

Isotopic Study of Bromine: Determining Bromine Isotope Fractionation During Evaporation and Diagenesis

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Stable isotopes of bromine ($\delta^{81}\text{Br}$) and chlorine ($\delta^{37}\text{Cl}$) provide new opportunities to trace geochemical processes in various natural systems. While chlorine isotopes have long been applied in diverse hydrologic and geochemical fields, bromine isotopes have only recently drawn attention. Recent analytical advances have revealed unexpectedly large $\delta^{81}\text{Br}$ variations in formation waters and evaporite deposits, yet the controls on the $\delta^{81}\text{Br}$ variability remain incompletely understood. Resolving the fractionation mechanisms and the relationship between bromine and chlorine isotopes is essential. Understanding $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ systematics can support interpretations of evaporite basin evolution, and groundwater sources and mixing, and identification of diagenetic overprints in the subsurface.

This thesis integrates three complementary approaches, including a global synthesis of published $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ datasets, controlled seawater evaporation experiments, and analyses of paleo-evaporite sequences. The integrated work provides insights into when and how stable bromine isotopes fractionate, and when and why its isotopic behavior decouples from that of stable chlorine isotopes. The synthesis of published datasets harmonizes unconnected studies to enable a comparison of the isotopic behaviors of bromine and chlorine across hydrologic and lithologic settings. The laboratory experiments isolate mineral-specific isotopic behavior and incorporation of bromine during sequential mineral precipitation under well-constrained conditions relevant to natural evaporative concentration of seawater. The analyses of paleo-evaporite sequences reveal how depositional signatures can be subsequently modified by post-depositional processes, and how such processes alter the isotopic and geochemical signature of bromine from chlorine.

The global comparison of $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values in groundwater and surface waters reveals a consistent pattern: $\delta^{81}\text{Br}$ often diverges from $\delta^{37}\text{Cl}$, with broader scatter and distinct behaviors across settings. The data show that $\delta^{81}\text{Br}$ values often cannot be predicted from $\delta^{37}\text{Cl}$ values alone, highlighting that the two halogens respond to overlapping but non-identical processes differently. Multiple regression approaches and the comparisons among them indicate additional fractionation pathways, beyond simple mass-dependent behavior, differentially affect bromine and chlorine. Relatively high $\delta^{81}\text{Br}$ values often cluster under specific geologic or hydrologic contexts, including organic complexation/decomposition, atmospheric interaction, elevated temperature-pressure regimes, and cryogenic processes. The comprehensive review provides a structured map of where

bromine and chlorine behave similarly, where they diverge, and what that implies for interpreting natural datasets.

Controlled seawater evaporation experiments demonstrate that bromine isotopes fractionate during sequential mineral precipitation, and crucially, that detectable shifts are observed before halite saturation. To better understand the underlying mechanisms, a laboratory evaporation series using synthetic seawater was conducted with continuous monitoring and stepwise sampling of brines, precipitates, and gas traps. Precipitates were characterized mineralogically, and both precipitates and coexisting brines were analyzed for $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values to evaluate isotope fractionation during evaporation and mineral formation. Carbonates, gypsum, and halite have distinct $\delta^{81}\text{Br}$ signatures consistent with differing pathways of Br incorporation, while $\delta^{37}\text{Cl}$ values are consistently higher in minerals than in coexisting brines. Capture of bromine in the gas phase sampled during the experiment confirms volatilization as an additional fractionation pathway for bromine isotopes. These experimental results explain why $\delta^{81}\text{Br}$ values can vary widely, and differently from $\delta^{37}\text{Cl}$, during progressive evaporation, mineral formation, and volatilization.

Analyses of paleo-evaporite sequences show that primary depositional signals can be systematically reshaped by post-depositional modification. To evaluate depositional and post-depositional signals, basin-wide stratigraphic sampling for Br, Cl, $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ analysis across evaporite horizons and locations in the Salina Formation in the Michigan Basin was combined with lithological characterization. Br/Cl ratios were examined with petrographic indicators of diagenetic overprints, and basin-evolution context from previous studies was integrated. Paired measurements of $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ were then linked to these signatures. Consistent with the compiled groundwater and surface water datasets, evaporite $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values often show weak correlation, reflecting multiple fractionation pathways rather than a single control acting on both isotopes simultaneously. Diagenetic processes often produce path-dependent shifts: either $\delta^{37}\text{Cl}$ or $\delta^{81}\text{Br}$ values can increase, decrease, or remain unchanged depending on the processes involved (e.g., dissolution-reprecipitation, fluid-salt interaction, thermal regimes, organic interaction). The $\delta^{81}\text{Br}$ – $\delta^{37}\text{Cl}$ dataset provides clear basin-evolution interpretations in complex evaporite records.

The combined results establish that bromine isotopes are particularly sensitive to specific geochemical processes and that their variability cannot be explained by chlorine isotope systematics alone. This research contributes three main advances: (1) it provides a systematic review and defines

the variability of bromine isotopes associated with diverse hydrogeologic settings; (2) it demonstrates experimentally that bromine isotopes fractionate significantly during evaporation and mineral precipitation, including prior to halite saturation; and (3) it shows that natural evaporite systems preserve complex isotopic signatures that integrate depositional and post-depositional processes, and that these signals are better understandable when both halogens are considered. Overall, this thesis develops a conceptual framework for bromine isotope geochemistry and demonstrates the value of Br-Cl dual isotope systematics to disentangle overlapping depositional and diagenetic processes, with implications for groundwater studies and evaporite basin evolution.

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Chapter 1

Introduction

1.1 Background

Halogen concentrations and ratios (e.g., Cl and Br concentrations, Cl/Br, Br/Cl $\times$ 1,000), have long been used as geochemical tracers in groundwater systems to evaluate origin, evolution, and mixing due to their conservative behavior (Carpenter, 1978; Hanor, 1994). Chlorine isotopes ($\delta^{37}\text{Cl}$) have likewise been widely applied to problems in hydrogeology, diagenesis, and geochemical tracing (Barnes and Sharp, 2017; Eggenkamp, 2014a; Kaufmann et al., 1984). More recently, bromine stable isotopes ($\delta^{81}\text{Br}$) have emerged as a promising complementary tracer. Accumulating evidence from recent studies suggests that bromine isotopes can undergo significant isotopic fractionation in natural systems (e.g., Eggenkamp and Coleman, 2000; Frape et al., 2007; Shouakar-Stash, 2008; Hanlon et al., 2017; Ercan et al., 2019; Stotler et al., 2021). This indicates that bromine isotopes may provide insights into subsurface and surface geochemistry that cannot be obtained from chlorine isotopes alone. Despite this potential, with many uncertainties regarding their variability across environmental conditions, the mechanisms driving bromine isotope fractionation remain incompletely understood and their relationship to chlorine isotope systematics remains unresolved.

Early studies assumed that bromine isotopes would fractionate negligibly due to the small relative mass difference between its two stable isotopes (^{79}Br and ^{81}Br), and for decades the Br isotope system received little attention. The advent of improved analytical precision in the early 2000s enabled resolution of natural $\delta^{81}\text{Br}$ variability (Eggenkamp and Coleman, 2000). Subsequent studies reported $\delta^{81}\text{Br}$ values well beyond the expected narrow ranges in diverse environments including brines, formation waters, and evaporite deposits (Eggenkamp et al., 2019b; Frape et al., 2007; Hanlon et al., 2017; Shouakar-Stash, 2008; Shouakar-Stash et al., 2007, 2005b; Stotler et al., 2021, 2010). In many cases, $\delta^{81}\text{Br}$ values are reported alongside $\delta^{37}\text{Cl}$ values and used for tracing fluid origin and evolution, yet the two isotopic systems frequently exhibit distinct behaviors. For example, in salt deposits, $\delta^{37}\text{Cl}$ values decrease systematically with progressive evaporation and increasing Br/Cl ratios, whereas $\delta^{81}\text{Br}$ values show no simple correlation with either Br/Cl ratios or the degree of evaporation (Eggenkamp et al., 2019b; Tan et al., 2006). These observations suggest that multiple fractionation pathways, distinct from those governing chlorine isotope systematics, contribute to bromine isotope variability.

Several mechanisms have been proposed to explain the observed isotopic variability of bromine. Physical processes with established directionality include volatilization, ^{79}Br -enriched in the gaseous phase, leaving residual brines relatively higher in $\delta^{81}\text{Br}$ values (Hanlon et al., 2017), and diffusion, which yields a kinetic isotope effect whereby ^{79}Br diffuses slightly faster than ^{81}Br , producing a relative ^{81}Br enrichment in the source (Eggenkamp and Coleman, 2009; Strydom et al., 2022). During evaporative concentration and mineral precipitation, mineral-brine partitioning can also fractionate bromine isotopes. Although the larger ionic radius of bromide relative to chloride limits incorporation into mineral lattices, fractionation could occur when bromide is substituted into the lattice, adsorbed to the surfaces, or entrapped in fluid inclusions. For example, in chloride-evaporite systems (e.g., halite, sylvite, bischofite), minerals exhibit varying preference for either ^{81}Br or ^{79}Br , yielding variable $\delta^{81}\text{Br}$ values (Eggenkamp et al., 2019b; Gao and Liu, 2021). Biogeochemical influences may also modify $\delta^{81}\text{Br}$ values. Organic and microbial processes may preferentially utilize ^{79}Br during deposition or diagenesis; subsequent degassing of ^{79}Br -rich volatiles would enrich the residual phase relatively enriched in ^{81}Br (Stotler et al., 2021; Wang, 2017).

Despite the potential for recording the imprints of various processes, including mixing and evolution of brines, evaporation and mineral precipitation, and other biological or physical processes, systematic studies of $\delta^{81}\text{Br}$ remain scarce, and the global distribution of values is poorly constrained. Existing data are geographically uneven, often reported without paired complementary hydrochemical information, and the processes driving isotopic divergence remain underexplored. More importantly, there is still no unifying framework that explains how bromine isotopes vary across hydrological and geological contexts and their responses to depositional processes and diagenetic alterations.

This thesis addresses these gaps by integrating three complementary approaches: (1) synthesis of published global Br-Cl isotope datasets, (2) controlled laboratory experiments on isotopic fractionation during evaporation and mineral precipitation, and (3) analysis of natural evaporite deposits to evaluate depositional and post-depositional signatures. Together, these approaches establish a mechanistic basis for bromine isotope fractionation, clarify its relationship with chlorine isotopes, and test its potential as an environmental tracer. The following chapters present a global review (*Chapter 2*), experimental investigations (*Chapter 3*), and natural case studies in evaporites (*Chapter 4*), and close with integrated conclusions in *Chapter 5*. Ultimately, this research contributes to the broader field of isotope geochemistry by demonstrating how bromine isotopes can serve as powerful tracers of fluid and evaporite origin, evolution, and post-depositional alteration.

1.2 Objectives

The objective of this research is to explain the behavior and fractionation mechanisms of bromine stable isotopes across controlled laboratory conditions and natural water bodies and evaporite environments, and to evaluate their applicability as environmental tracers, with particular emphasis on comparison to chlorine isotopes and the potential for dual halogen isotope tracing. This thesis will address each of the following specific objectives through independent chapters:

- Compile and synthesize existing literature and datasets on bromine isotope geochemistry to assess current understanding, establish the basis of isotopic distribution, and suggest potential fractionation pathways.
- Conduct controlled laboratory experiments to evaluate bromine isotopic behavior during selected geochemical processes (e.g., evaporation, sequential evaporite mineral precipitation, volatilization) and relate these patterns to mechanistic controls.
- Characterize bromine isotope compositions in natural paleo-evaporite settings and distinguish pre-/syn-depositional signals from post-depositional modifications.
- Integrate experimental and natural datasets to develop a conceptual framework for bromine isotope-based environmental tracing and explore the potential of combined Br-Cl isotope systematics.

1.3 Scope

The analytical focus of this thesis is on $\delta^{81}\text{Br}$, supported by $\delta^{37}\text{Cl}$, hydrogeochemistry, and key environmental parameters (e.g., salinity, temperature). The research spans three main settings:

- Subsurface and surface waters (including fresh to highly saline water or brine).
- Controlled laboratory systems mimicking evaporation of seawater and sequential evaporative mineral precipitation.
- Natural evaporite deposits with well-characterized geological and hydrological context.

The thesis is organized into five chapters with an integrated approach combining literature synthesis and review, controlled laboratory experiments, and analyses of natural paleo-evaporite systems. *Chapter 2* provides a comprehensive review of previous applications of bromine isotopes as geochemical tracers

across diverse geological and hydrological contexts. It identifies knowledge gaps, particularly the limited understanding of isotopic behavior during specific geochemical processes, and establishes the basis of isotopic distribution and the rationale for future field of investigations. *Chapter 3* presents controlled laboratory experiments designed to quantify bromine isotope fractionation associated with distinct processes such as seawater evaporation, mineral precipitation, and volatilization. By analyzing chemical conditions and measuring isotopic shifts during sequential evaporative mineral precipitation, the experimental study identifies mineral-specific fractionation signatures and explores their mechanistic basis. *Chapter 4* investigates bromine and chlorine isotope systematics in natural evaporite sequences within a single Silurian age Formation. These paleo evaporite systems, shaped by prolonged evaporation and deposition, followed by complex diagenetic histories, provide valuable natural analogues for the processes studied experimentally and opportunity to differentiate post-depositional processes from pre/syn-depositional signatures. The scope of each chapter is summarized below for clarity.

- **Chapter 2** – Literature review of bromine isotope geochemistry, compilation of published datasets, and identification of knowledge gaps.
- **Chapter 3** – Experimental investigations of bromine and chlorine isotope fractionation during seawater evaporation and mineral precipitation under controlled conditions.
- **Chapter 4** – Analysis of natural paleo evaporite systems, with emphasis on distinguishing depositional from diagenetic signals.
- **Chapter 5** – Integrated conclusions, implications for bromine and chlorine isotopes as environmental tracers, and recommendations for future study.

Chapter 2

Bromine and Chlorine Isotope Geochemistry in Groundwater: A Review

2.1 Introduction

Chloride and bromide, two halogens in natural waters, generally behave conservatively except during precipitation of evaporite minerals or, less commonly, certain silicate minerals. Due to this near-conservative behavior, their concentrations and Br/Cl ratios have long been applied as reliable tracers of fluid sources and salinity evolution (Carpenter, 1978; McCaffrey et al., 1987; Rittenhouse, 1967). Chlorine isotope compositions ($\delta^{37}\text{Cl}$) have been used as geochemical tracers in diverse contexts, including tracing halite dissolution (Eastoe et al., 2007; Eastoe and Guilbert, 1992; Eggenkamp et al., 1995), identifying mixing between brines of different origins (Shouakar-Stash et al., 2007; Stotler et al., 2010), and investigating hydrothermal alteration processes (Ransom et al., 1995; Spivack et al., 2002). Recent analytical advances have extended this utility to include bromine isotope systems ($\delta^{81}\text{Br}$) (Shouakar-Stash et al., 2005b). While $\delta^{37}\text{Cl}$ variation in natural waters rarely exceeds $\pm 2\text{‰}$, published $\delta^{81}\text{Br}$ values span over 5‰, and their observed behavior and distribution often deviate from theoretically predicted equilibrium fractionations (Eggenkamp, 2014a). This discrepancy suggests that additional fractionation pathways such as organic matter degradation may influence bromine more readily than chlorine (Stotler et al., 2021; Wang, 2017), yet the direction and magnitude of such pathways remain poorly constrained.

Although the number of studies reporting $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values together has increased in recent years (e.g., Bagheri et al., 2014; Wang, 2017; Hanlon et al., 2017; Eissa, 2018; Yu et al., 2019), most have focused on chlorine isotopes or local hydrochemical problems, such as seawater intrusion or basin-scale salinity evolution. In such site-specific contexts, bromine isotopes are often reported but seldom interpreted in depth. Despite the geochemical compatibility of Br and Cl, many studies report weak correlations between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values (Eggenkamp, 2025; Shouakar-Stash, 2008), implying that these isotopes can be fractionated independently under certain geological or hydrochemical conditions. Consequently, no comprehensive synthesis has yet evaluated how both isotopes vary across the full range of surface and subsurface water reservoirs, from crystalline shields to evaporite basins, or identified which geological or hydrochemical factors (e.g., salinity, ionic concentrations and ratios, lithology,

temperature-pressure conditions, organic content) systematically influence their co-variation or decoupling. Addressing this knowledge gap is important for assessing recent hypotheses of secular variation in seawater $\delta^{81}\text{Br}$ (Eggenkamp, 2025; Shouakar-Stash, 2008).

This study compiles a global dataset of groundwater and surface water samples reporting both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values, along with associated geological and hydrochemical data. The dataset contains 1,110 subsurface and 88 surface or sea-ice samples from 24 regions worldwide. These data are analyzed with respect to lithology and geologic age of the host rock, salinity, temperature/pressure regime, and selected ionic parameters (e.g., Br, Cl, Li, Mg/Ca). This synthesis aims to characterize the global distribution of bromine and chlorine isotopes in natural waters and to evaluate plausible fractionation pathways, including evaporation-precipitation sequences, halite cycling, dolomitization, organic reactions, cryogenic processes, and hydrothermal alteration, that shape their isotopic patterns and divergence. The resulting framework provides new constraints on bromine isotope geochemistry and highlights priorities for future experimental and field-based studies.

2.2 Data Compilation

A comprehensive literature review was conducted to compile published studies reporting bromine isotope compositions ($\delta^{81}\text{Br}$) in groundwater and surface water bodies. Through this search, a total of 1,110 groundwater and 88 surface water or sea-ice samples were compiled here. The literature referenced here includes studies that report $\delta^{81}\text{Br}$ values as well as those that provide complementary data (e.g., hydrochemical and geological parameters) from the same samples or locations.

Because the primary objective of this review is to evaluate the overall distribution of $\delta^{81}\text{Br}$ in subsurface water bodies worldwide, the main inclusion criterion was the availability of $\delta^{81}\text{Br}$ values along with chlorine isotope composition ($\delta^{37}\text{Cl}$) for comparison. Clear documentation of sampling locations, depths, and associated geological information (e.g., rock type, geologic period, stratigraphic unit) was also required for effective geological assessment. However, all available datasets were compiled without exclusion to evaluate the overall $\delta^{81}\text{Br}$ data richness.

The compiled database encompasses a wide range of salinities and water types, and includes 56 surface waters samples from lake and creek waters, 32 sea-ice samples, and numerous groundwaters and pore water samples from across a range of depths, and from every continent except South America (Figure 2-1; Table 2-1). Samples come from diverse geological settings such as sedimentary basins, coastal sabkhas,

oil fields, and crystalline and metamorphic terranes; the dominance of samples from sedimentary basins in the dataset is consistent with estimates that 39% of Earth's bromine resides in these environments (Eggenkamp, 2014a). While this makes it important to understand the distribution of bromine isotopes in sedimentary settings, the inclusion of other geological contexts is essential for capturing bromine behavior across the wide range of subsurface reservoirs and developing a more comprehensive framework to interpret bromine isotope systematics.

The dataset includes: 656 $\delta^{81}\text{Br}$ and 769 $\delta^{37}\text{Cl}$ values (34 and 45 of which, respectively, are from surface waters, and 32 from sea-ice), major ion concentrations (ranging between 793 values for bicarbonate concentrations to 1,303 values for chloride concentrations), and trace element concentrations where available (e.g., 945 bromide and 294 lithium concentrations); additional parameters such as temperature are also included to facilitate a comprehensive assessment. Hydrochemical quality control was performed by evaluating charge balance error and reviewing the original publications for indications of unreliable data. Data flagged as unreliable are not considered in the subsequent discussions.

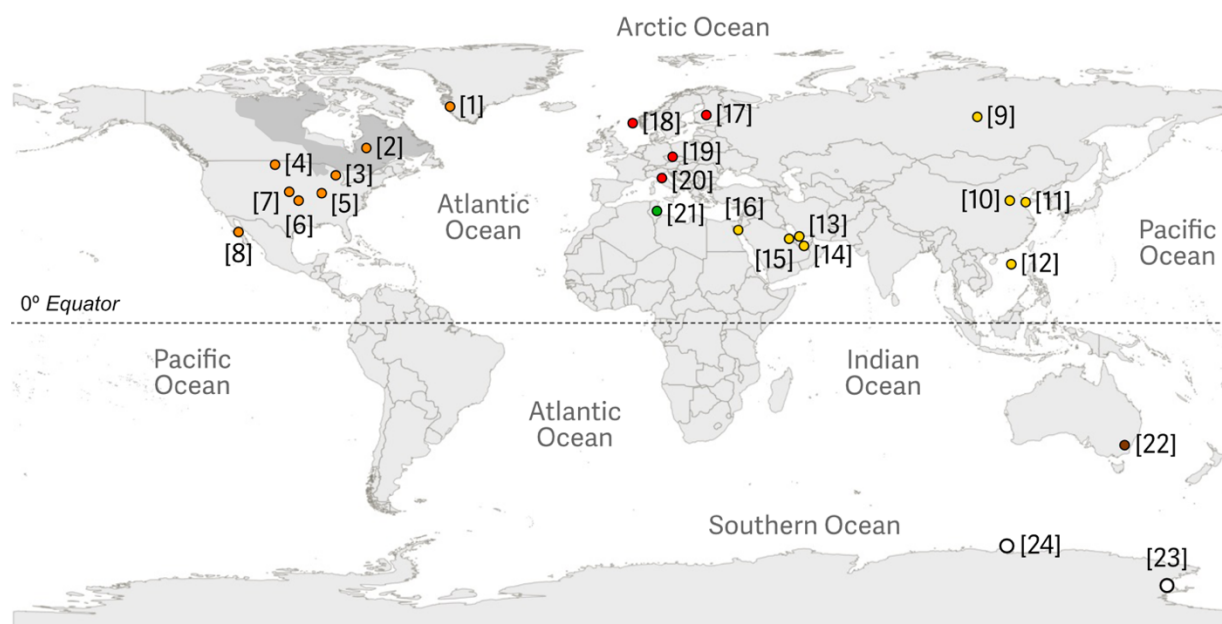


Figure 2-1. Global distribution of datasets used in this study. Each circle marks the approximate location of a study included in the dataset, and the bracketed number corresponds to the entry in Table 2-1. Sampling localities for dataset [2] are dispersed across the Canadian Shield; the relevant portion of the Shield is therefore shaded in gray. Circle colors differentiate continents, providing quick visual comparison of geographic coverage. The dashed line denotes the Equator.

Table 2-1. Geographic and geologic settings and sample type for each dataset. Site numbers correspond to those plotted on the map in Figure 2-1.

Location	Geologic Description*	Sample Type**	Source(s)
<i>North America</i>			
[1] Greenland Icesheet, Greenland	Archean gneisses reworked in the Paleoproterozoic with structural complexities	(Sub-permafrost and talik) groundwater, lake water	Henkemans et al. (2018)
[2] Canadian Shield, Canada	Precambrian crystalline rocks that have been metamorphosed and deformed. Metasediments, banded iron formation, intrusive plutonic and volcanic rocks.	Groundwater	Stotler et al. (2010)
[3] Michigan Basin, Canada and USA	Cambrian to Carboniferous sedimentary rock sequence (sandstone, evaporite, shale, dolostone, etc.) in intracratonic basin	Formation fluid, groundwater, porewater	Shouakar-Stash, (2008) and references therein; Skuce (2014); Skuce et al. (2015); Wang (2017)
[4] Williston Basin, Canada and USA	Cambrian to Cretaceous sedimentary rocks, predominantly marine origin	Formation fluid	Shouakar-Stash (2008) and references therein
[5] Illinois Basin, USA	Cambrian marine sedimentary rocks, sandstone with alternating clay-rich shale	Porewater	Giunta et al. (2017)
[6] Cherokee Basin, USA	Pennsylvanian coal, shale, and limestones	Formation water, gas	Stotler et al. (2021)
[7] Saline lakes in Nebraska and Kansas, USA	Saline lakes in a tectonically inactive, closed basin. Lakebeds have complex mineralogy including various sodium-sulfate/carbonate minerals with underlying Permian halite- and anhydrite-bearing sandstones.	Lake water, gas, precipitate	Hanlon et al. (2017)
[8] Las Tres Vírgenes, Cerro Prieto, and Los Azufres Geothermal Fields, Mexico	Cenozoic volcanic complex including deltaic sedimentary rocks and sedimentary sandstone and andesite, with high geothermal anomaly	Groundwater	Pinti et al. (2019); (2020)

<i>Asia</i>			
[9] Siberian Platform, Russia	Cambrian to Jurassic sedimentary rocks and sediments, including terrigenous carbonate and evaporites	Formation brine, spring and lake waters	Shouakar-Stash et al. (2007)
[10] North China Plain, Hebei, China	Cenozoic sedimentary sequence underlain by Precambrian bedrock consisting of metamorphic rock over marine carbonate	Formation water, brine, lake water, seawater	Chen et al. (2014) and references therein
[11] Coastal aquifer in Laizhou Bay, China	Quaternary unconsolidated marine sediments with minor amounts of evaporites	Groundwater, river water, seawater	Du et al. (2015)
[12] South China Sea oil field, China	Cenozoic sedimentary basin of shale, mudstone, and interbedded sandstone	Formation water	Yu et al. (2019)
[13] Kangan gas field, Iran	Permian to Triassic anticline formation as a gas reservoir predominantly consists of limestone and dolomite overlain by shale	Formation water, spring water,	Bagheri et al. (2014)
[14] Coastal sabkha in United Arab Emirates	Holocene sand dunes and oxidized reddish-brown carbonate underlain by Miocene carbonate	Shallow sabkha water, deep brine	Saeed et al. (2021)
[15] Coastal sabkhas in Saudi Arabia	Holocene deposits on Miocene to Eocene irregularly eroded sandy carbonate and evaporite	Shallow brine, deep groundwater	Hussain et al. (2020)
[16] Coastal aquifers (Wadi Watir and Dabab) in Sinai, Egypt	Precambrian granitic, metamorphic, and volcanic rocks covered by Quaternary sand deposits with local outcrops of Cambrian sedimentary rock	Groundwater, seawater	Eissa et al. (2016); Eissa (2018)
<i>Europe</i>			
[17] Fennoscandian Shield, Finland	Precambrian gneiss, greenstone belt, granites, schists, serpentinite, and other metamorphic rocks, with red sand stones and shale interlayers	Groundwater	Stotler et al. (2010)

[18] Oseberg Field, Norway	Jurassic mudrocks covered by Cretaceous mudrocks and marls in transition zone between tectonically active graben and platform	Formation water	Eggenkamp and Coleman, (2000); Ziegler et al. (2001)
[19] Bohemian Massif, Czech Republic	Tertiary sediments and Carboniferous continental sedimentary basins	Groundwater	Frape et al. (2007)
[20] Northern Apennine Foredeep, Italy	Tertiary turbidites and evaporites (marine), overlying Triassic to Neogene carbonate succession	Groundwater	Boschetti et al. (2011)
<i>Africa</i>			
[21] Coastal aquifer in Djebeiana, Tunisia	Mio-Pleistocene continental deposits of alternating clays, marls, and coarse sands with conglomerates	Groundwater (shallow and deep)	Moussaoui et al. (2023)
<i>Australia</i>			
[22] Lake George Basin, NSW, Australia	Ordovician fractured rock consists of phyllite and quartzite (Pittman Fm.)	Core crush/leach extract, groundwater, creek water, lake water	Short (2017)
<i>Antarctica</i>			
[23] McMurdo Dry Valleys, Antarctica	Blood Falls (hypersaline discharge of the Taylor Glacier)	Englacial brine, (supraglacial water, hypersaline lake water)	Lyons et al. (2019)
[24] Southern Ocean off East Antarctica	Ocean sea-ice collected from Sea Ice Physics and Ecosystems eXperiment (SIPEX-2) voyage	Sea-ice	Vallelonga et al. (2021)

**Geologic Description* describes the primary lithology from where subsurface water samples are sampled.

***Sample Type* includes the samples for which both bromine and chlorine isotopic values are available.

2.3 Bromide and Chloride Concentrations in Groundwater

2.3.1 Background: Known Sources, Processes, and Behaviors

Understanding the concentrations and geochemical behavior of bromide (Br) and chloride (Cl) in groundwater provides a necessary foundation for interpreting their isotopic systematics, since the processes that control solute abundances can also impact isotopic fractionation. Groundwater Br and Cl concentrations can span several orders of magnitude, reflecting diverse sources and hydrochemical processes. Br and Cl behave conservatively in most groundwater systems, precipitating into minerals primarily only after halite saturation is reached, so their concentrations and ratios serve as reliable indicators of solute origin (McCaffrey et al., 1987; Rittenhouse, 1967). Cl can also partition into silicate lattices formed during hydrothermal or metamorphic alteration, particularly amphibole, biotite, and serpentine, whereas Br, owing to its larger ionic radius, is incorporated much less readily (Stober and Bucher, 1999). Because Cl commonly constitutes over 95% of the total anion mass in formation waters, identifying its source remains a key to understanding overall solute origins (Hanor, 1994).

In sedimentary strata and basins, salinities can vary from only a few milligrams per liter in shallow meteoric aquifers (e.g., Central Valley in California, USA) to more than 10^5 mg/L in evaporite-rich settings (e.g., the Michigan and Williston Basins, USA-Canada) (Kharaka and Hanor, 2014). Two dominant processes often explain elevated Br and Cl concentrations in formation waters: (1) subaerial evaporation of seawater, concentrating both halides until halite (NaCl) precipitates; and (2) subsurface dissolution of evaporites, where mainly halite dissolution increases Cl concentration relative to Br (Hanor, 1987; McCaffrey et al., 1987). By contrast, crystalline rock aquifers do not frequently host significant in-situ halite or other evaporite deposits; instead, Br and Cl concentrations can be elevated by: (1) silicate hydration during regional metamorphism or hydrothermal overprinting; (2) leakage of fluid inclusions; (3) migration of external brines (sedimentary or metamorphic fluids) through fracture systems; or (4) long-term diffusive filtration brine migration from adjacent sedimentary basins (Boumaiza et al., 2024; Frape et al., 2014; Stober and Bucher, 1999; Stotler et al., 2010). Mafic or ultramafic lithologies often show elevated Br/Cl ratios, which potentially reflect enhanced Br retention in specific mineral phases as well as the selective leaching of Br-bearing phases during water-rock interaction (Frape et al., 2014; Stotler et al., 2010).

2.3.1.1 Main Processes Controlling Br-Cl Systematics

During subaerial evaporation of seawater or groundwater, both Br and Cl concentrations initially increase, following a log-linear segment of the Seawater Evaporation Trajectory (SET; solid red line in Figure 2-2) (Carpenter, 1978; McCaffrey et al., 1987). Once halite saturation is reached (“H” on the SET, Figure 2-2), Cl is preferentially removed into the precipitating salt, so the residual brines become progressively Br-rich, and the trajectory “flattens” toward higher Br/Cl ratios. Conversely, when halite dissolution occurs, whether by freshwater or seawater, both Br and Cl concentrations increase, though Cl typically dominates due to low Br content in halite (e.g., orange dashed arrows). The slope of the Br-Cl relationship during dissolution may vary depending on the specific halite

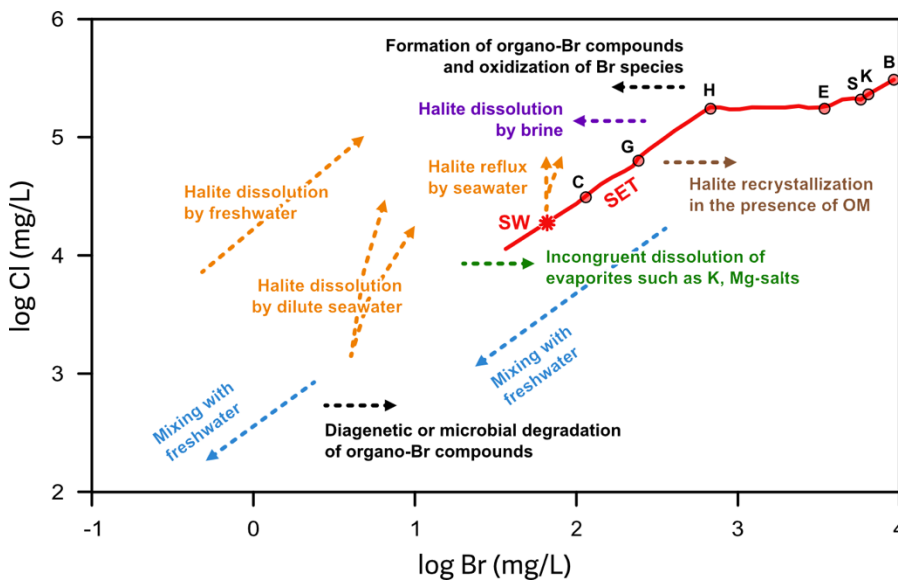


Figure 2-2. Conceptual diagram showing the evolution of Cl and Br concentrations during evaporation, dissolution of evaporites, and mixing. Arrows represent the general direction of each process (e.g., evaporation, evaporite dissolution, mixing) from an example initial concentration, rather than quantitative trajectories. The seawater evaporation trajectory (SET) is from *Carpenter (1978)* and *McCaffrey et al. (1987)*; and initial evaporite precipitation points are from *Matray (1988)*. Possible evolution scenarios including mixing and dissolution are from several sources (*Hanor, 1987; Rittenhouse, 1967; Warren, 2016*). Abbreviations: SW = seawater, C = calcite saturation, G = gypsum saturation, H = halite saturation, E = epsomite saturation, S = sylvite saturation, K = carnallite saturation, B = bischofite saturation.

composition, especially the Br content (Rittenhouse, 1967), and the location will depend on the initial composition of the dissolving fluid. In cases where bedded halite dissolve during brine mixing (i.e., halite dissolution by brine), Cl concentrations may remain relatively consistent while Br concentration decreases (purple dashed arrow), reflecting the low Br content in bedded halite (Rittenhouse, 1967). Beyond the fundamental evaporation and dissolution pathways, incongruent dissolution of K-Mg-Cl evaporites (e.g., carnallite) can further enrich Br relative to Cl (green dashed arrow), when subsequent precipitation of sylvite (KCl) occurs as those evaporites dissolve, thereby leaving Cl concentration largely unaffected (green dashed arrow; (Worden, 2018, 1996). Repeated cycles of halite dissolution and reflux can also enrich Br concentrations beyond those expected from simple halite dissolution or a single-stage seawater evaporation process (Hanor, 1987).

Processes involving organic interactions add more complexity, by affecting Br concentrations in groundwater, but typically leaving Cl concentrations less affected. Organic-rich sediments can release or consume Br through diagenetic reactions, shifting Br/Cl ratios away from inorganic pathways such as evaporation or halite dissolution (Land and Prezbindowski, 1981; Worden, 2018, 1996). The net effect of groundwater interaction with organobromine (organo-Br)-rich sediments depends on the balance between the formation and degradation of organo-Br compounds, which are influenced by environmental conditions such as redox state and pH (Heeb et al., 2014; Leri et al., 2010; Leri and Myneni, 2012). For example, under anoxic conditions, microbial degradation of organo-Br compounds, where bacteria can remove Br from the organic structure through anaerobic respiration, can release Br into the groundwater (Heeb et al., 2014). Similarly, coal seams and organic-rich shales or sediments may release Br through microbial degradation (Vainikka and Hupa, 2012; Worden, 2018). Recrystallization of halite in the presence of organic matter can inhibit Br incorporation into new halite crystals, leaving higher concentration of Br in solution (Hanor, 1987). In contrast, Br can be removed from the aqueous system if it is incorporated into organo-Br compounds or oxidized to volatile Br₂, although this pathway is less common and typically limited to shallow groundwater environments (Rittenhouse, 1967). In shallow groundwater or surface water environments, photolysis and hydrolysis can contribute to the breakdown of organo-Br compounds, particularly in environments exposed to sunlight (Hanlon et al., 2017; Heeb et al., 2014). The net effects of these processes are to alter Br concentrations, typically more than Cl, resulting in either elevated or reduced Br/Cl ratios, depending on the dominant pathway. This behavior is schematically represented in Figure 2-2 as a leftward or rightward divergence from the SET.

Collectively, groundwater Br/Cl mass ratio signatures reflect cumulative influence of every process discussed above. Baseline seawater ($\text{Br/Cl} \approx 0.0035$) shifts to lower values when halite or other evaporites dissolve in meteoric water or seawater, and to higher values when Cl is sequestered in precipitating halite, K-/Mg-evaporites, or by the release of Br during organic diagenesis or reflux cycling (Hanor, 1987; Heeb et al., 2014; Vainikka and Hupa, 2012; Worden, 2018, 1996). In net these processes result in a broad range of Br/Cl ratios (from 0.00075 to 0.018) in formation waters in various sedimentary basins (Hanley and Koga, 2018). Crystalline aquifers, typically with limited in-situ halite, often inherit ratios from a signature shaped by seawater or hydrothermal-metamorphic-igneous rock fluid histories, left in the rock matrix or adjacent brines; yet Br/Cl ratios can further increase where Cl is lost from the rock matrix by diffusion or is partitioned into amphibole and biotite during hydrothermal overprinting, pronounced in mafic and ultramafic hosts (Boumaiza et al., 2024; Stober and Bucher, 1999; Stotler et al., 2010). Thus, the Br/Cl ratio is an integrated signature of groundwater's evaporative history, diagenetic overprint, and host-rock lithology.

2.3.1.2 Other Notable Processes or Influences

Additional processes can further modify Br and Cl concentrations, although observations that confirm or quantify these effects may be more limited. Dolomitization may preferentially affect Br, as observed in dolomitized carbonate intervals with elevated Br/Cl ratios, complicating the halogen record in carbonate reservoirs (Johnson et al., 2009; Schoenherr et al., 2009). Br can also co-precipitate with calcium carbonate, particularly aragonite, although incorporation can vary depending on crystal form and salinity due to halide competition (Okumura and Kitano, 1986). Experimental studies on scapolite and subduction zone fluids suggests that mineral-fluid partitioning under high pressure, high temperature conditions can either enrich or deplete Br in fluids, depending on mineral preferences and the stability of Br-bearing species (Hammerli et al., 2024; Louvel et al., 2020). Tectonic processes can also drive brine migration across sedimentary basins, crystalline shields, or thrust belts, introducing contrasting Br/Cl signatures into local groundwater systems (Bethke and Marshak, 1990; McCaig et al., 2000). In addition, Cl-specific trends have also been reported. For instance, significantly low Cl concentrations in sub-seafloor porewaters have been interpreted as a result of upward advection of Cl-depleted fluids, sourced from deeply stored dilute formation waters, as well as from clay dehydration (Hesse et al., 2006). All of these processes underscore the complexity of Br-Cl systematics in subsurface waters.

2.3.2 Br-Cl in the Compiled Dataset

In the datasets examined in this study (Table 2-1), Br concentrations range between 0.041 and 8,587 mg/L ($n=945$), while Cl concentrations range between 1 and 577,210 mg/L ($n=1030$) (Table 2-2). The mean Br and Cl concentrations are 632 and 82,083 mg/L, respectively. These values, especially the upper extremes of Br, far exceed the typical values ($\sim 3,000$ mg/L) in formation waters originating from simple halite dissolution by meteoric or seawater (McCaffrey et al., 1987; Shouakar-Stash, 2008). The elevated Br concentrations and the large concentration range for both halides suggests that many samples have complex salinity evolutionary histories, such as multiple evaporite dissolution-reprecipitation cycles or diagenetic processes involving organic matter (Hanor, 1994; Land and Prezbindowski, 1981).

Table 2-2. Summary statistics for chlorine and bromine concentrations and their ratios along with their isotope values of 1,110 groundwater samples.

	Br (mg/L)	Cl (mg/L)	Br/Cl	$\delta^{81}\text{Br}$ (‰)	$\delta^{37}\text{Cl}$ (‰)
Minimum	0.041	1	5.8×10^{-7}	-1.94	-3.86
Maximum	8,587	577,210	0.35	+3.35	+2.07
Mean	632	82,083	0.0068	+0.55	-0.05
Standard Deviation	963	86,364	0.012	0.76	0.53
n	945	1030	940	622	724

A comparison of Br and Cl concentrations reveals a moderate positive correlation ($R^2 \approx 0.6$, $p < 0.001$; Figure 2-3), broadly consistent with seawater evaporation trajectory (SET) (Carpenter, 1978; McCaffrey et al., 1987). Yet, many samples deviate from the SET, implying mixed sources derived from diverse geological contexts and processes, such as salt precipitation and reflux or organic influences (Figure 2-3) (e.g., Shouakar-Stash, 2008; Skuce, 2014; Wang, 2017). Similarly, Br/Cl ratios exhibit considerable variability (Table 2-2), far beyond the near-constant 0.0035 ratio typical of modern seawater. Br/Cl ratios higher than seawater (i.e., to the right of the SET) often indicates advanced evaporation, incongruent dissolution of Cl salts, or organics-driven Br enrichment, whereas lower ratios (i.e., to the left of the SET) typically reflect halite dissolution (Figure 2-3) (Fuge, 1988; Rittenhouse, 1967; Warren, 2016; Worden, 1996).

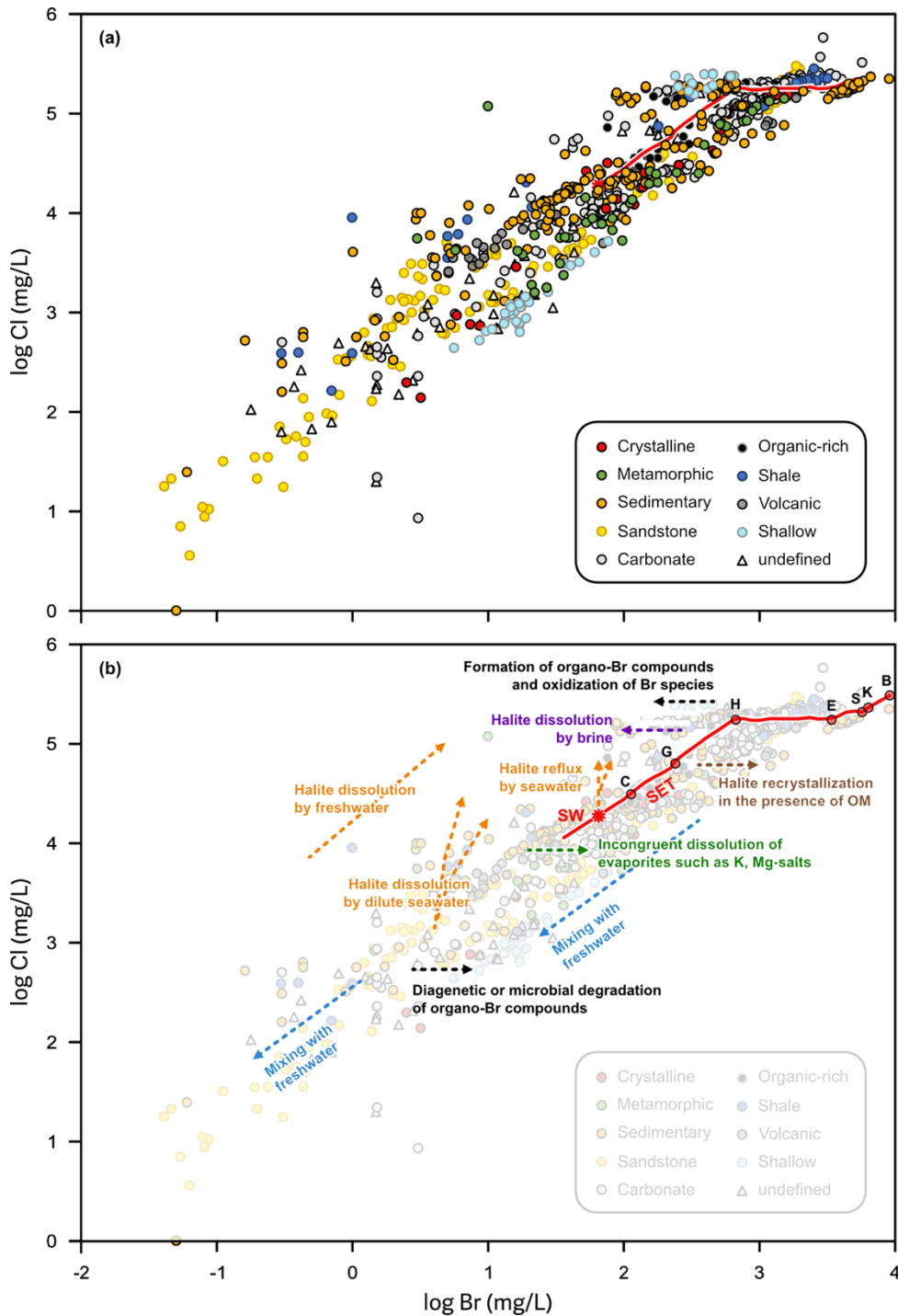


Figure 2-3. (a) Cl vs. Br concentrations of groundwaters collected from formations of different rock types in a log scale. (b) The processes from Figure 2-2 are overlaid as arrows to illustrate potential salinity pathways and evolution in these systems.

Despite encompassing a wide range of geologic settings, there is no spatial trend for Br-Cl concentrations in the compiled dataset, and only a very weak, though statistically significant correlation with depth ($R^2 \approx 0.03$, $p < 0.001$). Instead, local salinity sources and geochemical processes, such as evaporation, evaporite dissolution, and organic matter interactions, appear to drive the observed patterns (Figure 2-3). Grouping samples by rock type further reveals distinct Br-Cl distributions for each lithology, showing how variations in lithology, hydrologic regimes, and diagenetic pathways can differentially influence halide evolution (Figure 2-4); these trends will be described below.

In waters hosted in several rock types (including undifferentiated sedimentary units, carbonate rocks, organic-rich strata, and certain shallow groundwater samples), Br concentrations exhibit substantial variability while Cl concentrations remain consistently elevated, creating “horizontal” trends on a Br-Cl plot (Figure 2-4d, f, g, and i). Such patterns suggest that the evolution of salinity in these settings is dominated by processes such as repetitive halite dissolution-precipitation cycles, incongruent dissolution of K-Mg-Cl salts, or microbial diagenesis within organic-bearing strata (Land and Prezbindowski, 1981; Worden, 2018, 1996). In these environments, although Cl concentrations are maintained by ongoing salt cycling, variations in bromine indicate that additional factors (such as organic matter interactions) exert a more significant influence on its concentration. For example, fluids hosted by organic-rich strata have notably high salinities and slightly low Br/Cl ratios. These signatures likely arise from a combination of extensive evaporite recycling and the uptake of Br during the formation of organo-Br compounds (Heeb et al., 2014; Worden, 1996).

Conversely, waters hosted in sandstone-dominated formations (Figure 2-4e) typically exhibit a more linear Br-Cl relationship that plots below the theoretical SET. Their comparatively simple trend implies limited halite cycling and diagenetic overprinting, so salinity is governed mainly by conservative mixing between meteoric water and evaporated marine-derived brine. Shale-hosted waters (Figure 2-4h) tend to exhibit a more scattered Br-Cl distribution, possibly due to additional processes such as selective Br release during organic-matter degradation or diffusive filtration that perturb the two halides to different degrees. Shallow coastal groundwaters, meanwhile, appear to separate into two distinct groups: a low-salinity group, produced by mixing highly evaporated brines with meteoric water, and a higher-salinity group reflecting more direct seawater intrusion followed by partial evaporation and, in some cases, oxidation of Br-species or microbial or photolytic loss of Br to gas phase.

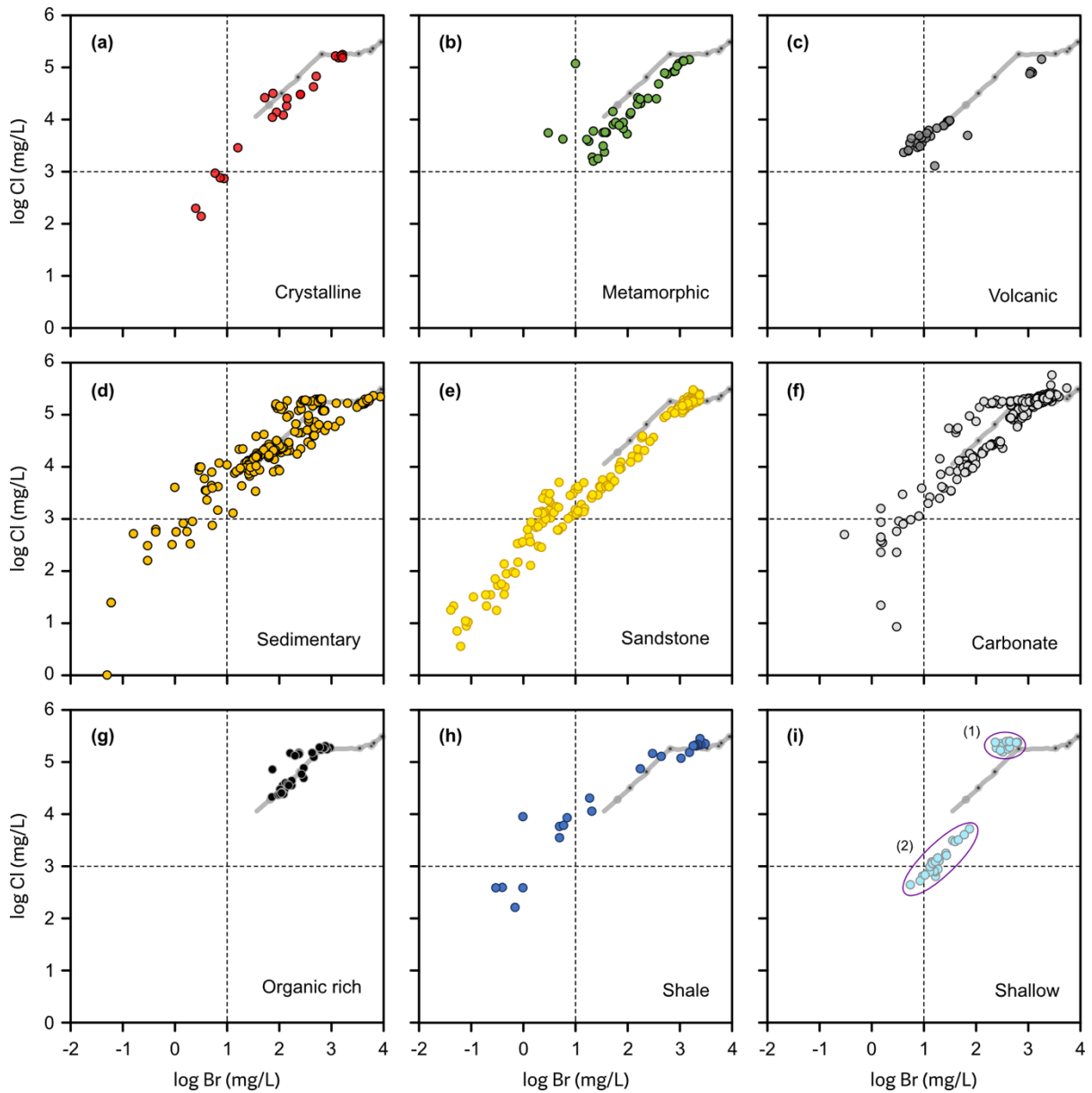


Figure 2-4. Log-log scatterplots of Cl versus Br concentrations for the compiled dataset, grouped by host rock types. Individual panels (a-i) display, respectively, crystalline, metamorphic, volcanic, undifferentiated sedimentary rocks, sandstone, organic-rich, shale, and shallow coastal aquifer samples. The solid gray curve reproduces the seawater-evaporation trajectory (SET).

2.4 $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ Signatures in Groundwater and Surface Water

The compiled groundwater dataset includes both groundwater and surface water samples, with groundwater making up the majority. Groundwater samples display distinctive ranges for bromine ($\delta^{81}\text{Br}$) and chlorine ($\delta^{37}\text{Cl}$) isotope values (Figure 2-5a, b). $\delta^{81}\text{Br}$ values range from -1.94‰ to +3.35‰, with a mean of $0.55 \pm 0.76\text{‰}$ ($n = 622$), while $\delta^{37}\text{Cl}$ values range from -3.86‰ to +2.07‰, with a mean of $-0.05 \pm 0.53\text{‰}$ ($n = 724$) (Table 2-2). Most groundwater samples exhibit high $\delta^{81}\text{Br}$ values (83% of the data; $n = 517$), whereas the $\delta^{37}\text{Cl}$ values are tightly clustered around 0‰, with 81% of the data ($n = 584$) within $0 \pm 0.50\text{‰}$ (Table 2-2; Figure 2-5a, b). Equivalent histograms subdivided by host-rock type are provided in Appendix Figures A-1 and A-2 for direct lithological comparison. A smaller set of surface water samples from rivers, creeks, and lakes exhibits a narrower $\delta^{37}\text{Cl}$ spread (-1.58‰ to +0.93‰) and $\delta^{81}\text{Br}$ (-0.74‰ to +1.80‰) (Figure 2-5c, d). While much of the following discussion will focus on the larger groundwater dataset, a detailed discussion of surface water data is presented in Section 2.8.4.

Regression analyses provide insights into the relationship between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ and help distinguish between mass-dependent and anomalous fractionation behaviors. The slope and correlation of $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ can indicate whether fractionation is predominantly by processes affecting both isotopes at the same time, or whether additional Br or Cl-specific mechanisms are at work. Across the full groundwater dataset, the weak but statistically significant Pearson correlation of the Ordinary Least Squares (OLS) regression ($R^2 = 0.06$; $p < 0.001$) suggests that $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values are not well correlated. Given the diverse geologic and hydrochemical settings, a single OLS linear fit applied to the entire dataset does not adequately capture the isotopic covariance. The OLS assumes all uncertainty lies on the y-axis ($\delta^{81}\text{Br}$) and treats the x-axis ($\delta^{37}\text{Cl}$) as error-free, limiting its applicability when both variables carry uncertainty.

To better characterize the variance and behavior of the two isotopes, two alternative regression approaches are explored. The Reduced Major Axis (RMA) regression incorporates variance along both axes and yields $\delta^{81}\text{Br} = 1.82 (\pm 0.14) \times \delta^{37}\text{Cl} + 0.61 (\pm 0.06)$ ($R^2 = 0.16$, $n = 724$). The steep slope reflects the influence of high $\delta^{81}\text{Br}$ values, capturing the full variance (Figure 2-6). Meanwhile, the Theil-Sen robust median regression estimates the slope as the median of all pairwise point-to-point slopes, focusing on the main data cloud while remaining insensitive to extreme values (Wilcox and Keselman, 2012). Before fitting, 153 samples were excluded for meeting one or more criteria: (i)

$\delta^{37}\text{Cl}$ values beyond $\pm 3\text{‰}$, (ii) outliers by Mahalanobis distance criteria (distance exceeded the central cluster spread), or (iii) high-influence points flagged by Cook's distance (a single point altered the slope by $>20\%$). The remaining 571 samples define the 'main data cloud' used for robust regression and Residual Standard Error (RSE) calculation. As a result, the Theil-Sen regression gives $\delta^{81}\text{Br} = 0.53 (\pm 0.07) \times \delta^{37}\text{Cl} + 0.43 (\pm 0.02)$ ($n = 571$, $\text{RSE} = 0.69\text{‰}$). This slope closely matches the theoretical mass-dependent fractionation (~ 0.44), derived from the relative mass differences of Br and Cl stable isotopes (i.e., $(2/79) / (2/35) = 35/79$), implying that for most groundwater samples, a 1‰ shift in $\delta^{37}\text{Cl}$ is accompanied by a $\sim 0.5\text{‰}$ shift in $\delta^{81}\text{Br}$.

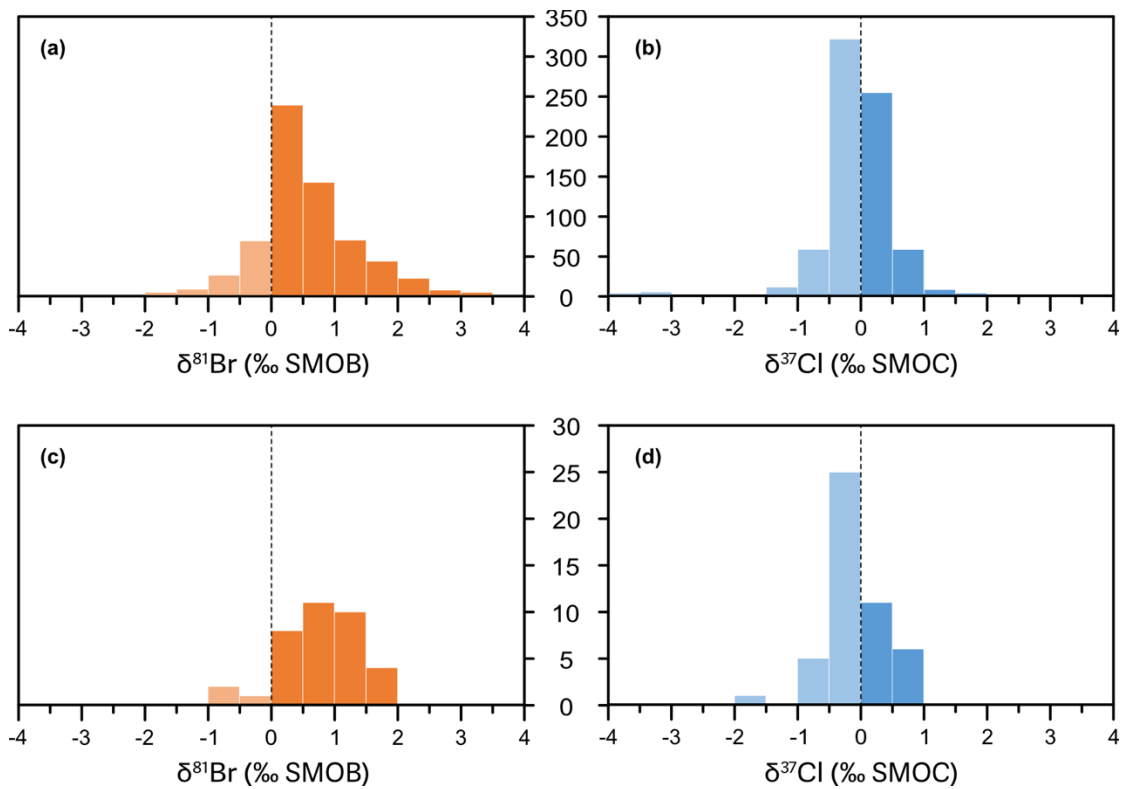


Figure 2-5. Histograms demonstrating the frequency distribution of bromine and chlorine isotope values of all groundwater samples (a, b) and surface water samples (c, d). Dark orange and blue shades represent relatively high isotope values while bright orange and blue shades represent relatively low values, relative to their respective reference standards.

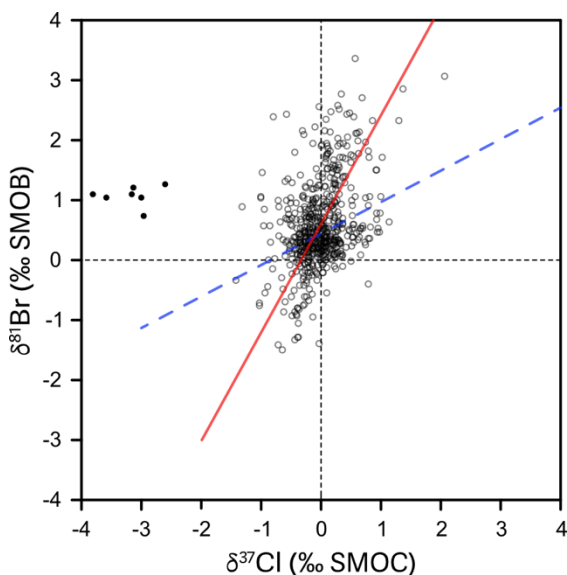


Figure 2-6. Scatterplot of $\delta^{81}\text{Br}$ vs. $\delta^{37}\text{Cl}$ for the compiled groundwater dataset. Open symbols define the data cloud. Black filled circles mark samples from a tectonically active transition zone where diffusion and membrane ultrafiltration drive $\delta^{37}\text{Cl}$ to unusually negative values (Eggenkamp and Coleman, 2000; Ziegler et al., 2001). Removing these samples increases the explained variation to $R^2 = 0.16$. The solid red line is the RMA fit ($\delta^{81}\text{Br} = 1.82 (\pm 0.14) \times \delta^{37}\text{Cl} + 0.61 (\pm 0.06)$; $R^2 = 0.16$, $n = 724$); the blue dashed line is the Theil-Sen fit ($\delta^{81}\text{Br} = 0.53 (\pm 0.07) \times \delta^{37}\text{Cl} + 0.43 (\pm 0.02)$; $n = 571$, $\text{RSE} = 0.69\text{‰}$).

Unlike the Theil-Sen regression's similarity to the mass-dependent expectation (~ 0.44), the RMA regression accommodates variance from extreme values and yields much higher slope (1.82 ± 0.14), reflecting a small number of relatively high $\delta^{81}\text{Br}$ values. These values affect the overall variance structure and suggest additional processes affecting Br isotopes in specific environments. The evolution of most groundwaters closely resembles the mass-dependent expectation, whereas the higher RMA slope indicates the disproportionate sensitivity of bromine isotopes and ^{81}Br enrichment in a few specific settings. The specific settings or processes might include gaseous bromine exchange or organic matter interactions that do not equivalently influence chlorine isotopes (Hanlon et al., 2017).

Although most samples plot near the Theil-Sen or RMA fit, a small subset of samples exhibits very low $\delta^{37}\text{Cl}$ values relative to $\delta^{81}\text{Br}$ (solid circles in Figure 2-6). These outliers originate from a

tectonically active transition zone where molecular diffusion and membrane ultrafiltration significantly altered $\delta^{37}\text{Cl}$ values without apparently similarly affecting $\delta^{81}\text{Br}$ (Eggenkamp and Coleman, 2000; Ziegler et al., 2001).

The comparative slopes derived from the Theil–Sen and RMA regressions thus provide complementary perspectives on $\delta^{81}\text{Br}$ – $\delta^{37}\text{Cl}$ relationships in groundwater. The Theil–Sen slope aligns with expectations for mass-dependent fractionation, whereas the steeper RMA slope incorporates the full variance, including additional fractionation influences. These reference slopes form an interpretive framework for evaluating isotopic patterns in diverse hydrogeologic settings and will be used in the following sections to assess whether isotopic relationships vary systematically with the geologic age of the host formation.

2.5 Br and Cl Isotopic Variations Across Geologic Periods

To evaluate the origin and evolution of halogen isotopes in groundwater hosted in formations of different geologic periods, $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values and their relationships are compared using the slopes derived from both the RMA and Theil–Sen regressions as interpretive references. In this framework, data clustering near the Theil–Sen slope may suggest the influence of mass-dependent fractionation, while slopes close to the steeper RMA fit likely reflect additional fractionation mechanisms. This comparative approach provides a consistent basis for interpreting isotopic trends across formations of varying geologic age, origin, and diagenetic history. It also facilitates direct comparison between periods by framing observations relative to the same reference slopes.

The compiled database indicates varying ranges of both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values in groundwaters hosted in formations of different geological ages. Across most periods, $\delta^{81}\text{Br}$ values consistently exhibit a wider range than $\delta^{37}\text{Cl}$ values (Table 2-3; Figure 2-7). Mean $\delta^{81}\text{Br}$ values remain positive, while varying between 0.28‰ and 1.07‰ except where data are sparse, whereas mean $\delta^{37}\text{Cl}$ values are generally confined within ± 0.5 ‰ from SMOC. Precambrian- and Paleozoic-hosted groundwaters tend to display the widest $\delta^{81}\text{Br}$ ranges, while younger formations such as those from the Cenozoic exhibit narrower spreads. These patterns might suggest that halogen isotope signatures in groundwater are at least partly modified by the distinct hydrochemical histories associated with each geologic period.

Distributions of $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$, and slopes of $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ (Figure 2-8) vary systematically across geologic periods, providing insights into the processes influencing halogen isotopes over time. Groundwater hosted in Cenozoic formations (Paleogene to Quaternary) typically plot close to the Theil-Sen fit, with smaller spreads and low correlation. In contrast, samples from older formations often exhibit a wider spread for $\delta^{81}\text{Br}$ relative to younger formations and plot more closely to the steeper RMA slope. Paleozoic datasets (Cambrian to Permian) yield OLS slopes of 0.66-2.16, whereas Cenozoic datasets show slopes of 0.05-0.28, the latter indicating a comparably wider range for $\delta^{37}\text{Cl}$. Due to the inability to estimate RMA or Theil-Sen slopes for low-correlation groups or groups with few data points, slope comparisons were based on ordinary least squares (OLS) estimates (Appendix Tables B-1 and B-2). Most period-specific regressions have low coefficients of determination ($R^2 < 0.40$), underscoring that even within a given age group, no single process consistently controls both halogen isotope systems.

Table 2-3. Statistical comparison of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values in waters hosted in rocks from different geological periods.

Era	Period	$\delta^{37}\text{Cl}$ (‰ _{SMOC})						$\delta^{81}\text{Br}$ (‰ _{SMOB})						Time (Ma)
		Mean	Stdev	Min	Max	Range	<i>n</i>	Mean	Stdev	Min	Max	Range	<i>n</i>	
Cenozoic	Quaternary	0.06	0.27	-0.85	0.74	1.59	114	0.38	0.48	-0.97	1.71	2.68	124	2.58 to present
	Neogene	0.01	0.46	-1.44	0.81	2.25	72	0.35	0.33	-0.41	1.22	1.63	69	23.03 – 2.58
	Paleogene*	-0.99 (<i>only one value available</i>)					1	1.46 (<i>only one value available</i>)					1	66.0 – 23.03
Mesozoic	Cretaceous	-0.55	0.49	-1.01	0.16	1.17	5	<i>Not available</i>						145.0 – 66.0
	Jurassic*	-3.23	0.40	-3.86	-2.65	1.21	7	1.07	0.17	0.74	1.27	0.53	7	201.3 – 145.0
	Triassic*	-0.23	0.06	-0.30	-0.18	0.12	5	0.32	0.06	0.28	0.36	0.09	2	251.9 – 201.3
	Permian													298.9 – 251.9
Paleozoic	Carboniferous	0.06	0.43	-0.81	2.07	2.88	74	1.03	0.95	-0.63	3.07	3.70	55	358.9 – 298.9
	Devonian	0.20	0.46	-1.11	1.82	2.93	124	0.77	0.66	-0.42	2.77	3.19	91	419.2 – 358.9
	Silurian	-0.04	0.37	-1.04	0.86	1.90	70	0.28	0.96	-1.29	2.31	3.60	56	443.8 – 419.2
	Ordovician	-0.32	0.35	-1.31	0.47	1.78	104	0.51	0.86	-1.50	2.15	3.65	79	485.4 – 443.8
	Cambrian	-0.11	0.37	-0.90	1.54	2.44	70	0.46	0.75	-1.41	3.35	4.76	59	541.0 – 485.4
	Precambrian	-0.04	0.42	-0.78	1.52	2.30	74	0.86	0.66	0.01	3.30	3.29	69	> 541

*Available from only one study each (see Table 1). Geologic time is based on the definitions of the International Chronostratigraphic Chart v.2020/03 (Cohen et al., 2020).

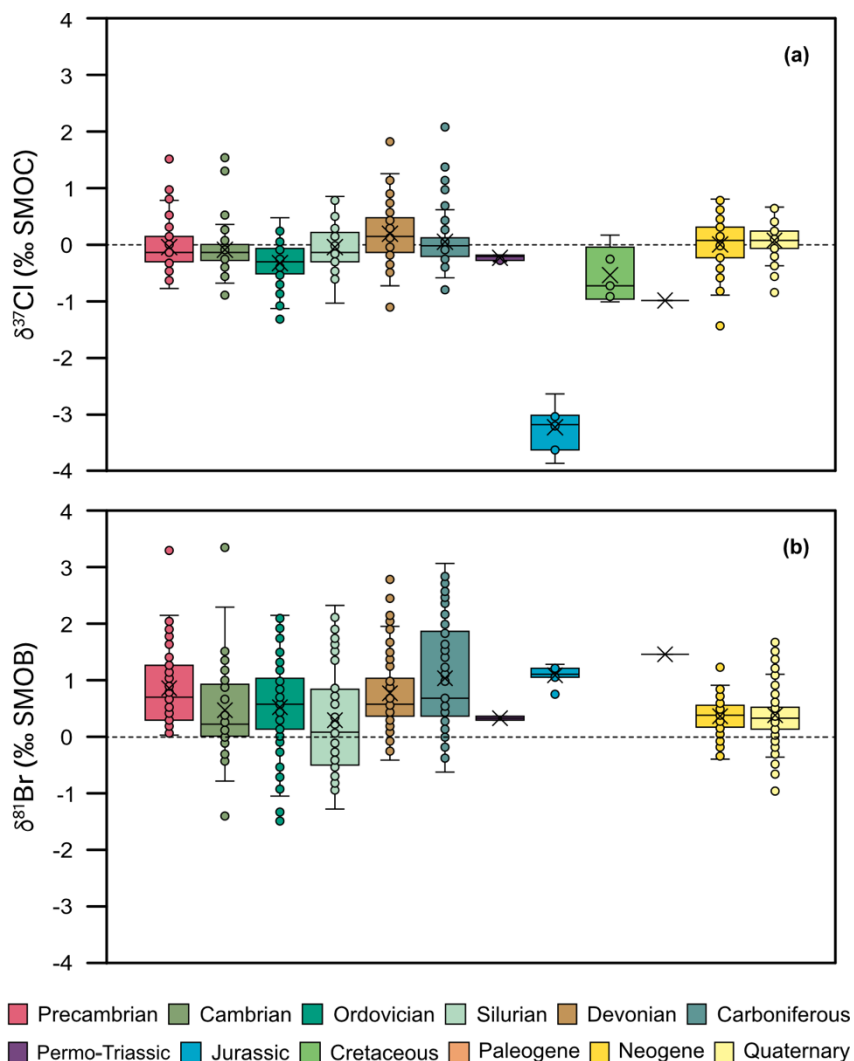


Figure 2-7. Box-and-whisker plot comparing the distribution of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values in waters hosted in rocks of different geologic periods. For each geologic period, circles show individual values; the box spans the interquartile range (IQR), the horizontal bar indicates the median, and the cross mark (x) denotes the mean. Whiskers extend to the minimum and maximum values that are within 1.5*IQR of the lower and upper quartiles; points beyond those limits are plotted as outliers. $\delta^{81}\text{Br}$ data are absent for waters hosted in Cretaceous units, and only single $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values are available for Paleogene units.

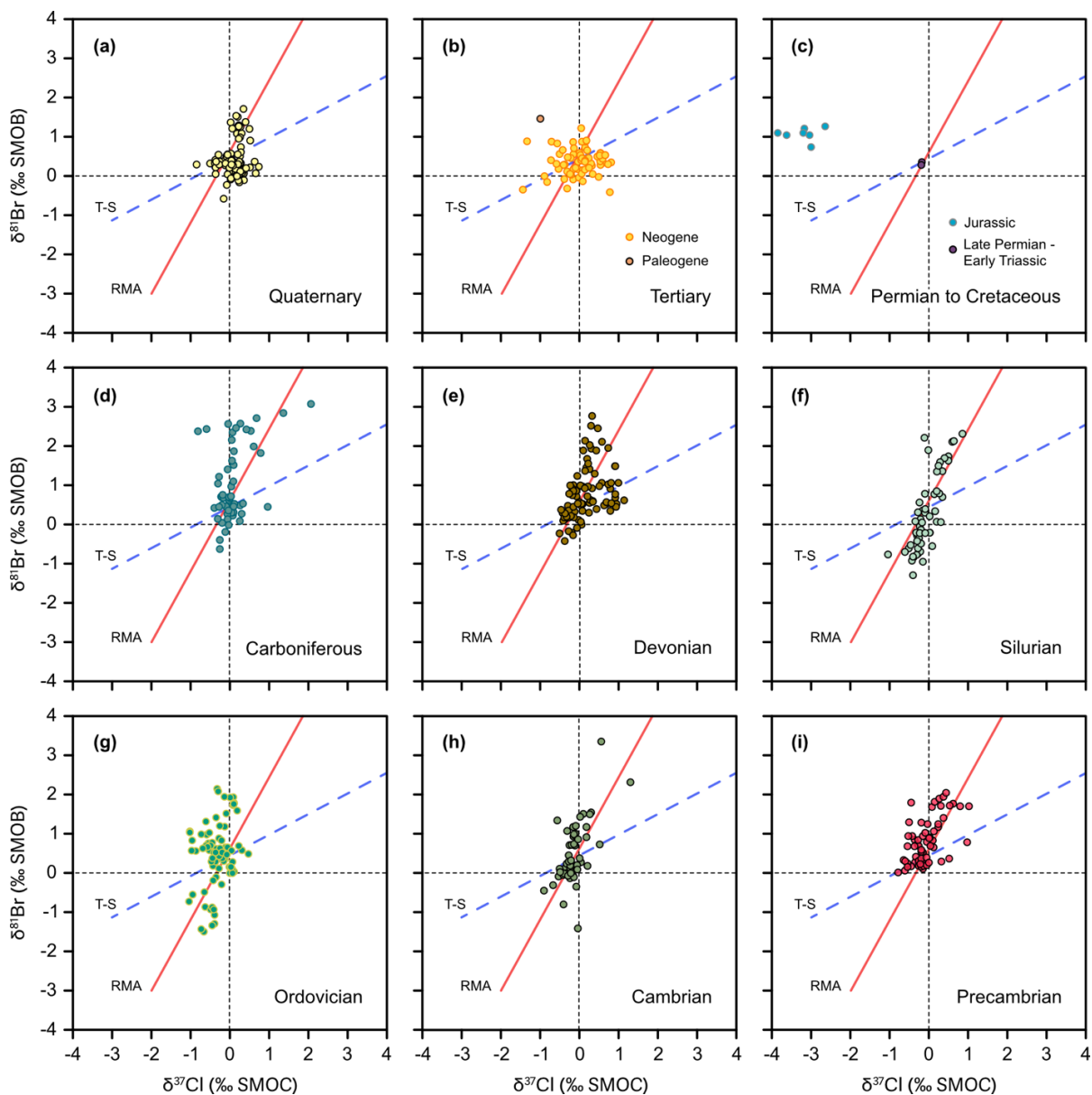


Figure 2-8. Scatterplots of $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ for groundwater samples grouped by host-formation age: (a) Quaternary, (b) Tertiary, (c) Permian–Cretaceous, (d) Carboniferous, (e) Devonian, (f) Silurian, (g) Ordovician, (h) Cambrian, and (i) Precambrian. Each point represents an individual sample, and point colors follow the period legend in panels (b) and (c). Dashed blue and solid red lines are Theil-Sen (T-S) and Reduced Major Axis (RMA) regression slopes, respectively, calculated for the entire dataset (see Section 2.4 and Figure 2-6 for details). Br-Cl log-log plots for the same host-formation ages are available in Appendix Figure A-3.

Interpretations of halogen isotope variations by geological age must consider two key uncertainties. First, while several authors argue that Phanerozoic seawater maintained a nearly constant $\delta^{37}\text{Cl}$ value (Eastoe et al., 2007; Eggenkamp et al., 1995; Kaufmann et al., 1984; Shouakar-Stash, 2008), the long-term evolution of seawater $\delta^{81}\text{Br}$ is poorly constrained. Large seawater $\delta^{81}\text{Br}$ shifts could be inferred from the variation observed in formation waters and from evidence that biological oxidation and redox processes affect Br (Eggenkamp, 2016; Eggenkamp et al., 2016; Shouakar-Stash, 2008). On this basis, some authors have proposed substantial seawater $\delta^{81}\text{Br}$ variation over geologic time (Eggenkamp, 2025; Shouakar-Stash, 2008). Eggenkamp (2016) reached a similar conclusion, but hypothesized only minimal variation throughout the Phanerozoic ($\sim 0.6\%$). Second, groundwaters are generally younger than their host rocks and may inherit evolving mixtures of meteoric recharge, formation waters, and diagenetic fluids, some of which may have migrated from formations of different ages (Holland et al., 2013; Osborn et al., 2012; Stotler et al., 2021). This underlies the rationale for use of primary halite deposits of different ages to assess secular seawater variation (Eggenkamp et al., 2019a). The halite archives indicate only modest variation in $\delta^{81}\text{Br}$ over the past ~ 2 Ga (Eggenkamp et al., 2019a), in contrast to the much larger range observed in formation- and groundwaters. The latter therefore largely reflects diagenetic overprint rather than original seawater composition and variation.

Formation age is often linked to sampling depth in sedimentary basins, but neither $\delta^{81}\text{Br}$ nor $\delta^{37}\text{Cl}$ correlates meaningfully with depth ($R^2 \approx 0.05$; $p < 0.001$). Instead, lithology exerts a strong influence: sedimentary evaporite-rich formations, such as from the Silurian and Ordovician, often exhibit relatively low $\delta^{81}\text{Br}$ values (Shouakar-Stash, 2008 and references therein; Skuce, 2014; Skuce et al., 2015; Short, 2017; Wang, 2017), while Precambrian crystalline terranes with complex lithologies, lacking substantial halite, generally show relatively high $\delta^{81}\text{Br}$ values (Chen et al., 2014; Eissa, 2018; Eissa et al., 2016; Shouakar-Stash, 2008; Stotler et al., 2010). Many Cenozoic samples originate from shallow aquifers where meteoric recharge dilutes halide concentrations and limits fractionation, producing isotopic values near the seawater baseline.

Although differences between geologic periods could suggest secular variation in seawater $\delta^{81}\text{Br}$, they may equally reflect local controls such as variations in initial fluid, lithology and diagenetic history. Depth alone does not explain the observed variability, with gravitational settling at depth proposed as a potential long-term halogen isotope fractionation process (Giunta et al., 2017), depth-

related interpretations require careful consideration. Given the complex interplay of environmental and geological factors, it remains an open question which sample types or terranes would best preserve the seawater bromine isotopic signature. The combined evidence underscores the need for further research to disentangle the influence of evolving ocean chemistry from various processes that shape halogen isotope records. Integrating halite archive records, groundwater datasets, and targeted sampling of diverse lithologies and depths will be essential for clarifying the controls on halogen isotope signatures in subsurface waters.

2.6 Br and Cl Isotope Variations in Groundwater from Different Rock Types

Groundwaters in the dataset were regrouped by host-rock lithology, including crystalline, metamorphic, volcanic, and sedimentary sub-types, to examine how rock-specific water-rock interactions shape Br- and Cl-isotopic signatures (Figure 2-9). This classification allows comparison of isotopic patterns across different geologic settings while retaining regression-based interpretive framework established in Section 2.4 (Figure 2-10). Across lithologies, $\delta^{81}\text{Br}$ values show greater variability than $\delta^{37}\text{Cl}$ values. Mean $\delta^{37}\text{Cl}$ values are all between -0.29‰ and +0.27‰, whereas mean $\delta^{81}\text{Br}$ values are consistently relatively high but vary more by roughly a factor of three (between +0.09‰ and +1.55‰) compared to $\delta^{37}\text{Cl}$. This suggests that bromine isotopes may respond more strongly to water-rock interaction and/or lithology-dependent processes such as halite dissolution-reprecipitation and reflux cycling in evaporite-rich sedimentary basins (Eastoe et al., 2007; Shouakar-Stash, 2008); microbial debromination of organobromine compounds in organic-rich shale- and coal-bearing formations (Shouakar-Stash, 2008; Stotler et al., 2021; Wang, 2017); and high-temperature Br volatilization in volcanic terranes (Pinti et al., 2020; Rizzo et al., 2013). In comparison, chlorine isotopes respond to basin-scale salinity-controlling processes, including evaporation, halite cycling, and large-scale diffusive or membrane filtration (Eastoe et al., 2007; Shouakar-Stash, 2008; Stotler et al., 2010) and therefore exhibit less variation among different lithologies.

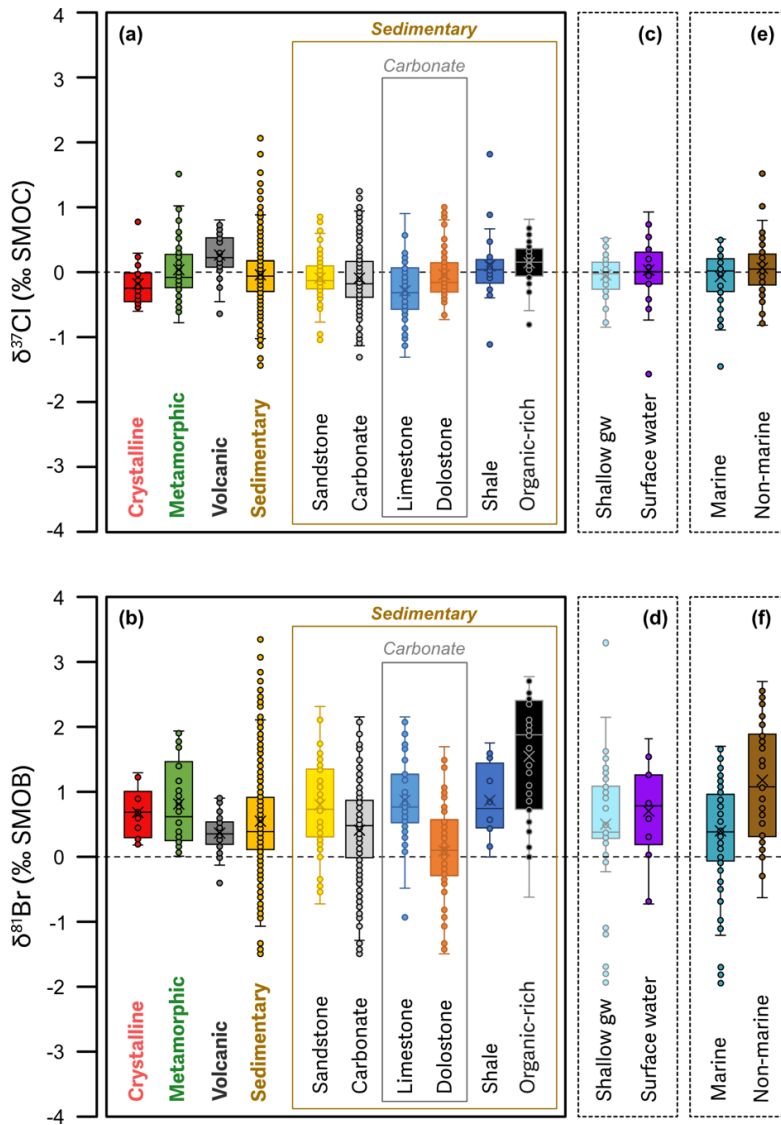


Figure 2-9. Box-and-whisker plots of $\delta^{37}\text{Cl}$ (top; a, c, e) and $\delta^{81}\text{Br}$ (bottom; b, d, f) for water bodies from various settings. (a, b) Groundwater grouped by host-rock lithology (crystalline, metamorphic, volcanic, sedimentary, and sedimentary sub-types). (c, d) (Near-)surface waters (shallow groundwater <5 m, creeks, lakes, springs). (e, f) Terrigenous vs. marine groundwater. Each box spans the inter-quartile range (IQR); the central bar marks the median; crosses (×) indicate the mean; whiskers extend to the smallest and largest values within $1.5 \times \text{IQR}$. Circles indicate individual data points, and those beyond the whiskers are statistical outliers ($<Q_1 - 1.5 \text{ IQR}$ or $>Q_3 + 1.5 \text{ IQR}$). Note: some overlaps occur (e.g., Carbonate includes Limestone and Dolostone); samples lacking clear lithologic description of host-rock are not shown.

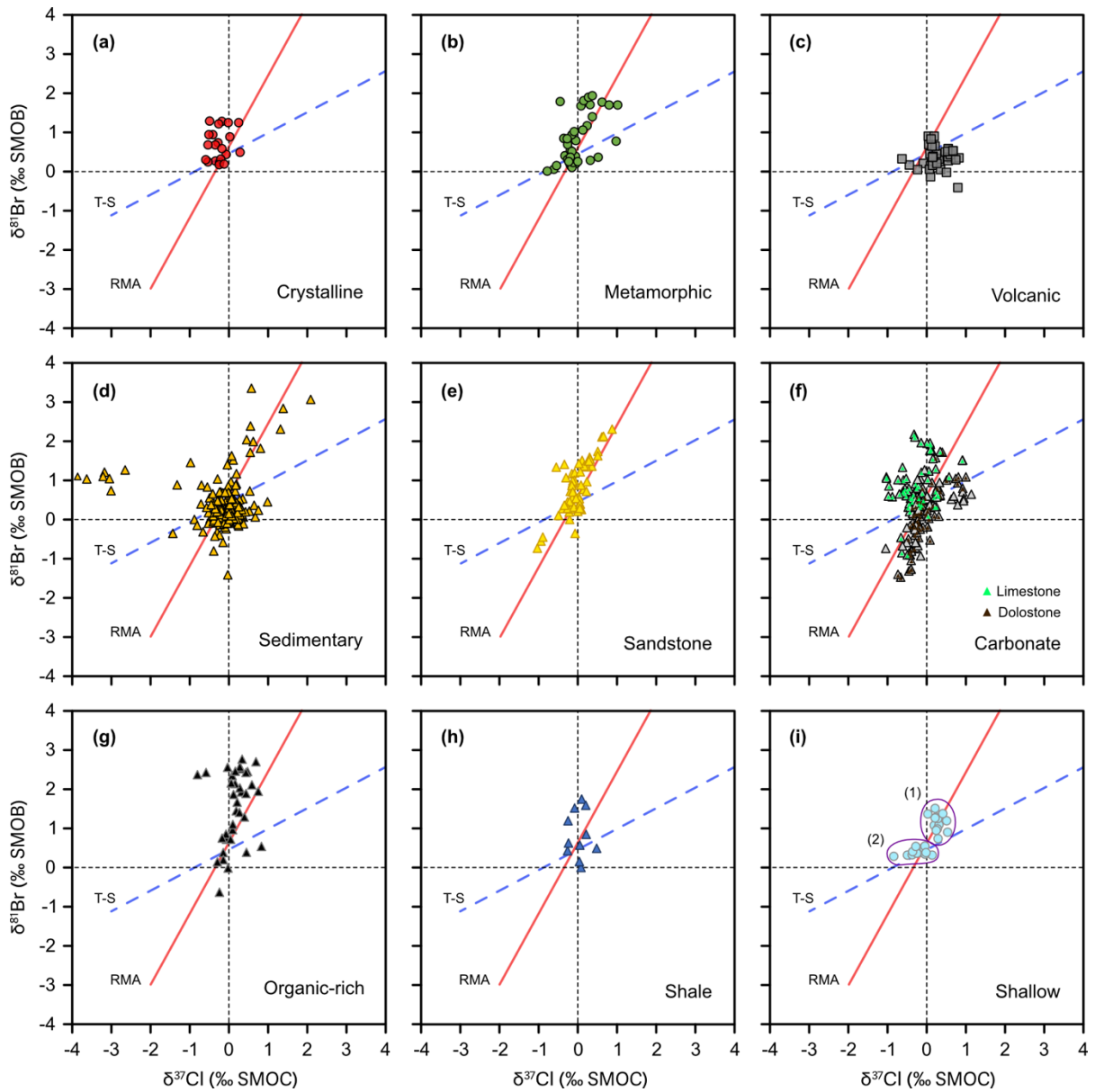


Figure 2-10. $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ for groundwaters grouped by host-rock lithology. Panels (a-i) correspond to crystalline, metamorphic, volcanic, undifferentiated sedimentary, sandstone, carbonate (limestone, dolostone), organic-rich, shale, and shallow aquifer groundwaters. Only samples with both isotopes measured are plotted; hence some data shown in Figure 2-9 are absent here. Dashed blue and solid red lines represent Theil-Sen (T-S) and Reduced Major Axis (RMA) regression slopes, respectively, calculated for the entire dataset (see Section 2.4 and Figure 2-6 for details). Corresponding log-log Br-Cl plots are in Figure 2-4.

2.6.1 Crystalline, Metamorphic, and Volcanic Settings

In **crystalline** rocks (those not specified whether igneous, sedimentary or metamorphic by the original authors), $\delta^{37}\text{Cl}$ values are often relatively low while $\delta^{81}\text{Br}$ values are relatively high (Figure 2-9b and Figure 2-10a). The Br-Cl concentrations typically plot near the seawater evaporation trajectory (SET; Figure 2-4), which could imply slightly evaporated seawater diluted by meteoric recharge (McCaffrey et al., 1987; Rittenhouse, 1967). However, fluids hosted in many crystalline rocks have complex histories of water-rock interactions that can affect fluid chemistry even though they plot along or near the SET (Boumaiza et al., 2024; Frape et al., 2014). The lack of linear trend between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ suggests that no single process governs both halide isotope systems simultaneously. Some crystalline-hosted waters show large variations in $\delta^{81}\text{Br}$ while $\delta^{37}\text{Cl}$ values remain within a smaller range, suggesting processes that selectively mobilize or fractionate Br, such as mixing with Br-rich fluids or mineralogical controls that reduce Br retention (e.g., Br release from felsic lithologies) (Stotler et al., 2010). Conversely, others show a wide range in $\delta^{37}\text{Cl}$ but little change in $\delta^{81}\text{Br}$, consistent with selective Cl fractionation through diffusive filtration or serpentinite-related Cl-removal (Frape et al., 2007; Stotler et al., 2010), processes that do not fractionate the two halides in the same way. When compared with the dataset-wide correlations established earlier (Section 2.4), most crystalline-rock samples deviate from both the Theil–Sen reference or RMA slope, likely reflecting localized leakage or diffusive processes of either Br or Cl.

In **metamorphic** settings, $\delta^{81}\text{Br}$ values remain relatively high, yet both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values span a broader range than in most crystalline and volcanic-hosted samples (Figure 2-9b). When compared with the overall dataset correlations, most metamorphic-hosted samples plot near the RMA or Theil–Sen slopes but include notable outliers of relatively high $\delta^{81}\text{Br}$ values with variable $\delta^{37}\text{Cl}$ values. The scatter is greatest in low Br concentration samples, while at higher Br concentrations, above a few hundred mg/L, the $\delta^{81}\text{Br}$ range narrows to $\sim 0.3\text{‰}$ (see Appendix Figure A-4). Multiple processes in metamorphic settings, such as high-temperature/pressure water-rock interactions, redox changes, and diffusion during metamorphic uplift, strongly modify halogen abundances and can fractionate Br isotopes, leading to net removal of Br from the groundwater system (Hammerli and Rubenach, 2018; Stotler et al., 2010). Thus, the low-Br samples with varying $\delta^{81}\text{Br}$ values may capture an early stage of metamorphic volatilization, with the preferential loss of ^{79}Br . Conversely, continued circulation through low-permeable networks can result in selective loss of Cl through diffusion and/or membrane

filtration, while interaction with mafic/ultramafic host rocks may supply additional Br. Evidence for the existence of such long-residence fluids in metamorphic settings is supported by studies of ancient, chemically evolved deep groundwater, some of which have been preserved for millions to billions of years (Boumaiza et al., 2024; Holland et al., 2013; Warr et al., 2018). In this context, the narrow $\delta^{81}\text{Br}$ range with elevated Br concentration, and a lack of a clear marine signature might reflect an end-member representing long-residence fluids that have undergone substantial geochemical evolution in a nearly closed system.

The $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values in groundwaters from **volcanic** settings tend to cluster near zero, but lie predominantly in the first quadrant of the $\delta^{81}\text{Br}$ – $\delta^{37}\text{Cl}$ plot (Figure 2-10c). In these settings, Br–Cl concentrations generally remain below halite saturation with relatively low Br/Cl ratios, mostly consistent with previously reported values for volcanic rocks (Dolejš and Zajacz, 2018 and references therein). These may be attributed to the preferential loss of Br as volatile species through high-temperature processes or from diffusion during volcanic deposition (Hanley and Koga, 2018; Symonds et al., 1994). While such gaseous loss appears to leave $\delta^{37}\text{Cl}$ values relatively unaffected (Pinti et al., 2020; Rizzo et al., 2013), $\delta^{81}\text{Br}$ values can shift either toward enrichment in ^{81}Br if ^{79}Br is lost in the vapor/gaseous phase, or toward depletion in ^{81}Br if ^{81}Br is partitioned into volcanic glass. The overall distribution of $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values is not well explained by either the Theil–Sen or RMA slopes, suggesting that high-temperature volcanic processes affect bromine and chlorine isotopes in ways distinct from other lithologies.

2.6.2 Sedimentary Settings

Groundwaters hosted in sedimentary rocks exhibit the widest ranges in both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values and are typically accompanied by high total dissolved solids (TDS) values. Mean TDS is ~170 g/L, considerably higher than for crystalline (84 g/L), metamorphic (57 g/L), and volcanic (44 g/L) settings. This elevated salinity often indicates extreme evaporation and/or prolonged water-rock interaction (Rittenhouse, 1967; Carpenter, 1978; Kharaka and Hanor, 2003; Shouakar-Stashet al., 2007). To explore how lithology-specific processes influence Br and Cl isotope systematics, sedimentary-hosted samples are subdivided further by dominant lithology (e.g., sandstone, carbonate, shale, and organic-rich units), based on the best available geological descriptions (Figure 2-10d to h).

Sandstone-hosted groundwaters exhibit the strongest correlation between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values ($R^2 \approx 0.57$, $p < 0.001$; Figure 2-10e) and a similarly high correlation between Br and Cl concentrations that plot just below the SET (Figure 2-4e). Although the Br-Cl pattern is consistent with meteoric dilution of slightly evaporated seawater, the isotope data suggests complexity beyond simple mixing. A high OLS slope of ~ 1.4 in $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ indicates that $\delta^{81}\text{Br}$ varies much more widely than $\delta^{37}\text{Cl}$. Such a steep slope is inconsistent with processes that strongly fractionate Cl (e.g., ongoing halite precipitation/dissolution or matrix diffusion). Compared to the Theil-Sen and RMA slopes for the overall dataset, sandstone-hosted samples plot close to the RMA fit but deviate from the Theil-Sen fit, the latter representing the major data cloud and close to the mass-dependent fractionation expectation. This deviation reinforces the interpretation that Br-specific enrichment dominates over mass-dependent fractionation in these settings. The data instead suggests selective addition of Br-enriched brines that have migrated from deeper basin strata or adjacent formations. Repeated halite reflux or interaction with organic-rich layers at depth can enrich these brines in Br without greatly perturbing Cl; subsequent mixing with meteoric recharge in overlying sandstones broadens $\delta^{81}\text{Br}$ while leaving $\delta^{37}\text{Cl}$ comparatively unchanged.

Groundwaters hosted in **carbonate**-dominated rocks show a characteristic distribution in $\delta^{81}\text{Br}$: values are frequently low in dolostone-dominated settings but relatively high in limestone-dominated settings (Figure 2-9 and Figure 2-10f). Dolomitization, a process that removes Mg from the groundwater thereby lowering Mg/Ca ratios, can coincide with elevated Br contents in the rock matrix, particularly where early cementation or local hydrothermal circulation has affected dolomite (Johnson et al., 2009; Schoenherr et al., 2009); it could therefore also affect $\delta^{81}\text{Br}$ values. A plausible isotopic fractionation mechanism is selective removal of Br, with ^{81}Br preferentially removed, into dolomite cements or as fluid inclusions, leaving the residual fluid isotopically light while exerting little influence on Cl. Dedolomitization, in contrast, is commonly driven by meteoric water or Ca-rich brines and also can be initiated when gypsum dissolution supplies Ca, triggering dolomite dissolution (Back et al., 1983; Plummer et al., 1990). This reaction should release Br previously sequestered during dolomitization (potentially enriched in ^{81}Br), without adding equivalent amount of Cl; subsequent mixing can then modify $\delta^{37}\text{Cl}$, making both isotopes vary. Carbonate-hosted groundwaters plot close to either the RMA or Theil-Sen fit, suggesting that multiple overprinting processes affect the overall isotopic values rather than a single dominant process. The combined effect of ^{81}Br

sequestration during dolomitization and release during dedolomitization, with selective Cl modification during mixing, likely explain the dual isotope trends observed in Figure 2-10f.

Organic-rich aquifers exhibit the widest $\delta^{81}\text{Br}$ range, yet $\delta^{37}\text{Cl}$ values remain narrowly distributed near 0‰ (Figure 2-10g). Br concentrations are generally high, implying organically driven Br release into groundwater or extensive evaporite cycling (Figure 2-4g). When plotted against the overall dataset slopes, organic-rich samples deviate from the Theil–Sen fit and scatter around the RMA fits, underscoring the dominance of local (bio)geochemical and mixing processes rather than a single mass-dependent fractionation trend. Two orthogonal trends are evident: a vertical trend (high $\delta^{81}\text{Br}$ values at near-constant $\delta^{37}\text{Cl}$) likely driven by microbial debromination of organobromine compounds, which preferentially consume ^{79}Br without affecting Cl; and a horizontal trend ($\delta^{37}\text{Cl}$ shifts at near-constant $\delta^{81}\text{Br}$) attributed to mixing with halite-derived Cl, leaving $\delta^{81}\text{Br}$ almost unchanged (Shouakar-Stash, 2008; Stotler et al., 2021; Wang, 2017). Together, these patterns suggest a decoupling of Br and Cl isotope fractionation pathways, with organic-matter degradation being the primary driver of Br isotope variability while Cl is largely controlled or remains buffered by regional Cl-rich brines. The mechanisms related to organic matter and associated redox conditions are discussed further in Section 2.8.3.

In **shale**-dominated aquifers, $\delta^{81}\text{Br}$ values vary less than in organic-rich settings, and $\delta^{37}\text{Cl}$ remains narrowly distributed near 0‰ (Figure 2-10h). Here, the shale group refers to units not classified as organic-rich (i.e., excluding organic-rich shales that are considered separately in the previous paragraph), and therefore generally represents shales with low to moderate organic content. Br concentrations are typically lower, likely reflecting the limited presence of organic matter. Isotopic patterns instead imply halide exchange with clay minerals and diffusive release from long-residence formation waters trapped within the low-permeable shale matrix (Shouakar-Stash, 2008; Wang, 2017). Some clay mineral surfaces often retard Cl more strongly than Br, allowing Br to be released more readily. In contrast, diffusion often mobilizes Cl more rapidly than Br, due to its smaller hydrated radius, gradually increasing Br/Cl ratios in residual porewaters. The net effect thus depends on the balance between these two processes. Shale aquitards can therefore act as both reservoirs and sources for halides, yielding measurable isotope fractionation. While organic-rich shales are excluded from this group, shale-rich successions may still contain localized intervals with elevated organic content; in such cases, biogeochemical processes (e.g., microbial debromination) could further contribute to Br isotope variability. Shale-hosted groundwaters commonly deviate from the Theil-Sen

fit and plot around the RMA, suggesting that lithology-specific interactions exert the dominant control on Br and Cl isotopes.

2.6.3 Shallow Aquifers

Shallow groundwaters from coastal and sabkha regions (< 5 m, locally ≤ 10 -20 m in some hand-dug wells) plot near, but not exactly on, the SET in the Br-Cl diagram (Figure 2-4i). In the log-log Br-Cl plot, as well as in the $\delta^{37}\text{Cl}$ vs. $\delta^{81}\text{Br}$ plot (Figure 2-10i), these waters fall into two distinct compositional groups ((1) and (2) in Figure 2-10i and Figure 2-4i). The first group (1) contains brines with high Cl and Br concentrations but Br/Cl ratios lower than seawater, indicating a dominant halide contribution from halite dissolution by brine, which maintains high Cl concentrations. This group shows a slightly wider $\delta^{81}\text{Br}$ range with narrow $\delta^{37}\text{Cl}$. The second group (2) plots just below the SET and remains below halite saturation (saturation index with respect to halite < 0 , calculated using PHREEQC), representing mixing of evaporated seawater with fresher meteoric recharge ((2) in Figure 2-4i). In this group, $\delta^{37}\text{Cl}$ variability slightly exceeds that of $\delta^{81}\text{Br}$, likely reflecting variable $\delta^{37}\text{Cl}$ input or deposition.

Two main processes appear to account for the combined Br-Cl concentration and isotope patterns. First, mixing with other brines, particularly ascending geologic brines from deeper formations, or dissolution of halite by these geologic brines (Saeed et al., 2021) can maintain high Cl concentrations while lowering Br concentrations. Without significant halite precipitation, this process largely preserves the original $\delta^{37}\text{Cl}$ signature, while minor changes in $\delta^{81}\text{Br}$ is possible. Second, dilution by meteoric- and/or seawater in coastal areas lowers Cl concentrations increases Br/Cl ratios, and generally leaves $\delta^{81}\text{Br}$ values clustered near zero, with $\delta^{37}\text{Cl}$ values varying according to the proportion and isotopic composition of those inputs (Eissa et al., 2016; Gwynne et al., 2013; Shouakar-Stash, 2008). Even small contributions can alter the original $\delta^{37}\text{Cl}$ signature in low Cl waters. In addition, surface-related processes described in Section 2.8.4, such as volatilization, and photolytic or microbial oxidation, can selectively enrich ^{81}Br without significantly affecting $\delta^{37}\text{Cl}$, further broadening the $\delta^{81}\text{Br}$ range observed in some shallow aquifers. Overall, the relatively larger $\delta^{37}\text{Cl}$ range observed in certain shallow aquifers (Figure 2-10e, f) may reflect external Cl sources and largely trace the proportion meteoric input, such as the input of low $\delta^{37}\text{Cl}$ values via precipitation (Eastoe, 2016), whereas the broader $\delta^{81}\text{Br}$ spread likely reflects a combination of various brine mixing and potential surface-related processes.

2.6.4 Marine versus Terrigenous Systems

Groundwaters hosted in marine versus terrigenous settings show contrasting halide isotopic patterns that may reflect differences in halide sources, hydrochemical evolution, and associated fractionation processes. Marine-sourced groundwaters, typically from coastal aquifers or formations of known marine depositional origin, have both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values centered near 0‰ (mean $\delta^{37}\text{Cl} = -0.07 \pm 0.38\text{‰}$; mean $\delta^{81}\text{Br} = +0.41 \pm 0.79\text{‰}$), but with a substantial spread (Figure 2-9e, f). By contrast, non-marine groundwaters, defined here as those from terrigenous geological settings with minimal direct seawater influence, more frequently exhibit relatively high values in both isotopes (mean $\delta^{37}\text{Cl} = +0.06 \pm 0.43$; mean $\delta^{81}\text{Br} = +1.19 \pm 0.91$).

In marine systems, halides are primarily inherited directly from seawater, resulting in isotope compositions that remain near the marine baseline. In contrast, terrigenous systems evolve without continuous marine input and often receive continental solutes from local lithology and weathering, including Ca, Mg, SO_4 , and HCO_3 -rich inputs (Deocampo and Jones, 2013). Such differences in major ion chemistry influence the type and sequence of mineral precipitation, leading to hydrochemical evolution pathways that diverge from those of marine environments. Thus, the overall enrichment in both ^{81}Br and ^{37}Cl observed in terrigenous groundwaters likely reflects a combination of solute sources enriched in the heavier isotopes and water-rock interactions that preferentially remove lighter isotopes or progressively enrich heavier isotopes over time.

2.7 Hydrochemical Controls on Br and Cl Isotopic Signatures

The halogen isotope behavior in groundwater systems suggests a complex interplay of source fluids, evaporative concentration, mineral precipitation, and water-rock interactions. Although bromine and chlorine share similar chemical properties and generally behave conservatively, their isotopic systems often respond differently to secondary processes, sometimes showing contrasting distributions (Eissa et al., 2016; Gwynne et al., 2013; Wang, 2017). In formation waters, the chlorine isotope system is primarily controlled by the original seawater input and modestly modified by processes such as halite dissolution, subareal evaporation, shale dewatering, and diffusion (Eastoe et al., 2001; Eggenkamp, 2025). In contrast, bromine isotope fractionation pathways are less clearly understood and appear to be influenced by additional processes that have yet to be fully elucidated (Eggenkamp, 2014a; Eggenkamp et al., 2019b; Eissa et al., 2016). To better understand the isotopic distribution and behavior of both halides, key hydrochemical parameters, including salinity (i.e., total dissolved

solids), ion concentrations and their ratios, and conservative tracers such as lithium, are examined here as indicators of the processes influencing both halide isotopic systems.

2.7.1 Trends with Total Dissolved Solids (TDS)

Groundwater samples with available major ion concentrations are classified into three groups based on total dissolved solids (TDS), following the classification by Robinove et al. (1958): fresh (<1 g/L), saline (1-35 g/L), and brine (>35 g/L). Although Robinove et al. (1958) and other schemes (National Ground Water Association, 2010; Winslow et al., 1968) further subdivide the saline range (e.g., slightly, moderately, and very saline) or apply alternate terms such as “brackish” depending on application context, the Robinove et al. (1958) classification is a practical approach centered around seawater salinity (~35 g/L) for hydrochemical interpretation.

Distinct variations in $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values are observed across the three salinity classes (Table 2-4; Figure 2-11). Freshwater samples exclusively display relatively high $\delta^{81}\text{Br}$ values, whereas $\delta^{37}\text{Cl}$ values remain narrowly distributed around 0‰. As salinity increases, $\delta^{81}\text{Br}$ values in both saline waters and brines exhibit broader distributions, with more samples showing relatively low $\delta^{81}\text{Br}$ values more frequently: ~6.5% of saline samples (11 of 169) and over 20% of brine samples exhibit $\delta^{81}\text{Br}$ values < 0‰. The mean $\delta^{81}\text{Br}$ also decreases with increasing TDS, from 1.07‰ in freshwater to 0.63‰ in saline water and +0.57‰ in brine. Conversely, $\delta^{37}\text{Cl}$ values remain less variant across salinity classes (Table 2-4), with only a few brines showing very low values.

Table 2-4. Summary of bromine and chlorine isotopic values in groundwater, categorized by total dissolved solids (TDS) values into fresh (<1 g/L), saline (1-35 g/L), and brine (>35 g/L). For each group, the mean $\pm$ standard deviation, range, and sample count (*n*) are shown.

Water Type	$\delta^{81}\text{Br}$ Mean (‰)	$\delta^{81}\text{Br}$ Range (‰)	<i>n</i>	$\delta^{37}\text{Cl}$ Mean (‰)	$\delta^{37}\text{Cl}$ Range (‰)	<i>n</i>
Fresh	+1.07 $\pm$ 0.78	+0.07 to +2.15	6	+0.03 $\pm$ 0.28	-0.42 to +0.58	12
Saline	+0.63 $\pm$ 0.65	-1.81 to +3.35	169	+0.03 $\pm$ 0.49	-1.44 to +2.07	197
Brine	+0.57 $\pm$ 0.86	-1.94 to +2.84	363	-0.13 $\pm$ 0.56	-3.86 to +1.54	421

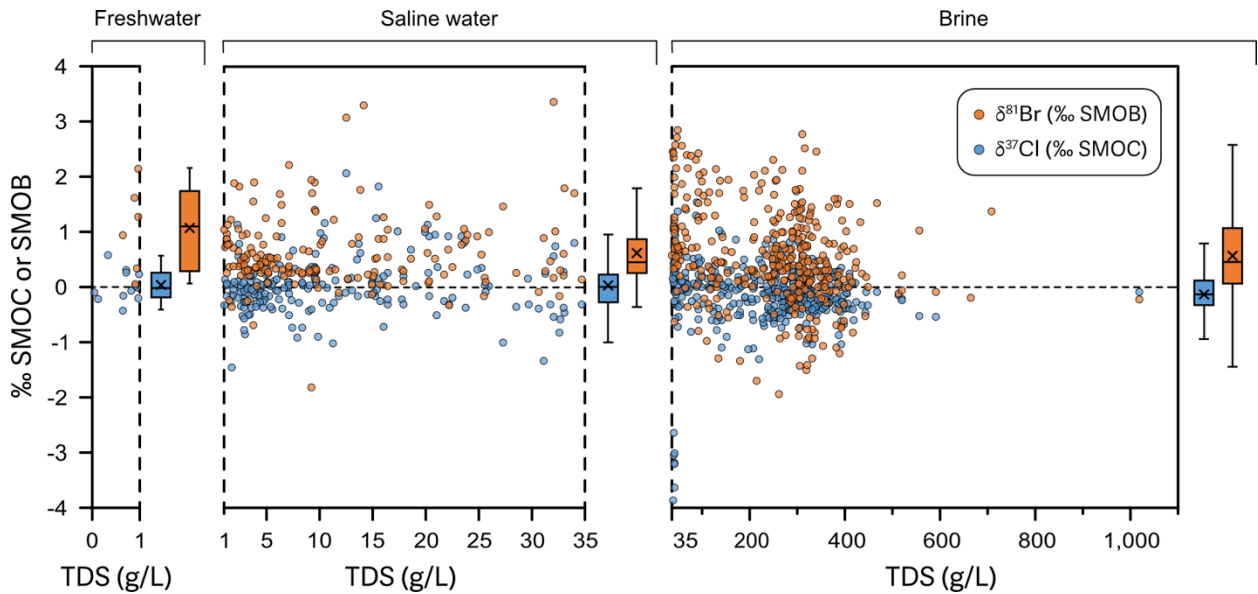


Figure 2-11. Distributions of $\delta^{81}\text{Br}$ (orange) and $\delta^{37}\text{Cl}$ (blue) values plotted against total dissolved solids (TDS, g/L), classified into freshwater (<1 g/L), saline water (1-35 g/L), and brine (>35 g/L). Box plots on the right of each scatterplot summarize the data distributions, showing means (crosses), medians (central lines), and interquartile ranges (IQR) with whiskers extending to the minimum and maximum values excluding outliers beyond 1.5*IQR.

These patterns imply that bromine isotopes are more susceptible to fractionation at elevated salinity. In low-TDS settings, processes favoring the retention of ^{81}Br (or removal of ^{79}Br) appear to dominate. Yet, the substantial $\delta^{81}\text{Br}$ variability observed in brines, despite their high bromide concentrations, suggests that isotopic shifts likely involve active fractionation processes at higher salinity. However, in higher salinity conditions, the broadening of $\delta^{81}\text{Br}$ distributions suggests the presence of overlapping or competing fractionation mechanisms with different directions and magnitudes.

2.7.2 Evaporative Concentration and Mineral Precipitation

Evaporation fundamentally modifies groundwater chemistry by concentrating solutes and promoting sequential mineral precipitation. These processes, which occur in both surface and subsurface environments, progressively reshape the composition of the residual brine and affect the distribution of bromine and chlorine (Carpenter, 1978; Deocampo and Jones, 2013; McCaffrey et al., 1987;

Rittenhouse, 1967). The chemical evolution depends strongly on the initial solution stoichiometry and its subsequent change during evaporation (Rittenhouse, 1967; Carpenter, 1978; McCaffrey et al., 1987; Deocampo and Jones, 2013).

In marine systems, the evaporative mineral precipitation sequence is well established and leads to systematic changes in Br/Cl ratios. Modern seawater follows a sequence of calcite → gypsum → halite → Mg- and K-salts. Halite, the first precipitate that incorporates Cl as a major component, initially tends to exclude Br but gradually incorporates increasing amounts as evaporation proceeds, thereby increasing the Br/Cl ratios in the residual brine (Braitsch, 1971; Siemann and Schramm, 2000). Later-forming minerals, such as polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), can incorporate up to several hundred ppm Br, although this may vary with hydrochemical conditions (Braitsch, 1971; Deocampo and Jones, 2013; Eggenkamp, 2025). Br incorporation into evaporite minerals is thought to occur through multiple pathways: substitution for crystal lattice (e.g., Cl in halide minerals), as well as entrapment in fluid inclusions, or surface adsorption (e.g., gypsum, polyhalite). The relative importance of these mechanisms likely varies with mineralogy and depositional setting.

Non-marine systems exhibit different chemical evolution pathways. Groundwaters in terrigenous settings or closed-basin alkaline lakes often begin low Ca^{2+} and elevated HCO_3^- , Na^+ and K^+ concentrations; these conditions favor the precipitation of Na-carbonates (e.g., trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$), gaylussite ($\text{CaCO}_3\text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$), natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)) long before halite forms, and gypsum may not precipitate (Deocampo and Jones, 2013). In these settings, the Br distribution coefficients between salt and brine are poorly constrained (Eggenkamp, 2025); Br could be sequestered earlier, adsorbed onto Na-carbonate salts, or retained in the evolving brine until later stages. These uncertainties complicate direct comparison of Br behavior between marine and non-marine evaporitic systems.

Consequently, equivalent TDS values in marine and terrestrial environments do not reflect equivalent fluid evolution, mineral assemblages, or halogen partitioning behavior. Differences in the geochemical context between marine and non-marine settings must be considered when interpreting $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values. The following subsections examine the $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values with evaporation-related processes in two steps: (1) the use of lithium concentration as a proxy for

evaporation progress, and (2) the isotopic evolution of Br and Cl during evaporation and mineral precipitation stages.

2.7.2.1 Lithium Concentration as a Proxy for Evaporation

Lithium (Li) serves as a conservative tracer for evaporation because it remains largely in solution and is minimally incorporated into precipitating minerals. Its progressive concentration during evaporation makes it a useful proxy for assessing the extent of evaporative evolution. In modern seawater, Li concentration is around 0.17 $\mu\text{g/g}$ and rises steadily as evaporation proceeds; it reaches about 1.37 $\mu\text{g/g}$ at the onset of halite precipitation, 4.57 $\mu\text{g/g}$ at polyhalite precipitation, and continues to rise during subsequent sulfate and chloride salt precipitation stages (Mertineit and Schramm, 2019).

In this study, Li concentration data are available for 302 samples, with measured values ranging between 0.003 and 366 mg/L. Most of the concentrations fall far below the threshold typically associated with Li-bearing mineral precipitation. While Li precipitation thresholds can vary, concentrations exceeding $\sim 1,000$ mg/L are commonly associated with the Li_2SO_4 formation, and some brines may exceed 20,000 mg/L without significant formation of Li-bearing salts, depending on the brine composition (Ogawa et al., 2014). The observed range in the dataset is therefore consistent with conservative Li behavior, supporting its use as an evaporation intensity index.

Li concentrations exceeding ~ 26 $\mu\text{g/g}$ in brines have previously been interpreted as possible indicators of additional inputs, such as pegmatites, dissolution of Li-bearing silicates, or hydrothermal sources (Bradley et al., 2017; Lindsey et al., 2021; Sharma et al., 2022). However, no such lithologic contributions are evident in the present dataset, and there is no geologic evidence for Li-bearing lithologies in the sampled regions. This absence of external sources supports the interpretation that Li enrichment in these samples primarily reflects progressive evaporative concentration rather than lithologic contributions.

2.7.2.2 $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ during Evaporative Mineral Precipitation

To evaluate how progressive evaporation and mineral precipitation influence halogen isotope behavior, $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values are examined in relation to Li concentrations, which serve as a proxy for evaporation extent (Figure 2-12). As evaporation progresses and minerals sequentially precipitate, the isotope systems of bromine and chlorine respond differently due to variations in how Br and Cl

are incorporated into minerals. For chlorine, residual brine typically becomes isotopically lighter with evaporite mineral precipitation, reflecting the preferential incorporation of ^{37}Cl into precipitating minerals such as halite (Eastoe et al., 2007, 2001; Eggenkamp et al., 1995; Luo et al., 2012). Consequently, $\delta^{37}\text{Cl}$ values in the residual brine tend to become lower, decreasing further at later stages during K, Mg-chloride mineral (e.g., carnallite, bischofite) precipitation (Figure 2-12b).

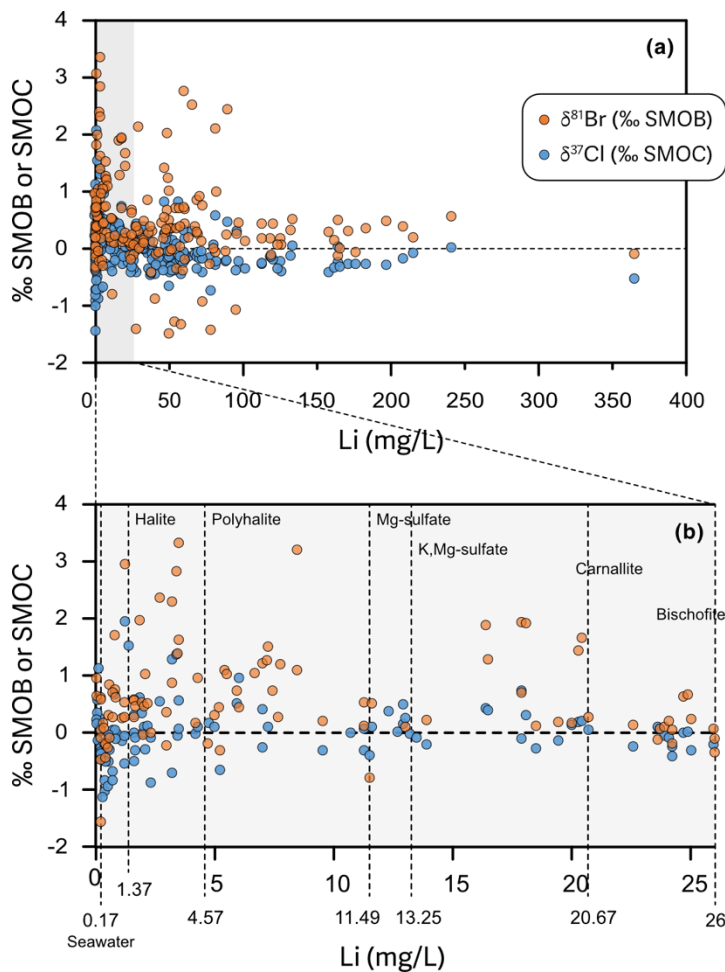


Figure 2-12. Bromine and chlorine isotope values versus lithium concentrations. (a) Full Li concentration range for the dataset; (b) Expanded view of the Li concentration range associated with evaporative mineral precipitation.

Bromine isotopes, however, exhibit a more complex, non-monotonic trend across mineral precipitation stages. At early stages ($\text{Li} < \sim 1.37 \text{ mg/L}$), $\delta^{81}\text{Br}$ values tend to increase, suggesting that ^{79}Br is preferentially incorporated into early-forming minerals, potentially including calcite (or aragonite), gypsum, or early halite, thus enriching the residual brine in ^{81}Br . As evaporation continues and Li concentrations increase above $\sim 5 \text{ mg/L}$, $\delta^{81}\text{Br}$ values decrease, then increase again during sulfate mineral precipitation (e.g., epsomite, kainite), followed by another variation associated with carnallite and bischofite, with variations within each mineral precipitation stage. This variable $\delta^{81}\text{Br}$ trends likely reflect a mineral-specific fractionation dynamics, such as changes in dominant Br-partitioning pathways and competing fractionation effects.

Experimental observations provide insight into potential mechanisms for these trends (*Chapter 3*). In early stages, Br may be incorporated into calcite, aragonite, or gypsum via lattice substitution or physical entrapment (e.g., fluid inclusion, surface occlusion). Aragonite, in particular, may prefer ^{79}Br incorporation, contributing to early ^{81}Br enrichment in the brine. Halite typically excludes Br from its lattice, but rapid crystallization can result in Br entrapment through fluid inclusion, occlusion, or lattice-substitution. In later stages, hydrous minerals may incorporate Br through substitution at hydrated sites, where competition with OH^- or H_2O for structural sites and changes in Br hydration state can influence isotope partitioning (Bureau and Métrich, 2003; Louvel et al., 2020). For minerals like carnallite and bischofite, a preferential incorporation of ^{79}Br has been proposed (Eggenkamp et al., 2019b). Although these mechanisms are not yet fully quantified, they help explain the complex $\delta^{81}\text{Br}$ trends observed during progressive evaporation and support the greater sensitivity of bromine isotopes to mineralogical and chemical changes compared to chlorine.

2.7.3 Water-Rock Interaction

2.7.3.1 Halite Dissolution

The dissolution of evaporitic minerals, particularly halite, can significantly modify fluid halogen signatures. Halite dissolution and seawater evaporation followed by halite precipitation produce distinct hydrochemical signatures that can be differentiated using major ion concentrations and their ratios (e.g., Na, Ca, Cl, Br, Br/Cl, Ca/Na). These parameters are used in this study to define two compositional groups in the dataset (Figure 2-13b to d). Group 1 is characterized by Br/Cl ratios $< \sim 0.001$, a near unity Na-Cl trend, and Na concentrations greater than Ca, consistent with dissolved halite (Deocampo and Jones, 2013; Eastoe et al., 2001; Eggenkamp, 2025). Group 2 shows elevated

Br/Cl ratios, Cl/Na molar ratios $> \sim 1$, and relatively elevated Ca/Na ratios, indicating brines that underwent seawater evaporation followed by halite precipitation.

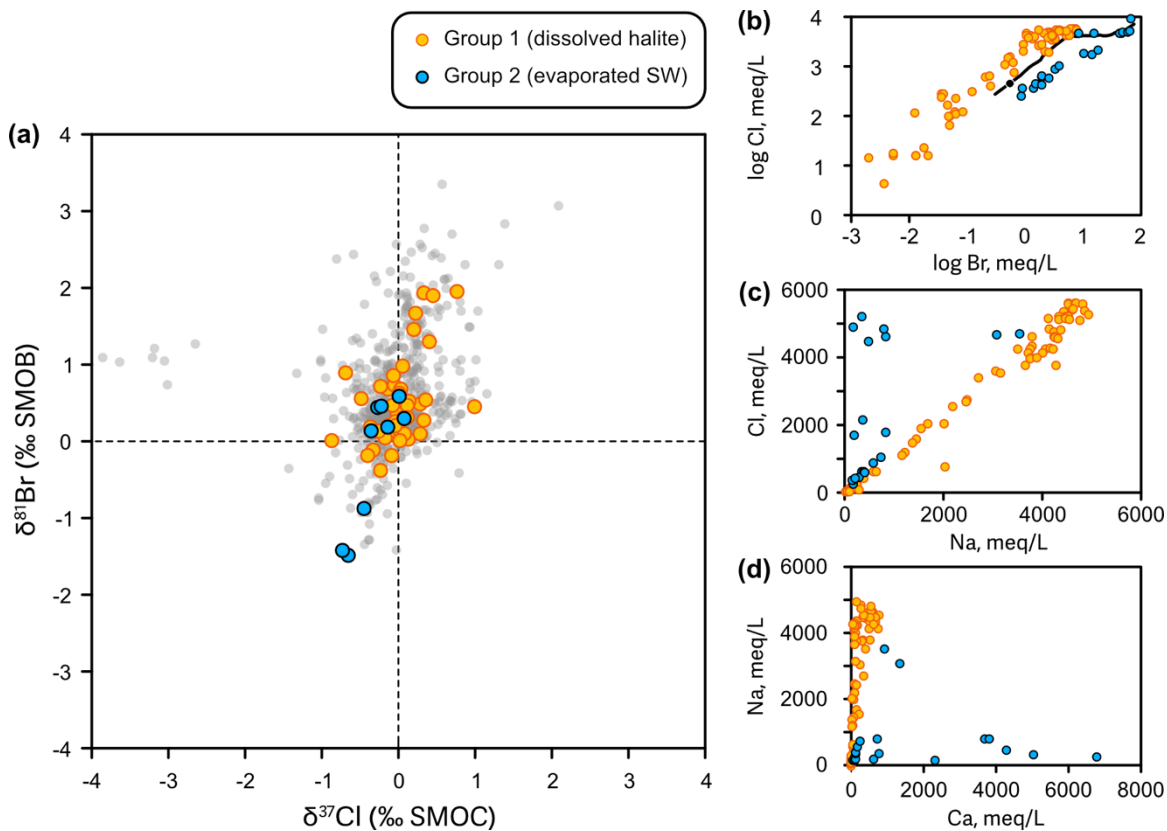


Figure 2-13. (a) $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ values for the compiled groundwater dataset. Gray circles indicate all samples with both isotope values available; colored symbols highlight the two hydrochemical groups identified in this study. Group 1 (orange) represents brines produced primarily by halite dissolution, and Group 2 (blue) corresponds to evaporated seawater that has precipitated halite. See panels b-d for hydrochemical parameters used to differentiate the two groups; (b) $\log \text{Cl}$ versus $\log \text{Br}$, with the solid black line showing the Seawater Evaporation Trajectory (see Figure 2-2); (c) Cl versus Na ; and (d) Na versus Ca concentrations. All concentrations are in meq/L.

Groundwaters dominated by halite dissolution (Group 1) display a predictable chemical and isotopic pattern: near-unity Na-Cl stoichiometry, low Br/Cl ratios, and high Na/Ca ratios. $\delta^{81}\text{Br}$ values are predominantly relatively high, and $\delta^{37}\text{Cl}$ values generally fall within the range expected for complete halite dissolution (between -0.2‰ and +0.5‰; Eggenkamp et al., 2019a). Relatively lower $\delta^{37}\text{Cl}$ values can arise where incongruent dissolution preferentially leaches ^{35}Cl (Eastoe et al., 2001). In either case, halite dissolution, whether complete or incongruent, yields brines with relatively high $\delta^{81}\text{Br}$ values, mostly > 0‰.

In contrast, brines predominantly influenced by evaporated seawater and halite precipitation (Group 2) exhibit chemical evidence of Cl loss and Br enrichment. These samples plot near the seawater evaporation trajectory in Br-Cl space, past halite saturation, and in some cases, show partial influence from freshwater mixing (Figure 2-13b; see also Figure 2-2). Their $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values are generally lower than those of Group 1, consistent with theoretical predictions and observations for evaporated seawater that precipitated halite (Eastoe et al., 2001, 1999; Eggenkamp et al., 1995). Some overlap in $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values between two groups may reflect partial dissolution of halite by freshwater, as suggested by their Br-Cl trends. Overall, comparison of the two groups aligns with earlier findings that groundwater influenced predominantly by halite dissolution tends to be more enriched in ^{81}Br than those derived solely from evaporated seawater (Jiang et al., 2022). If dissolved halite later re-precipitates (i.e., reflux halite), the resulting halite crystals are expected to inherit these relatively high $\delta^{81}\text{Br}$ values.

2.7.3.2 Dolomitization

Dolomitization and dedolomitization could be important water-rock interaction processes that can modify halogen isotope signatures, particularly bromine, in carbonate-hosted groundwaters. During dolomite formation, magnesium is removed from solution, causing Mg/Ca ratios to decrease; this ratio serves as a useful indicator of dolomitization process. Previous studies have shown that dolomitization can modify Br concentrations, likely through selective partitioning during dolomite formation (Johnson et al., 2009). Early dolomitization processes may also result in elevated Br contents in evaporites such as halite (Schoenherr et al., 2009), implying that dolomitization may correspond to a decrease in Br concentration in the associated fluid. Although halogen isotope values were not analyzed in these earlier works, the observed systematic changes in Br concentrations suggest that dolomitization could affect $\delta^{81}\text{Br}$ values through similar partitioning effects.

In the dataset reviewed here, groundwater from dolostone-dominated settings exhibits a moderate positive correlation between Mg/Ca ratios and $\delta^{81}\text{Br}$ values ($R^2 \approx 0.33$, $p < 0.05$; circles in Figure 2-14b). This $\delta^{81}\text{Br}$ -Mg/Ca relationship is absent in comparable limestone-dominated settings ($R^2 \approx 0.019$, $p < 0.05$; crosses in Figure 2-14b), suggesting that the fractionation mechanism is specific to dolomite regimes. In contrast, $\delta^{37}\text{Cl}$ values exhibit no consistent increase or decrease with Mg/Ca either in either dolostone- or limestone-dominated settings; instead, they remain within a relatively

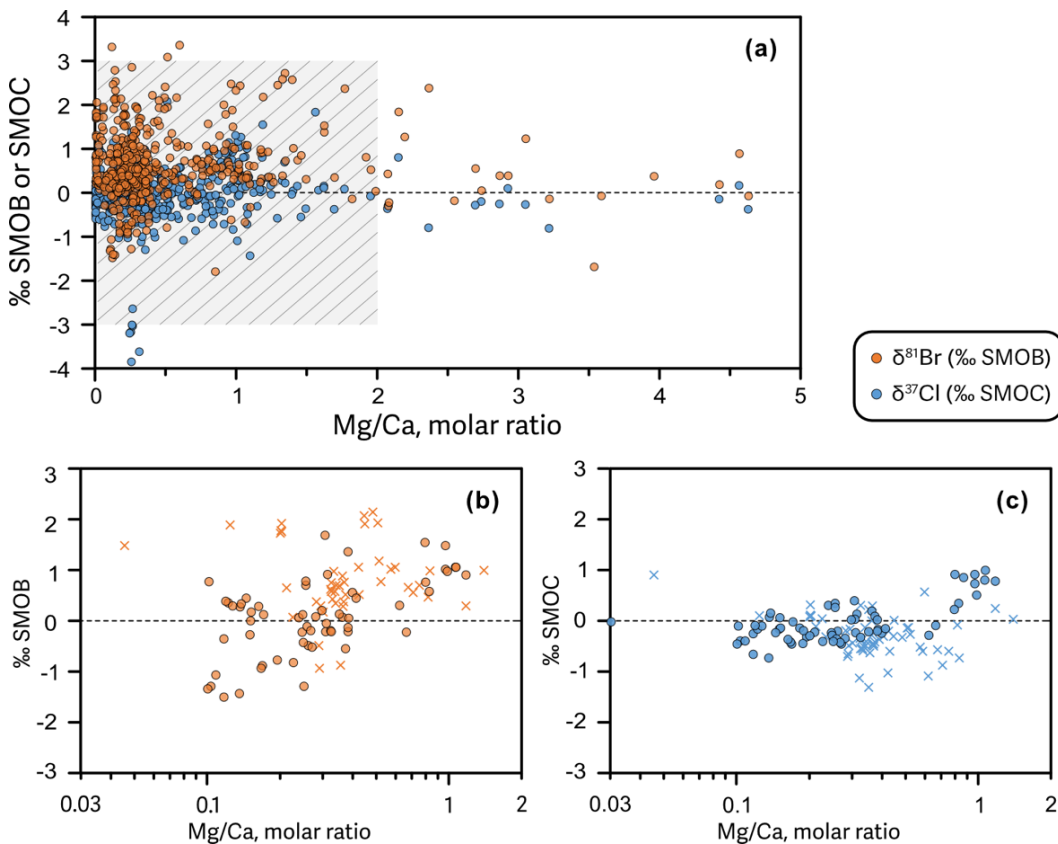


Figure 2-14. (a) $\delta^{81}\text{Br}$ (orange) and $\delta^{37}\text{Cl}$ (blue) versus Mg/Ca molar ratios for all lithologies. The gray shaded area marks the range of Mg/Ca ratios and isotopic values typical of carbonate-hosted groundwaters. (b) $\delta^{81}\text{Br}$ vs. Mg/Ca for carbonate aquifers, with filled circles for dolostone and crosses for limestone. (c) $\delta^{37}\text{Cl}$ vs. Mg/Ca for the same samples as in (b). A subset of high-Mg/Ca samples exhibit a sudden $\delta^{37}\text{Cl}$ increase, coupled with low TDS, low Br, and relatively high Cl, tentatively reflecting freshwater-influenced halite dissolution.

narrow range, often with relatively low $\delta^{37}\text{Cl}$ (Figure 2-14c). These patterns suggest that dolomitization (or dedolomitization) introduces a fractionation process that more selectively affects $\delta^{81}\text{Br}$ than $\delta^{37}\text{Cl}$. One plausible explanation is the preferential incorporation of ^{81}Br into dolomite during crystal growth, progressively depleting the fluid in ^{81}Br while leaving $\delta^{37}\text{Cl}$ values largely unchanged. Overall, these observations suggest that (de)dolomitization provides a lithology-specific fractionation pathway for bromine isotopes, calling for further investigation.

2.8 Other Controls

Beyond the major processes discussed in earlier sections—evaporation, mineral precipitation, and water–rock interaction—halogen isotope compositions in groundwaters and brines can also be influenced by a range of environmental settings. These include high-temperature and high-pressure regimes, cold regions subject to seasonal freezing, organic-rich and redox-active conditions, and shallow or surface water bodies experiencing atmospheric interaction. Although these factors may operate locally or episodically, they can impart distinct $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ signatures that should be considered when interpreting halogen isotope data.

2.8.1 Extreme Heat and Pressure

High-temperature and high-pressure environments, such as hydrothermal systems or deep geothermal reservoirs, may play an important role in shaping halogen isotope signatures distinct from those in low-temperature groundwater. In typical low-temperature natural groundwater systems, chlorine isotopes exhibit minimal fractionation, with deviations rarely exceeding $\pm 2\text{‰}$ (Eastoe and Guilbert, 1992; Kaufmann et al., 1984). By contrast, diagenetic alteration at elevated temperatures, such as mineral-fluid interaction at active margins ($\sim 100^\circ\text{C}$) or the alteration of oceanic basalts (up to 350°C), can produce significantly lower $\delta^{37}\text{Cl}$ values, some falling below -4‰ (e.g., Ransom et al., 1995; Spivack et al., 2002). Although such extreme fractionation appears to be confined to settings with substantial hydrothermal activity and continuous fluid flow, and such significant hydrothermal activity was not reported in the studies included in the database here, these cases suggest the potential for thermal conditions to induce pronounced changes in chlorine isotope compositions.

Geothermal groundwaters in the compiled dataset have temperatures exceeding 80°C and up to 274°C under deep burial and/or hydrothermal activity, and exhibit relatively low $\delta^{37}\text{Cl}$ values but a wide $\delta^{81}\text{Br}$ range that often includes relatively high values (Figure 2-15, S-S and P) (Pinti et al., 2020,

2019; Shouakar-Stash, 2008). Such isotopic patterns imply open, advective regimes in which rapid water-rock exchange keeps the system far from isotopic equilibrium. If kinetic fractionation alone was responsible for both halogen isotope fractionations, $\delta^{37}\text{Cl}$ should vary more widely than $\delta^{81}\text{Br}$ (Eggenkamp, 2025 and reference therein). Instead, the narrow $\delta^{37}\text{Cl}$ range implies either an additional Br-specific fractionation process or a mechanism that limits further Cl isotope fractionation while Br continues to fractionate. Overall, these patterns are consistent with high-temperature, non-equilibrium alteration driven by hydrothermal circulation rather than closed-system equilibrium processes.

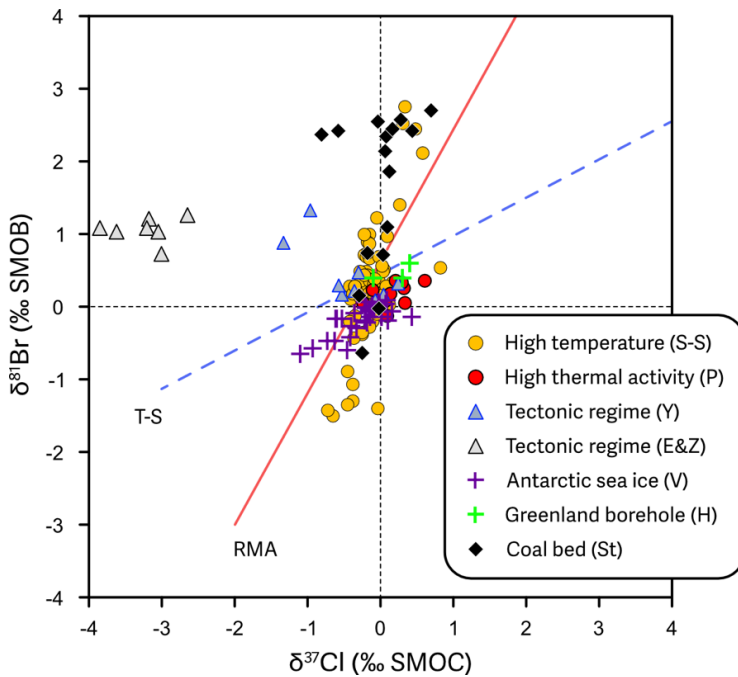


Figure 2-15. $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ values for datasets reporting high-temperature anomalies, tectonic activity as a major hydrochemical control (current or past), or from cold-regions or organic-rich coal beds. Abbreviations in the legend correspond to the first author(s) of each dataset: S-S = *Shouakar-Stash (2008)*; P = *Pinti et al. (2019)*; Y = *Yu et al. (2019)*; E&Z = *Eggenkamp and Coleman, (2000) & Ziegler et al. (2001)*; V = *Vallelonga et al. (2021)*; H = *Henkemans et al. (2018)*; St = *Stotler et al. (2021)*. High temperature (S-S) reports temperature $>80^\circ\text{C}$ and Tectonic regime (Y) mentions (past) tectonic activities as one of major hydrochemical control. Dashed blue and solid red lines represent Theil-Sen (T-S) and Reduced Major Axis (RMA) regression slopes, respectively, calculated for the entire dataset (see Section 2.4 and Figure 2-6 for details).

Tectonically active settings, on the other hand, exhibit a wide $\delta^{37}\text{Cl}$ range, with relatively low values overall, paired with comparatively narrow and relatively high $\delta^{81}\text{Br}$ values (Figure 2-15, Y and E&Z). These regions are characterized by highly fractured or actively deforming rock masses (Eggenkamp and Coleman, 2000; Yu et al., 2019; Ziegler et al., 2001). Their relatively low and dispersed $\delta^{37}\text{Cl}$ values are attributed to diffusion or ion-filtration through compaction, or diffusion through interlayers (Hesse et al., 2006; Stotler et al., 2010; Yu et al., 2019; Ziegler et al., 2001) in low-permeable rock matrices adjacent to fractures, while the fractures themselves act as high-flow pathways. The broader dispersion of $\delta^{37}\text{Cl}$ values compared to $\delta^{81}\text{Br}$ likely reflects the combined influence of mass-dependent diffusion together with additional processes such as ion exchange and mixing with halite-sourced chloride, which perturb Cl more strongly than Br. In contrast, the consistently high but less variable $\delta^{81}\text{Br}$ values are plausibly explained by preferential diffusive loss of ^{79}Br , which enriches the residual fluid in ^{81}Br but does not generate large variability. Such distinct isotopic responses highlight a clear decoupling between bromine and chlorine isotopes in tectonically active regions. This decoupling underscores that in these settings, $\delta^{37}\text{Cl}$ values reflect the combined influence of multiple processes, whereas $\delta^{81}\text{Br}$ records more selective fractionation.

2.8.2 Cold Regions

Halogen isotopes in cold-region environments show distinct $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ signatures compared to high-temperature systems. $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values from high-latitude environments, including Antarctic sea-ice cores (Vallelonga et al., 2021) and Greenland sub-permafrost brines (Henkemans et al., 2018), exhibit $\delta^{81}\text{Br}$ values that cluster near 0‰, with a much narrower range than those observed in high-temperature systems, whereas $\delta^{37}\text{Cl}$ values span a substantially wider range (Figure 2-15, V and H). This characteristic pattern may reflect a physical “freeze-out” process, in which freezing and ice formation remove water as ice while excluding most ions from the ice lattice, thereby concentrating them in the residual brine (i.e., ion exclusion).

Laboratory freezing experiments confirm that freezing may influence the Cl isotope fractionation. Although chloride ions are largely excluded from the ice lattice during freezing, a small amount of ^{37}Cl can still become structurally incorporated. Experiments show that freeze-out preferentially incorporates ^{37}Cl into the ice (Zhang and Frape, 2003; see also Stotler, 2008). This leads to slight ^{37}Cl enrichment in the ice and corresponding depletion in the residual brine. Although the extent of fractionation varies with freezing conditions (e.g., rapid batch freezing vs. slow column freezing),

enrichment in ^{37}Cl of the ice relative to the parent fluid occurs even at modest sub-zero temperatures (-2 to -3 °C). Rapid freezing in batch experiments produced only minor fractionation ($\leq 0.2\%$), whereas slow freezing with gravity drainage in a column experiment yielded much larger differences (fractionation factor $\alpha \approx 1.0005$) through increased incorporation of structurally bound chloride rather than interstitial brine within the ice matrix (Zhang and Frape, 2003). Bromine, which has not yet been investigated experimentally under similar conditions, likely remains largely dissolved in the brine and experiences minimal isotopic fractionation.

Field data align with these experimental observations, potentially explaining the broader $\delta^{37}\text{Cl}$ but relatively limited $\delta^{81}\text{Br}$ variability in cold settings. In natural sea-ice, however, the measured $\delta^{37}\text{Cl}$ values predominantly reflect the history of brine retention and gravity drainage during repeated melt-freeze cycles, rather than equilibrium partitioning between ice and brine at the moment of freezing. Antarctic sea-ice shows systematic depletion in ^{37}Cl where brine rejection and gravity drainage are efficient, whereas $\delta^{81}\text{Br}$ values stay within 1‰ (Vallelonga et al., 2021). Greenland sub-permafrost brines show the complementary and opposite trend, with relatively high values for both $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$, yet $\delta^{37}\text{Cl}$ values spanning a relatively narrow range (Henkemans et al., 2018). Repeated freeze-thaw concentration cycles in permafrost settings should expel dense brine downward during each freezing episode, while the overlying permafrost layer prevents subsequent dilution, allowing progressive enrichment in ^{37}Cl . If seasonal thawing and evaporation-salt precipitation occur before refreezing, additional enrichment, including enrichment in ^{81}Br , may be superimposed via ion exclusion.

Taken together, these studies show that halogen signatures in cold-region systems are governed predominantly by physical ion-exclusion mechanisms, including brine drainage efficiency. In Antarctic sea-ice, the $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ regression gives an OLS slope of ~ 0.47 ($R^2 = 0.55$, $p < 0.05$), close to the ~ 0.44 expected when a single physical process fractionates both isotopes in proportion to their mass differences, and also close the Theil-Sen regression slope of 0.53 ± 0.07 (see Section 4). Consequently, any interpretation of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values in (sub)permafrost brines, sea-ice, or polar lake waters must account for the freeze-thaw history and the efficiency brine separation from ice, as these controls can readily overshadow isotopic produced by other processes. However, as noted for sub-permafrost brines at Lupin, freeze-thaw history, groundwater residence time, and mixing of different source waters can weaken or obscure this cryogenic signal (Stotler et al., 2009); thus, complementary indicators such as Br/Cl ratios should also be considered.

2.8.3 Organic Interaction and Redox Conditions

Redox conditions and interactions with organic matter can play a significantly role in shaping halogen isotope signatures in groundwater. In particular, reduced environments have been associated with relatively high $\delta^{81}\text{Br}$ values while $\delta^{37}\text{Cl}$ remains more variable, suggesting a greater sensitivity of bromine to redox-driven processes compared to chlorine (e.g., Stotler et al., 2021; Wang, 2017). This pattern represents a potentially important control on the distribution of $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values in organic-rich aquifers.

Observations from the Cherokee Basin support this interpretation (Figure 2-15; Stotler et al., 2021). Groundwater samples from reduced environments tend to exhibit elevated $\delta^{81}\text{Br}$ values with more variable $\delta^{37}\text{Cl}$ values (Stotler et al., 2021). This can be explained by organic matter preferentially consuming lighter bromine isotopes (^{79}Br) during diagenesis or transforming ^{79}Br into organobromine compounds, leaving the residual groundwater enriched in ^{81}Br with no consistent influence on $\delta^{37}\text{Cl}$. A similar tendency has been reported at the Bruce Nuclear Site, where elevated $\delta^{81}\text{Br}$ values coincide with high total organic carbon (TOC), while $\delta^{37}\text{Cl}$ values show no clear trend (Wang, 2017). These findings indicate that organic processes associated with reduced environments can preferentially enrich the residual groundwater in ^{81}Br , highlighting bromine's higher sensitivity to these processes relative to chlorine.

A comparable pattern is also evident in the Bakken Formation, an organic-rich shale with TOC contents up to 35% (Shouakar-Stash, 2008). Formation waters from this unit consistently exhibit relatively high $\delta^{81}\text{Br}$ values, in several cases exceeding +2‰, while $\delta^{37}\text{Cl}$ values are more variable. The relatively high $\delta^{81}\text{Br}$ values, coupled with elevated Br concentrations (74-934 mg/L), suggest that these signatures cannot be explained by evaporated seawater origin alone. Instead, they likely reflect interaction with organic matter during deposition and subsequent diagenesis, processes that have enhanced bromine isotope fractionation relative to chlorine (Shouakar-Stash, 2008).

Because inflow and mixing with waters from other formations can mask or alter this ^{81}Br enrichment signal, especially under low Br concentration conditions, it is advisable to interpret these patterns with caution. Integrating halogen isotope data with hydrogeological and hydrochemical context, including redox conditions, TOC measurements, and groundwater flow characterization, is helpful in attributing isotope patterns to organic effects.

2.8.4 Atmospheric Interaction in Surface Water Environments

Surface water samples, including creeks, springs, rivers, and lakes, plot over a broad range in both the Br-Cl and $\delta^{37}\text{Cl}$ - $\delta^{81}\text{Br}$ plots (Figure 2-16a, b). In the log-log Br-Cl plot, concentrations span several orders of magnitude for both Cl and Br, with data points scattered widely. This variability reflects the combined influence of diverse hydrological inputs and surface processes, as surface waters are subject to rapid and spatially heterogeneous inputs such as evaporation, halite dissolution or precipitation, meteoric recharge, and runoff. Within this scatter, samples with high Cl concentrations are predominantly lake waters, with ongoing evaporation concentration and possible halite precipitation and reflux (Chen et al., 2014; Hanlon et al., 2017; Short, 2017; Shouakar-Stash et al., 2007). In contrast, some creek, spring, and river waters exhibit relatively low Cl concentrations possibly influenced by meteoric recharge and surface runoff (Bagheri et al., 2014; Du et al., 2015; Short, 2017; Shouakar-Stash et al., 2007).

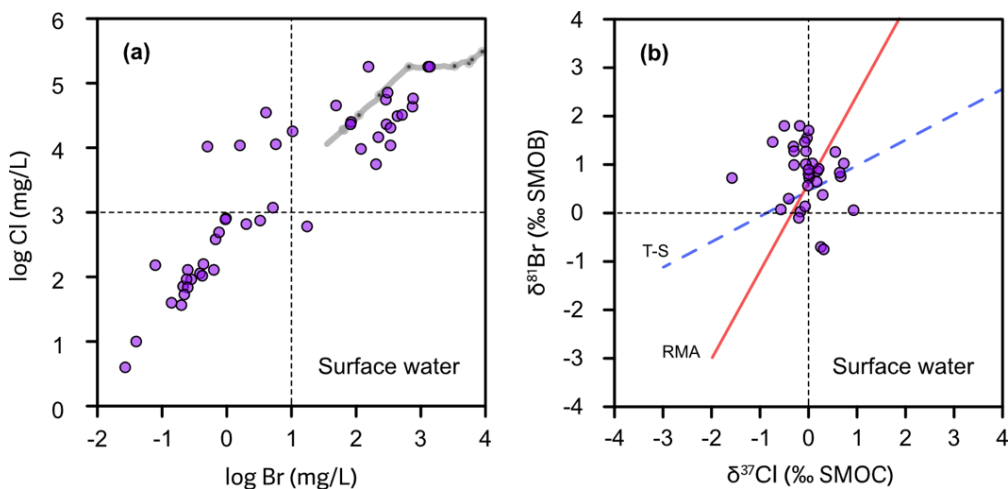


Figure 2-16. (a) Log-log Br-Cl plot for surface water samples. The solid grey line indicates seawater evaporation trajectory (SET). (b) $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ values for the same samples. Samples shown here include lakes, springs, rivers, and creeks from seven different studies (Bagheri et al., 2014; Chen et al., 2014; Du et al., 2015; Eissa et al., 2016; Hanlon et al., 2017; Short, 2017; Shouakar-Stash et al., 2007). Dashed blue and solid red lines represent Theil-Sen (T-S) and Reduced Major Axis (RMA) regression slopes, respectively, calculated for the groundwater dataset (see Section 2.4 and Figure 2-6 for details).

High-salinity lake waters often exhibit Cl concentrations several times higher than seawater, and Br/Cl ratios generally lower than seawater, consistent with halite precipitation. They exhibit varying $\delta^{37}\text{Cl}$ values (-1.58‰ to +0.66‰), and $\delta^{81}\text{Br}$ values mostly remain relatively high (+0.07‰ to +1.80‰). Low-salinity surface waters, such as creeks and springs, are readily affected by precipitation and runoff that could dissolve salt stored in the sediments or bed. During this process, halide concentrations can increase, and Br/Cl ratios can vary depending on various factors such as Br adsorption capacity of the sediments. These samples exhibit comparably wide $\delta^{37}\text{Cl}$ values (-0.74‰ to +0.93‰), likely reflecting variable mixing of low $\delta^{37}\text{Cl}$ meteoric inputs and ongoing halite precipitation, and $\delta^{81}\text{Br}$ values similarly remain relatively high (+0.02‰ to +1.47‰), with two exceptions of isotopically light creek waters.

Across all surface waters samples, the $\delta^{37}\text{Cl}$ - $\delta^{81}\text{Br}$ distribution does not align with either the Theil–Sen or RMA slopes derived for the groundwater dataset (Figure 2-16b; see also Section 2.4), and no statistical correlation between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ is observed ($R^2 = 0.0059$, $p < 0.001$). This indicates that dominant fractionation processes in surface water environments differ from those in subsurface aquifers. In addition, the lack of a $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ correlation further suggests that the processes affecting bromine and chlorine isotopes may act independently in these settings. Despite variable salinity and halide concentrations, most surface waters consistently exhibit ^{81}Br enrichment.

A plausible explanation for this consistent ^{81}Br enrichment is atmospheric interaction, such as volatilization or oxidation of bromine species, in which ^{79}Br is preferentially removed as gaseous HBr or Br_2 , enriching the residual fluid in ^{81}Br (Hanlon et al., 2017). Photolytic or microbial oxidation may also enhance this enrichment without affecting $\delta^{37}\text{Cl}$. The variability in $\delta^{37}\text{Cl}$ values, instead, is governed largely by halite precipitation, which removes ^{37}Cl into evaporite minerals and leaves the fluid isotopically lighter, and meteoric inputs that typically have low $\delta^{37}\text{Cl}$ values (Eastoe, 2016); while relatively high $\delta^{37}\text{Cl}$ values can arise from dissolution of pre-existing halite deposits (Eggenkamp et al., 1995; Shouakar-Stash et al., 2007). On average, surface waters exhibit higher $\delta^{81}\text{Br}$ values (mean = $0.77 \pm 0.43\text{‰}$, $n = 34$) than shallow groundwaters ($0.54 \pm 0.99\text{‰}$, $n = 45$) and all groundwater samples (0.55 ± 0.76 , $n = 622$), consistent with the greater influence of surface processes that selectively remove ^{79}Br .

2.9 Summary and Conclusions

A global dataset is compiled from all publicly available groundwater and surface water analyses that report both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values, and includes available hydrochemistry such as major ion concentrations, Br/Cl ratios, and other hydrochemical parameters. Around 1,110 subsurface and 88 surface or near-surface samples from 24 regions across diverse geological settings are reviewed in this study. Across all settings, bromine isotope ($\delta^{81}\text{Br}$) values range between -1.94‰ and +3.35‰, and chlorine isotope ($\delta^{37}\text{Cl}$) values between -3.86‰ and +2.07‰. While $\delta^{37}\text{Cl}$ values in most lithologies remain centered within ± 0.5 ‰ of the seawater baseline, $\delta^{81}\text{Br}$ values vary more widely, by nearly a factor of three between various lithological settings.

Regression analyses (Reduced major axis, Theil-Sen, and Ordinary Least Squares) of $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ reveal that main cloud of groundwater samples (Theil-Sen; slope: 0.53 ± 0.07) might follow a $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ relationship close to mass-dependent fractionation slope (~ 0.44), but the full dataset exhibits a steeper RMA slope (1.82 ± 0.14) driven by a subset of ^{81}Br -enriched samples. This divergence suggests that additional fractionation pathways, such as organic matter degradation, atmospheric interaction, high-temperature processes, and freeze-out ion-exclusion, are affecting bromine isotopic compositions preferentially. In contrast, outliers with strongly negative $\delta^{37}\text{Cl}$ values are linked to tectonically active zones where diffusion and membrane ultrafiltration fractionation chlorine preferentially.

Several mechanisms are suggested to control halogen-isotope variations: (i) Evaporative mineral precipitation – sequential precipitation of evaporite minerals typically lowers $\delta^{37}\text{Cl}$ in the residual brine as ^{37}Cl is preferentially incorporated into salts, while $\delta^{81}\text{Br}$ exhibits mineral-specific and non-monotonic trends, depending on the stage and type of mineral precipitation; (ii) Halite dissolution and reflux – complete halite dissolution increases Br/Cl ratios and $\delta^{37}\text{Cl}$ values in brine, while reflux cycling enriches ^{81}Br ; (iii) Dolomitization and dedolomitization might selectively influence $\delta^{81}\text{Br}$, potentially lowering $\delta^{81}\text{Br}$ during dolomite formation and raising during dedolomitization, without consistently altering $\delta^{37}\text{Cl}$; (iv) High-temperature and tectonically deformed systems often produce isotopic decoupling between Br and Cl, by selectively affecting either $\delta^{37}\text{Cl}$ or $\delta^{81}\text{Br}$; (v) Organic-related processes tend to yield relatively high $\delta^{81}\text{Br}$ values through microbial debromination that preferentially remove ^{79}Br , while not as equally altering $\delta^{37}\text{Cl}$; (vi) Cryogenic processes – freeze-out preferentially incorporates ^{37}Cl into ice when brine drainage is available, whereas $\delta^{81}\text{Br}$ typically

remains unaltered; and (vii) Atmospheric interactions, such as volatilization or photolytic/microbial oxidation of bromine species, preferentially remove ^{79}Br into gaseous phase, enriching residual fluid in ^{81}Br with little to no effect on $\delta^{37}\text{Cl}$. The $\delta^{37}\text{Cl}$ variability depends largely on halite precipitation or dissolution and meteoric mixing.

Collectively, the combined $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ approach suggests these isotopes are a sensitive tracer of halite cycling, brine mixing, organic redox reactions, cryogenic processes, and atmospheric interaction. There are many processes that make bromine isotopes vary more while leaving chlorine isotope values within a smaller range (and vice versa), making the use of both $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ an especially sensitive tracer of halite cycling, organic redox reactions and cryogenic brine evolution. Future priorities include experimental calibration of Br partitioning into non-marine evaporites, quantification of high-temperature fractionation factors, and targeted sampling across lithologies to better disentangle overlapping fractionation pathways. The global synthesis and process-based framework provided here offer a qualitative baseline for such next-step studies and interpreting halogen isotope variations in both modern and ancient hydrological systems.

Chapter 3

Experimental Insights into Chlorine and Bromine Isotope Fractionation during Evaporation of Multicomponent Brines

3.1 Introduction

Chloride and bromide behave conservatively in most aqueous systems (McCaffrey et al., 1987), making the stable isotope compositions of chlorine ($\delta^{37}\text{Cl}$) and bromine ($\delta^{81}\text{Br}$) useful for fingerprinting the origin and evolution of brines. $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ are increasingly recognized as valuable geochemical tracers of salinity evolution, fluid-rock interaction, and evaporite formation, yet their isotopic behavior remains incompletely understood. While $\delta^{37}\text{Cl}$ has been studied across a range of geochemical conditions (Eastoe, 2016; Eastoe et al., 2007, 2001; Eggenkamp, 1994; Strydom et al., 2022), $\delta^{81}\text{Br}$ has only recently become analytically accessible with sufficient precision, with most studies focused on compositions in fluids (Eggenkamp, 2025; Eggenkamp and Coleman, 2000). In formation and basin fluids, $\delta^{81}\text{Br}$ values span a wide range (up to $\sim 5\text{‰}$), influenced by processes such as mixing of brines from different sources, halite dissolution and reflux, prolonged water-rock interaction, and other lithologic or geologic controls (Chen et al., 2014; Eggenkamp and Coleman, 2000; Frape et al., 2007; Shouakar-Stash, 2008; Stotler et al., 2010); see also *Chapter 2*) These studies reveal large $\delta^{81}\text{Br}$ variations far exceeding the small fractionation factors predicted from equilibrium Br-salts precipitation and those calculated theoretically (Eggenkamp, 2016; Eggenkamp et al., 2016; Gao and Liu, 2021). More recently, $\delta^{81}\text{Br}$ values have been measured in natural evaporite sequences, mainly paleo halite deposits. These studies show a relatively small range of $\delta^{81}\text{Br}$ variation ($\sim 1\text{‰}$) and no strong correlation between $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$, typically attributed to exclusion of Br^- from the halite lattice, entrapment of Br-rich residual brines in fluid inclusions, and diagenetic process such as dissolution-recrystallization (Eggenkamp et al., 2019b; Ercan et al., 2019); *Chapter 4*). Collectively, these findings indicate that $\delta^{81}\text{Br}$ values in nature are governed by multiple kinetic and physicochemical processes beyond simple mineral-fluid equilibrium (Eggenkamp et al., 2016), underscoring the need for further studies.

Despite these recent evaporite studies, $\delta^{81}\text{Br}$ investigations in such settings remain still scarce and the mechanisms underlying the observed variability and decoupling of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ are not yet fully resolved. In particular, $\delta^{81}\text{Br}$ behavior during sequential precipitation of minerals such as Ca-

carbonates, gypsum, halite, and Mg-rich salts during seawater evaporation has not been systematically examined. The divergent evolution of $\delta^{81}\text{Br}$ from $\delta^{37}\text{Cl}$ observed in these natural halite deposits implies that the two halogens respond to distinct mineralogical and physicochemical controls (Eggenkamp et al., 2019b). Experimental and field studies have suggested multiple processes that could produce the $\delta^{81}\text{Br}$ variability, including exclusion of Br^- from the halite lattice during rapid crystallization, kinetic isotope effects related to its trace abundance, trapping of Br-rich residual fluids in inclusions, water-rock interaction, and selective volatilization of Br in both natural systems (Eggenkamp, 2025; Eggenkamp et al., 2019b; Hanlon et al., 2017; Stotler et al., 2021). Eggenkamp et al. (2016) experimentally demonstrated that the direction and magnitude of Br and Cl isotope fractionation depend on the co-precipitating cation, suggesting mineral-specific behavior. However, controlled laboratory studies have yet to quantify the magnitude, direction, and sequence of $\delta^{81}\text{Br}$ fractionation during evaporation of multicomponent brines.

To address this gap, the objectives of this study are to evaluate halogen isotope evolution during seawater evaporation and mineral precipitation, and to distinguish the respective influence of lattice partitioning, fluid inclusion, and volatilization. These were pursued through controlled evaporation experiments using synthetic seawater, in which $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values were tracked across brine, precipitate, and gaseous phases over the course of stepwise mineral precipitation. This approach provides a basis for understanding mineral-specific fractionation patterns in a multicomponent matrix and assessing how incorporation and exclusion pathways shape the isotopic evolution. This study offers the first experimental framework for Br-Cl isotope evolution during multistage evaporation-precipitation in multicomponent seawater systems and new insights on the processes governing Br-Cl isotope systematics.

3.2 Methodology

3.2.1 Synthetic Seawater Precipitation

For this experiment, 40 liters of synthetic seawater was prepared using analytical-grade reagents with purities exceeding 99% dissolved in ultra-pure Milli-Q water. The preparation followed a slightly modified formulation based on (Kester et al., 1967), with minor substitutions and adjustments to accommodate available chemical compounds (see Appendix Table C-1). To minimize unintended precipitation of carbonates (e.g., SrCO_3) during preparation, the synthetic seawater was initially prepared as two separate stock solutions and left at room temperature for at least 48 hours, with

occasional manual agitation (e.g., gentle inversion or swirling) to promote dissolution and prevent stratification. The solutions were then combined and left for another 24 hours to ensure complete mixing. The final composition of the synthetic seawater matches modern natural seawater to within 0.8-2.7% for all major constituents except HCO_3^- , which is 17% higher in synthetic seawater, likely due to atmospheric CO_2 absorption during stirring or partial precipitation of CaCO_3 during mixing (Table 3-1). Achieving an exact match was challenging due to insoluble residues or CaCO_3 precipitates, which contributed to slight deviations from the target composition. Because these residues could act as nucleation sites for unintended precipitation, they were carefully excluded from the final seawater batch by allowing them to settle at the bottom of the storage container, after which only the clear solution was transferred to the evaporation pan, leaving the insoluble material behind.

Table 3-1. Chemical composition of the synthetic seawater used in the evaporation experiments, compared with that of modern natural seawater (*Millero et al., 2008*). All concentrations are reported in mg/L. Natural seawater values were converted from g/kg to mg/L using a density of 1.025 kg/L for direct comparison.

	Cl^-	Na^+	SO_4^{2+}	Mg^{2+}	Ca^{2+}	K^+	HCO_3^-	Br^-	Sr^{2+}
Natural seawater	19,837	11,051	2,780	1,316	422	409	107	69	8.1
Synthetic seawater	19,470	10,832	2,741	1,285	419	402	125	68	7.9
% difference	1.9%	2.0%	1.4%	2.3%	0.8%	1.6%	17%	1.4%	2.7%

3.2.2 Experimental Setup

Evaporation was conducted inside a 200-L polypropylene chamber (100 x 50 x 40 cm), equipped with several instruments to control the experimental environment and monitor key parameters (Figure 3-1). A 150-watt ceramic heat lamp (ExoTerra), suspended approximately 25 cm above the brine, provided constant heat, while a circulation fan prevented thermal stratification. The heat lamp was controlled by a digital temperature controller (ITC-308, Inkbird) to keep brine temperature within $\pm 0.5^\circ\text{C}$ ($30 \pm 0.5^\circ\text{C}$ in Run 1 and $28 \pm 0.5^\circ\text{C}$ in Run 2) and prevent overheating. Air temperature, logged by thermo-

hygrometer (RHT-10, ExTech; Appendix Figures D-1 and D-2), remained at $31 \pm 0.7^\circ\text{C}$ and $29 \pm 0.7^\circ\text{C}$, respectively; relative humidity stabilized near $70 \pm 0.4\%$, with variations at the beginning and the end of evaporation. Bubble-wrap on the chamber side walls near the air inlet buffered temperature differences between the lab air and the chamber interior, preventing condensation on the wall without obscuring visual inspection. The chamber remained closed and airtight with silicone applied to holes and crevices, and the connections between the lid and the chamber taped with electrical tape (poly-vinyl chloride) for the duration of each experiment.

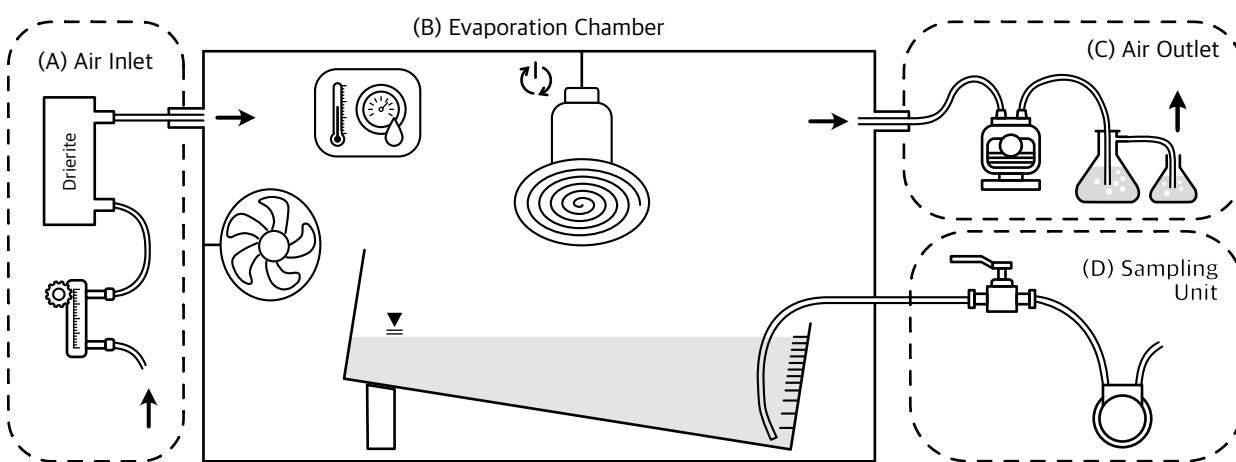


Figure 3-1. Schematic diagram of the experimental evaporation system. (A) Inlet for dry compressed air, passed through a Drierite column; (B) sealed evaporation chamber with temperature control; (C) outlet connected to two serial KOH traps for capturing any volatiles; and (D) peristaltic sampling port enabling brine sampling without compromising chamber seal.

Airflow into and out of the chamber was carefully controlled (Figure 3-1A, C). Building-supplied compressed air entered the chamber after passing through a Drierite drying column at a flow rate of 16 L/min, which was controlled by a gas flowmeter. Outflow was maintained at the same rate with the help of a diaphragm pump to prevent pressure build-up within the chamber. The exhaust stream was directed and bubbled sequentially through two Erlenmeyer flasks, each successive flask containing 500 mL and 200 mL, respectively, of ~ 0.2 M KOH solutions to oxidize and trap volatile bromine-containing gases as KBr and/or KBrO (aq). The two-flask series ensured complete capture of Br gas.

To evaluate potential background contamination, blank KOH solutions were also prepared and treated with the same building-supplied compressed air used in the experiments, but without brine present. These blanks served as a control to confirm that any Br measured in the experimental traps was attributable only to the evaporation, not to the air supply or laboratory setup.

To ensure reproducibility and reliability of the results, two separate experimental runs were conducted under otherwise identical conditions, with minor modifications. Synthetic seawater (7.2 L) was placed in a 17-L polypropylene container (46 x 31 x 18 cm) serving as an evaporation pan (Figure 3-1B). In Run 1 the pan remained level, resulting in a relatively consistent rate of evaporation throughout the process; in Run 2 the same pan was tilted by approximately 13° to enable brine sampling later into the evaporation process and to allow precipitates to settle sequentially along the down-slope wall. Graduated volume marks on the pan wall provided an immediate estimate of water volume loss; the evaporation degree was later calculated using Mg^{2+} concentrations.

3.2.3 Sampling and Analyses

3.2.3.1 Sampling

The peristaltic sampling port (Figure 3-1D) with ball valve allowed brine to be withdrawn periodically without disrupting the sealed environment of the chamber. Once the ball valve was opened, a low-speed peristaltic pump (<0.3 L/min) pumped brine directly into Nalgene bottles. The slow flow rate minimized pressure perturbations and prevented exchange of chamber air with room air. Sampling was performed at specific stages, corresponding to either specific reductions in brine volume or the visual appearance of a new mineral phase. Sample volumes ranged from 20-120 mL, with larger volumes early in the evaporation run to compensate for low halide concentrations. The total fluid volume removed during evaporation was 420 mL in Run 1 and 570 mL in Run 2. Immediately after collection, bottles were closed, sealed, and stored at room temperature until analysis to minimize the potential for mineral precipitation.

All precipitates were collected only after evaporation was complete and no visible brine remained. To ensure complete removal of residual surface moisture from the salt cake, the chamber was kept warm for up to 24 additional hours, then allowed to cool to room temperature. The dried salt cake was then scraped with ethanol-cleaned stainless-steel tools and subdivided according to their position within the container, using the graduated volume marks on the pan wall as a guide to identify potential variations in the precipitates, particularly as it was expected different mineral phases would

settle in distinct layers. Each fraction was double-bagged, labelled, and stored dry and dark at room temperature prior to chemical and isotopic analyses.

At the end of each run, the 0.2 M KOH solutions in the two serial flasks used to trap gaseous phases were weighed and combined, yielding approximately 600 mL of solution after accounting for ~100 mL evaporative loss during the experiment. This combined solution was divided into two portions: ~100 mL was reserved for chlorine analysis, and the remaining ~500 mL for bromine. From each portion, 5 mL aliquots were allocated to concentration measurements, and the rest was dedicated to isotopic analysis.

3.2.3.2 Analyses

Ionic determinations were completed using a variety of methods. Chloride (Cl^-) and bromide (Br^-) concentrations in brine samples were determined using an ICS-2000 ion chromatography (IC) system, configured to analysis of anions using Dionex IonPac AS18 Column, at University of Waterloo (UW). For some samples, Br^- concentrations were below the IC detection limit. Concentrations of Br^- in these samples and other major and trace elements (Na, Mg, K, Ca, S, Sr, Li, B, Al, Si, P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Te, Ba, Tl, Pb, Th, U) in all brine samples were determined by ICP-MS at the Analytical Geochemistry Laboratory, University of Saskatchewan.

Precipitated salt samples were completely dissolved in a measured volume of ultrapure water and analyzed for Cl^- , Br^- , and SO_4^{2-} concentrations at UW using the same IC configuration as for brine analysis. The IC results for dissolved solids were initially obtained in mg/L and subsequently converted to mg/g by normalizing to the measured mass of each solid sample and the volume of ultrapure water added for dissolution.

Bromine and chlorine stable isotope compositions ($\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$) were determined using gas chromatography-continuous flow-isotope ratio mass spectrometry (GC-CF-IRMS), following methods described by Shouakar-Stash et al. (2005b, 2005a), at the University of Waterloo-Environmental Isotope Laboratory (UW-EIL). The $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values are reported using the conventional δ -notation:

$$\delta_{\text{Sample}} = \left(\frac{R_{\text{Sample}} - R_{\text{Standard}}}{R_{\text{Standard}}} \right) \times 1000\text{‰}$$

where $R = {}^{81}\text{Br}/{}^{79}\text{Br}$ or ${}^{37}\text{Cl}/{}^{35}\text{Cl}$. Values are reported relative to Standard Mean Ocean Bromide (SMOB) or Standard Mean Ocean Chloride (SMOC), respectively, as the standard. The maximum allowable precision at the UW-EIL is 0.10‰ (1 σ) for both isotopes.

3.3 Results

3.3.1 Brine Chemistry versus Degree of Evaporation

Magnesium (Mg^{2+}) provides a reliable proxy for progress of evaporation because it remains entirely in solution until Mg-sulfate minerals begin to precipitate near 70 $\times$ seawater concentration (i.e., $\sim$ 98.6% water volume loss; McCaffrey et al., 1987). The Mg^{2+} concentration in the residual brine increases with the fraction of water evaporated, and the slope of the Mg^{2+} steepens markedly as the remaining water volume drops rapidly in later stages of evaporation (Figure 3-2a). Thus, Mg^{2+} concentration exhibits a strong linear correlation with the degree of evaporation calculated as the ratio of the initial seawater volume to the remaining brine volume ($R^2 = 0.989$, $p < 0.05$ in Run 2; Figure 3-2b), making it a reliable metric for tracking evaporation. Based on the conservative and predictable behavior, evaporation degree is therefore expressed throughout this paper as:

$$\text{Evaporation degree } (\times \text{ seawater}) \approx \frac{(\text{Molality } \text{Mg}^{2+})_{\text{brine}}}{(\text{Molality } \text{Mg}^{2+})_{\text{seawater}}}$$

In addition to its conservative behavior, another advantage of using Mg^{2+} as a proxy is its ability to correct for the sampling-induced skew that would appear when calculating a volumetric-based evaporation degree. Because water was periodically removed for chemical and isotopic analyses, relying solely on the remaining volume to estimate evaporation can overestimate the actual extent of water loss. The differing timing and volume of brine sampling in Run 1 and Run 2 resulted in inconsistent apparent volumetric evaporation degree (differing slopes in Figure 3-2b), due to unequal cumulative sampling volumes. Instead using Mg^{2+} concentration to determine evaporation degree ensures consistency between the two runs and provides a more reliable and comparable framework for interpreting chemical evolution. Based on this correction, the highest measurable evaporation degree in these experiments is approximately 18 $\times$ seawater in Run 2, corresponding to $\sim$ 95% loss of the initial water volume.

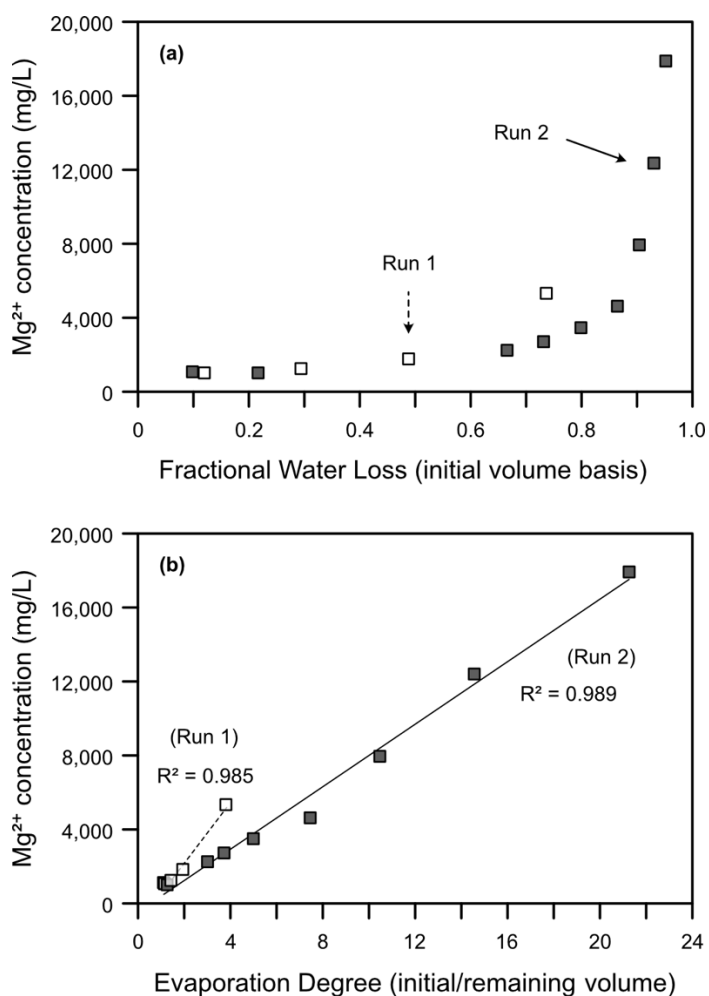


Figure 3-2. Relationship between Mg^{2+} concentration and (a) the fractional water volume loss relative to the initial seawater volume, and (b) the evaporation degree, calculated as the ratio of initial seawater volume to the remaining brine volume. Open symbols represent results from Run 1; filled symbols represent Run 2.

Concentration versus evaporation curves for major ions and halides (Ca^{2+} , Na^+ , Mg^{2+} , K^+ , SO_4^{2-} , Cl^- , Br^-) reveal distinctive trends based on their participation into mineral precipitation (Figure 3-3). Mg^{2+} , K^+ , SO_4^{2-} , and Br^- concentrations increase linearly with evaporation (Figure 3-3c, d, e), indicating conservative behavior throughout the experiment, consistent with previous studies (McCaffrey et al., 1987). In contrast, Ca^{2+} , Na^+ , and Cl^- concentrations and electrical conductivity (EC) values show inflection points associated with mineral precipitation (Figure 3-3a, b, e, f).

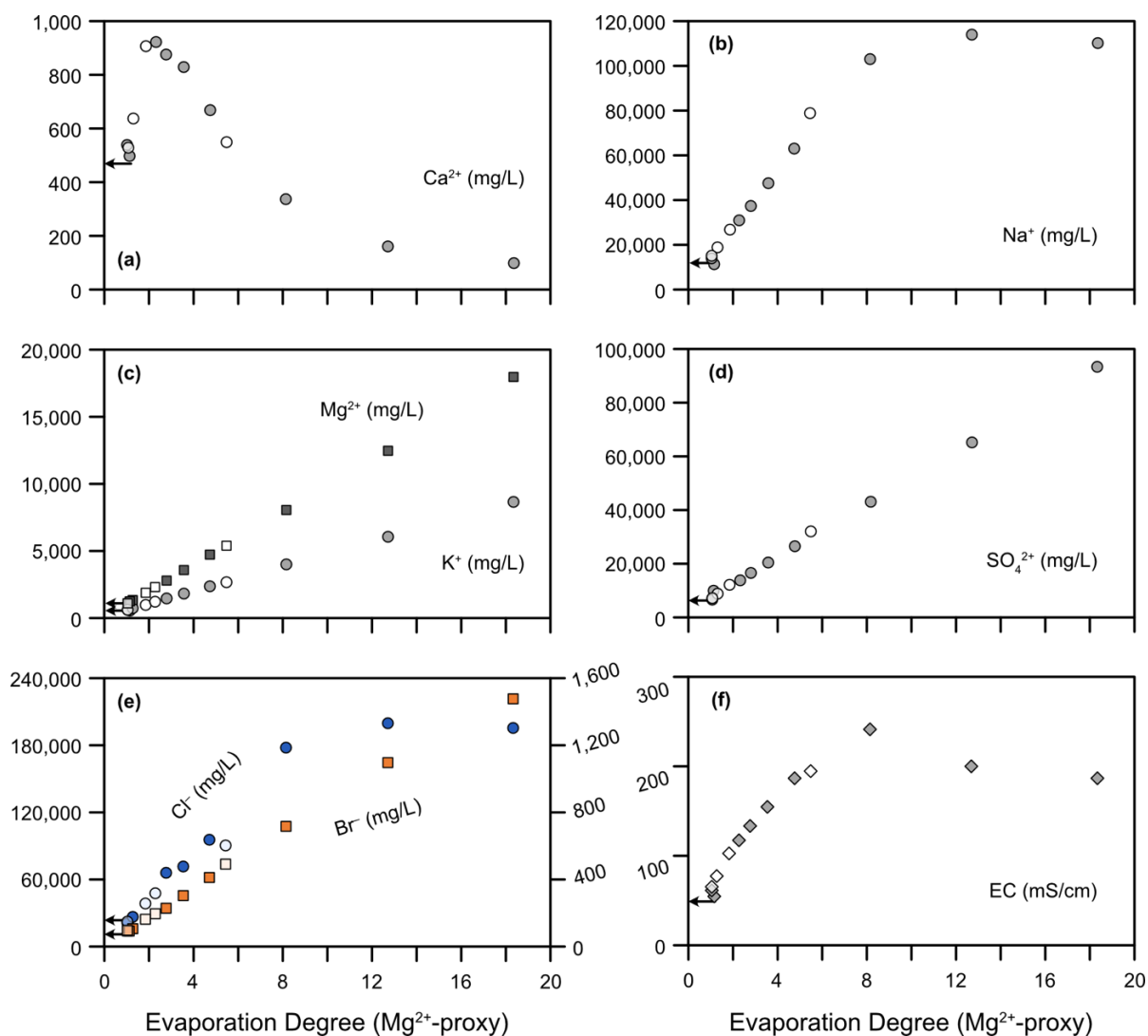


Figure 3-3. Evolution of solute concentrations and electrical conductivity (EC) as a function of evaporation degree, calculated from Mg^{2+} concentration. Open symbols represent Run1; filled symbols represent Run 2. In (e), circles indicate Cl^- concentrations (open for Run 1, filled blue for Run 2) and squares indicate Br^- concentrations (open for Run 1, filled orange for Run2).

Two noticeable inflection points are marked: Ca^{2+} concentration decreases at $\sim 2\times$ seawater due to CaCO_3 precipitation, while Na^+ and Cl^- concentrations, as well as EC, plateau or decrease around $\sim 9\times$ seawater concentration, marking the start of halite precipitation. The CaCO_3 precipitation stage typically begins after $\sim 50\%$ water is lost and is expected to yield a small fraction of the total salt mass

(~0.6%, ~1.5 g from 7.2 L seawater). A minor inflection near ~4-5× seawater, attributed to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation (McCaffrey et al., 1987), is only vaguely reflected in the EC curve (Figure 3-3f). The absence of a clear inflection in the SO_4^{2-} curve is likely due to a relatively small amount of gypsum precipitation (estimated to be ~9 g total, ~5,000 mg SO_4^{2-}), which is proportionally small compared to the overall SO_4^{2-} concentration (Figure 3-3d). The second major inflection at ~9× seawater marks the onset of halite (NaCl) precipitation, corresponding to approximately 90% water loss and accounts for ~78% of the total salt mass (~197 g). These two inflection points at ~2× and ~9× seawater are therefore used to define two primary stages in the evaporation sequence: an early Ca-dominated precipitation phase and a later halite-dominated precipitation phase.

3.3.2 Mineralogy of Precipitation and Solid Phase Evolution

Only the mineralogy of precipitate samples from the second experimental run (Run 2) was studied, as the salt cake from the first run formed as a single horizontal layer, making it impossible to distinguish precipitates formed at different stages of evaporation. Complete evaporation during Run 2 produced a single salt-cake that was subdivided into six positional fractions based on the graduated volume marks on the brine pan wall (Table 3-2). Microscopic observations of each fraction are summarized in the subsections below. The earliest precipitate accumulated on the upper walls (ES 2-1), whereas the deepest bottom layer (ES 2-5) records the final stage of brine evolution and mineral precipitation. From the 0.5 L mark and below, salt crystals are observed both on the wall (ES 2-3W) and on the bottom (ES 2-3B) of the pan, showing that from this point and onward, salt began precipitating simultaneously at both interfaces. In this zone, the wall and bottom samples are treated as sample subsets and are described individually (ES 2-3W and ES 2-3B in Table 3-2). Below the 0.2 L mark, precipitates occur almost exclusively as bottom accumulations (ES 2-4). Given the shallow-pan setting of the experimental system, nucleation begins at the air-water interface, rather than at the bottom, which is more typical of deeper, stratified brines (Lugli, 2009; Warren, 2006).

Table 3-2. Positional fractions of the salt-cake and dominant mineral assemblages.

Photomicrographs in Figures 3-4 to 3-8 illustrate representative textures for each fraction.

	Pan interval	Dominant mineral texture	SO ₄ , mg/kg	Cl, mg/kg	Br, mg/kg	Br/Cl ×1,000
ES 2-1 (Fig. 3-4)	> 1.4 L (wall)	Micro-cubic halite + acicular aragonite needles	110,000	543,000	151	0.278
ES 2-2 (Fig. 3-5)	1.4-0.5 L (wall)	Cloudy chevron halite + spherulitic gypsum	156,000	439,000	300	0.683
ES 2-3W (Fig. 3-6)	0.5-0.2 L (wall)	Chevron halite	166,000	427,000	679	1.59
ES 2-3B (Fig. 3-6)	0.5-0.2 L (bottom)	(Chevron halite) + radiating gypsum needles	150,000	412,000	419	1.02
ES 2-4 (Fig. 3-7)	0.2-0.1 L (bottom)	Clear halite + trace Ca-phases	131,000	433,000	300	0.693
ES 2-5 (Fig. 3-8)	< 0.1 L (bottom edge)	Massive hopper halite + residual brine overprint	98,000	471,000	251	0.534

3.3.2.1 ES 2-1 – Earliest wall crust (Figure 3-4)

Salts precipitated on the wall above the 1.4 L mark formed a thin radial coating consist of 50- to 100- μm subhedral cubic halite plates (Figure 3-4a, b) intergrown with sparse needle-like calcium carbonate crystals that effervesce vigorously in cold 10% HCl (Figure 3-4c). This fraction shows relatively low SO₄ and Br contents compared to other fractions. The relatively high Mg/Ca ratio of the brine and the early, low salinity condition favor aragonite over calcite (Zhong and Mucci, 1989). No fluid inclusions are visibly observed, and a low Br concentration and Br/Cl ratio is measured for this fraction. These precipitates correspond to brine samples EV 2-1 through EV 2-5.

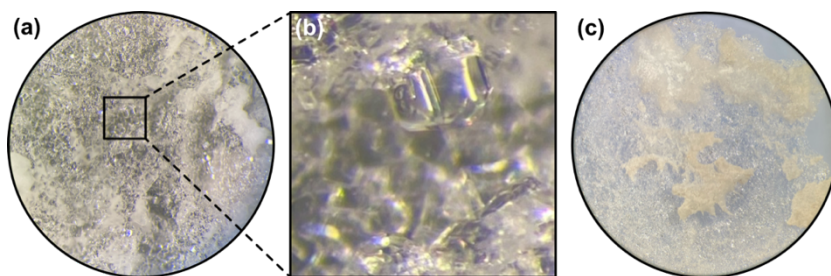


Figure 3-4. Photomicrographs of ES 2-1 (> 1.4 L mark), representing the earliest wall crust. (a) Microcrystalline cubic halite (field width ~3.5 mm); (b) enlarged halite cube with edge length $\approx$ 0.1 mm; (c) intergrown of acicular aragonite (CaCO₃) needles and halite, with no visible fluid (field width ~14 mm).

3.3.2.2 ES 2-2 – Cloudy intermediate layer (Figure 3-5)

Precipitates that accumulated between 1.4 L and 0.5 L marks correspond to brine samples between EV 1-7 and 2-7, a brief interval of high local supersaturation for CaSO_4 (and/or CaCO_3) before bulk NaCl (super)saturation was reached. This set of precipitates form a cloudy or milky whitish appearance (Figure 3-5a), commonly associated with abundant fluid inclusions in previous studies (Goldstein and Reynolds, 1994; Lowenstein and Hardie, 1985; Warren, 2016). Microscopy shows chevron halite crystals with parallel stepped ridges (Figure 3-5b, c), rather than the small cubic halite seen in ES 2-1, intergrown with early Ca-rich acicular needles, most plausibly gypsum, with possible minor aragonite/calcite (Figure 3-5d, e). The spherulitic clusters of acicular needles is typical of gypsum that nucleates rapidly, further supported by relatively higher contents of SO_4 in ES 2-2 than ES 2-1.

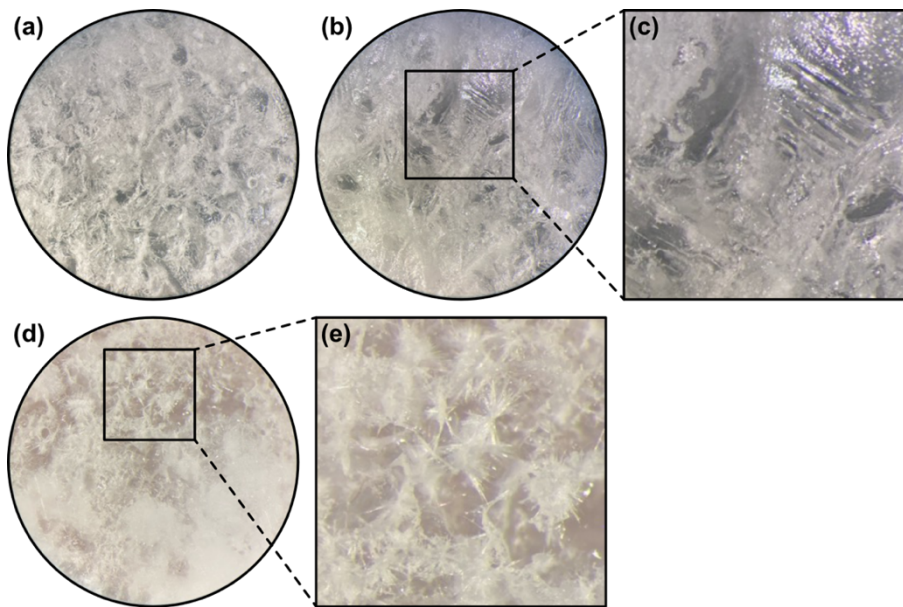


Figure 3-5. Photomicrographs of fraction ES 2-2 (1.4–0.5 L marks), showing cloudy halite with abundant fluid inclusions and early Ca-sulfate precipitation. (a) Overall cloudy appearance with pervasive fluid inclusions (field width ~14 mm); (b) hopper halite plates showing stepped {001} terraces (field width ~14 mm); (c) close-up of halite crystal (field width ~6.3 mm); (d) radially arranged acicular needles (field width ~3.5 mm) (e) enlarged view of the needle bundles (each star-burst bundle ~0.1-0.2 mm diameter; field width ~1.1 mm).

3.3.2.3 ES 2-3W and B – Wall and bottom layers (Figure 3-6)

To assess vertical heterogeneity, this interval was subdivided into a wall fraction (ES 2-3W) and a bottom fraction (ES 2-3B). The wall subfraction (ES 2-3W) is dominated by granular mosaics of chevron halite plates (Figure 3-6a). The clear chevron halite records the moment Na^+ and Cl^- reached supersaturation. This fraction exhibits lower SO_4 content than the bottom fraction (Table 3-2). The bottom subfraction (ES 2-3B) contains radiating star-burst bundles of 2-3 mm acicular gypsum needles (Figure 3-6b, c). The needles extend into open cavities on the chamber wall, do not effervesce in acid, and are thus identified as bottom-nucleated gypsum. Halite veneers locally coat the needles.

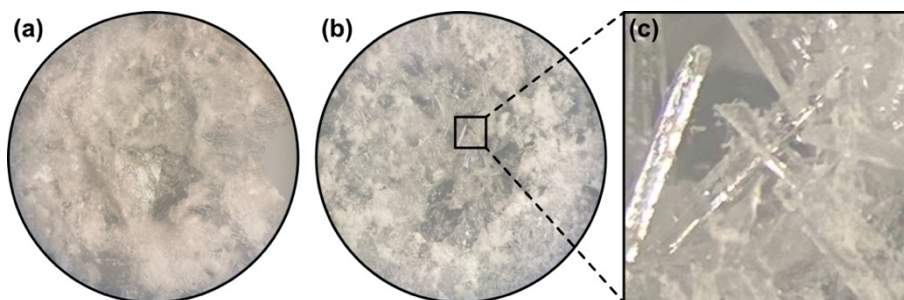


Figure 3-6. Photomicrographs of ES 2-3 wall and bottom fractions. (a) Wall fraction (ES 2-3W) shows granular chevron halite with coarse Ca-phase cores (field width ~22 mm); (b) bottom fraction (ES 2-3B) includes radiating gypsum needles extending into cavity spaces (field width ~14 mm); (c) close-up of individual gypsum needles (field width ~1.5 mm).

3.3.2.4 ES 2-4 – Major halite precipitation stage (Figure 3-7)

Between 0.2 L and 0.1 L marks, clear, coarsely crystalline halite crystals dominate, with minor Ca-phase (calcite or gypsum) pillar. The minor occasion of gypsum pillar might be bottom growth or once-floating gypsum, new halite has formed on the surface, burying the earlier-formed gypsum or calcite crystals underneath. This fraction has lower SO_4 content than the preceding fractions (ES 2-3W and ES 2-3B), consistent with a reduced presence of Ca-phases (Table 3-2). Br content and Br/Cl ratio are also lower, while Cl content is slightly higher, reflecting the dominance of halite.

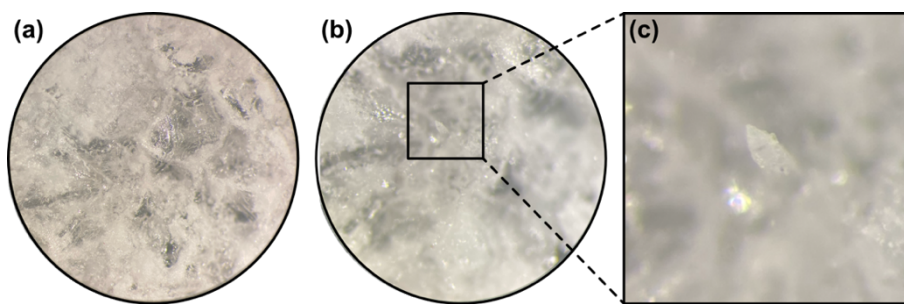


Figure 3-7. Photomicrographs of ES 2-4 (0.2-0.1 L marks), representing the main halite precipitation stage. (a) Chevron or hopper halite crystals (field width ~14 mm); (b) pillar-like crystal in center (field width ~14 mm); (c) close-up of the center of (b; field width ~ 3.6 mm).

3.3.2.5 ES 2-5 – The final precipitate (Figure 3-8)

The final precipitate fraction collected below 0.1 L mark, from the bottom, consists almost entirely of hopper halite crystals, predominantly centimeter-scale. Slight surface pitting and a thin brine film suggest minor interactions with the final residual solution. SO_4 content is lowest here, but Br concentration remains slightly elevated.

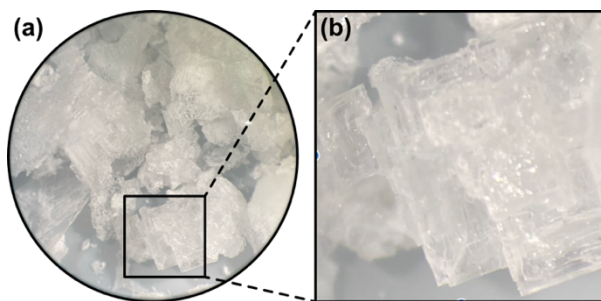


Figure 3-8. Photomicrographs of ES 2-5 (<0.1 L mark, bottom edge), representing the final stage of precipitation. (a) Aggregates of hoppers of halite (field width ~18 mm); (b) detailed view of hopper morphology (field width ~5 mm).

3.3.2.6 Precipitate Chemistry

Bulk precipitate chemistry shows halite-dominated matrices (~78% total salts) with mid-stage sulfate enrichment and a transient bromine maximum that wanes in the late halite stage. Across all fractions, Cl remains high (412,000-543,000 mg/kg), consistent with halite being present in every sample (Table 3-2). SO₄ is relatively elevated in the intermediate fractions (ES 2-2, ES 2-3W/B) and lowest in the final fraction (ES 2-5). Br increases from 151 mg/kg (ES 2-1) to a peak in ES 2-3 (679 mg/kg in ES 2-3W; 419 mg/kg in ES 2-3B), then declines through ES 2-4 (300 mg/kg) to ES 2-5 (251 mg/kg). The Br/Cl ratio follows the same pattern, rising from $\sim 0.28 \times 10^{-3}$ (ES 2-1) to $\sim 1.59 \times 10^{-3}$ (ES 2-3W) and decreasing to $\sim 0.53 \times 10^{-3}$ (ES 2-5).

These chemical trends correspond well with the observed mineralogy and textures. The SO₄ highs in ES 2-2 and ES 2-3 coincide with spherulitic/radiating gypsum (ES 2-3B) and with cloudy chevron halite (ES 2-2) that is widely associated with abundant fluid inclusions. No K- or Mg-bearing evaporites (e.g., polyhalite, carnallite) were detected optically or by bulk chemistry, so relatively elevated Br contents in ES 2-2 to ES 2-3 is best explained by retention of Br-rich residual brine in inclusions rather than by discrete high-Br minerals (Raup and Hite, 1993). The subsequent decline in Br and Br/Cl into ES 2-4 and ES 2-5 is consistent with clearer, coarser halite and reduced inclusion abundance; notably, grinding away inclusions in modern solar salt can lower bulk Br by $\geq 50\%$ (Amdouni, 2010). Overall, the precipitate chemistry summarizes to pervasive halite (high Cl), mid-stage sulfate and inclusion maxima (high SO₄ and Br), and late halite overprint with diminished Br.

3.3.3 Halogen Isotope Variation in Brine, Precipitates, and Gas

Both chlorine ($\delta^{37}\text{Cl}$) and bromine ($\delta^{81}\text{Br}$) isotope values of the brine exhibit systematic changes with progressive evaporation. Overall (including brine, precipitates, and gas) $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values range between -0.26‰ and $+0.45\text{‰}$, and between -0.17‰ and $+0.71\text{‰}$, respectively (Figure 3-9). Amongst the groups, $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values range between -0.26‰ and $+0.45\text{‰}$, and $+0.15\text{‰}$ and $+0.71\text{‰}$, respectively for brine, and between $+0.01\text{‰}$ and $+0.33\text{‰}$, and between $+0.16\text{‰}$ and $+0.39\text{‰}$, respectively, for precipitates. The gas phase captured in KOH solution throughout the entirety of the evaporation experiment is depleted in ^{81}Br , with the lowest $\delta^{81}\text{Br}$ value of any of the sample media ($-0.17 \pm 0.03\text{‰}$).

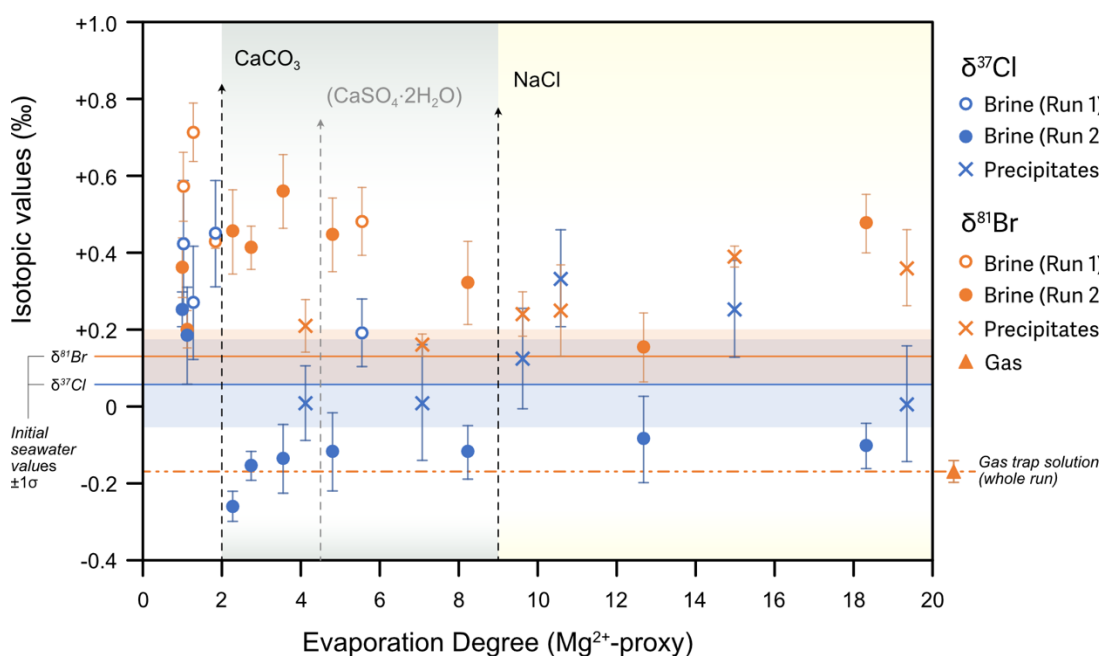


Figure 3-9. Evolution of $\delta^{37}\text{Cl}$ (blue) and $\delta^{81}\text{Br}$ (orange) values in brine (circles), precipitates (crosses), and the gas-trap solution collected over the whole run (triangle) as a function of evaporation degree, calculated from Mg^{2+} concentrations. Horizontal lines and shaded $\pm 1\sigma$ bands represent the initial $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values of synthetic seawater. Shaded backgrounds indicate distinct mineral precipitation stages: Ca-phase (grey) and halite (yellow), as defined in Section 3.3.1 and Figure 3-3. Vertical dashed lines mark the approximate onset of precipitation of CaCO_3 (at $\sim 2\times$ seawater concentration), CaSO_4 ($\sim 4\text{--}5\times$), and NaCl ($\sim 9\times$). Precipitate data points are positioned along the x-axis based on their inferred formation stages rather than direct measurement. Error bars represent $\pm 1\sigma$ analytical precision.

In brine, the values for both isotopes rise steeply from the initial values for the synthetic seawater ($\delta^{37}\text{Cl} = +0.06 \pm 0.11\text{‰}$; $\delta^{81}\text{Br} = +0.13 \pm 0.07\text{‰}$) during the early stage of evaporation, before their trends diverge. At the end of the early stage of evaporation, $\delta^{37}\text{Cl}$ values reach a maximum of $+0.45\text{‰}$ at $\sim 1.8\times$ seawater, while $\delta^{81}\text{Br}$ values peak at $+0.71\text{‰}$ at $\sim 1.3\times$ seawater. The appearance of CaCO_3 needles at $\sim 2\times$ seawater coincides with an abrupt fall in $\delta^{37}\text{Cl}$ values to -0.26‰ . The $\delta^{37}\text{Cl}$ values then rebound slightly to a value of $\sim -0.10\text{‰}$, where it remains (within analytical uncertainty) for the remainder of the evaporation experiment. Conversely, brine $\delta^{81}\text{Br}$ values exhibit a wider

variation. After reaching its early maximum, the $\delta^{81}\text{Br}$ values show a little variation between evaporation degree ~ 2 and ~ 4 , varying within a narrow range of approximately ± 0.05 around 0.5‰ . The values then gradually decrease to a minimum of $+0.15\text{‰}$ at $\sim 13\times$ seawater, within the halite precipitation stage, and subsequently rise again through the remainder of this stage, reaching $+0.48\text{‰}$ in the final sample collected at $\sim 18\times$ seawater.

Isotopic signatures in the precipitated salts generally mirror those of the brines throughout evaporation, but in places diverges from the liquid-phase trends. Every precipitated fraction is enriched in ^{37}Cl relative to the contemporaneous brine: $\delta^{37}\text{Cl}$ values range between $+0.01\text{‰}$ (last halite) and $+0.33\text{‰}$ (earliest precipitate), yielding a relative enrichment in the precipitates compared to brine of between $+0.15\text{‰}$ and $+0.40\text{‰}$. In contrast, $\delta^{81}\text{Br}$ values in the precipitates range between $+0.16\text{‰}$ and $+0.39\text{‰}$, exhibiting either enrichment or depletion in ^{81}Br relative to its contemporaneous brine. The $\delta^{81}\text{Br}$ values in the early Ca-rich crusts containing Ca-carbonate or -sulfate (ES 2-1, 2-2, and 2-3W) tend to be more depleted in ^{81}Br and are 0.08 - 0.35‰ lower than the coexisting brine. Halite-dominated samples formed between $\sim 10\times$ and $\sim 18\times$ seawater are initially enriched in ^{81}Br by 0.24‰ , while later precipitated halite (or halite that interacted with remaining late-stage brine) is depleted in ^{81}Br by 0.12‰ .

The gas phase trapped in the KOH solutions provides direct evidence for bromine volatilization, but not for chlorine volatilization. The bromine captured in the serial KOH traps ($\delta^{81}\text{Br} = -0.17 \pm 0.03\text{‰}$) is depleted in ^{81}Br , approximately 0.65‰ lower than the final brine and 0.31‰ lower than the initial seawater value. No Cl or trapped chlorine was detected in the gas trapped solutions, confirming negligible chlorine volatilization under experimental conditions. Although the Cl^- and Br^- concentrations in the KOH solutions are below the detection limit for IC, faint yellow AgBr precipitate formation during sample preparation for isotopic analysis and successful $\delta^{81}\text{Br}$ measurements verify minimal but detectable bromine capture, while AgCl did not precipitate and was not available for $\delta^{37}\text{Cl}$ measurements. The experimental blank of building-supplied compressed air revealed no detectable bromine or AgBr precipitate, indicating the air supply was not the source of the gaseous bromine and did not contaminate the sample.

3.4 Discussion

3.4.1 Br/Cl Variability

The evolution of Br/Cl ratios in both brine and precipitates during evaporation reflects variable incorporation or exclusion of Br via lattice substitution, fluid inclusion, and/or some other processes. In brine, the Br/Cl ratio increases steadily once halite begins to precipitate at $\sim 9\times$ seawater (Figure 3-10) due to preferential incorporation of Cl^- into halite (NaCl), whereas the Br/Cl ratios of precipitates remain consistently lower than those of the contemporaneous brine. This pattern generally aligns with expectations for halite crystallization, where Br^- is excluded from the halite lattice (Valyashko, 1956). However, measured Br/Cl ratios for all precipitate fractions in this study are higher than values predicted from the distribution coefficient ($b = \text{Br}_{\text{precipitate}}/\text{Br}_{\text{brine}}$). Literature b values are ~ 0.13 for early halite and ~ 0.073 for late halite precipitating near carnallite saturation (Braitsch and Herrmann, 1963; Herrmann et al., 1973; Kühn, 1968). In this context, multiplying b by the Br concentration of the brine yields the predicted Br content of the precipitate, and assuming a fixed Cl content of 60.6 wt.% in halite converts this to a predicted Br/Cl ratio. For the brines in this study, this calculation predicts $\text{Br/Cl} \times 1000$ values of ~ 0.066 for early halite and ~ 0.18 for late halite (Table 3-3); by comparison, measured $\text{Br/Cl} \times 1000$ ratios range from 0.28 (ES 2-1) to 1.59 (ES 2-3W), which remain higher than the predicted values.

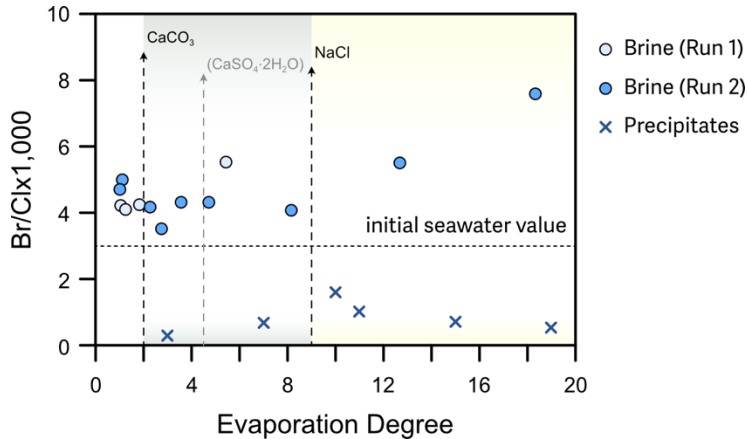


Figure 3-10. Br/Cl ratios in brine (circles) and precipitated salts (crosses) as a function of evaporation degree, calculated from Mg^{2+} concentrations. Horizontal dashed line indicates the

initial Br/Cl ratio of the synthetic seawater. Shaded background and vertical dashed lines mark the approximate onset of mineral precipitation stages as described in Figure 3-9.

Table 3-3. Comparison of Br/Cl×1000 ratios in brine and precipitates throughout the evaporation sequence. Expected Br/Cl ratios in precipitates are calculated by multiplying the distribution coefficient ($b = \text{Br}_{\text{precipitate}}/\text{Br}_{\text{brine}}$) by the Br concentration of the contemporaneous brine and converting to Br/Cl ratios assuming a fixed Cl content of 60.6 wt.% in halite. Measured Br and Cl contents for each fraction are listed in Table 3-2.

Mineral phase	b	Br/Cl×1000		
		Brine, this study	Precipitate, predicted	Precipitate, measured
Halite, first precipitate	0.13	4.3 (307 mg Br/L; EV 2-5)	0.066 (307*0.13/606)	0.278 (ES 2-1) 0.683 (ES 2-2) 1.59 (ES 2-3W)
Late halite, at carnallite saturation	0.073	7.6 (1480 mg Br/L; EV 2-9)	0.18 (1480*0.073/606)	1.02 (ES 2-3B) 0.693 (ES 2-4) 0.534 (ES 2-5)

The elevated Br/Cl ratios in early precipitates (ES 2-1 through ES 2-3W) are primarily driven by Br enrichment, rather than Cl depletion (Table 3-2). This enrichment likely results from the incorporation of residual brine into fluid inclusions during mineral precipitation, when residual brine remains abundant and in continuous contact with the growing crystals. In addition, the increase in Br/Cl ratios of the precipitates generally follows that of the brine, implying that evolving Br-enriched brine trapped in these fluid inclusions contributed to the observed enrichment. Supporting evidence for the presence of fluid inclusions includes cloudy textures observed in precipitates (e.g., ES 2-2), which are widely associated with inclusion-rich halite (Goldstein and Reynolds, 1994; Lowenstein and Hardie, 1985), and elevated SO₄ contents (e.g., ES 2-3W), suggesting entrapment of sulfate-rich residual brine in halite (Lazar and Holland, 1988), possibly with minor gypsum. The relatively rapid pace of evaporation in this study may have further promoted fluid inclusion entrapment; modern solar salts, which precipitate relatively rapidly, are also known to contain 3-5 vol% trapped brine inclusions (Amdouni, 2010; Eggenkamp et al., 2019a).

$\delta^{37}\text{Cl}$ values in precipitates show a positive correlation with Br/Cl ratios, increasing from +0.01‰ to +0.33‰ (Figure 3-11). In one previously studied paleo-evaporite basin (*Chapter 4*), only a weak Br/Cl- $\delta^{37}\text{Cl}$ correlation was observed, whereas another paleo-halite sequence reported an opposite trend with $\delta^{37}\text{Cl}$ decreasing as Br/Cl increased (Eggenkamp et al., 2019b). Instead, the results of this study resemble isotopic patterns observed in modern table salt produced via solar evaporation (Eggenkamp et al., 2019a). The positive trend observed for modern table salt has been attributed to kinetic fractionation, where rapid precipitation isolates the crystal from the brine before equilibrium can be established (Eggenkamp et al., 2019a). Although samples in this study were not harvested prematurely, the intense evaporation (>95% of the brine volume lost in less than two weeks) likely created similar disequilibrium. This would allow ^{37}Cl -rich brine to be incorporated into the growing lattice faster than isotopic exchange could occur, resulting in a progressive increase of $\delta^{37}\text{Cl}$ in precipitates.

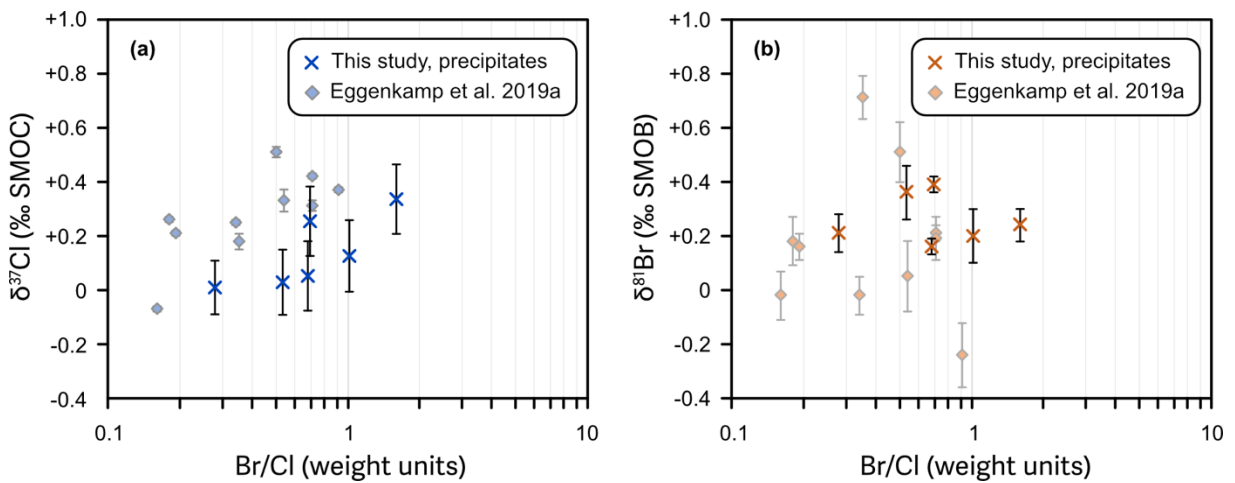


Figure 3-11. $\delta^{37}\text{Cl}$ (a, blue) and $\delta^{81}\text{Br}$ (b, orange) values in precipitates as a function of Br/Cl ratios. Crosses represent data from this study; diamonds indicate values from Eggenkamp et al. (2019a) for primary halite formed in modern solar salt settings. Error bars represent $\pm 1\sigma$ analytical uncertainty.

In contrast, $\delta^{81}\text{Br}$ values in precipitates range between +0.16‰ and +0.39‰ but show no systematic relationship with Br/Cl ratios (Figure 3-11). This implies that the incorporation and isotopic

fractionation of bromine are not solely governed by a single mechanism such as fluid inclusion. While fluid inclusion might explain elevated Br/Cl ratios in early-stage precipitates, through entrapment of evolving Br-enriched brine, likely driven by rapid crystal growth and associated inclusion/occlusion of interstitial fluids, $\delta^{81}\text{Br}$ values appear to be influenced by other mechanisms. These include preferential volatilization of ^{79}Br , confirmed by the relatively low $\delta^{81}\text{Br}$ value in the trapped gas, and potentially inefficient incorporation of Br into the lattice, which may suppress equilibrium-driven isotopic fractionation. The overall $\delta^{81}\text{Br}$ trend in solution evolves independently from Br/Cl ratios throughout evaporation, suggesting that vapor loss, lattice exclusion, and residual brine enrichment can each play distinct roles to the observed isotopic variations.

3.4.2 Evolution of Chlorine and Bromine Isotopic Ratios

The $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values in brine, precipitated salts, and trapped gas collectively record a sequence of halide isotopic evolution during evaporation and precipitation of Ca-bearing and halite salts (Figure 3-9). Each stage or process leaves a characteristic isotopic imprint that can be tied to one or more dominant fractionation mechanisms, including precipitation, fluid inclusion, and selective volatilization. The isotopic record divides into two stages: an early enrichment in both ^{37}Cl and ^{81}Br followed by variable, opposite $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ trends during Ca-phase precipitation ($2\text{--}9\times$ seawater), and a late enrichment in ^{37}Cl in precipitation and ^{81}Br in brine coincident with halite precipitation ($>9\times$ seawater) and Br volatilization.

Previous experimental study of simplified binary salt systems (e.g., NaCl, NaBr, CaCl_2 , CaBr_2 , NH_4Cl , NH_4Br) demonstrated that halide isotope fractionation varies by co-precipitating cation (Eggenkamp et al., 2016). While both the magnitude and direction of fractionation are generally cation-sensitive, $\delta^{81}\text{Br}$ fractionation remains small in the binary systems (e.g., $10^3\ln\alpha$ values range from -0.07 ± 0.05 for NaBr to $+0.11 \pm 0.05$ for NH_4Br). The multi-ion seawater matrix used in this study reveals more complex isotopic trends with larger variations in $\delta^{81}\text{Br}$ values, suggesting additional or complex interactions. The following subsections examine these isotopic trends in detail, highlighting the distinct fractionation behaviors during (i) Ca-phase precipitation, (ii) halite-dominated precipitation, and (iii) bromine volatilization.

3.4.2.1 Isotopic behavior during Ca-phase precipitation

When brine concentration reaches approximately $2\times$ seawater, CaCO_3 becomes supersaturated, initiating precipitation of carbonate minerals. During this phase, $\delta^{37}\text{Cl}$ value in the brine abruptly decreases from a maximum of $+0.45\text{‰}$ to a minimum of -0.26‰ , followed by a rebound to around -0.1‰ (Figure 3-9). In contrast, $\delta^{81}\text{Br}$ value varies, increasing to $+0.71\text{‰}$ prior to CaCO_3 precipitation, but then decreasing slightly during this phase.

The earliest precipitate (ES 2-1) that formed during this stage contains aragonite needles intergrown with cubic halite (Figure 3-4c). It exhibits $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values close to the initial seawater, but is slightly enriched in ^{37}Cl by $\sim +0.15\text{‰}$ and depleted in ^{81}Br by $\sim -0.35\text{‰}$ relative to the coexisting brine. These isotopic offsets are consistent in direction with binary Ca-halide systems ($10^3\ln\alpha \approx +0.04 \pm 0.02$ for CaCl_2 and -0.06 ± 0.04 for CaBr_2 ; Eggenkamp et al., 2016) but exceed their magnitudes, suggesting additional fractionation processes through multi-cation/anion interactions or co-precipitation of other minerals in a multicomponent seawater matrix.

Halide incorporation into solids at this stage appears to occur via multiple pathways, mainly through precipitation of aragonite and possibly microcubic halite. Optical evidence (Figure 3-4c) confirms the presence of aragonite needles in ES 2-1, which can accommodate >142 mg/kg Cl and ~ 40 mg/kg Br (Kitano et al., 1975; Okumura and Kitano, 1986). The elevated Br content (150 mg/kg; Table 3-2) likely reflects efficient lattice-scale Br substitution into rapidly growing acicular aragonite under low salinity, where competition with Cl is reduced (Okumura and Kitano, 1986). Microcubic halite, although present, is less likely to have contributed to Br uptake given its relative slow growth habit, indicated by clear, well developed cubic faces (Desarnaud et al., 2018) and its lower Br/Cl ratios compared to other samples. These observations suggest that Br incorporation, and the relatively low $\delta^{81}\text{Br}$ values in the earliest precipitate, were dominated by aragonite lattice substitution, with possible minor contributions from brine entrapped as fluid inclusions.

As evaporation progresses and NaCl concentration increases, calcite replaces aragonite as the dominant Ca-phase (Zhong and Mucci, 1989). Calcite incorporates only ~ 43 mg/kg Cl and <1 mg/kg Br (Kitano et al., 1975; Okumura and Kitano, 1986). In this study, ES 2-2 and ES 2-3W exhibit higher SO_4 and lower Cl contents relative to ES 2-1, a compositional shift that aligns with the transition from aragonite to calcite dominance (Kitano et al., 1975). Although these samples contain more Br than can be explained by calcite substitution alone, their relatively small isotopic offsets

between brine and precipitates suggest that excess Br was incorporated mainly via brine trapped as fluid inclusions or adhered films (second and third “x” in Figure 3-9).

Gypsum precipitation also occurs during this phase, as indicated by gypsum needles in ES 2-3B and high SO₄ content in ES 2-3W. Gypsum is known to form through bottom-nucleation in meromictic settings, or even in well-mixed shallow settings, during rapid changes in water salinity, often trapping abundant brine inclusions (Warren, 2016). The relatively high Br content in gypsum-bearing precipitates, combined with minimal isotopic offset from the brine, supports the interpretation that Br was primarily incorporated via fluid inclusion rather than lattice substitution. Fluid inclusions tend to preserve the isotopic composition of the trapped brine and thus would not induce significant isotopic fractionation.

Taken together, during the Ca-precipitation phase, a transition from chemically selective to physically passive Br incorporation is evident. Early-stage aragonite incorporates Br primarily through lattice substitution, producing measurable isotopic fractionation, whereas later calcite and gypsum retain Br largely through physical entrapment in fluid inclusions, without significant isotopic fractionation. The relatively stable $\delta^{37}\text{Cl}$ values in both brine and precipitates throughout this interval ($\sim 8\text{-}10\times$ seawater) further support this mechanism shift.

3.4.2.2 Halite-dominated stage

Following the Ca-precipitate phase, the evaporation-precipitation sequence transitions to the halite-precipitate phase as the brine reaches NaCl supersaturation starting at approximately $9\times$ seawater. This stage marks a transition in halite crystallization habit, from sub-100 μm microcubes to millimetre-scale hopper and chevron plates. These indicate a change toward more active and prevalent halite growth under high supersaturation conditions. Such morphological changes are often accompanied by limited trace ion incorporation, where kinetic effects during rapid growth can influence both trace element incorporation and isotopic fractionation (Desarnaud et al., 2018).

During this stage, Br contents in the precipitates decrease with progressive evaporation, from 419 mg/kg to 251 mg/kg, while Cl contents gradually increase from 412,000 to 471,000 mg/kg (ES 2-3B through ES 2-5; Table 3-2). The Br contents exceed those expected by equilibrium partitioning alone ($\text{Br}_{\text{halite}}/\text{Br}_{\text{brine}} \approx 0.13$; Braitsch and Herrmann, 1963), implying that kinetic processes such as fluid inclusion or surface adsorption are important during early, rapid halite crystal formation. As crystals enlarge, the incorporation of Br into NaCl decreases, and concurrently, the decreasing influence of

other Br-entrapping minerals such as gypsum may also contribute to the observed lower bulk Br contents in later-stage halite precipitates.

Precipitate $\delta^{81}\text{Br}$ values increase from $+0.20\text{‰}$ near the onset of halite precipitation to $+0.39 \pm 0.03\text{‰}$ in ES 2-4, followed by a minimal decrease to $+0.36 \pm 0.10\text{‰}$ in ES 2-5. This trend broadly mirrors the $\delta^{81}\text{Br}$ values of the brine, which increase from $+0.15\text{‰}$ to $+0.48\text{‰}$ between $\sim 9\times$ and $\sim 18\times$ seawater. However, the $\delta^{81}\text{Br}$ offsets between precipitate and brine are greater than those expected from equilibrium lattice substitution into halite alone ($10^3\ln\alpha_{\text{precipitate_brine}} \approx -0.07 \pm 0.05\text{‰}$ for NaBr; Eggenkamp et al., 2016), indicating that additional fractionation processes contribute the enrichment of brine in ^{81}Br . The isotopically light trapped gas ($\delta^{81}\text{Br}$ of -0.17‰) confirms selective loss of ^{79}Br to the gas phase, which would enrich the residual brine in ^{81}Br .

In contrast, $\delta^{37}\text{Cl}$ values in the brine remain nearly constant (within analytical uncertainty) at -0.1‰ , while precipitates are consistently enriched in ^{37}Cl relative to the brine. The isotopic offset decreases from $\sim 0.4\text{‰}$ to $\sim 0.1\text{‰}$ ($+0.33\text{‰}$ in ES 2-4 to $+0.03\text{‰}$ in ES 2-5). The overall enrichment in ^{37}Cl of precipitation aligns with laboratory determined equilibrium fractionation factors for NaCl precipitation ($10^3\ln\alpha_{\text{precipitate_brine}} \approx +0.35 \pm 0.08\text{‰}$ for NaCl; Eggenkamp et al., 2016) and is consistent with observations in natural paleo salt sequences where $\delta^{37}\text{Cl}$ decreases about 0.30‰ as Br/Cl ratios increase (Eggenkamp et al., 2019b).

Combined, these observations provide an isotopic mass balance for the halite-dominated stage. During early NaCl supersaturation, rapidly growing halite crystals tend to incorporate ^{37}Cl and modest amounts of Br, via near-lattice substitution, as well as potentially via fluid inclusions or surface adsorption. As crystals enlarge and brine volume decreases, both the incorporation of Br and the Cl isotopic offset between brine and precipitates decrease. Simultaneously, volatilization of ^{79}Br may play a secondary role to residual brine enrichment in ^{81}Br . The interplay of these processes leads to the observed decrease in $\delta^{37}\text{Cl}$ offsets and increase in $\delta^{81}\text{Br}$ offsets between brine and precipitates during the later stages of evaporation-precipitation. These patterns are more complex than those observed in binary salt systems and are thus more representative of natural settings of multicomponent seawater systems.

3.4.2.3 Bromine volatilization and $\delta^{81}\text{Br}$ evolution

At the end of the experiment, bromine captured in the KOH traps was significantly depleted in ^{81}Br ($\delta^{81}\text{Br} = -0.17 \pm 0.03\text{‰}$), approximately 0.31‰ lower than the initial seawater and 0.65‰ lower than the final brine. This confirms preferential volatilization of the lighter Br isotope, ^{79}Br , which was previously observed in a field study of an active evaporative environment (Hanlon et al., 2017). A simple isotope mass balance shows that shifting brine from +0.13‰ to +0.48‰ with gas at -0.17‰ would require loss of ~53% of the total Br (~260 mg for a ~490 mg Br inventory), indicating that the captured vapor alone cannot explain the ~0.34‰ rise in $\delta^{81}\text{Br}$. Volatilization thus provides clear directional evidence for ^{79}Br loss, while the magnitude of the ^{81}Br enrichment reflects overall limited ^{81}Br (or preferred ^{79}Br) incorporation into solids. As evaporation progresses and brine volume decreases, the isotopic impact of volatilization becomes significant.

In natural environments, volatilization of Br may occur through both inorganic and organic pathways, further increasing the fractionation effect beyond the laboratory observation. Inorganic reactions include photochemical or oxidant-driven generation of Br_2 , HOBr , or HBr from hypersaline surface films or sea salt aerosols (Sander et al., 2003; Vogt et al., 1996). Organic pathways involve microbially or abiotically mediated formation of volatile organobromine compounds (e.g., CHBr_3 , CH_2Br_2), especially in environments rich in dissolved organic carbon (DOC) and nutrients (Ziska et al., 2013). Substantial amounts of sediment-bound organobromine found widely in marine sediments indicate that such natural production pathways are common and can serve as a source of volatile Br species to the atmosphere (Leri et al., 2010). The present experiment minimized organic effects by using synthetic seawater with negligible DOC, yet still yielded ^{79}Br -enriched gas. This implies that inorganic volatilization alone under high salinity can drive measurable $\delta^{81}\text{Br}$ fractionation, and that natural environments where organic pathways operate, the effect could be even greater.

Although $\delta^{81}\text{Br}$ measurements of the Br volatile species remain rare, available field observations support evolution of $\delta^{81}\text{Br}$ through volatilization. Gases emitted from salt flats were depleted in ^{81}Br compared to associated brines and salts (e.g., -1.02 to -0.72‰ in gases vs. +0.07 to +1.47‰ in brines; Hanlon et al., 2017). Similarly, Br-bearing gases recovered from a coalbed methane field exhibited $\delta^{81}\text{Br}$ value (-0.81‰), significantly lower than water samples in the area (Stotler et al., 2021). These field observations are consistent with the experimental results presented here and reinforce the interpretation that volatilization selectively removes ^{79}Br , enriching the residual fluid in ^{81}Br . Because chlorine lacks comparable volatile species under similar conditions, this process is likely an important

driver of bromine isotope fractionation in late-stage brine evolution. Precipitation of Br-bearing salts may also occur at this stage, but the small brine volume in this study likely limited their formation or observation. Such precipitation, if significant in natural systems, could additionally contribute to the divergent $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ trajectories observed.

3.4.3 Reproducibility and Geometry Effects

Replicate experiments carried out in a flat pan (Run 1) and a 13°-tilted pan (Run 2) produced comparable isotopic trends across the shared evaporation interval. For the first seven brine samples, up to $\sim 10\times$ seawater, the Mg-normalized evaporation degree and paired $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values agree within $\pm 0.05\text{--}0.20\text{‰}$, well within analytical uncertainty, confirming that the isotopic signals are reproducible across both geometries. The Mg proxy also performs consistently between runs, validating its use as a concentration index for both setups.

Despite this overall agreement, subtle differences arise from the tilted geometry. In Run 2, the upslope wall and edge experience a thinner brine layer and therefore reach local supersaturation earlier than the bulk solution. This produces stratified Ca-phase and halite precipitates, in contrast to the more uniformly distributed salt cake formed in the level pan in Run 1. In addition, the downslope corner in the tilted pan retains brine longer, allowing extended sampling to a final evaporation degree of $18\times$ seawater. Conversely, the flat geometry in Run 1 supports a more constant evaporation rate, providing a better baseline for early- and mid-stage comparisons.

Other conditions such as air temperature and relative humidity remained nearly identical between the two runs (Appendix Figures D-1 and D-2), indicating that the observed isotopic differences are attributable to the evaporation pan geometry rather than these external factors. Run 1 thus offers a cleaner signal for capturing early-stage isotopic behaviors under steady evaporation, while Run 2 enables access to late-stage samples and stratigraphic precipitates, each geometry offering advantages.

3.5 Conclusion

This study provides the first observation of both chlorine- and bromine-isotopic variations during complete evaporation of synthetic multi-ion seawater. Using two replicate runs (one in a flat pan and one tilted at 13°), halogen isotope evolution in brine, precipitates, and gas across the full evaporation sequence were studied. The close agreement in $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values between both runs

demonstrates that using a Mg-based proxy of degree of evaporation relative to seawater concentration yields consistent and reproducible fractionation trajectories.

Three main mechanisms explain the isotopic behaviors of Cl and Br: kinetic uptake by Ca-carbonates, fluid inclusion or lattice inclusion in halite crystals, and preferential ^{79}Br volatilization. Rapid nucleation of aragonite $\pm$ calcite enriches residual brine in ^{37}Cl ($\delta^{37}\text{Cl}$ up to +0.45‰), while the precipitates remain close to initial seawater $\delta^{37}\text{Cl}$ values but depleted in ^{81}Br relative to initial seawater by up to 0.35‰. These offsets match previously published Ca-halide equilibrium fractionation factors, supporting carbonate precipitation as the initial control on halogen isotopic divergence between brine and precipitate. As halite crystallizes and transitions from microcubes to hopper crystals, $\delta^{37}\text{Cl}$ values in precipitates decrease from +0.33‰ to +0.03‰, and $\delta^{81}\text{Br}$ values increase from +0.24‰ to +0.36‰, while the residual brine evolves toward higher $\delta^{81}\text{Br}$ with little change in $\delta^{37}\text{Cl}$.

The progressive increase in $\delta^{81}\text{Br}$ in brine cannot be explained by equilibrium fractionation via lattice substitution alone. Selective volatilization of ^{79}Br , evidenced by the isotopically light bromine gases trapped in KOH ($\delta^{81}\text{Br} = -0.17\text{‰}$), also contributes. Although the volatilized mass was small, the accompanying isotopic shift ($\sim -0.33\text{‰}$) in the final brine is significant, especially given the reduced fluid volume and diminishing inclusion capacity at late evaporation stages. The absence of detectable Cl in the gas phase confirms that volatilization selectively modifies $\delta^{81}\text{Br}$.

These results demonstrate that halogen isotope evolution in multi-ion brines arises from a complex interplay of chemical partitioning, physical entrapment, and phase-specific losses. The findings in this study provide a systematic baseline for interpreting Cl-Br isotope records during seawater evaporation and mineral precipitation, where multi-phase and multi-mineral precipitation sequences act together to shape halogen isotope compositions.

Given the early stage of this line of research and the need to refine the mechanisms identified, several recommendations are provided here for future studies: (i) increase sampling frequency, especially just prior to the onset of and during the key mineral precipitation events; (ii) conduct mineralogical characterization and analysis (e.g., XRD) to better resolve phase-specific or mineral-specific isotope signatures; (iii) perform halide mass balances, including quantification of total halide content in each mineral and volatile phases; (iv) repeat the experiments under varied temperature conditions; and (v) evaluate potential organic or microbial influences on Br isotope fractionation.

Chapter 4

Bromine and Chlorine Isotopic Values of Evaporites from the Salina Formation, Michigan Basin

4.1 Introduction

Recent advances in chlorine and bromine isotope geochemistry have highlighted intriguing research questions about fractionation pathways in bromine isotopes in natural settings. For instance, observations often reveal larger Br isotope variations than Cl, and substantially greater ranges than those predicted by theoretical models and laboratory experiments (Eggenkamp, 2016; Eggenkamp et al., 2016; Gao and Liu, 2021). It remains unclear why these two compatible halogens respond differently to some fractionation pathways, and exactly how certain geologic processes, such as salt precipitation, compaction, and brine migration, alter bromine isotope compositions (Eggenkamp, 2014b; Eggenkamp et al., 2019a, 2019b; Eggenkamp and Coleman, 2009; Hanlon et al., 2017; Shouakar-Stash, 2008). While some efforts have been made to understand these isotopic variations through laboratory experiments and theoretical calculations, focusing on certain processes (i.e., diffusion, compaction, salt precipitation and gas volatilization); however, these do not yet explain the full extent of the isotopic behavior and distribution of bromine in natural systems (Czarnacki and Hałas, 2012; Eggenkamp and Coleman, 2009; Strydom et al., 2022). Advancing our understanding of the mechanisms and magnitudes of bromine isotope fractionation is thus critical to improve its usefulness as a geochemical tracer in paleo-environmental reconstructions, as well as to elucidate the behavior of halogens in natural settings.

Groundwater chloride and bromide geochemistry within sedimentary basins shows wide variability, particularly in systems influenced by evaporite deposits (Hanor, 1994; Kharaka and Hanor, 2003; Worden, 2018). These variations reflect a complex interplay of processes, including halite dissolution-reprecipitation, water-rock interaction, and mixing with brines of different solute origins (Babel and Schreiber, 2014; Cendón et al., 2004; Küster et al., 2009; McIntire, 1963). While halogen concentrations can reflect these processes to some extent, they often yield ambiguous interpretations due to overlapping signatures from multiple sources and subsequent diagenetic modification. In this context, halogen isotopes, particularly $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$, have been increasingly applied to characterize brine mixing and fluid evolution; yet most studies have focused on the

dissolved phase in modern groundwater systems (Chen et al., 2014; Eggenkamp, 2025; Gwynne et al., 2013; Jiang et al., 2022; Shouakar-Stash, 2008). By contrast, significantly fewer studies have explored the halogen isotopes solid phases within evaporitic basins (Eggenkamp et al., 2019b, 2019a; Ercan et al., 2019). Among those, most examined halite-rich intervals at limited spatial or stratigraphic scales, often without integrated comparisons to co-occurring Ca-bearing minerals or across multiple lithologic and diagenetic contexts. As a result, significant questions remain regarding how different depositional and post-depositional processes affect Cl and Br isotope distributions in evaporite-bearing rock sequences. In particular, the potential of $\delta^{81}\text{Br}$ as an indicator of diagenetic alteration (e.g., organic or microbial degradation of organic-Br) has only recently begun to be explored and remains poorly constrained (Stotler et al., 2021; Wang, 2017). A broader, basin-scale, multi-lithology investigation is needed to determine how isotopic compositions are preserved or overprinted across diverse geological contexts.

The goal of this study is to elucidate how depositional and post-depositional processes govern Cl and Br isotope distributions in rock records. This will be accomplished by characterizing the Cl and Br contents and isotopic compositions in multiple lithologies and horizons of the Silurian Salina Formation across the Michigan Basin. The Salina Fm. was deposited through repeated cycles of marine inflow and intense evaporation and includes thick halite beds interlayered with carbonates, anhydrites, and shale, and is known to host elevated halogen concentrations (Harrison III and Voice, 2017; Mesolella et al., 1974). The formation also shows some evidence of substantial diagenetic modification, including halite dissolution, brine reflux, burial compaction, and fluid-rock interaction, which makes it an excellent natural laboratory for exploring how evaporation-deposition and post-depositional processes shaped halogen isotopic signatures (Das et al., 1990; McIntosh and Walter, 2005; Sarg, 1982). This will advance our understanding of halogen systematics in evaporitic rock records and the interplay of geological and geochemical processes that affect these signatures in sedimentary basins.

4.2 Background: Chloride and bromide geochemistry during evaporation of seawater and precipitation of evaporative minerals

During seawater evaporation and subsequent mineral deposition, chloride (Cl) and bromide (Br) concentrations and their relative proportions in the evaporating seawater change, due to their differing behaviors and inclusion in various evaporite minerals (Figure 4-1). Initially, Cl and Br both behave

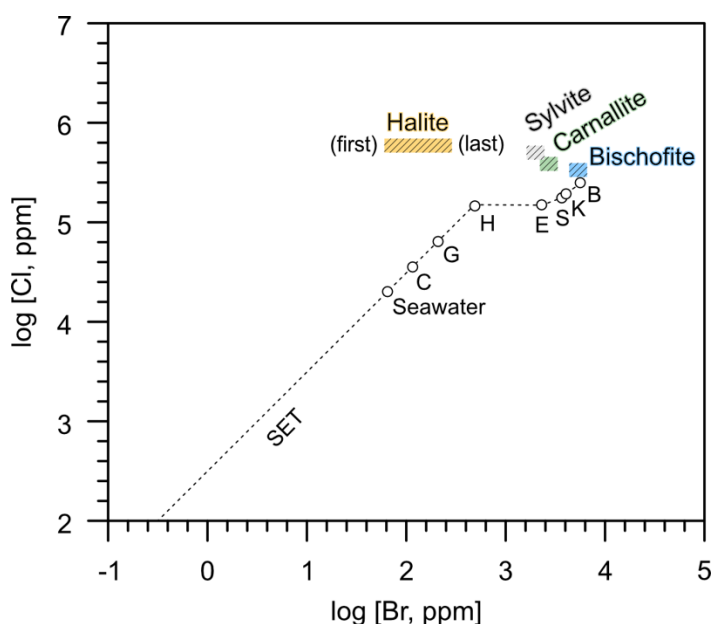


Figure 4-1. Log-log plot of Br vs. Cl concentrations (in ppm) during progressive seawater evaporation, along with the Br and Cl contents in the resulting evaporite minerals. The dashed line indicates the seawater evaporation trajectory (SET; *Carpenter, 1978; McCaffrey et al., 1987*), illustrating how Br and Cl concentrations in brine evolve as major salt phase precipitates in turn: calcite (C), gypsum (G), halite (H), epsomite (E), sylvite (S), carnallite (K), and bischofite (B) (*Matray, 1988*). Shaded areas indicate the typical Br-Cl ranges in evaporites including “first” through “last” halite (yellow), sylvite (grey), carnallite (green), and bischofite (blue) (refer to the main text for details).

conservatively, remaining in solution at a constant Br/Cl ratio until halite saturation (McCaffrey et al., 1987). Early precipitates, such as calcite (CaCO_3) and gypsum/anhydrite (CaSO_4), do not include halogens in their crystal structures, so negligible amount of Cl or Br is removed from the brine at those stages. Once halite (NaCl) begins to precipitate, Cl is readily incorporated into its crystal lattice, while only minor, variable amounts of Br enter halite via surface adsorption, occlusion or fluid inclusion, or substitution in a crystal lattice, causing the Br/Cl ratio in the residual brine to rise (Carpenter, 1978; McIntire, 1963; Valyashko, 1956). Continued evaporation leads to precipitation of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), sylvite (KCl), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) progressively, each having a larger Br partition coefficient than halite, with Cl and Br concentrations

further increasing in the brine as water volume decreases (Harvie et al., 1980). As these later salts incorporate Br more efficiently than halite, the net rise in the Br/Cl ratio in brine may slow or even reverse, depending on how efficiently these minerals incorporate Br (Braitsch, 1971).

Br contents and Br/Cl ratios can be used not only to infer the stage of evaporation at which a mineral formed but also to detect overprinting by diagenetic or tectonic processes in evaporative settings, thus can be used to fingerprint primary and secondary origins (Eggenkamp, 2025; Kühn, 1968; Siemann and Schramm, 2000). Solid phase Br contents vary widely, while Cl contents in evaporite minerals exhibit a narrow range, fixed by their chemical formula. (Braitsch, 1971; Eggenkamp, 2025; Siemann and Schramm, 2000). During evaporation, the first halite that forms at ~ 10.6 times seawater salinity, typically contains 60-75 ppm Br ($\text{Br/Cl} \times 1000 \sim 0.1-0.125$, mass ratio), suggesting a lower limit for primary halite (Braitsch, 1971; Herrmann et al., 1973; Schreiber and Tabakh, 2000; Valyashko, 1956). As salinity increases further, Br contents in last halite to precipitate can reach ~ 270 ppm Br, with $\text{Br/Cl} \times 1000$ ratios increasing to ~ 0.45 (Schreiber and Tabakh, 2000). With continued evaporation and as Br/Cl ratios continue to increase in the brine, Br contents in the subsequent minerals also increase, with Br contents in sylvite around 2000 ppm and $\text{Br/Cl} \times 1000$ of $\sim 3-4$ (Braitsch, 1971; McCaffrey et al., 1987). Carnallite precipitates in advanced Br-rich brines and incorporates significant amounts of Br, thus its Br content often rises to ~ 2600 ppm, and the $\text{Br/Cl} \times 1000$ ratio increases to ~ 10 (Braitsch, 1971; Schreiber and Tabakh, 2000). By the bischofite precipitation stage, Br concentrations in brine can exceed 0.4 wt.% Br (varying between 0.431% and 0.608%), so the Br content in bischofite may reach up to ~ 6000 ppm ($\text{Br/Cl} \times 1000 \sim 17$) (Braitsch, 1971; McIntire, 1963).

While the initial Br-Cl signatures in evaporites are largely set by seawater evaporation and early mineral precipitation, post-depositional alterations such as brine reflux or salt tectonics can significantly modify Br-Cl contents and ratios. Reflux occurs when dense, saturated brine plumes descend into underlying or adjacent formations, causing partial dissolution and recrystallization of evaporite minerals, during later interactions with subsurface fluids under temperature-pressure condition changes, compaction, or uplift (Babel and Schreiber, 2014; Warren, 2018, 2016). In halite, (partial-)dissolution and recrystallization typically lowers Br content (< 60 ppm) by preferentially removing Br into the brine, thus reducing the Br/Cl ratios in the solid (Stoessell and Carpenter, 1986; Cendón et al., 2004). In contrast, salt tectonics (i.e., halokinesis) can trap pockets of highly evolved

brine with decreased volume under pressure and alter halite to have exceptionally high Br content, exceeding several thousand ppm, over 4000 ppm (Risaçher and Fritz, 2000; Küster et al., 2009).

4.3 Study Area: The Salina Formation in the Michigan Basin

The Salina Formation in the Michigan Basin is a sedimentary rock sequence composed of cyclic deposition of evaporites and interbedded evaporitic carbonates during the Silurian period (Mesoella et al., 1974). This formation extends across Michigan, USA, through Ontario, Canada, and into Pennsylvania and New York, USA in both the Michigan and the Appalachian Basins (Figure 4-2a). During the middle Paleozoic era, the Michigan Basin was consistently tropical to subtropical and formed a restricted and isolated embayment due to structural arches surrounding the basin, including the Algonquin and Findlay Arches (Catacosinos et al., 1991; Davis, 1964). Restricted seawater circulation resulted in cyclic evaporation and refreshing, forming repeated deposits of halite, gypsum, anhydrite, dolomite, and calcite enriched with high halide concentrations (Mesoella et al., 1974).

The Salina Formation is subdivided into units based on mineralogical dominance and depositional cycles: A-1 Evaporite, A-1 Carbonate, A-2 Evaporite, A-2 Carbonate, B, C, D, E, F, and G Units (Landes, 1945; Mesoella et al., 1974) (Figure 4-2d; see Appendix F for detailed explanation of each unit). Cyclic deposition of carbonates and evaporites is attributed to sea-level fluctuations driven by tectonic and/or climatic changes, with carbonate deposits corresponding to high sea levels and evaporites to low sea levels (Fisher, 1977; Sloss, 1969). The A-1 and A-2 Carbonates, deposited in environments conducive to the accumulation and preservation of organic matter, are noted by their higher organic content compared to the other units within the Salina Formation (Harrison III and Voice, 2017).

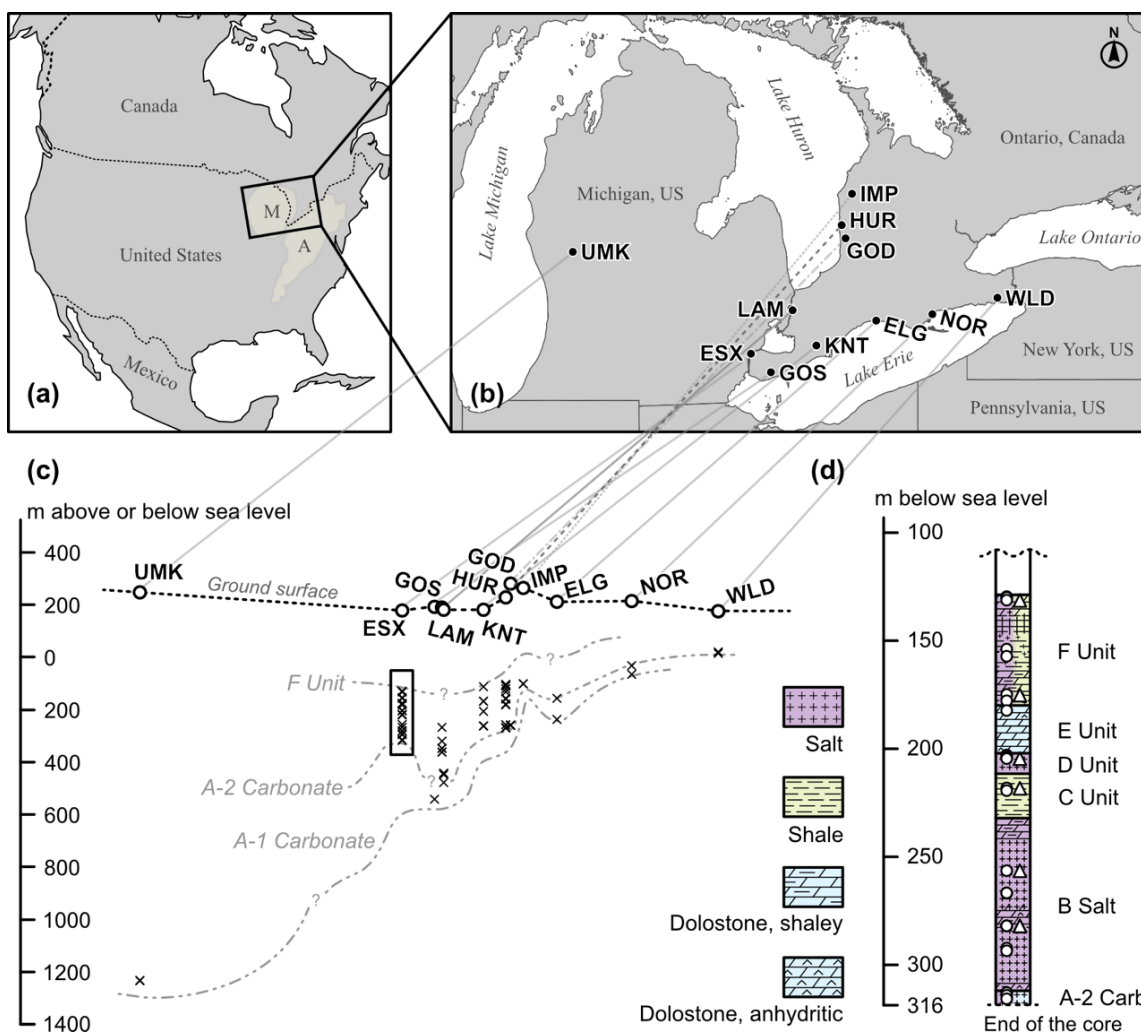


Figure 4-2. (a) Map highlighting the study area, with “M” and “A” denoting the relative locations of the Michigan and Appalachian Basins, respectively. (b) Enlarged map of the study area showing the locations of cores from which evaporite samples were collected. (c) Schematic cross-section of the Salina Formation, along the transect from UMK to WLD. The distance between each core is relative to the distance from UMK. (d) Representative stratigraphic column illustrating the general stratigraphic framework of the Salina Formation succession at ESX. Circles mark the locations where Cl isotope values are available, while triangles indicate where Br isotope values are available.

In the Michigan Basin, the Salina evaporite sequences are thickest at the basin center, transitioning to thinner layers along the margins (i.e., from UMK towards WLD in the Figure 4-2c). The central subsidence of the basin, driven by the Taconic orogeny and sediment loading, led to concentrated brine deposition in the basin center and selective salt dissolution at the margins (Harrison III and Voice, 2017). Marginal deposits in Ontario that are presently at shallow depths or exposed to the surface have been influenced by post-depositional processes including glacial meltwater, exhibit evidence of varying diagenetic and post-diagenetic processes, including selective dissolution and deformation of overlying strata (McIntosh and Walter, 2005; Wang and Frape, 2015). The Salina Formation is continuous into the Appalachian Basin, dipping southeastward, showing greater deformation and alteration toward the east driven by the Alleghenian and Acadian orogenies, which resulted in enhanced hydrothermal diagenesis in the Michigan Basin toward the Appalachian orogen (Figure 4-2a; (Basler et al., 2021; Catacosinos et al., 1991; Hatcher Jr et al., 1989).

4.4 Materials and Methods

4.4.1 Sample Selection

Samples were selected from 12 boreholes from locations across the Michigan Basin portion of the Salina Formation, encompassing a wide range of lithologies, depositional environments, and degrees of diagenetic alteration (Figure 4-2b, c). A total of 74 samples were obtained, including 18 archived samples at the University of Waterloo, previously characterized for other geochemical and geological features, and 56 samples acquired from the Ontario Oil, Gas, and Salt Resources Library (OGSRL). Selection criteria for sampling from OGSRL included geographic locations, stratigraphic position, lithologic diversity, and evidence of diagenetic processes.

The final set of 74 samples includes 44 halite, 23 carbonate, 6 gypsum/anhydrite, and 1 shale samples from various stratigraphic units, categorized based on the dominant mineral phase in each bulk analysis (Table 4-1). These samples span various stratigraphic units and were collected from both basin center and margin localities, covering a wide range of depositional environments and diagenetic histories (Figure 4-2). For example, one set of samples is from a core close to the basin center (UMK), while another comes from the basin margin, where the formation occurs as shallow bedrock beneath the unconsolidated overburden (WLD).

Some cores are sampled more densely and extensively to examine vertical (i.e., stratigraphic) variations in isotopic and chemical trends, allowing comparisons among samples deposited in similar depositional environments but differing in lithology or diagenetic overprint. Core selection prioritized those with thick halite layers within it to ensure sufficient Br for analysis. Halite is most abundant in the B and F Units, and the A-2 Unit, one of the most extensively studied stratigraphic intervals in the Salina Formation; therefore, these were the main contributors to the sample set. The selected samples encompass diverse lithologies, including organic-rich carbonates, halite-dominant evaporites, and anhydrite-bearing evaporites, each reflecting distinct depositional settings and diagenetic histories (Table 4-1).

Table 4-1. Distribution of samples by stratigraphic unit and dominant lithology. The sample count reflects the number of samples collected from each stratigraphic unit of the Salina Formation, grouped by their dominant mineral phase (i.e., halite, carbonate, gypsum/anhydrite, and shale) in each bulk analysis.

Unit	Halite	Carbonate	Gyp/Anh	Shale	Total
F	10	4	1	0	15
E	0	3	0	0	3
D	5	0	0	0	5
C	6	1	1	1	9
B	12	2	2	0	16
A-2	10	7	1	0	18
A-1	1	6	1	0	8
Total	44	23	6	1	74

4.4.2 Sample Characterization

The samples were initially grouped into two broad categories: (1) halite-dominant samples, and (2) non-halite samples or those containing unrecognizable amounts of halite (e.g., carbonates such as calcite, dolomite, gypsum, or anhydrite). To differentiate dolostone (dolomite-dominant) from limestone (calcite-dominant) within the carbonate group, acid-test was performed using dilute nitric acid (HNO₃) on both uncrushed and crushed material. Anhydrite samples were identified by characteristic laminations (e.g., undulated laminations between halite layers), consistency with

stratigraphic unit descriptions, and corroboration with prior analyses (Kennell, 2008). Each sample reflects a dominant mineral phase rather than being entirely monomineralic. Due to the naturally low bromide contents in many of the minerals, bulk analyses requiring 4-30 g per sample were conducted. While the bulk analyses preclude precise separation of individual mineral components, it is sufficient for the study's main goal of assessing halogen isotope trends in a basin-wide formation scale.

After the dominant mineralogy was determined, each sample was evaluated in greater detail to understand its depositional context and textural features, including lithologic ordering within the core, the characteristic of the strata, and evidence of diagenetic alterations. Further focus was given to finding dissolution features, secondary mineral overgrowths, veins (e.g., salt-filled fractures within shale), and any potential hydrothermal overprint. Where available, previously published data, such as strontium isotope ratios or geological descriptions of each sample, was also incorporated to aid in refining the interpretation of depositional and post-depositional processes.

4.4.3 Sample preparation

All samples were first crushed and ground using a mortar and pestle until the particles were smaller than 1 mm, when the material felt smooth with no remaining gritty texture either in the mortar and pestle or to the touch. The finely ground samples were then prepared as solutions using a crush-leach/crush-dissolve technique for chemical and isotopic analyses. Specifically, 4-30 g of ground sample was mixed with ~200 mL ultrapure water and allowed to leach/dissolve for 24-48 hours or longer for less-soluble, non-halite lithologies such as anhydrites. While most halite-dominant samples dissolved almost completely during this leaching process, some non-halite samples, such as carbonate- or anhydrite-rich samples left behind insoluble residues (ranging <1 g to ~3 g). Because the goal was to capture both soluble and potentially lattice-bound halogens (particularly Br), these residues were not discarded; instead, they were acid-digested (e.g., nitric and sulfuric acid) and included in the subsequent separation and preparation steps for bromine isotope analysis. This approach ensured that both readily soluble and less-soluble mineral-bound bromine fractions were accounted for the isotopic measurements. The final halide contents were calculated based on the total mass of the original powdered sample.

4.4.4 Chemical and isotopic analyses

The leachate solutions (plus residues, if any) were analyzed for chlorine and bromine isotopic compositions ($\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$) and Cl and Br concentrations. The $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values were analyzed at the University of Waterloo Environmental Isotope Laboratory (UW-EIL). For $\delta^{37}\text{Cl}$ analysis, samples were prepared according to the method originally developed by (Taylor and Grimsrud, 1969), later improved by Kaufmann (1984) and Eggenkamp et al. (2010). For $\delta^{81}\text{Br}$ analysis, Br was separated from chlorine first, following the method described in Shouakar-Stash et al. (2005b). Isotopic measurements were performed on a gas chromatography-continuous flow-isotope ratio mass spectrometry (GC-CF-IRMS) system utilizing an Agilent 7890B gas chromatograph equipped with a CTC Analytics PAL Headspace Autosampler and a Thermo-253 continuous flow mass spectrometer. Analytical precision was evaluated based on the standard deviation of a minimum of four replicate runs per sample, with an acceptable precision of $\pm 0.1\%$.

For concentration measurements, the leachates were further diluted by additional factors of between 5 and 50, depending on the expected concentrations. Cl and Br concentrations were determined using ICS-2000 ion chromatography (IC) configured to analysis of anions using Dionex IonPac AS18 Column at University of Waterloo. The Br concentration detection limit was as low as ~ 0.01 mg/L but varied with dilution rate and relative concentrations of other anions. In samples where Br concentrations were below the IC detection limit, an inductively coupled plasma-mass spectrometer (ICP-MS) at the University of Saskatchewan's Analytical Geochemistry Laboratory was used, enabling Br determinations at ppb levels. Measured concentrations in mg/L were subsequently converted to solid-phase contents in mg/g (equivalent ppm) to enable direct comparison across all solid samples.

4.5 Results

4.5.1 Overall Range and Distribution of Cl and Br Contents

The analyzed dataset comprises 74 samples from multiple stratigraphic units of the Salina Formation, representing halite-, carbonate-, gypsum/anhydrite-, and shale-dominant lithologies (Table 4-1). Chloride (Cl) and bromide (Br) contents vary widely within the samples studied (Table 4-2). Halite-dominant samples (hereafter, referred to simply as halite) exhibit Cl contents that range between $\sim 141,000$ and $2,316,000$ ppm and Br contents between ~ 2 and $64,250$ ppm. In contrast, samples

dominated by calcium bearing minerals, such as carbonate, gypsum, anhydrite (hereafter, referred to as Ca-bearing minerals), exhibit Cl contents ranging between 100 and 223,000 ppm and Br contents between ~1 and 47,500 ppm. Overall, Cl contents are significantly lower in Ca-bearing minerals compared to halite-dominant samples, while Br contents vary widely across both groups.

The Cl and Br contents in halite-dominant samples span a wide range, reflecting various stages of brine evolution and mineral deposition (Figure 4-3). Samples with low Br contents (< 60 ppm) with low Br/Cl ratios, circled in red in Figure 4-3, are indicative of salt reflux processes wherein dissolution-recrystallization preferentially removed Br while leaving Cl contents remaining relatively constant (Stoessell and Carpenter, 1986; Cendón et al., 2004). Conversely, samples with high Br contents (up to 64,250 ppm), circled in blue in Figure 4-3, are likely associated with advanced stages of evaporation or halokinetic processes that concentrated Br (Küster et al., 2009).

Ca-bearing minerals (e.g., dolomite, calcite, anhydrite) display a broad range of the Br/Cl ratios, revealing a more complex formation history. Samples from the organic-rich A-1 and A-2 Units (black circles in Figure 4-3) generally fall below the seawater evaporation trajectory (SET), implying precipitation during earlier stages of evaporation and Salina Formation history, when brine salinity was lower. Their elevated Br contents and Br/Cl ratios may reflect contributions from organo-bromine in these units (Heeb et al., 2014; Leri et al., 2010; Leri and Myneni, 2012). In contrast, Ca-bearing minerals from other units (blue circles in Figure 4-3) tend to have higher Cl contents and lie above the SET, suggesting formation later in the evaporation sequence. The decreased Br/Cl ratios in these samples, compared to those from the A-1 and A-2 Units, may reflect the dissolution of pre-existing halite and mixing with seawater or freshwater during the later stages of brine evolution (e.g., Risaçher and Fritz, 2000; Lüders et al., 2010).

Table 4-2. Chloride (Cl) and bromide (Br) contents (in ppm) for each lithology (halite, carbonate, gypsum/anhydrite, shale) within the stratigraphic units, along with the Br/Cl×1000 ratio shown in the row immediately below. Where multiple samples were available, concentration range with the mean value in parenthesis are listed; a single value indicates only one sample. *n/a* describes no available samples.

Unit	Halite		Carbonate		Gyp/Anh		Shale	
	Cl	Br	Cl	Br	Cl	Br	Cl	Br
F	203,000-970,000 (562,000)	22.4-800 (183)	377-223,000 (108,000)	14.9-66 (43)	1,355	1.43	<i>n/a</i>	<i>n/a</i>
	0.0231-1.04		0.171-175		1.06		-	
E	<i>n/a</i>	<i>n/a</i>	1,140-103,000 (47,400)	6.67-47,500 (15,800)	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>
	-		0.177-41800		-		-	
D	141,000-703,000 (550,000)	49-545 (155)	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>
	0.0749-3.86		-		-		-	
C	152,000-687,000 (404,000)	55.6-38,600 (7,840)	82,900	101	22,600	31	97,500	61.3
	0.0809-111		1.21		1.37		0.628	
B	311,000-852,000 (520,000)	34.7-19,000 (3,060)	467-29,700 (15,100)	4.44-66.7 (35.6)	15.8-157,000 (78,500)	9.51-14.7 (12.1)	<i>n/a</i>	<i>n/a</i>
	0.0564-53.7		2.25-9.52		0.0934-60		-	
A-2	336,000-723,000 (477,000)	28-64,000 (12,600)	363-2,260 (1,260)	0.959-4,070 (602)	162,000	39.6	<i>n/a</i>	<i>n/a</i>
	0.0426-191		0.0100-2850		0.245		-	
A-1	144,000	2.33	100-3,400 (911)	0.973-65.2 (21.5)	8,100	80	<i>n/a</i>	<i>n/a</i>
	0.0163		1.01-200		9.88		-	

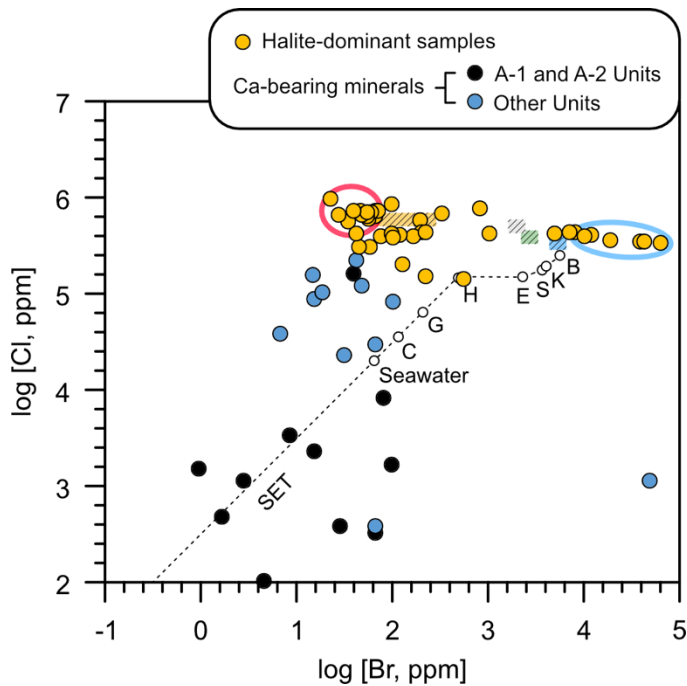


Figure 4-3. Distribution of Br vs. Cl contents in halite-dominant samples (yellow circles) and calcium-bearing minerals (black and blue circles). Ca-bearing samples are subdivided into those from the organic-rich A-1 and A-2 Units (black) and those from other units (blue). The dashed line indicates the SET, with letters along the SET denote major mineral precipitation stages (see Figure 4-1). Red circle highlights low-Br halite (< 60 ppm Br), interpreted as reflux-related, and blue circle highlights high-Br halite that is often associated with advanced evaporation or salt tectonics (i.e., halokinesis).

4.5.2 Overall Distribution of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ Values

The isotopic compositions of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ within the rock sequence studied display significant variability across the sampled intervals. The $\delta^{37}\text{Cl}$ values range from -1.81‰ to $+1.33\text{‰}$, with a mean and standard deviation of $+0.08 \pm 0.51\text{‰}$, while $\delta^{81}\text{Br}$ values range from -1.78‰ to $+1.76\text{‰}$, with a mean and standard deviation of $+0.17 \pm 0.84\text{‰}$ (Figure 4-4a, b). The ranges of both isotopes are larger than previously reported for paired values from salt deposits and rock formations at various locations and of different geologic ages (Eggenkamp et al., 2019b, 2019a; Ercan et al., 2019) (Figure 4-4e, f). The majority of $\delta^{37}\text{Cl}$ values cluster between -0.50‰ and $+0.50\text{‰}$, which broadly

corresponds to ± 1 standard deviation around the mean (Figure 4-4a). In contrast, $\delta^{81}\text{Br}$ values exhibit a broader distribution, with a slight skew towards more positive values with peaks both above and below 0‰ (Figure 4-4b). A weak positive linear correlation ($R^2 = 0.016$) between $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ (Figure 4-5) is not statistically significant ($p\text{-value} > 0.05$).

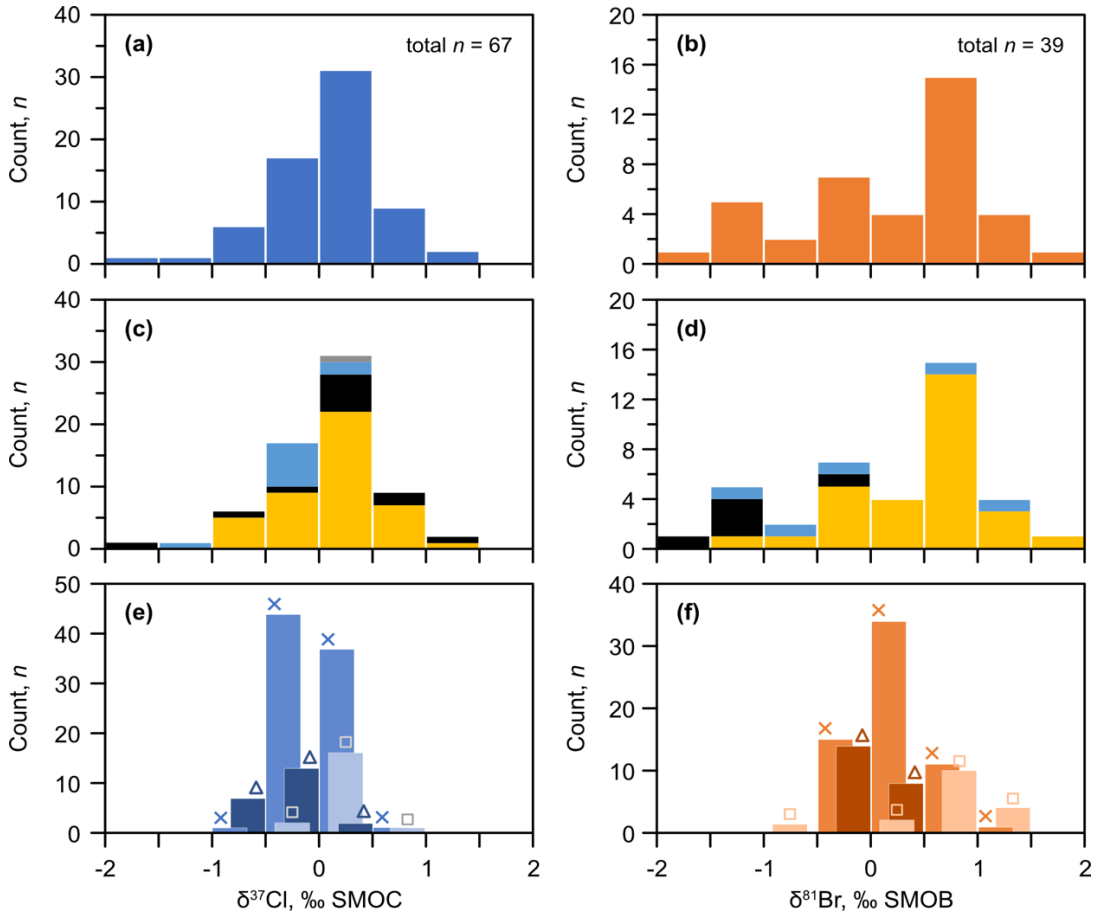


Figure 4-4. Histograms showing the distribution of isotope values of chlorine ($\delta^{37}\text{Cl}$) and bromine ($\delta^{81}\text{Br}$): (a, b) for all Salina Formation samples analyzed in this study; (c, d) Salina samples subdivided by dominant mineral group (halite-dominant samples in yellow, Ca-bearing minerals from the A-1 and A-2 Units in black and from other Units in blue; and (e, f) data from earlier studies. Earlier studies include primary halite samples from various locations and ages (crosses; *Eggenkamp et al., 2019a*), Miocene halite (squares; *Ercan et al., 2019*), and Permian evaporites (triangles; *Eggenkamp et al., 2019b*).

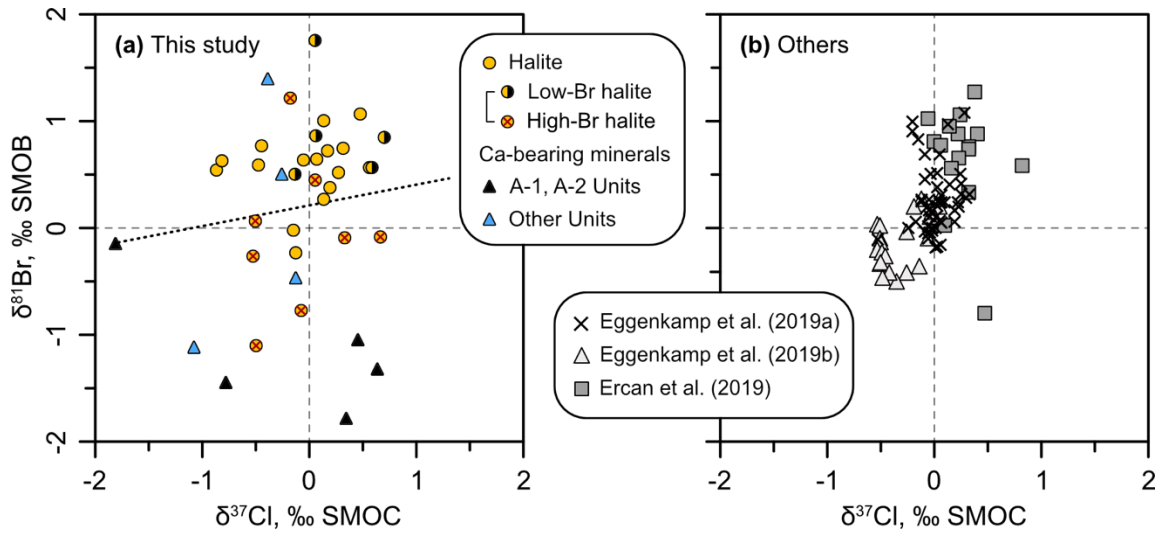


Figure 4-5. Scatterplots illustrating the relationship between chlorine ($\delta^{37}\text{Cl}$) and bromine ($\delta^{81}\text{Br}$) isotopic values. (a) Data from this study, with different symbols and fill styles indicating mineralogical and geochemical groupings: yellow circles = halite samples, further distinguished as low-Br halite (half-filled black) and high-Br halite (red crossed); black triangles = Ca-bearing minerals from the A-1 and A-2 Units; blue triangles = Ca-bearing minerals from other units. A dotted regression line is shown, reflecting a weak positive correlation ($R^2=0.016$, $p>0.05$). (b) Published data from previous studies for comparison: crosses = primary halite from various locations (Eggenkamp et al., 2019a); squares = Miocene halite (Ercan et al., 2019); and triangles = Permian evaporites (Eggenkamp et al., 2019b).

4.5.3 $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ Values Across Lithologies

The $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values exhibit divergent behavior based on mineralogic characteristics across the rock sequence studied in this project. Halite-dominant samples reveal a wide range of $\delta^{37}\text{Cl}$ values (-0.87‰ to +1.33‰) and an even wider range of $\delta^{81}\text{Br}$ values (-1.10‰ to +1.76‰) (Figure 4-5). Larger deviations in $\delta^{81}\text{Br}$ values than $\delta^{37}\text{Cl}$ values in halite samples are consistent with previous studies (Eggenkamp et al., 2019a; Ercan et al., 2019). Yet, the overall range of $\delta^{81}\text{Br}$ values cannot be explained by simple evaporation-deposition models that are available from theoretical calculations or experiments (Eggenkamp et al., 2016; Gao and Liu, 2021). While previous studies predominantly

reported positive $\delta^{37}\text{Cl}$ values for halite samples (shown as crosses and squares in Figure 4-5b), this study found both enriched and depleted $\delta^{37}\text{Cl}$ values in halite samples.

Ca-bearing minerals exhibit a wide range of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values. A potential negative correlation between $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ is observed in these samples (Figure 4-5), though the limited number of samples prevents statistical validation ($p\text{-value} > 0.05$). Notably, Ca-bearing minerals from organic-rich layers, such as those from A-1 and A-2 Carbonates (black symbols in Figure 4-4d and Figure 4-5), consistently exhibit depleted $\delta^{81}\text{Br}$ values and high Br/Cl ratios (Table 4-2). Specifically, these samples have Br/Cl $\times$ 1000 mass ratios ranging from 0.245 to 200, with an average of 36.7. In comparison, Ca-bearing minerals from other units have Br/Cl $\times$ 1000 mass ratios ranging between 0.0934 and 2.25, with an average of 0.671 (excluding two outliers, dolomite-dominant sample with Br/Cl $\times$ 1000 mass ratios of: 175 and 41800).

4.6 Discussion

4.6.1 Variability of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ Values

The $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values in this study exhibit a wider overall range than previously reported (Eggenkamp et al., 2019a, 2019b; Ercan et al., 2019) (Figure 4-4). This study is the first to report both halogen isotope values for evaporites other than halite, such as Ca-bearing minerals, encompassing various locations and stratigraphic horizons within a basin, offering a more comprehensive view of isotopic fractionation. It is therefore reasonable to find a broader range of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values in this study as they reflect various processes that can affect the isotopic values, such as evaporation, lithological changes due to depositional environment, and post-depositional diagenesis, whereas earlier works primarily focused on halite or halite-dominant samples within a single evaporative sequence.

A lack of a statistically significant correlation between $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ ($R^2 = 0.016$; Figure 4-5a) suggests that chlorine and bromine isotopes are affected differently by the fractionation mechanisms in this study, with bromine showing a broader overall distribution and potentially higher fractionation sensitivity to brine evolution and diagenesis. Several factors appear to control these observed variations in $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values. First, progressive evaporation stages appear to yield distinct fractionation effects on chlorine and bromine, as suggested by single-mineral precipitation

experiments and observations of natural salt sequence (Eggenkamp et al., 2019b; Luo et al., 2014, 2012). However, the extent to which these findings can be generalized, particularly for bromine, still requires further validation (Eggenkamp, 2015; Eggenkamp et al., 2019b). Second, lithology, particularly early-stage Ca-bearing phases (e.g., calcite, gypsum), likely introduce additional fractionation pathways for bromine not often captured by existing studies that focus primarily on chloride salts (e.g., halite, sylvite, carnallite). Additionally, post-depositional diagenesis (e.g., dissolution, recrystallization, and high temperature or pressure diagenesis) can selectively alter local isotopic values, possibly affecting $\delta^{81}\text{Br}$ more strongly than $\delta^{37}\text{Cl}$. Notably, different subsets of Salina Formation samples in this study experience these processes to varying degrees, depending on stratigraphic position, fluid pathways, and lithologic composition. These relationships are explored in the following subsections through detailed comparisons of isotopic values and halogen contents across different diagenetic contexts, including reflux, recrystallization, and hydrothermal alteration. As a result, these factors help explain the overall variability in $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values that is not captured by theoretical calculations or experimental determinations (Eggenkamp et al., 2016; Gao and Liu, 2021).

4.6.2 Cl^- and Br^- vs. $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$: Brine Evolution and Mineral Deposition

The concentrations of Cl and Br, as well as their mass ratios ($\text{Br}/\text{Cl} \times 1000$), offer useful insights into brine evolution and mineral deposition (Braitsch, 1971; McCaffrey et al., 1987; Valyashko, 1956). In many seawater evaporation models, the Br/Cl ratio increases systemically during halite precipitation (Harvie et al., 1980; McCaffrey et al., 1987), leading to progressive Br enrichment in both brine and precipitating halite. Data from the Salina Formation show an overall decrease in $\delta^{37}\text{Cl}$ values with increasing Br/Cl ratios: $\delta^{37}\text{Cl} = -0.080 \times \ln(\text{Br}/\text{Cl} \times 1000) + 0.060$, but this is a weak correlation across different rock types ($R^2 = 0.160$, $p < 0.05$), (Figure 4-6a; Table 4-3). A similar, but more tightly correlated ($R^2 = 0.951$) decreasing trend ($\delta^{37}\text{Cl} = -0.130 \times \ln(\text{Br}/\text{Cl}) - 1.053$) was reported from a Permian evaporite sequence (Eggenkamp et al., 2019b). The greater variability in $\delta^{37}\text{Cl}$ values observed in this study is attributed to the more diverse sample set of Salina samples spanning multiple cores, stratigraphic horizons, and mineral assemblages, contrasting with the single evaporite sequence in Eggenkamp et al. (2019b).

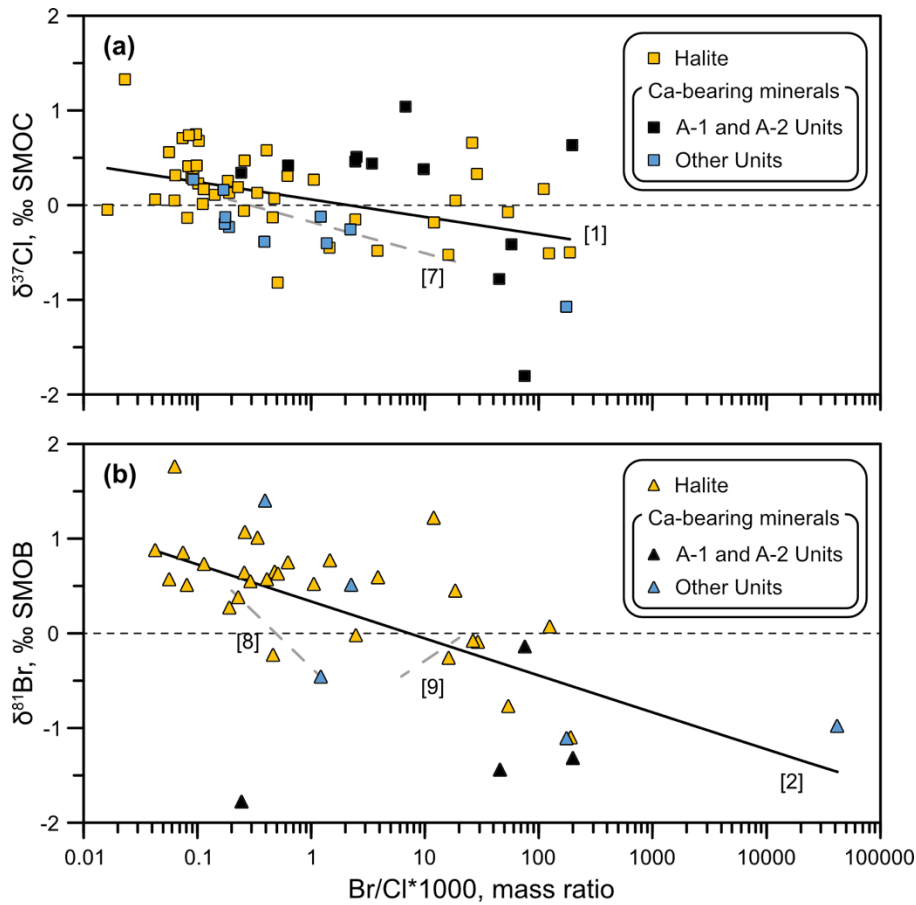


Figure 4-6. Scatterplots illustrating the relationship between Br/Cl mass ratios (x-axis) and isotope values of chlorine ($\delta^{37}\text{Cl}$) (y-axis, panel (a)) and bromine ($\delta^{81}\text{Br}$) (y-axis, panel (b)). Black solid lines represent trendlines considering all samples from this study [1-2], whereas grey dashed lines are from a Permian evaporite sequence [7-9] (*Eggenkamp et al., 2019b*). Note that the *Eggenkamp et al. (2019b)* data span a smaller range of Br/Cl*1000 ratios, between 0.25 and 18. Numerical equations and correlation coefficients (R^2) for each trendline can be found in Table 4-3.

Table 4-3. Equations for the various relationships between Br/Cl mass ratios and the isotopic values of Cl and Br ($\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$). Equations [1-2] and [7-9] correspond to the lines shown in Figure 4-6. Equations [1-6] are for data from this study (considering all samples, halite-dominant samples, or Ca-bearing minerals), and [7-9] reference data from *Eggenkamp et al. (2019b)* for Permian evaporites.

Br/Cl ratios vs. $\delta^{37}\text{Cl}$	Br/Cl ratios vs. $\delta^{81}\text{Br}$	Source, sample type
[1] $\delta^{37}\text{Cl} = -0.080 \times \ln(\text{Br/Cl} \times 1000) + 0.062$ ($R^2=0.159$, $p < 0.05$)	[2] $\delta^{81}\text{Br} = -0.169 \times \ln(\text{Br/Cl} \times 1000) + 0.340$ ($R^2=0.396$, $p > 0.05$)	This study, all samples
[3] $\delta^{37}\text{Cl} = -0.074 \times \ln(\text{Br/Cl} \times 1000) + 0.086$ ($R^2=0.179$, $p > 0.05$)	[4] $\delta^{81}\text{Br} = -0.157 \times \ln(\text{Br/Cl} \times 1000) + 0.459$ ($R^2=0.444$, $p < 0.05$)	This study, halite
[5] $\delta^{37}\text{Cl} = -0.083 \times \ln(\text{Br/Cl} \times 1000) + 0.019$ ($R^2=0.099$, $p > 0.05$)	[6] $\delta^{81}\text{Br} = -0.095 \times \ln(\text{Br/Cl} \times 1000) + 0.296$ ($R^2=0.126$, $p > 0.05$)	This study, Ca-bearing minerals
[7] $\delta^{37}\text{Cl} = -0.130 \times \ln(\text{Br/Cl}) - 1.053$ ($R^2=0.951$)	[8] $\delta^{81}\text{Br} = -0.498 \times \ln(\text{Br/Cl}) - 3.80$ ($R^2=0.862$); [9] $\delta^{81}\text{Br} = 0.342 \times \ln(\text{Br/Cl}) + 1.276$ ($R^2=0.413$)	Eggenkamp et al. (2019b), Permian evaporite sequence

The overall trend of $\delta^{37}\text{Cl}$ is largely defined by halite samples, while Ca-bearing minerals exhibit more scatter (Figure 4-6). Br/Cl $\times$ 1000 ratios in evaporitic minerals directly precipitated from seawater evaporation may range from $\sim$ 0.1 in early halite to greater than 6.3 in carnallite or sylvite and up to $\sim$ 17 in bischofite (Braitsch, 1971; Herrmann et al., 1973; McCaffrey et al., 1987; McIntire, 1963; Schreiber and Tabakh, 2000; Valyashko, 1956). These ratios can shift further through diagenetic processes such as halite recrystallization, fluid interaction, and preferential leaching of Br during reflux or pressure compaction (Cendón et al., 2004; Küster et al., 2009; Stoessell and Carpenter, 1986). Within this range, most samples from this study tend to follow the general trend of decreasing $\delta^{37}\text{Cl}$ values with increasing Br/Cl ratios until roughly 3.5-13, corresponding to halite to

carnallite saturation thresholds in seawater. This reflects isotope partitioning during progressive evaporation and halite precipitation, where $\delta^{37}\text{Cl}$ values decrease as halite continues to form and Br becomes concentrated in the residual brine.

Beyond this Br/Cl threshold, however, $\delta^{37}\text{Cl}$ values among halite samples become widely scattered. This variability likely reflects multi-stage precipitation and diagenetic overprints, where evolved high-Br brines interacted with pre-existing halite layers, leading to partial dissolution and reprecipitation that altered the original isotopic signature. For instance, some high-Br halite samples from thick halite intervals, which show enriched $\delta^{37}\text{Cl}$ values, show partial recrystallization as the only apparent diagenetic feature observed petrographically, suggesting complex fluid evolution and halite reworking. These observations are consistent with previous reports showing that halite affected by multiple diagenetic stages can develop highly variable Cl isotopic values, likely due to (incongruent) dissolution and reprecipitation associated with brine-rock interaction (Eastoe et al., 2001); reflux and halokinetic processes may contribute to such isotopic complexity, and their direct influence on $\delta^{37}\text{Cl}$ remains to be explicitly demonstrated.

Unlike the two-stage pattern observed in a Permian sequence, where $\delta^{81}\text{Br}$ values initially decreased at lower Br/Cl ratios and later increased at higher Br/Cl ratios ([8] and [9] shown on Figure 4-6b; (Eggenkamp et al., 2019b), the $\delta^{81}\text{Br}$ values in this study consistently decrease with increasing Br/Cl ratios. Notably, halite samples exhibit the strongest correlation between $\delta^{81}\text{Br}$ and Br/Cl ratios ($R^2 = 0.444$, $p < 0.05$; Table 4-3), yet no corresponding increase in $\delta^{81}\text{Br}$ values is observed at Br/Cl values of 6-18. Given the single salt sequence from a previous study (Eggenkamp et al., 2019b) involving the Permian record exhibited different trends at earlier vs. later stages of evaporation, the moderate and consistent linear trend observed in this study is intriguing, as it is observed across the basin in multiple repeated evaporation sequences. Further, the likely recycling of brines, possibly via multiple diagenetic processes, complicates Cl-Br geochemistry in the Salina salts. These complications underscore the need for caution when inferring brine histories solely from either halite Br/Cl ratios or isotopic values of Cl or Br. In basins where brine recycling or dissolution-reprecipitation is significant, elevated Br/Cl ratios may not directly reflect a precipitation stage or degree of evaporation from gradual evaporation-deposition history (Cendón et al., 2004; McCaig et al., 2000) and may complicate the isotopic signals.

4.6.3 Unit-by-Unit Variations

Cl and Br contents and their isotopic compositions ($\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$) display notable variation across the stratigraphic units examined in this study (see Table 4-2 for Cl and Br contents). Although direct comparisons between units are complicated by differing lithologies (e.g., halite-dominant vs. carbonate-dominant) and variable diagenetic and post-diagenetic histories (e.g., dissolution and recrystallization), discernable trends and contrasts appear when halogen contents and isotopic values are compared by unit (Figure 4-7).

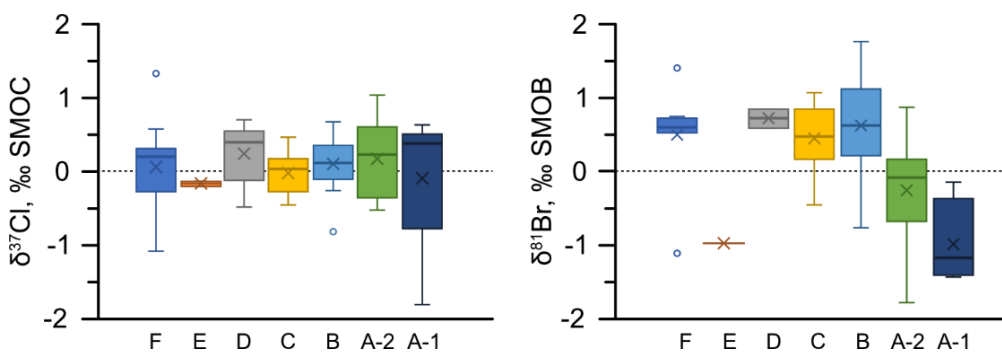


Figure 4-7. Box-and-Whisker plots illustrating the distribution of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values across each stratigraphic unit (F through A-1 Units.) Each box extends from the first to third quartile, with a central line for the median, an X for the mean, whiskers for the minimum and maximum values, and open circles indicating outliers (outside 1.5 times interquartile range).

Units dominated by halite, such as F, D, and B Units, generally exhibit elevated Cl contents, while their Br contents do not directly correlate with the abundance of halite. Conversely, samples from carbonate-rich units tend to exhibit lower overall Cl contents, but in some cases, exceptionally high mean Br contents. For example, the E Unit exhibits the highest mean Br content (15,800 ppm) despite containing fewer halite samples. This elevated mean is partly attributed to a single dolomite sample enriched in Br yet low in Cl, thus insufficient for $\delta^{37}\text{Cl}$ analysis, reinforcing that carbonate minerals, particularly in organic-rich facies, can retain substantial amounts of Br. Comparisons between the A-1 and A-2 Carbonates highlight that the A-2 Unit commonly exhibits both higher Cl and Br contents than the A-1 Unit. This difference aligns with the observation that the samples from A-2 Units often

show signs of dissolution-precipitation processes because of frequent interaction with adjacent halite layers.

In terms of isotopes, the A-1 and E Units, both largely carbonate-dominated, exhibit the lowest average $\delta^{81}\text{Br}$ values (-0.99‰ and -0.98‰, respectively). This pattern suggests that carbonate lithologies may be associated with depleted $\delta^{81}\text{Br}$ signatures (Figure 4-7). While the specific mechanism remains uncertain, one plausible interpretation is that organic-rich diagenesis promotes the preferential retention of ^{79}Br in the solid phase, thereby lowering $\delta^{81}\text{Br}$ values during organic diagenesis. In contrast, the D Unit, composed entirely of halite-dominant samples, exhibits a narrower isotopic range for both $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values, reflecting less complex halogen behavior in relatively pure halite systems (Eggenkamp et al., 2019a).

Unit-level observations emphasize that multiple factors, including lithology, stratigraphic context, and diagenetic history, collectively determine Cl-Br distributions and isotopic patterns across the formation. High Br contents coupled with negative $\delta^{81}\text{Br}$ values are more frequently observed in carbonate-rich intervals, supporting the idea that organic matter may promote ^{79}Br retention during post-depositional alteration, thereby lowering $\delta^{81}\text{Br}$ values in the residual solid when preserved. Halite-dominant units, on the other hand, exhibit a wide range of isotopic compositions, reflecting variable processes such as progressive evaporation, brine recycling, and structural modification (e.g., halokinesis). These behaviors highlight the importance of interpreting Cl-Br systematics within the facies-specific and diagenetic framework and discussing how these processes are noted in halite vs. Ca-bearing lithologies.

4.6.4 Halite vs. Ca-bearing Minerals: Distinct Isotopic Signatures and Diagenetic Processes

4.6.4.1 Halite

Halite samples from this study exhibit a wide range of $\delta^{37}\text{Cl}$ values (-0.87‰ to +1.33‰, $n = 44$) and an even broader range of $\delta^{81}\text{Br}$ values (-1.10‰ to +1.76‰, $n = 29$). While most $\delta^{37}\text{Cl}$ values cluster within previously reported primary halite ranges (-0.53‰ to +0.51‰) (Eastoe et al., 1999; Eggenkamp et al., 2019a, 1995), the occurrence of more extreme values in both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ suggests the influence of additional fractionation processes beyond simple precipitation from evaporating seawater. In particular, $\delta^{81}\text{Br}$ values appear highly susceptible to the diagenetic processes,

which can drive $\delta^{81}\text{Br}$ to deviate largely from simple evaporation-deposition models and theoretical calculations (Eggenkamp et al., 2016; Gao and Liu, 2021). Such diagenetic processes may include brine reflux, where partial dissolution can promote the preferential removal of ^{79}Br and $\delta^{81}\text{Br}$ enrichment in the remaining halite. Hydrothermal fluid interactions may also induce isotopic exchange or diffusion, further modifying $\delta^{81}\text{Br}$ signatures.

As shown in Figure 4-5, halite samples exhibit greater variability in $\delta^{81}\text{Br}$ than in $\delta^{37}\text{Cl}$. This suggests that although Cl is the main structural component of halite, Br is more geochemically labile, and its isotopes may be more readily affected by various syn- and post-depositional processes. These include, but are not limited to, reflux, recrystallization, fluid-rock interaction, burial compaction, hydrothermal fluid interaction, and potentially microbial or organic reactions. Each of these processes may induce Br isotope fractionation in different directions or magnitudes depending on local geochemical conditions.

A notable distinction is observed between low-Br halite (< 60 ppm, which is less than the first halite precipitated from evaporating seawater, 60-75 ppm) and high-Br halite (exceeding several thousand ppm) (Figure 4-3). The low-Br halite samples likely reflect salt reflux and repeated brine recycling that preferentially removes Br relative to Cl (Herrmann et al., 1973; Warren, 2016). Notably, these low-Br halite occurrences are not confined to any specific stratigraphic unit, nor do they exhibit a clear geographic pattern. On the contrary, the elevated Br contents can be explained by (i) precipitation from highly evaporated brine beyond sylvite saturation, or (ii) halokinetic processes that concentrate Br in residual brines via halite bed thinning under pressure (Küster et al., 2009; Risacher et al., 2006). In the Michigan Basin, halite and sylvite from case (i) often are reported in the basin center and within the A-1 Unit (Harrison III and Voice, 2017; Mesolella et al., 1974). The high Br-halite samples in this study come from A-2, B and C Units along the basin margins, near the Chatham Sag, a structural low that likely functioned as brine conduits or pathway during basin evolution (e.g., LAM, KNT in Figure 4-2); and are frequently associated with polyhalite ($2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) vein fillings or recrystallized halite, reinforcing the role of halokinesis that induced changes in pressure or fluid chemistry during that process in Cl and Br systematics of high-Br halite (Nollet et al., 2005; Schlöder et al., 2008). Linking the distinct geochemical characteristics of low-Br halite, indicative of salt reflux, and high-Br halite, linked to salt tectonics, facilitates a discussion of the diagenetic modifications influencing the isotopic signatures ($\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$).

4.6.4.1.1 Low-Br halite and reflux

Several halite-dominant samples in this study contain < 60 ppm Br, potentially indicating salt reflux. Reflux, previously described as the downward migration of dense brines that dissolve salts, can selectively remove Br from the salt phase. Among these low-Br halite samples, Cl contents tend to be elevated, and $\delta^{37}\text{Cl}$ values show mild enrichment relative to the broader halite dataset; in fact, almost none of the samples within this group have depleted $\delta^{37}\text{Cl}$ values (Figure 4-8). This absence of depleted $\delta^{37}\text{Cl}$ values aligns with expected isotopic behavior during reflux: as ^{35}Cl preferentially dissolves into the brine, the residual halite becomes enriched in ^{37}Cl , resulting in more positive $\delta^{37}\text{Cl}$ values (Eastoe et al., 2001; Eggenkamp et al., 1995).

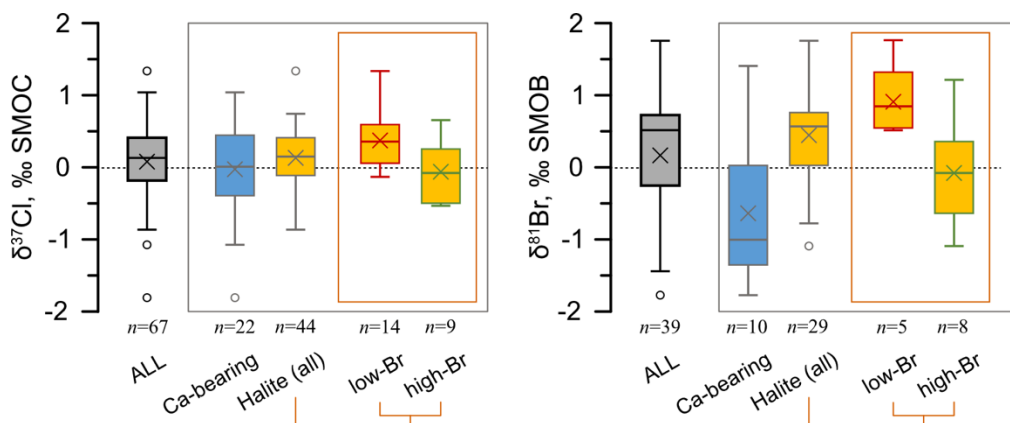


Figure 4-8. Box-and-Whisker plots illustrate the distribution of chlorine ($\delta^{37}\text{Cl}$, left) and bromine ($\delta^{81}\text{Br}$, right) isotope values by dominant-rock type, highlighting distinct trends among Ca-bearing minerals, all halite-dominant samples, and halite subgroups with low-Br (<60 ppm) or high-Br (> thousands ppm). Each box represents interquartile range (IQR), with a central line at the median and an 'X' marking the mean value. Whiskers extend to the minimum and maximum values within 1.5 times IQR, and empty circles beyond these bounds represent outliers.

Due to their low Br contents, nine samples did not yield Br isotope ratios; however, the other five samples yielded $\delta^{81}\text{Br}$ values with a range between +0.51‰ and +1.76‰. Notably, the highest $\delta^{81}\text{Br}$ value of +1.76‰ represents the maximum observed in this study, and the overall $\delta^{81}\text{Br}$ range for low-

Br halite samples is significantly greater than that for high-Br halite or Ca-bearing minerals (Figure 4-5a and Figure 4-8). The elevated $\delta^{81}\text{Br}$ values observed in low-Br halite samples may reflect both the isotope effects of reflux, where lighter ^{79}Br is preferentially removed, enriching the residual salt in ^{81}Br , and the increased susceptibility of small Br inventories to fractionation. In such low-concentration systems, minor shifts in isotopic partitioning can result in larger apparent $\delta^{81}\text{Br}$ variations, magnifying the impact of diagenetic processes even in samples lacking petrographic signs of alteration.

These enriched $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values suggest that reflux processes preferentially remove the lighter isotopes (^{35}Cl and ^{79}Br), leaving the residual salt enriched in the heavier isotopes (^{37}Cl and ^{81}Br). Although no clear trend has been established for Br; brine interaction with salt, through processes such as incongruent dissolution and subsequent recrystallization, has been shown to gradually elevate the $\delta^{37}\text{Cl}$ in the residual halite as ^{35}Cl preferentially partitions into the fluid (Eastoe et al., 2007, 2001; Eggenkamp et al., 1995). Consequently, elevated $\delta^{81}\text{Br}$ values with reduced Br content in the salt may therefore serve as a useful marker for reflux in evaporitic settings. While these results are intriguing, the limited sample size requires further analysis to support these preliminary interpretations. Moreover, these observations imply that the reflux fluid itself could be enriched in the lighter isotopes of both halides – a hypothesis that calls for further investigation to fully constrain its impact on evaporite formation and fluid evolution.

4.6.4.1.2 High-Br halite and salt tectonics (*halokinesis*)

In contrast to the low-Br halite samples (<60 ppm Br), several halite-dominant samples in this study exhibit thousands of ppm Br, with values reaching up to 64,250 ppm. These samples are commonly found within the thick and relatively pure halite layers of the A-2 and B Evaporites, which underwent syn-sedimentary and post-depositional subsidence, or within shale layers of the C Shale (Mesolella et al., 1974). Because evaporites consist of ductile salts and shale, they readily compact under burial and become prone to halokinesis as well as deformation by changes in overburden pressure (Davison, 2009; Hudec and Jackson, 2007). Under these settings, primary minerals alter (e.g., gypsum dehydration) and generate fluid pressure changes that can fracture the salt or shale, leading to the precipitation of secondary minerals (e.g., polyhalite) within these fractures (Howell and van der Pluijm, 1999; Schreiber and Tabakh, 2000; Warren, 2016). During these processes, halite may be reworked by high-Br brines, further increasing its Br content (Küster et al., 2009;

Rittenhouse, 1967). In relatively pure and thick halite intervals, such as the A-2 and B Evaporites, Br may be further enriched in brine pockets by the migration and concentration of fluid-inclusions carrying evolved brines with elevated Br concentrations (Warren, 2016). Although large-scale halokinesis is often reported in tectonically active settings (e.g., continent-continent collisions), it can also affect intracratonic basins such as the Michigan Basin, where episodic movement of salt occurred under long-term subsidence and density drive flow. Indeed, Silurian bedded halite in the adjacent Appalachian Basin shows comparable halokinetic and significant salt migration features under Appalachian orogenic stresses (Howell and van der Pluijm, 1999; Warren, 2016).

The high-Br halite samples in this study show a relatively broad range of both $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values. Many of these samples tend to exhibit $\delta^{37}\text{Cl}$ values mostly within $\pm 0.5\text{‰}$ and slightly lower $\delta^{81}\text{Br}$ values compared to other halite containing rock units studied (Figure 4-5a and Figure 4-8). In contrast, one sample from a polyhalite vein filling within the C Shale, interpreted to reflect mobilization under geologic pressure, shows a higher $\delta^{81}\text{Br}$ value ($+0.45\text{‰}$) and a lower $\delta^{37}\text{Cl}$ value ($+0.05\text{‰}$) relative to adjacent salts. Vein-hosted polyhalite in evaporite sequences is commonly associated with fracturing induced by salt flow and differential loading (Howell and van der Pluijm, 1999; Warren, 2016). Previous work suggests that halokinesis can elevate $\delta^{37}\text{Cl}$ values relative to primary bedded halite when significant dissolution occurs; however, in some cases no measurable change is observed between secondary and primary halite (Eastoe et al., 2007). Thus, the effect of halokinesis on $\delta^{37}\text{Cl}$ likely depends on the extent of dissolution and the dynamics of fluid cycling within the salt body.

Our data further suggest that salt tectonics may lower $\delta^{81}\text{Br}$ values in the original salt unit, while fully mobilized salt or secondary mineralization preserves or generates higher $\delta^{81}\text{Br}$ values with slightly elevated $\delta^{37}\text{Cl}$ values. In summary, when halokinesis is accompanied by extensive brine interaction that reworks the original halite, mobilizing ^{35}Cl and ^{81}Br , the residual salt tends to exhibit higher $\delta^{37}\text{Cl}$ values and lower $\delta^{81}\text{Br}$ values. Conversely, if brine interaction is limited, the $\delta^{37}\text{Cl}$ may remain relatively unchanged, with only a slight decrease in $\delta^{81}\text{Br}$ as Br content increases; in this case, the mobilized salt may retain a lower $\delta^{37}\text{Cl}$ and higher $\delta^{81}\text{Br}$ signature than the adjacent salt body. Furthermore, the extent of dissolution and fluid migration accompanying halokinesis can significantly influence the resulting isotopic signatures. This variability highlights the need to carefully evaluate the contributions of these diagenetic processes when interpreting the isotopic record in high-Br halite.

4.6.4.2 Ca-bearing minerals

Ca-bearing minerals (e.g., dolomite, calcite, anhydrite) appear to exhibit a negative correlation between $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values, in contrast to the positive correlation observed in halite-dominant samples (Figure 4-5a). Although these minerals are often neglected in evaporite halogen studies, they can record important diagenetic pathways for Cl and Br. Because only a small number of samples ($n = 10$) produced both Cl and Br isotope results, the correlation is not statistically significant ($p > 0.05$); however, the observed trend suggests that Ca-bearing minerals might follow distinct fractionation pathways for Cl and Br—either during formation or subsequent diagenesis. Among the six anhydrite/gypsum-dominant samples, only one yielded both $\delta^{37}\text{Cl}$ (+0.34‰) and $\delta^{81}\text{Br}$ (-1.78‰) values, thus limiting the discussion primarily to calcium carbonate, such as dolomite and calcite. These early precipitates did not yield Br isotopes due to the extremely low Br content; however, selective incorporation of ^{79}Br may help explain the overall $\delta^{81}\text{Br}$ values range of Ca-bearing minerals (Figure 4-8).

Ca-bearing minerals span a wide range of Cl and Br contents and variable Br/Cl ratios, reflecting multiple depositional and post-depositional processes (Figure 4-3). In the A-1 and A-2 Units, interpreted as quiet depositional settings characterized by anoxic-oxic transitions and interbedded shale lamina, these minerals often plot below the seawater evaporation trajectory (SET). It is important to note that these fractionation patterns not only reflect early evaporative processes but are also significantly influenced by organic diagenesis. In contrast, Ca-bearing minerals from other stratigraphic units show elevated Cl contents and more variable Br/Cl ratios, implying more complex diagenetic histories, including salt dissolution and secondary mineral precipitation (Lüders et al., 2010; Risaçher and Fritz, 2000). Outside of the A-1 and A-2 Units, Ca-bearing mineral samples exhibit dissolution vugs and fenestral porosity in dolomite or anhydrite, that is infilled by halite, halite replacing gypsum, and salts precipitated within anhydrite/dolomite/shale fractures. Consequently, where Ca-bearing minerals have repeatedly interacted with halite through dissolution and reprecipitation, they tend to acquire Cl-Br chemical signatures resembling those of halite, displaying varying but overall elevated Cl and Br contents (Figure 4-3). In these cases, isotopic signatures of Cl and Br become more halite-like, contrasting with Ca-bearing minerals in the A-1 and A-2 Units, which exhibit no evident overprint of reworked halite (Figure 4-6; blue vs. black symbols).

4.6.4.2.1 Organic diagenesis and shale influence

There is a notable deviation from typical isotopic trends observed in organic-rich horizons, specifically within the A-1 and A-2 Units (Figure 4-6). These units, particularly the A-1, generally exhibit finer-grained textures that favored the preservation of organic matter, often expressed as greater organic material accumulation within carbonate intervals (Appendix A; Mesolella et al., 1974). Samples from these organic-rich intervals exhibit a broader range of $\delta^{37}\text{Cl}$ values (-1.81‰ to +1.04‰) compared to other units (-1.08‰ to +0.27‰), including an unusual rise and subsequent drop in $\delta^{37}\text{Cl}$ values with increasing Br/Cl ratios, diverging from the typical halite trend (Figure 4-6). The presence of shale lamina in these intervals may facilitate diffusive exchange, resulting in lower Cl contents with lower $\delta^{37}\text{Cl}$ values (Hesse et al., 2006; Stotler et al., 2010). Indeed, the lowest $\delta^{37}\text{Cl}$ value was recorded in a shaley laminated dolomite-dominant sample from the A-1 Carbonate Unit. Similar influences may be anticipated in other stratigraphic intervals wherever fine-grained shale and laminae facilitate differential diffusion or compaction-driven ion-filtration, which may alter isotopic compositions by selectively retarding or excluding lighter halide isotopes (Hesse et al., 2006; Stotler et al., 2010).

The Ca-bearing minerals in these organic-rich units consistently exhibit negative $\delta^{81}\text{Br}$ values (-1.78‰ to -0.14‰) and elevated Br/Cl ratios (Figure 4-5a and Figure 4-6b), indicating a preferential enrichment of the lighter isotope, ^{79}Br . Previous studies have shown that organic and microbial activity strongly influences bromine geochemistry, preferring to oxidize Br over Cl, thus influencing $\delta^{81}\text{Br}$ values more than $\delta^{37}\text{Cl}$ values (Blei et al., 2010; Eggenkamp, 2016; Hanlon et al., 2017; Leri et al., 2014, 2010). In sedimentary basin porewater and groundwater, elevated $\delta^{81}\text{Br}$ values often correlate with high organic contents (i.e., TOC) of the strata, due to the preferential consumption of ^{79}Br during organic or microbial oxidation reactions, leaving the residual fluid enriched in ^{81}Br (Stotler et al., 2021; Wang, 2017). In this study, organic-rich intervals exhibit the negative $\delta^{81}\text{Br}$ values with elevated Br/Cl ratios, suggesting preferential retention of ^{79}Br in the solid rock phase. Organic diagenesis thus appears to be one of the major controls on the isotopic fractionation of bromine within organic-rich carbonate rock matrix.

The preferential retention of ^{79}Br in organic-rich dolomite or calcite cement suggests that Ca-bearing minerals are capable of sequestering significant amounts of Br with the existence of organic matter during post-depositional organic or microbial diagenesis. Moreover, the observed combination

of negative $\delta^{81}\text{Br}$ values and elevated Br/Cl in the rock record implies that this process likely occurred after deposition. During the process, ^{79}Br may have been reserved within the mineral matrix; otherwise, the ^{79}Br consumption could have led to the escape of volatile bromine species (e.g., HBr, CH_3Br) via microbial or photolytic processes (Blei et al., 2010; Hanlon et al., 2017; Horst et al., 2014). These halogenated volatiles can be preserved in fluid inclusions or other mineral-bound domains for geologic timescales without escaping, unless mechanically or thermally disturbed (Mulder et al., 2013) until analysis involving grinding, leaching, and strong acidification.

The occurrence of high Br contents and negative $\delta^{81}\text{Br}$ values in organic-rich dolomite and calcite highlights the role of organic diagenesis in shaping halogen geochemistry in sedimentary basins, creating complex $\delta^{37}\text{Cl}$ – $\delta^{81}\text{Br}$. Rather than adhering to simple evaporation-halite precipitation models, these intervals reflect additional fractionation pathways involving microbial or organic interactions. When combined with the influence of shale laminae, known to enhance diffusive exchange and lower both $\delta^{37}\text{Cl}$ values, both Cl and Br isotope systems may exhibit negative values, often accompanied by low Br/Cl ratios. As such, the combined Cl and Br isotopic signatures in Ca-bearing minerals provide valuable constraints on pre- and post-depositional organic alteration processes.

4.6.5 Hydrothermal Influence on Isotope Signatures

Hydrothermal alteration, driven by high-temperature brines that often ascend from deeper stratigraphic intervals or basement rocks, provide another diagenetic pathway that can reshape evaporite geochemistry, including Cl and Br. In the Michigan Basin, fluid-driven diagenesis has been studied in various stratigraphic intervals and areas, especially where faults and fractures act as conduits for hydrothermal fluids (Coniglio et al., 2003, 1994; Dunseith et al., 2021; Kennell, 2008). During this process, marine evaporites that initially record late Silurian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values can be overprinted by diagenetic fluids enriched in radiogenic Sr (^{87}Sr), elevating Sr isotope ratios (Burke et al., 1982; Denison et al., 1997; Schreiber and Tabakh, 2000). Although elevated Sr isotope ratios may sometime result from clays or carnallite (KMgCl_3) (Baadsgaard, 1987; Schreiber and Tabakh, 2000), this process has not been identified in the present samples in this study.

Observations from Goderich 1 samples reveal distinct isotopic patterns associated with hydrothermal influence (Figure 4-9). In halite with elevated Sr isotope ratios, indicative of hydrothermal alteration (e.g., sample H1 in Figure 4-9), a decrease in $\delta^{81}\text{Br}$ values ($\Delta = -0.30\text{‰}$), an increase in $\delta^{37}\text{Cl}$ values ($\Delta = +0.38\text{‰}$), and lower Br/Cl ratios are observed relative to nearby

unaltered halite (e.g., sample H3 in Figure 4-9). Sample H3, halite containing minor gypsum/anhydrite, exhibits an Sr isotope ratio near the lower bound of formation water values in the A-2 Unit (denoted as “D” in Figure 4-9), reflecting the concentrated brine that accumulates in the basin center (Dollar, 1988; Shouakar-Stash, 2008). From H3 to H1, $\delta^{81}\text{Br}$ values gradually decrease while $\delta^{37}\text{Cl}$ values gradually increase, although $\delta^{37}\text{Cl}$ values change only marginally (within error) from H2 to H1. Similarly, sample F, halite containing undulating iron-oxide layers, likely due to the exsolution, exhibits a $\delta^{37}\text{Cl}$ value similar to H3, yet its Sr isotope ratio and $\delta^{81}\text{Br}$ value suggest partial hydrothermal influence. This suggests that some diagenetic processes related to hydrothermal alteration may predominantly affect $\delta^{81}\text{Br}$ values while exerting a lesser impact on $\delta^{37}\text{Cl}$.

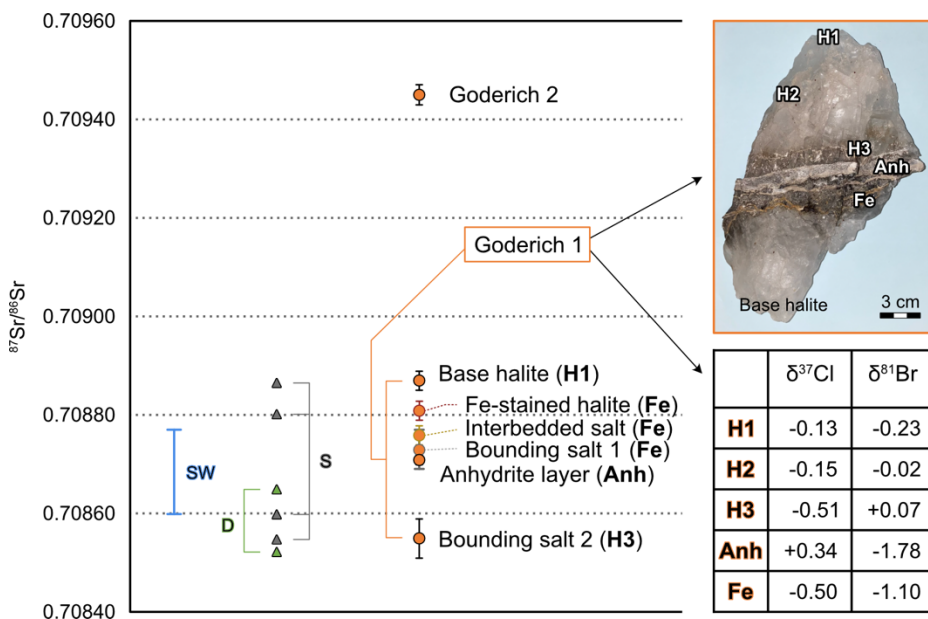


Figure 4-9. Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of halite and anhydrite samples from Goderich 1 and Goderich 2. Blue bar on the left indicates approximate $^{87}\text{Sr}/^{86}\text{Sr}$ range for late Silurian seawater (SW; *Burke et al., 1982; Denison et al., 1997*), and triangles represent $^{87}\text{Sr}/^{86}\text{Sr}$ values of formation waters from the A-1 Unit (D = from *Dollar, 1988*; S = from *Skuce et al., 2015*). The table on the right lists $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values, highlight isotopic variations within the Goderich 1 sample.

A similar isotopic trend is observed in a dolomite body, where secondary calcite filling dissolution vugs exhibits a decrease in $\delta^{81}\text{Br}$ values ($\Delta = -0.28\text{‰}$) and an enrichment in $\delta^{37}\text{Cl}$ values ($\Delta = +0.18\text{‰}$) relative to its dolomite host. Although Sr data for the dolomite are unavailable, limiting independent confirmation of hydrothermal influence, these observations imply that hydrothermal fluids preferentially remove heavier bromine isotopes (^{81}Br), yielding a more pronounced shift in $\delta^{81}\text{Br}$ compared to $\delta^{37}\text{Cl}$. Further research in other hydrothermally altered settings is needed to refine our understanding of how these processes drive bromine fractionation and the broader geochemical evolution of evaporite systems. With confirmation, $\delta^{81}\text{Br}$ measurements may serve as a sensitive indicator of hydrothermal alteration, especially when combined with other geochemical or petrographic proxies.

The Goderich 2 sample, a non-bedded halite with abundant fluid inclusions, exhibits an elevated Sr isotope ratio (+0.0009 relative to H3), suggesting hydrothermal deposition or significant alteration. Its fluid inclusions, containing both gas and liquid phases, indicate interaction with high-temperature fluids followed by rapid cooling (Kennell, 2008). This sample is relatively enriched in both ^{37}Cl and ^{81}Br , implying extensive fluid-rock interaction may lead to re-equilibration of the salt and result in enrichment of both chlorine and bromine isotopes. In contrast, the anhydrite layer (sample A in Figure 4-9), exhibits an Sr isotope ratio close to late Silurian seawater, consistent with anhydrite's suggested preservation of its original seawater composition (Kennell, 2008; Stueber et al., 1984). Very negative $\delta^{81}\text{Br}$ value in this sample may suggest the contrasting starting point of anhydrite versus halite under – which may result in different behavior under hydrothermal influence.

4.7 Summary and Conclusions

This study details how two halogen isotopic systems ($\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$) in a paleo rock sequence across a sedimentary basin record the interplay of multiple depositional and diagenetic processes, including repeated seawater evaporation, reflux, halokinesis, organic diagenesis, and hydrothermal alteration. By examining a range of lithologies and stratigraphic intervals in the Salina Formation, the scope of halogen isotope studies in evaporitic settings has expanded beyond halite-dominant samples. Notably, this is the first study to document $\delta^{81}\text{Br}$ values lower than -1.0‰ in natural rock samples, and samples with a positive-negative isotope composition ($\delta^{37}\text{Cl} > 0\text{‰}$, while $\delta^{81}\text{Br} < 0\text{‰}$) are exceptionally rare, having not been observed in either groundwater or rock samples to our knowledge.

The halogen geochemical and isotopic results reveal complex trends that vary across stratigraphic units and mineral phases. Overall, the samples show a wide range of Cl and Br contents, with halite Br contents ranging from <60 ppm due to reflux processes up to ~64,000 ppm under extreme enrichment. The $\delta^{37}\text{Cl}$ values range between -1.81‰ and +1.33‰, whereas $\delta^{81}\text{Br}$ values extend from -1.78‰ to +1.76‰. These ranges exceed those found in earlier studies, largely reflecting the broader range of sample types selected for this study, including multiple evaporite minerals (e.g., halite vs. Ca-bearing minerals) deposited during multiple evaporation cycles and subjected to various diagenetic overprints. This study identified:

- No significant correlation ($R^2 = 0.016$, $p > 0.05$) between $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$, suggesting that chlorine and bromine isotopic systems respond differently to fractionation pathways during and after deposition.
- Bromine isotopes ($\delta^{81}\text{Br}$) exhibit larger deviations than chlorine isotopes ($\delta^{37}\text{Cl}$), suggesting greater sensitivity to specific fractionation processes such as organic diagenesis (i.e., potential selective retention of ^{79}Br in organic-rich environments) or hydrothermal alteration.
- Low-Br halite (< 60 ppm Br), interpreted as a product of reflux, tends to show enrichment in both ^{37}Cl and ^{81}Br relative to other halite samples. This suggests that reflux processes preferentially remove lighter isotopes (^{35}Cl and ^{79}Br) into brines, leaving the residual halite enriched in heavier isotopes (^{37}Cl and ^{81}Br).
- Halite samples with exceptionally high Br contents (thousands of ppm) likely represent advanced evaporation and/or localized salt tectonics (halokinesis). Under overburden pressure, halite may undergo reworking via dissolution-precipitation with highly concentrated brines, promoting Br enrichment. During the process, ^{35}Cl and ^{81}Br can be preferentially mobilized into the dense fluid phase, typically resulting in lowered $\delta^{81}\text{Br}$ values and modestly elevated $\delta^{37}\text{Cl}$; however, the extent and direction of this fractionation depend on the extent and nature of salt mobilization.
- Ca-bearing minerals exhibit a widespread in $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ values, with an apparent negative trend. However, the correlation is not statistically significant ($p > 0.05$). In organic-rich intervals (e.g., A-1 and A-2 Carbonates), elevated Br/Cl ratios with negative $\delta^{81}\text{Br}$ values point to ^{79}Br retention in organic phases.

- A subset of halite and dolomite samples with elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show decreased $\delta^{81}\text{Br}$ and slightly increased $\delta^{37}\text{Cl}$ values, implying that hydrothermal fluids can preferentially mobilize ^{81}Br from the rock phase. These findings highlight the potential of $\delta^{81}\text{Br}$ as a sensitive proxy for detecting hydrothermal overprinting in evaporite-bearing systems.

These findings highlight that repeated evaporation and diagenetic processes, including dissolution-reprecipitation and brine recycling complicate Cl and Br chemical and isotopic systematics in evaporative and sedimentary basins. $\delta^{81}\text{Br}$ values appear particularly susceptible to alteration by post-depositional diagenetic processes, whereas $\delta^{37}\text{Cl}$ values remain relatively less variable yet still responsive to reflux or halokinetic processes. Importantly, high Br contents in non-halite lithologies indicate that Br isotope fractionation is not restricted to halite-dominated settings but can be strongly modified by controls outside halite-dominated facies, such as oxidative reaction of organic or microbial activity, and diagenetic processes related to lithologic context.

Taken together, this study highlights the value of integrating $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ data with other geochemical proxies (e.g., Sr isotopes, TOC) to better constrain the diagenetic and post-diagenetic processes, such as hydrothermal alteration and organic activity, on Cl-Br geochemistry. Assessing Cl and Br isotopic compositions other evaporite basins across multiple evaporite cycles will reveal how broadly these complex patterns in $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ apply. In sum, this study highlights the need for multi-phase, multi-isotope approaches to accurately reconstruct paleo-brine evolution and to unravel the diagenetic overprints affecting evaporite-bearing sequences.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

This thesis examined the isotopic systematics of bromine and chlorine ($\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$) to advance the understanding of bromine stable isotope geochemistry and its utility as an environmental tracer. By combining a synthesis of global datasets, controlled laboratory experiments, and analysis of natural evaporite systems, the research demonstrates that bromine isotopes undergo substantial fractionation across depositional and diagenetic processes. The findings collectively highlight both the unique behavior of bromine compared to chlorine and the interpretive value of considering the two halogens together. Beyond interpretation, the isotope framework has practical utility for subsurface applications, helping separate processes ranging from brine concentration and mineral precipitation to fluid-mineral interaction and identifying diagenetic overprints.

A global synthesis of groundwater and surface water datasets (*Chapter 2*) reveals that $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values often diverge across various lithologic and hydrologic settings, with $\delta^{81}\text{Br}$ in particular exhibiting greater scatter. Regression analyses between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ suggest that most samples broadly follow a mass-dependent trend, but subsets show enrichments in either heavy or light bromine (^{81}Br or ^{79}Br) that cannot be explained by chlorine systematics. This observation prompted experimental testing of isotope fractionation between fluid and minerals and comparison with natural evaporite sequences to identify the processes responsible.

Laboratory experiments (*Chapter 3*) demonstrate that bromine isotopes fractionate during sequential seawater evaporation and mineral precipitation. Unlike chlorine, where heavier isotopes (^{37}Cl) consistently partition into minerals (e.g., aragonite, calcite, gypsum, and halite), the preference for either ^{79}Br or ^{81}Br depends on the host mineral phase and composition and mode of incorporation. For example, carbonates (aragonite/calcite) may favor ^{79}Br through kinetic uptake, while gypsum accommodates Br largely in fluid inclusions with minimal isotopic fractionation. Halite appears to exhibit variable isotopic preferences influenced by precipitation rates and incorporation pathways (e.g., lattice substitution, fluid inclusion, surface adsorption). These findings overall show that bromine isotope variability is more pronounced than previously assumed and that significant fractionation can occur well before halite saturation is reached.

The investigation of paleo-evaporite deposits (*Chapter 4*) extends these insights by revealing that post-depositional processes further modify isotopic signatures. The isotopic records in evaporite minerals reflect both primary depositional fractionation and later diagenetic overprints. Dissolution of the evaporite minerals tends to release lighter isotopes (^{79}Br and ^{35}Cl) into fluids, while recrystallization disfavors Br incorporation, lowering Br/Cl ratios in the solid phase. Repetitive dissolution-recrystallization cycles (i.e., reflux) therefore complicate the isotopic signature. Additional diagenetic processes drive systematic but decoupled isotopic responses of bromine and chlorine: halokinesis generally increases $\delta^{37}\text{Cl}$ values or produces only a subtle change, while lowering $\delta^{81}\text{Br}$ values; hydrothermal alteration similarly yields higher $\delta^{37}\text{Cl}$ values while lowering $\delta^{81}\text{Br}$ values; and interactions with organic diagenesis produce little or no change in $\delta^{37}\text{Cl}$, while $\delta^{81}\text{Br}$ varies in direction and magnitude depending on the specific pathway. Evidence of organic-mediated reactions and volatilization (*Chapter 3*) highlights selective fractionation pathways unique to bromine, which lack chlorine analogues. These findings help explain why natural datasets show broader $\delta^{81}\text{Br}$ variability and highlight the need to integrate depositional and diagenetic perspectives when interpreting isotopic signatures. Considered with the *Chapter 3* experiments, the *Chapter 4* results indicate how diagenetic reworking can amplify, invert, or erase early partitioning signals, providing practical criteria to distinguish primary imprints from late-stage modification at basin scale.

This thesis makes three central contributions. First, it establishes the current state of knowledge on bromine isotope geochemistry through a systematic review, thereby providing a baseline for future studies. Second, it experimentally demonstrates that bromine isotopes fractionate significantly and variably during mineral precipitation. Third, it shows that natural evaporite systems preserve complex isotopic signatures that can be evaluated through the combined use of bromine and chlorine isotopes. In conclusion, this thesis demonstrates that bromine isotopes are sensitive to a range of geochemical processes and can provide unique insights when integrated with chlorine isotopes and other geochemical imprints or hydrological context. By bridging experimental and natural observations, it contributes to the development of a conceptual framework for bromine isotope geochemistry.

Beyond these contributions, the results of this thesis also clarify how bromine isotopes can be most effectively interpreted and applied in natural systems. The combined experimental, global water, and paleo-evaporite datasets show that bromine isotopes can fractionate not only during evaporation and mineral-fluid partitioning, but also throughout the subsequent geochemical history of rocks and groundwater. $\delta^{81}\text{Br}$ is more sensitive than $\delta^{37}\text{Cl}$ to mineral-specific incorporation pathways, organic

or redox-related processes, and volatilization; accordingly, deviations in $\delta^{81}\text{Br}$ - $\delta^{37}\text{Cl}$ from mass-dependent trends often reflect selective Br fractionation pathways that chlorine does not record. When the two isotopes are considered together, they allow identifying additional processes that modify Br behavior beyond simple evaporation. Effective application of Br isotopes requires integrating isotopic data with hydrochemical information, especially Br and Cl concentrations and their ratios, as well as lithologic context, in order to distinguish primary evaporative signals from later modification. This combined approach provides a refined framework for interpreting halogen isotope behavior in complex hydrogeologic systems.

Chapters 2-4 indicate a practical interpretive hierarchy for applying bromine and chlorine isotopes in evaporitic settings: evaluate atmospheric and/or physical processes (e.g., volatilization, diffusion), then assess mineral-brine partitioning during evaporative concentration, and finally consider diagenetic overprints (e.g., reflux, halokinesis, hydrothermal processes, organic interaction). $\delta^{37}\text{Cl}$ values tend to track evaporation progress more monotonically, whereas $\delta^{81}\text{Br}$ values serve as a selective proxy reflecting incorporation pathways tied to substitution or adsorption, including in halite and Ca-bearing minerals. In practice, using $\delta^{37}\text{Cl}$ values as the baseline and reading $\delta^{81}\text{Br}$ values as the diagnostic deviation improves discrimination between primary depositional signals and later remobilization or overprinting.

Nonetheless, limitations remain. The available datasets are geographically limited and often lack paired isotopic or hydrochemical information. Laboratory systems, while controlled, cannot reproduce the full complexity of natural environments, such as microbial activity, organic interactions, or long-term pressure-temperature effects. Addressing these gaps will require expanded sampling across diverse environments, as well as extended experiments incorporating additional geochemical variables. The following recommendations outline potential directions for future work.

5.2 Recommendations for Future Research

Some of the findings from this thesis remain suggestive rather than definitive, and several key questions have occurred throughout the course of this research. Future research should therefore address the following areas:

- (1) Global baseline and secular variations

Special attention should be paid to secular variations of $\delta^{81}\text{Br}$, which may provide the foundation for discussing its evolution. A systematic survey of $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ in waters and evaporite systems together will help establish a global baseline for Br isotope variation and allow testing of the secular $\delta^{81}\text{Br}$ variation. In addition, the assumption that $\delta^{81}\text{Br}$ values in ocean water is globally homogeneous is plausible and logical but remains unvalidated and should be critically examined. Ocean depth profiles may also provide a natural laboratory for assessing the influence of light, oxygen, density, and temperature on $\delta^{81}\text{Br}$.

(2) Mineral incorporation mechanisms

The mechanisms by which bromine incorporates into different minerals remain poorly constrained. Results from this study suggest that incorporation or inclusion pathways strongly influence isotopic fractionation, yet the competition of Br with other anions (e.g., OH^-) in mineral lattices and fluid regimes is not fully understood. Further experimental work, potentially requiring interdisciplinary collaboration, is needed to understand these mechanisms. A clearer understanding of Br incorporation into mineral lattice or at surface level will directly refine interpretations of both experimental and natural datasets.

(3) Cross-environment validation

The adaptability of bromine isotopes as tracers depends on testing fractionation pathways across contrasting environments. This includes extending beyond marine evaporites to terrestrial geologic and hydrochemical systems. Water-rock interactions specific to lithology should be systematically disentangled, as the co-occurrence of some lithologies (e.g., shale and organic-rich settings) currently obscures interpretations.

(4) Role of non-halide minerals

Minerals such as amphibole and biotite are known to be important halogen sinks but remain largely unexplored in terms of bromine isotopes. Amphibole is a major sink for halogen and shows Br concentration trends similar to Cl (Kusebauch et al., 2015). $\delta^{37}\text{Cl}$ values are slightly higher for minerals where Cl is bonded to +2 cations (e.g., micas, amphiboles) than those where Cl is bonded to +1 cations (e.g. halite) (Schauble et al., 2003). Biotite, another halogen-bearing mineral, incorporates less Cl than amphibole, but Br concentration increases with alteration, producing exceptionally high Br/Cl ratios near shear zones (Kusebauch et al.,

2015). These minerals may preserve isotopic evidence of Br-Cl decoupling and thus represent important targets for future studies.

(5) Temperature and pressure dependence

Expanded laboratory experiments should systematically explore the effects of temperature and pressure on Br isotope fractionation. In particular, competition between Br and OH during incorporation into mineral lattice or fluid complexes (Bureau and Métrich, 2003) and the relationship between temperature and Br/Cl ratios in fluid inclusions (Kozłowski and Karwowski, 1974) suggest that pressure and thermal conditions could play a significant role in determining isotopic behavior, a view further supported by high-pressure studies of Br speciation and partitioning in slab-derived fluids and melts (Louvel et al., 2020). Yet these effects still lack quantitative and isotopic assessment.

(6) Integration with other tracers and processes

Bromine isotopes should be studied in concert with chlorine and other geochemical tracers to establish dual- or multi-isotope tracer frameworks. This integration will enhance the capacity to distinguish depositional and post-depositional signatures. Additionally, fractionation associated with transitions involving gaseous phase, microbial activity, and organic transformations should be given more attention as these processes may selectively alter $\delta^{81}\text{Br}$ without producing equivalent shift in $\delta^{37}\text{Cl}$.

In summary, future research on bromine isotopes should move toward establishing global reference frameworks, resolving mineral-scale incorporation mechanisms, and testing fractionation pathways across diverse environments. By extending investigations to non-halide minerals, integrating multiple tracers, and incorporating biotic and volatile processes, the field can transition to a robust, predictive framework. Such advances will not only strengthen the role of bromine isotopes as environmental tracers but also refine their contribution to the broader understanding of halogen geochemistry in Earth systems.

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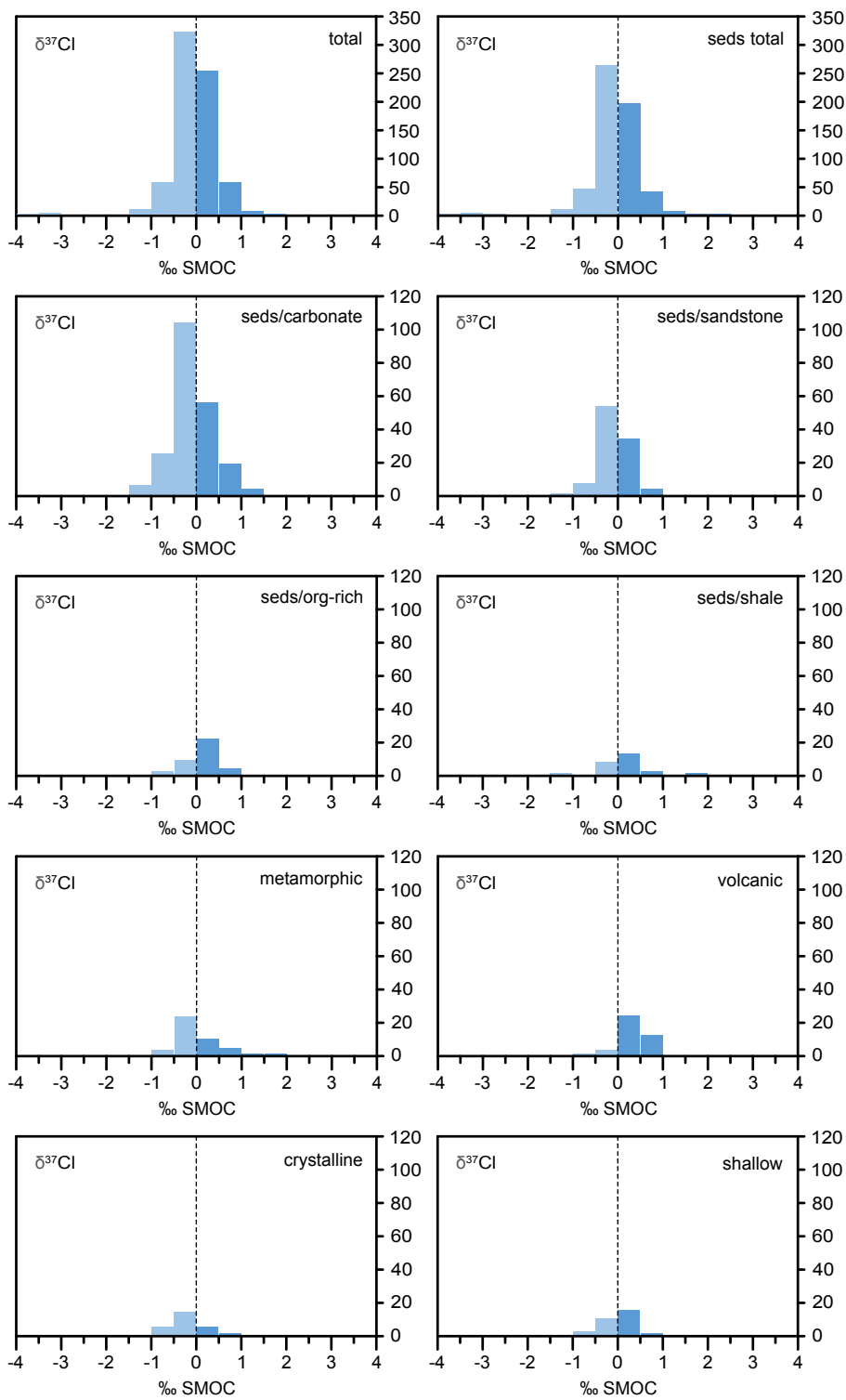
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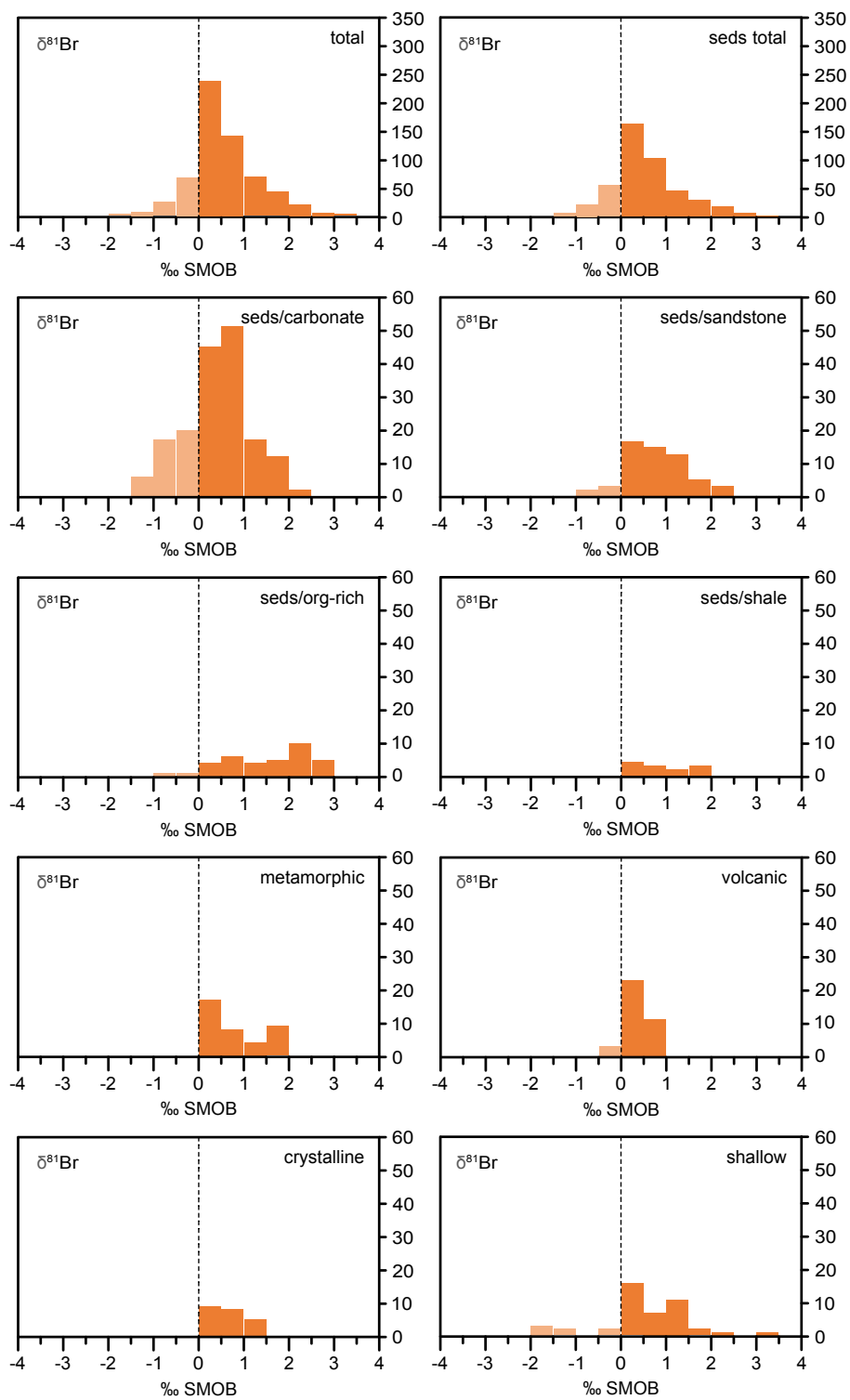
Appendices

Appendix A

Additional Figures for Chapter 2



(see p.143 for caption)



(see p.143 for caption)

Figure A-1 (p.141). Frequency distributions of $\delta^{37}\text{Cl}$ values (blue) for groundwater samples in the compiled dataset, shown for (a) all samples (“total”), (b) all sedimentary settings, and (c–j) individual lithological subgroups: carbonate, sandstone, organic-rich, shale, metamorphic, volcanic, crystalline, and shallow aquifer settings. The y-axis represents the number of samples within each bin, and the x-axis shows $\delta^{37}\text{Cl}$ values in 0.5‰ intervals.

Figure A-2 (p.142). Frequency distributions of $\delta^{81}\text{Br}$ values (orange) for groundwater samples in the compiled dataset, shown for (a) all samples (“total”), (b) all sedimentary settings, and (c–j) individual lithological subgroups: carbonate, sandstone, organic-rich, shale, metamorphic, volcanic, crystalline, and shallow aquifer settings. The y-axis represents the number of samples within each bin, and the x-axis shows $\delta^{81}\text{Br}$ values in 0.5‰ intervals.

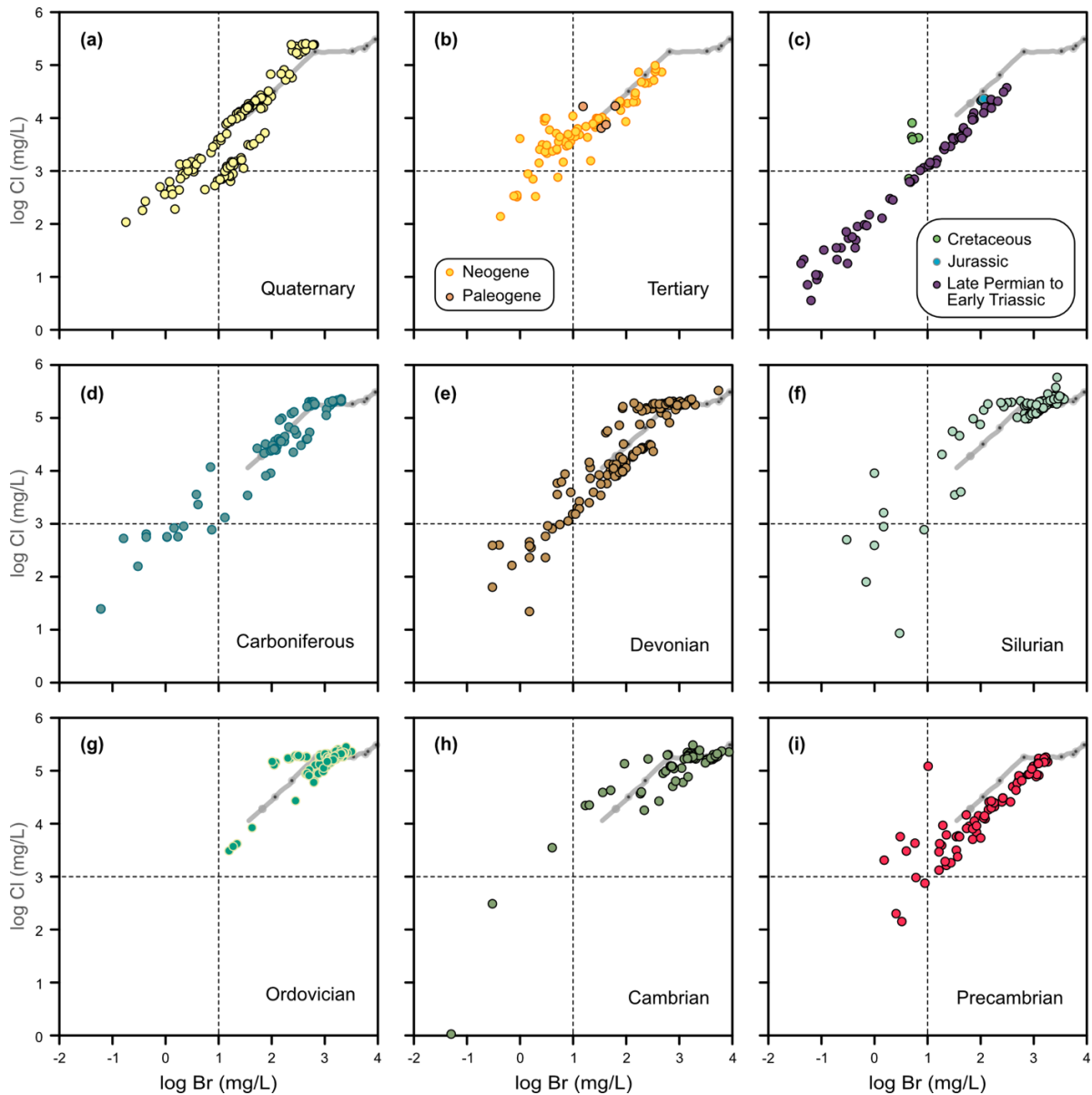


Figure A-3. Log-log plots of bromide versus chloride concentrations (mg/L) for groundwater samples grouped by host-formation age: (a) Quaternary, (b) Tertiary (Neogene and Paleogene), (c) Mesozoic (Cretaceous, Jurassic, and Late Permian to Early Triassic), (d) Carboniferous, (e) Devonian, (f) Silurian, (g) Ordovician, (h) Cambrian, and (i) Precambrian. Each point represents an individual sample. Grey curves indicate the theoretical seawater evaporation trajectory (SET). Variations in slope and scatter reflect lithology-specific salinity sources and evolutionary pathways, including evaporative concentration, halite dissolution, and mixing processes (see Figure 2 for more processes).

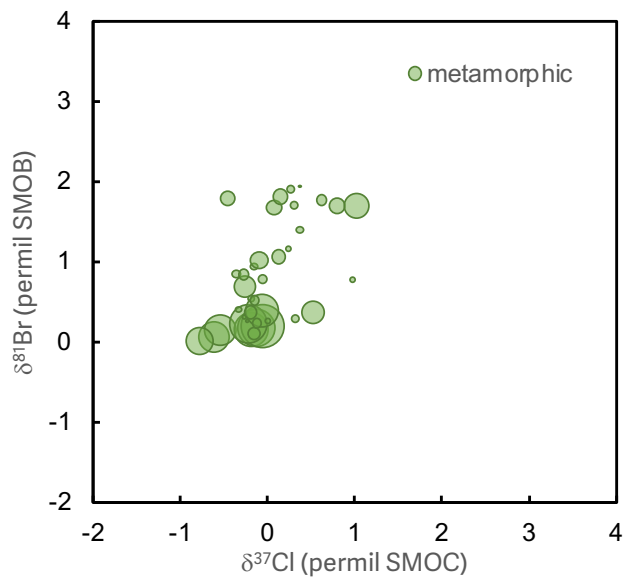


Figure A-4. Relationship between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values for groundwater samples hosted in metamorphic terranes. Each circles represents an individual sample, with marker size proportional to bromide concentrations.

Appendix B

Statistical and Methodological Considerations for $\delta^{37}\text{Cl}$ - $\delta^{81}\text{Br}$ Data

This appendix summarizes the regression framework used to evaluate relationships between $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ in the compiled *Chapter 2* dataset. Three regression approaches are applied to evaluate $\delta^{81}\text{Br}$ vs. $\delta^{37}\text{Cl}$ relationship. **Ordinary Least Squares (OLS)** assumes error-free independent variable (X-axis), all measurement error lies in dependent variable (Y-axis), and minimizes vertical residuals, making it sensitive to outliers. **Reduced Major Axis (RMA)** accounts for variance in both variables and is appropriate for symmetric relationships when both X and Y contain error. The slope is determined based on the ratio of standard deviations of X and Y, while accounting for residuals in both the X and Y directions. Thus, the resulting slope tends to be steeper or flatter than OLS, depending on variance structure. It is commonly used in natural sciences, geoscience, and biology, where data are observational. **Theil-Sen estimator** is a non-parametric, outlier-resistant method that captures the core linear trend of a data cloud without being skewed by outliers. It is frequently used for environmental and geochemical datasets, where the central trend of a relationship needs to be evaluated with the presence of extreme values.

OLS regression equations (slope, intercept) and goodness-of-fit statistics (R^2 and p -values) are summarized by host-formation age in Table B-1 in the following page. Summary statistics for RMA and Theil–Sen regressions are compiled in Table B-2 in the following page. Geologic periods with insufficient variance or sample size are reported as “NA” (see table notes for criteria).

Table B-1. Summary of ordinary least squares (OLS) regression parameters for $\delta^{37}\text{Cl}$ versus $\delta^{81}\text{Br}$ relationships in groundwater samples grouped by host formation age. Slope, intercept, and coefficient of determination (R^2) with associated p -values are shown for each geologic period. Periods with insufficient data for regression are indicated by “NA”. Notes specify cases where only one study is available or where $\delta^{81}\text{Br}$ or $\delta^{37}\text{Cl}$ values are unavailable.

Geologic Period	Slope	Intercept	R^2 ; p -value	Notes
Quaternary	0.278	0.391	0.026; <0.05	
Neogene	0.050	0.357	0.005; <0.05	
Paleogene	NA	NA	NA	Only one value available.
Cretaceous	NA	NA	NA	No available $\delta^{81}\text{Br}$ data
Jurassic	0.040	1.199	0.009; <0.05	One study available
Permo-Triassic	NA	NA	NA	One study available; no available $\delta^{37}\text{Cl}$
Carboniferous	0.910	0.949	0.186; <0.05	
Devonian	0.662	0.660	0.173; <0.05	
Silurian	2.165	0.393	0.622; <0.05	
Ordovician	0.753	0.726	0.087; <0.05	
Cambrian	1.458	0.657	0.392; <0.05	
Precambrian	0.866	0.847	0.327; <0.05	

Table B-2. Summary statistics and regression parameters for $\delta^{37}\text{Cl}$ versus $\delta^{81}\text{Br}$ relationships in groundwater samples grouped by host formation age. Columns show the number of samples (n), standard deviations (SD) of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$, and Pearson correlation coefficients (r). Reduced Major Axis (RMA) and Theil–Sen slopes and intercepts are reported where applicable; “NA” indicates insufficient variance or correlation ($r < 0.4$) or too few data points to calculate regression parameters. Notes (1) and (2) denote these cases, respectively.

Geologic Period	n	SD $\delta^{37}\text{Cl}$	SD $\delta^{81}\text{Br}$	r	RMA			Theil-Sen	
					slope	intercept	r^2	slope	intercept
Quaternary	97	0.248	0.428	0.192	NA ⁽¹⁾	NA ⁽¹⁾	NA ⁽¹⁾	0.080	0.310
Neogene	68	0.469	0.325	0.072	NA ⁽¹⁾	NA ⁽¹⁾	NA ⁽¹⁾	0.080	0.358
Paleogene	1	NA	NA	NA	NA ⁽²⁾	NA ⁽²⁾	NA ⁽²⁾	NA ⁽²⁾	NA ⁽²⁾
Cretaceous	0	NA	NA	NA	NA ⁽²⁾	NA ⁽²⁾	NA ⁽²⁾	NA ⁽²⁾	NA ⁽²⁾
Jurassic	7	0.404	0.170	0.094	NA ⁽¹⁾	NA ⁽¹⁾	NA ⁽¹⁾	0.010	1.131
Permo-Triassic	2	0.007	0.057	1	NA ⁽²⁾	NA ⁽²⁾	NA ⁽²⁾	8.000	1.800
Carboniferous	55	0.451	0.952	0.431	0.841	0.186	0.186	1.111	0.75
Devonian	91	0.414	0.661	0.415	0.507	0.173	0.173	0.699	0.503
Silurian	54	0.352	0.966	0.789	0.425	0.622	0.622	2.302	0.426
Ordovician	77	0.335	0.856	0.294	NA ⁽¹⁾	NA ⁽¹⁾	NA ⁽¹⁾	0.609	0.655
Cambrian	59	0.319	0.748	0.627	0.795	0.393	0.393	1.333	0.593
Precambrian	64	0.384	0.581	0.572	0.894	0.327	0.327	0.905	0.806

Appendix C

Artificial Seawater Recipe (40-L, 35‰) and a Short “How-To”

The following formula (Table C-1) was used to create the 40 L artificial seawater used for the experiments in this study.

Table C-1. Salt masses used for making 40 L artificial seawater.

Salts	g used
NaCl	1111.89
MgCl ₂ ·6H ₂ O	215.98
MgSO ₄	132.82
CaCl ₂	45.67
KCl	29.87
Na ₂ CO ₃	3.1
KBr	2.11
NaBr	1.76
CaCO ₃	0.962
SrCl ₂	0.586

Mixing the salt masses in Table B-1 in 40 L of deionized (ultrapure, <18 MΩ cm) water produces a composition close to that of natural seawater (see also Table 3-1). The recipe is adapted from Kester et al. (1967) and adjusted based on available stock.

The container was prepped by pre-rinsing it with ultrapure water. To avoid premature precipitation (particularly of carbonates) and to ensure complete dissolution, salts were added sequentially, and the container was periodically inverted and gently agitated. The general order was: NaCl, Mg-salts, the rest of chloride salts, Na₂CO₃, Br-salts, followed by SrCl₂ and CaCO₃. Each addition of salts was made only after the previous one had fully dissolved. The container was kept covered and sealed during preparation to minimize evaporation.

Appendix D

Supplementary Figures and Supporting Discussions for Chapter 3

D.1 Additional Figures

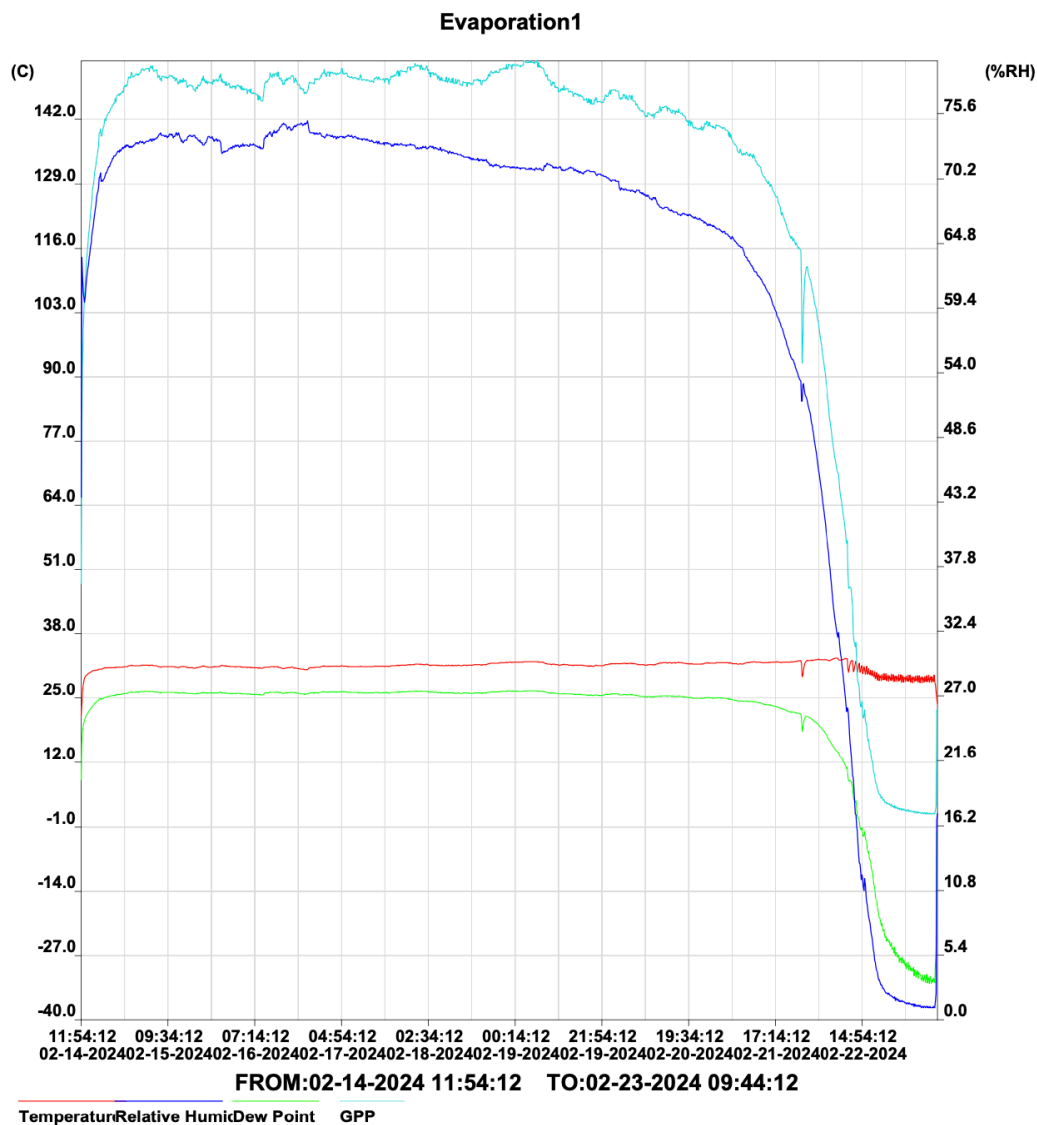


Figure D-1. Continuous 10-minute records (RHT-10, ExTech) of air temperature (red), dew point (green), relative humidity (blue), and humidity ratio (cyan) over the experimental duration. Throughout most of the run, air temperature remained stable at $\sim 31 \pm 0.7$ °C, relative humidity near $70 \pm 0.4\%$, with minor deviations observed at the onset and termination of evaporation.

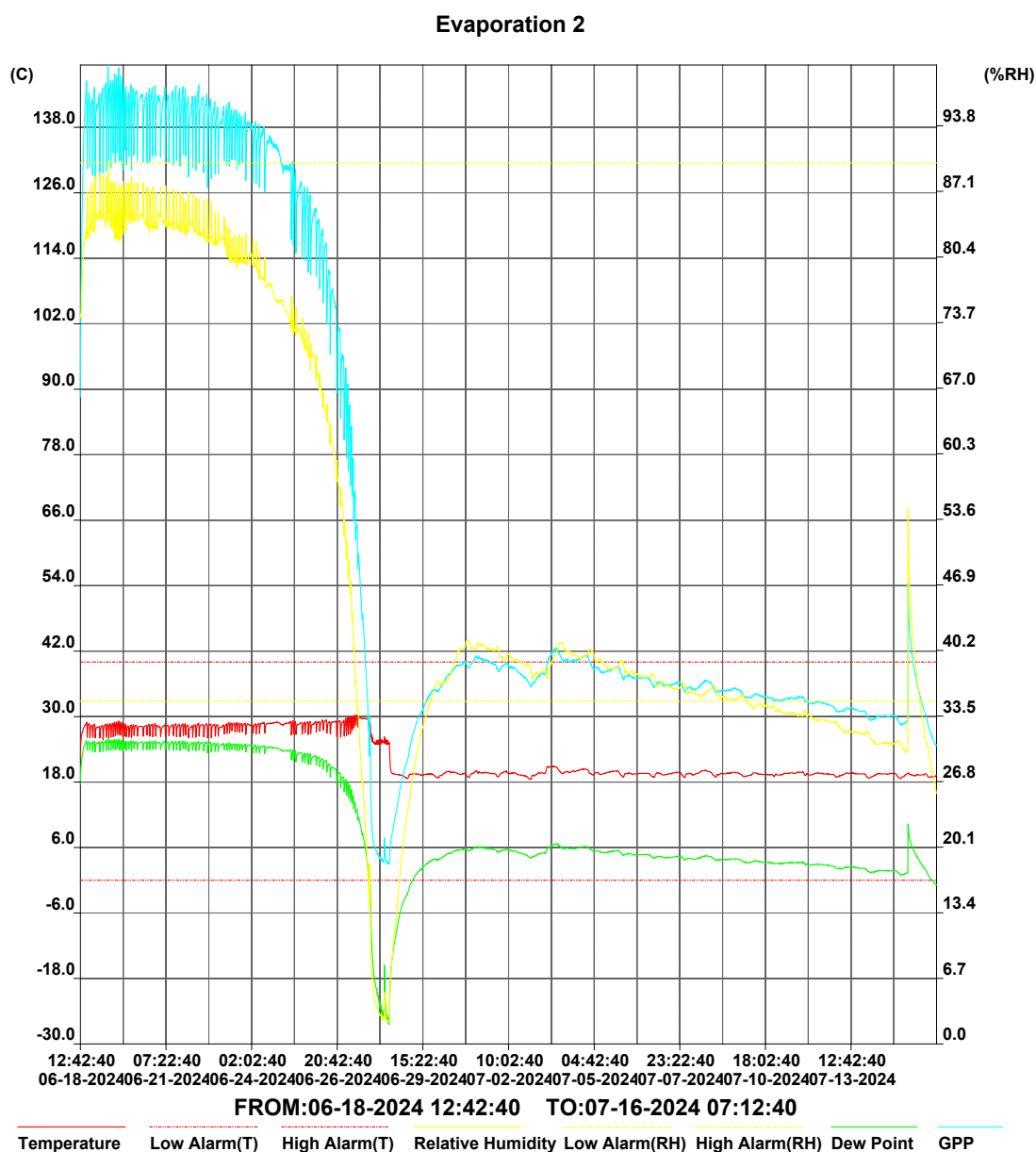


Figure D-2. Continuous 10-minute records (RHT-10, ExTech) of air temperature (red), dew point (green), relative humidity (yellow), and humidity ratio (cyan) over the experimental duration. Throughout most of the run, air temperature remained stable at $\sim 28 \pm 0.8$ °C, relative humidity near $81 \pm 4\%$, with most deviations observed during early-stage evaporation. The sharp drop in all sensors marks the termination of the experiment. Data acquired after this point were collected during removal and chamber disturbance and are therefore excluded from interpretation.

D.2 Interpretation of Needle-like Crystals in the Run 2

Table D-1. Summary of Zhong and Mucci (1989) and Application to this study.

	Findings of Zhong and Mucci (1989)	Relevance to this experiment
Rate control	Precipitation rates of calcite and aragonite obey $\log R = n \log(\Omega - 1) + \log k$; saturation state (Ω) is the prime driver.	Early in evaporation, Ω rises steeply $\rightarrow$ surface nucleation can be rapid for both needle-like aragonite and gypsum.
Aragonite vs. calcite	At 25 °C, once Ω_{calcite} exceeds ~ 2.6 ($\approx \Omega_{\text{aragonite}} > 1.7$), aragonite grows faster than calcite.	Early brine likely surpassed this Ω threshold, making aragonite kinetically favored.
Salinity (S) effect	Calcite rates are independent of salinity for $S = 5$ -44. Aragonite rates decrease two- to five-fold as salinity rises from 5 to 44, yet remain faster than calcite at the same Ω .	At $S \approx 35$, aragonite growth is slightly slower than at low salinity but still faster than calcite, so needle-like aragonite is plausible.
Other modifiers	Phosphate, sulfate, and temperature can all shift polymorph selection.	At 31°C in synthetic seawater, so no strong inhibition is expected.

Application to ES 2-1 and ES 2-2:

Brine conditions early in the run (31°C, $S \approx 35\%$) likely exceeded Ω thresholds for aragonite dominance, consistent with wall-coating needles interpreted as aragonite. For definitive distinction between aragonite and gypsum, XRD or Raman analyses would be required (e.g., aragonite 2 θ peaks at 26.2°, 27.2°, 33.1° versus gypsum at 11.6°, 20.7°, 29.1°. Elevated Br/Cl ratios may also suggest abundant fluid inclusions, compatible with rapidly grown, porous aragonite.

D.3 Preparation of Thin Sections of Soluble Salts

For further mineralogical characterization or investigations of the precipitates (i.e. soluble salts) from seawater/brine evaporation, conventional thin-section preparation methods are inadequate for water-soluble or soft salt minerals, as grinding may cleave off fragments from the sample and polishing can lead to dissolution. Thus, alternative approaches are required to prepare water-soluble samples, such as halite, into a thin-section analysis. Below are three possible methods from previous studies:

Method 1. Thin section of halite (Walker, 1969):

1. Prepare an aluminum mold the size of a standard thin section, 13 mm thick.
2. Pour 5 mm of liquid casting plastic (e.g., epoxy resin, acrylic, polyester) into the mold.
3. Place a 4 mm thick rough-cut sample on the hardened plastic surface.
4. Pour another 5 mm thick layer of casting plastic over the sample.
5. After complete curing, grind the mold down to the halite on one side and to within 2 mm of the sample on the other side. For grinding, use *supersaturated NaCl solution* or *glycol* as the fluid to prevent dissolution.
6. Polish the exposed side and recover it with a 2 mm thick plastic layer; then grind the other side to the thickness of a normal thin section.
7. Pour a 1 mm layer of plastic over the surface and, after gardening, polish the entire casting.

Method 2. Thin section of rock salt having fluid inclusions (Wang et al., 2016):

Use *anhydrous ethanol* as (i) the cooling liquid for cutting blade, (ii) the grinding fluid, (iii) the wetting agent for polishing power (polishing solution), and (iv) the cleaning liquid. This avoids dissolution and deformation and preserves the original geological features, including fluid inclusions, in rock salt. (*Paper in Chinese; only abstract available in English.*)

Method 3. Salt minerals (Yu et al., 1965):

This method is specifically applicable to Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), and natural alkali ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 10\text{H}_2\text{O}$).

1. Rough-grind a piece of salt mass with emery, using the *saturated solution of the salt* as lubricant, until a plane surface is obtained; then switch to oil instead of water.
2. Cement the salt slab to a glass mount with soft gum previously conditioned to a semi-solid; keep the cohering temperature $\leq 40^{\circ}\text{C}$, then rapidly cool with cold water flow.
3. Mount the cover glass with cold gum.
4. For loose grains, it is necessary first to dip the sample into liquid polyethylene (using ethylene diamine anhydrous or triethanolamine as hardening agent). After solidification, proceed as above.

D.4 Fractionation Factors ($10^3 \ln \alpha$) for Brines, Precipitates, and Gas

Table D-2. Summary of fractionation factors for chlorine and bromine between artificial seawater and brine, precipitate, and gas phases at different evaporation stages. Evaporation degree is expressed using Mg concentration as a conservative proxy. All fractionation factors are calculated relative to the artificial seawater baseline. NA: Not available.

Sample #	Type	Evap Degree	$10^3 \ln \alpha \text{ Cl}_{\text{SW-X}}$			$10^3 \ln \alpha \text{ Br}_{\text{SW-X}}$		
			brine	precipitate	gas	brine	precipitate	gas
EV 0	Seawater	0	0	0		0	0	
EV 2-1	Brine	1.14	0.13			0.07		
EV 1-1	Brine	1.05	0.36			0.44		
EV 2-2	Brine	1.03	0.19			0.23		
EV 1-3	Brine	1.28	0.21			0.58		
EV 1-5	Brine	1.84	0.39			0.30		
EV 2-3	Brine	2.28	-0.32			0.32		
EV 2-4	Brine	2.78	-0.21			0.28		
ES 2-1	Precipitate			-0.05			0.08	
EV 2-5	Brine	3.57	-0.19			0.43		
EV 2-6	Brine	4.73	-0.18			0.31		
EV 1-7	Brine	5.46	0.13			0.35		
ES 2-2	Precipitate			-0.01			0.03	
EV 2-7	Brine	8.16	-0.18			0.19		
ES 2-3W	Precipitate			0.27			0.07	
ES 2-3B	Precipitate			0.07			0.11	
EV 2-8	Brine	12.7	-0.14			0.02		
ES 2-4	Precipitate			0.20			0.26	
EV 2-9	Brine	18.3	-0.16			0.34		
ES 2-5	Precipitate			-0.03			0.23	
EG 2	Gas				NA			-0.31

Appendix E

Chapter 3 Data Table

Table E-1. Sample list and results; units in mg/L (liquids) and mg/kg (solids); EV: evaporation; SD: standard deviation.

	Type	EV (Mg-proxy)	EC (mS/cm)	Cl ⁻	Na ⁺	SO ₄ ²⁺	Mg ²⁺	Ca ²⁺	K ⁺	HCO ₃ ⁻	Br ⁻	Sr ²⁺	δ ³⁷ Cl	SD	δ ⁸¹ Br	SD
EV 0	Seawater	0.00	-	19470	10832	2741	1285	419	402	125	68	7.90	0.06	0.11	0.13	0.07
EV 2-1	Brine	1.14	54.50	18700	11150	6150	1110	499	481	-	93	6.16	0.18	0.13	0.20	0.05
EV 1-1	Brine	1.05	65.70	22400	14900	7190	1020	526	497	-	94	5.32	0.42	0.17	0.57	0.09
EV 2-2	Brine	1.03	60.80	21000	13800	6651	1010	540	493	-	98	5.25	0.25	0.05	0.36	0.08
EV 1-3	Brine	1.28	77.30	27200	18700	8508	1250	639	611	-	111	6.52	0.27	0.15	0.71	0.08
EV 1-5	Brine	1.84	102.30	39000	26600	12223	1800	908	868	-	164	9.39	0.45	0.14	0.43	0.02
EV 2-3	Brine	2.28	116.60	47950	30800	13871	2230	920	1110	-	199	11.10	-0.26	0.04	0.45	0.11
EV 2-4	Brine	2.78	132.70	66650	37400	16237	2710	877	1350	-	233	12.50	-0.16	0.04	0.41	0.06
EV 2-5	Brine	3.57	154.80	71700	47700	20252	3480	829	1700	-	307	15.10	-0.14	0.09	0.56	0.10
EV 2-6	Brine	4.73	186.40	96200	62900	26243	4620	667	2280	-	413	16.30	-0.12	0.10	0.45	0.10
EV 1-7	Brine	5.46	195.20	90333	78900	31756	5330	547	2570	-	496	16.30	0.19	0.09	0.48	0.09
EV 2-7	Brine	8.16	241.50	178300	103000	42840	7960	337	3890	-	721	18.50	-0.12	0.07	0.32	0.11
EV 2-8	Brine	12.70	200.50	200500	114000	65309	12400	162	5980	-	1100	14.40	-0.09	0.11	0.15	0.09
EV 2-9	Brine	18.34	186.30	195900	110000	93170	17900	100	8610	-	1480	11.30	-0.10	0.06	0.48	0.08
ES 2-1	Solid	-	-	543000	-	110000	-	-	-	-	151	-	0.01	0.10	0.21	0.07
ES 2-2	Solid	-	-	439000	-	156000	-	-	-	-	300	-	0.05	0.13	0.16	0.03
ES 2-3 W	Solid	-	-	427000	-	166000	-	-	-	-	679	-	0.12	0.13	0.20	0.10
ES 2-3 B	Solid	-	-	412000	-	150000	-	-	-	-	419	-	0.33	0.13	0.24	0.06
ES 2-4	Solid	-	-	433000	-	131000	-	-	-	-	300	-	0.25	0.13	0.39	0.03
ES 2-5	Solid	-	-	471000	-	98000	-	-	-	-	251	-	0.03	0.12	0.36	0.10
EG	Gas	-	-	-	-	-	-	-	-	-	-	-	BAL*	-	-0.17	0.03

*BAL: Below analytical level, reflecting insufficient Cl in the KOH-captured gas to precipitate enough AgCl for Cl isotope analysis.

Appendix F

Detailed Description of Salina Formation Units

F.1 A-1 and A-2 Units

The **A-1 Evaporite** primarily consists of halite with interbedded anhydrite and sylvite, with thickness and mineral composition varying with proximity to reef complexes. Notably, sylvite deposition is a prominent feature in the basin center (Harrison III and Voice, 2017). Biomarker data indicate that the source rocks—organic-rich laminites within inter-reef A-1 mudstones—were deposited under hypersaline, strongly reducing conditions (Gardner and Bray, 1984; Obermajer, 2000; Warren, 2016). The **A-1 Carbonate**, overlying the A-1 Evaporite, is characterized by dense brown dolomite overlain by dark gray to black limestone or limy shale, indicative of greater organic material accumulation (Mesolella et al., 1974). This shift from evaporitic to carbonate deposition was driven by a relative sea-level rise and basin transgression, which reduced salinity and allowed finer carbonate sediments to accumulate. The slower sedimentation rates and less evaporitic conditions in the carbonate interval resulted in finer-grained textures and favored the preservation of organic matter, particularly in the basin center (Mesolella et al., 1974).

The subsequent **A-2 Evaporite** deposition mirrors the A-1 Evaporite in its halite-dominated composition but lacks sylvite beds, suggesting a greater hydrologic inflow that prevented potash salt precipitation. Laterally, the A-2 Evaporite grades into interlaminated anhydrite and dolomite. Overlying the A-2 Evaporite, the A-2 Carbonate marks another environmental transition of a relative sea-level rise and basin transgression. Dissolution of older halite deposits near the basin margins during A-2 Carbonate deposition underscores syn-sedimentary subsidence and brine migration pathways (Mesolella et al., 1974). Similar to the A-1 Carbonate, the **A-2 Carbonate**, contains coarser carbonate grains that thicken near pinnacle reefs, where dolomitization is prominent (Mesolella et al., 1974). This transition indicates that as the depositional environment shifted from highly evaporitic to less saline conditions, carbonate sedimentation became more favorable. Organic matter is also abundant in the basin-center sections of the A-2 Carbonate, which formed under conditions conducive to organic preservation. Unlike the evaporite units, the slower sedimentation rates and reduced salinity in these carbonates favored the retention of organic matter. Dissolution of older halite deposits near the basin margins during A-2 Carbonate deposition further underscores the interplay of syn-sedimentary subsidence and brine migration (Mesolella et al., 1974).

F.2 B Unit

During deposition of the Salina Formation at the beginning of the Cayugan (Late Silurian), sea-level regression led to the formation of interbedded salts, including halite, gypsum, anhydrite, and potash salts, in the Michigan basin center under a highly evaporitic regime (Briggs et al., 1978; Gill, 1977). Subsequent sea-level rise deposited transgressive deposits, and, together with thick salt accumulation, contributed to subsidence and the development of a geosyncline in the basin center (Mesolella et al., 1974; Tremper, 1973). Consequently, the B Evaporite, which has the greatest lateral extent of the formation, is divided into two subfacies: the lower B Salt and the upper B Unit. Furthermore, oxygen and carbon isotopic analyses provide additional insights into the environmental conditions during the deposition of the Salina Formation: $\delta^{13}\text{C}$ values indicate a transitions from anoxic bottom conditions to oxic conditions during the deposition of the B Evaporite, while organic-rich carbonate units, such as the A Carbonate, were deposited in shallow-water evaporitic settings adjacent to sabkha environments (O'Shea et al., 1988).

The **B Salt** primarily consists of halite with occasional gypsum intervals near its base, suggesting deposition in shallow water. In these facies, halite frequently underwent recrystallization and enlargement, distorting interlayered dolomitic carbonates that likely represent primary bedding (Harrison III and Voice, 2017). Thickness variations within the B Unit provide further insights into depositional dynamics: the B Unit thickens where the underlying A-2 Evaporite is thinner, suggesting localized changes in accommodation space; and similarly, the overlying C Unit thickens where the B Salt is thinner, reflecting reciprocal sedimentary relationships (Tremper, 1973). Notably, the B Unit marks the first significant lateral expansion of the Salina Formation into Ohio, Pennsylvania, and New York, making it an important correlation marker for the Ohio and Indiana Basins (Droste and Shaver, 1985; Mesolella et al., 1974). Evidence also suggests that increased water exchange occurred through an entrance strait connecting the Michigan Basin to the northern Ohio salt basin via southeastern Michigan, a factor that likely influenced both the extent and composition of these evaporitic deposits (Harrison III and Voice, 2017).

F.3 Upper Salina Deposits (C through G Units)

Above the B Evaporite, isotopic evidence suggests the widespread development of subaerial prograding sabkhas across the basin. Additionally, $\delta^{18}\text{O}$ values indicate that Silurian oceans were depleted in ^{18}O by 5-6‰ compared to modern oceans, further supporting interpretations of unique

paleoenvironmental conditions (Bailey, 2005). The upper Salina deposits comprise the C, D, E, and F Units, (and include the G Unit in some locations). The C Unit, often referred to as the **C shale**, is dominated by gray dolomitic shale and shaly (argillaceous) dolomites interbedded with nodular to laminar anhydrite and minor halite. Secondary fractures in the shale are mainly filled with orange to reddish-brown salt (Harrison III and Voice, 2017). The upper part of the C Unit contains rounded, frosted quartz grains of eolian origin, which serve as excellent correlation markers across the Michigan, Ohio, Allegheny, and Indiana Basins; and the e (Droste and Shaver, 1985; Lilienthal, 1978; Sonnenfeld and Al-Aasm, 1991). This unit generally thickens in the northern part of the basin, especially where the B Salt is locally thinner (Tremper, 1973).

The D Unit, or the **D Salt**, typically consists of halite with some gypsum crystals and is frequently replaced by halite (Harrison III and Voice, 2017). The D Salt shares similar geochemical and textural characteristics with the B Salt, although it is generally much thinner and has a smaller areal extent, predominantly in the basin center. The unit is split into two subunits by a thin dolomite intercalation (Sanford, 1969) and, toward the east and south, contains three distinct halite units (Jacoby, 1969). Along the basin margin, the halite transitions into thinner anhydrite and shale (Tremper, 1973), and the unit continues into Ohio, and northern and western Pennsylvania similarly to the C Unit (Mesolella et al., 1974).

The **E Unit** is composed mostly of red and greenish-gray mudstone, interbedded in its lower part with thin dolomitic carbonate stringers and interrupted by occasional intervals of reddish-brown salt and nodular anhydrite—resembling the fracture-filling salt found in the C Shale (Harrison III and Voice, 2017; Tremper, 1973). The E Unit reaches a thickness of up to 36 m, comparable to that of the C Unit, and on the western side of the basin, it contains a very porous dolomite known as the “Kintigh zone” (Burns, 1962).

The F Unit, so-called the **F Salt**, is the thickest and more intensively studied unit, with a maximum thickness of ~330 m. Due to the thickness and easy accessibility, this is one of the most extensively studied units of the Salina Formation. This unit is discussed further in the following section.

The uppermost **G Unit**, generally the second thinnest unit of the Salina Formation, consists mainly of dark dolomitic shale with occasional anhydrite interbeds and thins toward the basin margins (Sonnenfeld and Al-Aasm, 1991). The dolomite content in the G Unit typically increases toward the margins, although local uplift and erosion can also control its distribution.

F.4 F Salt

The F Salt, the thickest and one of the most intensively studied units of the Salina Formation (maximum thickness ~330 m), has been investigated extensively through cores such as TB-7 (e.g., Harrison III and Voice, 2017). The F Salt comprises up to six distinct salt cycles, each separated by interbeds of shale, dolomite, and anhydrite. The lower salt cycles are more extensive, whereas the upper cycles retreat into the Michigan Basin and are increasingly replaced by shales along the basin margins. Tremper (1973) interpreted this abrupt thinning of salt near the margins as a result of redissolution processes.

Within the F Salt, textural differences are evident: for example, F-1 is less recrystallized compared to the coarsely recrystallized F-2, suggesting variations in diagenetic history or depositional environment. The upper part of the Salina Formation, including the F Salt, exhibits evidence of increased clay influx, suggesting that humid periods became more frequent at the expense of prolonged dry periods. This climatic shift likely influenced the depositional environment and contributed to the observed lithological transitions.

Appendix G

Sample Lists for Chapter 4

G.1 Sample List 1: Archived Samples and Description

Table F-1. Archived Samples List and Descriptions. Pictures and notes on characteristics of each sample are available on the subsequent pages.

Sample ID	Old label	Location	Unit	Depth (m)	Dominant rock/mineral, key feature
UMK-2	UMK 29	Newaygo, MI, USA (Western flank of the Michigan Basin)	A-1 Carb	1479.57	Shaley dolomite (no vugs)
UMK-3-C	UMK 30	Newaygo, MI, USA	A-1 Carb	1482.31	Carbonate (calcite)
UMK-3-D	UMK 30	Newaygo, MI, USA	A-1 Carb		Shaley dolomite (vuggy)
GOS-1	IMP Gosfield 6-4 WD 2409.5 ft	Essex, ON, Canada	A-1	734.42	Carbonate/Dolomite (no lamination)
LAM-1	27 OGS Lambton 1505.55	Lambton, ON, Canada (Eastern flank of the Michigan Basin)	F	458.89	Dolomite with micritic halite
LAM-3	29 OGS Lambton 1675 ft+ 40 cm	Lambton, ON, Canada	E	510.54	Shaley dolomite
LAM-4-H1	S2-33-537.20; OGS 82-1 Lambton 537.20m	Lambton, ON, Canada	C	537.20	Halite (top massive piece)
LAM-4-H2	OGS 82-1 Lambton 537.20m	Lambton, ON, Canada	C	537.20	Vein filling orange plunging halite + polyhalite
LAM-6-A	OGS 82-1 Lambton 553.21m (A1-28-553.21)	Lambton, ON, Canada	C	553.21	Anhydrite (chicken wired texture with a small amount of plunging salt)

LAM-6-D	OGS 82-1 Lambton 553.21m (Dol/Clay-28- 443.21 with Halite vein)	Lambton, ON, Canada	C	553.21	Dolomite and illite with intermittent thin orange halite filling
GOD-1	<i>n/a</i>	Goderich, ON, Canada	A-2	540	Halite (chunky cube)
GOD-2-H1-3	<i>n/a</i>	Goderich, ON, Canada	A-2	540	Halite (H1 = top base halite, 2 = middle base halite, 3 = bounding salt)
GOD-2-F	<i>n/a</i>	Goderich, ON, Canada	A-2	540	Halite with Fe-stains
GOD-2-A	<i>n/a</i>	Goderich, ON, Canada	A-2	540	Anhydrite layer ca. 1-cm-thick
IMP-1	Imp Huron 9-XI 1199ft	Huron, ON, Canada	A-1	264.87	Anhydrite
IMP-2	Imp Huron 9-XI 1199ft	Huron, ON, Canada	A-1	264.87	Clear halite

G.2 Sample List 1: Photographs

G.2.1. UMK Series (Newaygo, MI)



Figures G-1 (left) and G-2 (right). UMK-2 sample consists of dark, shaley dolomite with thin, muddy laminations, suggesting deposition in a low-energy environment.



Figures G-3 (left) and G-4 (right). UMK-3-C/D samples display dark dolomite with vuggy textures with shaley laminations; evidence of secondary calcite precipitation indicates possible hydrothermal alteration.

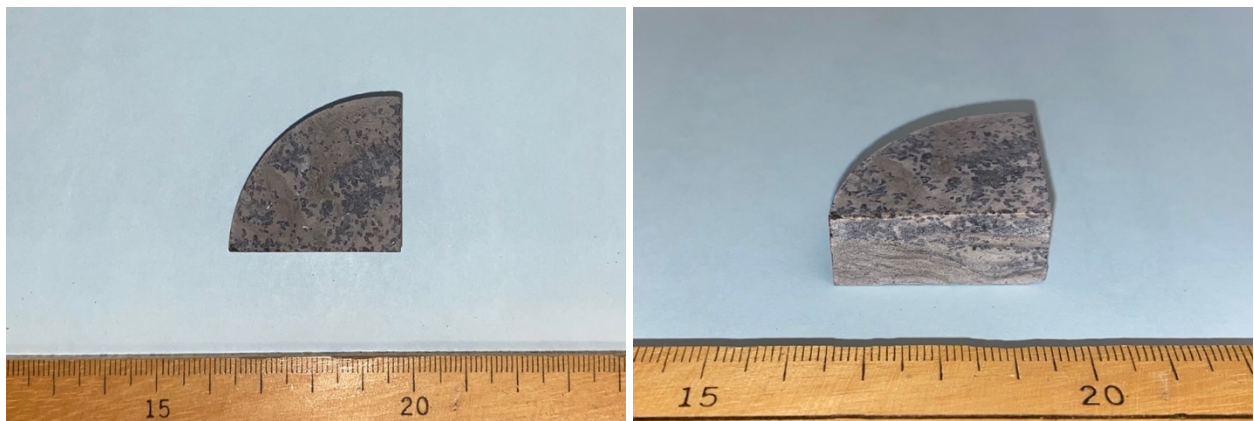
G.2.2. GOS-1 (Essex, ON)



Figure G-5. GOS-1 sample represents a carbonate bank environment with dolomite and minimal laminations.

G.2.3. LAM Series (Lambton, ON)

Likely represent an intertidal setting, as indicated by varying muddy laminations and features of halite bottom growth. The region's proximity to a brine channel (e.g., an entrance strait such as the Chatham Sag) is also evident.



Figures G-6 (left) and G-7 (right). LAM-1 sample exhibits distinct laminations, indicative of bottom growth, and halite precipitations that partly replaced gypsum, resulted in micritic halite.

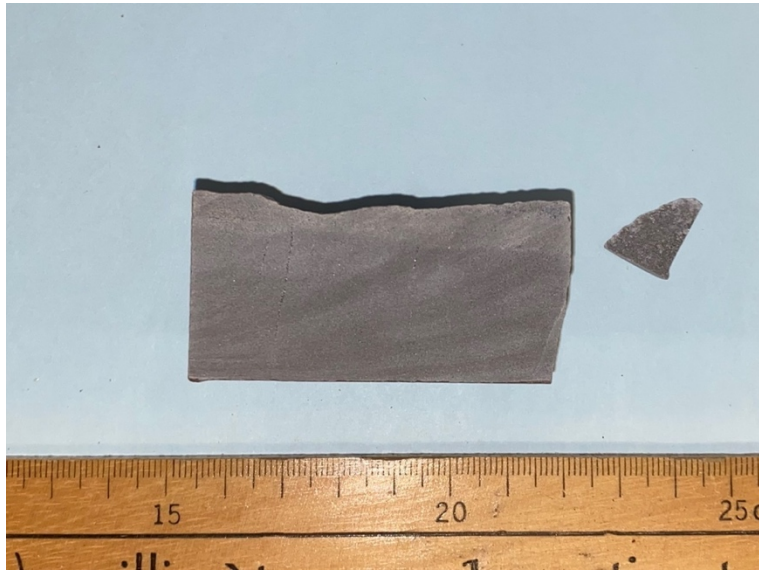


Figure G-8. LAM-3 sample contains shaley laminations of dolomite, characteristic of a slope facies.



Figures G-9 (left) and G-10 (right). LAM-4 samples feature an abrupt transition between anhydrite and dolomite, with massive orange plunge halite and halite veins (H1: massive top; H2: vein) within the dolomite body, and a basal anhydrite and carbonate body.



Figures G-11 (top left), G-12 (top right), and G-13 (bottom). LAM-6 samples display anhydrite within dolomite/illite, along with a thin orange halite vein deposit. Anhydrite body displays chicken wired texture.

G.2.4. GOD Series



Figure G-14. Pure halite with a lot of blurry fluid inclusions.

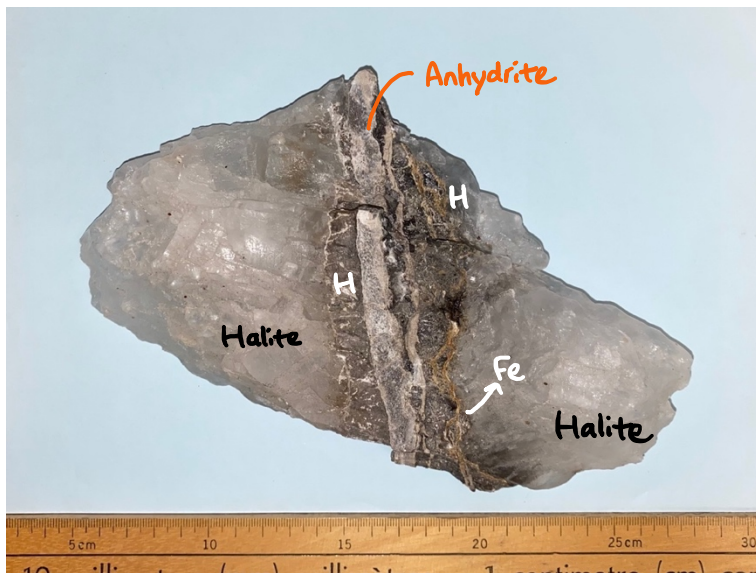


Figure G-15. Halite based on both sides cut by anhydrite layer with some iron-stains in the bounding halite.

G.2.5. IMP Series



Figure G-16. Anhydrite including halite precipitated within dissolved-out vugs.

G.3 Sample List 2: OGSRL Samples and Description

Table G-2. Sample list and metadata for OGSRL cores collected from multiple localities across southern Ontario. Samples include halite-, carbonate-, and anhydrite-bearing units from F to A-1 intervals. Coordinate values are in decimal degrees.

#	Label on the bag	Lat	Long	Unit	Depth	Dominant mineral
ESX-2	1118-100-38	42.29296417	-83.08473222	F Salt	307.47	Halite
ESX-3	1118-100-39	42.29296417	-83.08473222	F Salt	308.09	Halite
ESX-4	1118-100-42	42.29296417	-83.08473222	F Salt	309.04	Halite
ESX-5	1118-108-34	42.29296417	-83.08473222	F Salt	331.84	Halite
ESX-6	1118-109-33	42.29296417	-83.08473222	F Salt	335.13	Halite
ESX-7	1118-118-30-C	42.29296417	-83.08473222	F Unit	352.80	Calcite
ESX-8	1118-118-30-S	42.29296417	-83.08473222	F Unit	352.80	Halite
ESX-9	1118-119-29	42.29296417	-83.08473222	F Unit	355.76	Dolomite
ESX-10	1118-121-27	42.29296417	-83.08473222	E Unit	360.13	Dol/Anh
ESX-11	1118-133-21	42.29296417	-83.08473222	D Salt	380.98	Halite
ESX-12	1118-133-22	42.29296417	-83.08473222	D Salt	381.82	Halite
ESX-13	1118-133-23	42.29296417	-83.08473222	D Salt	382.22	Halite
ESX-14	1118-133-24	42.29296417	-83.08473222	D Salt	382.48	Halite
ESX-15	1118-141-18	42.29296417	-83.08473222	C Shale	395.90	Polyhalite
ESX-16	1118-141-19	42.29296417	-83.08473222	C Shale	397.27	Shale/Dol
ESX-17	1118-161-17	42.29296417	-83.08473222	B Salt	434.32	Halite
ESX-18	1118-166-15	42.29296417	-83.08473222	B Salt	444.48	Halite
ESX-19	1118-166-16	42.29296417	-83.08473222	B Salt	444.75	Halite
ESX-20	1118-175-11	42.29296417	-83.08473222	B Salt	459.84	Calcite
ESX-21	1118-175-12	42.29296417	-83.08473222	B Salt	459.96	Halite
ESX-22	1118-175-10	42.29296417	-83.08473222	B Salt	460.06	Halite
ESX-23	1118-181-7	42.29296417	-83.08473222	B Salt	470.14	Halite
ESX-24	1118-181-9	42.29296417	-83.08473222	B Salt	471.51	Halite
ESX-25	1118-192-5	42.29296417	-83.08473222	A-2 Salt	490.83	Halite
ESX-26	1118-192-6	42.29296417	-83.08473222	A-2 Salt	491.83	Halite
ESX-27	1118-193-2	42.29296417	-83.08473222	A-2 Carb	493.59	Anh/Carb (no fizz)
LAM-8	538-175-5	42.7865	-82.4465	B	623.69	Halite

LAM-9	538-176-7	42.7865	-82.4465	B	628.25	Halite
LAM-10	538-177-8	42.7865	-82.4465	B	630.85	Halite
LAM-11	538-187-2	42.7865	-82.4465	A-2 Carb	660.53	Carbonate
KNT-1	860-178-1	42.3878225	-82.079895	F Unit	291.90	Anh/Gyp
KNT-2	860-214-8	42.3878225	-82.079895	B Salt	347.29	Dol/Hal
KNT-3	860-215-9	42.3878225	-82.079895	B Anh	348.75	Anhydrite
KNT-4	860-241-12	42.3878225	-82.079895	A-2 Carb	388.56	Carbonate (no fizz)
KNT-5	860-279-16	42.3878225	-82.079895	A-2 Salt	443.23	Halite
KNT-6	860-279-17	42.3878225	-82.079895	A-2 Salt	443.55	Halite
KNT-7	860-279-18	42.3878225	-82.079895	A-2 Salt	443.73	Halite
HUR-1	1072-96-1	43.7376533	-81.687863	F Salt	332.23	Halite
HUR-2	1072-96-2	43.7376533	-81.687863	F Salt	333.85	Halite
HUR-3	1072-98-7	43.7376533	-81.687863	F Salt	338.65	Halite
HUR-4	1072-98-8	43.7376533	-81.687863	F Salt	338.93	Dolomite (little fizz)
HUR-5	1072-102-9	43.7376533	-81.687863	F Salt	348.73	Halite
HUR-6	1072-107-11	43.7376533	-81.687863	E Unit	360.59	Carbonate
HUR-7	1072-117-15	43.7376533	-81.687863	D Salt	386.41	Halite/Anh
HUR-8	1072-118-18	43.7376533	-81.687863	C	388.07	Halite
HUR-9	1072-126-21	43.7376533	-81.687863	C	408.16	Halite
HUR-10	1072-127-25	43.7376533	-81.687863	C	410.19	Halite/Mg-Sulfate
HUR-11	1072-155-33	43.7376533	-81.687863	B Salt	488.92	Halite
HUR-12	1072-159-34	43.7376533	-81.687863	B Anh	495.67	Anhydrite
HUR-13	1072-159-35	43.7376533	-81.687863	B Anh	498.44	Halite
ELG-1	861-190-1	42.6707683	-81.161395	A-2 Carb	368.14	Dolomite (little fizz)
ELG-2	861-243-3	42.6707683	-81.161395	A-1 Carb	449.40	Dolomite/Anh
NOR-1	100-59-3	42.7406389	-80.294944	A-2 Carb	246.81	Carbonate
NOR-2	100-70-5	42.7406389	-80.294944	A-1 Carb	279.94	Carbonate
WLD-1	173-41-1	42.9245775	-79.292114	A-2	154.99	Carbonate
WLD-2	173-43-4	42.9245775	-79.292114	A-2	162.24	Carbonate

G.4 Sample List 2: Core Location Description and Sampling Notes

Core photographs are available through the OGS Library well cards database

(<https://www.ogslibrary.com/wellcards/index.php>). Photographs can be accessed by searching with the core license number (e.g., T011552). The license numbers of each core are provided below.

G.4.1 Essex (T011552, MTOX11-5, 1118)

- Sampling from this core covers the F Salt, E, D, C, B Salt, and A-2 Carbonate units.
- The core terminates in the A-2 Carbonate at a true vertical depth (TVD) of 500.15 m, with a base depth of 496.05 m.
- An adjacent core located in Lambton (~40 km away) records the following depths: F Shale (448-503 m), E Carbonate (505-525 m), C Shale (537-553? m), B Evaporite/Anhydrite (556-654 m), and A-2 Carbonate (654-694 m). Essex is approximately 200 m shallower than the Lambton interval.

G.4.2 Lambton (T001992, ARGOR65-1, 538)

- Samples from this core include deeper intervals of B Salt, A-2 Carbonate, A-2 Evaporite, and A-1 Carbonate.
- The C and shallower units (<553.21 m) are already covered by existing samples (“archived”).

G.4.3 Kent (T006045, OGS82-2Chatham, 860)

- Planned sampling targets the F, E, C, and B units as well as A-2 Carbonate, A-2 Shale, A-2 Anhydrite, and A-1 Carbonate.
- This core is located ~20 km from the Fletcher core, at a ground elevation 2–5 m higher.
- Intervals include: F Salt (270–310 m), E Carbonate (310–340 m), C Shale (340–370 m), B Evaporite (370–375 m), A-2 Carbonate (375–400 m), A-2 Evaporite (thin, 2-3 m at around 400 m depth), and A-1 Carbonate (400-420 m).

G.4.4 Huron Goderich (T003563, DOMTARGODERICH.S.T.#1, 1072)

- Samples from the A-2 interval (535-545 m) are already available.
- Additional sampling targets the F Salt, E, D, C, and B Salt units.

G.4.5 Elgin (T006078, OGS82-3, 861); Norfolk (F005446, U.S. Steel No.1–J.H. Lawrence No.1, 100); and Welland (T003723, Consumers’32271, 173)

- Sampling at these three locations focuses on the A-2 and A-1 carbonate intervals.
- Core coordinates and lithologic descriptions are provided in Table F-2.

Appendix H

Chapter 4 Data Table

Table H-1. Sample list and descriptions, including the original sample label, sample type (with core license number where applicable), and associated geological and locational information (e.g., coordinates, elevation, depth, stratigraphic group/formation and unit, and dominant mineralogy). See Table H-2 (pp.179-186) for corresponding chloride and bromide contents and chlorine and bromine isotopic values.

#	Original Sample Label	Type (License #)	Longitude (X)	Latitude (Y)	Ground Elevation (m asl)	Depth (m)	Actual Depth (m asl)	Group/ Formation	Stratigraphic Unit	Dominant mineral
UMK-2	UMK 29	Core cut	-85.82685	43.44074	248.00	1479.57	-1231.57	Salina	A-1 Carb	Dolomite
UMK-3-D	UMK 30	Core cut	-85.82685	43.44074	248.00	1482.31	-1234.31	Salina	A-1 Carb	Dolomite
UMK-3-C	UMK 30	Core cut	-85.82685	43.44074	248.00	1482.31	-1234.31	Salina	A-1 Carb	Calcite
ESX-2	1118-100-38	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	307.47	-129.82	Salina	F Salt	Halite
ESX-3	1118-100-39	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	308.09	-130.44	Salina	F Salt	Halite
ESX-4	1118-100-42	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	309.04	-131.39	Salina	F Salt	Halite
ESX-5	1118-108-34	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	331.84	-154.19	Salina	F Salt	Halite
ESX-6	1118-109-33	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	335.13	-157.48	Salina	F Salt	Halite
ESX-7	1118-118-30-C	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	352.80	-175.15	Salina	F Unit	Calcite

#	Original Sample Label	Type (License #)	Longitude (X)	Latitude (Y)	Ground Elevation (m asl)	Depth (m)	Actual Depth (m asl)	Group/ Formation	Stratigraphic Unit	Dominant mineral
ESX-8	1118-118-30-S	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	352.80	-175.15	Salina	F Unit	Halite
ESX-9	1118-119-29	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	355.76	-178.11	Salina	F Unit	Dolomite/Hal
ESX-10	1118-121-27	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	360.13	-182.48	Salina	E Unit	Dolomite/Anh
ESX-11	1118-133-21	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	380.98	-203.33	Salina	D Salt	Halite
ESX-12	1118-133-22	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	381.82	-204.17	Salina	D Salt	Halite
ESX-13	1118-133-23	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	382.22	-204.57	Salina	D Salt	Halite
ESX-14	1118-133-24	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	382.48	-204.83	Salina	D Salt	Halite
ESX-15	1118-141-18	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	395.90	-218.25	Salina	C Shale	Polyhalite
ESX-16	1118-141-19	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	397.27	-219.62	Salina	C Shale	Shale/Dol
ESX-17	1118-161-17	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	434.32	-256.67	Salina	B Salt	Halite
ESX-18	1118-166-15	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	444.48	-266.83	Salina	B Salt	Halite

#	Original Sample Label	Type (License #)	Longitude (X)	Latitude (Y)	Ground Elevation (m asl)	Depth (m)	Actual Depth (m asl)	Group/ Formation	Stratigraphic Unit	Dominant mineral
ESX-19	1118-166-16	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	444.75	-267.10	Salina	B Salt	Halite
ESX-20	1118-175-11	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	459.84	-282.19	Salina	B Salt	Calcite/Shale
ESX-21	1118-175-12	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	459.96	-282.31	Salina	B Salt	Halite
ESX-22	1118-175-10	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	460.06	-282.41	Salina	B Salt	Halite
ESX-23	1118-181-7	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	470.14	-292.49	Salina	B Salt	Halite
ESX-24	1118-181-9	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	471.51	-293.86	Salina	B Salt	Halite
ESX-25	1118-192-5	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	490.83	-313.18	Salina	A-2 Salt	Halite
ESX-26	1118-192-6	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	491.83	-314.18	Salina	A-2 Salt	Halite
ESX-27	1118-193-2	OGSRL core (T011552)	-83.08473222	42.29296417	177.65	493.59	-315.94	Salina	A-2 Carb	Carbonate/Anh (no fizz at all)
GOS-1	IMP Gosfield 6-4 WD 2409.5 ft	Core cut (F000369)	-82.777	42.08375	193.24	734.42	-541.18	Salina	A-1	Carbonate
LAM-1	27 OGS Lambton 1505.55 m	Core cut (T006044)	-82.46429806	42.80176028	190.80	458.89	-268.09	Salina	F	Dolomite/Hal

#	Original Sample Label	Type (License #)	Longitude (X)	Latitude (Y)	Ground Elevation (m asl)	Depth (m)	Actual Depth (m asl)	Group/ Formation	Stratigraphic Unit	Dominant mineral
LAM-3	29 OGS Lambton 1675 ft+ 40 cm	Core cut (T006044)	-82.46429806	42.80176028	190.80	510.54	-319.74	Salina	E	Dolomite
LAM-4-H1	S2-33-537.20	Core cut (T006044)	-82.46429806	42.80176028	190.80	537.20	-346.40	Salina	C	Halite/Anh
LAM-4-H2	OGS 82-1 Lambton 537.20m	Core cut (T006044)	-82.46429806	42.80176028	190.80	537.20	-346.40	Salina	C	Polyhalite
LAM-6-D	S1/C-28-553.21; Dol/Clay-28- 443.21 with Halite vein	Core cut (T006044)	-82.46429806	42.80176028	190.80	553.21	-362.41	Salina	C	Dolomite
LAM-6-A	S1/C-28-553.21; A1-28-553.21	Core cut (T006044)	-82.46429806	42.80176028	190.80	553.21	-362.41	Salina	C	Anhydrite
LAM-8	538-175-5	OGSRL core (T001992)	-82.4465	42.7865	182.30	623.69	-441.39	Salina	B	Halite
LAM-9	538-176-7	OGSRL core (T001992)	-82.4465	42.7865	182.30	628.25	-445.95	Salina	B	Halite
LAM-10	538-177-8	OGSRL core (T001992)	-82.4465	42.7865	182.30	630.85	-448.55	Salina	B	Halite
LAM-11	538-187-2	OGSRL core (T001992)	-82.4465	42.7865	182.30	660.53	-478.23	Salina	A-2 Carb	Carbonate
KNT-1	860-178-1	OGSRL core (T006045)	-82.079895	42.3878225	180.80	291.90	-111.10	Salina	F Unit	Anhydrite/Gyp

#	Original Sample Label	Type (License #)	Longitude (X)	Latitude (Y)	Ground Elevation (m asl)	Depth (m)	Actual Depth (m asl)	Group/ Formation	Stratigraphic Unit	Dominant mineral
KNT-2	860-214-8	OGSRL core (T006045)	-82.079895	42.3878225	180.80	347.29	-166.49	Salina	B Salt	Dolomite/Hal
KNT-3	860-215-9	OGSRL core (T006045)	-82.079895	42.3878225	180.80	348.75	-167.95	Salina	B Anh	Anhydrite
KNT-4	860-241-12	OGSRL core (T006045)	-82.079895	42.3878225	180.80	388.56	-207.76	Salina	A-2 Carb	Carbonate (no fizz at all)
KNT-5	860-279-16	OGSRL core (T006045)	-82.079895	42.3878225	180.80	443.23	-262.43	Salina	A-2 Salt	Halite
KNT-6	860-279-17	OGSRL core (T006045)	-82.079895	42.3878225	180.80	443.55	-262.75	Salina	A-2 Salt	Halite
KNT-7	860-279-18	OGSRL core (T006045)	-82.079895	42.3878225	180.80	443.73	-262.93	Salina	A-2 Salt	Halite
HUR-1	1072-96-1	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	332.23	-103.63	Salina	F Salt	Halite
HUR-2	1072-96-2	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	333.85	-105.25	Salina	F Salt	Halite
HUR-3	1072-98-7	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	338.65	-110.05	Salina	F Salt	Halite
HUR-4	1072-98-8	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	338.93	-110.33	Salina	F Salt	Dolomite (little fizz)
HUR-5	1072-102-9	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	348.73	-120.13	Salina	F Salt	Polyhalite

#	Original Sample Label	Type (License #)	Longitude (X)	Latitude (Y)	Ground Elevation (m asl)	Depth (m)	Actual Depth (m asl)	Group/ Formation	Stratigraphic Unit	Dominant mineral
HUR-6	1072-107-11	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	360.59	-131.99	Salina	E Unit	Carbonate
HUR-7	1072-117-15	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	386.41	-157.81	Salina	D Salt	Halite/Anh
HUR-8	1072-118-18	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	388.07	-159.47	Salina	C	Polyhalite
HUR-9	1072-126-21	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	408.16	-179.56	Salina	C	Halite
HUR-10	1072-127-25	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	410.19	-181.59	Salina	C	Polyhalite
HUR-11	1072-155-33	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	488.92	-260.32	Salina	B Salt	Halite
HUR-12	1072-159-34	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	495.67	-267.07	Salina	B Anh	Anhydrite
HUR-13	1072-159-35	OGSRL core (T003563)	-81.68786278	43.73765333	228.60	498.44	-269.84	Salina	B Anh	Halite
GOD-1	S1-Goderich2 Halite	Rock chunk (T010686?)	-81.6275025	43.59265528	279.70	540	-260.30	Salina	A-2	Halite
GOD-2-H1	S1-Goderich1 Halite	Rock chunk (T010686?)	-81.6275025	43.59265528	279.70	540	-260.30	Salina	A-2	Halite
GOD-2-H2	n/a	Rock chunk (T010686?)	-81.6275025	43.59265528	279.70	540	-260.30	Salina	A-2	Halite

#	Original Sample Label	Type (License #)	Longitude (X)	Latitude (Y)	Ground Elevation (m asl)	Depth (m)	Actual Depth (m asl)	Group/ Formation	Stratigraphic Unit	Dominant mineral
GOD-2-H3	S3-Goderich1	Rock chunk (T010686?)	-81.6275025	43.59265528	279.70	540	-260.30	Salina	A-2	Halite
GOD-2-F	Goderich1-Fe Stain	Rock chunk (T010686?)	-81.6275025	43.59265528	279.70	540	-260.30	Salina	A-2	Halite
GOD-2-A	A1-Goderich1	Rock chunk (T010686?)	-81.6275025	43.59265528	279.70	540	-260.30	Salina	A-2	Anhydrite
IMP-1 (HUR-A)	Imp Huron 9-XI 1199ft	Core cut (F012078?)	-81.53152778	44.08602778	264.87	365.46	-100.59	Salina	A-1?	Anhydrite
IMP-2 (HUR-H)	Imp Huron 9-XI 1199ft	Core cut (F012078?)	-81.53152778	44.08602778	264.87	365.46	-100.59	Salina	A-1?	Halite
ELG-1	861-190-1	OGSRL core (T006078)	-81.16139472	42.67076833	211.40	368.14	-156.74	Salina	A-2 Carb	Dolomite (little fizz)
ELG-2	861-243-3	OGSRL core (T006078)	-81.16139472	42.67076833	211.40	449.40	-238.00	Salina	A-1 Carb	Dolomite/Anh
NOR-1	100-59-3	OGSRL core (F005446)	-80.29494444	42.74063889	214.60	246.81	-32.21	Salina	A-2 Carb	Carbonate
NOR-2	100-70-5	OGSRL core (F005446)	-80.29494444	42.74063889	214.60	279.94	-65.34	Salina	A-1 Carb	Carbonate
WLD-1	173-41-1	OGSRL core (T003723)	-79.29211444	42.9245775	176.20	154.99	21.21	Salina	A-2	Carbonate
WLD-2	173-43-4	OGSRL core (T003723)	-79.29211444	42.9245775	176.20	162.24	13.96	Salina	A-2	Carbonate

Table H-2. Chloride and bromide content, chlorine and bromine isotope values with 1 standard deviations, and detailed sample descriptions (e.g., lithologic notes, reaction to acids). See Table H-1 (pp.172-178) for corresponding geological and locational information. BAL: Below analytical level. *Cl and Br contents are initially obtained in mg/L and subsequently converted to mg/g by normalizing to the measured mass of each solid sample and the volume of ultrapure water added for dissolution/leaching.

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
UMK-2	Dark shaley laminations with no dissolution features	-1.81	±0.09	-0.14	±0.02	0.374	0.0280
UMK-3-D	Dark shaley dolomite with dissolution vugs	0.45	±0.02	-1.04	±0.15	<i>not available</i>	<i>not available</i>
UMK-3-C	Massive carbonate at the bottom of shaley lamination of dolomite; readily breakable; likely hydrothermally deposited	0.63	±0.25	-1.32	±0.06	0.326	0.0652
ESX-2	Halite replaced gypsum, another ~15 cm halite layer that's separate by carbonate(?) layer from the lower salt interval	1.33	±0.08	-0.28	±0.05	970	0.0224
ESX-3	Halite; UVF fluorescent; skeletal clear salt (probably squeezed up from the lower thick salt)	0.32	±0.13	<i>not available</i>		728	0.0466
ESX-4	Halite; top of thick (>1 m) halite interval, coarsely recrystallized, with thin, muddy anhydrite layer	0.27	±0.05	0.52	±0.12	772	0.8000
ESX-5	Halite; still the part of the thickest halite interval, recrystallized halite between anhydrite layers	0.29	±0.10	<i>not available</i>		735	0.0656
ESX-6	Halite; coarsely crystalline rock salt with dispersed organic matter, cross-bedded, anhydrite interlayered	0.25	±0.15	<i>not available</i>		311	0.0569

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
ESX-7	halite & shaley carbonate mudstone with nodular anhydrite; fibrous reddish-brown salt filled fractures of laminated shaley carb mudstone with nodular anhydrite	-0.24	±0.14	<i>not available</i>		223	0.0422
ESX-8	halite & shaley carbonate mudstone with nodular anhydrite; fibrous reddish-brown salt filled fractures of laminated shaley carb mudstone with nodular anhydrite	0.07	±0.13	0.65	±0.05	686	0.3271
ESX-9	porous dolostone with brighter skeletal calcite lamina, halite filling in the moldic porosity	0.16	±0.09	<i>not available</i>		87.2	0.0149
ESX-10	Dolomite and anhydrite lenses; muddy laminations with dissolution vugs	-0.20	±0.11	<i>BAL</i>		37.7	0.0067
ESX-11	halite; with undulatory anhydrite lamina indicating absence of dissolution features, with dispersed organic matter	0.39	±0.12	<i>not available</i>		602	0.0557
ESX-12	Halite. Thick interval of clear salt, over 3 meters (haven't checked the total thickness)	0.23	±0.11	<i>not available</i>		651	0.0664
ESX-13	halite; has primary features (upside down chevron, right angle) indicating absence of dissolution event	0.70	±0.10	0.85	±0.08	654	0.0490
ESX-14	Halite with dispersed organic matter, within the thick interval, with anhydrite intervened - probably recrystallized halite	0.41	±0.09	<i>not available</i>		703	0.0588

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
ESX-15	Halite + polyhalite; ~1 m-thick and wide reddish brown polyhalite, cross-bedded (deeper-water slope deposits), interval within thicker shale unit, could be an early replacement of anhydrite by K- and Mg-rich brines.	-0.14	±0.14	0.51	±0.07	687	0.0556
ESX-16	dolomitic mudstone with anhydrite nodules (no fizz); seems like the host rock	0.04	±0.08	<i>not available</i>		98	0.0613
ESX-17	halite; with dispersed organic matter, top of the ~25 m thick salt interval	0.05	±0.17	1.76	±0.18	550	0.0347
ESX-18	halite; absence of dissolution features, with organic matter, with ~0.6 cm anhydrite layer	0.01	±0.11	<i>not available</i>		584	0.0653
ESX-19	halite; bedded, absence of dissolution events, with ~1 cm anhydrite layer	0.11	±0.06	<i>not available</i>		311	0.0445
ESX-20	fracture-cutting laminated shaley carbonate mudstone with nodular anhydrite	-0.26	±0.10	0.51	±0.08	29.7	0.0667
ESX-21	(same as #11) fracture-filling fibrous reddish brown polyhalite cement	0.56	±0.13	0.57	±0.04	709	0.04
ESX-22	halite; transition from pressurized salt to clear bedded salt layer	0.13	±0.04	1.01	±0.06	576	0.1948
ESX-23	halite; crystal halite with thin undulating anhydrite lamina, probably the main body of salt, with organic matter (brown layer's there)	0.68	±0.14	<i>not available</i>		630	0.0651

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
ESX-24	halite in mudstone lamina with nodular anhydrite, with a bit of organic matter	0.42	±0.10	<i>not available</i>		418	0.0413
ESX-25	Halite. Clear, planar cross-bedded (known to be generated by migration of large-scale, straight crest bedforms)	0.75	±0.15	<i>not available</i>		723	0.0709
ESX-26	Halite. Clear, darker with dispersed organic and mud laminae intervened, planar cross-bedded (no dissolution)	0.74	±0.15	<i>not available</i>		643	0.0544
ESX-27	carbonate; relatively bright suggesting less organic matter (dark inside when crushed), with muddy anhydrite laminations, no fizz at all.	0.46	±0.08	<i>not available</i>		1.12	0.0027
GOS-1	Dark, with no visible fractures or fillings	-0.78	±0.02	-1.44	±0.08	0.100	0.0045
LAM-1	Laminated dolomite + "dotted" halite precipitated in fenestral porosity; 82-1 represents inter pinnacle reef lithofacies zone	-1.08	±0.03	-1.11	±0.07	0.377	0.0660
LAM-3	Similar to LAM-2, but with lower (visual) content of anhydrite. Brittle without no visible fillings or fractures	<i>not available</i>	<i>not enough left</i>	-0.98	±0.15	1.14	47.5
LAM-4-H1	Top massive H (Orange halite + polyhalite within anhydrite body)	0.17	±0.1	<i>not available</i>	<i>not enough left</i>	347	38.6

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
LAM-4-H2	vertical H vein (orange-colored) in carbonate body, between two anhydrite layers; LAM-4-H2 generated more HBr bubbles (more actively) than LAM-4-H1 did.	0.05	±0.01	0.45	±0.02	434	8
LAM-6-D	Illite, dolomite; intermittent thin orange halite filling	-0.13	±0.07	-0.46	±0.07	82.9	0.101
LAM-6-A	anhydrite (chicken wire texture) w/ a bit of plunging salt	-0.40	±0.16	<i>not available</i>	<i>not enough left</i>	22.5	0.0310
LAM-8	halite w/ intermittent reddish-brown anhydrite	-0.08	±0.09	-0.77	±0.11	355	19.038
LAM-9	halite; a bit of dissolution features b/w anhydrite. layers	0.33	±0.15	-0.09	±0.10	408	11.887
LAM-10	halite; recrystallized b/w cal. layers	-0.18	±0.11	1.22	±0.11	415	4.9561
LAM-11	dolomite; dark, microbially laminated dolomites with intraclastic horizons of soft sediments with no disruption	<i>not available</i>		<i>not available</i>		1.43	4.0714
KNT-1	anhydrite/gypsum, 17 mm thick layer between muddy laminations (if it's softer than fingernail, it's gypsum. If not, prob anhydrite.)	<i>BAL</i>		<i>not available</i>		1.355	0.0014
KNT-2	porous laminated mudstone with anhydrite laminae, "dotted" halite filling in the moldic/fenestral porosity	<i>BAL</i>	<i>low Cl</i>	<i>BAL</i>	<i>low Br</i>	0.467	0.00444
KNT-3	anhydrite, chicken-wire texture	<i>BAL</i>	<i>low Cl</i>	<i>BAL</i>	<i>low Br</i>	0.158	0.00951

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
KNT-4	carbonate, dark, brittle, no other feature	1.04	±0.12	<i>not available</i>	<i>not enough left</i>	2.26	0.015
KNT-5	halite; clear bedded halite	-0.53	±0.11	-0.26	±0.06	435	7
KNT-6	halite; bedded halite with dispersed organic matter	0.06	±0.18	0.87	±0.09	658	0.028
KNT-7	3-6 mm thick dark carbonate interlayered; b/w carbonate layers	0.66	±0.14	-0.08	±0.10	386	10
HUR-1	halite; end of the thick halite layer, with dispersed organic matter	0.31	±0.10	0.75	±0.10	203	0.1274
HUR-2	halite, middle of the halite layer, clear, little if any organic	0.58	±0.14	0.57	±0.07	399	0.1639
HUR-3	halite, b/w thin anhydrite layers, beginning of the clear halite layer	-0.06	±0.12	0.64	±0.06	408	0.1050
HUR-4	muddy dolomite; features that had been filled with halite but dissolved.	-0.39	±0.17	1.40	±0.10	121	0.048
HUR-5	halite; clear polyhalite with coarse halite; orange plunge layer there	-0.87	±0.04	0.55	±0.05	404	0.1179
HUR-6	carbonate; halite filling fenestral porosity	-0.13	±0.13	<i>not available</i>		103	0.018
HUR-7	halite+anh, frequent intermittent anh layers	-0.48	±0.15	0.59	±0.13	141	0.545
HUR-8	halite, orange plunge layer/vein (#21 might be the source of this one's salt content)	-0.45	±0.14	0.77	±0.12	152	0.221

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
HUR-9	halite, clear, transparent (may have worked as a salt source for the above plunging halite/polyhalite)	0.19	±0.12	0.38	±0.09	425	0.0971
HUR-10	fibrous polyhalite seam; muggy and blurry (may be due to Mg)	0.47	±0.15	1.07	±0.08	381	0.100
HUR-11	halite, clear, a little translucent	-0.82	±0.15	0.63	±0.09	438	0.223
HUR-12	transition from nodular anhydrite to muddy dolostone with fracture filling halite	0.27	±0.12	BAL		157	0.01469
HUR-13	halite containing no organic matter; with minor calcite/anhydrite	0.17	±0.14	0.73	±0.05	852	0.097
GOD-1	clear cubic halite, with a lot of fluid inclusion	0.13	±0.06	0.27	±0.11	394	0.075
GOD-2-H1	Clear halite; top summit	-0.13	±0.01	-0.23	±0.07	433	0.200
GOD-2-H2	Clear halite; upper, middle	-0.15	±0.08	-0.02	±0.10	418	1.025
GOD-2-H3	Halite; upper, close to the anhydrite layer; light brown stain	-0.51	±0.08	0.07	±0.06	348	43
GOD-2-F	Fe-stained	-0.50	±0.09	-1.10	±0.09	336	64
GOD-2-A	Brittle; mostly anhydrite with some clear gypsum and halite as fillers/fillings in between; some are remaining undissolved after stirring on a hot plate	0.34	±0.14	-1.78	±0.22	162	0.0396

#	Sample Description	$\delta^{37}\text{Cl}$	Stdev/ notes	$\delta^{81}\text{Br}$	Stdev/ notes	Cl (mg/g)*	Br (mg/g)*
IMP-1 (HUR-A)	Anhydrite	0.38	±0.14	BAL	low Br	8.10	0.0800
IMP-2 (HUR-H)	clear halite or calcite (similar to UMK-3-C)	-0.05	±0.17	BAL	low Br	144	0.00233
ELG-1	carbonate, dark, laminated	-0.42	±0.09	BAL	low Br	1.68	0.0964
ELG-2	anhydrite/dolomite, dark, no other feature	0.51	±0.13	BAL	low Br	3.390	0.00855
NOR-1	carbonate, dark, no other feature	0.42	±0.15	BAL	low Br	1.511	0.000959
NOR-2	carbonate, relatively bright	not available		not available	low Br	0.365	0.000973
WLD-1	Carbonate, dark (less dark than WLD-2)	not available		not available	low Br	0.363	0.0223
WLD-2	Carbonate, dark	0.44	±0.12	not available	low Br	0.477	0.00164