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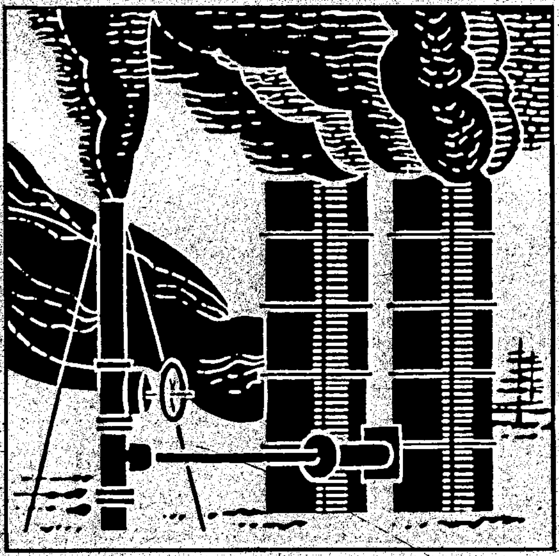

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FRACTIONATION OF BORON ISOTOPES IN ICELANDIC HYDROTHERMAL SYSTEMS

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SUMMARY - Boron isotope ratios have been determined in a variety of different geothermal waters from hydrothermal systems across Iceland. Isotope ratios from the high temperature meteoric water recharged systems reflect the isotope ratio of the host rocks without any apparent fractionation. Seawater recharged geothermal systems exhibit more positive $\delta^{11}B$ values than the meteoric water recharged geothermal systems. Water/rock ratios can be assessed from boron isotope ratios in the saline hydrothermal systems. Low temperature hydrothermal systems also exhibit more positive $\delta^{11}B$ than the high temperature systems, indicating fractionation of boron due to adsorption of the lighter isotope onto secondary minerals. Fractionation of boron in carbonate deposits may indicate the level of equilibrium attained within the systems.

1. INTRODUCTION

Hydrothermal systems in Iceland were sampled in order to elucidate the behaviour of boron isotopes being ^{10}B and ^{11}B, in hydrothermal systems during water-rock reactions. Sub-aerial hydrothermal systems in Iceland were examined as they are the closest analogue to sub-marine systems found along mid-ocean ridges. The results from Iceland may be extrapolated to indicate submarine water/rock reactions.

A range of different hydrothermal systems across Iceland were sampled. These systems include the high temperature meteoric water recharged systems at Nesjavellir, Krafla and Bjarnaflag (Figure 1), the high temperature seawater recharged systems at Reykjanes, the high temperature seawater/meteoric water recharged systems at Svartsengi, low temperature meteoric water recharged systems in the Southern Lowlands geothermal field and cool carbonate springs on the Snaefellsnes Peninsula.

Boron (B) is a particularly mobile element during water/rock reactions and is strongly partitioned into the aqueous phase at elevated temperatures, (>60 C) (Aggarwal, 1995). At these temperatures there appears to be no fractionation of B isotopes during the leaching of B from the host rock. At

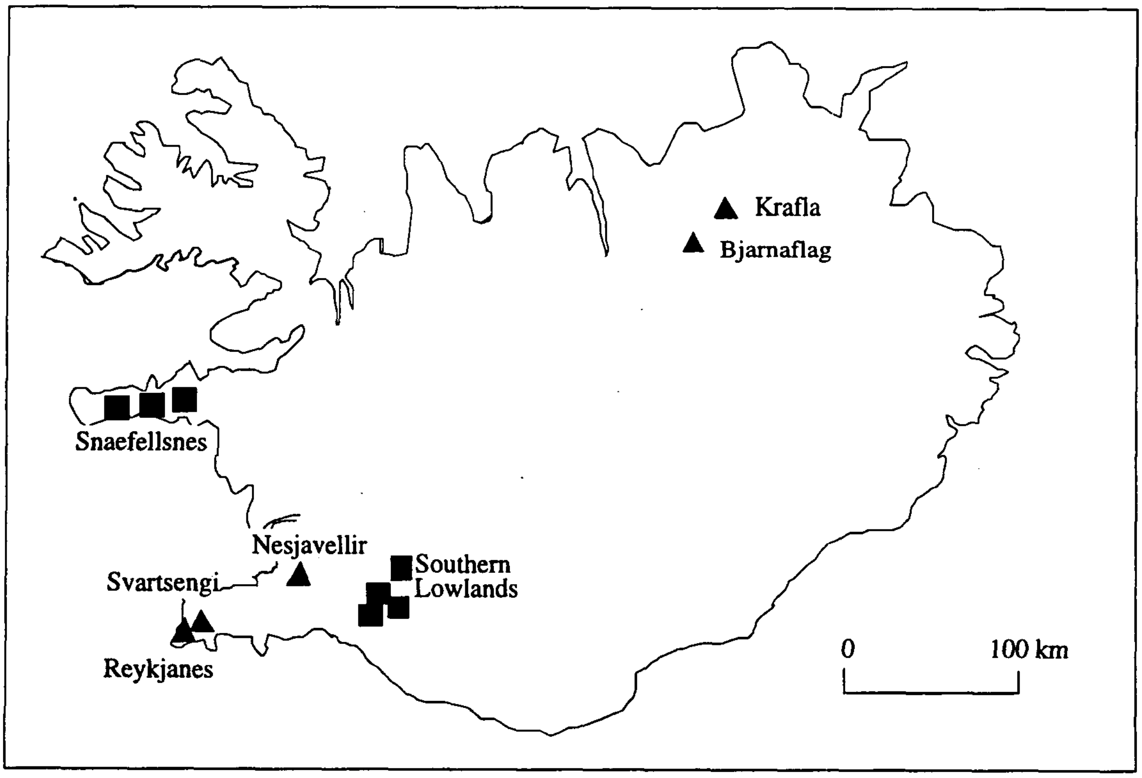

Figure 1. Location of high and low temperature geothermal systems in Iceland. ▲ Sampled high temperature geothermal system; ■ sampled low temperature geothermal system.

lower temperatures (<50 C), B is adsorbed by secondarylower temperatures, (<50 C), B is adsorbed by secondary minerals, e.g. clay minerals, resulting in the fractionation of the isotope ratios (Spivack and Edmond, 1987).

The rocks hosting the hydrothermal systems in Iceland are predominantly theoleitic basalts, and there is very little variation in the geology. If it is assumed that variations of the B isotopic ratios in the rocks are minor, then the B isotopic varitiations seen indicate the controls of temperature, pH, and pressure.

2. SAMPLE COLLECTION AND ANALYSIS

Geothermal water samples were collected after filtration through a 0.45μm filter, into precleaned high density polyethylene bottles. Samples from geothermal wells were collected using a steam separator, which allowed separation of the water phase from the steam phase. Both phases were collected and analysed.

Travertine deposits around the springs on Snaefellsnes were collected, as was scale from within some wells.

Boron concentrations in the geothermal waters were determined by both the curcumin method and an adapted azomethine-H method, (Aggarwal, 1995). Digestion of the carbonates was carried out using dilute HCl and mannitol, in a sealed teflon bomb, (Aggarwal, 1995).

Samples for B isotope analyses were purified using both the dicesium borate method, (Spivack and Edmond, 1986), and using a B specific ion exchange resin (Aggarwal and Palmer 1995).

Results are reported relative to NBS 951 as $\delta^{11}B$ values:

$$\delta^{11}B = \left\{ \left[\frac{{}^{11}B/{}^{10}B_{sample}}{{}^{11}B/{}^{10}B_{standard}} \right] - 1 \right\} \times 1000$$

3. RESULTS AND DISCUSSION

The results of the isotopic analyses are shown in Table 1 below. Errors in the B isotope ratios are typically ± 0.5‰.

Potential sources of B in all of the geothermal systems examined include the water recharging the hydrothermal system, the rock with which the water interacts and any contribution of B from a gaseous source. In the case of the meteoric water recharged hydrothermal systems, the contribution of B from the meteoric water is insignificant on two accounts. Assuming that lake waters are typical of water recharging these systems, B concentrations are less than 5μM (Aggarwal, 1995). In addition, it has been shown from submarine hydrothermal systems (Spivack and Edmond 1987), that at low temperatures, B is adsorbed onto clay minerals in the downwelling limbs of hydrothermal systems. It is therefore likely that in the meteoric water recharged hydrothermal system, there is no significant

Geothermal systems	Well/ Spring	Year sampled	B (μM)[1]	B/Cl (mol/mol)	$\delta^{11}B$ (‰)	CO_2[2] (mM)
High Temperature Systems						
Nesjavellir	6	1983	370	0.76	-3.4	ND[3]
	6	1985	310	0.12	-3.7	ND[2]
	6	1989	424	0.17	-3.2	ND[2]
	6	1991	345	0.09	-4.1	12.8
Krafla	16	1988	134	0.09	-3.5	ND[2]
	12	1991	222	0.14	-6.3	8.1
	15	1991	528	0.66	-6.7	9.7
Bjarnaflag	4	1991	73	0.05	-3.0	11.2
	11	1991	349	0.34	-2.4	6.8
Svartsengi	7	1991	798	0.0019	28.9	5.3
	8	1991	746	0.0022	27.3	5.1
Reykjanes	9	1992	809	0.0013	26.1	1.4
Low Temperature Systems						
Snaefellsnes	Olkelda	1991	90	0.014	-3.2	19
	Olkelda	1992	107	0.017	1.5	18.4
	Lysuholl	1991	35	0.018	-4.7	11
	Heggastadir	1992	5.3	0.022	17.5	11.3
	Raudamelur	1992	47	0.042	0.2	12.2
	Landbrot	1992	4.8	0.001	11.4	1.6
	Seawater[4]		426	0.00079	39.5	

Table 1. Boron isotopic composition and concentration of selected Icelandic hydrothermal systems.

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[1] Concentration shown is for the water phase collected after phase separation.

[2] CO_2 concentrations in geothermal wells are calculated as concentrations before phase separation using the geochemical code WATCH, (Arnorsson et al., 1983)

[3] ND = Not determined.

[4] Seawater data from Spivack and Edmond, (1987).

contribution of B from the water recharging these systems. In the case of Svartsengi, where there is about 65% seawater, as calculated on the basis of chloride concentration, (Arnorsson, 1978). The B concentrations and isotope ratios are elevated indicating this seawater involvement.

Examination of the steam phase of the high temperature geothermal systems showed no appreciable B concentrations. It therefore appears that B does not partition into the steam phase, and that the geothermal waters represent the isotopic composition of deep well fluids. Spivack and Edmond, (1987), have shown that during submarine water/rock reactions there is no fractionation of B. This would suggest that the waters reflect the isotopic compostion of the host rock.

B isotope ratios from the Nesjavellir well 6 between 1983 and 1991, show no significant variation, (within error). If there were any systematic variation during this period it may imply fractionation of B isotopes during water/rock reactions.

The geothermal waters in the high temperature, meteoric water recharged systems, therefore indicate that the host rocks have $\delta^{11}B$ values of between -2.4 ‰ and -6.7‰. The lighter isotope ratios tend to occur at Krafla where subsurface intrusions of granophyre have been found in the drill cutting material, (Kristmannsdottir *et al.*, 1976, Krsitmannsdottir *et al.*, 1977, Gudmundsson and Steingrimmson, 1981). Nesjavellir and Bjarnaflag exhibit $\delta^{11}B$ values between -2.4‰ and -4.1‰. This range in $\delta^{11}B$ coincides with the B isotope ratios found in glasses from oceanic basalts, (Chaussidon and Jambon, 1994).

Assuming that the granophyre in the Krafla systems is solely responsible for the lighter B isotope ratios, it would suggest that as magmas become more evolved (fractionated), the $\delta^{11}B$ of the magma becomes more negative (lighter).

The Svartsengi geothermal system shows the more positive $\delta^{11}B$ value. If it is assumed that the source of B in this field is from the seawater and the host rock, then the B isotope ratio of the geothermal water would be expected to lie between 40‰ (seawater) and -3‰ (rock). Reykjanes, a seawater recharged geothermal field shows a $\delta^{11}B$ value of 26‰. If the Reykjanes and Nesjavellir systems are end members in a mixing model (if it is assumed that geology of all three hydrothermal systems are identical), the Svartsengi system would be predicted to have a $\delta^{11}B$ of 20‰ based on Cl concentrations (Figure 2).

The higher than expected B concentrations and $\delta^{11}B$ at Svartsengi may be explained by higher water/rock ratios in the low temperature (downwelling limb) part of the hydrothermal system, or lower water/rock ratios in the high temperature (upwelling) part of the system, than occurs at Reykjanes. It is difficult to ascertain which of these two parts of the hydrothermal system controls the B concentration and isotope ratio. However, evidence from alkali trace metals, (Aggarwal, 1995), indicates that lower water/rock ratios in the high temperature part of the hydrothermal systems are more likely. These lower water/rock ratios may suggest that at Svartsengi, the rocks are less permeable than at Reykjanes. This higher rock permeability at Reykjanes may result from submarine volcanic activity resulting in more fractured rocks.

The low temperature hydrothermal systems sampled on the Snaefellsnes Peninsula, exhibit a wider range in $\delta^{11}B$ than the high temperature systems. Samples collected from Olkelda (a cold carbonate spring), in two subsequent years show $\delta^{11}B$ of -3.2‰ and 1.5‰. This variation is yet to be accounted for. Lysuholl is another carbonate rich spring, however, unlike Olkelda the water exits at 56 C. Of all the Snaefellsnes springs, this spring shows the most negative $\delta^{11}B$ value. This is because at 56 C, little or no B is adsorbed onto secondary minerals, which would otherwise result in fractionation. Heggastadir which is only at 7 C, shows the most positive $\delta^{11}B$, as a consequence of the fractionation of B during adsorption onto secondary minerals. It may be speculated from the high CO_2 content of these Snaefellsnes springs that some of the B may also be

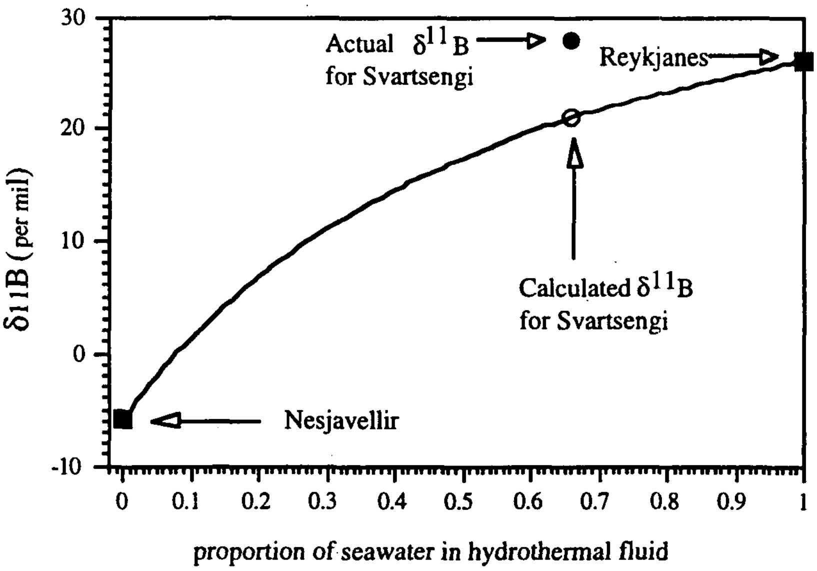

Figure 2. Mixing model for Svartsengi based on end member geothermal systems at Reykjanes and Nesjavellir. Proportion of seawater is based on chloride concentrations.

derived from the same source as the CO_2. B is known to be transported in volcanic gases (Quisefit *et al.*, 1989), and is easily volatilised as BF_3 and BCl_3, (Ishikawa, T., Nakamura, E. 1990). It is therefore likely that in the Snaefellsnes springs some B is derived from a juvenile magmatic source, however as yet there is no firm evidence to substantiate this.

Travertine deposits around the Lysuholl spring show a $\delta^{11}B$ of -22‰, while the geothermal water has a $\delta^{11}B$ value of -4.7‰. This constitutes a fractionation of 17.3‰ between the calcite in the travertine and the water. This is not particularly surprising, as it is only the tetrahedral form of the hydrated borate species, ($B(OH)_4^-$) that is incorporated into the calcite lattice. ^{10}B, preferentially partitions into this tetrahedral form resulting in isotopic fractionation. It is interesting to note that the level of fractionation (17‰) is similar to that observed in marine biogenic carbonates by Hemming and Hanson, (1992). If significant amounts of travertine are formed by the geothermal fluids at Lysuholl, the $\delta^{11}B$ of the sampled spring water may not indicate the true $\delta^{11}B$ of the fluid before travertine formation. It is likely that the $\delta^{11}B$ of the deep fluid is somewhat more positive.

Scale recovered from within the well of Svartsengi well 8, shows a $\delta^{11}B$ value of 17.4‰. This suggests that the scale (which is predominantly calcite), fractionates B by some 9‰. This is much less than that observed in the deposit around Lysuholl. If the temperature at which the scale is formed is taken into account, and the associated fractionation considered, using the data of Kakihana et al. (1977), there is still a large difference in fractionation between the two different calcite deposits. The difference may be explained if the rates at which the deposits form is examined. The scale deposit formed within the well results from the flashing of the geothermal fluids as it ascends. The calcite is therefore formed quickly and is not in equilibrium with the coexisting fluid. In the case of Lysuholl, equilibrium between the calcite and the fluid is established (as has been shown by REE partitioning, Aggarwal, 1995), resulting in a higher degree of fractionation.

4. CONCLUSIONS

Geothermal waters from meteoric water recharged hydrothermal systems show similar $\delta^{11}B$ values to MORB. Where seawater recharges the hydrothermal systems (Reykjanes and Svartsengi), the geothermal waters show more positive $\delta^{11}B$ values indicating the contribution of seawater derived B. The $\delta^{11}B$ value for the Svartsengi geothermal system cannot be predicted from a mixing model using Nesjavellir and Reykjanes as end-members. This has been interpreted to indicate that B isotope ratios are sensitive to water/rock ratios where B is derived from both the host rock and the water recharging the system. Travertine formed at Lysuholl, is in equilibrium with the coexisting geothermal fluid and shows a higher degree of fractionation than that formed within a geothermal well. It may therefore be possible to use B isotope ratios in carbonate vein deposits to indicate if equilibrium has been attained in the formation of the deposit.

5. ACKNOWLEDGEMENTS

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