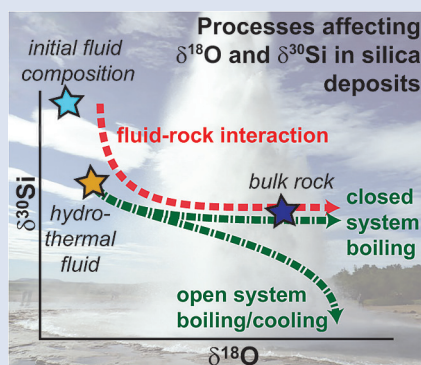# Silicon and oxygen isotopes unravel quartz formation processes in the Icelandic crust

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Abstract

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Quartz formation processes in the Icelandic crust were assessed using coupled $\delta^{18}O$ and $\delta^{30}Si$ systematics of silica deposits formed over a wide temperature range (<150 to >550 °C). Magmatic quartz reveals $\delta^{18}O$ (-5.6 to +6.6 ‰) and $\delta^{30}Si$ (-0.4 ± 0.2 ‰) values representative of mantle- and crustally-derived melts in Iceland. Hydrothermal quartz and silica polymorphs display a larger range of $\delta^{18}O$ (-9.3 to +30.1 ‰) and $\delta^{30}Si$ (-4.6 to +0.7 ‰) values. Isotope modelling reveals that such large variations are consistent with variable water sources and equilibrium isotope fractionation between fluids and quartz associated with secondary processes occurring in the crust, including fluid-rock interaction, boiling and cooling. In context of published $\delta^{18}O$ and $\delta^{30}Si$ data on hydrothermal silica deposits, we demonstrate that large ranges in $\delta^{30}Si$ values coupled to insignificant $\delta^{18}O$ variations may result from silica precipitation in a hydrothermal fluid conduit associated with near-surface cooling. While equilibrium isotope fractionation between fluids and quartz seems to prevail at high temperatures, kinetic fractionation likely influences isotope systematics at low temperatures.

Introduction

Quartz is among the most abundant minerals in the continental crust and a major constituent of many plutonic, sedimentary and metamorphic rocks (*e.g.,* Götze, 2009). Under magmatic conditions, quartz may crystallise at ~700 °C and numerous metamorphic reactions involve the consumption and production of quartz. Because of its common association with hydrothermal and ore deposits, the origin of quartz and its paragenesis continues to be a subject of considerable discussion.

Over the past decades, oxygen isotopes have been applied as a tracer for the source(s) of crustal fluids (*e.g.,* Bowman *et al.,* 1994). However, Si isotopes have only gained interest recently due to improved analytical techniques. Silicon isotopes of quartz and other silica polymorphs range from -5 to +5 ‰ and have been used for reconstruction of past geological environments (Fig. 1). $\delta^{30}Si$ systematics in Precambrian chert deposits have been used to constrain environmental conditions during their formation (*e.g.,* Robert and Chaussidon, 2006; Marin-Carbonne *et al.,* 2014). However, silicon isotope data from more recent quartz deposits formed under variable temperatures and fluid compositions, are still limited (Geilert *et al.,* 2015). Such data are critical to constrain the processes (*e.g.,* fluid-rock

interaction) that lead to the formation of secondary quartz in the Earth's crust, and can contribute to better understand the origin and formation conditions of ancient silica deposits.

Often adopted as a potential analogue for Earth's earliest continental crust (Reimink *et al.,* 2014), the Icelandic crust represents a continental-type crust with characteristics typical of the oceanic crust. Iceland's crustal lithology is dominated by basalts with silicic volcanics and volcaniclastic sediments also being common (Sæmundsson, 1979). Hydrothermal activity occurs over a wide temperature range (<10 to >400 °C; Arnórsson *et al.,* 2008), resulting in low-grade metamorphism within the crust (Kristmannsdóttir, 1979). Quartz is a common secondary mineral in hydrothermal systems whereas primary quartz is not common within the dominantly basaltic crust (Browne, 1978). This makes Iceland an ideal locality for studying secondary quartz formation processes taking place in the crust.

To assess quartz formation processes over a wide temperature range (<150 to >550 °C), $\delta^{18}O$ and $\delta^{30}Si$ isotopic and chemical composition in quartz and silica polymorphs from magmatic and hydrothermal settings in Iceland were studied using secondary ion mass spectrometry (SIMS) and electron microprobe analysis (EMPA). Applying isotope modelling approaches (Stefánsson *et al.,* 2017), fluid sources, chemical

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reactions and associated isotope fractionations were quantified for various processes occurring in the curst, including fluid-rock interaction, fluid phase separation (boiling) and cooling. Implications of this dataset and the isotope modelling were further extended to explain the origin of ancient hydrothermal silica deposits.
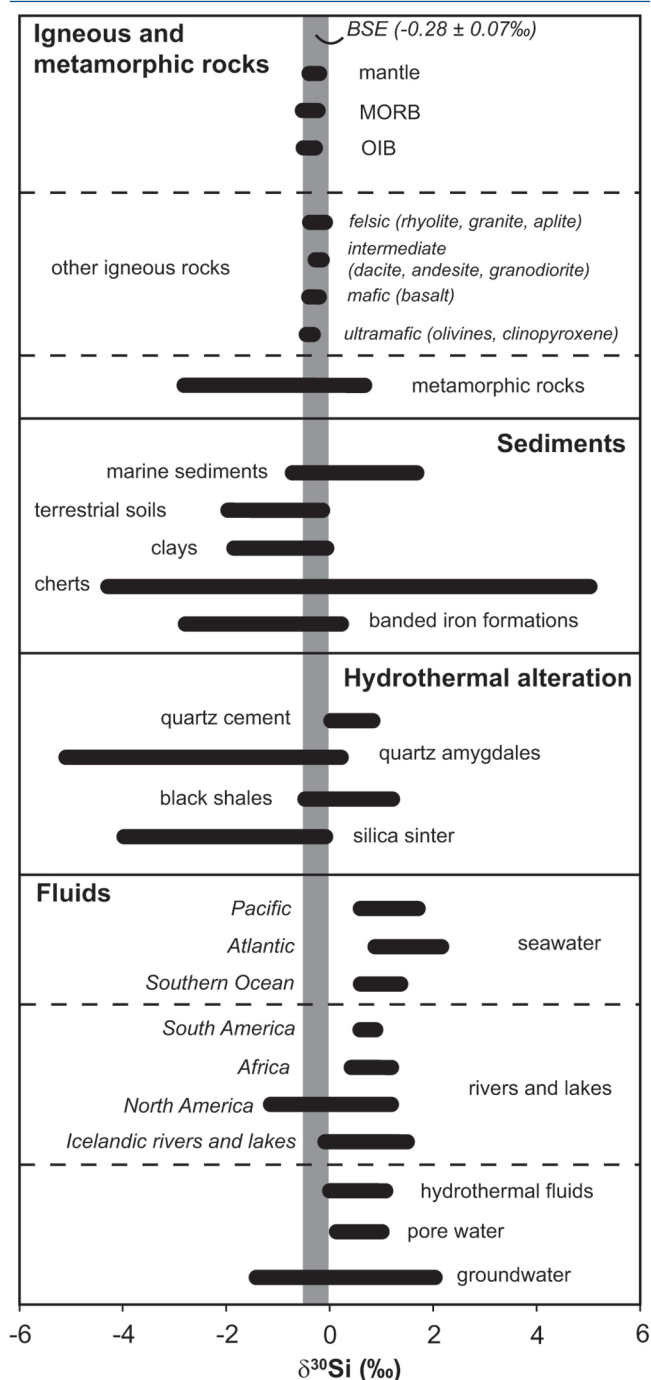

Figure 1 Compilation of $\delta^{30}Si$ values for different rock types and fluids. Data taken from Douthitt (1982), De La Rocha *et al.* (2000), André *et al.* (2006), Robert and Chaussidon (2006), Georg *et al.* (2007a,b, 2009), Fitoussi *et al.* (2009), Steinhoefel, *et al.* (2009, 2010), Savage *et al.* (2010, 2011, 2012), Van den Boorn *et al.* (2010), Abraham *et al.* (2011), Armytage *et al.* (2011), Heck *et al.* (2011), Chakrabarti *et al.* (2012), Delvigne *et al.* (2012), Marin-Carbonne *et al.* (2012, 2014), Opfergelt *et al.* (2012), von Strandmann *et al.* (2012), Fan *et al.* (2013), Zambardi *et al.* (2013), Geilert *et al.* (2015), Stefurak *et al.* (2015), Brengman *et al.* (2016), Chen *et al.* (2016), Pollington *et al.* (2016). BSE = bulk silica earth (see Supplementary Information for more details).

Methods and Results

Quartz-bearing samples were collected from multiple locations throughout Iceland (Fig. S-1) including (1) magmatic (primary) quartz (n = 9) associated with crustal xenoliths and micro-granites (>550 °C), (2) hydrothermal (secondary) high-temperature quartz (~200 to 400 °C; n = 48) and (3) hydro-thermal low-temperature quartz and silica polymorphs (<150 °C; n = 20). Oxygen ($\delta^{18}O_{V-SMOW}$) and silicon ($\delta^{30}Si_{NBS28}$) isotope composition of quartz and silica polymorphs were analysed *in situ* using SIMS and trace elements of the same grains using EMPA. Details on sample selection, processing, analysis and results are given in the Supplementary Information (SI).

Oxygen isotopes in magmatic quartz display $\delta^{18}O$ values of -5.6 to +6.6 ‰, while silicon isotopes show a very limited range of $\delta^{30}Si$ values of -0.7 to -0.2 ‰ (Fig. 2). In contrast, both $\delta^{18}O$ (-9.3 to +30.1 ‰) and $\delta^{30}Si$ (-4.6 to +0.5 ‰) of hydrothermal quartz display a much greater range. Trace element concentrations of quartz agree with existing quartz data from other magmatic and hydrothermal settings (Götze, 2009; Table S-2). Al and Ti in magmatic quartz range from 57 to 77 ppm and 56 to 140 ppm, respectively, while Al and Ti in hydrothermal quartz and silica polymorphs span a wide range (Al = 28-2140 ppm; Ti = 20-80 ppm). Additionally, trace element concentrations in hydrothermal quartz do not show any distinct correlation with $\delta^{18}O$ and $\delta^{30}Si$ that would allow us to further distinguish different formation conditions (Fig. S-3).

Controls on $\delta^{18}O$ and $\delta^{30}Si$ in Hydrothermal Quartz

Oxygen and silicon isotope values of both ancient and modern hydrothermal silica deposits vary significantly with $\delta^{18}O$ ranging from -10 to +30 ‰ and $\delta^{30}Si$ ranging from -5 to +2 ‰ (Geilert *et al.,* 2015; Brengman *et al.,* 2016; Pollington *et al.,* 2016; this study). Silica and oxygen are both reactive elements and their isotope ratios in minerals and fluids may change significantly upon crustal processes and associated chemical reactions. The observed wide range in isotopic values of hydrothermal silica deposits highlights the need for quantification of such processes and their effects on the isotope systematics. Processes of importance in hydrothermal systems include fluid-rock interaction, phase separation (boiling) and temperature changes (cooling). Such processes lead to changes in the relative abundance of elements of various sources, *e.g.,* the water to rock ratio, changes in aqueous species and gas concentrations and quantity of secondary minerals formed, which may all influence isotopic characteristics of fluids and minerals (Stefánsson *et al.,* 2017).

Origin of Primary $\delta^{18}O$ and $\delta^{30}Si$ Characteristics

The $\delta^{18}O$ values of igneous rocks in Iceland are generally thought to represent derivation from a mantle source ranging in $\delta^{18}O$ from +5 to +6 ‰ (Hemond *et al.,* 1993). However, as a result of extensive fluid-rock interaction involving a low-^{18}O meteoric water component, strong $\delta^{18}O$-depletions from such a mantle source are commonly observed in Icelandic rocks (Muehlenbachs *et al.,* 1974). Such fluid-rock interaction likely affected xenoliths from the 1875 Askja eruption from our sample suite that show notable depletion in $\delta^{18}O$ (-5.5 ± 0.4 ‰; Fig. 2a).
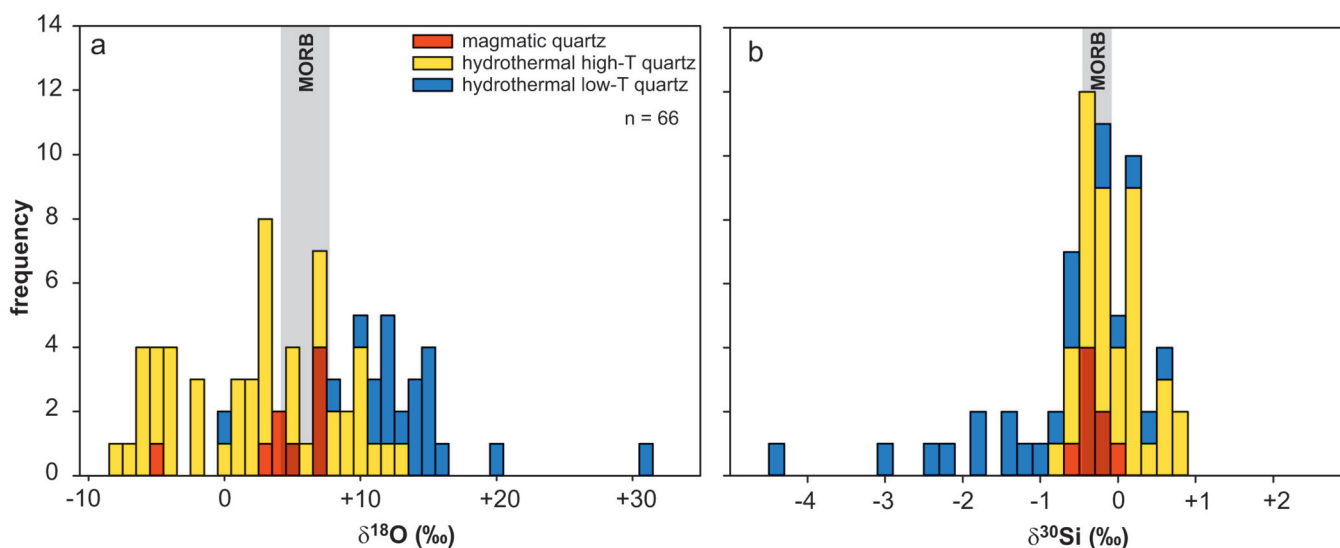
Figure 2 Variation in (a) $\delta^{18}O$ and (b) $\delta^{30}Si$ values of magmatic quartz (>550 °C), hydrothermal high-temperature (~200-400 °C) quartz and low-temperature (<150 °C) quartz and other silica polymorphs. The isotopic values are compared to $\delta^{18}O$ and $\delta^{30}Si$ values for MORB (Eiler *et al.*, 2000; Savage *et al.*, 2010).

Despite strong $\delta^{18}O$-depletions in the Askja xenoliths, their $\delta^{30}Si$ values display only a limited range (Fig. 2b). Indeed, $\delta^{30}Si$ values measured in magmatic quartz (-0.75 to -0.19 ‰) in this study agree with values reported for whole rock and glass samples of igneous rocks from Iceland and elsewhere (Figs. 1, 2b; Table S-1). Recent studies showed that the silicon isotopic composition of Earth's mantle is relatively homogenous ($\delta^{30}Si$ = -0.29 ± 0.07 ‰) and not greatly affected by magmatic processes (Savage *et al.*, 2010). As a result, the $\delta^{30}Si$ values of magmatic quartz (this study) likely represent magmatic values. This implies that the measured $\delta^{30}Si$ values have not been affected by interaction of the xenoliths with meteoric water and/or other secondary processes.

Assessing Secondary Silica Mineralisation Processes in the Icelandic Crust

The large range in $\delta^{18}O$ and $\delta^{30}Si$ values of hydrothermal quartz and silica polymorphs (Fig. 2) are considered to reflect the source(s) of the elements and isotope fractionations associated with hydrothermal processes and reactions. These processes and their effects on the $\delta^{18}O$ and $\delta^{30}Si$ values in quartz can be quantified using isotope modelling approaches (Fig. 3a,b; detailed description in SI).

Comparison of our dataset with the results of the isotope models reveals that silica in hydrothermal high-temperature quartz predominantly originates from the primary (basaltic) rocks that generally display a limited range in $\delta^{30}Si$ values (-0.29 ± 0.07 ‰; Savage *et al.*, 2010, Fig. 3c,d). Upon progressive fluid-rock interaction, the silica is dissolved from the rock by the hydrothermal fluid and precipitates as hydrothermal quartz. The model predicts that the observed decrease in $\delta^{30}Si$ values (+0.66 to -1.01 ‰) compared to the isotopic values characteristic for basaltic rocks and meteoric water (+0.68 ‰, Georg *et al.*, 2007a) and/or seawater (+1.16 ‰; De La Rocha *et al.*, 2000) results from isotope fractionation upon progressive fluid-rock interaction, boiling and cooling. In contrast, oxygen in quartz has multiple sources with the $\delta^{18}O$ values dominated by the source water at low rock-water ratio (ξ < 0.1 mol basalt/kg water) and the primary rock at high rock-water ratio (ξ = 0.1-10 mol basalt/kg water; Figs. 3, S-4). The $\delta^{18}O$ value of the source water also varies. Seawater can be approximated to a value of 0 ± 1 ‰ (vSMOW), while meteoric water will

depend on the geographical location, with values of -7.5 ± 1 ‰ in the south but -12.5 ± 1 ‰ in the north of Iceland (Árnason, 1976).

Hydrothermal low-temperature quartz and silica polymorphs are typically formed by precipitation of dissolved silica upon cooling at or near the surface (*e.g.*, Neuhoff *et al.*, 1999; Geilert *et al.*, 2015). In most cases, the source waters are high-temperature hydrothermal fluids with elevated silica concentrations (Geilert *et al.*, 2015). The trends observed in Figure 3d are consistent with these silica phases having $\delta^{30}Si$ values similar to, or more negative than, the primary host rocks. The depletion of ^{30}Si in the silica minerals cannot be explained by simple fluid-rock interaction and equilibrium fractionation. According to our model, equilibrium fractionation associated with fluid-rock interaction would result in precipitation of quartz with $\delta^{30}Si$ values ranging from +2 to +0.5 ‰ and, depending on the fluid source, $\delta^{18}O$ values of +10 ± 5 ‰ or +15 ± 5 ‰. Instead, the observed $\delta^{18}O$ and $\delta^{30}Si$ values follow a trend predicted by boiling of high-temperature hydrothermal fluids to surface (100 °C) followed by cooling (Fig. 3d). The model predicts that the fluid becomes progressively more negative in $\delta^{30}Si$ than the corresponding silica minerals. However, recent measurements of silica precipitates and coexisting hydrothermal water suggest the opposite, *i.e.* that the boiled water is enriched in ^{30}Si relative to the solid precipitate (Geilert *et al.*, 2015). In line with previous findings (Geilert *et al.*, 2015; Roerdink *et al.*, 2015; Brengman *et al.*, 2016), this suggests that fractionation between silica deposits and fluids under low-temperature (<150 °C) hydrothermal conditions is likely controlled by kinetics and may strongly depend on precipitation rates.

Implications for Hydrothermal Silica deposits in the Geological Record

Coupled $\delta^{18}O$ and $\delta^{30}Si$ studies of ancient hydrothermal silica are still rare (Brengman *et al.*, 2016; Pollington *et al.*, 2016). Hydrothermal quartz precipitates such as quartz amygdales encased by quartz cement occur in a brecciated pillow basalt from the Isua Greenstone Belt in SW Greenland and display a broad range of $\delta^{30}Si$ values with insignificant variations of $\delta^{18}O$ (Brengman *et al.*, 2016). A similar isotopic trend has been observed in quartz cements of hydrothermal origin within the

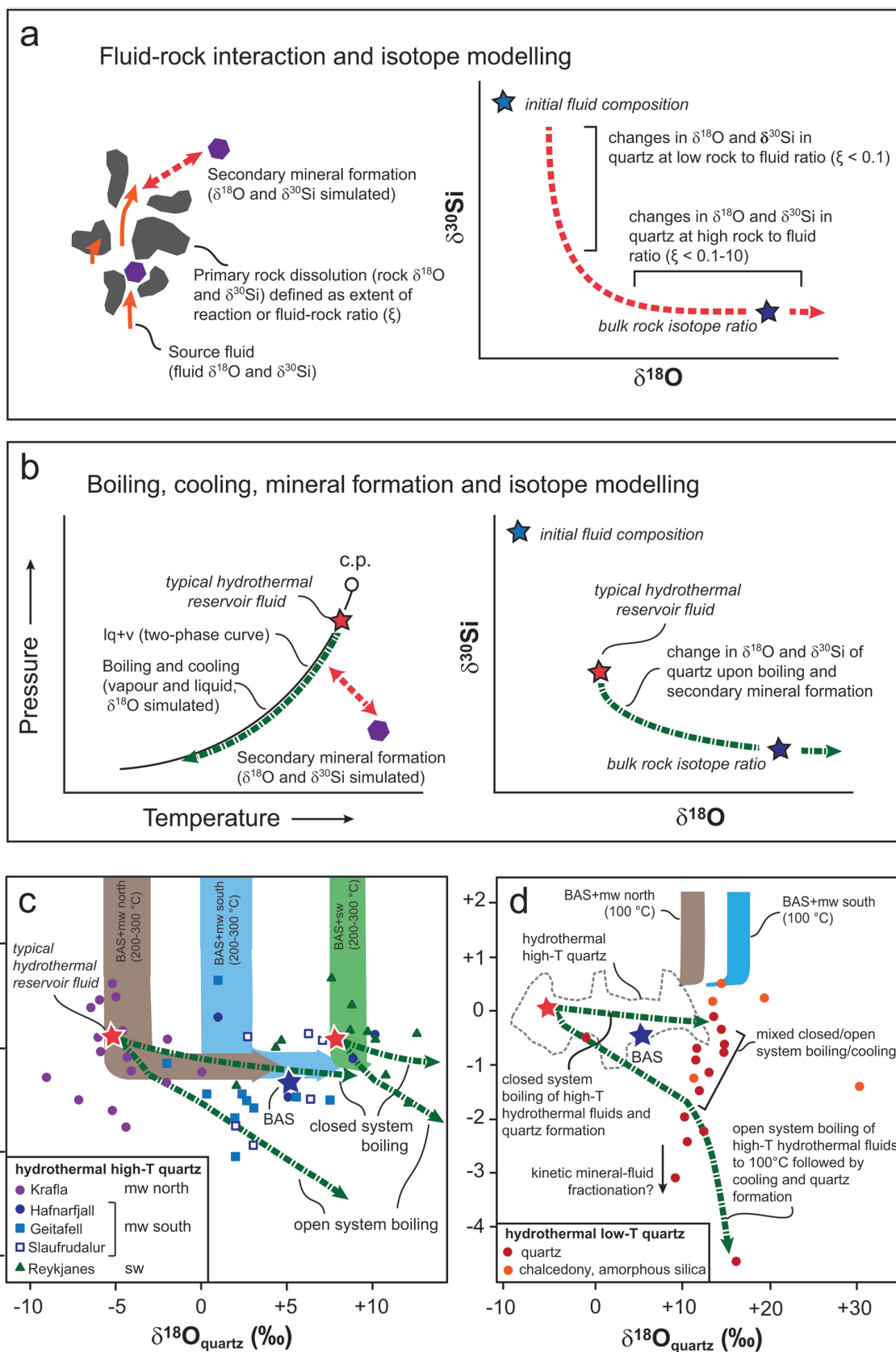**Figure 3** The conceptual chemical and isotope model involves **(a)** fluid-rock interaction with various source fluids and **(b)** boiling followed by cooling and mineral formation; **(c)** isotope systematics in hydrothermal high-temperature quartz largely match the predicted reaction path for progressive fluid-rock interaction (shaded areas) and boiling (arrows). $\delta^{30}Si$ decreases with increasing rock-fluid ratio (ξ) whereas $\delta^{18}O$ values in quartz both depend on the source water and rock-fluid ratio; **(d)** most of the isotope variations in hydrothermal low-temperature quartz and silica polymorphs can be explained by boiling and cooling of a hydrothermal fluid (arrows). Silica deposits with low $\delta^{30}Si$ and constant $\delta^{18}O$ values may result from open system boiling of a high-temperature fluid followed by cooling and quartz or opal formation. BAS = basalt, mw = meteoric water, sw = seawater. Analytical uncertainties of $\delta^{30}Si$ and $\delta^{18}O$ are listed in Tables S-7 and S-8.
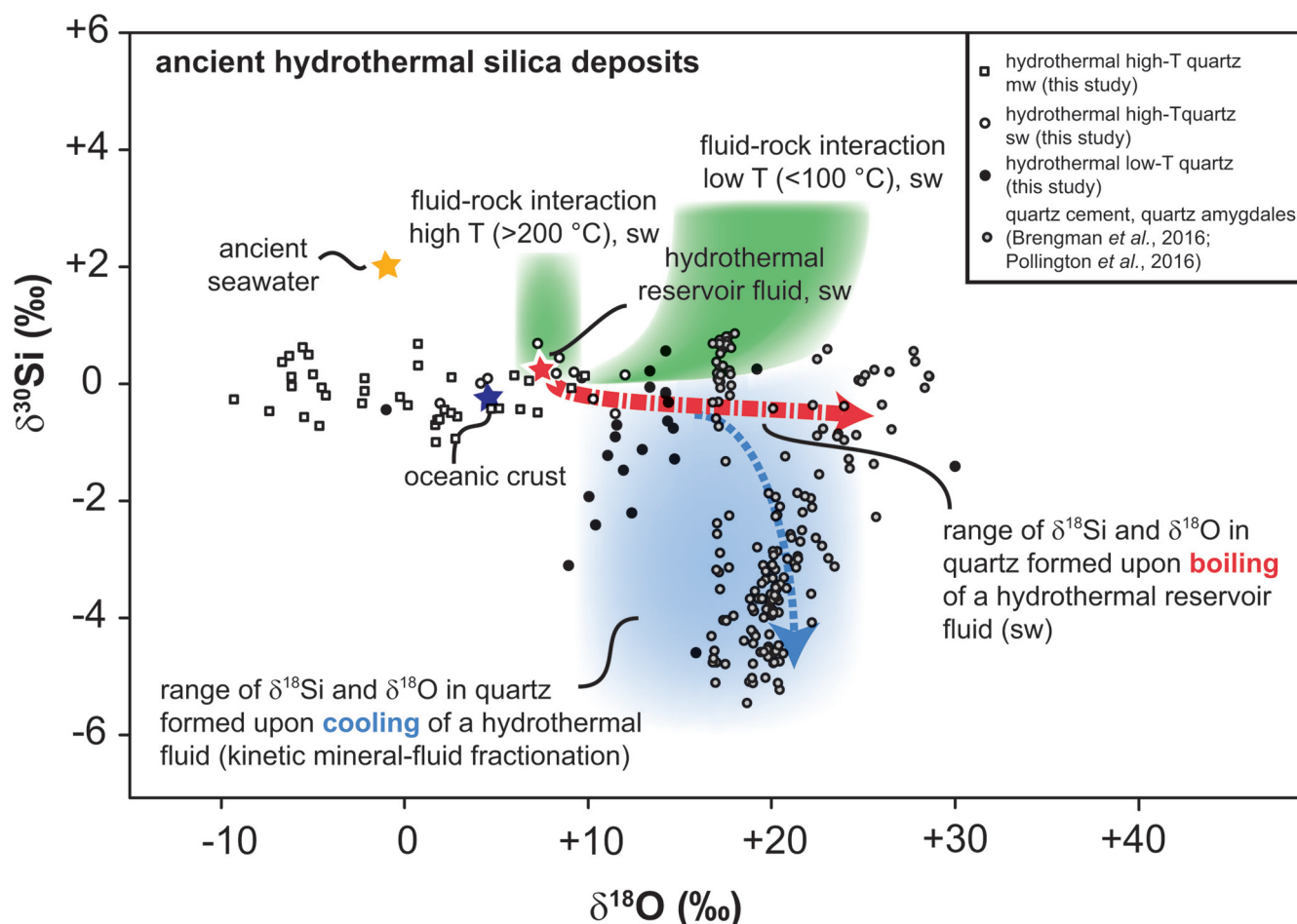
Figure 4 δ^{30}Si *versus* δ^{18}O values of ancient, hydrothermally altered quartz cement and amygdales (Brengman *et al.*, 2016; Pollington *et al.*, 2016). A highly variable but largely negative range in δ^{30}Si values is likely to result from quartz precipitating out of a boiling and cooling fluid involving kinetic fluid-quartz/opal fractionation during rapid temperature decrease. For modelling, the isotope composition of ancient seawater was used (Marin-Carbonne *et al.*, 2014). mw = meteoric water, sw = seawater.

Cambrian Mt. Simon Formation in central North America (Pollington *et al.*, 2016). Such trends have been interpreted as the result of (1) rapid quartz formation from thermal fluids and kinetic isotope fractionation (Brengman *et al.*, 2016) or (2) quartz cement precipitation from hydrothermal fluids that leached ^{30}Si-depleted silicon from the surrounding highly weathered Precambrian rocks (Pollington *et al.*, 2016). The results of the present study indicate that such trends are also typical for open system silica precipitation from a hydrothermal fluid conduit and near-surface cooling, where the chemical and isotope composition of the fluid and silicates changes along the fluid flow path (Fig. 4). Differences in δ^{18}O values between silica deposits may not only result from varying temperature conditions but may also derive from variation in the source water. Furthermore, despite the sedimentary origin of cherts and banded iron formations (BIFs), these rocks have often been exposed to hydrothermal alteration (*e.g.*, Van den Boorn *et al.*, 2007). Thus, the interaction between seawater, hydrothermal fluids and host rocks might have an effect on the Si and O composition even in those silica deposits.

Despite the lack of fractionation factors between fluids and precipitating minerals, this study demonstrates that progressive fluid-rock interaction and the reactions involved may have a strong influence on the oxygen and silicon isotopic characteristics of hydrothermal fluids and associated secondary minerals over a wide temperature range. Fractionation between fluids and minerals of reactive elements like silicon and oxygen are dependent on the source(s) and chemical reactions, aqueous and gas speciation changes as well as

secondary mineral formation. Such processes could lead to δ^{30}Si and δ^{18}O variations in hydrothermal silica deposits of >2 ‰ and >20 ‰, respectively, for a system dominated by a single source of both primary rock and water.

Conclusions

The δ^{18}O and δ^{30}Si systematics of quartz were determined *in situ* using SIMS to assess crustal quartz formation processes in Iceland. Magmatic quartz records δ^{18}O of -5.6 to +6.6 ‰ and δ^{30}Si of -0.4 ± 0.2 ‰ representative of mantle- and crustally-derived melts in Iceland. Hydrothermal quartz and silica polymorphs (<150 to 400 °C) record a much greater range with δ^{18}O of -9.3 to +30.1 ‰ and δ^{30}Si of -4.6 to +0.7 ‰. Isotope modelling reveals that these large variations in the δ^{18}O and δ^{30}Si values are caused by a combination of processes such as fluid-rock interaction, cooling, boiling and associated changes in aqueous and gas speciation of the fluids as well as type and quantity of secondary minerals formed upon these processes. Comparison of the results of this study suggests that the large ranges observed in δ^{30}Si values and insignificant δ^{18}O variations observed in quartz cements and quartz amygdales of hydrothermal origin may result from silica formation in a hydrothermal fluid conduit at or near the surface associated with cooling. Equilibrium fractionation of δ^{18}O and δ^{30}Si between fluids and minerals seems to prevail at hydrothermal high-temperature conditions (~200-400 °C), whereas kinetic fractionation is likely to influence isotope systematics at lower temperatures.

Acknowledgements

Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article1811.

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