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Triple oxygen isotope systematics as a tracer of fluids in the crust: A study from modern geothermal systems of Iceland

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ABSTRACT

Triple oxygen isotope systematics of ancient hydrothermally altered rocks has been previously used to constrain environmental conditions of the Precambrian. To validate those studies, we report high-precision triple oxygen isotope measurements (expressed as $\Delta'^{17}O$ with reference slope 0.528) of quartz, epidote and well fluids from modern geothermal areas of Iceland, Krafla and Reykjanes, as well as measurements from the extinct 6 Ma Geitafell hydrothermal system. At these systems, basalts reacted with distinct fluid sources at temperatures ranging from 250 to 400 °C. Resolvable difference between isotope compositions of surface waters and rocks enables novel insights into boiling, isotope exchange at variable water-rock ratios, and remelting of altered rock. Our measurements of δD, $\Delta'^{17}O$, and $\delta'^{18}O$ in well fluids show that the reactions proceeded at water-rock ratios of 0.1 to 2, and reveal the addition of meteoric water in the Reykjanes system, and near-surface boiling and steam-liquid separation at Krafla. The $\delta'^{18}O$ and $\Delta'^{17}O$ values of fluids shift due to exchange with rocks at high temperature following the slope 0.51 in the triple isotope space. Near-surface boiling and steam-liquid separation cause shifts in δD and $\delta'^{18}O$ values of the fluids. Their $\Delta'^{17}O$ values do not change significantly owning to the shallow slope of liquid-vapor equilibrium fractionation relative to the reference line slope. Epidote $\delta'^{18}O$ and $\Delta'^{17}O$ values in all three localities closely resemble the isotope composition of local fluid sources. The measured slope of triple oxygen isotope fractionation between quartz and epidote at 250–400 °C is 0.526 ± 0.001. We suggest that triple oxygen isotope composition of epidote can be used as a direct first-order proxy for the equilibrium fluid $\delta'^{18}O$ and $\Delta'^{17}O$ values. The calibrated quartz-water equilibrium fractionation for triple oxygen isotopes yields general agreement with the local fluid sources, within ± 1.5‰ of their $\delta^{18}O$ values, while the $\Delta'^{17}O$ agree within ± 0.02‰. We present *in situ* $\delta^{18}O$ measurements in a quartz crystal from Krafla that show several ‰ heterogeneities which may affect the reconstructed equilibrium fluid values. We tested the effect of shallow crustal contamination on the $\Delta'^{17}O$ values of rhyolitic glasses from Krafla, including those quenched and extracted by drilling, that likely formed by assimilation of low-$\delta^{18}O$ hydrothermally altered crust. Our $\Delta'^{17}O$ measurements constrain the degree of crustal assimilation to 10–20 %. Our study shows that the $\Delta'^{17}O$ values measured in geothermal fluids, secondary minerals and low $\delta^{18}O$ contaminated magmas can provide key information on the conditions of water-rock reaction and magma genesis, and contain additional details that were not accessible through conventional analyses of δD and $\delta^{18}O$.

1. Introduction

Hydrothermal alteration of mid-ocean ridge basalts to greenschist facies mineral assemblages provides the dominant control on the isotope and elemental budget of seawater and notably modifies the composition of the oceanic crust (Muehlenbachs and Clayton, 1976; Alt and Teagle, 2000). Since oxygen is the most abundant element both in water and rocks and has distinct isotope compositions in these reservoirs, the alteration can be monitored and quantified by the $^{18}O/^{16}O$ ratio. The advent of high precision triple oxygen isotope measurements enables us to use hydrothermally altered rocks as tracers of fluids in the past and thereby better understand details of past hydrothermal processes. In this paper, we explore the effects of high-temperature alteration of basaltic crust using simultaneous measurements of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios in continental and near-coastal hydrothermal systems of Iceland. Aided by hydrogen isotope ratios, we

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hope to better distinguish the intertwined effects of temperature, fluid isotope composition, mixing of fluids, boiling, and exchange at variable water-rock ratios in controlling the isotope compositions of hydrothermally altered rocks. The systematic mass-dependent relationship between $^{17}O/^{16}O$ and $^{18}O/^{16}O$ in geothermal fluids and minerals reported here promises to provide a variety of useful applications ranging from ore potential and geothermal exploration to studies of ophiolites, paleoclimate proxies, and tracking recycling of isotope compositions through the main terrestrial reservoirs.

1.1. Hydrogen and oxygen isotope studies of hydrothermal systems

In areas of extensive magmatism hydrothermal systems are charged with fluids from local sources that move through the crust by convective groundwater flow and react with the host rocks at high temperature (Norton, 1984; Criss and Taylor, 1986; Hayba and Ingebritsen, 1997; Manning and Ingebritsen, 1999). Due to high-temperature exchange reactions between fluid and rock, alteration minerals have H- and O-isotope values that are close to being in equilibrium with hydrothermal fluids. The ratios of hydrogen and oxygen isotopes, D/H and $^{18}O/^{16}O$, are widely used to investigate fluid sources, temperature of water-rock interaction and processes that occur in hydrothermal systems such as exchange reactions, boiling, and mixing of various fluid reservoirs (Taylor, 1971; Ohmoto and Rye, 1974; Taylor, 1974; Gregory and Taylor, 1981).

In fossilized hydrothermal system, where fluids are no longer present, measurements of $\delta^{18}O$ in coexisting mineral pairs, combined with δD measurements of hydrous minerals and fluid inclusion studies, are used for isotope equilibrium calculations involving mineral-mineral and mineral-water calibrations. Combined H- and O-isotope measurements can fingerprint isotope composition of initial fluids (e.g. Taylor, 1974, Taylor, 1977; Ohmoto and Rye, 1974; Truesdell and Hulston, 1980; Dilles et al., 1992; Giggenbach, 1992; Pope et al., 2014), however the δD values of ancient hydrous minerals rarely reflect equilibrium with the original hydrothermal fluids at high-temperature ($>$ 250 °C) due to subsequent retrogressive exchange at lower temperature ($<$ 100 °C), hydration and weathering (Kyser and Kerrich, 1991; Graham, 1981). Thus, the source of fluids in ancient hydrothermal systems cannot necessarily be determined from $\delta^{18}O$ measurements alone without making assumptions about the isotope composition of fluids or equilibrium temperature. Moreover, the isotope composition of initial fluids may be significantly overprinted due to high-temperature exchange with rocks, varying temperature of alteration, contributions of steam and brine, and addition of magmatic fluids.

Introducing a new isotope parameter $^{17}O/^{16}O$, measured simultaneously with $^{18}O/^{16}O$, enables a new ability to constrain the isotope signature of initial fluids. The unique and systematic relationship between triple oxygen isotope compositions of meteoric waters, seawater and rocks (Landais et al., 2008; Luz and Barkan, 2010; Uemura et al., 2010; Pack and Herwartz, 2014; Sharp et al., 2018) along with recently calibrated equilibrium fractionations (Sharp et al., 2016; Wostrbrock et al., 2018) provide a promising basis to track temperature and O-isotope signature of fluid at the same time. Similarly to $\delta^{18}O$ – δD systematics, the $\delta^{18}O$ - $\delta^{17}O$ systematics of hydrothermal minerals can identify processes that affect isotope composition of the fluid phase, such as boiling, mixing of distinct fluids and isotope exchange with rocks. Unlike combined δD and $\delta^{18}O$ measurements, $\delta^{17}O$ and $\delta^{18}O$ values are obtained concurrently by mass spectrometers from single aliquots of sample O_2 gas.

In this study we investigate the $\delta^{18}O$ - $\delta^{17}O$ relationship in fluids and minerals from active high-temperature (250–400 °C) hydrothermal systems at Reykjanes and Krafla located in southwest and northern Iceland respectively, and at an exposed subvolcanic section in the 6 Ma Geitafell central volcano in southeast Iceland (Fig. 1). These systems serve here as natural laboratories, where distinct fluids with previously determined isotope compositions are reacting with mantle-derived rocks at known temperatures. Using the previous analyses of local precipitation and groundwater recharge sources (Fig. 2) and measurements of fluid pressure and temperature in the geothermal wells, we are able to test the applications of $\Delta'^{17}O$ values under well-defined conditions. We used drill cuttings of quartz and epidote from known depths at Reykjanes and Krafla where temperature in the boiling systems can be determined at specified depth from the boiling point-water depth curve. Quartz and epidote were targeted because their co-occurrence, especially in veins and vesicles, is indicative of hydrothermal alteration at temperatures above 250 °C (Bird and Speiler, 2004), and they are not susceptible to isotope exchange at low temperatures. We also used samples of well fluids from Reykjanes that are dominated by seawater that underwent boiling at depth and isotope exchange with rocks, and from Krafla, where meteoric water boils close to the surface after reaction with rocks at depth.

Measurements from the 6 Ma Geitafell system are used here to validate our findings in the active hydrothermal systems. We test the ability to reconstruct the triple oxygen isotope values of ancient meteoric water at Geitafell similarly to using combined $\delta^{18}O$ and δD values (see Pope et al., 2014). The zoning of alteration minerals and the pattern of isotope ratios in the host rocks of the Geitafell system display a “bull's eye” pattern that formed in response to a temperature gradient and circulation of meteoric water around the cooling intrusion (Taylor and Forester, 1979). This study is also a next logical step in validating previous triple oxygen isotope investigations of ancient hydrothermally altered rocks (Herwartz et al., 2015; Zakharov et al., 2017; Zakharov and Bindeman, 2019). Those investigations applied the triple oxygen isotope approach to resolve ancient environment conditions using lithologies that experienced aqueous alteration billions of years ago. Since the triple oxygen isotope composition of high-temperature minerals is not easily reset, even during regional metamorphism, the current paper provides basis for validating the findings in those previous studies.

1.2. $\delta'^{18}O$ and $\Delta'^{17}O$ definitions

Mass-dependent fractionation of triple oxygen isotopes between entities A and B obeys the relationship (Urey, 1947; Matsuhisa et al., 1978; Cao and Liu, 2011):

$$\ln {}^{17}\alpha_{A-B} = \theta \cdot ln^{18}\alpha_{A-B} \tag{1}$$

where $^{17,18}\alpha_{A\text{-}B}$ are the ratios of $^{17}O/^{16}O$ or $^{18}O/^{16}O$ in A to that in B. The value of θ, the triple isotope exponent, is a temperature-dependent variable typically ranging between 0.5 and 0.5305 for equilibrium and kinetic processes (Matsuhisa et al., 1978; Cao and Liu, 2011; Hayles et al., 2017). Since the relationship between $^{17}\alpha$ and $^{18}\alpha$ is exponential, we adopt linearized delta notation expressed through natural logarithm and denoted by a prime symbol (ʹ) (Miller, 2002):

$$\delta'^{x}O = 1000ln(1 + \frac{\delta^{x}O}{1000}) \tag{2}$$

where x is either 17 or 18. The $\delta^{x}O$ value in Eq. 2 is the conventionally defined delta-notation:

$$\delta^{x}O = 1000(\left(\frac{^{x}O}{^{16}O}\right)_{sample} \Big/ \left(\frac{^{x}O}{^{16}O}\right)_{VSMOW} - 1) \tag{3}$$

where VSMOW (Vienna Standard Mean Oceanic Water) represents a standard with isotope ratios close to that of seawater. Using the linearized notations for triple oxygen isotope fractionation, the θ value can be expressed as a slope in the $\delta'^{17}O$ – $\delta'^{18}O$ coordinates:

$$\theta_{A-B} = \frac{\delta'^{17}O_A - \delta'^{17}O_B}{\delta'^{18}O_A - \delta'^{18}O_B} \tag{4}$$

where A and B are two substances in equilibrium, for example quartz and water, quartz and epidote. When measuring fractionations in triple

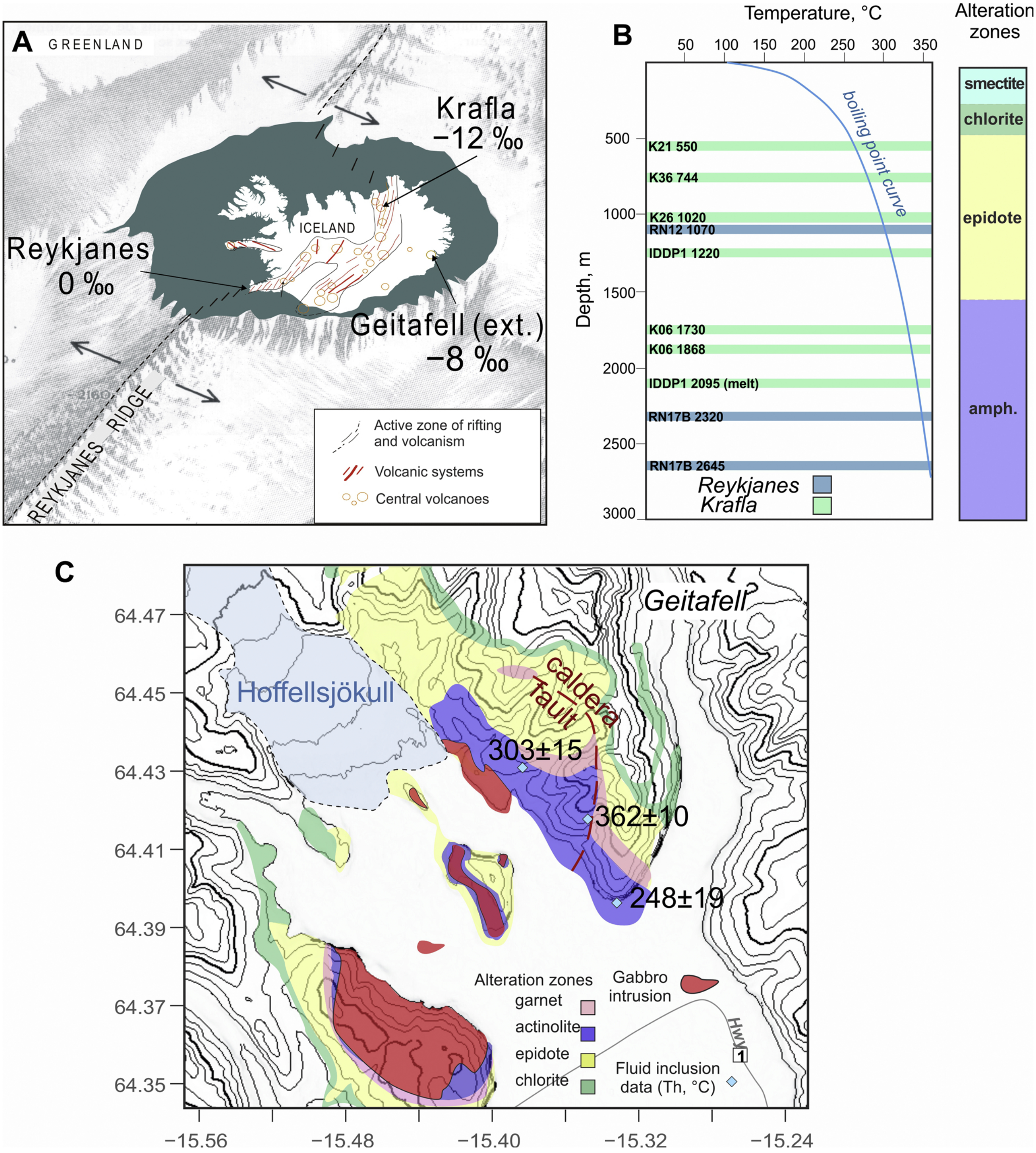

Fig. 1. (A) Locations of the geothermal systems of Iceland studied here. The Reykjanes and Krafla systems are currently active, while the 6 Ma Geitafell extinct volcano hosts a fossilized hydrothermal system eroded to the depth of about 2 km (Friðleifsson, 1983). (B) The temperature of alteration for Reykjanes and Krafla systems can be approximated by the boiling point of water at depth. The temperatures are consistent with characteristic alteration mineral zones from top to bottom: smectite, chlorite, epidote and amphibole. The depth of collected samples is shown with horizontal bands, including the depth of intersection of rhyolite magma by IDDP1. (C) General pattern of alteration at the Geitafell subvolcanic system. The gabbro intrusion is surrounded by a concentric pattern of alteration zones (Friðleifsson, 1983; Thorlacius, 1991) similar to the ones observed in the downward profiles recovered from drill holes in the modern hydrothermal systems. The average homogenization temperature (Th, °C in the legend) of fluid inclusions measured in quartz veins surrounding the intrusion is shown with blue diamonds (after Troyer et al., 2007). These values were used as an approximate estimate of temperature of quartz-water equilibrium for corresponding samples (303 °C for GER16 and 362 °C for GER34 in Table 1). Topographic contour lines are drawn every 100 m. White area represents elevation of about 5 m above sea level.

oxygen isotope system, instead of using the slopes in $\delta'^{18}O$ – $\delta'^{17}O$ coordinates, it is more illustrative to use $\Delta'^{17}O$ notation, often termed ^{17}O-excess. Deviations of $\delta'^{17}O$-$\delta'^{18}O$ fractionations from a reference line with slope of λ_{RL} are then expressed as $\Delta'^{17}O$:

$$\Delta'^{17}O = \delta'^{17}O - \lambda_{RL}\cdot\delta'^{18}O \tag{5}$$

Following definitions in previous studies of silicate rocks and precipitation (e.g., Landais et al., 2008; Luz and Barkan, 2010; Pack et al., 2016), in the Eq. 5 we use the reference line with the slope of λ_{RL} = 0.528.

1.3. Isotope signals in hydrothermal systems

The δD, $\delta^{18}O$ and $\Delta^{17}O$ values of fluids and rocks in hydrothermal

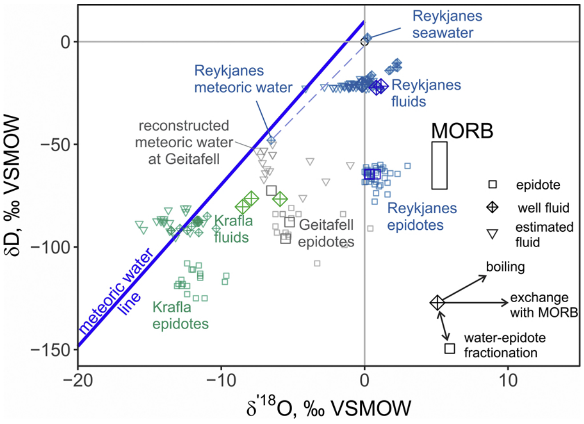

Fig. 2. Compiled δD and $\delta^{18}O$ data for well fluids and epidotes at the Reykjanes, Krafla and Geitafell systems. The data gathered from Pope (2011; 2014; small symbols) and multiple measurements from this study (large symbols). The Reykjanes fluids are derived from seawater ($\delta^{18}O$ and δD = 0 ‰) with minor amount of local meteoric water with $\delta^{18}O$ of -6.5 ‰ (Ólafsson and Riley, 1978). Krafla fluids are derived from meteoric water with $\delta^{18}O$ of -13 ‰ and δD of -90 ‰. Geitafell epidote indicates meteoric waters with $\delta^{18}O$ of about -8 ‰. Compositional field of mid-ocean ridge basalt (MORB) represents initial unaltered rock. Isotope shifts experienced by hydrothermal fluids and water-epidote fractionation are shown schematically in the lower right corner. Boiling vector shows the values of remaining liquid fraction.

systems are distinctive owing to evaporation and condensation that surface waters undergo. Since VSMOW is used as a standard for the definition of δD, $\delta^{18}O$ and $\Delta^{17}O$, all three values are close to 0 ‰ in modern seawater. In the globally averaged meteoric water, hydrogen and oxygen isotopes are related through the equation also known as the global meteoric water line (Craig, 1961):

$$\delta D = 8 \cdot \delta^{18}O + 10 \tag{6}$$

Likewise, the $\delta'^{17}O$ value in meteoric water is related to the $\delta'^{18}O$ through the effects of water-vapor fractionation and relative humidity (Luz and Barkan, 2010). As shown in the recent compilation of meteoric water values (Sharp et al., 2018), the traditionally used single meteoric water line with the slope of 0.528 and y-intercept of 0.033 in $\delta'^{17}O$-$\delta'^{18}O$ coordinates (Luz and Barkan, 2010) may not be representative of precipitation globally. Using the compilation from Sharp et al. (2018), we approximate the slope and y-intercept of the meteoric water line by fitting a linear regression across the range of $\delta'^{18}O$ values between -40 and 0‰. The linear regression yields coefficients:

$$\delta'^{17}O = 0.5272(0.0001) \cdot \delta'^{18}O + 0.016(0.002) \tag{7}$$

where standard errors are given in parenthesis. This equation takes into account the diversity of processes that compose the isotope signature of meteoric waters (re-evaporation, humidity and water-vapor fractionation) including hydrologic cycle in the high-latitude regions such as Iceland. Combined with Eq. (5), triple oxygen isotope meteoric water line in coordinates specific for any reference slope can be expressed through $\Delta'^{17}O$:

$$\Delta'^{17}O = (0.5272 - \lambda_{RL}) \cdot \delta'^{18}O + 0.016 \tag{8}$$

We use these global meteoric water relationships (Fig. 3) to approximate the isotope composition of precipitation at the localities studied here. Using the global $\delta^{18}O$ – δD relationship is justified since the correlation between these values in meteoric waters is very tight ($r^2 > 0.95$; see Craig, 1961) and previous studies showed that the local precipitation is close to the global meteoric water line (Árnason, 1976). As for the $\delta^{18}O$ - $\Delta'^{17}O$ relationship, we report 95% prediction intervals resulting in a meteoric water "band" (see Fig. 3B). This is done to emphasize the poor fit ($r^2 = 0.23$) of the linear regression line caused by the scatter in the $\Delta'^{17}O$ of meteoric waters across the range of $\delta'^{18}O$ values (Fig. 3B). Using the prediction intervals allows us to consider the possible variability within the original local precipitation caused by local isotope effects (e.g. relative humidity, re-evaporation, water-vapor fractionation) when we sample the well fluids or when we derive equilibrium fluid values from mineral analyses.

In each of the three localities, water-rock interaction involved distinctly different reservoirs of surface waters – meteoric water and seawater – reacting with basaltic rocks that have relatively uniform H- and O-isotope composition (Hattori and Muehlenbachs, 1982; Eiler, 2001). The triple oxygen isotope compositions of these reservoirs differ due to small but systematic mass-dependent variations in fractionation of $^{17}O/^{16}O$ relative to $^{18}O/^{16}O$. Mantle rocks have negative $\Delta'^{17}O$ values ranging between −0.06 and −0.05‰ (Herwartz and Pack, 2014; Pack et al., 2016) with δD values of -70 ± 10‰ (Kyser and O'Neil, 1984; Dixon et al., 2017). The effect of isotope exchange between rocks and fluids at high temperature leads to shifts in the $\delta^{18}O$ and $\Delta'^{17}O$ values of the fluids, and to a lesser extent, in their δD values. We show associated isotope shifts in fluids and its effect on equilibrium quartz and epidote (Fig. 3). In addition, liquid-vapor separation and mixing between seawater and meteoric water affects the stable isotope composition of the fluids and minerals in shallow continental systems (Fig. 3).

The Reykjanes, Krafla, and Geitafell systems have well characterized δD and $\delta^{18}O$ compositions of the hydrothermal fluids, local fluid sources and alteration minerals (Fig. 2; Árnason, 1976; Ólafsson and Riley, 1978; Sveinbjornsdottir et al., 1986; Darling and Ármannsson, 1989; Pope et al., 2014, 2016). Reykjanes is a seawater-dominated hydrothermal system where fluids have salinity of local seawater and $\delta^{18}O$ close to those of seawater, with an average value of −1.1‰ and a δD of about −23‰ reflecting a contribution from steam and a small addition of local meteoric water (Ólafsson and Riley, 1978; Pope et al., 2009). At Krafla, the meteoric-derived fluids have $\delta^{18}O$ values close to those of local precipitation, ranging between −13 and −12‰, and δD values between −94 and −87‰ (Darling and Ármannsson, 1989; Pope et al., 2016). Geitafell has a multi-phase intrusion of gabbro and a several-kilometer radius areole of hydrothermally altered tholeiitic lavas (Friðleifsson, 1983) where Pope et al. (2014) measured δD and $\delta^{18}O$ in epidote and determined that hydrothermal fluids were derived from meteoric water with $\delta^{18}O$ of about −8 ± 1‰ and δD of about −60 ± 10‰.

2. Methods

2.1. Oxygen isotope measurements

All stable isotope analyses of solids were carried out at the University of Oregon Stable Isotope Lab. For oxygen isotope analyses we used quartz and epidote from all three localities, volcanic glasses from Krafla well IDDP-1 (single chunks of dark glass) and surface exposures (sample KRF14), and one sample of hydrothermal garnet from Geitafell. All samples were examined with a stereo microscope for inclusions of other minerals prior to analysis. Small samples (1.5–2 mg) were placed in a vacuum chamber and pre-treated with BrF_5 overnight to remove the absorbed moisture and reactive compounds. The oxygen was liberated from the samples by heating them with a CO_2 laser in presence of BrF_5. Extracted oxygen was transported in a stainless steel ¼-inch tube vacuum line, and traces of remaining reagent and other fluorine-containing byproducts were removed by cryogenic traps and reaction with Hg-vapor in a mercury diffusion pump. After the purification, oxygen gas was trapped on a 5 Å molecular sieve by cooling to liquid nitrogen temperature. Subsequently released, the gas was carried though a GC-column by He-flow at the rate 30 mL/minute and room temperature. After about 3 min of elution time, oxygen gas was trapped on a 5 Å molecular sieve immersed in liquid nitrogen. The gas was further trapped on another, smaller volume 5 Å molecular sieve immersed in liquid nitrogen and introduced into a MAT 253 gas-source isotope-ratio mass spectrometer at 50–60 °C. Each measurement consisted of at least 24 cycles of sample-reference gas comparisons with intermittent

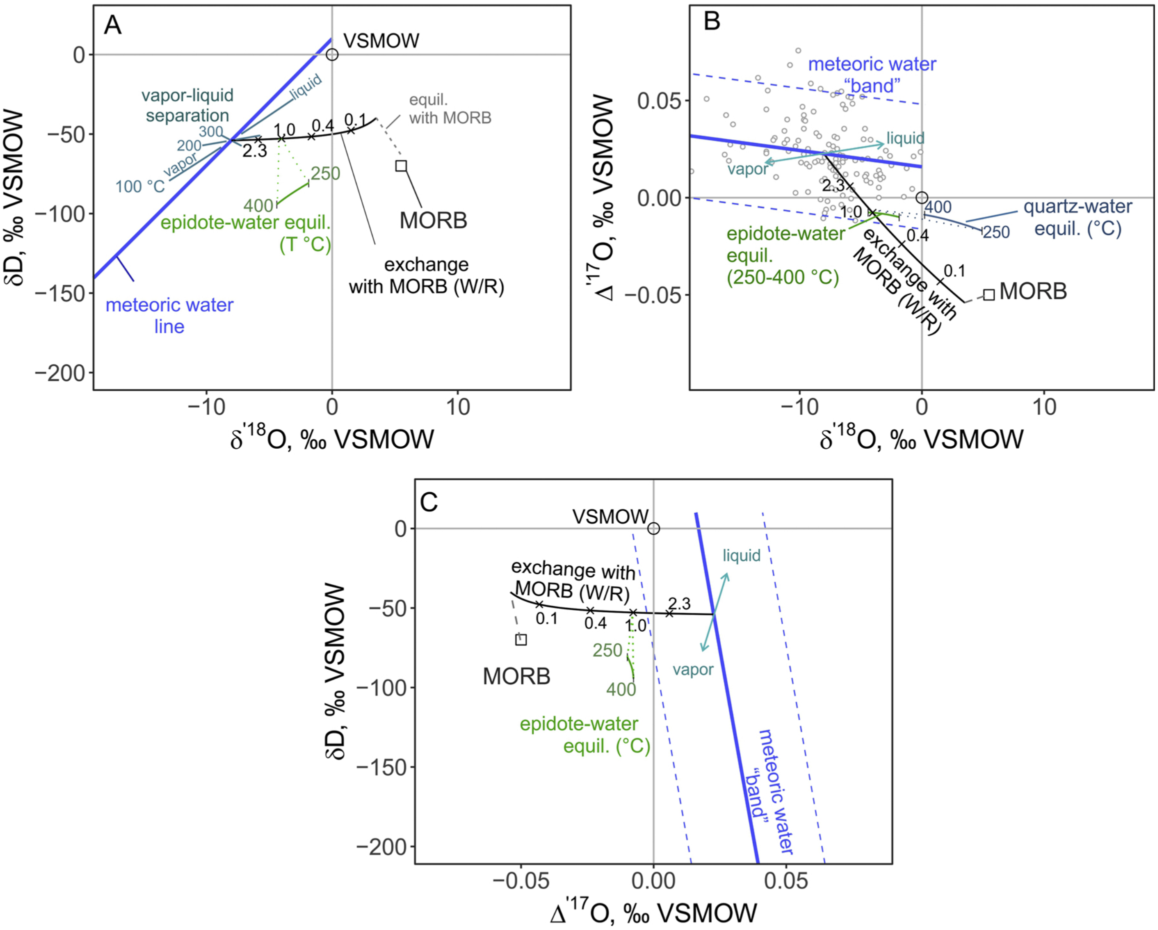

Fig. 3. Systematics of water-rock interaction between meteoric water and mid-ocean ridge basalt (MORB) for the three stable isotope parameters plotted in coordinates: conventional δD-$\delta^{18}O$ (A), $\delta'^{18}O$ – $\Delta'^{17}O$ (B) and $\Delta'^{17}O$-δD (C). The processes of isotope exchange (solid black line), boiling (blue straight lines), quartz-water fractionation (light blue curve) and epidote-water fractionation (green curve) at 250-400 °C are depicted for interaction between unaltered MORB and pristine meteoric water that has $\delta'^{18}O$ of -8 ‰ (on the global meteoric water line, Craig, 1961). Meteoric water "band" refers to the regression line (solid blue; mean slope 0.5272) and 95 % prediction intervals (dashed blue) that are based on the compilation of $\Delta'^{17}O$ values in meteoric waters (open grey circles in B; Luz and Barkan, 2010; Sharp et al., 2018 and references therein). Tick marks on the solid black curve and numbers indicate water-rock ratios (W/R) of isotope exchange reactions. Quartz-water equilibrium at 250-400 °C is after (Sharp et al., 2016). Epidote-water equilibrium slope is approximated by the quartz-water fractionation at high temperature (> 250 °C; see Methods).

equilibration of pressure in the bellows of the mass spectrometer (see Methods in Bindeman et al., 2018; Zakharov and Bindeman, 2019). A subset of samples collected from the Geitafell extinct volcano was analyzed for $^{18}O/^{16}O$ ratio only via conversion of O_2 gas to CO_2 in a heated platinum-graphite converter for a more rapid analysis.

The measurements of well fluids were carried out at the IPM, Okayama University, Japan using fluorination line with a Ni-reactor tube. A few microliters of fluid samples were injected into the reactor and fluorinated using BrF_5 at 250 °C to liberate O_2 gas. The rest of the procedure can be found in Tanaka and Nakamura (2013).

The $\delta^{18}O$ and $\delta^{17}O$ of fluid samples were calibrated to the VSMOW2-SLAP2 scale using the VSMOW2 ($\delta^{18}O_{VSMOW2} \equiv 0 \pm 0.124$ and $\delta^{17}O_{VSMOW2} \equiv 0 \pm 0.070$, N = 5, 2SD) and SLAP2 ($\delta^{18}O_{VSMOW2}$ = -55.283 ± 0.226 and $\delta^{17}O_{VSMOW2}$ = -29.572 ± 0.141, N = 3, 2SD) values measured during this study at the Okayama University. The $\delta'^{18}O$ and $\Delta'^{17}O$ values of silicates were measured at the University of Oregon using the reference gas that has values $\delta^{17}O$ = 12.042 ± 0.067 ‰ and $\delta^{18}O$ = 23.587 ± 0.084 ‰ (mean ± 2SD). These values were determined by analyzing it against the VSMOW2-SLAP2-calibrated reference gas at the IsoLab, University of Washington. Since we did not measure VSMOW2 and SLAP2 during analyses of silicates, we used San Carlos olivine (SCO) as an internal standard within each session to monitor the accuracy. As reported previously (Pack et al., 2016), the SCO values are $\delta'^{17}O$ = 2.677 ± 0.086‰ and $\delta'^{18}O$ = 5.140 ± 0.161‰ (mean ± 1SD) calibrated to VSMOW2-SLAP2 scale. Each analysis was adjusted to the difference between these and measured values of SCO within the session. The uncorrected values reported against the reference gas are assembled in Supplementary Table 1. The measurements of SCO (n = 9) yielded $\delta'^{17}O$ = 2.890 ± 0.185‰ and $\delta'^{18}O$ = 5.606 ± 0.301‰ (mean ± 1SD).

We also measured $\delta^{18}O$ values *in situ* in a quartz crystal extracted from the Krafla well K36 at depth of 744 m using a secondary ion mass spectrometer (SIMS) CAMECA IMS-1280 at the WiscSIMS lab, University of Wisconsin. First, a polished section of quartz was imaged using a FEI Quanta field emission gun scanning electron microscope equipped with a cathodoluminescence (CL) grayscale detector at the University of Oregon. The $\delta^{18}O$ values were analyzed from 10-μm-diameter spots by SIMS. A polished grain of UWQ-1 quartz standard ($\delta^{18}O$ = 12.33‰; Kita et al., 2009) was mounted with the samples and used as a bracketing standard. The precision during the analyses was ± 0.4‰ or better (2 standard errors).

2.2. Hydrogen isotopes

Hydrogen isotopes were analyzed using a high temperature thermal conversion elemental analyzer (TC/EA) that is connected to the MAT

Table 1
Hydrogen and triple oxygen isotope measurements of minerals and fluids from Reykjanes, Krafla and Geitafell systems.

Drill hole/sample	Depth, m	Material	$\delta'^{18}O$	± 1SE	$\Delta'^{17}O$ (λ_{RL} = 0.528)	± 1SE	δD	± 1SE	H_2O, wt. %
Reykjanes									
RN12	1070	epidote	0.932	0.002	0.008	0.006			
RN12	1070	epidote	1.676	0.004	−0.023	0.007			
RN12	1070	quartz	5.582	0.004	−0.023	0.010			
RN12	1070	quartz	5.793	0.004	−0.029	0.013			
RN17B	2645	epidote	0.760	0.003	−0.032	0.006	−65	2	1.98
RN17B	2645	epidote	0.342	0.004	−0.013	0.010			
RN17B	2320	epidote	0.706	0.003	−0.021	0.007			
RN10		well fluids	1.141	0.001	−0.025	0.002	−21.7	1.9	
RN12		well fluids	−0.200	0.001	−0.017	0.002	−20.9	1.6	
RN12		well fluids	−0.125	0.001	−0.015	0.002	−20.9	1.6	
RN25		well fluids	0.818	0.001	−0.015	0.002	−22.4	2.1	
Krafla									
K06	1730	epidote	−13.482	0.006	0.014	0.014			
K06	1868	epidote	−13.732	0.003	0.033	0.009			
K36	744	quartz	−2.091	0.012	0.007	0.012			
K36	744	quartz	−1.482	0.008	0.017	0.008			
K36	744	quartz	−1.910	0.009	−0.008	0.009			
IDDP-1	1220	quartz	−5.048	0.004	−0.033	0.008			
IDDP-1	1220	quartz	−3.759	0.003	−0.022	0.007			
IDDP-1	1220	epidote	−10.777	0.003	−0.006	0.008			
K26	1020	quartz	−7.281	0.004	−0.010	0.007			
K21	550	quartz	−5.591	0.004	0.001	0.007			
IDDP-1	2095	rhyolitic glass	2.726	0.005	−0.069	0.010			
IDDP-1	2095	rhyolitic glass	2.724	0.008	−0.066	0.009			
IDDP-1	2095	rhyolitic glass	3.080	0.007	−0.040	0.007			
KRF14		rhyolitic glass	2.813	0.007	−0.059	0.007			
IDDP-01		well fluids	−7.903	0.001	0.007	0.002	−76.4	2.0	
KJ36		well fluids	−8.507	0.001	0.014	0.002	−80.4	2.0	
Klafla pool		powerplant discharge	−5.898	0.001	0.008	0.002	−76.6	2.1	
Geitafell (collected from surface exposures)									
GER 5		epidote	−5.234	0.005	0.005	0.011	−88	2	2.47
GER 5		quartz	2.073	0.003	−0.021	0.007			
GER1		garnet	−5.737	0.004	0.029	0.010			
GTF 25		epidote	−5.517	0.004	0.030	0.010	−96	2	2.29
GTF 25		quartz	2.219	0.004	0.002	0.009			
GTF28		epidote	−6.500	0.004	0.019	0.009	−73	2	1.73
GER16		quartz	−2.284	0.003	−0.003	0.008			
GER16		quartz	−1.011	0.004	−0.013	0.008			
GER34		quartz	1.978	0.004	−0.014	0.007			
GER34		quartz	1.451	0.003	0.019	0.007			

253 at the University of Oregon, using a continuous flow mode where gases from samples and standards are transported in He carrier gas (see methods in Hudak and Bindeman, 2018). Each solid sample and standard were wrapped in a silver foil capsule and dried in a vacuum oven overnight, then transported to the auto sampler where they were purged with He carrier gas. In the TC/EA's furnace lined with a glassy carbon column, samples experienced pyrolysis at 1450 °C, and all of the H_2O in the minerals was pyrolized to H_2 and CO gas. Extracted gas carried by He into a gas chromatograph where H_2 is resolved from CO, which was discarded. The CONFLOIII device was used to lower the sample pressure to atmospheric, suitable for introduction into the mass spectrometer, which also meters pulses of monitoring gas. Mica standards, USGS57 and USGS58 (δD = −91 and −28‰, respectively; Qi et al., 2017), were included in each analytical session to monitor the accuracy of analysis. The δD values of fluid samples were determined using the same TC/EA set up through multiple injections directly into the glassy carbon column.

2.3. Equilibrium fractionation calculations

We used the calibrations by Sharp et al. (2016) and Wostbrock et al. (2018) to derive the $\delta'^{18}O$ values of equilibrium fluids using measurements of quartz:

$$\delta'^{18}O_{quartz} - \delta'^{18}O_{water} = \frac{4.28 \pm 0.07 \times 10^6}{T^2} - \frac{3.5 \pm 0.2 \times 10^3}{T} \tag{9}$$

and the $\Delta'^{17}O$ of equilibrium fluids:

$$\Delta'^{17}O_{quartz} - \Delta'^{17}O_{water} = \left(\frac{4.28 \pm 0.07 \times 10^6}{T^2} - \frac{3.5 \pm 0.2 \times 10^3}{T}\right) \times \left(0.5305 - \frac{1.85 \pm 0.02}{T} - \lambda_{RL}\right) \tag{10}$$

where T is equilibrium temperature in Kelvins. At 250–400 °C, fractionation is such that $\delta'^{18}O_{quartz} - \delta'^{18}O_{water}$ and $\Delta'^{17}O_{quartz}$-$\Delta'^{17}O_{water}$ give about +4-9‰ and −0.04 to −0.01‰ respectively. At this temperature range, epidote has $\delta^{18}O$ values within ± 1.5‰ of the equilibrium fluids (Zheng, 1993). The approximate $\Delta'^{17}O$ fractionation for epidote-water could be derived from Eq. 10 by substitution of the first term with the incremental calibration of $^{18}O/^{16}O$ ratio given by Zheng, 1993:

$$\Delta'^{17}O_{epidote} - \Delta'^{17}O_{water} \approx \left(\frac{4.05 \times 10^6}{T^2} - \frac{7.81 \times 10^3}{T} + 2.29\right) \times \left(0.5305 - \frac{1.85 \pm 0.02}{T} - \lambda_{RL}\right) \tag{11}$$

In general, the $\Delta'^{17}O_{mineral}$-$\Delta'^{17}O_{water}$ fractionation is expected to approach the high-temperature fractionation limit with increasing temperature, though at different rates for different mineral species. In this study, the second term in Eq. 11 is borrowed from quartz-water fractionation (Eq. 10). Even though that part of the equation has not been calibrated for epidote-water fractionation and the factor -1.85 is likely not correct, we assume that it may serve as a valid approximation for the high-temperature systems (250–400 °C), where triple oxygen isotope fractionation approaches its high-temperature limit. From the Eqs. 10 and 11 it is clear, when the T is high, the second term (or θ value in Eq. 4) approaches 0.5305 (Matsuhisa et al., 1978; Bao et al., 2016; Hayles et al., 2018).

To provide an additional estimate of the temperature of alteration in the Geitafell fossilized hydrothermal system, we used the empirical calibration for quartz-epidote equilibrium fractionation given in Matthews (1994):

$$1000ln^{18}\alpha_{quartz-epidote} = \delta'^{18}O_{quartz} - \delta'^{18}O_{epidote} = (2 + 0.75 \times Xps)10^6/T^2 \tag{12}$$

where Xps is mole proportion of pistacite in epidote, calculated as the proportion of iron in formula coefficient units, $Fe^{3+}/(Al + Fe^{3+})$. We used the Xps value of 0.2, which is an average value based on previous measurements for Krafla and Reykjanes epidotes (see Sveinbjornsdottir, 1991).

3. Results

3.1. Measured $\delta'^{18}O$, $\Delta'^{17}O$ and δD values

The $\delta'^{18}O$, $\Delta'^{17}O$ and δD values of minerals and well fluids from Reykjanes and Krafla and mineral separates from Geitafell are reported in Table 1. Quartz, epidote, measured well fluids and estimated equilibrium fluids are graphically presented in Figs. 4–6.

The $\Delta'^{17}O$ values of Reykjanes well fluids range between -0.03 and -0.02‰, in general agreement with a seawater-dominated origin of the fluids. The three measurements of Krafla fluids, that range in $\delta'^{18}O$ between -8 and -6‰, are several ‰ higher than the local precipitation ($\delta'^{18}O$ = -13‰) since they represent the remaining liquid of the fluids that underwent boiling and steam-liquid separation in the near surface environment (Ármannsson et al., 2014; Pope et al., 2016). One samples has a high $\delta'^{18}O$ value of -5.9‰. This sample (Krafla pool; Table 1) represents the power plant discharge at Krafla. The Krafla fluid samples have distinctly high $\Delta'^{17}O$ values of about +0.01‰.

The $\delta'^{18}O$ and $\Delta'^{17}O$ values of Reykjanes epidotes are close to seawater values, varying between 0 and +1 ‰, and -0.03 and +0.01 ‰ respectively (Fig. 4). The Krafla epidotes have low $\delta'^{18}O$ values, between -14 and -11 ‰, and high $\Delta'^{17}O$ values of -0.01 and +0.03 ‰. Geitafell epidotes have $\delta'^{18}O$ values between -7 and -5 ‰, and $\Delta'^{17}O$ values between +0.01 and +0.03‰. The quartz samples are consistent with equilibrium fractionation at the temperature range between 250 and 400 °C being about 5–9‰ higher than the well fluids and epidotes. Their $\Delta'^{17}O$ values are about 0.01–0.03 ‰ lower than the respective fluid sources and epidotes (Figs. 4 and 5). Our measurements constrain apparent fractionation of triple oxygen isotopes between quartz and epidote as shown in the Eq. 4. The mean and standard error of the slope in $\delta'^{17}O$-$\delta'^{18}O$ coordinates is 0.526 ± 0.001. We show the quartz-epidote fractionation measured at each locality along with the 95 % confidence intervals (Fig. 4 and 5). This value corresponds to measured fractionation at the temperature range 250–400 °C and does not necessarily represent equilibrium fractionation between the two minerals.

In this study, we used a silicate standard (SCO) that has $\delta'^{18}O$ value about 20 ‰ higher than the lowest values measured in Krafla epidotes. It would be a good practice for future workers to develop a low $\delta^{18}O$ silicate standard with the $\Delta'^{17}O$ value calibrated to SLAP2-VSMOW2 scale. Then the values reported here could be corrected for a possible scale distortion effect using the values in Supplementary Table 1 and the reference gas value (see Methods section). The documented examples of scale distortions in other mass spectrometers show that the difference between true and measured $\Delta'^{17}O$ is on the order of 0.001 - 0.050 ‰ for the 60 ‰ $\delta'^{18}O$ range of the VSMOW2-SLAP2 scale (Schoenemann et al., 2013; Pack et al., 2016; Yeung et al., 2018). We suggest that the measurements used here are appropriate for studying hydrothermal processes for the following reasons: i) the span of $\delta'^{18}O$ in studied samples is less extreme than the VSMOW2-SLAP2 range; ii) the fluid samples reported here are calibrated to VSMOW2- SLAP2 and their values compare well to the mineral data.

3.2. Computed equilibrium fluids

Using the boiling point-depth to estimate temperature, the $\delta'^{18}O$ values of equilibrium fluids were computed based on quartz measurements and the Eq. 9 and 10 (Sharp et al., 2016; Wostbrock et al., 2018). From Eq. 12, Geitafell samples GER 5 and GER 25 yield equilibrium temperatures of 270 and 254 °C respectively, which were then used to compute equilibrium fluid values. The uncertainty of $\delta'^{18}O$ and $\Delta'^{17}O$ values of equilibrium fluids was estimated by propagating the uncertainties in fractionation factors and the analytical errors through the equations (9) and (10). We used the average values of analytical standard errors (SE): 0.005 ‰ for $\delta'^{18}O$ and 0.010 ‰ for $\Delta'^{17}O$. The uncertainty of ± 30 °C was used as the largest possible error on the temperature estimates given by the variations in the well log measurements, quartz-epidote thermometry, and pressure corrections associated with fluid inclusion microthermometry used for samples GER 16 and GER 34. The resulting propagated uncertainty of equilibrium fluids are 1.151 ‰ for $\delta'^{18}O$ and 0.011 ‰ for $\Delta'^{17}O$ (1SE). It is worth mentioning that the equilibrium fractionation of $\Delta'^{17}O$ values between water and quartz is not resolvable at the temperature range of 350-400 °C due to analytical uncertainty of ~0.01 ‰.

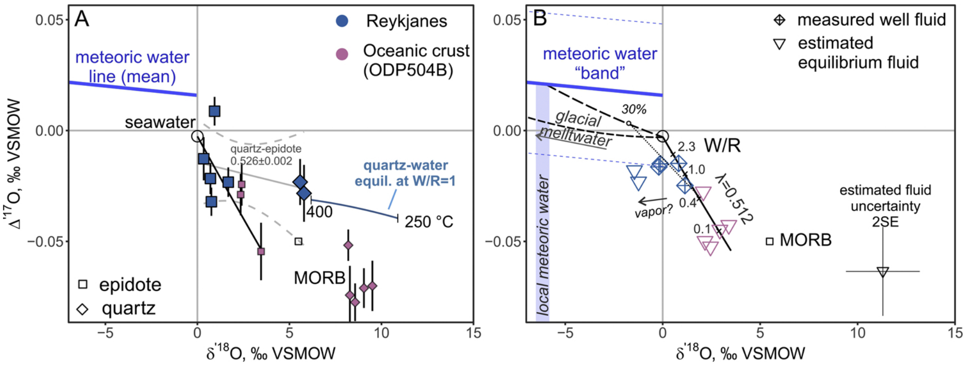

Fig. 4. Triple oxygen isotope values of minerals (A) and fluids (B) from Reykjanes. A – Values plotted for quartz and epidote from Reykjanes, and from modern oceanic crust as sampled by the drill hole ODP 504B in east Pacific Ocean (Zakharov and Bindeman, 2019). The apparent fractionation of triple oxygen isotopes between quartz and epidote at Reykjanes is shown with grey line and 95% confidence intervals (dashed). Quartz-water equilibrium at 250-400 °C is shown with the blue curve (Sharp et al., 2016). B – Values plotted for estimated equilibrium fluids computed from quartz-water fractionation (Eq. 10) and for well fluids measured directly. For both Reykjanes and modern oceanic crust, seawater (open circle) is the dominant fluid involved in alteration of mid-ocean ridge basalts (MORB). The seawater exchanged with rocks at high temperature becomes higher in $\delta'^{18}O$ and lower in $\Delta'^{17}O$ following the slope of $\lambda = 0.512$ in $\delta'^{17}O$ – $\delta'^{18}O$ space (black solid curve). Mixing line with local meteoric water at Reykjanes is shown as a dashed curve with maximum percent fraction of local meteoric water marked at 30 %. Contribution of vapor phase is shown with an arrow.

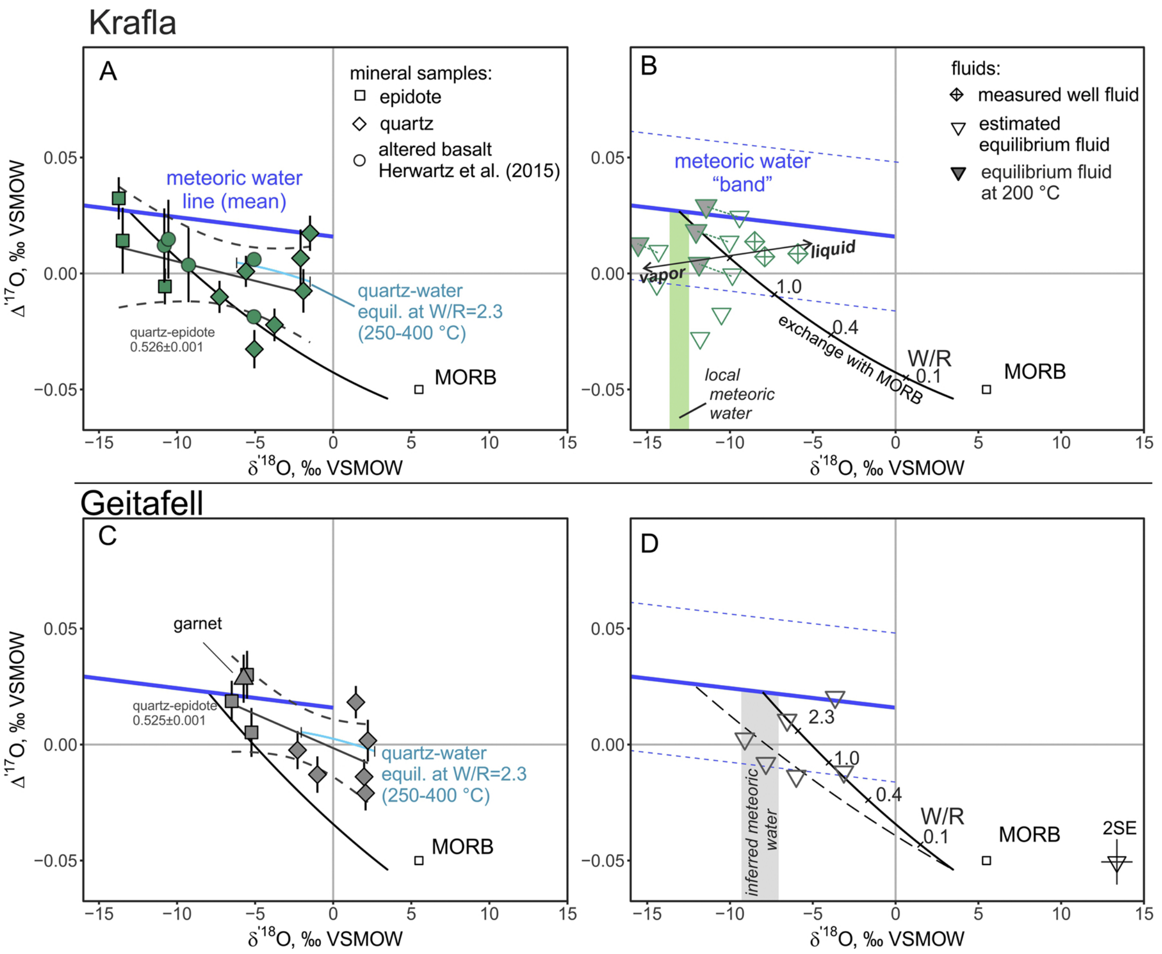

Fig. 5. The $\delta'^{18}O$ – $\Delta'^{17}O$ values of minerals (A and C) and fluids (measured and computed; B and D) from Krafla and Geitafell systems. The apparent fractionation of triple oxygen isotopes between quartz and epidote is shown with grey line and 95% confidence intervals (dashed). The vertical bands on the right panels show the $\delta'^{18}O$ values of local fluid sources (measured directly or inferred from δD values). Additionally, exchange with meteoric water that has composition of precipitation at Krafla is shown for Geitafell with dashed curve. The well fluids at Krafla system originated from exchange with rocks and liquid-vapor separation, which is reflected by their high $\delta'^{18}O$ values with $\Delta'^{17}O$ similar to those computed from quartz-water equilibrium. The four samples of quartz collected at shallow depth (< 1000 m) at Krafla were used to calculate equilibrium fluids (grey-filled symbols) at the temperature of local thermocline of 200 °C (Sveinbjornsdottir et al., 1986).

3.3. In situ $\delta^{18}O$ measurements of Krafla quartz

The cathodoluminescence (CL) image and the heterogeneous $\delta^{18}O$ values measured *in situ* in a quartz crystal from Krafla are shown on Fig. 7A. The CL-pattern reveals features indicative of precipitation at different temperatures manifested by different brightness (Fig. 7A). The $\delta^{18}O$ values measured *in situ* vary between -2 and 0 ‰ for most of the crystal, while the some of the CL-dark outermost rims are about −4 ‰. We show the effect of decreasing temperature and evolving fluids on the triple oxygen isotope composition of equilibrium quartz in Fig. 7B.

3.4. Distribution of $\delta'^{18}O$ values at the Geitafell system

In addition to the triple oxygen isotope measurements, we present the spatial distribution of $\delta'^{18}O$ values measured in quartz and epidote separates from Geitafell. The values are reported in Supplementary Table 2. The value of $\delta'^{18}O_{quartz}$ - $\delta'^{18}O_{epidote}$ ranges between 5 and 10 ‰, approaching the minimum near the contact of the Geitafell intrusion (Fig. 8). This range of fractionation is consistent with a temperature of alteration between 200 and 450 °C computed from Eq. 12. In addition, we measured pyroxene and magnetite separates from a sample of the gabbro intrusion, which returned $\delta^{18}O$ values of 4.69 and 2.06 ‰, respectively (sample Geit-I-8; Supplementary Table 2). Assuming that the minerals record original igneous values, the $\delta'^{18}O_{pyroxene}$ – $\delta'^{18}O_{magnetite}$ fractionation gives 2.6 ‰, which corresponds to equilibrium temperature of 890 °C (calibration from Chiba et al., 1989). However, preservation of original igneous signals by these minerals, especially magnetite, needs to be verified.

4. Discussion

Our measurements of minerals and fluids are quite consistent with their respective fluid sources, confirming that $\Delta'^{17}O$ measurements provide useful constraints for tracking water-rock interaction. These results validate previous studies of ancient submarine and continental hydrothermal systems that focused on the paleoenvironmental conditions of the early Paleoproterozoic (e.g. Herwartz et al., 2015; Zakharov et al., 2017; Zakharov and Bindeman, 2019; Zakharov et al., 2019). In these works, $\Delta'^{17}O$ values were measured to derive $\delta^{18}O$ of seawater or to evaluate mean annual temperature using estimated $\delta^{18}O$ values of local precipitation (Dansgaard, 1964). Below we consider how triple oxygen isotope measurements can be used to constrain the nature of combined isotope shifts owing to boiling, and isotope exchange, and temperature of mineral alteration based on calibrated thermometers. In addition, we explore the processes of crustal assimilation of hydrothermally altered rocks by mantle-derived magmas using the triple oxygen isotope coordinates.

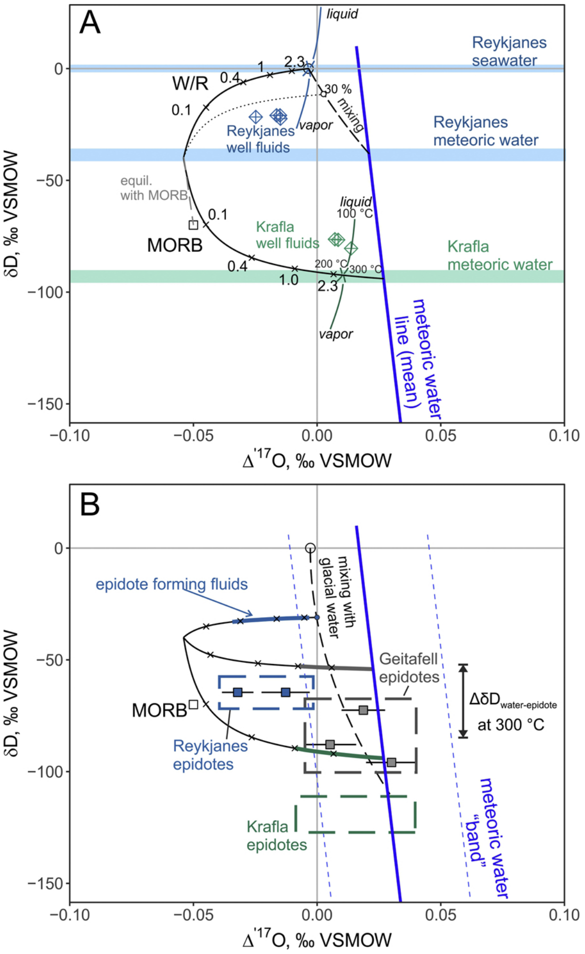

Fig. 6. Combined $\Delta'^{17}O$ and δD measurements of well fluids (A) and epidotes (B). A - The Reykjanes well fluids are best explained by small contribution of local meteoric water, subsurface boiling and isotope exchange with rocks. Krafla fluids represent residual liquid fraction after steam separation, which explains the heavy δD values compared to the exchange trend. B – The $\Delta'^{17}O$ and δD values of epidotes are shown as boxes (compiled data from here and Pope et al., 2014). Where combined measurements are available for the same sample, the values are shown with square symbols. At Geitafell these values are consistent with the reconstructed meteoric water ($\delta^{18}O$ of -8 ‰), while epidotes from Reykjanes may record contribution of low $\delta^{18}O$ and δD glacial waters (see Pope et al., 2009). Krafla epidotes reflect equilibrium fluids close to pristine local meteoric water.

4.1. *Triple oxygen isotope shifts in fluids*

The distinctly different slopes in the triple oxygen isotope space (see Fig. 3) allow us to interpret the origin of fluids in a new dimension. We use $\Delta'^{17}O$ directly measured in well fluids to capture possible isotope shifts occurring in modern hydrothermal systems that enable us to establish a basis for interpreting the mineral data and for understanding fossilized systems.

In the seawater-dominated Reykjanes system, the $\delta'^{18}O$ of well fluids are close to those of seawater with $\Delta'^{17}O$ around -0.02 ‰ (Fig. 4). Their $\delta'^{18}O$ values range between -0.2 and +1.1 ‰, not quite as high as in seawater-derived fluids measured at submarine vents (+0.5-2 ‰; Shanks, 2001). Together with the low δD values (-20 ‰), the isotope compositions of Reykjanes fluids hint at participation of meteoric water in the measured fluids (Arnórsson, 1978; Pope, 2011). The combined hydrogen and triple oxygen isotope values of these fluids reflect a combination of exchange with rocks at high temperature and up to 30 wt. % involvement of local meteoric water (see Fig. 6). The $\Delta'^{17}O$ values slightly below 0 ‰ are interpreted as the effect of isotope exchange with rocks at high temperature reflecting the water-to-rock mass ratios (W/R) between 0.1 and 1 (Fig. 4). Finally, some contribution of steam to the well fluids is manifested by the δD values that are shifted negatively from the trajectories of exchange with MORB (Figs. 4 and 6).

Boiling that occurs in shallow hydrothermal systems should follow a slope similar to the meteoric water line in the $\delta'^{18}O$ – $\Delta'^{17}O$ space due to equilibrium fractionation between vapor and liquid ($\theta_{\text{vapor-liquid}}$ = 0.529; see Eq. 4). This value was constrained from low temperature experiments (< 50 °C; Barkan and Luz, 2005) and is likely higher, closer to 0.53, for boiling water at depth. Thus, boiling affects $\delta'^{18}O$ and δD values of fluids in accordance with liquid-vapor equilibrium fractionation (Horita and Wesolowski, 1994), causing only small variations in $\Delta'^{17}O$. The well fluids at Krafla are derived from local meteoric waters ($\delta'^{18}O$ = - 13 ‰) and are enriched in heavy isotopes of oxygen so that their values approach -8 ‰ due to boiling and steam separation that occurs near the surface (Pope et al., 2016). At a temperature close to 100 °C, and the values of oxygen isotope fractionation, $\theta_{\text{liquid-vapor}}$ = 0.529 (Barkan and Luz, 2005) and $1000\ln^{18/16}\alpha$ close to 5‰ (Horita and Wesolowski, 1994), the $\delta^{18}O$ of remaining liquid can be computed as $R_{liquid} = R_{bulk} \cdot(1\text{-}f^{\alpha})\cdot(1\text{-}f)^{-1}$. The measured values ($\delta'^{18}O$ between -8 and -6‰) correspond to about 70–90 % of remaining liquid fraction (value *f*) of the fluid that originally had $\delta'^{18}O$ of around -10‰ due to isotope exchange with rocks. Essentially, boiling and liquid-vapor separation would result in the $\Delta'^{17}O$ shifts of only about 0.005‰ (Fig. 5). The $\Delta'^{17}O$ values of these fluids are however shifted negatively by 0.01 ‰ with respect to the meteoric water line (Fig. 6), which we interpret to result from isotope exchange with rocks, as supported by previous measurements of unseparated geothermal fluids at Krafla (Ármannsson et al., 2014; Pope et al., 2016). The δD values actually clarify the effect of water-rock isotope exchange combined with shallow boiling and steam loss that occurred between 100 and 200 °C (see Fig. 6). Consistent with the δD values of measured fluids and their triple oxygen isotope values, the isotope shifts measured in Krafla well fluids correspond to W/R ratio of about 1-2. We thus conclude, that the $\Delta'^{17}O$ values of Krafla fluid samples are less affected by the isotope exchange than the Reykjanes fluids, however carry a strong signature of boiling.

In all three systems we measured $\Delta'^{17}O$ shifts that range between -0.01 and -0.02 ‰ and about +0.5 to +2 ‰ shifts in $\delta^{18}O$. Thus, water-rock interaction produces hydrothermal fluids that evolve along the slope of 0.510-0.516 in $\delta'^{17}O$-$\delta'^{18}O$ space, with the mean value of 0.512 for submarine systems (see Fig. 4B). Our estimate is based on the measurements of epidote and quartz extracted from modern oceanic crust, where fluids appear to be shifted the most. This is similar to the previous estimate of 0.5105 provided by the study of bulk rock samples of altered oceanic crust (Sengupta and Pack, 2018). The value of this slope represents the input of high-temperature water-rock interaction in the triple oxygen isotope budget of hydrosphere, and it is an important variable because it allows assessment of the slope and extent of other fluxes (see Sengupta and Pack, 2018).

4.2. *Mineral record of $\Delta'^{17}O$ in fluids in the crust*

At Reykjanes and Krafla, the measured $\Delta'^{17}O$ values of minerals are reflective of equilibrium fluids that were present at depth in the recent past, which for the most part are similar to the modern-day well fluids (Sveinbjornsdottir et al., 1986). Supporting this are epidotes that have $\Delta'^{17}O$ and $\delta'^{18}O$ values close to the modern-day sources of fluids owing to small equilibrium fractionation at high temperature ($10^3\ln^{18/16}\alpha_{\text{epidote-water}}$ = 0–1.5 ‰ at 275–360 °C; Zheng, 1993). Epidotes from Krafla and Geitafell, fall within the range of meteoric water values, while at Reykjanes, epidote compositions are very similar to seawater (Figs. 4 and 5). Also, one sample of garnet from the Geitafell system has triple oxygen isotope composition close to that of meteoric water. It is expected, that the $\Delta'^{17}O$ of minerals with small fractionation would be close to that of fluids, i.e. within about 0.01 ‰ at these temperatures

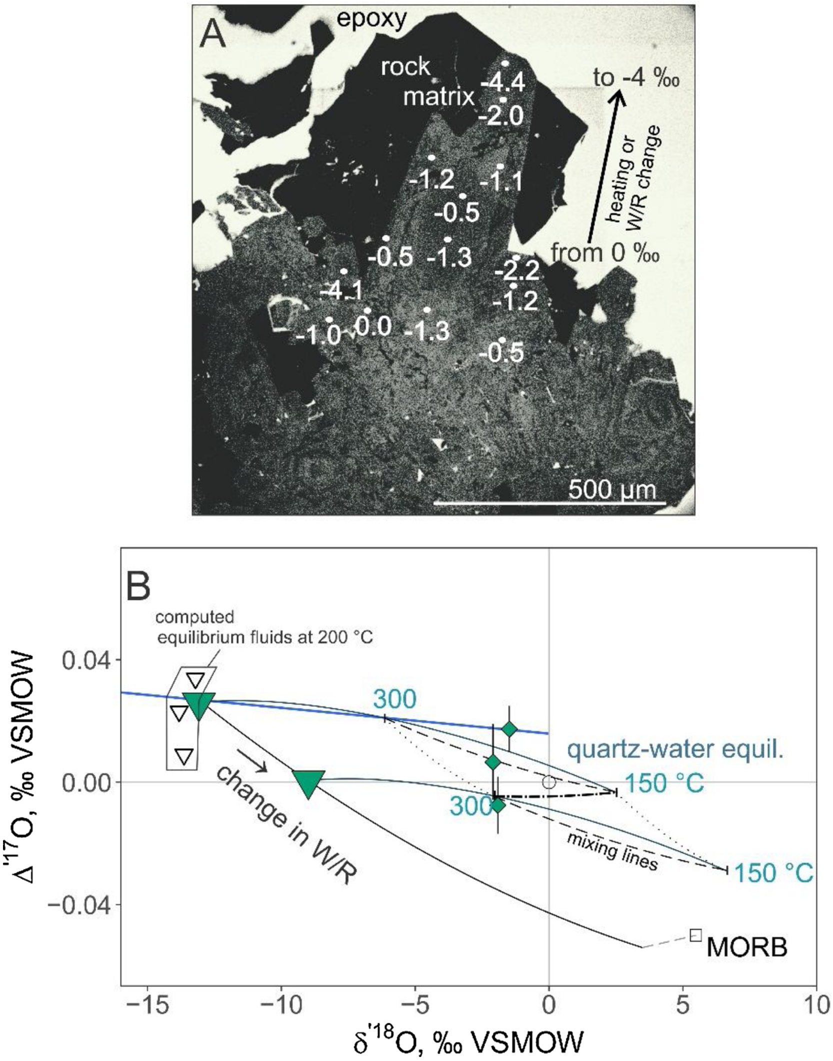

Fig. 7. A – Cathodoluminescent image of quartz (grey; center) from Krafla collected at depth of 744 m and analyzed by SIMS for oxygen isotopes. The $\delta^{18}O$ values (shown in white) vary from -4 ‰ from to about 0 ‰, which translates to temperature change from 190 to 270 °C assuming a fixed value of equilibrium fluids ($\delta'^{18}O$ = -13 ‰). B – The combined effect of variable temperature and variable water-rock ratio (W/R) on the triple oxygen isotope composition of equilibrium quartz. The two concave down curves indicate equilibrium fractionation between quartz and two arbitrarily chosen fluid compositions (filled triangles): initial meteoric water (on the blue line) and a shifted fluid (on the black curve). The tick marks on the curves show quartz compositions at 150 and 300 °C. Mixing between equilibrium compositions are shown with dashed (variable temperature, fixed W/R), dotted (variable W/R, fixed temperature) and dashed-dotted (variable temperature, variable W/R) curves. The reconstructed equilibrium fluids at 200 °C based on measurements of quartz from Krafla (collected at depth 744 m) are shown with open triangles.

(Hayles et al., 2018). This small range, ± 0.01‰, is at the limit of analytical precision, thus precluding meaningful determination of the reason for small variations in the $\Delta'^{17}O$ of epidotes. Nevertheless, epidotes provide promising first-order estimates of $\Delta'^{17}O$ in equilibrium fluids and they reveal reaction with rocks in instances where the fluids were shifted, as were epidotes recovered from modern oceanic crust (Fig. 4).

Using the calibrated quartz-water fractionation (Eq. 9 and 10; Sharp et al., 2016; Wostbrock et al., 2018), we find that the $\delta'^{18}O$ values of computed equilibrium fluids at Reykjanes are lower by about 1 ‰ than the directly measured modern-day well fluids and epidotes, while the $\Delta'^{17}O$ values are close to that of seawater-derived fluids (Fig. 4). Involvement of ancient (Pleistocene) meteoric or glacial low $\delta^{18}O$ water (Sveinbjornsdottir et al., 1986; Pope et al., 2014) would explain these values, as suggested by the low δD values of epidotes (Fig. 6). That suggests that the $\delta'^{18}O$ values of epidotes are within 1 ‰ of their equilibrium fluids. Equilibrium fluids computed from quartz-water fractionation at Krafla and Geitafell plot within the 95 % prediction intervals around the meteoric water line which agrees well with the estimated values of local fluid sources and with the epidote values (Fig. 5). The negative shifts in the $\Delta'^{17}O$ of equilibrium fluids compared to meteoric water likely resulted from isotope exchange with rocks at high temperature, while negative $\delta'^{18}O$ shifts could be a result of combined effects of isotope exchange and liquid-steam separation with a high input of steam (see Fig. 5).

As an example of ancient hydrothermal alteration, the epidote and quartz $\delta'^{18}O$-$\Delta'^{17}O$ measurements from the 6 Ma Geitafell system indicate that the $\delta'^{18}O$ values of equilibrium fluids range between − 9 and − 3 ‰, resembling previous estimates that were based on δD-$\delta^{18}O$ values of epidotes (Pope et al., 2014). The $\Delta'^{17}O$ values of the Geitafell epidote (+0.01 to +0.03 ‰) are consistent with that of inferred meteoric water with $\delta'^{18}O$ of -8 ± 1 ‰, they plot directly on the meteoric water line (Fig. 5). This value is generally corroborated by the equilibrium fluids computed from quartz, however those are lower in $\Delta'^{17}O$ than epidote values and a bit more scattered. The value of -8 ‰ is somewhat high for precipitation in the interior of Iceland, where Geitafell was originally formed at 6 Ma (Fig. 1; Friðleifsson, 1983). In comparison, precipitation at the Krafla system located in the interior of the island has $\delta^{18}O$ of around -13 ‰. It is possible to interpret some of the reconstructed fluids as a result of meteoric water with $\delta'^{18}O$ lower than -8 ‰ combined with isotope exchange (see Fig. 5D). However, the δD values of epidotes and reconstructed equilibrium fluids (Pope et al., 2014) indicate a meteoric water source with the $\delta^{18}O$ value of -8 ± 1 ‰ corroborating our $\Delta'^{17}O$ estimates (see Fig. 3 and Fig. 6).

We notice that the $\Delta'^{17}O$ values of equilibrium fluids derived from quartz measurements are consistently lower than those of epidote. This could be partially explained by the wide range of temperatures and isotope shifts recorded by quartz. Compared to epidote, quartz forms over a large span of temperatures including late-stage veins at low temperature, as low as 150 °C. Thus, we realize that the applied mineral-water calibration might yield inaccurate equilibrium fluids due to inaccurate choice of equilibrium temperature and due to

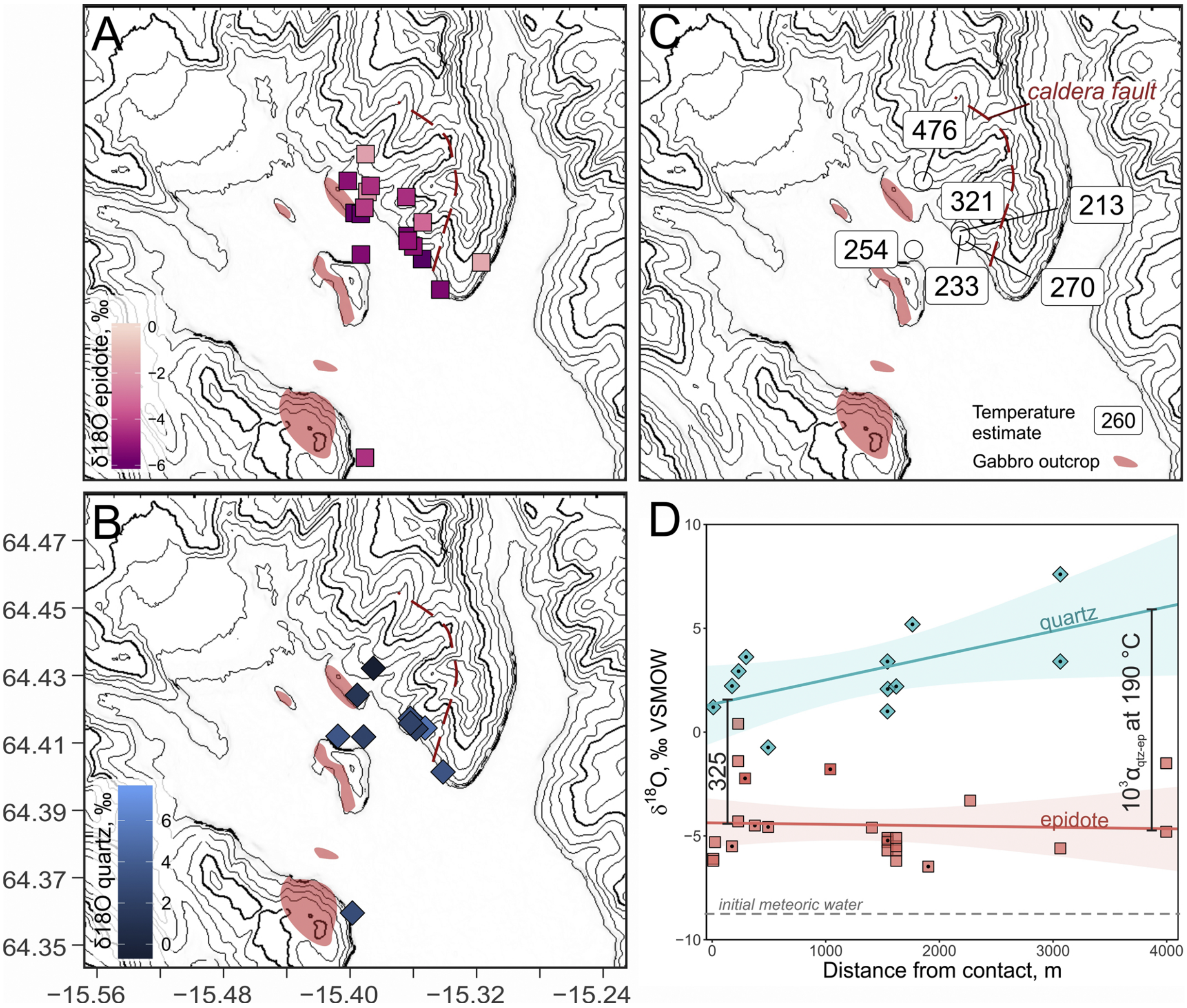

Fig. 8. Spatial distribution of $\delta'^{18}O$ values in epidote (A) and quartz (B) from the host rocks of the Geitafell intrusion shown in the map view (see lithological legend in Fig. 1). The equilibrium temperatures computed from mineral pair measurements extracted from the same sample are shown in (C). The $\delta'^{18}O$ values plotted as a function of distance from the intrusion contact shown in panel (D). Based on the $\delta'^{18}O_{quartz-epidote}$ fractionation, the temperature around the intrusion is > 325 °C near the contact and 190 °C away from it. The data is compiled from Pope et al., 2014 and this study (dotted symbols in D). The isotope equilibrium is consistent with the mineralogical pattern of alteration and the fluid inclusion data (see Fig. 1).

heterogeneities of oxygen isotope composition within quartz crystals as revealed by SIMS (Fig. 7). This particular crystal (Fig. 7A) was extracted from a relatively shallow depth of 744 meters, where borehole temperature measurements indicate a thermocline in which temperatures are consistently lower than the boiling point of water (Sveinbjornsdottir et al., 1986). In this case equilibrium temperature of 200 °C is likely a more accurate estimate (Fig. 7). The 4 ‰ variation measured within the crystal may be related to a change in temperature or/and transition from rock- to meteoric-water-dominated fluid isotope composition. The spatial distribution of $\delta^{18}O$ values in the rocks surrounding the Geitafell intrusion display a pattern also consistent with non-isothermal equilibrium fractionation of oxygen isotope ratios between quartz and water around plutons (Fig. 8) that were emplaced in the shallow crust causing circulation of meteoric waters around them (see Taylor, 1974,;Taylor and Forester, 1979). The $\delta^{18}O$ values of epidote meanwhile vary much less than those of quartz, partly due to its smaller fractionation factor and partly, due to a high and narrow range of temperatures recorded by the mineral (rarely above or below 250–400 °C ; Bird and Spieler, 2004). Additionally, epidote is typically found in areas of high permeability within hydrothermally altered matrix, where water/rock ratios are high (Bird and Spieler, 2004). We thus suggest that $\Delta'^{17}O$ values of epidote (and garnet) can be used as a direct proxy for $\Delta'^{17}O$ values of equilibrium fluids, while caution is needed when using quartz-water calculations to reconstruct equilibrium fluids.

4.3. Implications for magmatic assimilation and origin of low $\delta^{18}O$ rhyolites

In areas of extensive magmatism shallow hydrothermally altered rocks can be assimilated by partial melts to yield low- $\delta^{18}O$ igneous rocks. Similarly to radiogenic isotopes and trace elemental ratios, triple oxygen isotope composition of contaminated magmas can trace the input of hydrothermally altered rock. In Krafla, erupted rhyolites, such as glasses quenched by drilling of hole IDDP-1 and high silica rocks exposed on the surface carry a low-$\delta^{18}O$ signature from assimilated hydrothermally altered crust (Elders et al., 2011). We construct the trajectory of assimilation of shallow hydrothermally altered rocks in triple oxygen isotope space (Fig. 9) based on our measurements of epidote and quartz, rhyolitic glasses and the previous measurements of altered basalts by Herwartz et al. (2015) recalibrated to more accurate standards (Pack et al., 2016). These measurements provide the basic information needed to estimate the effect of crustal assimilation on the triple oxygen isotope composition of contaminated magmas. Since magmatic differentiation occurs at high temperature, the $\Delta'^{17}O$ values of primitive and evolved magmas do not vary significantly at the level

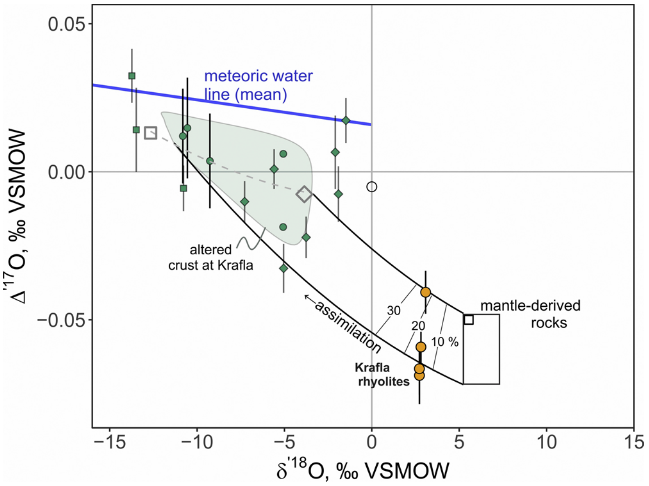

Fig. 9. Triple oxygen isotope systematics of assimilation of low $\delta^{18}O$ hydrothermally altered crust at Krafla by mantle-derived magmas. The contribution of low $\delta'^{18}O$ and high $\Delta'^{17}O$ hydrothermally altered crust from Krafla is resolved due to its distinct isotope signature compared to the isotope composition of uncontaminated magmas. Measurements of volcanic glasses quenched by the drilling hole IDDP-1 and surface rhyolites are consistent with assimilation of 10–20 % of hydrothermally altered crust by mantle-derived melts. The composition of hydrothermally altered crust is shown with the shaded region based on the previous measurements of whole rock samples (data from Herwartz et al., 2015 recalibrated to SCO composition from Pack et al., 2016). The whole rock samples are in agreement with high-temperature alteration of the crust since their values can be reproduced by mixing (dashed grey curve) between average values of epidote (open square) and quartz (open diamond).

of analytical precision in the range of values $\Delta'^{17}O$ = -0.06 ± 0.01 ‰ (Tanaka and Nakamura, 2013; Pack and Herwartz, 2014; Pack et al., 2016; Sharp et al., 2018). Thus, incorporation of hydrothermally altered rocks with distinct isotope composition ($\Delta'^{17}O$ = +0.02 ± 0.01 ‰), could be resolved within the analytical precision. We estimate that the low-$\delta^{18}O$ rhyolitic magmas from Krafla, including those quenched and extracted by drill hole IDDP-1, were derived from assimilation of 10-20 % hydrothermally altered crust ($\delta^{18}O$ between −10 and −5 ‰) and 80-90 % uncontaminated magmas (Fig. 9). These estimates agree well with previous calculations based on combined oxygen and hydrogen isotope composition of the quenched glasses yielding about 20 % material assimilated (Elders et al., 2011). This approach for estimating the amount of assimilant through isotope mass balance might help to resolve the nature of recycled material in other geological situations where the contaminant has very high $\delta^{18}O$ and low $\Delta'^{17}O$ values, such as low temperature sedimentary rocks (e.g. shales with $\Delta'^{17}O$ = -0.10 ± 0.01 ‰; Bindeman et al., 2018).

5. Conclusions

We have presented high-precision measurements of $\Delta'^{17}O$ in hydrothermal minerals and fluids from the Icelandic geothermal areas Krafla and Reykjanes and from the fossilized hydrothermal system at Geitafell. The measurements provide a record of isotope exchange between rocks and variable fluid sources, such as seawater and meteoric waters of different isotope composition. We found the following:

1 Similar to combined δD and $\delta^{18}O$ measurements of hydrous minerals, the triple oxygen isotope measurements can fingerprint initial fluids, constrain temperature of alteration and effective water-rock ratios. Our results support previous triple oxygen isotope studies of the early Paleoproterozoic rocks that recorded composition of ancient precipitation (Herwartz et al., 2015; Zakharov et al., 2019) and seawater (Zakharov and Bindeman, 2019).

2 Measurements of high-temperature minerals, such as epidote and garnet, provide a close estimate of $\Delta'^{17}O$ in the equilibrium fluids. In our case, epidote has isotope compositions almost identical to the local fluid sources at Reykjanes and Krafla. Geitafell epidotes record isotope composition of 6 Ma meteoric water with $\delta'^{18}O$ of -8 ± 1 ‰.

3 The $\Delta'^{17}O$ measurements of geothermal fluids collected at the surface present a novel way to resolve the effects of isotope exchange with rocks at high temperature and boiling, which complements the conventional δD-$\delta^{18}O$ measurements. The negative $\Delta'^{17}O$ shifts in fluids are due to high-temperature exchange between rocks and local fluid sources, whereas shifts in $\delta'^{18}O$ without a significant change in $\Delta'^{17}O$ are due to boiling and vapor-liquid separation.

4 Quartz is used here to derive equilibrium fluid values via calibrated equilibrium fractionation. The estimated fluids range within ± 1.5 ‰ and ± 0.02 ‰ in $\delta'^{18}O$ and $\Delta'^{17}O$ of the well fluids at respective localities. However, caution is needed when interpreting the derived equilibrium fluid values due to the presence of multiple generations of equilibrium compositions within single crystals as shown here with the *in situ* $\delta^{18}O$ measurements.

5 The $\delta'^{18}O$- $\Delta'^{17}O$ values of contaminated magmas might be used to inform about the amount of assimilated material. The measurements of low $\delta^{18}O$ rhyolites from Krafla are consistent with assimilation of 10-20 % of high-temperature hydrothermally altered crust.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chemgeo.2019.119312.

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