

## Sulfur isotope ratios of Icelandic rocks

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**Abstract.** Sulfur isotope ratios have been determined in 27 selected volcanic rocks from Iceland together with their whole rock chemistry. The  $\delta^{34}\text{S}$  of analyzed basalts ranges from  $-2.0\text{‰}$  to  $+0.4\text{‰}$  with an average value of  $-0.8\text{‰}$ . Tholeiitic and alkaline rocks exhibit little difference in  $\delta^{34}\text{S}$  values but the intermediate and acid rocks analyzed have higher  $\delta^{34}\text{S}$  values up to  $+4.2\text{‰}$ . It is suggested that the overall variation in sulfur isotope composition of the basalts is caused by degassing. The small range of the  $\delta^{34}\text{S}$  values and its similarity to other oceanic and continental basalts, suggest that the depleted mantle is homogeneous in its sulfur isotope composition. The  $\delta^{34}\text{S}$  of the depleted mantle is estimated to be within the range for undegassed oceanic basalts,  $-0.5$  to  $+1.0\text{‰}$ .

hira et al. 1973). The average  $\delta^{34}\text{S}$  values for a large number of submarine fresh basalts from mid ocean ridges and oceanic islands have been determined to  $+0.6\text{‰}$  (Grinenko et al. 1975),  $+0.7\text{‰}$  (Sakai et al. 1982) and  $+0.3 \pm 0.5\text{‰}$  (Sakai et al. 1984). Degassed basalts from Kilauea had lower average  $\delta^{34}\text{S}$  values of  $-0.8\text{‰}$  (Sakai et al. 1982).

The purpose of the present study is to determine the  $\delta^{34}\text{S}$  of selected volcanic rocks from Iceland in order to estimate the  $\delta^{34}\text{S}$  of the mantle beneath Iceland and to compare it with  $\delta^{34}\text{S}$  values from other geotectonic environments.

### Methods

#### Selection of samples

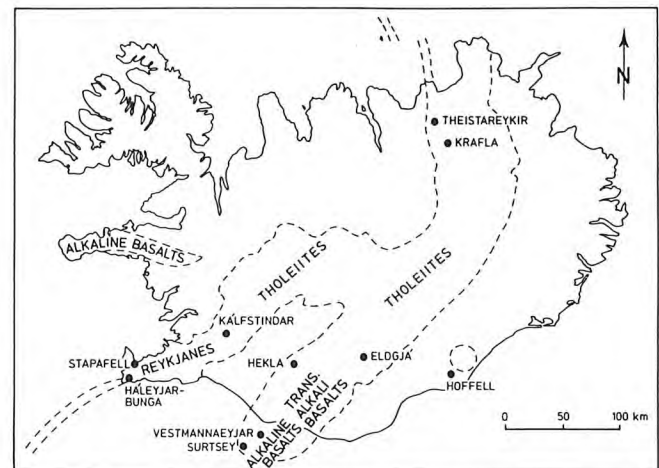
The samples selected cover a range in chemical composition representative of the rock suites occurring in Iceland. The tholeiitic rock suite, dominating the rift zones, is represented by samples from the Krafla-Namafjall and Theistareykir fissure swarms in N Iceland. In addition a few samples from the propagating rift in SE Iceland were analyzed. In order to estimate the sulfur isotope

### Introduction

In Iceland evolved rocks are more abundant than on the submerged ocean ridges. Isotope studies have demonstrated significant differences in the isotope ratios of Icelandic rocks (Muehlenbachs et al. 1974; Sun and Jahn 1975; O'Nions et al. 1976; Zindler et al. 1979; Hattori and Muehlenbachs 1982; Schilling et al. 1982; Condominnes et al. 1983; Kurz et al. 1985) relative to MORB.

Jakobsson (1972, 1979) and Imsland (1983) recognized three main rock series in Iceland and showed that the rift zone volcanism is exclusively tholeiitic. The volcanism outside the rift zone is represented by transitional alkaline and alkaline rock series (Fig. 1). Some petrogenetic models (Oskarsson et al. 1982, 1985; Steinthorsson et al. 1985) suggest that the only primary mantle derived melts are of primitive olivine tholeiite composition. All other magmas are derived from olivine tholeiites by fractional crystallization in crustal magma chambers (O'Hara 1977) or by partial melting of hydrated crust. Other models of Icelandic basalt petrogenesis require mantle heterogeneities; Schilling (1973) suggested two different sources and variable mixing between the magmas to explain the chemical composition of Icelandic rocks. On a global scale, Sr and Nd isotope data (DePaolo and Wasserburg 1976; DePaolo 1979; Zindler and Hart 1986) support a chemically heterogeneous mantle.

Sulfur isotope measurements of MORB's and OIB's have shown little variation: Two dredged basalts from the Mid-Atlantic Ridge ranged from  $+0.3$  to  $+1.6\text{‰}$  (Kane-



**Fig. 1.** Petrologic distribution of rocks within the neovolcanic zone of Iceland. The tholeiitic rocks are confined to the rift zone, in contrast to the alkaline and transitional alkaline rock series formed in the off rifting zones. The sampling sites are shown as filled circles. Heimaey island belongs to the islands of Vestmannaeyjar



fractionation during degassing of basaltic magma, four pillow lavas of olivine tholeiite composition were analyzed. Samples that presumably have preserved a larger part of their original sulfur content were preferentially selected i.e. aphyric or glassy superficial parts of lava flows, volcanic spatter and bombs. The rocks are completely fresh postglacial volcanics apart from the pillows which formed during the last glaciation and a gabbro sample from Hoffell (SE-Iceland) of Pliocene age.

#### Analytical procedures

Chemical analyses of all fresh rocks were made at C.N.R.S. in Nancy, France with an optical emission spectrograph equipped with a plasma excitation source (Govindaraju et al. 1977) or at the Nordic Volcanological Institute in Reykjavik, Iceland by XRF or microprobe techniques.

A chemical extraction was designed to obtain  $\delta^{34}\text{S}$  ratios for sulfide sulfur, sulfate sulfur and total sulfur, because separated mineral phases seldom provide a complete picture of sulfur isotope systematics. Sulfur was extracted as  $\text{H}_2\text{S}$  from the powdered rocks at controlled temperature in a nitrogen gas flow. Evolved  $\text{H}_2\text{S}$  was precipitated as  $\text{CdS}$  and converted to  $\text{Ag}_2\text{S}$ . Extraction of total sulfur was made within (II) in dehydrated phosphoric acid at  $280^\circ\text{C}$  (Kiba et al. 1955; Sasaki et al. 1979). The recovery of sulfide and sulfate sulfur was made in several steps according to the methods developed by Schneider (1970). The sulfide extraction was performed with 12 M HCl acid in the presence of granular Al at  $100^\circ\text{C}$ . The residue was treated with a mixture of HCl, HI and  $\text{H}_3\text{PO}_2$  (Thode et al. 1961) to extract the sulfate remnant in the rock sample. Pyrite, if present will not be extracted as sulfide but will react under the sulfate fraction. However, the sulfides present in these Icelandic lavas studied are most likely pyrrhotite, pentlandite or some cupriferous mineral if the sulfide mineralogy is similar in Icelandic as Hawaiian lavas (Desborough et al. 1968) or submarine basalts (Kanehira et al. 1973; Mathez 1976).

The sulfur concentration in the rocks was determined by weighing the recovered amount of  $\text{Ag}_2\text{S}$  from the total sulfur extractions. This provides only a semiquantitative estimate, as some of the  $\text{CdS}$  and  $\text{Ag}_2\text{S}$  is lost on glass, tubing and filter papers. However, almost half of the determined rocks in this study have been analyzed by XRF using standard addition procedures (Parviainen and Oskarsson, unpublished data). Agreement between calculated amounts from the extractions and the XRF data are better than 90% apart from concentrations less than 50 ppm where the agreement is not as good. The analytical sulfur values in this study are estimated to have an uncertainty of  $\pm 5\%$ , apart from low concentration data where the uncertainty is around  $\pm 10\%$ . Blank test of the "Kiba reagent" did not reveal any measurable amount of sulfur dissolved from the glass.

$\text{Ag}_2\text{S}$  was mixed with a fivefold excess  $\text{Cu}_2\text{O}$ , and reacted at a temperature of  $1100^\circ\text{C}$  (Robinson and Kusakabe 1975) and the  $\text{SO}_2$  was measured with a Micromass 602 C mass spectrometer at the Naturhistoriska Riksmuseet in Stockholm.

The sulfur isotope composition is given in the conventional  $\delta$  notation relative to CDT (Cañon Diablo Troilite). The samples were run in duplicate whenever possible. The accuracy is well within  $\pm 0.2\%$  for most samples confirmed by repeated measurements at the Institute of Geological Sciences in London. However, smaller samples showed slightly less accuracy.

#### Results

The chemical compositions of the investigated rocks are listed in Table 1, and the sulfur contents and isotopic compositions are given in Tables 2 and 3. A brief petrographic characterization of each sample is included in Table 3. The sulfur content of all samples varies between 10–670 ppm and the distribution of  $\delta^{34}\text{S}$  is from  $-2.0$  to  $+4.2\%$  (Tables 2 and 3). The variation of the basalts  $\delta^{34}\text{S}$  is from  $-2.0$  to  $+0.4\%$  and the mean basalt  $\delta^{34}\text{S}$  is  $-0.8\%$ .

Table 1. Chemical composition in wt% of the selected Icelandic rocks. The Stapafield pillow lavas are represented by their mean (sample 20 SP mean) as well as samples 7 and 8. Tot. vol. (Total volatiles) =  $\text{CO}_2 + \text{S} + \text{H}_2\text{O}$

| No                      | 1     | 2     | 3     | 4      | 5     | 6      | 7-8     | 9       | 10    | 11    | 12     | 13    | 14    | 15    | 16    | 17    | 18    | 19     | 20      |
|-------------------------|-------|-------|-------|--------|-------|--------|---------|---------|-------|-------|--------|-------|-------|-------|-------|-------|-------|--------|---------|
| Sample                  | TH30  | TH5   | N218  | N131   | N508  | KRA727 | GJA80GC | KRA8111 | N206  | A-THO | D-2    | KAL   | SUR   | VEB   | B-ALK | H70T  | I-ICE | B-GAB  | SP mean |
| $\text{SiO}_2$          | 47.33 | 48.22 | 48.50 | 50.30  | 48.60 | 48.52  | 48.90   | 49.70   | 56.66 | 74.48 | 49.00  | 47.30 | 45.80 | 47.36 | 48.25 | 53.91 | 53.82 | 45.06  | 47.17   |
| $\text{TiO}_2$          | 0.78  | 1.16  | 2.40  | 1.95   | 2.12  | 1.53   | 1.48    | 2.07    | 1.64  | 0.27  | 0.27   | 1.46  | 2.28  | 3.04  | 4.22  | 1.92  | 1.99  | 3.24   | 1.72    |
| $\text{Al}_2\text{O}_3$ | 13.41 | 16.56 | 13.30 | 13.40  | 13.09 | 14.60  | 14.60   | 13.00   | 13.25 | 12.07 | 16.05  | 15.23 | 16.05 | 15.46 | 12.38 | 14.66 | 14.78 | 14.86  | 1.22    |
| $\text{Fe}_2\text{O}_3$ | 0.92  | 1.74  | -     | -      | 4.08  | 1.87   | -       | -       | 1.47  | 0.88  | 0.70   | 1.13  | 1.80  | 3.38  | 4.12  | 4.48  | 4.59  | 4.12   | 1.86    |
| FeO                     | 8.66  | 9.07  | 12.50 | 15.90  | 11.62 | 10.71  | 11.60   | 15.00   | 9.06  | 2.55  | 7.05   | 9.46  | 10.30 | 10.48 | 10.81 | 7.20  | 7.76  | 10.81  | 9.36    |
| MnO                     | 0.18  | 0.19  | 0.21  | 0.26   | 0.25  | 0.21   | 0.22    | 0.27    | 0.20  | 0.10  | 0.19   | 0.19  | 0.21  | 0.25  | 0.22  | 0.25  | 0.26  | 0.18   | 0.20    |
| MgO                     | 13.24 | 7.74  | 7.80  | 5.30   | 6.18  | 8.80   | 8.51    | 5.77    | 3.50  | 0.10  | 10.11  | 9.81  | 7.77  | 4.59  | 5.35  | 3.01  | 3.24  | 6.97   | 10.13   |
| CaO                     | 12.29 | 12.49 | 12.50 | 10.20  | 10.18 | 11.35  | 12.10   | 10.50   | 7.23  | 1.75  | 14.95  | 11.35 | 9.70  | 8.39  | 10.00 | 6.68  | 7.01  | 12.57  | 11.77   |
| $\text{Na}_2\text{O}$   | 1.53  | 2.18  | 2.10  | 2.55   | 2.52  | 2.11   | 2.04    | 2.38    | 3.07  | 4.31  | 1.78   | 2.08  | 4.03  | 4.45  | 2.97  | 3.93  | 3.86  | 2.21   | 1.96    |
| $\text{K}_2\text{O}$    | 0.04  | 0.12  | 0.17  | 0.40   | 0.36  | 0.24   | 0.15    | 0.29    | 1.19  | 2.72  | 0.02   | 0.13  | 0.63  | 1.11  | 0.77  | 1.34  | 1.27  | 0.27   | 0.27    |
| $\text{P}_2\text{O}_5$  | 0.07  | 0.10  | -     | -      | 0.25  | 0.17   | 0.15    | 0.22    | 0.34  | 0.04  | 0.02   | 0.14  | 0.40  | 0.62  | 0.56  | 0.87  | 0.99  | 0.14   | 0.25    |
| Tot. vol.               | 0.20  | 0.18  | -     | -      | 0.51  | 0.29   | -       | -       | 0.97  | 0.15  | 0.06   | 0.85  | 0.81  | 0.32  | 0.25  | 0.41  | 0.19  | 0.88   | 0.52    |
| Total                   | 98.65 | 99.85 | 99.48 | 100.26 | 99.76 | 100.40 | 99.75   | 99.20   | 98.58 | 99.42 | 100.20 | 99.13 | 99.78 | 99.45 | 99.90 | 98.66 | 99.76 | 101.51 | 99.41   |

**Table 2.** Concentration and isotopic composition of sulfur of 4 pillows from Stapafell on the Reykjanes peninsula

| Sample             | $\Sigma S$ conc (ppm) | $\delta^{34}S_{\text{sulfide}}$ (‰) | $\delta^{34}S_{\text{sulfate}}$ (‰) | $\delta^{34}S_{\text{ES}}$ (‰) |
|--------------------|-----------------------|-------------------------------------|-------------------------------------|--------------------------------|
| SP1 I <sup>a</sup> | 430                   | -1.4                                | +0.2                                | -1.3                           |
| SP1 R              | 460                   | -0.8                                | -0.1                                | -1.2                           |
| SP2 I              | 540                   | -1.4                                | 0.0                                 | -1.2                           |
| SP2 R              | 490                   | -1.4                                | -1.0                                | -1.0                           |
| SP3 I              | 360                   | -0.8                                | -                                   | -0.7                           |
| SP3 R              | 410                   | -1.3                                | -0.2                                | -1.2                           |
| SP4 I              | 340                   | -0.7                                | -                                   | -0.8                           |
| SP4 R              | 450                   | -1.4                                | +0.4                                | -1.1                           |
| Mean I             | 420                   | -1.1                                | +0.1                                | -1.0                           |
| Mean R             | 450                   | -1.2                                | -0.2                                | -1.1                           |
| Mean all           | 440                   | -1.2                                | -0.1                                | -1.1                           |

<sup>a</sup> The respective pillow is marked with a number from 1–4. *I* interior and *R* rim

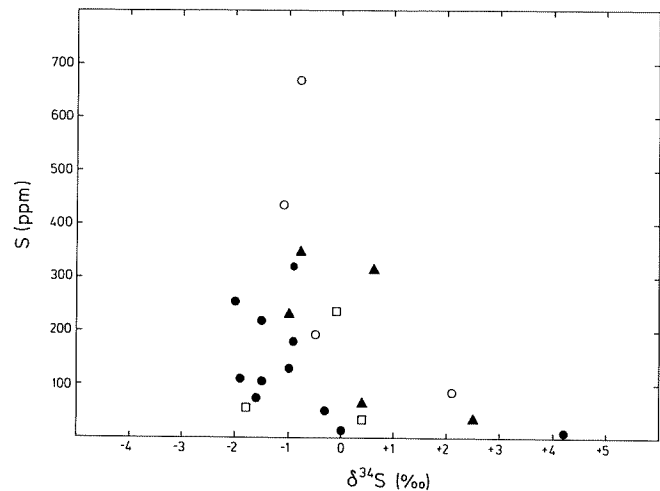
**Table 3.** Sulfur concentration and isotopic composition of Icelandic rocks. Added to the table is a short description of the samples

| No | Sample  | S conc (ppm) | $\delta^{34}S_{\text{sulfide}}$ (‰) | $\delta^{34}S_{\text{sulfate}}$ (‰) | $\delta^{34}S_{\text{ES}}$ (‰) |
|----|---------|--------------|-------------------------------------|-------------------------------------|--------------------------------|
| 1  | TH30    | 130          | -1.1                                | -                                   | -1.0                           |
| 2  | TH5     | 110          | -                                   | -                                   | -1.5                           |
| 3  | N218    | 10           | -                                   | -                                   | 0.0                            |
| 4  | N131    | 70           | -                                   | -                                   | -1.6                           |
| 5  | N508    | 320          | -                                   | -                                   | -0.9                           |
| 6  | KRA727  | 180          | -                                   | -                                   | -0.9                           |
| 7  | GJA80G  | 220          | -1.6                                | -0.9                                | -1.5                           |
| 8  | GJA80C  | 110          | -                                   | -1.8                                | -1.9                           |
| 9  | KRA8111 | 260          | -                                   | -                                   | -2.0                           |
| 10 | N206    | 50           | -                                   | -                                   | -0.3                           |
| 11 | A-THO   | 10           | -                                   | -                                   | +4.2                           |
| 12 | D-2     | 90           | -                                   | -                                   | +2.1                           |
| 13 | KAL     | 670          | -2.0                                | +4.1                                | -0.8                           |
| 14 | SUR     | 230          | -                                   | -                                   | -1.0                           |
| 15 | VEB     | 350          | -6.8                                | -0.5                                | -0.8                           |
| 16 | B-ALK   | 70           | -                                   | -                                   | +0.4                           |
| 17 | H70T    | 310          | -                                   | +1.0                                | +0.6                           |
| 18 | I-ICE   | 30           | -                                   | -                                   | +2.5                           |
| 19 | B-GAB   | 190          | +0.1                                | -                                   | -0.5                           |

**Characterisation:**

All samples are from lava flows unless otherwise noted 1 TH30. Olivine tholeiite. Theystareykir; 2 TH5. Olivine tholeiite. Theystareykir; 3 N218. Olivine tholeiite. Krafla-Namafjall; 4 N131. Tholeiite. Krafla-Namafjall; 5 N508. Tholeiite. Krafla eruption December 1975. Glassy; 6 KRA727. Olivine tholeiite. Krafla eruption September 1977. Glassy spatter; 7 GJA80G. Olivine tholeiite. Krafla eruption July 1980. Glassy surface of lava flow close to eruptive fissure; 8 GJA80C. Ditto but more crystalline from interior of flow; 9 KRA8111. Tholeiite. Krafla eruption in November 1981 glassy; 10 N206. Basaltic icelandite. Krafla-Namafjall; 11 A-THO. Rhyolite (Obsidian). Krafla-Namafjall; 12 D-2. Picrite. Reykjanes (Haleyjarbunga). Sulfur concentration in the sample highly variable, which suggests seawater contamination; 13 KAL. Olivine tholeiite. Kalfstindar. Glassy rim of pillow; 14 SUR. Alkali olivine basalt. Surtsey eruption 1963–1967; 15 VEB. Hawaiite. Heimey 1973. Volcanic bomb; 16 B-ALK. FeTi basalt. Eldgja; 17 H70T. Icelandite. Hekla 1970. Tephra; 18 I-ICE Ditto, but from lava flow; 19 B-GAB. Gabbro. Hoffell

The four pillow lavas from Stapafell (Fig. 1) are chemically homogeneous and represented with their mean in Table 1. The sulfur concentration in the pillow lavas ranges between 330–540 ppm and their sulfur isotope composition



**Fig. 2.** Sulfur concentration plotted against sulfur isotope composition of Icelandic rocks. The transitional alkaline and the alkaline rocks are represented by *triangles* and tholeiites represented by *circles* apart from the tholeiites from Reykjanes peninsula analysed by Sakai et al. (1980) which are included in the figure as *squares*. The *filled circles* are samples from Krafla-Namafjall and Theistareykir fissure swarms

shows little variation (Table 2). The sulfur isotope fractionation values between sulfate and sulfide, between 1–2‰, are to be compared with the largest  $\delta^{34}S$  fractionation between sulfide and sulfate found amounting to more than 6‰ in samples KAL (13) and VEB (15) (Table 3).

Glassy samples have higher sulfur concentration than the more crystalline rocks, exemplified by samples 7 and 8 from the Krafla eruption in July 1980. The glassy surface sample of the lava flow contains twice as much sulfur as the more crystalline interior sample. The glassy sample also has a slightly higher  $\delta^{34}S$  value but an overall relationship between the sulfur content and the sulfur isotope composition in all the samples (Fig. 2) is not observed.

The rock samples from the Krafla-Namafjall fissure swarm cover a composition from olivine tholeiite to rhyolite and a  $\delta^{34}S$  variation from -2.0 to +4.2‰ (Table 3). A simple relation between the chemical composition of the rock and its sulfur content or isotopic composition is not evident in the rocks as a whole nor in the Krafla-Namafjall data alone. However, the rhyolite, the two icelandites and the transitional rock series samples have slightly higher  $\delta^{34}S$  as compared to other samples.

**Discussion**

The sulfur content of the Stapafell pillow lavas ( $450 \pm 100$  ppm) is low compared to Moore and Fabbi's (1971) estimate of juvenile sulfur ( $800 \pm 150$  ppm), but close to the average sulfur concentration measured by them in samples from the interior of the pillows (540 ppm). All the Stapafell samples could have lost sulfur through cracks and joints as the sampled pillow rims (outer 2 cm) may be too wide to ensure only undegassed parts were sampled. The low sulfate content (inferred from the very low yield of the sulfate extraction) and the small fractionation between sulfate and sulfide in the pillows indicate that the isotopic disequilibrium between sulfate and sulfide is caused by de-

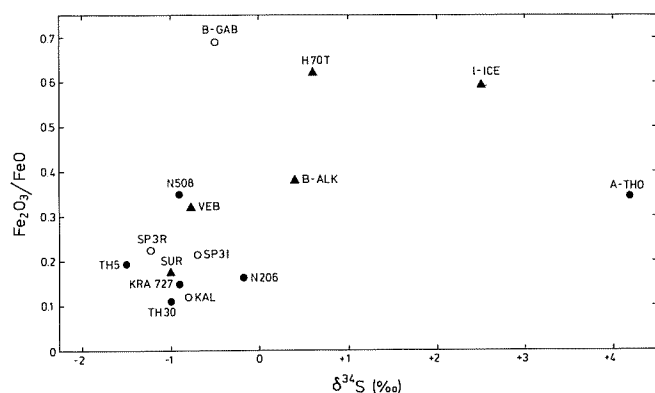


Fig. 3. Correlation of  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio with  $\delta^{34}\text{S}$  values. The *triangles*: alkaline and transitional alkaline rocks. *Filled circles*: tholeiites from Krafla-Namafjall and Theistareykir fissure swarms. *Open circles*: other tholeiites

gassing. The other rocks investigated in this study are also degassed with the exception of the Kalfstindar pillow (KAL), as inferred from the sulfur content and also from geological evidence (Gunnlaugsson 1977).

The sulfur isotope fractionation of 6.2‰ between sulfide and sulfate in the KAL and VEB samples points towards an isotope equilibrium temperature of around 850°C (Miyoshi et al. 1984). This temperature is lower than the solidus temperature of the olivine tholeiite, and the measured temperature of 1030°C in the erupting Heimaey lava (Thorarinsson et al. 1973). Miyoshi et al. (1984) noted that isotopic equilibrium between sulfide and sulfate was attained within 30 min at 810°C in solidified alkali-chloride melts. These observations confirm the results from studies of Kilauean basalts (Sakai et al. 1982) that sulfur isotope exchange is rapid and that equilibrium is attained at magmatic temperatures in silicate melts.

Very similar results are obtained by comparing subaerially degassed basalts of Hawaii and this study from Iceland. Firstly, very small fractionation is found between sulfide and sulfate in the rocks and secondly, the sulfate content of the rocks is low and thirdly, both the average  $\delta^{34}\text{S}$  values and the range in  $\delta^{34}\text{S}$  of the rocks are nearly the same. Sakai et al. (1982) suggested that heavy  $\text{SO}_2$  is lost from the magma and light sulfide is preferentially present in the solidified rocks, thus explaining the light sulfur in Kilauean tholeiites. The close similarity between the present Icelandic isotopic data with the Hawaiian ones suggests a similar interpretation for a majority of the samples. Volcanic gas samples from the Krafla eruption in July 1980 had  $\delta^{34}\text{S}$  values of +3.4‰, -0.4‰ and -1.2‰, decreasing through time (Torssander 1988) and this suggests that heavy sulfur was preferentially lost from the magma. The rock samples 7 and 8 from the same eruption confirm this further because enrichment of  $^{32}\text{S}$  must have occurred through time in the lava to yield the different sulfur isotope compositions of the two samples. A similar isotope composition in the Icelandic and Kilauean tholeiite magmas prior to degassing is thus suggested.

A plot of the  $\text{Fe}_2\text{O}_3/\text{FeO}$  versus  $\delta^{34}\text{S}$  (Fig. 3) indicates some correlation between high  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios and high  $\delta^{34}\text{S}$  values, with the exception of sample B-GAB. Deuteric oxidation could have occurred in many of the samples caus-

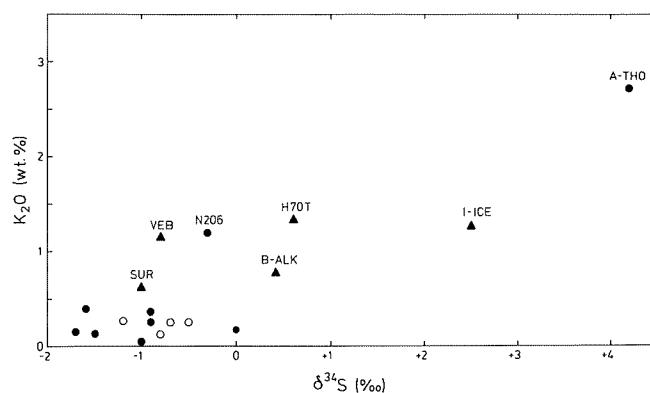


Fig. 4. Plot of  $\text{K}_2\text{O}$  versus  $\delta^{34}\text{S}$  in Icelandic rocks. Increased potassium concentration correlates with heavier  $\delta^{34}\text{S}$  ratios. Alkaline and transitional alkaline rocks plotted as *triangles*, tholeiites from Krafla-Namafjall and Theistareykir fissure swarms as *filled circles* and other tholeiites as *open circles*

ing the redox ratio between the ferric and ferrous ion to increase. Enrichment of  $^{34}\text{S}$  in the melt occurs during effervescence if the sulfate:sulfide ratio (and  $f_{\text{O}_2}$ ) is high (Sakai et al. 1982). Taylor (1986) showed that the initial degassing from Kilauean magma appeared to be dominated by reduction and decrease of  $\delta^{34}\text{S}$  in the melt and the more late stage subaerial degassing appeared to be dominated by oxidation and increase of  $\delta^{34}\text{S}$  in the molten rock. It is implied that the degassing process could be the main cause of the distribution of  $\delta^{34}\text{S}$ , even allowing some samples to become richer in  $^{34}\text{S}$  during effervescence, as seen in the  $\delta^{34}\text{S}$  data from the Hekla 1970 tephra (H70T) and lava (I-ICE) and the corresponding incrustations (Torssander 1988). Isotope balance calculations for the Hekla samples results in a  $\delta^{34}\text{S}_{\text{SS}} = -0.8\%$ , if the  $\Sigma\text{S}$  content is 700 ppm prior to degassing and if a Rayleigh distillation process is assumed.

Icelandic  $\delta^{18}\text{O}$  data (Muehlenbachs et al. 1974; Hattori and Muehlenbachs 1982) may be correlated with evolutionary indicators such as  $\text{K}_2\text{O}$ , where high  $\text{K}_2\text{O}$  and LIL abundances in general correlate with low  $\delta^{18}\text{O}$  values (Oskarsson et al. 1982). This has been taken to indicate large scale assimilation of hydrothermally altered basalts into magmas that evolve in very shallow (3–7 km) magma chambers because 1) The hydrothermal water is of meteoric origin causing the low  $\delta^{18}\text{O}$  values and 2) In Icelandic basalts, potassium has been shown to respond rapidly to these shallow assimilation processes due to the very low potassium abundances encountered in mantle derived rocks (Oskarsson et al. 1982). Figure 4 shows a correlation between  $\text{K}_2\text{O}$  and  $\delta^{34}\text{S}$ . During hydrothermal alteration in the geothermal system isotopically heavy  $\text{SO}_4^{2-}$  will leave the system continuously and the comparatively light  $\text{H}_2\text{S}$  will precipitate to some extent (Torssander 1986). This is due to the low solubility of sulfides relative to sulfates. Unlike the  $\delta^{18}\text{O}$  data, covariation with high  $\text{K}_2\text{O}$  and heavy sulfur could thus not be attributed directly to water-rock interaction, but if the higher  $\delta^{34}\text{S}_{\text{SS}}$  of the transitional alkaline rocks and intermediate and silicic rocks is due to partial melting and reworking of crust then the opposite relationship could be expected for the  $\delta^{34}\text{S}$  values.

Sulfur isotope fractionation during partial melting of the crust occurs if the distribution of sulfide and sulfate is different in the silicic melt and the hydrated basaltic host

rock. The formation of rhyolitic melt from a basic source is a chemical fractionation process in itself. The alkalis and silica are enriched in the rhyolite, whereas the iron oxides are left in the residue. The uptake of sulfur in the silicic melt can thus be supposed to involve the establishment of a high sulfate/sulfide ratio in the rhyolite compared to the residue and also compared to the mantle derived basalt. A similar high sulfate/sulfide ratio and enrichment of  $^{34}\text{S}$  could also result from fractional crystallization processes during the formation of silicic magma.

The  $\delta^{18}\text{O}$  values of basalts are lower in large highly evolved volcanic centers than in the less evolved ones (Sigvaldason 1979). An opposite relationship would then be expected for the  $\delta^{34}\text{S}$  values. The solubility of sulfur is lower in rhyolitic than in basaltic melts (Katsura and Nagashima 1974). With a small proportion of silicic melt to generate a more evolved tholeiite, the  $\delta^{34}\text{S}$  ratio will hardly change at all. A comparison between the average  $\delta^{34}\text{S}$  data for the evolved Krafla-Namafjall fissure swarm and the narrow Reykjanes fissure swarms, taking the  $\delta^{34}\text{S}$  data from Sakai et al. (1980) into account, shows that the tholeiites at Krafla and Reykjanes are very close in their average  $\delta^{34}\text{S}$  composition, being  $-1.2$  and  $-0.7\%$  respectively (samples 11: A-THO and 12: D-2 excluded). Comparing the range in  $\delta^{34}\text{S}$  reveals a similar picture, the range being nearly  $+0.5\%$  more positive in the Reykjanes specimens.

The fairly homogeneous sulfur isotope distribution in the alkaline rocks and tholeiitic rock series is a strong indication that the rocks have not changed their  $\delta^{34}\text{S}$  much through their crustal evolution. Imsland (1983) considered the productivity within the rift zone to be about 50% olivine tholeiites and about 50% of more evolved tholeiites including some 5% rocks of intermediate and silicic composition. It is therefore reasonable to estimate the sulfur isotope composition in Icelandic basalts around the mean  $\delta^{34}\text{S}$  for the basalts measured which is  $-0.8\%$ .

There is a marked consistency between  $\delta^{34}\text{S}$  data from the oceanic environment. The average  $\delta^{34}\text{S}$  ( $-0.6$  to  $-0.8\%$ ) and the range in  $\delta^{34}\text{S}$  (from  $-2.0$  to  $+0.5\%$ ) are similar in the degassed basalts of Kilauea (Sakai et al. 1982), Iceland and  $\delta^{34}\text{S}$  of sulfide sulfur from MORB's (Puchelt and Hubberten 1980; Grinenko et al. 1975; Sakai et al. 1984) while the average  $\delta^{34}\text{S}$  of total sulfur in submarine basalts varies from  $+0.3$  to  $+0.7\%$ . The good agreement between all these closely related studies and the results obtained for continental tholeiites (with  $\delta^{34}\text{S} = -0.03\%$  from Harmon et al. 1987; between 0 and  $+1.0\%$  from Smitheringale and Jenssen 1963 and Shima et al. 1963) suggest that the depleted mantle is homogeneous in its sulfur isotope composition. The heavier sulfur in Japanese volcanics with  $\delta^{34}\text{S}$  values from 0 to  $+9\%$  (Ueda and Sakai 1984) could arise from inhomogeneities in the mantle but also from ocean crust contamination (Ueda, oral communication). Thus, the sulfur isotope composition of the mantle could be estimated to be between  $-0.5$  and  $+1.0\%$ .

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## References

- Condomines M, Grönvold K, Hooker PJ, Muehlenbachs K, O'Nions RK, Oskarsson N, Oxburgh ER (1983) Helium, oxygen, strontium and neodymium isotopic relationships in Icelandic volcanics. *Earth Planet Sci Lett* 66:125-136
- DePaolo DJ (1979) Implications of correlated Nd and Sr isotopic variations for the chemical evolution of the crust and mantle. *Earth Planet Sci Lett* 43:201-211
- DePaolo DJ, Wasserburg GJ (1976) Nd isotopic variations and petrogenetic models. *Geophys Res Lett* 3:249-252
- Desborough GA, Anderson AT, Wright TL (1968) Mineralogy of sulfides from certain Hawaiian basalts. *Econ Geol* 63:636-644
- Grinenko VA, Dmitriev LV, Migdisov AA, Sharaskin AY (1975) Sulfur contents and isotope composition for igneous and metamorphic rocks from Mid-Ocean Ridges. *Geochem Int* 12:132-137
- Govindaraju K, Meville G, Chouard C (1976) Automated optical emission spectrochemical bulk analysis of silicate rocks with microwave plasma excitation. *Anal Chem* 48:1325-1331
- Gunnlaugsson E (1977) The origin and distribution of sulphur in fresh and geothermally altered rocks in Iceland. Ph D thesis, University of Leeds, Leeds
- Harmon RS, Hoefs J, Wedepohl KH (1987) Stable isotope (O, H, S) relationships in Tertiary basalts and their mantle xenoliths from the Northern Hessian Depression, West-Germany. *Contrib Mineral Petrol* 95:350-369
- Hattori K, Muehlenbachs K (1982) Oxygen isotope ratios of Icelandic crust. *J Geophys Res* 87:6559-6565
- Imsland P (1983) Iceland and the ocean floor: Comparison of chemical characteristics of the magmatic rocks and some volcanic features. *Contrib Mineral Petrol* 83:31-37
- Jakobson SP (1972) Chemistry and distribution pattern of recent basaltic rocks in Iceland. *Lithos* 5:365-386
- Jakobson SP (1979) Outline of the petrology in Iceland. *Jökull* 29:57-73
- Kanehira K, Yui S, Sakai H, Sasaki A (1973) Sulphide globules and sulphur isotope ratios in the abyssal tholeiite from the Mid-Atlantic Ridge near 30°N latitude. *Geochem J* 7:89-96
- Katsura T, Nagashima S (1974) Solubility of sulfur in some magmas at 1 atmosphere. *Geochim Cosmochim Acta* 38:517-531
- Kiba T, Tagaki T, Yoshimura Y, Kishi I (1955) Tin(II)-strong phosphoric acid. A new reagent for the determination of sulfate by reduction to hydrogen sulfide. *Bull Chem Soc Japan* 28:641-644
- Kurz DM, Meyer PS, Sigurdsson H (1985) Helium isotope systematics within the neovolcanic zones of Iceland. *Earth Planet Sci Lett* 74:291-305
- Mathez EA (1976) Sulfur solubility and magmatic sulfides in submarine basalt glass. *J Geophys Res* 81:4269-4275
- Miyoshi T, Sakai H, Chiba H (1984) Experimental study of fractionation factors between sulfate and sulfide in high temperature melts. *Geochem J* 18:75-84
- Moore JG, Fabbri BP (1971) An estimate of the juvenile sulfur content of basalt. *Contrib Mineral Petrol* 33:118-127
- Muehlenbachs K, Anderson AT, Sigvaldason GE (1974) Low  $^{18}\text{O}$  basalts from Iceland. *Geochim Cosmochim Acta* 38:577-588
- O'Hara MJ (1977) Geochemical evolution during fractional crystallization of a periodically refilled magma chamber. *Nature* 266:503-507
- O'Nions RK, Pankhurst RJ, Grönvold K (1976) Nature and development of magma sources beneath Iceland and the Reykjanes ridge. *J Petrol* 17:315-338
- Oskarsson N, Sigvaldson GE, Steinthorsson S (1982) A dynamic model of rift zone petrogenesis and the regional petrology of Iceland. *J Petrol* 23:28-74
- Oskarsson N, Steinthorsson S, Sigvaldason GE (1985) Iceland geochemical anomaly: Origin, volcanotectonics, chemical fractionation and isotope evolution of the crust. *J Geophys Res* 90:10011-10025

- Puchelt H, Hubberten HW (1980) Preliminary results of sulfur isotope investigations on deep sea drilling project cores from legs 52 and 53. Initial Rept Deep Sea Drilling Project 51-53, 2:1145-1148
- Robinson B, Kusakabe M (1975) Quantitative preparation of sulfur dioxide, for  $^{34}\text{S}/^{32}\text{S}$  analyse, from sulfides by combustion with cuprous oxide. *Anal Chem* 47:1179-1181
- Sakai H, Gunnlaugsson E, Tomasson J, Rouse JE (1980) Sulfur isotope systematics in Icelandic geothermal systems and influence of seawater circulation at Reykjanes. *Geochim Cosmochim Acta* 44:1223-1231
- Sakai H, Casadevall TJ, Moore JG (1982) Chemistry and isotope ratios of sulfur in basalts and volcanic gases at Kilauea volcano, Hawaii. *Geochim Cosmochim Acta* 46:729-738
- Sakai H, DesMarais DJ, Ueda A, Moore JG (1984) Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean floor basalts. *Geochim Cosmochim Acta* 48:2433-2441
- Sasaki A, Arikawa Y, Folinsbee RE (1979) Kiba reagent method of sulfur extraction applied to isotopic work. *Bull Geol Soc Japan* 30:241-245
- Schilling JG (1973) Iceland mantle plume: geochemical study of Reykjanes ridge. *Nature* 242:565-571
- Schilling JG, Meyer PS, Kingsley RH (1982) Evolution of the Iceland hotspot. *Nature* 296:313-320
- Schneider A (1970) The sulfur isotope composition of basaltic rocks. *Contrib Mineral Petrol* 25:95-124
- Sigvaldason GE (1979) Fluids in volcanic and geothermal systems. In: Rickard DT, Wickman FE (eds) *Chemistry and geochemistry of solutions at high temperatures and pressures*. Pergamon Press, Oxford, pp 179-196
- Shima M, Gross WH, Thode HG (1963) Sulfur isotope abundances in basic sills, differentiated granites and meteorites. *J Geophys Res* 68:2835-2847
- Smitheringale WG, Jensen ML (1963) Sulfur isotopic composition of the Triassic igneous rocks of eastern United States. *Geochim Cosmochim Acta* 27:1183-1207
- Steinthorsson S, Oskarsson N, Sigvaldason GE (1985) Origin of alkali basalt in Iceland: A plate tectonic model. *J Geophys Res* 90:10027-10042
- Sun SS, Jahn B (1975) Lead and strontium isotopes in post-glacial basalts from Iceland. *Nature* 255:527-530
- Taylor BE (1986) Magmatic volatiles: isotopic variation of C, H and S. In: Valley JW, Taylor HP, Jr, O'Neil JR (eds) *Stable isotopes in high temperature geological processes*. Mineralogical Society of America, Washington, pp 185-255
- Thode HG, Monster J, Dunford HB (1961) Sulfur isotope geochemistry. *Geochim Cosmochim Acta* 25:159-174
- Thorarinsson S, Steinthorsson S, Einarsson Th, Kristmannsdottir H, Oskarsson N (1973) The eruption on Heimay, Iceland. *Nature* 241:272-275
- Torssander P (1986) Origin of sulfur in Icelandic geothermal fluids. *Ext Abs Water-Rock Interaction 5*, Reykjavik 1986, pp 583-586
- Torssander P (1988) Sulfur isotope ratios of Icelandic lava incrustations and volcanic gases. *J Volcanol Geotherm Res* 35:227-235
- Ueda A, Sakai H (1984) Sulfur isotope study of Quaternary volcanic rocks from the Japanese Islands Arc. *Geochim Cosmochim Acta* 48:1837-1848
- Zindler A, Hart S (1986) Chemical geodynamics. *Ann Rev Earth Planet Sci* 14:493-571
- Zindler A, Hart SR, Frey FR, Jakobsson SP (1979) Nd and Sr isotope ratios and REE abundances in Reykjanes peninsula basalts: Evidence for mantle heterogeneity beneath Iceland. *Earth Planet Sci Lett* 45:249-262

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# Patterns and processes of oxygen isotope exchange in a fossil meteoric hydrothermal system, Cuillins Gabbro Complex, Isle of Skye, Scotland

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**Abstract.** Oxygen isotope compositions of whole rock specimens and mineral separates from the Cuillins Gabbro Complex, Isle of Skye, Scotland, are employed to determine the patterns and processes of  $^{18}\text{O}$  depletion in the Outer Unlayered Gabbro (OUG) and associated dikes. Whole rock  $\delta^{18}\text{O}$  values range from +4.8 to  $-1.1\text{‰}$  (SMOW) and dike  $\delta^{18}\text{O}$  values range from +4.7 to  $-2.8\text{‰}$ . Mineral separates from three OUG samples yield  $\delta^{18}\text{O}$  values from +5.3 to +4.8‰ for augite and +4.1 to +0.8‰ for plagioclase. An early, small-scale hydrothermal circulation system was initiated by the OUG prior to the large-scale hydrothermal convection established by the later Layered Cuillins Complex (LCC). Dikes were emplaced in the OUG after intrusion of the LCC and had only a minor effect on hydrothermal circulation in the OUG. There is evidence of enhanced fluid flow along dike/gabbro contacts. Isotopic compositions of augite separates demonstrate a normal  $\delta^{18}\text{O}$  value for the OUG magma with all  $^{18}\text{O}$  depletion in the OUG due to subsolidus exchange processes including diffusion and surface reaction. The mineral separates yield a pattern of  $^{18}\text{O}$  depletion consistent with a diffusion mechanism, the bulk of the exchange having occurred in the plagioclase. Secondary mineral formation played a subordinate role in the  $^{18}\text{O}$  depletion of the OUG. The calculated water to rock mass ratio necessary to effect the observed  $^{18}\text{O}$  depletion in the OUG is on the order of 0.2, although a much greater amount of water circulation probably occurred. The cooling duration required to explain the measured  $^{18}\text{O}$  depletion in the OUG by diffusion is very short (140 years at 750°C, 2400 years at 550°C) compared to the duration necessary for pure conductive cooling ( $10^5$  to  $10^6$  years). Rapid local cooling rates in the OUG due to meteoric water convection are consistent with the observed  $^{18}\text{O}$  depletion in OUG samples.

change with low- $^{18}\text{O}$  meteoric waters which circulated in large-scale hydrothermal convection cells driven by heat from the cooling intrusions. Further study by Forester and Taylor (1977) revealed that igneous rocks on Skye had undergone isotopic exchange of oxygen and hydrogen with meteoric waters over an area of approximately 100 km<sup>2</sup>. The average integrated water to rock mass ratio (the amount of water necessary to effect this depletion) was calculated to be approximately one. This required that a volume of at least 2000 km<sup>3</sup> of meteoric water cycled through the circulation system.

Oxygen and hydrogen isotope studies have revealed that many epizonal plutons had associated meteoric water circulation systems (e.g. Taylor 1971, 1974a; Williams 1980; Crowley and Giletti 1983). Because economically valuable ore deposits are sometimes associated with sites of former hydrothermal activity (Taylor 1973, 1974b; Casadevall and Ohmoto 1977; Bethke and Rye 1979), and because ancient meteoric hydrothermal circulation systems can yield valuable insights into the inner workings of modern-day geothermal fields, further, more detailed studies of these systems have been conducted.

We have measured oxygen isotope compositions of whole-rock and mineral separates from the Outer Unlayered Gabbro (OUG) of the Cuillins Gabbro Complex to evaluate: 1) the pattern of meteoric water circulation on scales varying from centimeters to kilometers; 2) the timing of dike emplacement relative to hydrothermal circulation events and the effect of dike emplacement on the patterns of meteoric water circulation; 3) the initial  $\delta^{18}\text{O}$  of the OUG magma; 4) the mechanisms of oxygen isotope exchange operative during the hydrothermal circulation; 5) the water to rock mass ratio necessary to effect the observed  $^{18}\text{O}$  depletions; and 6) the temperatures of exchange and duration of cooling for the OUG.

## Introduction

Oxygen isotope compositions of rocks from the Tertiary igneous intrusions on the Isle of Skye, Scotland, were first reported by Taylor (1968) and Taylor and Forester (1971), who found that  $\delta^{18}\text{O}$  values observed in many of the rocks were lower than those of normal igneous rocks. The  $^{18}\text{O}$  depletions in these rocks were attributed to oxygen ex-

## Geological setting

The Tertiary geology of Skye was first mapped in detail by Harker (1904). Reviews of the geology and petrology of the Tertiary igneous rocks of Skye can be found in Richey (1961), Brown (1969), Drury et al. (1976), and Thompson (1981, 1982). Figure 1 is a geological sketch map of a portion of the Tertiary plutons in the Isle of Skye. The oldest exposed rock is Precambrian Torridonian sandstone, unconformably overlain by Cambrian and Ordovician limestones. Jurassic sediments unconformably overlie the Paleozoic sediments. The pre-Tertiary sediments were then covered by Tertiary plateau basalts over most of Skye. There followed three major