Magmatic degassing as the primary source of salt in Archaean oceans

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ABSTRACT

The salinification of Earth's early oceans impacted both the climate and the evolution of life. However, available halogen data of Archaean seawater samples are at apparent odds with a conventionally assumed mantle origin of sea salt, highlighting a critical lack of mechanistic understanding of how the Archaean oceans became salty. Here, we present new triple halogen (Cl-Br-I) data from high temperature (~750–840 °C) fluid inclusions interpreted to have formed during late-stage crystallisation of a gabbroic intrusion in Iceland. Our data show that the magmatic degassing fractionates the halogens and generates fluids with high Br/Cl and I/Cl that match with Archaean seawater. These observations suggest that seawater salinity in the Archaean oceans was primarily regulated via fluids exsolved from cooling intrusions during genesis of early crust, and that the mantle had a modern-like halogen composition by 3.5 Ga. Our findings highlight the strong connection between the chemistry of the mantle, magmatic fluids and the oceans, with implications for understanding the chemical environments that guided the evolution of early marine organisms.

INTRODUCTION

Considerable effort has been dedicated to deciphering the chemical makeup of Archaean oceans (*e.g.*, Walker, 1983). The origin and abundance of sea salt are of particular interest due to its impact on the climate (Olson *et al.*, 2022), the solubility of oxygen and hence early life (Knauth, 1998), and its close link to the evolution of Earth's mantle and crust (Schilling *et al.*, 1978; Sharp and Draper, 2013). In the modern oceans, the dominant influx of solutes stems from riverine transport of continental weathering products, whereas Archaean solute fluxes were sourced mainly by magmatism and magmatic-hydrothermal activity (*e.g.*, Kamber and Webb, 2001). Accordingly, ocean salinity in the Archaean and Paleoproterozoic has been assumed to be mantle-derived (Schilling *et al.*, 1978; Marty *et al.*, 2018). However, available samples of Archaean seawater show higher Br/Cl and I/Cl relative to both the modern and the primitive mantle, challenging this explanation (Fig. 1). The mismatch could be explained by a shift of mantle halogen composition towards lower Br/Cl and I/Cl over time, fractionation of mantle-derived halogens during magmatic processes, or a hitherto unknown Br-I sink in Archaean oceans. Testing of these hypotheses is challenging because the halogen composition of the Archaean mantle is difficult to constrain (Kendrick, 2024) and the extent of halogen fractionation between melts and magmatic fluids—which distribute mantle halogens to the oceans at submarine hydrothermal systems—remains uncertain (Kendrick *et al.*, 2018).

In addition, magmatic temperature fluids (> 600 °C) have never been sampled *in situ* and fluid inclusion (FI) studies targeting fossil magmatic-hydrothermal high-T fluids have largely focussed on felsic, continental and/or convergent margin settings (*e.g.*, Audétat and Zhang, 2019). Hence, compositional data of magmatic fluids from mafic-dominated crustal environments that characterise the oceanic crust are limited, with no combined single-FI Cl-Br-I analyses available. This hampers our ability to estimate mantle-derived solute fluxes into the oceans, especially in the Archaean, when magmatism was dominantly mafic and submarine (Cawood and Hawkesworth, 2019).

To address this knowledge gap, we report the first triple halogen (Cl-Br-I) data for individual magmatic-temperature FIs in oceanic mafic-dominated crust. The data were collected from the fossil Vesturhorn volcanic complex in East Iceland, which offers an opportunity to investigate the effect of the magmatic fluid formation process on halogens at a modern setting resembling Archaean crust.

SAMPLES AND RESULTS

Here, we report halogen (Cl-Br-I) and trace element laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) data from quartz-hosted FIs. Full methodological details and datasets are provided in the Supplementary Information. The FIs occur in a miarolitic cavity within an exposed gabbroic intrusion belonging to the 3.7–4.3 Ma Vesturhorn volcanic complex (Martin *et al.*, 2011) in East Iceland. Iceland is arguably the best-available modern analogue of Early Earth crustal formation processes due to its high magma production rates and a thickened, oceanic plateau-type crust formed by a hot mantle plume (Reimink *et al.*, 2014). The simple geological context of Vesturhorn minimises fluid contributions from secondary, post-magmatic events, or external fluid sources (*e.g.*, seawater or sediments) which complicate interpretation of FI data at continental, submarine, or ancient settings.

The investigated miarolitic cavities occur within an aplitic vein that grades into a coarse-grained gabbroic host rock (Fig. S-1a). The cavities host two generations of quartz that are distinguished by their optical and cathodoluminescence (CL) colours, inclusion assemblages and Ti contents. The earliest-formed quartz (Phase 1) is represented by optically clear quartz cores with purple-to-violet CL colours, and high Ti contents (150±25 ppm; 1σ). The base of the Phase 1 quartz is intergrown with albite and K-feldspar within the aplite vein, forming a texture similar to micrographic granitoids (Fig. S-1d). Phase 1 quartz is overgrown by prismatic crystals of later-formed green quartz with actinolite inclusions (Phase 2) that is CL inactive and Ti-poor (1-2 ppm; Figs. 1a, S-1b,c,d). In this work, we focus on the most common FI assemblage consisting of co-occurring vapour-rich (70–90 % vapour, 10–30 % liquid at 20 °C) and brine FIs (liquid-vapour-multiple solid; Figs. 1c, S-1e,d,f). This assemblage forms inclusion trails that exclusively occur in the interior, actinolite-free Phase 1 quartz and terminate prior to the Phase 2 quartz overgrowth zones (Fig. S-1b) and are hence interpreted to be coeval with Phase 1 quartz. High homogenisation temperatures of the fluids (> 600° C) and high Ti concentrations of the host quartz suggests that the fluids were trapped at temperatures of 750–840 °C (Figs. 1a, S-2), compatible with a magmatic or near-magmatic formation environment. We interpret the FIs to represent magmatic fluids formed during late-stage crystallisation of the host gabbro from highly fractionated felsic residual melts, trapped during or following phase separation into a NaCl-poor vapour and a NaCl-rich brine, as is commonly observed in felsic plutons (Audétat and Zhang 2019).

The brine inclusions contain a (Na,K,Fe)Cl-rich aqueous fluid with a salinity of approximately 50 wt.% $NaCl_{eq}$ (Fig. S-3). Compared to most magmatic fluids associated with silicic plutons, the brines have high K-Fe contents relative to Na (Fig. S-3a) and have distinctly high Fe/Mn and Ba/Mn (Fig. S-4a,b). The major cation composition of the fluids was likely buffered by the host rock due to rapid fluid-rock equilibration at low water/rock ratios and high temperatures (Dolejš and Wagner, 2008). The brines are rich in Cu-Zn-Mo-Ag, similar to high-temperature FIs observed in deep parts of the active Reykjanes hydrothermal system in Iceland (Bali *et al.*, 2020) and continental granitic systems (Fig. S-3b).

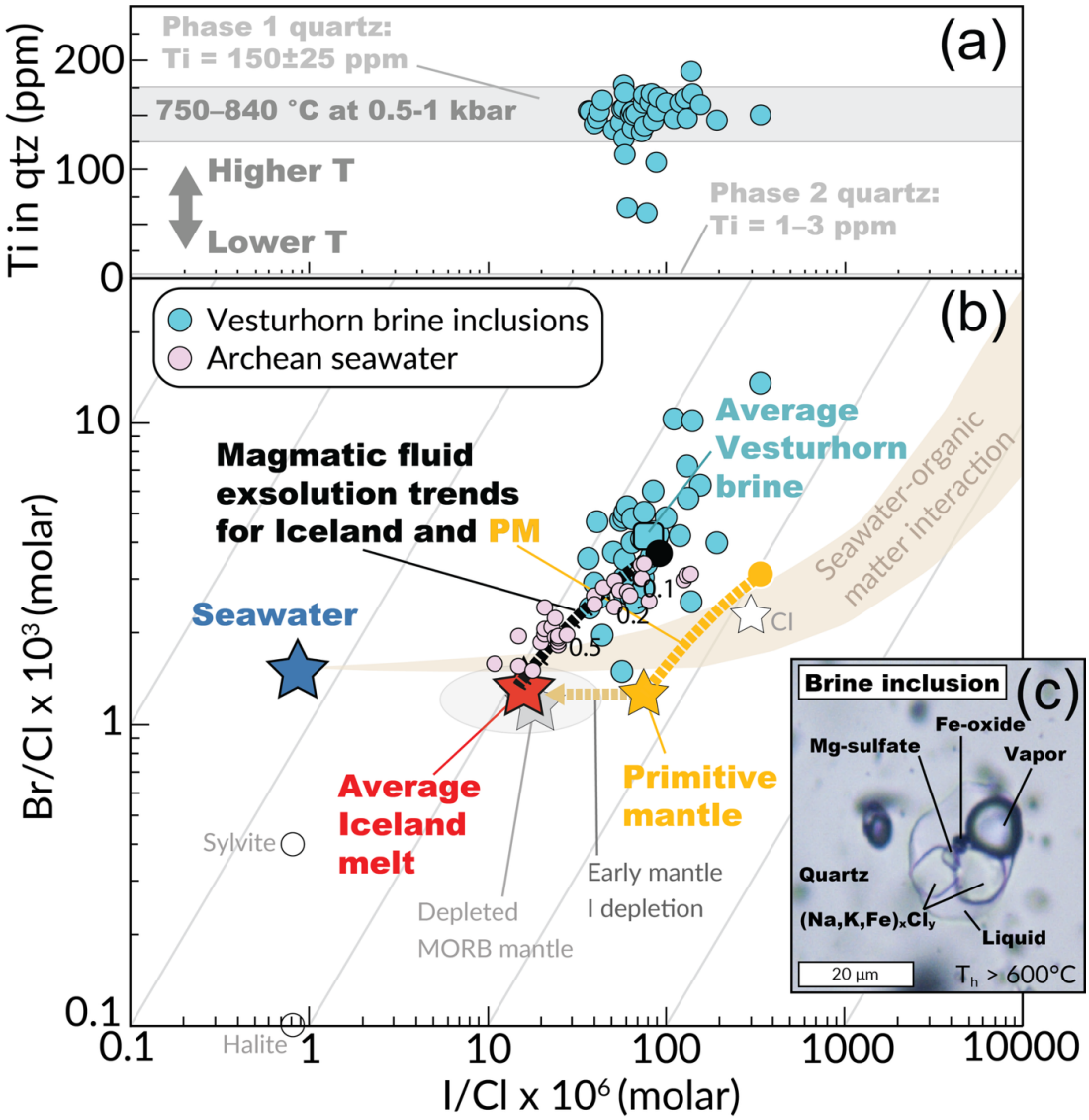

Figure 1 Halogen systematics of magmatic brines. **(a)** Brine inclusion host quartz Ti contents. Phase 1 quartz has high Ti contents of 150±25 ppm (1σ), indicating formation temperatures of 750–840 °C (Fig. S-2). Low Ti contents (<3 ppm) in Phase 2 quartz indicate a lower-T hydrothermal origin. **(b)** The halogen compositions of Vesturhorn FIs are distinct from Icelandic melts (Waters, 2021) but overlap with Archaean seawater (Channer *et al.*, 1997; Burgess *et al.*, 2020). Fluid exsolution trends are modelled assuming closed-system equilibrium fluid-melt partitioning (Tables S-3, S-4) from melt compositions representing an Iceland average basalt and the primitive mantle. The light brown field envelopes modern marine pore water compositions reflecting binary mixing of seawater and high-I/Cl organic matter (Kendrick *et al.*, 2018). **(c)** A typical Vesturhorn brine inclusion with multiple daughter phases. References for the plotted reservoir compositions are listed in the Supplementary Information.

DISCUSSION

Fractionation of halogens during magma degassing

Our new measurements provide the first empirical Cl-Br-I estimates for high-T magmatic fluids in an oceanic crustal environment and offer an opportunity to test melt-fluid partitioning behaviour of halogens in natural samples. Experimental studies show that Cl, Br and I are strongly hydrophilic and partition from a melt into an exsolved aqueous magmatic fluid phase, with $D_{fluid-melt}$ increasing from Cl to Br to I (Miranda *et al.*, 2025). Hence, fluid exsolution from intrusions is expected to fractionate the halogens, generating magmatic fluids with high Br/Cl, I/Cl and I/Br relative to the source melt. The Cl-Br-I ratios measured in the brine FIs are assumed to closely represent that of the bulk magmatic fluid, since halogens strongly partition

into the brine phase during vapour-liquid separation, and because Cl-Br-I are not thought to be significantly fractionated during during reaction with basaltic host rocks (Kendrick, 2018). Vapour-liquid separation of (Na,K)Cl-rich fluids can result in minor fractionation of Br/Cl, but produces brines with lower Br/Cl relative to the vapour (Seo and Zajacz, 2016), and hence does not explain the high Br/Cl brine values observed here.

We modelled the I/Cl and Br/Cl composition of magmatic fluids exsolving from Icelandic magmas, using a range of $D_{fluid-melt}$ calculated after Miranda *et al.* (2025; Figs. 1b, S-8; Tables S-3, S-4). Magmatic fluids develop higher Br/Cl (up to ~4×10^{-3}) and I/Cl (up to ~90 x 10^{-6}) relative to an average Icelandic undegassed melt composition (Br/Cl = 1.4×10^{3}, I/Cl = 15×10^{-6}; Waters, 2021). The magmatic fluid exsolution trend occupies an almost unpopulated field among published halogen data from geological environments (Fig. 1b). The Vesturhorn brines overlap with this trend, with average molar Br/Cl and I/Cl of 4.1×10^{-3} and 73×10^{-6}, respectively, equivalent to a loss of c. 10% of initial Cl from the melt. Conversely, exsolution of high Br/Cl and I/Cl fluids is expected to generate a complementary residual melt with lower Br/Cl and I/Cl (Table S-3). However, the effect on the residual melt is relatively minor at small degrees of halogen loss, and the modelled residual melt overlaps with Icelandic glass data at Cl loss of less than about 20% (Fig. S-10).

The high Br/Cl and I/Cl signature of the Vesturhorn fluids, together with their high formation temperatures (> 750°C), strongly support that the FIs trap a primary magmatic fluid prior to mixing with external fluids. Because mid-ocean ridge basalts and Icelandic melts have a near-identical halogen composition (Fig. 1b), the Vesturhorn FIs provide an accurate proxy of the halogen signature of magmatic fluids produced by modern ocean floor magmatism. Of particular note is that the elevated I/Cl of the Vesturhorn brines contrast sharply with the low I/Cl of modern seawater (0.9×10^{-6}), precluding seawater contribution, whereas their high Br/Cl is distinct from the seawater-organic matter mixing trend (Figs. 1b, S-10). Hence, Cl-Br-I systematics offer a uniquely suited geochemical tool for distinguishing between magmatic, marine organic matter and seawater-derived fluid sources in geological environments in general.

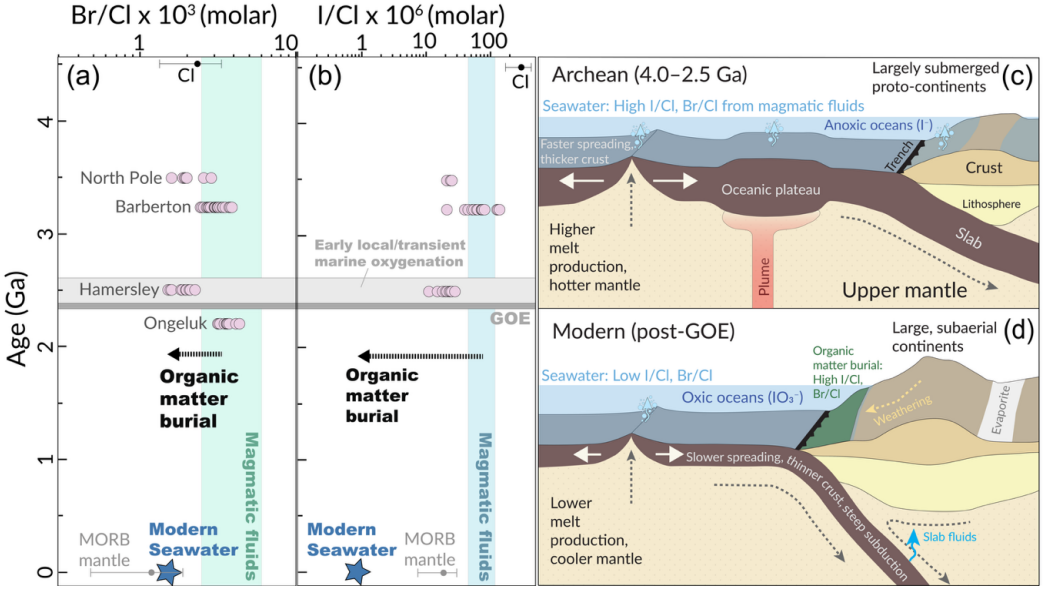

Figure 2 The **(a)** Br/Cl and **(b)** I/Cl evolution of Earth's oceans. The two cartoons illustrate the regime shift from **(c)** an Archaean anoxic ocean world, where magmatism is the primary halogen supplier to the oceans, to **(d)** the modern state, where the oceans' halogen budget is regulated by continental weathering, subduction and organic matter burial. The grey fields indicate the 2.4 Ga Great Oxygenation Event and possible earlier transient/localized oxygenation events (Liang *et al.*, 2025). References for the background data are listed in the Supplementary Information.

Halogen composition of Earth's early oceans and mantle

A key observation from our new halogen data is that the Vesturhorn Br/Cl and I/Cl signatures overlap with the halogen signature of Archaean seawater (Fig. 1B). This similarity provides independent evidence that the origin of salt in Archaean seas was magmatic and sourced from fluids formed during submarine magmatism, for reasons outlined below. The composition of Archaean seawater is known indirectly from compositions of sediments that precipitated from seawater (Veizer *et al.*, 1982; Kamber and Webb, 2001) and from FIs thought to preserve Archaean seawater or seawater-origin hydrothermal fluids (Channer *et al.*, 1997; Burgess *et al.*, 2020). Ocean salinity appears to have been close to its modern value of 3.5 wt.% NaCl since at least 3.0 Ga (Marty *et al.*, 2018). However, Archaean seawater (or hydrothermal fluids of seawater-origin) had higher Br/Cl ($1.5–4.3 \times 10^{-3}$) and I/Cl ($21–140 \times 10^{-6}$) relative to modern seawater (Br/Cl $=1.5 \times 10^{-3}$; I/Cl $= 0.87 \times 10^{-6}$; Figs. 1b, 2; Burgess *et al.*, 2020). This change in halogen composition reflects a wider biogeochemical regime shift in the Earth's oceans following the Great Oxygenation Event (GOE) at ~2.4 Ga, marking the large-scale oxygenation of the oceans and diversification of marine organisms (Holland, 2002), with major consequences for oceanic halogen budgets (Fig. 2). Post-GOE oceans are depleted in I and Br relative to Archaean seawater, as marine algae fixate the oxidised iodine species, IO_3^-, and to a lesser degree, Br, in seawater (Hardisty *et al.*, 2014). The lack of biological halogen sinks in pre-GOE oceans (Fusswinkel *et al.*, 2022) means that the observed Archaean seawater signatures reflect an inorganic high Br/Cl-I/Cl halogen source.

Continental weathering was limited during the Archaean, as the continental masses were submerged by oceans that covered up to 98% of global surface area (Flament *et al.*, 2008). Accordingly, volcanism forming the mafic oceanic crust, oceanic plateaus, as well as the proto-cratons occurred below sea level (Cawood and Hawkesworth, 2019). The low continental freeboard combined with higher rates of magmatism (Herzberg *et al.*, 2010) caused a ~50 times higher magmatic-hydrothermal/continental weathering solute input ratio into the oceans relative to the present (Fig. 2c; Kamber and Webb, 2001). Similarly, the halogen budget in Archaean oceans has been assumed to be mantle-buffered (Schilling *et al.*, 1978; Burgess *et al.*, 2020), although the Br/Cl and I/Cl of Archaean seawater do not match with either the modern upper mantle or estimated primitive mantle compositions (Fig. 1b).

Our data demonstrate that this mismatch could be caused by fractionation of the halogens during exsolution of magmatic fluids from a mantle-derived source melt. All published Archaean seawater halogen compositions fall close to the modelled magmatic fluid exsolution trend of Icelandic magmas, representative of the modern mantle, whereas no data overlap with the primitive mantle fluid exsolution trend (Fig. 1b). We propose that this overlap reflects an Archaean mantle that had a similar halogen composition to the modern, *i.e.* depleted in I relative to Cl compared to the primitive mantle. Our findings are compatible with the halogen mantle evolution model of Kendrick *et al.* (2020) suggesting that Earth's mantle may have reached modern mantle-like I/Cl values by 3.5 Ga—the age of the oldest Archaean seawater samples (Fig. 2)—due to early subduction of serpentinised lithosphere. Alternatively, mantle with a subchondritic I/Cl could be produced by preferential partitioning of I to the core during core-mantle differentiation (Jackson *et al.*, 2018) or collisional erosion of a Hadean halogen-rich surface reservoir during Earth's accretion (Sharp and Draper, 2013).

Regardless of the mechanism that caused early I depletion of the mantle, our observations suggest that the halogen input to the Archaean seas was dominantly magmatic and channelled via magmatic fluids emanating from cooling intrusions in the Archaean submarine crust (Fig. 2c). Magmatic fluid fluxes from intrusions to the oceans could be substantial, as intrusive magmatism contributes ~4–10 times more mass to the oceanic crust than extrusive volcanism (White *et al.*, 2006). A simple mass balance model shows that the flux of magmatic fluids to the Archaean oceans may have been sufficient to salinate the oceans to 0.5–1x modern seawater salinity within < 1.5 Ga (Fig. S-9). Notably, magmatic fluids with similar halogen signatures

may have formed both in Archaean mafic-dominated submarine crust as well as in submerged plateau-type proto-cratons.

This work demonstrates that the halogen composition of Earth's early oceans provide independent constraints on the timing and mechanisms of the contemporaneous evolution of Earth's mantle and crust. This insight should spark efforts to improve our currently patchy temporal resolution of Archaean and Proterozoic ocean halogen compositions (Fig. 2a,b). The implied high volume of magmatic fluid inputs to Archaean oceans has implications for understanding the chemical environments near Archaean submarine hydrothermal vents. Our data show that aqueous environments with high K/Na and high Zn and Mn concentrations—essential nutrients for protocells—are not exclusive to inland geothermal systems (Mulkidjanian *et al.*, 2012) but could also form near submarine vents with high magmatic fluid influx.

CONCLUSIONS

This study provides a new baseline composition for magmatic fluids produced during the genesis of oceanic crust. The results have implications for the chemistry of hydrothermal vents on the Archaean seafloor, where magmatic fluid fluxes may have been higher than in modern systems. The data confirm experimental evidence that Cl-Br-I fractionate during fluid exsolution from a silicate melt, resulting in a characteristic high Br/Cl and I/Cl magmatic fluid halogen signature that overlaps with Archaean seawater. Together, these observations reconcile the mismatch between mantle and seawater halogen signatures, providing compelling evidence that the salinity in the Archaean oceans had a dominantly magmatic origin and was sourced from a mantle that had a similar halogen composition to the modern by 3.5 Ga.

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