



The thermal springs of Bockfjorden, Svalbard: II: selected aspects of trace element hydrochemistry

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Abstract

Waters from the Trollkjeldene (Troll springs) and Jotunkjeldene (Jotun springs) thermal springs on northern Svalbard have been analysed by ICP-AES, ICP-MS and IC techniques for a wide range of major and trace elements. Although it is plausible that the thermal waters originate from a deep reservoir in siliceous rocks, it appears that a significant component of their hydrochemical signature is derived from dissolution of higher-level Hecla Hoek marbles. Rare earth elements (REEs) show some degree of enrichment of heavy REEs in the water phase, relative to the marbles and to the travertines that precipitate from the waters. A strong positive Eu anomaly is also observed in the waters, suggesting preferential mobilisation of Eu under reducing conditions. The ratio Nb/Ta is

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rather well-preserved between the marbles, the waters and the travertines. © 1999 CNR. Published by Elsevier Science Ltd. All rights reserved.

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1. Objective

The objective of this paper is to examine selected trace element parameters in waters and travertines from the Bockfjorden thermal springs on Svalbard, and to relate them to potential aquifer rocks in the vicinity. In particular, the paper focuses on four groups of elements that might be expected to exhibit chemically similar behaviour in the hydrogeological environment, but where minor fractionation between the components may yield interesting information on geochemical processes occurring in the hydrothermal system. These groups are:

1. the rare earth elements (REEs);
2. the element pairs Nb, Ta and Zr, Hf;
3. the group I alkali metals Li, Na, K, Rb and Cs;
4. the group II alkaline earth metals Be, Mg, Ca, Sr and Ba.

2. Note on terminology

The authors use three terms in this paper that require explanation. The terms are used in the context of tracing ratios of chemically analogous elements through the system: aquifer host rock to thermal waters to travertine deposits.

2.1. Fractionation

The term fractionation is used to describe the situation where the ratio of two or more chemically analogous elements (REEs, Nb/Ta, Li/Na) is not preserved between solid and solution phases (i.e. rock weathering or dissolution, precipitation of travertines). The term implies nothing about the processes involved in this apparent fractionation.

2.2. Immobile

The term immobile is applied to elements that show a tendency (relative to other chemically analogous elements) to be enriched or retained in the solid phase during rock weathering or travertine precipitation. As the behaviour of many elements depends strongly on hydrochemical conditions, the behaviour described

here should be regarded as specific to the Bockfjorden (and similar) geothermal systems.

2.3. Aquaphile

The opposite of immobile. This term describes elements showing a tendency to be enriched or retained in the solution phase.

3. Introduction

The thermal springs of Bockfjorden (or Bockfjord) are probably the northernmost documented thermal springs in the world. They lie at almost 80° N latitude on the northern coast of Spitsbergen (Svalbard). They were visited and sampled by the authors in July 1996. They emerge at three places, (i) the Jotunkjeldene springs (or Jotun springs), (ii) the Trollkjeldene springs (Troll springs) and (iii) the Gygrekjelda spring (immediately west of the Jotunkjeldene springs), all located on a major fault zone separating marbles, gneisses, mica

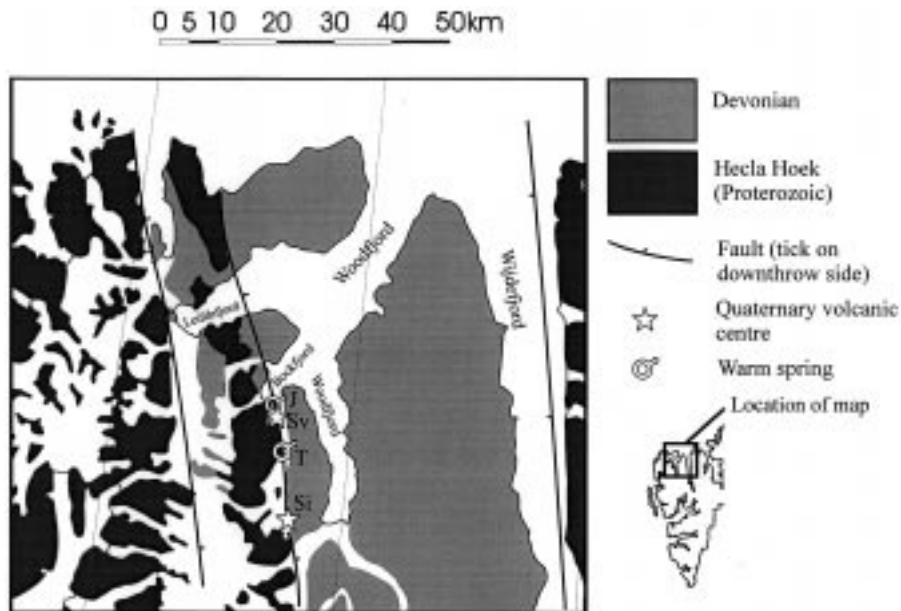


Fig. 1. Sketch map of the Woodfjord area of Northern Svalbard: J, Jotunkjeldene springs; Sv, Sverrefjellet; T, Trollkjeldene springs; Si, Sigurdfjellet. The white areas represent glaciated terrain or terrain covered by Quaternary (moraine/sandur) deposits. Inset shows map of Spitsbergen with location of main map (after Banks et al., 1997b; 1998). Hecla Hoek is a Precambrian complex of marbles, gneisses, mica schists, metadolerites and phyllites. Devonian is 'Old Red' sandstone (ORS) and associated sediments.

schists, metadolerites and phyllites of the Precambrian Hecla Hoek complex in the west from a down-faulted Devonian ‘Old Red’ Sandstone basin in the east. Quaternary alkaline olivine basaltic volcanic centres also lie on the fault zone (Fig. 1). The springs appear to emerge from Hecla Hoek marbles; it is possible that the hydrothermal system extends below these marbles to stratigraphically lower siliceous rocks of the Hecla Hoek such as gneisses.

The springs emerge in nine groups, six groups at Trollkjeldene (numbered 1–6 northwards), two at Jotunkjeldene (1 and 2) and one at Gygrekjelda. Each group of springs is associated with large deposits of travertine; at Trollkjeldene these are typically in the form of cascading concave-upwards basins, at Jotunkjeldene and Gygrekjelda they are massive convex-upwards mounds. The Gygrekjelda spring was recently described by Salvigsen and Høgvard (1998). In this paper only the Trollkjeldene and Jotunkjeldene springs are discussed.

The warmest springs in each group at Trollkjeldene are those situated highest up on the travertine deposits (the ‘A’ springs). Water from these A-springs infiltrates the travertine to emerge at lower levels as ‘B’- or ‘C’-springs, or at the base of the travertine slope, at the junction with the sandur flat at the end of Bockfjorden, as ‘D’-springs (Fig. 2). Fossil travertine deposits are found at a level higher than the highest currently active spring at Trollkjeldene area 6. Higher level fossil travertine deposits that are not associated with any currently active springs are also found at Trollkjeldene (area 7, between areas 5 and 6) and Jotunkjeldene (between areas 1 and 2).

Banks et al. (1997a; 1997b; 1998) have already considered the major ion chemistry of the waters. On the basis of major ion hydrochemistry, they found three clear groupings of springs:

1. the southern Trollkjeldene Spring Areas 1, 2 and 3 with Na-(Ca)-HCO₃⁻ composition;
2. the northern Trollkjeldene Spring Areas 5 and 6 with Na-HCO₃⁻ waters;
3. the Jotunkjeldene springs with Na-Cl⁻ waters.

On the basis of major ion chemistry, Banks et al. (1998) also drew the following conclusions:

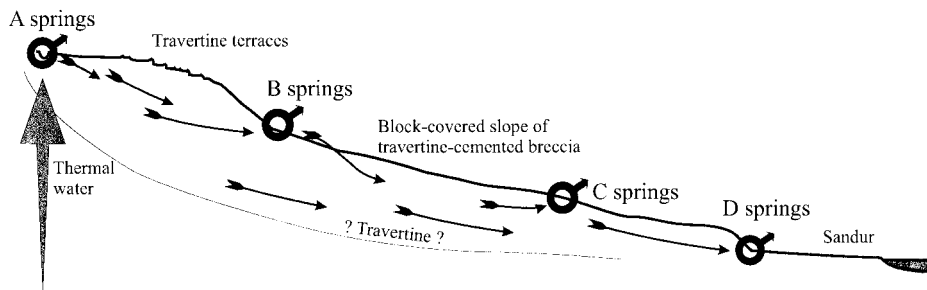


Fig. 2. Schematic cross-section of the structure and probable groundwater flow at the Trollkjeldene springs site, Svalbard (after Banks et al., 1998).

- There is a negative correlation between temperature and Eh, and temperature and pH. The warmest water, at 25.6°C, has an Eh of –270 mV, a pH of 6.83 and contains hydrogen sulphide. It is thus suggested that the ‘pristine’ thermal water source has a sub-neutral pH and is probably reducing. Many of the thermal waters also appear to emit bubbles of CO₂; although no gas samples were taken, the negative relationship of pH and temperature is indicative of degassing of CO₂ due to pressure release.
- Common geothermometers (Si, Na/K, enthalpy) yield widely varying temperatures for the thermal water source. The most likely solutions suggest temperatures at depth of 130–180°C for the Trollkjeldene Springs, with 10–30% thermal water diluted by 70–90% cold water. This corresponds—on the basis of the prevailing geothermal gradient of 0.079°C/m (Banks et al., 1998)—with a depth of 1.6–2.3 km. The Jotunkjeldene springs appear to be derived from a thermal water source a few tens of °C hotter. The thermometers are, however, of dubious applicability for such cool, aggressive, CO₂-bearing springs and the real reservoir temperatures are likely to be significantly lower than those cited above.
- Br/Cl ratios suggest that the chloride salinity of the water is not derived from water–rock interaction but rather from evaporitic deposits in the Devonian sandstones or from (fossil ?) sea-water. The sodium, potassium, sulphate and silicon concentrations appear to be controlled by near-equilibrium water–rock interactions at depth.

A suite of water and rock samples was also analysed for a large number of trace elements by ICP-MS techniques. This paper will address selected aspects of the trace element hydrochemistry, but will not attempt to provide an extensive documentation of data. For such a documentation, the reader is referred to the report by Banks et al. (1997a).

4. Groundwater sampling and analysis

At almost all A-springs and a number of B-, C- and D-springs, pH, temperature and Eh were measured in the field. At selected springs (seven A-springs at Trollkjeldene, 2 D-springs at Trollkjeldene, and Jotunkjeldene Springs 1JA3 and 2JB) samples were collected for laboratory analysis (of these, only nine samples were submitted for ICP-MS analysis). The selected A springs include the hottest springs of each spring area (except area 4). Additionally, a cold spring between spring areas 3 and 4 at Trollkjeldene was sampled (Sample K1). This is believed to be a permanent spring, as indicated by a verdant growth of spring moss, and is also believed to represent a discharge of non-thermal sub-permafrost groundwater. A sample was also taken from a thaw seepage from the active permafrost layer between spring areas 4 and 5 (sample K2).

For each sampled spring 2 × 100 ml samples of filtered water were taken in 100 ml polyethene bottles. These were rinsed thrice with spring water prior to

sampling and twice with filtered spring water. Samples were filtered with 0.45 µm Millipore filters. On arrival at the Geological Survey of Norway (NGU) laboratory, one flask of each sample was acidified with 0.5 ml/100 ml concentrated Suprapure[®] (Merck) HNO₃ to remobilize and preserve any precipitated or adsorbed metals. This sample was analysed for 32 parameters at NGU by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES—Ødegård and Andreassen, 1987) and then forwarded to the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) in Germany for analysis of a wide range of trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The second flask of each sample was sent to the Norwegian Agricultural University (NLH) for anion analysis by Ion Chromatography (IC). The flask was then returned to NGU for confirmatory IC analysis.

5. Rock sampling and analysis

Eleven samples of rock were collected from the Bockfjorden spring areas:

1. Sv1R — grey, fine-grained, Hecla Hoek marble from Trollkjeldene
2. Sv3R — travertine from an active travertine mound, Spring 5A4, Trollkjeldene
3. Sv5R — buff brecciated Hecla Hoek marble from Trollkjeldene
4. Sv10R — travertine from a fossil basin, spring area 1, Trollkjeldene
5. Sv11Ra — travertine from laminar layers in the wall of a fossil travertine basin, spring area 3, Trollkjeldene
6. Sv11Rb — travertine from porous layers in the wall of a fossil travertine basin, spring area 3, Trollkjeldene
7. Sv14R — fossil travertine, spring area 7, Trollkjeldene.
8. Sv15R — travertine from active basin, spring area 3, Trollkjeldene
9. Sv17R — coarser-grained marble, Hecla Hoek, Jotunkjeldene
10. Sv19R — frost-shattered mica-schist, Hecla Hoek, Jotunkjeldene
11. Sv28R — Devonian Old Red Sandstone, near Trollkjeldene

X-ray diffraction (XRD) analysis of travertine samples Sv3R, Sv10R and Sv15R showed them to be almost exclusively composed of calcite (Banks et al., 1997a).

At the Geological Survey of Norway, samples were prepared by crushing and fine milling in a clean agate mill. Further sample preparation and analysis were performed at the Bundesanstalt für Geowissenschaften und Rohstoffe in Germany.

For X-ray fluorescence (XRF) analysis, 1000 mg of milled samples were heated to 1030°C for 15 min to determine loss on ignition. After mixing the residue with 5.0 g lithium metaborate and 100 mg iodine pentoxide, the samples were fused at 1150°C for 20 min in Pt-Au crucibles to produce glassy XRF discs. Analysis was performed using a wavelength dispersive X-ray spectrometer, with both chromium (PW 1480) and rhodium (PW 1400) tubes to achieve optimal results for different elements. Monitor samples and more than 50 certified reference materials were used for calibration and matrix correction of results.

For Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis, 100 mg

of milled sample was added to 5 ml of concentrated ultrapure HNO_3 and 2 ml HF. The mixture was heated at 170°C for 24 h in a sealed Teflon bomb. The reaction vessel was then carefully opened and heated to near-dryness on a hotplate. Concentrated HCl (3 ml) was added and the samples were again heated in the sealed vessel at 150°C for 12 h. Finally, 1 ml HNO_3 and 1 ml HCl were added to the residue and the solution topped up with pure water to 100 g total (i.e. a total dilution factor of 1000), prior to ICP-MS analysis.

In both cases, results are cited as ppm relative to dry, non-ignited weight (Banks et al., 1997a).

6. Rare earth elements

The rare earth elements are a series of elements (57–71 atomic number, i.e. La–Lu), usually occurring in a +III oxidation state, which are regarded as being chemically analogous, behaving similarly in most geochemical contexts. Exceptions to this rule are cerium (which may have a +IV oxidation state and is generally more immobile than the other REEs) and europium (which may have a +II state and often substitutes in feldspars or carbonates). Many reactions will result in a minor degree of REE fractionation, which can yield useful information on geochemical processes. In many cases, water–rock interaction appears to result in a relative enrichment of heavy REEs in the groundwater phase and a negative cerium anomaly (Vlasov 1966; Banks et al., 1999). In the case of the Bockfjorden waters, where reducing conditions prevail in the hydrothermal system, the behaviour of Eu might be expected to be particularly anomalous (reduced to +II).

For the thermal water samples from Svalbard, concentrations of REEs as analysed by ICP-MS typically fall in the range <0.001 – 0.02 ppb (Figs. 3 and 4). The concentrations of each element exhibit the alternating high-low pattern characteristic of the cosmic abundance of REEs. Of the rock samples, the siliceous lithologies (schist and sandstone) contain considerably higher concentrations of REEs than the carbonates (Fig. 5). Concentrations of all REEs in the nine analysed thermal waters were normalised (ppb:ppb) with respect to average concentrations of the REEs in Devonian sandstone (Sv28R), Hecla Hoek mica schist (Sv19R), Hecla Hoek marble (Sv1R, Sv5R, Sv17R), and travertine (Sv3R, Sv10R, Sv11Ra, Sv11Rb, Sv14R, Sv15R) and with respect to sea-water composition as cited by Rollinson (1993).

For all normalised plots (Fig. 3) the thermal waters show some indication of relative enrichment in the water phase from light to heavy REEs (characterised by the Er/Nd or Er/La ratios, see Figs. 4 and 6), which is not present to the same extent in the cold waters. The thermal waters also exhibit a small negative Ce anomaly, as predicted by, for example, Vlasov (1966). Fig. 4 indicates that the negative Ce anomaly is strongest in the cold, presumably more oxidising groundwater K1 (Ce immobilised in +IV form). There is also a very strong positive Eu anomaly, which is strongest in the thermal waters (Figs. 4 and 6,

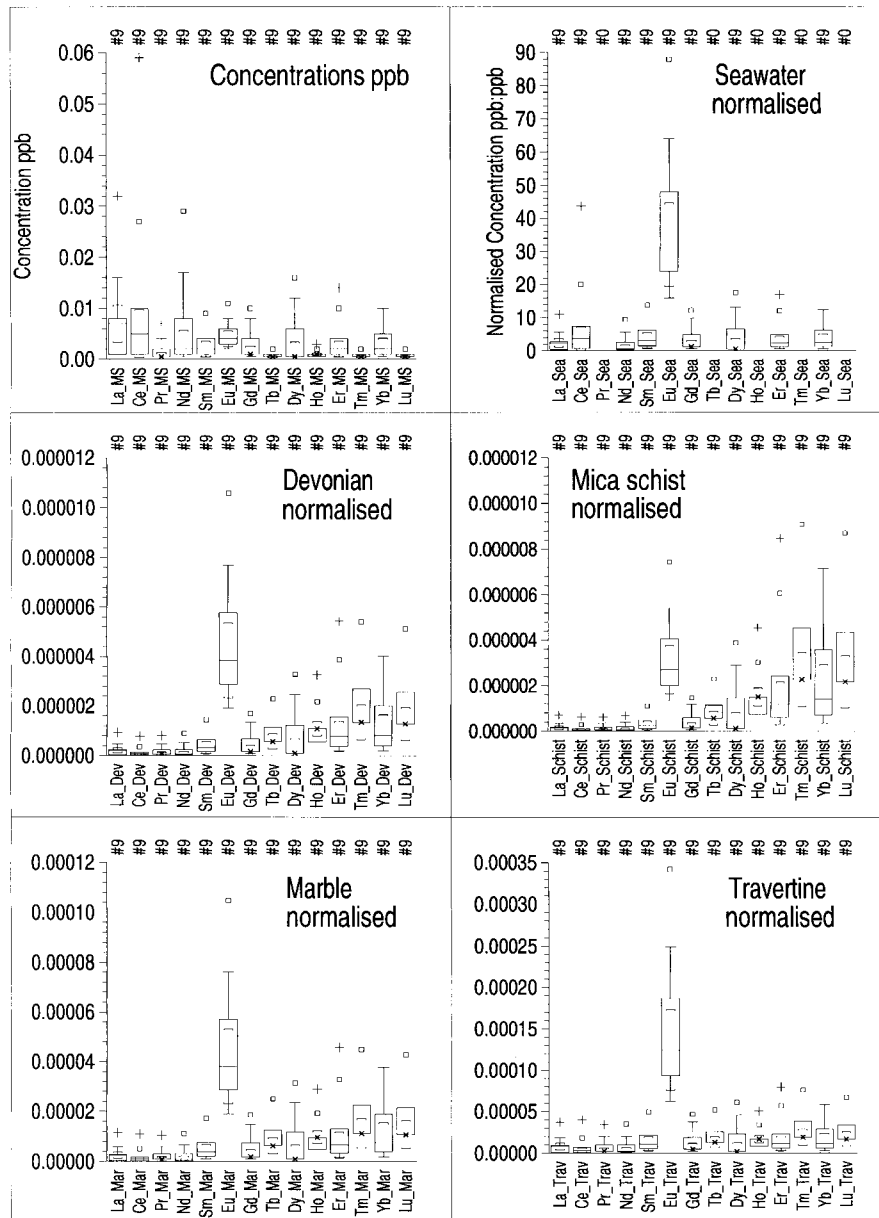


Fig. 3. Boxplots showing concentrations of REEs (rare earth elements) in nine thermal waters from Bockfjorden (in ppb, upper left), and concentrations normalised (ppb/ppb; i.e. dimensionless ratio, other five diagrams) with respect to average REE concentrations in travertines, marbles, mica schist and Devonian Old Red Sandstone from the Bockfjorden area, and sea-water (Rollinson, 1993). In boxplots, the box represents the interquartile range, with a horizontal line at the median value; whiskers represent extraquartile range, with squares and crosses representing outliers. Concentrations below analytical detection limit are set to half the detection limit.

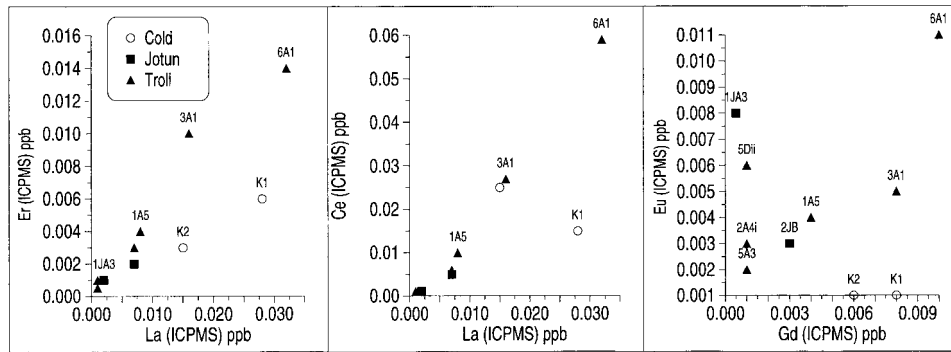


Fig. 4. x-y plots showing concentrations of (a) La vs Er, (b) La vs Ce and (c) Gd vs Eu, for the water samples from Bockfjorden (all in ppb). Concentrations below analytical detection limit are set to half the detection limit.

europium present in anomalous +II form). It is conceivable that this is an analytical artifact, as Ba may interfere strongly with Eu in ICP-MS analyses. This is regarded as unlikely, however; Eu results have been corrected for Ba using a method similar to that described by Hall et al. (1995, 1996), and a plot of Eu vs Ba reveals no residual correlation. If the strong positive Eu anomaly is real, it might indicate strong preferential weathering of Eu-enriched phases such as carbonates or calcic feldspars. It will, however, be seen from Fig. 5 that the marbles, although consisting dominantly of calcium carbonate, are not especially rich in Sr (for which Eu may substitute) and exhibit a rather low Eu content (Eu/La ratio in the range 0.037–0.092). The two cold groundwaters have Eu/La ratios (Fig. 6) of 0.036 and 0.067, implying that marble dissolution is an adequate explanation for the REE signature of these waters. The nine thermal

Table 1

The ratios of median concentrations and median normalised concentrations of Eu, Er, La and Nd, for the nine thermal waters and rock samples

Ratios of median concentrations	Eu/La	Er/La	Er/Nd
Non-normalised thermal water concentrations (<i>n</i> = 9)	0.57	0.29	1.0
Devonian ORS (<i>n</i> = 1)	0.030	0.075	0.080
Mica schist (<i>n</i> = 1)	0.033	0.037	0.038
Marbles (<i>n</i> = 3)	0.042	0.083	0.10
Travertines (<i>n</i> = 6)	0.021	0.21	0.21
Devonian-normalised thermal waters (<i>n</i> = 9)	19	3.8	13
Mica schist-normalised thermal waters (<i>n</i> = 9)	17	7.8	26
Marble-normalised thermal waters (<i>n</i> = 9)	15	2.6	8.5
Travertine-normalised thermal waters (<i>n</i> = 9)	15	1.4	4.7
Sea-water-normalised thermal waters (<i>n</i> = 9)	13	1.0	3.7
Sea-water ratios (after Rollinson, 1993)	0.043	0.29	0.27

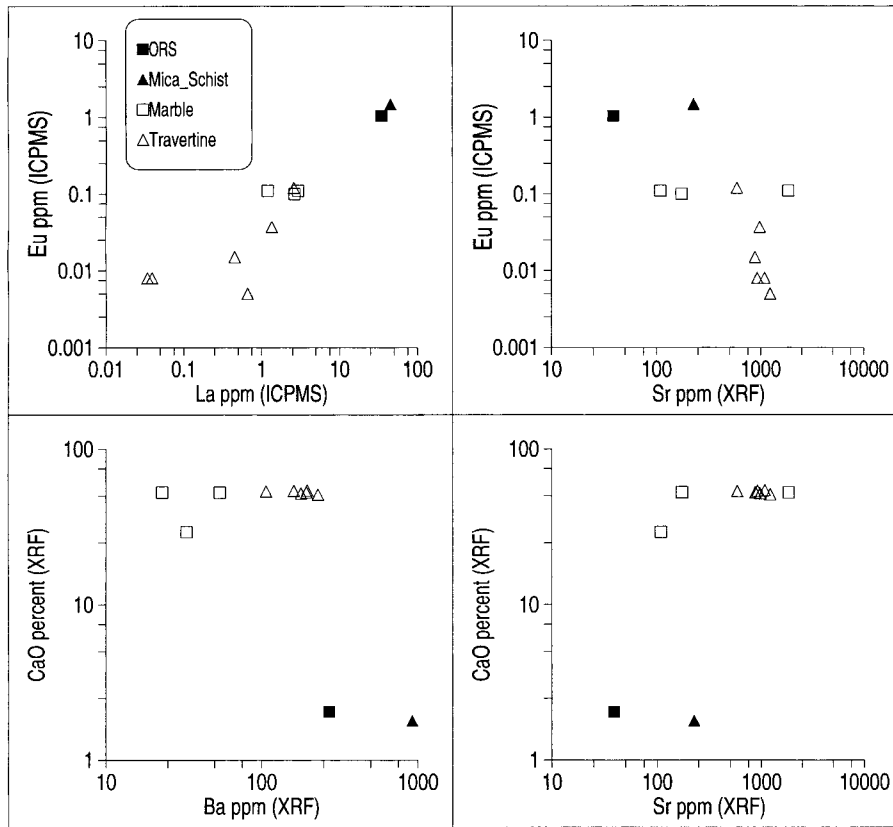


Fig. 5. x - y plots showing concentrations of (a) La vs Eu, (b) Sr vs Eu, (c) Ba vs CaO and (d) Sr vs CaO for rock samples from the Bockfjorden area. La and Eu by ICP-MS (ppm), Sr and Ba by XRF (ppm), Ca as CaO by XRF (%). Concentrations below analytical detection limit are set to half the detection limit.

groundwaters exhibit, however, Eu/La ratios in the range 0.31–6 (median 0.5), implying that processes other than mere carbonate dissolution from the Hecla Hoek marbles must be responsible for the Eu anomaly and that a strong Eu fractionation is occurring within the thermal waters (Table 1). Interestingly, the travertines do not reflect the high Eu content of the thermal water, with Eu/La ratios similar to the marbles (Fig. 6). If the analytical results are correct, they imply that Eu is preferentially enriched in the solution phase in the reducing thermal waters, whereas the other REEs are preferentially retained in the solid phases (low leaching from host rocks relative to Eu and high immobilisation in the travertines).

The enrichment in heavy REEs may be quantified by the ratios of non-anomalous REEs such as Er/La, or Er/Nd. These values are presented in Table 1 and Fig. 6. These ratios are similar in both thermal waters and travertines,

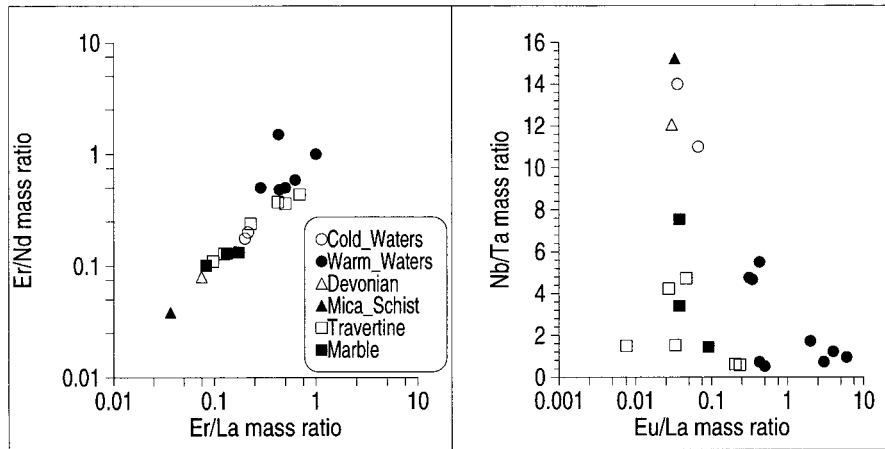


Fig. 6. x - y plots of mass ratios of (a) Er/La vs Er/Nd and (b) Eu/La vs Nb/Ta for rock and water samples from Bockfjorden. Determined by ICP-MS techniques on both water and rock samples. Where one component of the ratio returned a value below analytical detection limit, no point is plotted.

implying that the REE signature (except Eu) is preserved during calcite precipitation. The ratios are all higher in the waters than in the potential aquifer source rocks, confirming the relative enrichment in heavier REEs during weathering reactions. The least degree of fractionation is observed relative to the sea-water and to the marbles, suggesting that these may be the most probable sources for the thermal water REE signature (not unlikely, as one would expect intense marble dissolution by warm CO_2 -charged waters). However, the absolute concentrations of many REEs are generally somewhat higher than in standard sea-water, precluding fossil or current sea-water as the source of the REE signature.

7. Zr/Hf and Nb/Ta ratios

The two pairs of metals zirconium/hafnium and niobium/tantalum are often regarded as being chemical analogues. In many geological media, the ratio Zr/Hf lies in the range 25–200, whereas Nb/Ta lies in the range 10–20.

The two ratios were calculated for the Bockfjorden samples (using ICP-MS data) to ascertain whether a consistent signature could be traced from host rock to groundwater to travertine. This proved impossible in the case of Zr/Hf due to apparent analytical inconsistencies between rock and water analyses and these parameters will not be discussed further here. For the ratio Nb/Ta a more consistent picture was obtained. The marbles, the travertines and the thermal waters all exhibited a similar range of Nb/Ta ratios [although these were typically < 10 (Fig. 6)]. The silicate rocks (sandstone and schist) exhibited more typical Nb/

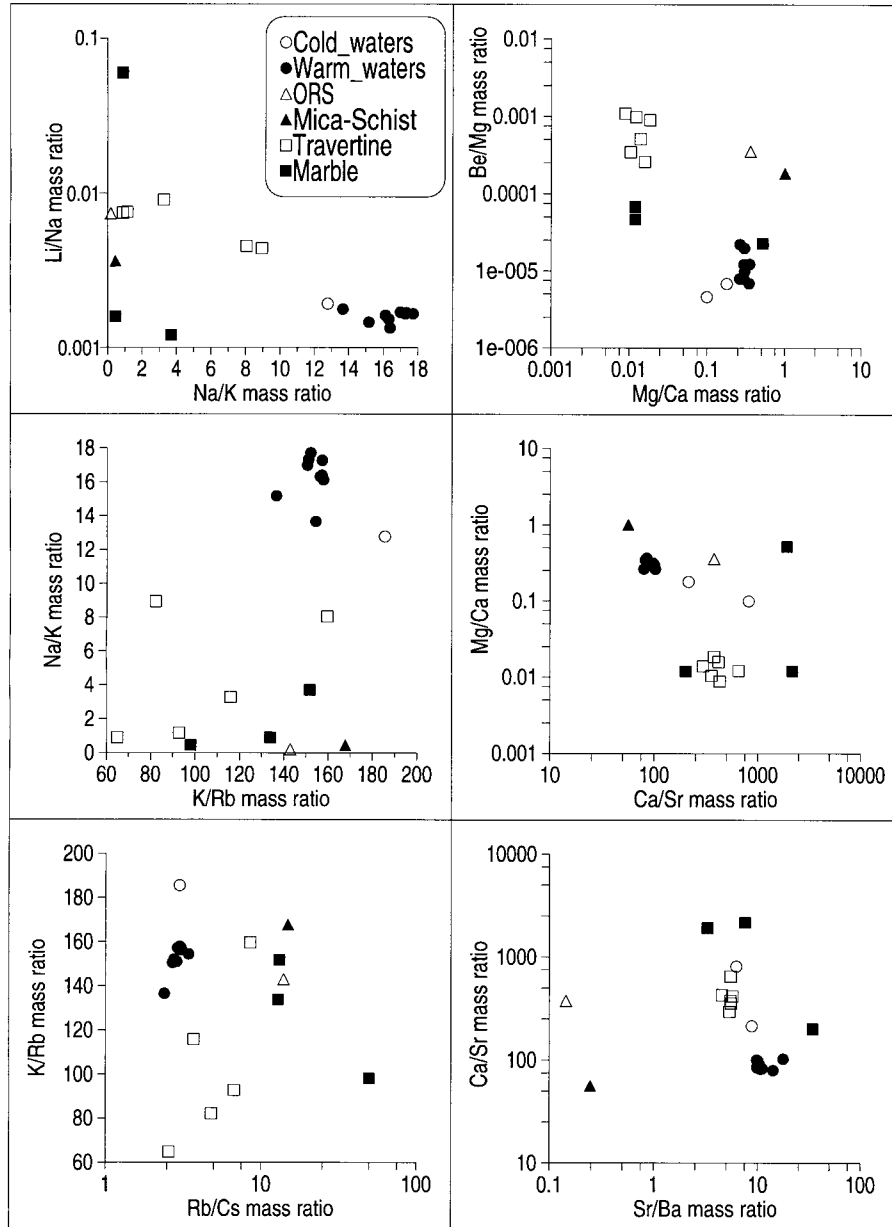


Fig. 7. x - y plots of mass ratios of (left) alkaline (group I) metals and (right) alkaline earth (group II) metals, according to increasing atomic number. For waters, Li, Rb, Cs and Be were determined by ICP-MS; Na, K, Mg, Ca, Sr, Ba by ICP-AES. For rock samples Li, Rb, Cs and Be were determined by ICP-MS; Na, K, Mg, Ca, Sr and Ba by XRF. Where one component of the ratio returned a value below analytical detection limit, no point is plotted.

Ta ratios in the range 10–20. The Nb/Ta ratio suggests, as do the REEs, that much of the trace element signature of the thermal waters is derived from the Hecla Hoek marbles. The Nb/Ta ratio is conservative during precipitation of calcite travertine from the waters. Interestingly, the cold groundwaters exhibit Nb/Ta ratios more comparable to the silicate rocks. No adequate explanation for this is found, as the two cold groundwaters appear to emerge from the Hecla Hoek marbles. These observations should be treated with some degree of caution, however, as analytical signals observed in blanks were of a similar order of magnitude to those real water samples with the lowest Nb and Ta concentrations (Banks et al., 1997a; 1997b).

8. Alkali metals

The ratio Na/K is used as the basis of several well-known geothermometers (Fournier, 1981), as it is believed that, at elevated temperatures, in silicate rocks, the ratio is approximately constant, but temperature-dependent. A consistent Na/K ratio was observed in the Bockfjorden waters (Banks et al., 1998) and it is hypothesised that the other alkali (group I) metals may behave similarly. Thus, the ratios Li/Na, Na/K, K/Rb and Rb/Cs have been calculated for both rocks and water, and are presented graphically in Fig. 7.

For all ratios, Li/Na, Na/K, K/Rb and Rb/Cs, the thermal waters exhibit a low variation; i.e. they may be useful in terms of geothermometry. The thermal waters exhibit similar Li/Na ratios to the marbles, although the Na/K ratio is much higher in the waters than the marbles. It is thus hypothesised either that (a) the Na/K ratio reflects an equilibrium with possible silicate (gneissic) rocks underlying the Hecla Hoek marbles at depth or (b) the Na/K ratio in the waters may partially be derived from a fossil saline water component in the geothermal system (Banks et al., 1998). The travertines all exhibit rather similar Li/Na ratios, but these are higher than in the thermal waters. The Na/K ratios of the travertines are generally lower than the thermal waters, implying that the K is being retained in secondary minerals in the travertine complex. It appears that Li and K generally exhibit a more immobile behaviour than Na, which is regarded as an aquaphile element.

The K/Rb ratio varies considerably for the travertines, but is generally lower than for the thermal waters. The thermal waters exhibit a similar K/Rb ratio to the potential host rocks, suggesting that the ratio is relatively conservative in the geothermal system. The travertine data show a tendency to slightly more immobile behaviour in Rb than in K.

The Rb/Cs ratio is relatively constant for the thermal waters and the travertines, at approximately the same value. The ratio is, however, lower in the waters than the potential aquifer host rocks, suggesting that Rb behaves in a more immobile manner than Cs in the Bockfjorden geothermal system.

Of the alkali metals it thus appears that Rb behaves in the most immobile manner in the Bockfjorden geothermal system, and sodium as the most aquaphile.

9. Alkaline earth metals

A similar series of ratios and diagrams may be constructed for the alkaline earth (group II) metals.

The plot of Be/Mg vs Mg/Ca shows extremely good definition of the various groups of rocks and waters. All the rocks exhibit higher Be/Mg ratios than the waters, confirming Be as a poorly soluble and immobile element. The warm waters are enriched in Be relative to the cold waters, and this enrichment is reflected in relatively high Be/Mg ratios in the travertines, where Be is preferentially precipitated on emergence in the spring waters.

The Mg/Ca ratio in the waters could be directly explained as being derived by congruent dissolution of Ca and Mg from the marbles. The travertines are, however, enriched in Ca relative to the Mg/Ca ratio in the warm waters, confirming the relatively pure nature of the travertine calcite. Mg appears thus not to be precipitated in the travertines at the same rate as calcium.

The Ca/Sr ratio in the warm waters is generally slightly lower than most of the potential host rocks, suggesting that Sr is preferentially mobile over calcium in the geothermal system. The aquaphile nature of Sr is confirmed by the fact that the travertines exhibit generally higher Ca/Sr ratios than the waters, implying that Sr is not precipitated in the travertines at the same rate as calcium.

The Sr/Ba ratio provides a clear distinction between the waters, marbles and travertines on the one hand (with a high Sr/Ba ratio) and the silicate rocks on the other (low ratio). This evidence again suggests that another component of the trace element signature is derived from the marbles rather than silicate rocks. The Sr/Ba signature of the waters is compatible with congruent weathering of these elements from the marbles. The travertines exhibit slightly lower Sr/Ba ratios than the waters, implying that barium is preferentially retained in the travertines.

Thus, of the alkaline earths, Be, Ba and Ca tend to behave in an immobile manner in the Bockfjorden thermal system, whereas Mg and Sr tend to be more aquaphile.

10. Conclusions

In cool, CO₂-rich thermal springs in complex geology, the applicability of common geothermometers is problematic. It has thus proven impossible to define with any certainty the maximum reservoir temperature or depth for the Bockfjorden system. Although the springs emerge from Hecla Hoek marbles, it is conceivable that the hydrothermal reservoir extends to the siliceous (e.g. gneissic) rocks underlying the marbles, and that part of the chemical signature of the thermal waters may reflect thermal equilibria attained therein (Banks et al., 1998). It is likely, however, that this signature has been modified by passage through the Hecla Hoek marbles. In particular, REEs, the ratio Nb/Ta and several trace group I and II elements provide strong evidence of their derivation from the marbles.

The rare earth elements show a minor enrichment in heavy REEs in the thermal water phase, compared to the marbles, and also a strong positive Eu anomaly. This may provide evidence of the occurrence of Eu in its reduced +II form in the geothermal system. Fractionation of REEs during precipitation of travertines is again minor, with the exception of Eu.

The Nb/Ta ratio is rather similar for the thermal waters, the marbles and the travertines, while the siliceous rocks exhibit a higher ratio.

Of the group I and II metals, pairs of elements typically exhibit differing behaviour in the various dissolved and solid phases. Of the group I elements, Na is the most and Rb the least aquaphile. Of the group II elements, Ca, Ba and (particularly) Be behave in an immobile manner, and Sr and Mg in an aquaphile manner. For all pairs of elements within group I and group II, the thermal waters all exhibit a low variability in ratios, suggesting that they may be useful either as geothermometers or geochemical natural tracers. The scope of the current work does not, unfortunately, permit a full assessment of this possibility. In order to demonstrate the potential utility of these trace elements in geothermometry, empirical studies would be needed in a range of geothermal systems where reservoir temperatures are already known via independent means.

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