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Exceptionally high whole-rock δ^{18}O values in intra-caldera rhyolites from Northeast Iceland

Sylvia E. Berg[1,2,*], Valentin R. Troll[1], Chris Harris[3], Frances M. Deegan[1], Morten S. Riishuus[2], Steffi Burchardt[1] and Michael Krumbholz[1]

[1] Department of Earth Sciences, Section for Mineralogy, Petrology and Tectonics, Uppsala University, Villavägen 16, 752 36 Uppsala, Sweden
[2] Nordic Volcanological Center, Institute of Earth Sciences, University of Iceland, Sturlugata 7, Askja, 101 Reykjavik, Iceland
[3] Department of Geological Sciences, University of Cape Town, Rondebosch 7701, South Africa

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ABSTRACT

The Icelandic crust is characterized by low δ^{18}O values that originate from pervasive high-temperature hydrothermal alteration by ^{18}O-depleted meteoric waters. Igneous rocks in Iceland with δ^{18}O values significantly higher than unaltered oceanic crust (~5.7‰) are therefore rare. Here we report on rhyolitic intra-caldera samples from a cluster of Neogene central volcanoes in Borgarfjörður Eystri, Northeast Iceland, that show whole-rock δ^{18}O values between +2.9 and +17.6‰ ($n = 6$), placing them among the highest δ^{18}O values thus far recorded for Iceland. Extra-caldera rhyolite samples from the region, in turn, show δ^{18}O whole-rock values between +3.7 and +7.8‰ ($n = 6$), consistent with the range of previously reported Icelandic rhyolites. Feldspar in the intra-caldera samples ($n = 4$) show δ^{18}O values between +4.9 and +18.7‰, whereas pyroxene ($n = 4$) shows overall low δ^{18}O values of +4.0 to +4.2‰, consistent with regional rhyolite values. In combination with the evidence from mineralogy and rock H_2O contents, the high whole-rock δ^{18}O values of the intra-caldera rhyolites appear to be the result of pervasive isotopic exchange during subsolidus hydrothermal alteration with ^{18}O-enriched water. This alteration conceivably occurred in a near-surface hot spring environment at the distal end of an intra-caldera hydrothermal system, and was probably fed by waters that had already undergone significant isotope exchange with the country rock. Alternatively, ^{18}O-enriched alteration fluids may have been produced during evaporation and boiling of standing water in former caldera lakes, which then interacted with the intra-caldera rock suites. Irrespective of the exact exchange processes involved, a previously unrecognized and highly localized δ^{18}O-enriched rock composition exists on Iceland and thus probably within the Icelandic crust too.

Keywords: Northeast Iceland, high ^{18}O values, hydrothermal alteration, intra-caldera lakes.

Introduction

Iceland is an oceanic plateau that sits atop the Mid-Atlantic Ridge (MAR) and the impinging Icelandic mantle plume (Sigmundsson, 2006; Thordarson and Larsen, 2007). Because of Iceland's cold sub-polar oceanic climate, it receives high rates of precipitation that, in combination with active volcanism and crustal extension, promote deep-seated meteoric-hydrothermal systems (Muehlenbachs *et al.*, 1974; Eiler, 2001). Hydrothermally altered crust on Iceland is generally characterized by δ^{18}O values that are lower than those of the mantle (Muehlenbachs *et al.*, 1974; Gautason and Muehlenbachs, 1998; Bindeman *et al.*, 2012), and thus crustal assimilation by ascending magmas creates a wide range of sub-mantle δ^{18}O values in Icelandic igneous rocks (e.g. O'Nions and Grönvold, 1973; Óskarsson *et al.*, 1982; 1985; Hattori and Muehlenbachs, 1982; Björnsson, 1985;

*E-mail: e.sylviaberg@gmail.com
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MacDonald *et al.*, 1987; Eiler, 2001; Bindeman, 2008; Bindeman *et al.*, 2012; Geiger *et al.*, 2016). In this context, $\delta^{18}O$ values above +7‰ for Icelandic igneous rocks are extremely rare, and include a devitrified and hydrated pitchstone from Öræfajökull and hydrated acidic xenoliths from Hekla volcano that show $\delta^{18}O$ values of around +10‰ (e.g. Muehlenbachs *et al.*, 1974; Condomines *et al.*, 1983; Hemond *et al.*, 1993; Prestvik *et al.*, 2001). Igneous rocks with $\delta^{18}O$ values exceeding the range that can be produced by closed-system fractionation from a mantle-derived magma (+5.7 to ~7‰; Valley *et al.*, 2005; Bindeman, 2008) are thought typically to have assimilated material altered at low temperature or undergone isotope exchange at low temperature themselves (e.g. Bindeman, 2008; Donoghue *et al.*, 2008; 2010; Deegan *et al.*, 2012). Whereas S-type granites are generally characterized by $\delta^{18}O$ values in excess of +10‰, because their sedimentary protoliths underwent near-surface low-temperature oxygen exchange (e.g. Savin and Epstein, 1970; O'Neil *et al.*, 1977), low-temperature alteration processes on Iceland are less likely to produce high $\delta^{18}O$ values because Icelandic meteoric waters are ^{18}O-depleted (–7.7 to –15‰, Árnason, 1976; Hattori and Muehlenbachs, 1982; Rozanski *et al.*, 1993). Moreover, the rate of chemical weathering on Iceland is relatively low because of the generally low mean annual air temperatures, although it should be noted that a 5 to 10°C warmer climate in the Neogene compared to today would have allowed for slightly increased weathering rates (Óskarsson *et al.*, 2012). However, the frequent absence of soils within formerly buried flood lavas in the study region support the assumption of rapid burial and consequently low surface-weathering rates.

In this paper, we present whole-rock oxygen isotope data for 12 broadly rhyolitic rock samples from the Borgarfjörður Eystri region, Northeast Iceland, of which a sub-group of intra-caldera rhyolites display unusually high whole-rock $\delta^{18}O$ values. For several crucial samples we also analysed oxygen isotopes in feldspar and pyroxene mineral phases, to offer possible explanations for the anomalously high $\delta^{18}O$ values detected.

Geological setting

Dyrfjöll, Breiðavik, Kækjuskörð and Herfell are the eroded remnants of a cluster of Neogene central volcanoes around Borgarfjörður Eystri in Northeast Iceland (Berg *et al.*, 2014). These volcanoes produced voluminous rhyolite lavas and ignimbrite deposits around 12 Ma, which together make up ≥20% of the surface rock exposures in the area (relative to the 10–12% silicic outcrop typical for Iceland, Gústafsson *et al.*, 1989; Burchardt *et al.*, 2011; Martin *et al.*, 2011; Óskarsson and Riishuus, 2013). During this extremely violent eruptive phase, the Njarðvik, Dyrfjöll, Breiðavik and Herfell collapse calderas formed and voluminous intra- and extra-caldera ignimbrite sheets and rhyolitic lavas were deposited (Fig. 1, Gústafsson *et al.*, 1989; Burchardt *et al.*, 2011). At Dyrfjöll and Breiðavik calderas, the caldera infill is overlain by olivine basaltic hyaloclastites and remnants of pillow lavas that provide evidence for the existence of caldera lakes following rhyolite eruption and caldera collapse (Figs 1 and 2, see Gústafsson, 1992). The hyaloclastites are, in turn, overlain by regional flood basalts. The thickness of the caldera-bounded hyaloclastite deposits suggests that the intra-caldera lakes were of substantial size and may have reached ≤350 m depth (Gústafsson, 1992). These Neogene caldera lakes were probably similar to modern Icelandic caldera lakes, such as Öskjuvatn at Askja volcano that formed after the 1875 explosive eruption (Sigurdsson and Sparks, 1978). In contrast, the Herfell caldera appears to have been completely filled with a thick succession of ignimbrites that can be traced for several kilometres beyond the caldera. Hyaloclastites are absent at Herfell and the ignimbrite infill is overlain directly by olivine basalt lavas belonging to the regional flood basalt suite (cf. Óskarsson and Riishuus, 2013). Hyaloclastites are also absent in the Njarðvik caldera, implying that Herfell and Njarðvik did not host extensive caldera lakes (cf. Walker, 1975; Lipman, 1984; Gústafsson, 1992). The present-day elevation of the Dyrfjöll caldera is ~600 m above sea level, but glacial erosion is estimated to have removed nearly two kilometres of former overburden (Gustafsson, 1992). At the time of formation ~12–14 Ma, magmatism in the area is thought to have occurred on the shoulder of the Neogene volcanic rift (Gustafsson *et al.*, 1989; Óskarsson and Riishuus, 2013), making it probable that the Dyrfjöll volcano reached up to 2000 m in elevation. Moreover, as hyaloclastites only occur in some of the calderas in the region investigated, it is probable that the Neogene sea level did not reach this elevation, consistent with subaerial emplacement structures observed in the adjacent and capping flood-basalt flows (Óskarsson and Riishuus, 2013).

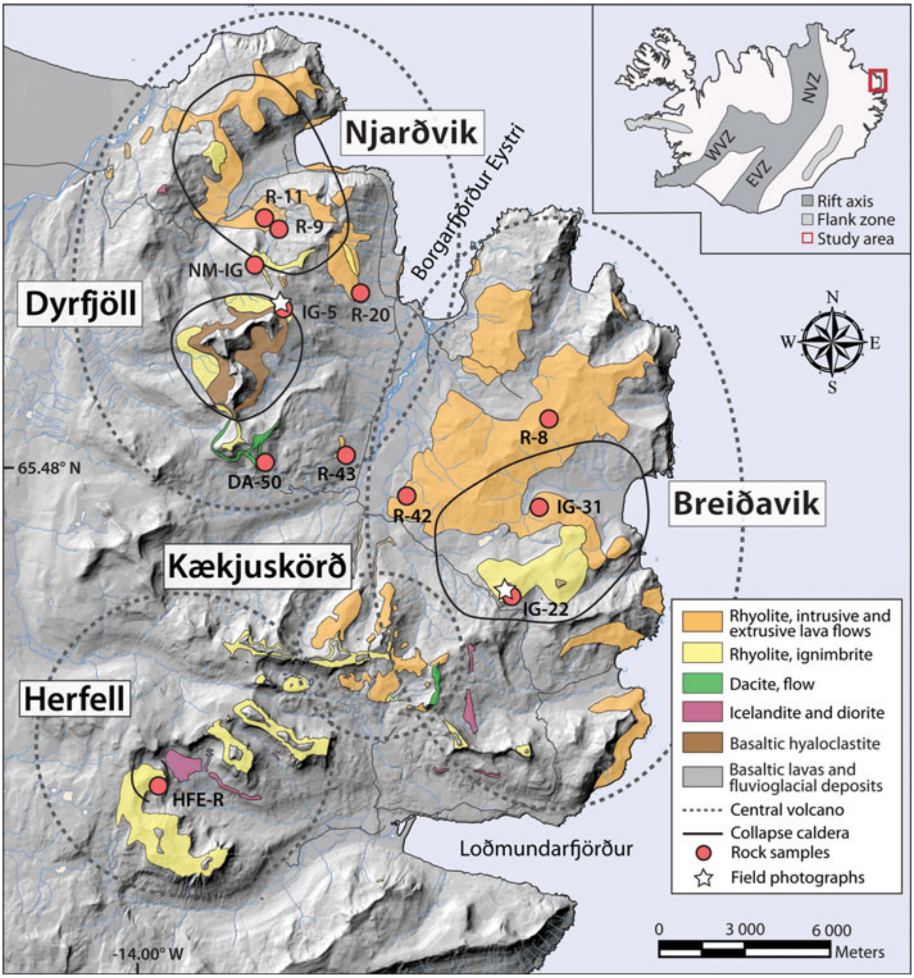

FIG. 1. Geological map of the Borgarfjörður Eystri region in Northeast Iceland, created using the Landmælingar Íslands IS 50 V database together with geological rock units compiled from Gústafsson *et al.* (1989) and Gústafsson (1992), as well as more recent field observations from the region (Berg *et al.*, 2014). Inset shows field area with a red box. Silicic rocks are shown in orange, yellow and green; intermediate rocks in pink; and hyaloclastite deposits in brown. Grey background shading represents basaltic lavas and fluvio-glacial deposits. Sample locations are marked with red circles and approximate caldera margins are indicated with black solid lines. Stippled lines indicate the approximate outline of the individual volcanic centres in the area (Gústafsson *et al.*, 1989; Gústafsson, 1992; Burchardt *et al.*, 2011; Berg *et al.*, 2014). White stars represent the locations of field photographs in Fig. 2.

We sampled intra-caldera rocks from the various volcanic centres in the region ($n = 6$), including four rhyolitic ignimbrites, one rhyolite intrusion and one rhyolite lava (see Fig. 1 and Tables 1 and 2). The Dyrfjöll ignimbrite was sampled at Urdalsvarp and represents a marginal caldera infill (IC-URD-IG-5). Two ignimbrite units were sampled within the Breiðavik caldera: one from Hvítserkur mountain that lies close to the inferred margin of the Breiðavik caldera (IC-HE-IG-22); and another that crops out close to a silicic dome within the central part of Breiðavik caldera (IC-HFE-IG-31). The Herfell ignimbrite was sampled inside the Herfell caldera, but close to the caldera's boundary (IC-HFE-R-1); and a rhyolite intrusion and a lava flow were sampled inside the Njarðvik caldera (IC-HV-R-9 and IC-HV-RD-11).

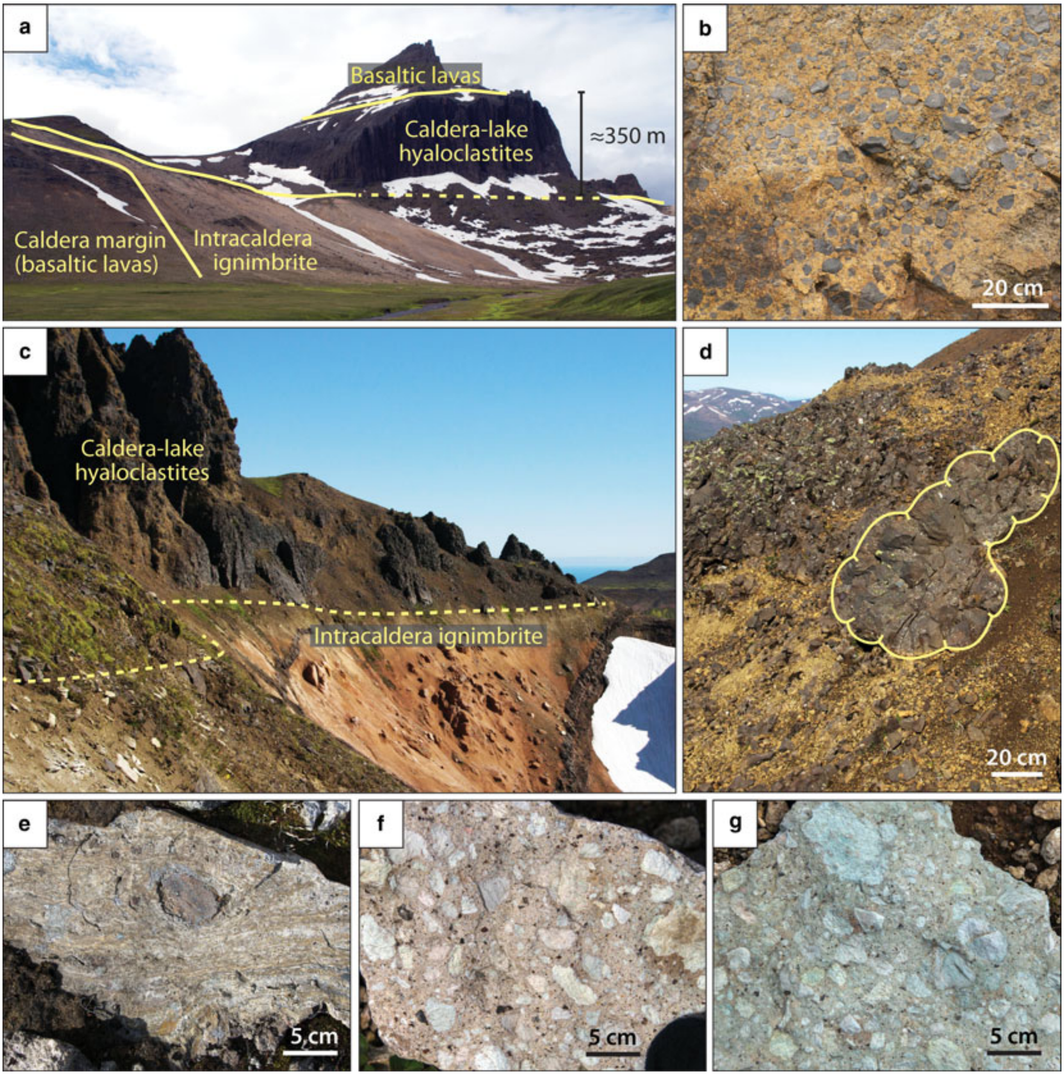

FIG. 2. Field photographs of (*a*) Urdalsvarp valley at the margin of Dyrfjöll caldera, showing 350 m thick hyaloclastite deposits that formed in a caldera lake setting (photo location marked with a white star in Fig. 1); (*b*) close-up of basaltic hyaloclastite breccia deposits; (*c*) the marginal intra-caldera Hvítserkur ignimbrite of the Breiðavik caldera overlain by hyaloclastite deposits; (*d*) these hyaloclastites comprise common basaltic pillow structures. (*e*–*g*) Representative hand specimens of intra-caldera rhyolitic ignimbrite samples from Herfell (*e*) and Dyrfjöll (*f*–*g*), showing welded to lithic-rich rhyolite samples with intense yellow, pink and green alteration colours.

For comparison, we also sampled six representative extra-caldera rhyolites from the region, including one rhyolitic ignimbrite, one dacitic lava flow and four rhyolitic lava flows. Although the Njarðvik ignimbrite from Náttmálafjall (IC-NM-IG-1) was sampled close to the outer margin of the caldera, it is distal to its source here. The remaining lava flow samples were collected at a distance of ~1500 to 4000 m to the Njarðvik, Dyrfjöll and Breiðavik calderas (see Fig. 1).

Methods

All rock samples were washed and cut to remove weathered surfaces, and thin sections were

TABLE 1. Mineral abundances (wt.%) from X-ray diffraction analysis of ignimbrites from Borgarfjörður Eystri, Northeast Iceland.

	Intra-caldera rhyolites				Extra-caldera rhyolite
Sample name	IC-URD-IG-5	IC-HE-IG-22	IC-HF-IG-31	IC-HFE-R-1	IC-NM-IG-1
Location	Dyrfjöll, Urdadalsvarp	Breiðavik, Hvítserkur	Breiðavik, Hvítafjall	Herfell	Njarðvik
Anorthoclase	7.0	9.9	26.4	36.9	n.d.
Plagioclase	n.d.	3.2	16.9	8.0	43.4
K-feldspar	n.d.	n.d.	23.7	15.1	15.3
Quartz	n.d.	3.0	1.6	10.7	35.8
Cristobalite*	n.d.	1.4	31.4	23.9	n.d.
Tridymite	n.d.	n.d.	n.d.	5.4	n.d.
Heulandite–clinoptilolite	8.9	34.7	n.d.	n.d.	n.d.
Mordenite	n.d.	47.8	n.d.	n.d.	n.d.
Phillipsite	n.d.	n.d.	n.d.	n.d.	5.5
Opal-C	23.1	n.d.	n.d.	n.d.	n.d.
Amorphous**	61.0	n.d.	n.d.	n.d.	n.d.

n.d. = not detected; *cristobalite may include opal-C; **amorphous refers to X-ray amorphous material.

subsequently prepared for petrographic observations. Samples were processed further by jaw crushing and milling of hand-picked rock fragments in an agate ball mill at Uppsala University. A portion of each pulverised sample was analysed by X-ray diffraction (XRD) with Rietveld refinement at Activation Laboratories Ltd., Canada. The powdered sample was spiked with known quantities of corundum to permit accurate determination of the mineral proportions present before loading the sample into a sample holder prior to analysis. Following quantification of the crystalline components, the remaining sample content up to 100% was considered to be amorphous material. A Panalytical X'Pert Pro diffractometer equipped with a Cu X-ray source and an X'celerator detector was used for the XRD analyses. The operating conditions were as follows; voltage: 40 kV; current: 40 mA; range: 5–70°2θ; step size: 0.017°2θ; time per step: 50.165 s; divergence slit: fixed; angle: 0.5°. Crystalline mineral phases were identified using the PDF-4 Minerals ICDD database (powder diffraction files from the International Centre for Diffraction Data, http://www.icdd.com/).

Major-element oxides were determined from rock powders by X-Ray Fluorescence (XRF) at ACME Analytical Laboratories Ltd, Vancouver, Canada. Loss on ignition (LOI, i.e. volatile content determined through loss on ignition) was measured by the weight difference after ignition of sample splits at 1000°C. Trace and rare-earth elements were measured by inductively coupled plasma mass spectrometry (ICP-MS) after preparation by multi-acid digestion (HNO_3–$HClO_4$–HF) at ACME Analytical Laboratories Ltd, Vancouver, Canada. Sample duplicates have reproducibilities of <0.10 wt.% for major elements and <10 ppm for trace elements. Accuracy was assessed using internal reference materials with reproducibilities of <0.10 wt.% for major elements and <5 ppm for trace elements.

We measured oxygen isotope ratios of 12 whole-rock samples and additional hand-picked mineral separates from four distinct rhyolite ignimbrites from Borgarfjörður Eystri, using both conventional and laser fluorination methods at University of Cape Town, South Africa. All isotope ratios were measured off-line using a Thermo DeltaXP mass spectrometer and all values are reported in standard δ-notation, where $\delta = (R_{sample}/R_{standard} - 1) \times 1000$ and $R = {}^{18}O/{}^{16}O$.

The oxygen isotope composition of 14 whole-rock powders (including two duplicate samples) were analysed using a conventional silicate extraction line (described by Harris and Ashwal, 2002). Approximately 10 mg of powdered sample was dried in an oven at 50°C and degassed under vacuum at 200°C. Silicates were reacted with ClF_3

TABLE 2. Sample description of rhyolites from Borgarfjörður Eystri, Northeast Iceland, including major and trace elements, and oxygen isotope values.

	Intra-caldera rhyolites					
Sample name	IC-URD-IG-5	IC-HE-IG-22	IC-HF-IG-31	IC-HFE-R-1	IC-HV-R-9	IC-HV-RD-11
Location	Dyrfjöll, Urdadalsvarp	Breiðavik, Hvítserkur	Breiðavik, Hvítafjall	Herfell	Njarðvik, Innri Hvannagilsá	Njarðvik, Innri Hvannagilsá
GPS coordinates*	65°31.738′N, 013°54.361′W	65°25.905′N, 013°45.289′W	65°27.187′N, 013°43.855′W	65°22.769′N, 014°1.800′W	65°33.389′N, 013°54.841′W	65°33.560′N, 013°55.199′W
Rock type	Rhyolite, ignimbrite	Rhyolite, ignimbrite	Rhyolite, ignimbrite	Rhyolite, ignimbrite	Rhyolite lava flow	Rhyolite intrusion
wt.% oxide						
SiO_2	69.30	66.60	73.90	77.03	68.80	74.30
Al_2O_3	11.81	11.53	11.49	12.72	13.41	13.15
Fe_2O_3	1.65	2.56	2.65	1.53	3.51	2.13
CaO	2.18	1.83	1.33	0.28	1.79	0.29
MgO	0.53	0.76	0.55	0.05	0.55	0.25
Na_2O	2.34	3.21	3.57	4.55	4.22	2.91
K_2O	2.83	2.57	3.88	4.16	2.73	4.16
MnO	0.05	0.07	0.04	0.04	0.07	0.02
TiO_2	0.17	0.35	0.43	0.09	0.47	0.29
P_2O_5	0.02	0.05	0.06	–	0.10	0.03
Cr_2O_3	0.01	0.00	0.00	–	0.01	0.02
LOI	8.98	10.87	1.18	0.47	4.41	2.50
Total	99.87	100.40	99.14	100.91	100.07	100.05
Trace elements in ppm						
Ba	713.0	448.0	605.0	852.0	503.0	628.0
Be	7.0	8.0	6.0	7.0	2.0	2.0
Co	1.5	4.9	4.8	–	4.6	1.2
Cs	1.3	1.1	0.4	0.7	0.7	0.6
Ga	24.0	22.2	22.3	33.0	16.7	25.7
Hf	8.9	8.9	8.1	8.5	14.3	13.1
Nb	58.5	50.9	53.3	87.0	20.9	63.2
Rb	56.6	66.1	61.7	96.0	58.7	93.2
Sn	9.0	7.0	6.0	9.0	3.0	8.0
Sr	102.3	61.0	72.0	26.0	134.5	80.6
Ta	3.6	3.7	4.0	6.4	1.8	4.6
Th	7.7	6.3	6.5	9.1	7.5	11.7
U	2.2	1.4	1.7	2.8	2.1	4.0
Zr	168.2	181.4	190.4	167.0	417.2	299.4
Y	113.2	99.7	80.5	130.0	53.1	97.9
La	21.0	25.1	19.4	27.0	41.7	83.1
Ce	58.0	60.2	46.3	67.1	96.6	167.7
Pr	8.4	8.8	6.8	11.1	11.2	20.4
Nd	36.1	38.8	26.0	49.5	43.2	76.0
Sm	12.2	13.0	9.4	17.2	9.3	16.4
Eu	1.7	1.8	1.8	2.2	2.1	1.6
Gd	15.6	15.0	10.4	20.8	9.0	16.0
Tb	3.1	3.1	2.2	3.9	1.6	3.0
Dy	19.7	18.5	13.4	25.2	9.7	18.0
Ho	4.2	4.3	3.2	5.2	2.14	3.8
Er	12.2	11.2	8.8	14.3	6.0	10.8
Tm	1.8	1.7	1.3	2.2	0.9	1.6
Yb	11.5	11.0	9.3	14.3	5.7	9.7
Lu	1.6	1.6	1.2	2.2	1.0	1.4
Pb	4.2	5.4	3.2	8.0	2.9	3.8

(continued)

TABLE 2. (*contd.*)

	Intra-caldera rhyolites					
Sample name	IC-URD-IG-5	IC-HE-IG-22	IC-HF-IG-31	IC-HFE-R-1	IC-HV-R-9	IC-HV-RD-11
Location	Dyrfjöll, Urdadalsvarp	Breiðavik, Hvítserkur	Breiðavik, Hvítafjall	Herfell	Njarðvik, Innri Hvannagilsá	Njarðvik, Innri Hvannagilsá
GPS coordinates*	65°31.738′N, 013°54.361′W	65°25.905′N, 013°45.289′W	65°27.187′N, 013°43.855′W	65°22.769′N, 014°1.800′W	65°33.389′N, 013°54.841′W	65°33.560′N, 013°55.199′W
Rock type	Rhyolite, ignimbrite	Rhyolite, ignimbrite	Rhyolite, ignimbrite	Rhyolite, ignimbrite	Rhyolite lava flow	Rhyolite intrusion
Ni	0.9	7.2	5.8	–	0.9	1.9
$\delta^{18}O$ (‰)						
Whole rock[†]	15.6 ± 0.2	18.5 ± 0.2	9.7 ± 0.2	5.4 ± 0.2	2.9 ± 0.2	3.3 ± 0.2
Duplicate analyses	15.4 ± 0.2	16.6 ± 0.2	n.d.	n.d.	n.d.	n.d.
Average	15.5 ± 0.2	17.6 ± 0.2	n.d.	n.d.	n.d.	n.d.
Pyroxene	4.2 ± 0.2	4.0 ± 0.2	n.d.	4.2 ± 0.2	n.d.	n.d.
Pyroxene magma[#]	4.5 ± 0.2	4.3 ± 0.2	n.d.	4.5 ± 0.2	n.d.	n.d.
Feldspar	16.5 ± 0.2	18.7 ± 0.2	n.d.	4.9 ± 0.2	n.d.	n.d.
Zircon[§]	3.0 ± 0.2	2.5 ± 0.2	n.d.	3.0 ± 0.1	3.2 ± 0.1	3.3 ± 0.2
Zircon magma[§]	4.5 ± 0.2	4.0 ± 0.2	n.d.	4.5 ± 0.1	4.7 ± 0.1	4.8 ± 0.2

	Extra-caldera rhyolites					
Sample name	IC-NM-IG-1	IC-GG-R-8	IC-TH-R-42	IC-SS-R-43	IC-BK-R-20	IC-K-DA-50
Location	Njarðvik	Breiðavik, Gagnheiði	Breiðavik, Thverá	Breiðavik, Sesseljuhamrar	Dyrfjöll, Bakkaá	Dyrfjöll, Kambur
GPS coordinates*	65°32.495′N, 013°54.265′W	65°29.175′N, 013°43.034′W	65°27.757′N, 013°50.269′W	65°28.935′N, 013°52.119′W	65°31.665′N, 013°50.696′W	65°28.921′N, 013°55.934′W
Rock type	Rhyolite, ignimbrite	Rhyolite lava flow	Rhyolite lava flow	Rhyolite lava flow	Rhyolite lava flow	Dacite lava
wt.% oxide						
SiO_2	70.10	73.90	73.60	73.40	75.50	68.10
Al_2O_3	13.52	13.21	13.91	13.52	11.86	14.07
Fe_2O_3	3.41	2.55	1.54	1.69	1.69	5.46
CaO	0.49	0.80	0.82	0.85	0.36	2.38
MgO	0.05	0.03	0.08	0.09	0.35	0.57
Na_2O	4.41	5.18	4.76	4.96	2.97	5.04
K_2O	3.28	3.43	3.76	3.46	4.71	2.24
MnO	0.01	0.08	0.01	–	0.02	0.07
TiO_2	0.35	0.19	0.22	0.24	0.22	0.59
P_2O_5	0.07	–	0.02	–	0.02	0.13
Cr_2O_3	–	0.00	–	0.00	0.01	–
LOI	3.47	0.68	0.94	0.96	1.89	1.36
Total	99.16	100.05	99.66	99.17	99.60	100.01
Trace elements in ppm						
Ba	654.0	778.0	779.0	760.0	576.0	464.0
Be	3.0	4.0	–	4.0	5.0	3.0
Co	–	0.4	0.4	0.4	1.4	3.3
Cs	–	0.8	0.1	0.1	0.4	0.3
Ga	23.0	27.9	25.6	25.3	19.3	21.6
Hf	11.3	19.3	13.5	17.7	10.7	16.6
Nb	47.0	75.3	55.7	68.3	54.5	38.6
Rb	69.0	70.2	73.7	69.9	99.7	38.3

(continued)

TABLE 2. (*contd.*)

	Extra-caldera rhyolites					
Sample name	IC-NM-IG-1	IC-GG-R-8	IC-TH-R-42	IC-SS-R-43	IC-BK-R-20	IC-K-DA-50
Location	Njarðvik	Breiðavik, Gagnheiði	Breiðavik, Thverá	Breiðavik, Sesseljuhamrar	Dyrfjöll, Bakkaá	Dyrfjöll, Kambur
GPS coordinates*	65°32.495′N, 013°54.265′W	65°29.175′N, 013°43.034′W	65°27.757′N, 013°50.269′W	65°28.935′N, 013°52.119′W	65°31.665′N, 013°50.696′W	65°28.921′N, 013°55.934′W
Rock type	Rhyolite, ignimbrite	Rhyolite lava flow	Rhyolite lava flow	Rhyolite lava flow	Rhyolite lava flow	Dacite lava
Sn	7.0	9.0	7.0	9.0	4.0	4.0
Sr	151.0	89.4	120.4	130.4	31.8	232.1
Ta	3.2	5.5	4.1	4.9	4.2	2.9
Th	8.4	9.9	11.1	9.9	11.3	5.4
U	2.2	2.9	1.6	2.5	3.3	1.5
Zr	420.0	569.1	451.4	536.5	276.1	640.2
Y	48.0	117.0	55.5	95.1	46.7	76.3
La	111.0	79.8	61.8	87.7	65.3	56.0
Ce	142.0	184.9	133.7	139.6	136.9	121.0
Pr	11.5	22.5	16.9	22.5	16.7	15.3
Nd	29.1	87.2	65.7	88.5	63.6	61.3
Sm	4.7	20.1	14.1	18.7	12.7	14.4
Eu	0.8	4.0	3.2	3.9	1.4	3.5
Gd	4.6	20.0	12.4	18.0	11.0	13.6
Tb	0.9	3.6	2.2	3.2	1.9	2.4
Dy	7.5	21.0	12.9	18.5	11.6	14.0
Ho	2.0	4.6	2.6	3.9	1.9	3.1
Er	6.7	13.0	6.8	10.1	5.5	8.0
Tm	1.1	1.9	1.0	1.5	0.8	1.3
Yb	8.3	12.4	6.9	10.2	5.1	8.4
Lu	1.4	1.9	1.0	1.4	0.9	1.2
Pb	–	1.4	1.4	0.9	2.4	0.4
Ni	–	–	0.1	0.1	0.5	1.7
$\delta^{18}O$ (‰)						
Whole rock[†]	3.7 ± 0.2	4.0 ± 0.2	6.9 ± 0.2	7.0 ± 0.2	7.5 ± 0.2	7.8 ± 0.2
Duplicate analyses	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Average	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pyroxene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pyroxene magma[#]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Feldspar	3.3 ± 0.2	n.d.	n.d.	n.d.	n.d.	n.d.
Zircon[§]	3.0 ± 0.1	2.9 ± 0.1	2.6 ± 0.1	2.9 ± 0.2	3.0 ± 0.1	3.3 ± 0.2
Zircon magma[§]	4.5 ± 0.1	4.4 ± 0.1	4.1 ± 0.1	4.4 ± 0.2	4.5 ± 0.1	4.8 ± 0.2

‘–’ indicates analysis below detection limit; n.d. = not determined; LOI = loss on ignition. *Reported as: degrees, decimal minutes. [†] Values reported relative to SMOW (‰). [#] Calculated using conversion factor from Harris *et al.* (2005). [§] See Berg (2016).

(Borthwick and Harmon, 1982) and the liberated O_2 was converted to CO_2 using a hot platinized carbon rod (Vennemann and Smith, 1990; Harris and Ashwal, 2002; Fagereng *et al.*, 2008). Further details of the extraction methods of oxygen from silicates can be found in Vennemann and Smith (1990) and Fagereng *et al.* (2008). Samples were run on the conventional line together with duplicate samples of the internal quartz standard MQ ($\delta^{18}O = 10.1‰$) that was used to calibrate the raw data to the SMOW scale (Standard Mean Ocean Water; e.g. Sharp, 2007). During the course of this study, analyses of MQ gave a 2σ variation of 0.16‰. The O-isotope ratios of mineral separates were analysed by laser fluorination using purified O_2 gas. The internal standard MON GT ($\delta^{18}O = 5.38‰$, Harris and Vogeli, 2010) was used to calibrate the raw data to the SMOW scale. The long-term average difference in δ^{18}O values of duplicates of MON GT analysed during this study was 0.13‰, and corresponds to a 2σ value of 0.16‰.

Results

The rhyolites in the study region can be classified into three textural groupings: (1) unwelded to welded and partly glassy ignimbrite deposits; (2) vitrophyric lava flows; and (3) microcrystalline lava flows to slightly coarser sheet intrusions (Gústafsson 1992; Berg *et al.*, 2014). The welded ignimbrites (1) display fiamme and eutaxitic textures, whereas unwelded ignimbrites contain abundant well-preserved pumice fragments and undeformed-to-cuspate glass shards. The ignimbrites investigated have phenocryst assemblages comprising primarily of plagioclase (up to 500 µm in size) and quartz (≤200 µm), minor clinopyroxene, altered biotite and small 'iddingsitized' olivine (<50 µm). The ignimbrites also contain a diverse assortment of lithic clasts, including gabbroic plutonic fragments, basaltic enclaves, as well as felsic xenoliths (see Fig. 3). Overall the matrix is partly glassy, however devitrified glass shards, perlitic cracks and spherulitic textures are ubiquitous especially within the intra-caldera rock suite (cf. Ross and Smith, 1961; Lofgren, 1971*a*,*b*). Vitrophyric rhyolite lavas in region (2) are porphyritic (5–15 area%) with a phenocryst assemblage consisting mainly of plagioclase feldspar, quartz, clinopyroxene and minor olivine (≤1 mm in size) set in a dominantly glassy and laminated groundmass. Glomerocrysts of plagioclase and clinopyroxene can be observed in the vitrophyric rhyolites and dacites (see Berg, 2016 for further details). The microcrystalline to coarsely-crystalline rhyolite flows and intrusions (3) are porphyritic (5–10 area%), with a phenocryst assemblage consisting mainly of plagioclase feldspar (≤1 mm), altered clinopyroxene (≤1 mm), as well as minor quartz (≤1 mm) and pyrite (≤200 µm). The groundmass is composed of quartz, alkali-feldspar, minor Fe-Ti oxides and biotite.

In general, the intra-caldera rhyolites appear to be more affected by secondary mineralization and mineral replacements relative to the extra-caldera suite. In hand specimen, all of the intra-caldera rhyolites show alteration colours that range from white to yellow, pink and green. Moreover, a range of alteration features and alteration minerals can be observed, including chlorite, zeolite, recrystallized quartz aggregates, mineral veining and secondary spherulites. Groundmass plagioclase and clinopyroxene are commonly replaced by sericite and chlorite, respectively, and microcrystalline quartz is also widespread in the groundmass. This secondary alteration appears to be most intense in ignimbrite samples IC-URD-IG-5 and IC-HE-IG-22, which were taken from the margins of the Dyrfjöll and Breiðavik calderas.

Five whole-rock samples including four intra-caldera rhyolites and one extra-caldera sample were selected for XRD analyses with Rietveld refinement and the results are presented in Table 1. The extra-caldera sample shows a fairly typical rhyolitic mineral assemblage of dominantly plagioclase, quartz and potassium feldspar with minor zeolite (phillipsite). In contrast, the intra-caldera samples are highly variable in terms of their mineral content. Sample IC-URD-IG-5, for instance, is extremely silicified, containing 61% amorphous material and 23% opal-C (opal consisting of disordered α-cristoballite). Two more samples, IC-HFE-R-1 and IC-HF-IG-31, contain high-temperature silica phases, consisting of 24% cristoballite (+5% tridymite) and 31% cristoballite, respectively. Finally, sample IC-HE-IG-22 is distinct from the other intra-caldera samples owing to the fact that up to 83% of the sample mass can be accounted for by the zeolite minerals heulandite and mordenite.

When plotted on a TAS diagram, the intra- and extra-caldera samples analysed range from subalkaline high-silica dacite to rhyolite with SiO_2 contents between 69 and 77 wt.% (on a volatile-free basis, see Fig. 4*a*, Le Maitre *et al.*, 1989). By employing Harker plots for selected fluid-mobile major and trace elements (Na_2O, CaO, Rb, Pb, Fig. 4*b–e*), we can see that the extra-caldera rhyolites overlap frequently with the documented data range for evolved rocks in Iceland, which define linear or curvilinear trends towards rhyolite compositions and which typically reflect magma differentiation processes (Wood, 1978; Gunnarsson *et al.*, 1998; Troll and Schmincke, 2002). The intra-caldera rhyolites, in contrast are scattered relative to the unaltered Icelandic rhyolites with respect to their major- and trace-element compositions (c.f. Donoghue *et al.*, 2008; 2010).

Whole-rock oxygen isotope values of the extra-caldera rhyolites range from +3.7 to +7.8‰ ($n = 6$), which are similar to the values obtained previously for Icelandic rhyolites (Fig. 5, Condomines *et al.*, 1983; Sigmarsson *et al.*, 1992; Hemond *et al.*,

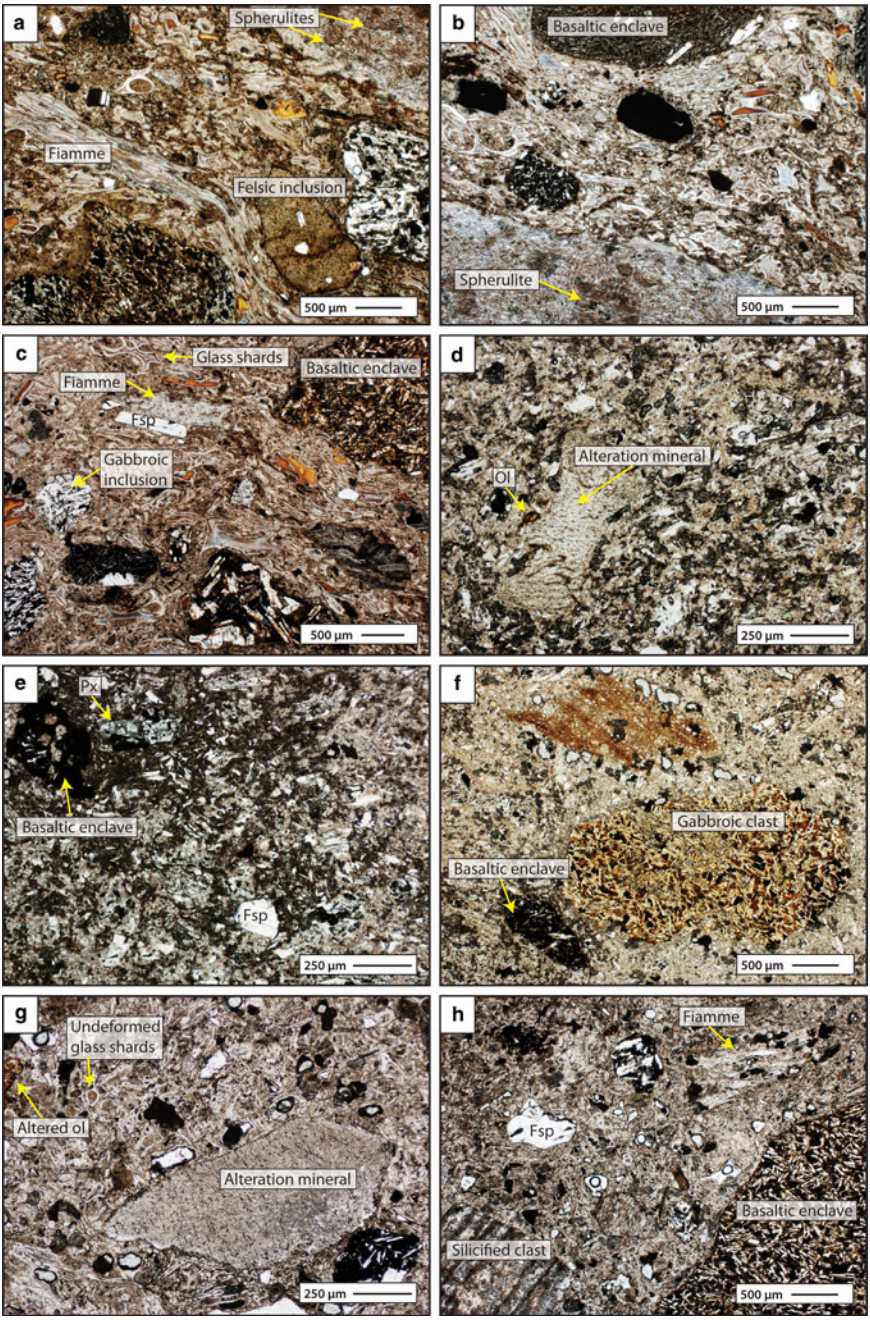

FIG. 3. Representative thin-section micrographs of intra-caldera rhyolites from Borgarfjörður Eystri. (*a–c*) Sample IC-HFE-IG-31 shows a slightly welded groundmass texture with dispersed feldspar crystals, as well as a variety of inclusions. (*d–f*) Sample IC-URD-IG-5 is hypocrystalline and poorly welded, with frequent secondary mineralization domains as well as basaltic and gabbroic inclusions. The basaltic enclaves sometimes show relict crenulated contacts to the host groundmass. Sample IC-HE-IG-22 (*g–h*) is hypocrystalline with secondary, sericite, zeolite and silica mineralization common throughout. All micrographs are shown in plane-polarised light (fsp = feldspar, px = pyroxene, ol = olivine).

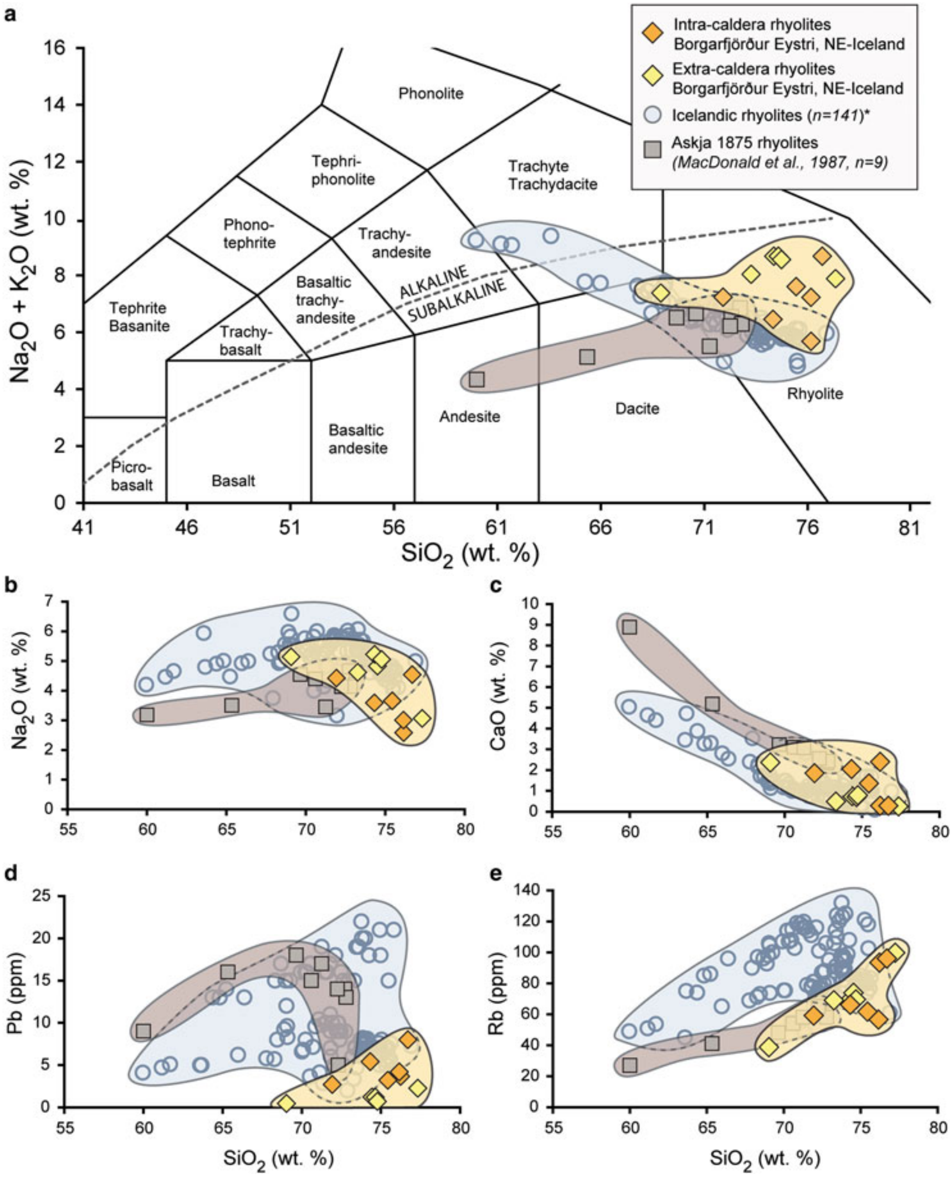

FIG. 4. Major- and trace-element plots of intra- and extra-caldera rhyolites from Borgarfjörður Eystri are shown in orange and light yellow, respectively, while unaltered Icelandic rhyolites are shown in blue (*data compiled from GEOROC database, http://georoc.mpch-mainz.gwdg.de/georoc/). The rhyolites from the Askja 1875 eruption are singled out and are shown here in brown (MacDonald *et al.*, 1987). (*a*) On a Total Alkali *vs.* silica diagram (TAS, Le Maitre *et al.*, 1989) the samples from Borgarfjörður Eystri classify as subalkaline dacite to rhyolite and define a group that shows considerable spread relative to the comparative literature data from Iceland. (*b*–*e*) Plots of selected fluid-mobile major and trace elements (Na_2O, CaO, Pb and Rb) *vs.* SiO_2 for Borgarfjörður Eystri dacite to rhyolite samples relative to Icelandic rhyolites. Note, Askja rhyolite samples are singled out again as an example of a cogenetic suite. The documented Icelandic dacite to rhyolite compositions define broad curvilinear trends on all plots, representing dominantly magmatic differentiation processes, whereas the altered Borgarfjörður Eystri rhyolites are more widely scattered, particularly the intra-caldera samples, which records the loss and gain of fluid-mobile elements during secondary hydrothermal overprinting as well as zeolite and secondary silica formation.

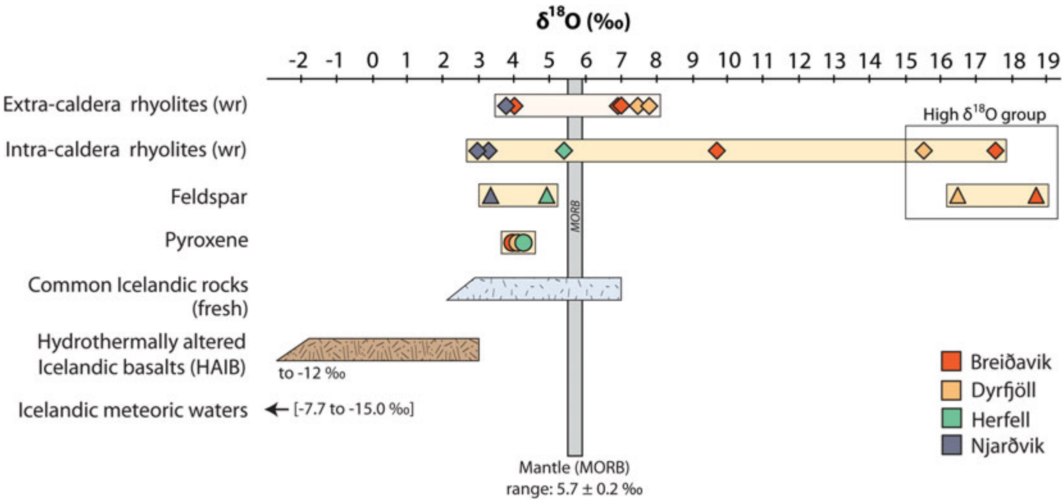

FIG. 5. Oxygen isotope variation in whole-rock and mineral separates of intra- and extra-caldera rhyolites from Borgarfjörður Eystri. Each volcanic system has been assigned a specific colour (see inset). Duplicate analyses were performed for the Dyrfjöll and Hvítserkur ignimbrites of the high $\delta^{18}O$ group (see Table 2). Literature $\delta^{18}O$ values of fresh Icelandic rocks (after Condomines *et al.*, 1983; Sigmarsson *et al.*, 1992; Hemond *et al.*, 1993; Gunnarsson *et al.*, 1998; Hards *et al.*, 2000; Prestvik *et al.*, 2001; Macpherson *et al.*, 2005), and hydrothermally altered Icelandic basalts (HAIB, after Hattori and Muehlenbachs, 1982; Bindeman *et al.*, 2012) are presented in blue and brown, respectively. Literature values of meteoric waters are from Árnason (1976), Hattori and Muehlenbachs (1982) and Rozanski *et al.* (1993).

1993; Gunnarsson *et al.*, 1998; Hards *et al.*, 2000; Prestvik *et al.*, 2001; Macpherson *et al.*, 2005, Carley *et al.*, 2017). The intra-caldera samples, in turn, range from +2.9 to +17.6‰ ($n = 6$), and notably, the Dyrfjöll and Breiðavik (Hvítserkur) rhyolite samples have $\delta^{18}O$ values of +15.5 and +17.6‰, respectively (Fig. 5). These $\delta^{18}O$ values are higher than any Icelandic igneous rock reported previously and duplicate analyses of these samples were carried out to ensure analytical reproducibility (Table 2). Notably, all the extra-caldera rhyolites in this study show LOI values of <3.5 wt.% and are thus within the range of Icelandic rhyolites in the literature in which the LOI values are known to reach up to 5 wt.% (GEOROC database, http://georoc.mpch-mainz.gwdg.de/georoc/). In contrast, the intra-caldera samples have highly variable LOI values, ranging from 0.5 up to 11.0 wt.% (Table 2). A subgroup of these samples shows exceedingly high LOI values (>9 wt.%, see Fig. 6) and concomitant high degrees of replacement by secondary minerals (Figs 2 and 3).

Feldspar separates from the intra-caldera samples show values from +4.9 to +18.7‰ ($n = 3$), which broadly overlap the respective whole-rock $\delta^{18}O$ values. Conversely, the $\delta^{18}O$ values of pyroxene separates from the intra-caldera sample suite define a narrow range of +4.0 to +4.2‰ ($n = 3$, see Fig. 5 and Table 2). Assuming that mineral $\delta^{18}O$ values below +5.5‰ reflect magmatic values, we can use the conversion factor from Harris *et al.* (2005) to estimate $\delta^{18}O$ magma values from pyroxene (which is preferable because it shows less variability than feldspar). A range of magma $\delta^{18}O$ values from +4.3 to +4.5‰ is derived from pyroxene for the rhyolite parental magmas by this approach, which is consistent with pristine magma $\delta^{18}O$ values calculated from zircon from these samples (Berg, 2016, Fig. 7 and Table 2). These low $\delta^{18}O$ magma values are also in good agreement with the range of primary $\delta^{18}O$ magma values reported from other silicic eruptions on Iceland (Bindeman, 2008; Bindeman *et al.*, 2012; Carley *et al.*, 2014; Schattel *et al.*, 2014, Geiger *et al.*, 2016; Carley *et al.*, 2017).

Discussion

The variations in oxygen isotope ratios among the intra- and extra-caldera rhyolites define a sub-group of high $\delta^{18}O$ intra-caldera samples that differs vastly

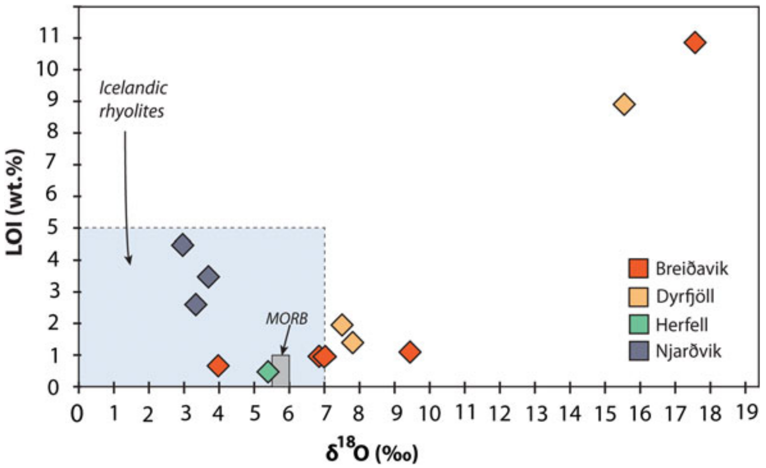

FIG. 6. Whole-rock δ^{18}O variation relative to LOI (loss on ignition) values of the Borgarfjörður Eystri rhyolite samples. Literature values for Icelandic rhyolites are from the GEOROC database, http://georoc.mpch-mainz.gwdg.de/georoc/. The intra-caldera rhyolites span a wide range in δ^{18}O values, which is also reflected in the δ^{18}O composition of feldspar. The high δ^{18}O group notably correlates with elevated LOI values.

from our regional sample suite and from Icelandic rhyolites in general. In the following discussion we use a combination of field observations, petrography and geochemical data to explain the variations in our data set and the processes that could have produced the exceptionally high δ^{18}O values.

Magmatic vs. hydrothermal signatures

The δ^{18}O values of igneous rocks typically reflect a combination of their original magmatic values (e.g. preserved in phenocrysts), and superimposed subsolidus changes to magmatic δ^{18}O values (e.g. Taylor, 1968; Cousens *et al.*, 1993; Bindeman, 2008; Deegan *et al.*, 2012). Mantle-derived basaltic magmas have δ^{18}O values of 5.7 ± 0.2‰ that can increase by up to ~1‰ through closed-system fractional crystallization (Valley *et al.*, 2005; Bindeman, 2008). The addition of external (e.g. crustal or fluid) components can then result in magma δ^{18}O values being shifted above or below this range. The δ^{18}O values resulting from open-system magmatic processes can be distinguished from secondary processes through e.g. study of alteration mineralogy (phyllosilicates, silica, zeolites) and water content of a rock (Taylor, 1968; Götze *et al.*, 2001; Donoghue *et al.*, 2010; Deegan *et al.*, 2012). In such cases, original magmatic oxygen isotope ratios may be preserved in some mineral phases that are more resistant to secondary isotope exchange, such as quartz or zircon (Valley *et al.*, 2005; Bindeman, 2008; Budd *et al.*, 2017) and oxygen isotope disequilibrium between co-existing minerals and/or whole-rock can help determine the degree of overprint by post-crystallization processes (e.g. Cousens *et al.*, 1993; Harris *et al.*, 2005).

Intra- and extra-caldera rhyolites from Njarðvik and Herfell have LOI values that are within the documented range for Icelandic rhyolites (≤5 wt.%, Figs 6 and 7; Owen *et al.*, 2013; GEOROC database), and they have δ^{18}O values similar to reported whole-rock δ^{18}O values of Icelandic rhyolites (Condomines *et al.*, 1983; Sigmarsson *et al.*, 1992; Hemond *et al.*, 1993; Gunnarsson *et al.*, 1998; Hards *et al.*, 2000; Prestvik *et al.*, 2001; Macpherson *et al.*, 2005, Carley *et al.*, 2017). The Herfell ignimbrite yields a magma δ^{18}O estimate from pyroxene that overlaps with magma values estimated from magmatic zircon from the same rock unit (Berg, 2016) and from detrital zircon in the region (Carley *et al.*, 2017). This particular sample is thus interpreted to reflect a magmatic δ^{18}O value (Figs 1, 5 and 7, Table 2). In contrast, rhyolites from the Breiðavik and Dyrfjöll volcanic centres are more variable in terms of both their oxygen isotope ratios and LOI values (Figs 6 and 7). The extra-caldera samples plot together with common Icelandic rocks, and the extra- and intra-caldera samples that are mildly elevated in δ^{18}O have low LOI, whereas intra-caldera samples with elevated δ^{18}O usually show high LOI as well (see Figs 6 and 7).

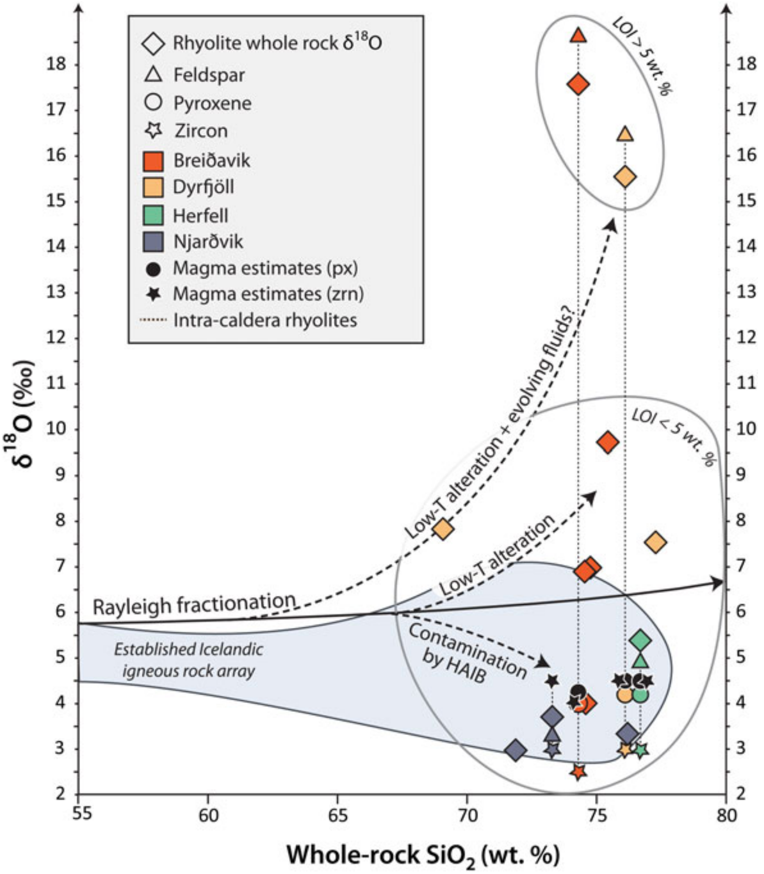

FIG. 7. Oxygen isotope values *vs.* SiO_2 content. Minerals and whole rocks are plotted with their measured isotopic compositions, and are colour coded for each volcanic centre. Selected magma estimates from relatively robust minerals pyroxene (px) and zircon (zrn) are presented with black solid symbols. Pyroxene $\delta^{18}O$ data were converted to magma values following the method outlined in Harris *et al.* (2005). Zircon data and magma estimates are presented in Berg (2016). The intra- and extra-caldera rhyolites show both positive and negative variation around the Raleigh fractionation trend (e.g. Bindeman, 2008), which indicates disequilibrium with alteration fluids. Note that feldspar and some whole rocks are more susceptible to alteration than pyroxene, and that high $\delta^{18}O$ values correlate with the hydrous content of the rocks (see sample IC-HE-IG-22 and IC-URD-IG-5). HAIB = hydrothermally altered Icelandic basalts. LOI = loss on ignition. Icelandic reference field drawn after Sigmarsson *et al.* (1992), Hemond *et al.* (1993), Gunnarsson *et al.* (1998), Hards *et al.* (2000), Prestvik *et al.* (2001) and Macpherson *et al.* (2005).

The extensively hydrated Dyrfjöll and Breiðavik (Hvítserkur) intra-caldera rhyolites samples (LOI = 9–11 wt.%) have whole-rock and feldspar $\delta^{18}O$ values >15‰, i.e. the whole-rocks are ~10‰ higher than the values recorded in their co-existing pyroxene and zircon (Berg, 2016). While the pyroxene and zircon values reflect predominantly magmatic values, the high $\delta^{18}O$ whole-rock and mineral values are not representative of the original magma, and the elevated $\delta^{18}O$ values in Dyrfjöll and Breiðavik (Hvítserkur) intra-caldera rhyolites thus reflect various degrees of secondary alteration processes after deposition. This hypothesis is consistent with the relative paucity of 'igneous' minerals and the presence of opal-C and zeolites in the intra-caldera Dyrfjöll and Breiðavik samples, respectively (Table 1). Secondary alteration would also be consistent with the apparent strong susceptibility of rock groundmass and feldspar to hydrous alteration processes as opposed to pyroxene (cf. Taylor, 1968; Gregory *et al.*, 1989; Cousens *et al.*, 1993). Alternatively, it may be argued that late-stage magmatic assimilation affected the groundmass and feldspar compositions only (cf. Duffield and Ruiz, 1998), but this model is unlikely because assimilation processes on Iceland usually shift magma towards lower $\delta^{18}O$ values (cf. Bindeman, 2008; Bindeman *et al.*, 2012; Gurenko *et al.*, 2015). Moreover, the samples with the highest $\delta^{18}O$ values also have high LOI values and distinct alteration mineralogy, consisting of high-temperature silica, opal-C and zeolites. This convincingly argues against a crustal assimilation origin of the exceptionally high $\delta^{18}O$ values reported in this investigation.

The large oxygen isotope variability in the investigated dacitic-to-rhyolitic whole-rock and mineral pairs from Borgarfjörður Eystri (+2.9 to +17.6‰) must therefore reflect a two-stage evolution for the high $\delta^{18}O$ group, that we envisage as follows: (1) Sub-mantle $\delta^{18}O$ magma values (<5.7‰) recorded in regional whole rocks, pyroxene and some feldspar crystals reflecting combined fractional crystallization of mantle-derived magmas and a degree of assimilation of hydrothermally altered ^{18}O-depleted crust (cf. MacDonald *et al.*, 1987; Valley *et al.*, 2005; Lackey *et al.*, 2008; Bindeman *et al.*, 2012: Zierenberg *et al.*, 2013; Geiger *et al.*, 2016). (2) Variable degrees of post-magmatic, secondary alteration of groundmass and feldspar then occurred in intra-caldera hydrothermal settings, which resulted in the observed hydrothermal alteration mineralogy and the high $\delta^{18}O$ whole-rock and feldspar values for these specific samples (cf. Taylor, 1968). Preferential groundmass alteration is not unusual during secondary alteration processes, and has been documented previously for ignimbrite and rift-zone intrusive rocks elsewhere (e.g. Cousens *et al.*, 1993; Deegan *et al.*, 2012), and effectively reflects an incomplete or partial alteration process. Accepting that the high $\delta^{18}O$ and LOI values reflect hydrothermal alteration (stage 2), then the single sample from Breiðavik caldera with elevated $\delta^{18}O$ but low LOI is probably also part of this group. This sample may have undergone further dehydration, e.g. due to re-heating inside the active Breiðavik caldera (e.g. due to proximity to a small intrusion; Donoghue *et al.*, 2010). The detailed processes that characterize stage 2 are discussed in more detail below.

Origin of high-$\delta^{18}O$ values

A number of processes could be responsible for the high-$\delta^{18}O$ values recorded in several intra-caldera rhyolites from Borgarfjörður Eystri. Below we will discuss: (1) low-temperature hydration; (2) low-temperature hydrothermal alteration; (3) high-temperature isotope exchange processes; and (4) isotope fractionation in fluids by evaporation.

Low-temperature hydration

Glassy volcanic rocks with high H_2O contents are not normally considered compositionally representative of their parent melt, but are commonly products of post-emplacement rehydration. This is the case for explosive eruptive products that lost most of their volatiles during eruption (e.g. Taylor, 1968; Lofgren, 1971*b*; Troll and Schmincke, 2002; Seligman *et al.*, 2016). Icelandic rhyolites usually have LOI contents up to 5 wt.% (Owen *et al.*, 2013; GEOROC database), for example, the Thorsmörk ignimbrite in southern Iceland has a LOI of 3.85 wt.% (Jørgensen, 1980), and the Solheimar ignimbrite from Katla has a LOI of 0.70 wt.% (Lacasse *et al.*, 2007). Sub-solidus hydration processes on Iceland have been shown to dominantly involve meteoric water (Árnason, 1976; Sveinbjörnsdóttír and Johnsen, 1992). Present-day meteoric waters in coastal areas on Iceland show $\delta^{18}O$ values from –8 to –11‰ (Árnason, 1976; Hattori and Muehlenbachs, 1982), and the long-term weighted mean $\delta^{18}O$ value of precipitation in Reykjavik is –7.7‰ (Rozanski *et al.*, 1993). Meteoric waters in Neogene Iceland were probably marginally less depleted in ^{18}O compared to today, because of a warmer Earth and Iceland's slightly lower latitude at 12–14 Ma (e.g. Hattori and Muehlenbachs, 1982; Sheppard, 1986). It follows, therefore, that the intra-caldera rhyolites with elevated $\delta^{18}O$ values and high water contents (LOI = 9 to 11 wt.%), cannot be derived by simple addition of meteoric water, which would lower rather than raise the $\delta^{18}O$ value of the hydrated whole-rock suite.

Low-temperature hydrothermal alteration

The intra-caldera rhyolites with elevated LOI and $\delta^{18}O$ values show a variety of alteration colours and secondary zeolite and silica mineralization (Figs 2*e*–*g* and 3, Tables 1 and 2). Hydrothermal alteration processes on Iceland usually involve the formation of phyllosilicates at a temperature of ~200°C (i.e. kaolinite, smectite, illite, montmorillonite – Kristmannsdóttir, 1982; Gislason and Eugster, 1987) and secondary quartz and/or zeolites at ~150–200°C (Walker, 1960; Walker and Carmichael, 1962; Franzson *et al.*, 2002). Indeed, our quantitative XRD results indicate that our two samples with exceptionally high δ^{18}O values, IC-URD-IG-5 (15.4‰) and IC-HE-IG-22 (16.6‰) contain secondary opal-C and the zeolite-group minerals heulandite–clinoptilolite and mordenite, respectively (see Table 1). Assuming that Neogene Icelandic meteoric water also had a δ^{18}O value of ca. –7.7‰ (Rozanski *et al.*, 1993), clinoptilolite that formed in equilibrium with this water would have a δ^{18}O value of ∼+25‰ at ambient temperature, because the clinoptilolite-water fractionation is +32.9‰ at 20°C (Feng *et al.*, 1999). However, the clinoptilolite-water fractionation decreases significantly at higher temperatures, and Δclinoptilolite-water is +11.4‰ at 200°C, +17.6°C at 100°C and +25.7‰ at 50°C (Feng *et al.*, 1999). Note that fractionation factors for heulandite and mordenite are not available, but it is unlikely that the different zeolites would have significantly different per mil fractionation factors. Similarly, secondary silicification during hydrothermal alteration increases the δ^{18}O value of the rock because of a large silica-water fractionation factor at low-temperature, i.e. Δquartz-water is +11.6‰ at 200°C, +20.7‰ at 100°C and +28.7‰ at 50°C (Matsuhisa *et al.*, 1979; Götze *et al.*, 2001). As a consequence, near-surface hot-spring-type alteration at low temperature in Neogene Iceland could have locally produced a zeolite and silica-rich assemblage with high δ^{18}O values. The mineralogy of the altered intra-caldera rhyolites throughout our sample suite justifies the involvement of secondary replacement minerals to cause ^{18}O enrichment. To reach δ^{18}O whole-rock values of +18‰, the intra-caldera rhyolites would be required to have almost fully equilibrated isotopically with the fluid at 50°C because water with a δ^{18}O value of –7.7‰ would be in equilibrium with quartz with a δ^{18}O value of 21.0‰ and zeolite (clinoptilolite) with a δ^{18}O value of 18.0‰. This scenario, however, is at odds with our mineralogical observations (Fig. 3), as some minerals, such as pyroxene, apparently maintained their original magmatic δ^{18}O values. The data in total leads us to surmise that unrealistically low temperatures (<50°C) would be required during alteration to compensate for pyroxene with magmatic δ^{18}O values by producing exceedingly high groundmass δ^{18}O values. Alternatively, shifts in the isotope composition of the alteration fluids that affected the groundmass of the samples need to be considered, in the sense that alteration fluids affecting the groundmass became progressively more positive with ongoing duration of the alteration process (see next section).

High-temperature isotope exchange processes

Fluids in geothermal systems and hot springs are predominantly sourced from local precipitation (Hoefs, 1973; Árnason, 1976; Donoghue *et al.*, 2010). Circulating ^{18}O-depleted waters in Neogene Iceland (e.g. –7.7‰; Rozanski *et al.*, 1993) would tend to progressively increase their δ^{18}O values along fluid pathways during the course of medium- to high-temperature exchange with the country rock (the 'oxygen shift' of Hoefs, 1973). Such water-rock isotopic exchange is thought to be slow at temperatures <200°C, yet geothermal steam waters at Hekla record an isotopic shift of +7.5‰ and thermal water at the Theistareykir high-temperature field in Northeast Iceland shows an oxygen isotopic shift of up to +6.5‰ (Hoefs, 1973; Sveinbjörnsdóttír *et al.*, 2013). Therefore, at the distal end of a hydrothermal circulation cell, geothermal fluids may become significantly enriched in ^{18}O (e.g. Hoefs, 1973; Donoghue *et al.*, 2008). Hydrothermal alteration in a near-surface hot-spring environment (∼100 to 200°C) fed by waters that already exchanged oxygen at high temperature with the country rock would then produce alteration minerals (clay, zeolites and silica) considerably enriched in ^{18}O. For example, if the alteration fluid is –1‰ rather than –7.7‰, the alteration minerals would be ∼7‰ higher, which would permit crystallization of zeolite and silica with δ^{18}O values ≥+20 and +17‰, respectively, during equilibration at 100°C (cf. Matsuhisa *et al.*, 1979; Feng *et al.*, 1999). By considering a lower temperature for this process, a greater zeolite/silica-water fractionation has to be assumed. The wide range of δ^{18}O values recorded in the intra-caldera rhyolites studied could hence be accounted for by epithermal (∼100 to 200°C) interaction with evolved fluids that had undergone previous O-isotope shifts by progressive water-rock interaction during hydrothermal circulation.

Evaporation of thermal pools

Another process by which the δ^{18}O composition of fluids can be raised is through Rayleigh-type distillation during evaporation (Craig, 1963). In a subaerial and evaporating hydrothermal system, the residual liquid becomes enriched in ^{18}O (Craig, 1963; Faure, 1986). Progressive vapour loss through evaporation from, for example, a hot or even boiling lake would therefore increase the δ^{18}O value of the remaining water gradually and any mineral that eventually precipitates from such a fluid would similarly become enriched in ^{18}O. In fact, when quartz precipitates from an aqueous liquid in an open hydrothermal system undergoing

30% vapour loss and a temperature decline from 300 to 150°C, Rayleigh distillation will increase the δ^{18}O value of the quartz by ~10‰ (cf. Chiba *et al.*, 1989; Rhodes and Oreskes, 1999; Donoghue *et al.*, 2008). As a result of evaporation processes, shallow surface brines in modern Iceland usually have δ^{18}O values that are 3‰ higher than the brine water measured in drill holes at these sites (e.g. +2 and –1‰ respectively, Ólafsson and Riley, 1978). It is thus plausible that boiling and evaporation can drive the meteoric-hydrothermal alteration fluids towards further enrichment and promote subsequent high δ^{18}O whole-rock values in the vicinity of crater and caldera lakes.

Model for high-δ^{18}O intra-caldera rhyolites in Borgarfjörður Eystri

Fossil geothermal systems associated with central volcanoes are common in the Quaternary and Neogene formations of Iceland (Arnórsson, 1995), and might have also provided favourable conditions for boiling water systems within e.g. the Dyrfjöll and Breiðavik calderas. A ~10‰ increase in the δ^{18}O value of meteoric waters is possible via Rayleigh evaporation in such pools upon hydrothermal heating and associated vapour flux (e.g. Giggenbach and Stewart, 1982). The high δ^{18}O waters of a caldera lake can then feed back into the hydrothermal system via e.g. caldera faults and fractures (e.g. Walter and Troll, 2001; Troll *et al.*, 2002; Donoghue *et al.*, 2008), thus promoting infiltration of the underlying rock succession and permitting progressive fluid-rock interaction. This would lead to progressively ^{18}O-enriched fluids over the lifetime of such a circulating hydrothermal system and would result in elevated δ ^{18}O values in the altered rocks that host the high-level (near surface) part of the system.

In this respect, we note that caldera margins are particularly susceptible to low-temperature hydrothermal alteration because fumarole activity at these localities is usually cooler than in the centre of the caldera (e.g. Taylor, 1968; Walter and Troll, 2001; Donoghue *et al.*, 2008). Importantly, the intra-caldera rhyolites with the highest δ^{18}O values (IC-URD-IG-5 and IC-HE-IG-22) are found at the margins of former intra-caldera lakes (Fig. 1), where epithermal (~100 to 200°C) alteration was probably dominant. This is similar to the occurrence of altered, marginal intra-caldera tuffs in other settings, such as those at Fuente de Los Azulejos on Gran Canaria. There, low-temperature hydrothermal caldera margin rocks show intense weathering colours from green to pink and a mineral assemblage of zeolites, clays, sheet silicates and secondary silica with δ^{18}O compositions of up to +18‰ (Donoghue *et al.*, 2008). Although at lower latitude than Iceland, the Fuente de Los Azulejos caldera margin rocks are also enriched in ^{18}O beyond the equilibrium fractionation of the phases involved when local meteoric water is taken as the dominant water source. Similarly, magma-rock interaction involving circulating hydrothermal fluids has been suggested to have played a significant role in the formation of the Los Azulejos rocks by producing ^{18}O enriched hydrothermal fluids. This leads us to suggest that δ^{18}O enriched hydrothermal fluids may be widespread in intra-caldera and caldera-margin settings.

With this model for the high δ^{18}O sample group, the variation among the intra-caldera rhyolites is explained by the presence of former caldera lake water that fed fumarole activity, thus enabling localized formation of exceptionally ^{18}O enriched hydrothermal fluids that are now bound in a range of hydrous replacement minerals. The lower δ^{18}O values in intra-caldera samples from both Njarðvik and Herfell calderas coincide with an absence of hyaloclastites in these two calderas, which hints at the absence of major caldera lakes and suggests a comparatively dry environment at these sites. The H_2O-poor, intra-caldera rhyolite with mildly elevated δ^{18}O values from the centre of Breiðavik caldera (δ^{18}O = 9.7‰, IC-HF-IG-31), in turn, was probably affected initially by the enriched ^{18}O hydrothermal waters of the caldera lake, much like the high-δ^{18}O group, but was subsequently dehydrated during later heating, conceivably during a magmatic resurgence episode in the central part of the caldera. A similar situation was reported by e.g. Donoghue *et al.* (2010) from Gran Canaria. There, the intra-caldera cone sheet swarm contains individual intrusive sheets that are hydrothermally altered, but some were subsequently dehydrated due to later incoming cone sheet intrusions, thus offering an analogue for the Icelandic sample in question.

Summary and implications

Extra-caldera rhyolites on Iceland record regional low δ^{18}O magmatic signatures and an element of 'regular' low-temperature alteration, whereas the δ^{18}O compositions of some of the intra-caldera rhyolites reported here are among the highest δ^{18}O values thus far known for igneous rocks on Iceland. Although at this time we present a relatively small δ^{18}O dataset, our new data are consistent with: (1)

secondary alteration textures; (2) geographical position of samples at the margins of former caldera lake settings; (3) whole-rock H_2O contents; (4) alteration mineralogy; and (5) scatter in major- and trace-element compositions of altered high-silica rocks versus well defined evolutionary trends of unaltered intermediate and high-silica rock suites on Iceland. It appears that the high-$\delta^{18}O$ intra-caldera rhyolites of our study underwent hydrothermal alteration by fluids with higher $\delta^{18}O$ values than local meteoric waters on Iceland. Fluid enrichment may have been achieved through progressive wall-rock exchange, or it may have been an effect of surface evaporation in caldera lake settings, or a combination of these processes. Thus, low-temperature meteoric waters were potentially capable of feeding circulating hydrothermal systems with ^{18}O-enriched fluids in the investigated intra-caldera lake setting, proably as a result of fractionation due to interaction with the rocks encountered during the course of fluid circulation. Another factor to achieve exceptionally enriched ^{18}O fluids could be evaporation in hot or boiling intra-caldera lakes. Large oxygen isotopic shifts are plausibly linked to caldera margins because of intense fracturing and rapid heat loss of the system at these sites (e.g. Donoghue *et al.*, 2008), which may reflect a more widespread phenomenon in intra-caldera and especially caldera margin settings.

The wider implication of our finding is that high-$\delta^{18}O$ rocks may be locally present in the Icelandic crust as they might derive from old hydrothermal systems now buried under extensive lava piles. This implies that significant heterogeneity in $\delta^{18}O$ composition may exist locally within the Icelandic crust as spatially restricted domains that vastly exceed $\delta^{18}O$ mantle values. This realization could be important in relation to digestion of Icelandic crust by magma as discrete high-$\delta^{18}O$ pockets in buried central volcanoes may complicate $\delta^{18}O$ magmatic signatures if taken up by ascending melts. Indeed, high $\delta^{18}O$ domains in the Icelandic crust may also help to explain the occurrence of occasional high $\delta^{18}O$ zircon on Iceland as a result of partial melting of preconditioned, altered crust (cf. Gurenko *et al.*, 2015).

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