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**WATER/ROCK RATIO CALCULATIONS
IN HYDROTHERMAL SYSTEMS: A CASE
STUDY FROM BERGSLAGEN,
CENTRAL SWEDEN**

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WATER/ROCK RATIO CALCULATIONS IN HYDROTHERMAL SYSTEMS:
A CASE STUDY FROM BERGSLAGEN, CENTRAL SWEDEN

by

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ABSTRACT

Determination of water-rock (W/R) ratios in hydrothermal systems has economic importance for its ability to estimate volumes of ore which could be deposited by that system. Three different methods for water-rock calculation are presented in this work. The Hjulsjö alteration zones, West Bergslagen, central Sweden, of early Proterozoic age are selected as a case study. The alteration zones are located in felsic volcanic rocks, which are intruded by the Hjulsjö granite-granophyre complex. Exhalative- and skarn mineralization, which were mined in historic times, occur in the surroundings of the alteration zones, and some may be connected to these zones.

The W/R ratio calculation methods comprise:
1) an oxygen isotope method,
2) a Mg-enrichment method, and
3) a rare earth element (REE)-leaching method.

The oxygen isotope method results in W/R ratios for the most altered parts of the zones of 0.6 - 2.9 (300-400°C) and 0.5 - 1.4 (300-400°C) for closed and open systems respectively. The Mg-enrichment and REE-leaching methods are applied to samples through the alteration zones.

The Mg-enrichment method results in ratios between 16 -19 for mass based calculations and between 45 - 53 for volume based calculations for the most altered parts of the zones. The central zones all fall in the same range of W/R ratios, whereas the outer zones and meta-volcanic rocks are considerably lower, with ratios of 1 - 10 and 1 -3 respectively.

For the REE calculations, the most labile of these elements in the alteration zones, i.e. La, Ce, and Sm, are used. Calculations based on different fluid compositions for meta-volcanic rocks and outer alteration zones generally result in negligible to low W/R ratios. For outer zone samples very high and variable W/R ratios (in the range 400 to 6.106) are obtained.

The huge range in W/R estimates for the three calculation methods applied to the same alteration system may be explained by differences in reaching equilibrium for the specific system under consideration. If a given system is in equilibrium, no further registration of exchange between the fluid and the rock occurs; other systems, however, which are still out of equilibrium, may continue to undergo chemical exchange and register enhanced W/R ratios.

Consequently, the application of W/R ratio calculation must be carried out with circumspection and must be monitored by a variety of methods which accord with the mineralogy and petrology of the system. It is suggested that W/R ratio calculations based on a single method, as often reported in literature, may represent meaningless values.

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WATER/ROCK RATIO CALCULATIONS IN HYDROTHERMAL SYSTEMS: A CASE STUDY FROM BERGSLAGEN, CENTRAL SWEDEN

INTRODUCTION

In hydrothermal alteration systems calculation of water/rock (W/R) ratios is applied to estimate volumes of fluids, which potentially mobilise or deposit elements by interaction with rocks. Fluid flows in channels, along mineral boundaries, or by diffusion through the minerals. Estimates of W/R ratios may be economically important in that they assist int the determination of the possible volume of ore formed in mineralized sites related to a hydrothermal system.

An early Proterozoic fossil hydrothermal alteration system near the village of Hjulsjö, central Sweden, described in a set of publications (Baker and De Groot, 1983a,b; Jasinski, 1988; De Groot, 1990; De Groot and Baker, 1992), is selected as a case study for calculation of W/R ratios by a variety of methods. The alteration zones in this region are related to exhalative- and skarn mineralization, forming the mining province of Bergslagen, where mining was active for several centuries but has stopped completely a short time ago.

Geological description of the example area

The Hjulsjö alteration zones are situated in the 1.90 - 1.86 Ga volcano-sedimentary belt of western Bergslagen, central Sweden (Oen et al., 1982; Oen, 1987; Baker et al., 1988; Lundström, 1987, 1988; Parr, 1988; Allen et al., 1996). The West Bergslagen belt has a strong ensialic character (e.g. Van der Velden et al., 1982; Oen et al., 1982; Vivallo and Rickard, 1984; Baker et al., 1988) and comprises more than 10 km of felsic volcanic rocks and over 2 km of volcaniclastic sediments. Marbles, chert and iron-oxide lenses intercalate the volcanic rocks. The supracrustal rocks were intruded by diabase dykes and sills and by granitic plutons. A bimodal style of volcanism is characteristic for the Bergslagen belt (Van der Velden et al., 1982; Lagerblad, 1988).

Publications by Baker and De Groot (1983a) and De Groot and Baker (1992) include extensive descriptions of the geological and petrological situation of the Hjulsjö alteration zones. An alteration model of felsic rock minerals with saline fluids based on thermodynamics was presented by De Groot (1990). Baker and De Groot (1983a) and De Groot and Baker (1992) discussed the mechanisms of alteration, the mineralogy of the altered zones and the mobility of major and trace elements in the zones. Based on the high Mg-content of altered rocks in the West Bergslagen belt and on the marine depositional environment of carbonates (De Groot and Sheppard, 1988), intercalated in the volcanic rocks, it is assume that a significant component of the hydrothermal fluids is composed of (modified) seawater.

Only a summary of the Hjulsjö region is provided below and the interested reader is referred to the references cited above for more extended descriptions. Figure 1 shows the outline of the Hjulsjö alteration zones, hosted in felsic supracrustal rocks. The zones form an oval-shaped, concentric pattern. Bedding and foliation of the volcanic rocks, and the foliation in the alteration zones is oriented (sub-)vertical. The foliation of the zones generally follows the bedding of the volcanic rocks and, where the bedding bends into a NW direction around the Hjulsjö granophyre-granite complex (Baker, 1985a), it starts to make a sharp angle with the bedding continuing into a NNW direction. The felsic volcanic rocks intercalate lenses of stratiform carbonate, iron oxides and cherts/jaspilite. Diabase dykes and sheets intrude the felsic

Figure 1: Geological map of the Hjulsjö area. Shown are the Hjulsjö granite-granophyre intrusive complex (crossed pattern) and the meta-volcanic rocks (white) surrounding the complex in a circular pattern. Diabase dykes and sills (cross-striked pattern), carbonate - iron formation horizons or lenses (paralel lines with strikes) and faults (strike - dot lines marked with F) are also included. Bedding of the meta-volcanic rocks is shown by broken lines. Bedding and foliation are given by strikes into measured direction and direction of dip is given by solid and open circles respectively; all bedding and foliation is dipping at angles steeper than 70°, vertical positions are given by double circles. The alteration zones are shown by shaded areas. Lakes are shown with a gulfing pattern. A large scale map of Scandinavia is shown in the inset at the right lower corner; a crown marks the location of the major map. (Map after Baker and De Groot, 1983a).

volcanic rocks and the intrusive complex. In the northwestern parts of the zones, foliation starts to crosscut this bedding (Figure 1). The felsic volcanic rocks were metamorphosed into a greenschist facies assemblage. The intrusive complex of Hjulsjö is thought to provide the heat for the hydrothermal processes forming the Hjulsjö alteration zones and the Fe-(Mn)oxide mineralization of Ösjöberg-Sirsjöberg (Figure 1).

The alteration zones can be sub-divided into outer (OZ) and central (CZ) sub-zones as shown in Figure 2. The subdivision is based on the grade of alteration and the mineral assemblages (De Groot and Baker, 1992). Mobilisation of labile material increases towards the most altered central parts of the Hjulsjö zones, where quartz - mica - Mg-chlorite schist's are exten-
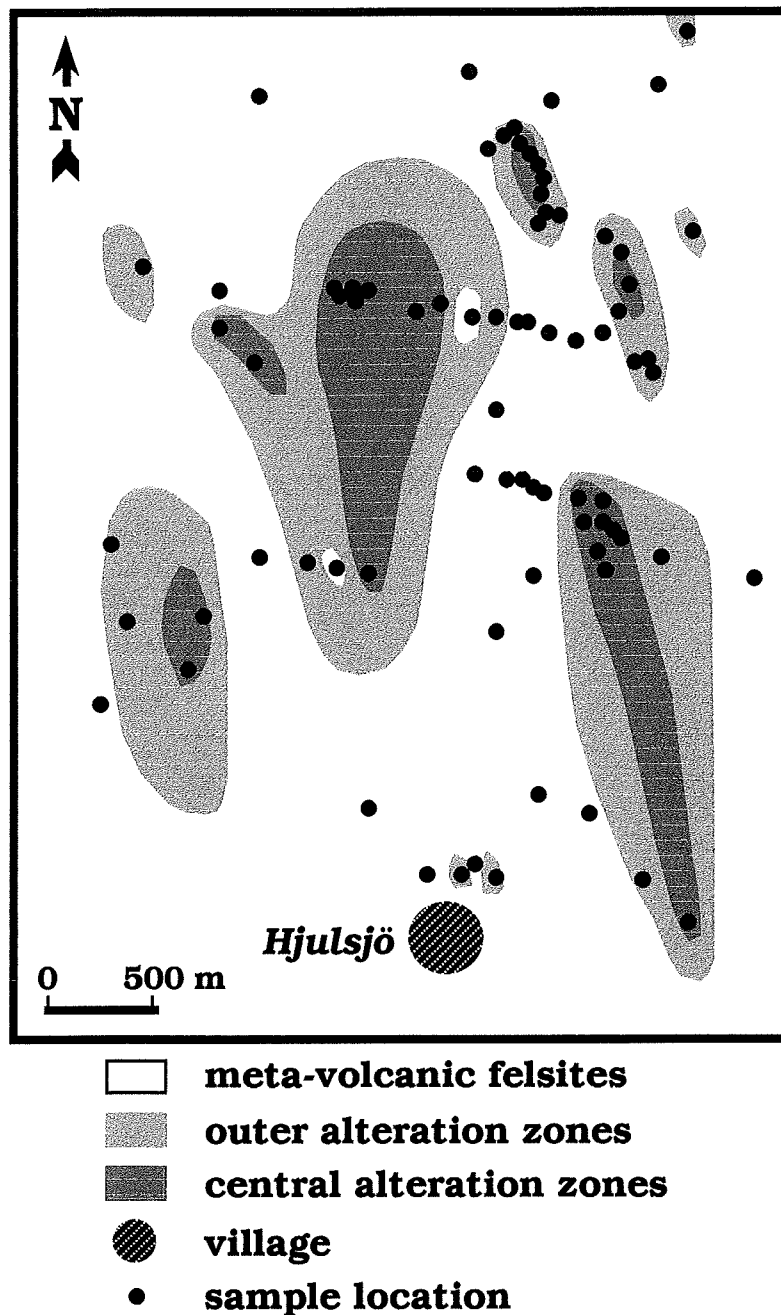
sively developed.

Figure 2: *The Hjulsjö alteration zones. The outer- (OZ) and central- (CZ) alteration zones are given in different shaded patterns. Sample locations are given in the map by solid circles.*

ANALYTICAL METHODS

Stable isotopes

Silicate mineral separates and whole rock samples are analysed for oxygen isotopes according to the procedure as described by Clayton and Mayeda (1963), with BrF_5 as oxidiser. O_2 is converted into CO_2 by a hot carbon rod under high vacuum conditions. The CO_2 is mea-

sured on a VG Sira 24 mass spectrometer and given in the standard delta notation (δ) in per mil (‰) against V-SMOW. Precision is better than ±0.2‰. The NBS-28 quartz standard gave a value of 9.42‰ (n=23) over the period of measuring. Measured values are corrected to NBS-28 = 9.6‰.

Chemical analysis

Major element (MgO) analysis was carried out by standard XRF techniques developed by ViéLeSage et al. (1979). Rare earth elements (REEs) were measured (±10%, 2σ) by INAA using the Interuniversity Reactor Institute (IRI) facilities at Delft, The Netherlands (De Bruin, 1983).

WATER/ROCK RATIO CALCULATIONS

Oxygen isotope method

Description

The oxygen isotope method is based on the exchange of oxygen isotopes between the rock minerals and fluids in a hydrothermal alteration system. Knowledge about starting and final oxygen isotopic compositions of the rock and the fluid is needed for application of this method. Formulae to calculate the W/R (water/rock) ratios of closed and open systems by use of oxygen isotopes are provided by Taylor (1979)(Table 1)

$$(1) \qquad W/R_{closed-system} = \frac{\delta^f_{rock} - \delta^i_{rock}}{\delta^i_{H2O} - (\delta^f_{rock} - \Delta)}, \text{ and } \qquad \Delta = \delta^f_{rock} - \delta^f_{H2O}$$

$$(2) \qquad W/R_{open-system} = \ln[W/R_{closed-system} + 1]$$

δ^i and δ^f are initial and final isotopic values respectively, for rock and water, all in the standard per mill (‰) notation against V-SMOW.

Isotopic data

Oxygen isotopic values of a group of the least altered samples, of mineral separates of the most altered rock from the central alteration zones (sample BJ550), and estimates for initial and final fluid compositions are given in Table 1. Oxygen isotopic composition of three least altered felsic volcanic rock samples (BJ34, BJ346, BJ517) are used to estimate a "fresh rock" value. The mean of the three samples is 7.9‰, which is used as value for $\delta^{18}O^i_{rock}$.

Sample BJ550 represents the most altered rock from the central alteration zones. Separates of quartz, as well as a mixture of muscovite and Mg-chlorite (sheridanite) are measured for their oxygen isotopic compositions. These minerals are considered to represent the most altered rock, comprising a 50% quartz - 50% muscovite/Mg-chlorite mixture, and result in a calculated rock isotopic value $\delta^{18}O^f_{rock}$ of 5.6‰.

Table 1. Oxygen isotopic values of rocks and fluids from the Hjulsjö alteration zones and their hosting rocks

SAMPLE	$\delta^{18}O$ (meas.)	$\delta^{18}O$ ($\pm$ ‰)
ROCKS:		
fresh volcanic rocks (rhyolitic composition):		
BJ 34	8.2	
BJ 346	8.2	
BJ 517	7.3	
mean fresh rocks:		**7.9**
most altered rocks of central zone:		
BJ 550　　Quartz	7.58	7.7 (±0.12)
	7.82	
Muscovite/	3.53	3.5 (±0.03)
Mg-chlorite	3.48	
mean calculated rock value:		**5.6**
FLUIDS:		
initial fluid:		
seawater [see text for explanation]		**0.0**
final fluid:		
1) BJ 550　　　　Quartz		7.7
quartz-water　　300°C: water		0.8
350°C: water		2.4
400°C: water		3.6
2) GP3J2　　　Mg-chlorite		2.4
chlorite-water　300°C: water		2.5
350°C: water		3.1
400°C: water		3.8
3) GP85/23B　　Mg-chlorite		1.8
chlorite-water　　　300°C: water		1.8
350°C: water		2.5
400°C: water		3.1
fractionations:　1)　after Clayton et al. (1972), and		
2,3) after Wenner and Taylor, (1971)		
calculated fluid at 350°C		**2.4**
[range 300° - 400°C		1.8 - 3.8‰]

Estimates of the fluid compositions are less easy to make. Not much is known about the compositions of early Proterozoic seawater, fresh water, or fluids circulating through the crust. These compositions must be estimated from indirect evidence, which is presented below. Support for a low ^{18}O fluid source for the hydrothermal system comes from the decreasing $\delta^{18}O$ trend for quartz and hydrous minerals with increasing alteration in the zones (Figure 3; Table 2)(De Groot, 1993, in prep.). Carbon isotopes from stratiform carbonates intercalating the felsic volcanic rocks hosting the Hjulsjö alteration zones, show "normal" marine carbonate val-

ues, suggesting a marine environment of deposition for the carbonates. This is supported by the regional Mg-enrichment trend in the volcanic rocks of the Bergslagen area, with no other reasonable source for the Mg than seawater (see the section on Mg enrichment calculations below for more extended discussions). For these reasons seawater is assumed to have formed the initial fluid in the Hjulsjö alteration zones. Seawater oxygen isotopic composition in the early Proterozoic is considered to have deviated very little from presentday value (Sheppard 1986; Muehlenbachs, 1986, 1987), and therefore the $\delta^{18}O^i_{H2O}$ for the Hjulsjö alteration zones is assumed to be about zero.
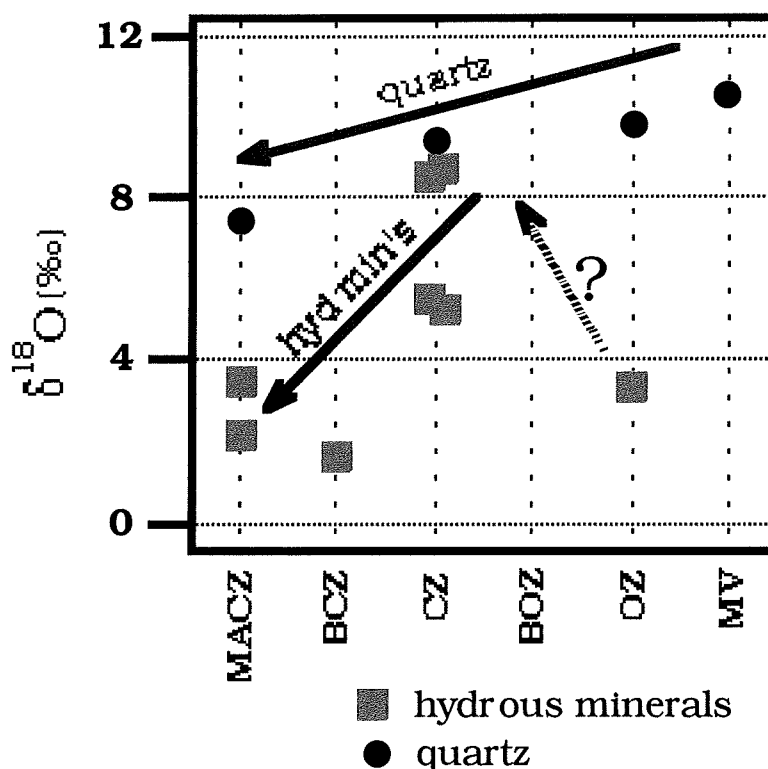
Figure 3. Oxygen isotopic values of quartz (solid circles) and hydrous mineral (light-grey squares) separates from different locations through the Hjulsjö alteration zones. Alteration grade increases from right (MV) to left (MACZ) in the diagram. MV = meta-volcanic rocks, OZ = outer alteration zone, BOZ = border between outer- and central alteration zones, CZ = central alteration zone, BCZ = border between most altered and central alteration zones, MACZ = most altered central alteration zone. Dark-grey arrows, marked with quartz and hyd min's (= hydrous minerals) show trends of oxygen isotope values through alteration zones; direction of arrow towards most altered alteration zones. Striked grey arrow marked with ? includes the oxygen isotope value from one hydrous mineral sample in the outer zone, deviating from the general trend. Oxygen isotopes in per mil. (‰) versus V-SMOW.

All minerals in the most altered parts of the Hjulsjö zones are either completely remobilized, or newly formed, and are assumed to be in isotopic equilibrium with the fluid causing alteration. Quartz ($\delta^{18}O$: 7.7‰) and Mg-chlorites ($\delta^{18}O$: 2.4 and 1.8‰) form the most altered parts of the Hjulsjö zones, and are in equilibrium with water with $\delta^{18}O$ values of 2.4‰ (quartz) and 3.1 and 2,5‰ (Mg-chlorites) at a temperature of 350°C, the estimated temperature for the Hjulsjö alteration system (De Groot, 1990; De Groot and Baker, 1992). If a temperature range of ± 50°C is included, the water $\delta^{18}O$ in equilibrium with the quartz varies between 0.8

and 3.6‰ and between 1.8 and 3.7‰ for the Mg-chlorites. $\delta^{18}O^i_{H2O}$ is assumed to have a value of 2.4‰ with a possible range of 0.8 to 3.7‰ at a temperature of 350°(±50°)C.

Water/rock calculations

Applying the formulas for closed systems and open systems, with the isotopic values given above, results for W/R ratios at 350°C of 0.96 (300°C: 2.88; 400°C: 0.61) and 0.67 (300°C: 1.36; 400°C: 0.49) are calculated (Table 5).

Table 2. Oxygen isotope values of quartz and hydrous mineral separates from the Hjulsjö alteration zones

SAMPLE	MINERAL	$\delta^{18}O$: meas.	mean ±[n]
BJ550	Quartz	7.58	7.7 ±0.12[2]
			7.82
	Muscovite/	3.51	3.5 ±0.03[2]
	Mg-chlorite	3.48	
1J1	Quartz	9.73	9.7
	Phlogopite	3.57	3.6
2J2	Quartz	9.23	9.2
	Phlogopite	8.43	8.4
	Muscovite	8.38	8.4
2J17	Quartz	10.79	10.7 ±0.07[2]
		10.65	
3J2	Mg-chlorite	2.47	2.4 ±0.11[2]
		2.25	
3J15	Muscovite	5.31	5.5 ±0.15[2]
			5.60
4J4	Mg-chlorite	5.71	5.7
GP85/23B	Mg-chlorite	1.84	1.8 ±0.07[2]
		1.71	

Notes: Isotopic values are related to the V-SMOW standard in the usual delta notation in per mil (‰). meas. = measured. Mean: mean of measured values, or, if single measurement, the single value. ±[n] = precision and number of measurements.

Rock Mg-enrichment calculation method

Description

This method is based on the circulation of a Mg-containing fluid (seawater) interacting with crustal rocks. During the fluid-rock interacting process elements from the rocks are mobilised, while others are deposited from the fluid in new formed minerals in the altered rocks. In this way Mg is completely stripped from the fluid and incorporated in new formed Mg-containing minerals in the altered rocks. If the change in Mg in the rocks (increase) and in the fluids (decrease) is known per unit volume, it is possible to calculate the amount of fluid which

exchanged with the rocks per unit volume. This can be represented as:

$$(3) \qquad W/R = \frac{Mg_{altered-rock} - Mg_{fresh-rock}}{Mg_{seawater}}$$

It is suggested that the approach provides estimates of the lower limits of W/R ratios, because of the assumption that the fluid actually exchanged completely with the rocks through which they are passing. This may not, in fact, be the case.

Regional Mg-enrichment in the West Bergslagen region

The West Bergslagen region is composed of at least 90 to 95 % felsic volcanics, volcanic derived clastics, and felsic intrusives (granites, granophyres and porphyries). A regional enrichment in Mg was recognised as soon as geochemistry was applied to the region in the first half of this century, and was discussed by different generations of geologists after discovery (e.g. Sundius, 1922; Geijer and Magnusson, 1944; Magnusson, 1970). Mg-enrichment by seawater is now a widely accepted explanation for the regional Mg-enrichment of the Bergslagen region, as exemplified by the exhalative ore mineralization or (sub)seafloor metamorphism models presented by Boström et al. (1979), Boström (1980), Vivallo (1985), Oen et al. (1986), Oen and Hellingwerf (1988), and Oen and Lustenhouwer (1992). This explanation is supported by carbonate-carbon isotopic values for stratiform carbonate horizons, intercalated in the felsic volcanics, which yield values of "normal" marine deposited carbonates (De Groot and Sheppard, 1988) and by fluid inclusion I and Br compositions of the Stripa granite, which may point to involvement of ancient (early Proterozoic?) seawater in the inclusion fluids (Irwin and Reynolds, 1995).

In considering possible sources for the Mg-enrichment in the West Bergslagen rocks, the mafic rocks and dolomites are excluded, because they are not voluminous enough to explain the regional Mg-enrichment. A mantle source is also out of the question, since there is no evidence for mantle contributions to the crustal rock compositions. The only reasonable source of fluid, considering the arguments given above, is seawater, which seeped down into the supracrustal rocks and, after being heated by active magmatic processes, interacted with the rocks in question.

Chemical data

Assuming that seawater is the most probable source of Mg in the altered rocks, the problem of the Mg content of early Proterozoic seawater arises. Seawater composition over the geologic time-scale was discussed by Holland (1978, 1984) where it was stated that changes by more than a factor of 3 in the concentration of any of the major ions, including Mg, in seawater was unlikely. Consequently, the present-day seawater Mg composition is assumed for early Proterozoic seawater, with the probable range as proposed by Holland (1978, 1984). Seawater Mg-compositions and MgO- and Mg-compositions for fresh (the group of 12 least altered rocks) and altered rocks of different parts of the Hjulsjö zones are given in Table 3. Both, mass and volume normalised calculations are carried out with the Mg enrichment model by formula (3) as presented above.

Table 3. Magnesium contents of fresh rocks, of different altered rocks from the Hjulsjo alteration zones, and of seawater

MgO	wt%	g/dm^3	g/kg
least altered rocks:			
[mean of 12 samples]*	0.56	14.92	5.61
mean density*:	2.659		
Hjulsjö zones altered rock samples:			
2J11: meta-volc. rock	0.78	21.03	7.80
2J21: outer alt. zone	0.80	21.57	8.00
2J18: outer alt. zone	1.31	35.32	13.10
2J3: central alt. zone	4.46	120.24	44.60
3J4: central alt. zone	4.64	125.09	46.40
BJ550: most alt. zone	4.62	124.56	46.20
density alt. rocks*:	2.696		

Mg		g/dm^3	g/kg
least altered rocks:			
[mean of 12 samples]		8.95	3.37
Hjulsjö zones altered rock samples:			
2J11: meta-volc. rock		12.62	4.68
2J21: outer alt. zone		12.94	4.80
2J18: outer alt. zone		21.19	7.86
2J3: central alt. zone		72.14	26.76
3J4: central alt. zone		75.05	27.84
BJ550: most alt. zone		74.74	27.72
Seawater:			
a) Bischoff and Dickson (1975)		1.25	1.29
b) Hajash and Chandler (1981)		1.45	1.50
c) Mitra et al. (1994)		1.23	1.27
density seawater:	1.035 (based on 35 ‰ salinity)		

Notes: volc. = volcanic; alt. = alteration. * from Baker and De Groot (1983a).

Water/rock calculations

Applying formula (3) to the Mg-compositions given in Table 3 results in W/R ratios from the most altered rocks of 16 to 19 for mass normalisation, and between 45 to 54 for volume normalisation. If we consider the variation in W/R ratios through the different alteration zones (Table 5), than it is obvious that the meta-volcanic rocks and the outer alteration zones were, in all cases, effected by lower W/R ratios ranging between 1 and 10. A slight increase is noted for the meta-volcanic rocks towards the outer alteration zone. The central alteration zone and the most altered sample fall within the same range of W/R ratio, of 17 ± 2 and 47 ± 5 for mass and volume normalised cases respectively. If we include the uncertainty of the Mg content of sea-

water (Holland, 1978, 1984), the ranges of most altered rocks is between 5 -58 for mass normalisation and 15 - 160 for volume normalisation. Again these calculations obtain minimum values, because they are based on complete stripping of Mg by the rock from the fluid during exchange, which may be far from complete.

Rare earth element leaching method

Description

The mobility of rare earth elements (REEs) in fluid-rock exchanging processes is reported in many publications. Exhalative fluids on the seafloor are strongly enriched in REEs compared to seawater, leaching the REEs from basaltic rocks (Michard et al., 1983; Klinkhammer et al., 1994; Mitra et al., 1994; James et al., 1995; James and Elderfield, 1996). In hydrothermally altered crustal rocks a strong REE mobility is reported in many works (i.e. Graf, 1977; Kerrich and Fryer, 1979; Alderton et al., 1980; Baker, 1985b; Bartley, 1986; Giuliani et al., 1987; Bau, 1991; Lottermoser, 1992; Ward et al., 1992; Bau and Dulski, 1995; Poitrasson et al., 1995). If the decrease in REEs in rocks during exchange with fluids is known, as well as the concomitant increase in fluid REE composition (or alternatively the REE composition of a fluid which originally was extremely low in REE) the amount of fluid needed to mobilise the REE from the altered rocks, and thus the W/R ratio, can be calculated.

Presented in the form of a formula the calculation is:

$$(4a) \qquad W/R = \frac{REE_{initial-rock} - REE_{final-rock}}{REE_{final-fluid} - REE_{initial-fluid}}$$

or alternatively, if initial fluid has very low REE:

$$(4b) \qquad W/R = \frac{REE_{initial-rock} - REE_{final-rock}}{REE_{fluid}}$$

Again, the calculated values represent lower limits of W/R ratios, because it is assumed that the fluid leached the maximum volume of REE from the rock. If lower concentrations were leached from the same rock volume, the actual W/R ratios would be larger than the calculated ones.

REE compositions at theWest Bergslagen region

Although the volcano-sedimentary basin of Bergslagen, in which the Hjulsjö alteration zones are developed, was a marine basin, its felsic composition is abnormal, and may invalidate comparison with basaltic seafloor hydrothermal processes. Therefore, besides use of actual seafloor hydrothermal REE compositions (Elderfield and Greaves, 1982; James et al., 1995; Mitra et al., 1994) for W/R ratio calculation, W/R ratio calculations by ground water REE compositions from granitic areas, such as Tibet and Bulgaria (Michard and Albarède, 1986) and the Carnmenellis batholith, SW England (Smedley, 1991), and by hydrothermal fluid REE compositions of the felsic Valles Caldera, New Mexico (Michard, 1989), are also considered.

The Hjulsjö hydrothermal system was most probably a sub-seafloor hydrothermal system, and highly comparable with actual active sub-seafloor hydrothermal systems. Adoption of REE-compositions of similar fluids for the Hjulsjö system is considered a valid procedure, even more if felsic rock related fluid REE-compositions are included in the model.

REE mobility in the Hjulsjö alteration zones is clearly shown by Baker and De Groot (1983) and De Groot and Baker (1992). Light REE are strongly leached from the altered rocks while Eu shows an increasing negative anomaly with grade of alteration (Figure 4). Heavy REE are only weakly leached or stay immobile (Figure 4). Strongly leached REEs, such as La, Ce and Sm are selected for W/R ratio calculation. La, Ce, and Sm compositions of the least altered rocks, of meta-volcanic rocks, and of outer-, central- and most altered zones are given in Table 4.
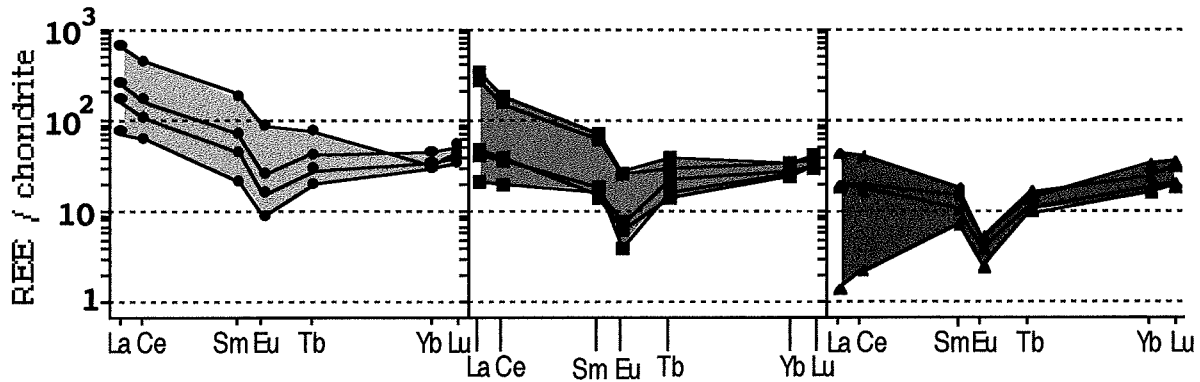
Figure 4. Chondrite-normalized (Evensen et al., 1978) compiled rare earth element diagrams for, from left to right, the meta-volcanic rocks, the outer alteration zone, and the central alteration zone respectively. See text for further explanation.

Fluid REE compositions

Compositions of seafloor hydrothermal fluids, ground waters from granitic areas and hydrothermal fluids from a felsic caldera system are given in Table 4. Seawater REE composition is several orders lower than the hydrothermal or ground water REE compositions, and is neglected in the calculations for that reason. Therefore formula 4b is applied for the REE-W/R ratio calculations below.

Water/rock calculations

Calculations of W/R ratios by seafloor hydrothermal fluids show negligible or low (sample 2J21; for Ce and Sm) W/R ratios for the meta-volcanic rocks and the outer alteration zones, while the central zones and the most altered sample have comparable W/R ratios of around 7-57 . 10^4 for La, around 19-85 . 10^4 for Ce, and around 0.4-33 . 10^4 for Sm, all rather similar values, be it that Sm-based ratios are comparatively low.

Calculations of W/R ratios by granitic ground waters is sub-divided into three cases: a) the Tibet ground waters, b) the Bulgarian ground waters, and c) the Carnmenellis fluids. Case a) and b) do not show La-based W/R ratios.

- Case a) results in W/R ratios of 0-19 . 10^4 (Ce) and of 0-45 . 10^4 (Sm) for the outer zone and of 111-135 . 10^4 (Ce) and of 140-155 . 10^4 (Sm) for the central and most altered zone.
- Case b) results in W/R ratios of 0 - 84 . 10^4 (Ce) and of 0-151 . 10^4 (Sm) for the outer zone and of 121-594 . 10^4 (Ce) and of 124-521 . 10^4 (Sm) for the central and most altered zone.
- Case c) results in W/R ratios of 0 (La), of 0 - 1 . 10^4 (Ce) and of 0-1.3 . 10^4 (Sm) for the

outer zone and of 19-85 . 10^4 (La), of 1.4-7.1 . 10^4 (Ce) and of 1.0-4.6 . 10^4 (Sm) for the central zone and most altered sample.

Cases a) and b) results in comparable ratios between 120 and 600 for the central and most altered zones, while case c), representing the Carnmenellis fluid composition, leads to values that are 2 orders smaller than the former cases. This difference in ratios results from the higher REE content of fluids in this example.

Table 4. Rare earth element (REE) compositions of fresh and altered rocks, of seawater, of seafloor hydrothermal fluids, of groundwaters in granitic areas, and of fluids in a felsic caldera hydrothermal system. All samples are given in gram REE/gram rock or fluid .

SAMPLE	La	Ce	Sm
ROCKS			
least alt. volcanics [mean of 12]	56.3 . 10^{-6}	98 . 10^{-6}	9.77 . 10^{-6}
2J11 - metavolcanic rock	64.8 "	108 . "	10.62 "
2J21 - outer zone	58.3 "	86 . "	7.65 "
2J18 - outer zone	82.6 "	117 . "	11.37 "
2J3 - central zone	5.1 "	13 . "	2.48 "
3J4 - central zone	12.5 "	28 . "	3.21 "
BJ550 - most altered zone	13.2 "	27 . "	3.11 "
SEAWATER[1]	5.1 . 10^{-15}	0.9 . 10^{-15}	0.80 . 10^{-15}
HYDROTHERMAL FLUIDS			
seafloor[2]	0.9-6 . 10^{-10}	3-20 . 10^{-10}	0.2-18 . 10^{-10}
Valles Caldera[3]	--	32-200 . 10^{-9}	8.4-16 . 10^{-9}
GROUNDWATERS IN GRANITIC AREAS			
Tibet[4]	--	63 . 10^{-12}	4.7 . 10^{-12}
Bulgaria[4]	--	14.3-58 . "	1.4-5.3 . "
Carnmenellis[5]	0.6-2.3 . 10^{-9}	1.2-4.9 . 10^{-9}	0.16-0.69 . 10^{-9}

Notes: 1) from Elderfield and Greaves (1982), Mitra et al. (1994) and James et al. (1995); 2) from Michard et al. (1983), Klinkhammer et al. (1994), James et al. (1995) and James and Elderfield (1996); 3) from Michard (1989); 4) from Michard and Albarède (1986); 5) from Smedley (1991).

Calculations of W/R ratios by the caldera waters again results in ratios about 3 to 4 orders smaller than the Tibet or Bulgarian based ratios and 1 to 2 orders smaller than the Carnmenellis based ratios. Ratios are between 0-0.04 . 10^4 (Ce) and 0-0.03 . 10^4 (Sm) for the outer zone and between 0.04-0.3 . 10^4 (Ce) and 0.04-0.09 . 10^4 (Sm) for the central and most altered zone. Again these are minimum W/R ratio values, since the fluids may not have leached

REE's at the volumes as given, which are assumed to be saturation values of REE in the fluids for those specific conditions.
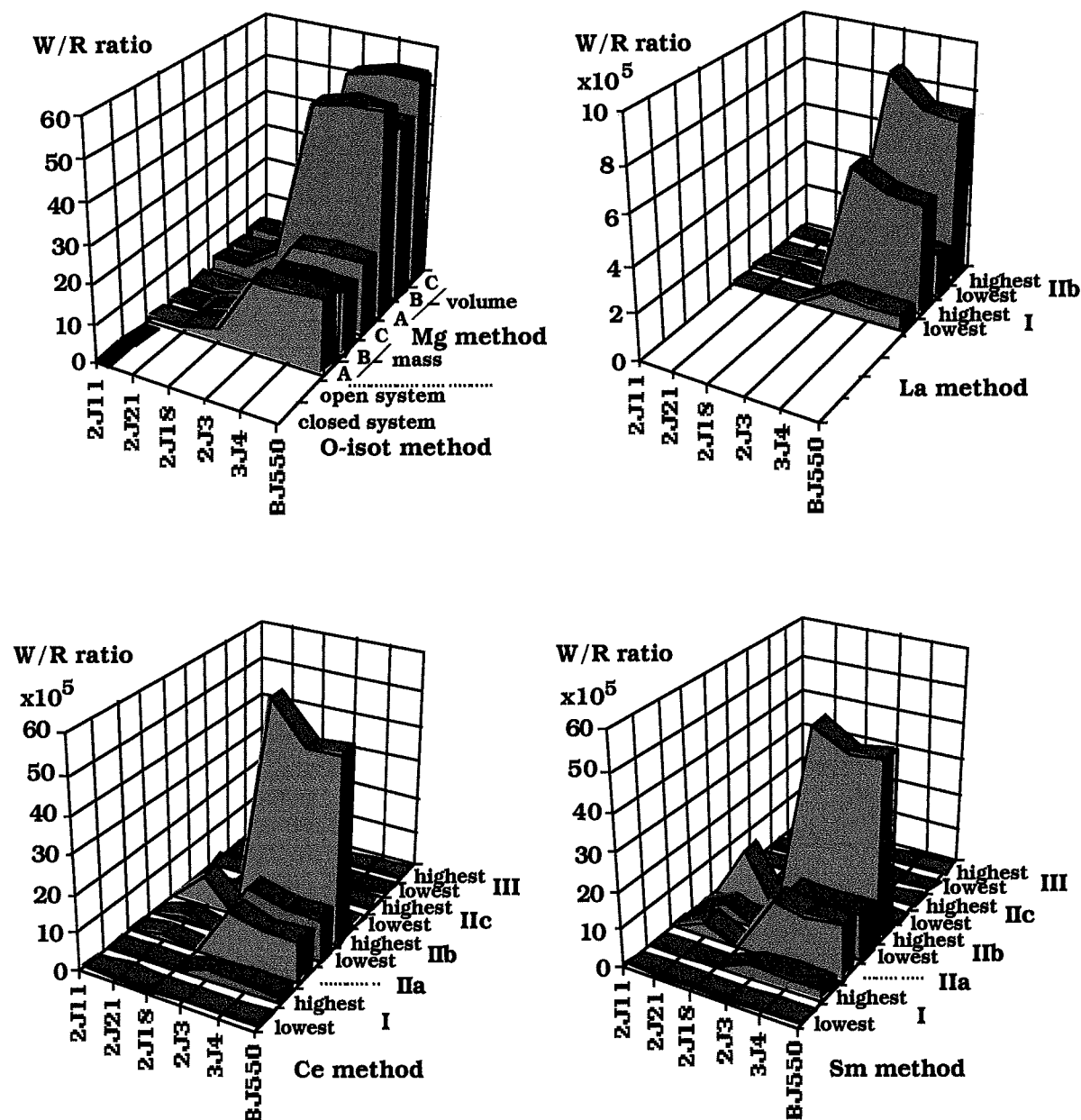

Figure 5. Block diagrams showing water-rock ratios obtained by the different calculation methods for meta-volcanic rock (2J11), outer alteration zone (2J21; 2J18), central alteration zone (2J3; 3J4), and most altered central alteration zone (BJ550) samples. Note the different scales of the diagrams. See Table 5 for W/R ratio values, obtained for La, Ce, and Sm by the use of different fluid compositions, and their codes (I, IIa, IIb, IIc, III) as also used in these diagrams; the lowest and highest values obtained by the different W/R ratio calculations by REEs are used, and marked, in the diagrams.

Table 5. Water-rock (W/R) ratio calculated values for the oxygen isotope exchange, the Mg-enrichment, and the REE-leaching methods .

OXYGEN ISOTOPE EXCHANGE METHOD		
	w/r ratio:	range:
closed system:	0.96 [350°C]	0.61 [300°C] - 2.88 [400°C]
open system:	0.67 [350°C]	0.49 [300°C] - 1.36 [400°C]

Mg-ENRICHMENT METHOD	MASS			VOLUME		
SEAWATER:	A	B	C	A	B	C
2J11 - metavolcanics	1.0	0.9	1.0	2.9	2.5	3.0
2J21 - outer zone	1.1	1.0	1.1	3.2	2.8	3.2
2J18 - outer zone	3.5	3.0	3.5	9.8	8.4	10.0
2J3 - central zone	18.1	15.6	18.4	50.6	43.6	51.4
3J4 - central zone	19.0	16.3	19.3	52.9	45.6	53.7
BJ550 - most altered	18.9	16.2	19.2	52.6	45.4	53.5

REE-LEACHING METHOD					
W/R-RATIO BY:	I	IIa	IIb	IIc	III
La [W/R ratios x 10^4]					
2J11 - metavolcanics	0	--	--	0	--
2J21 - outer zone	0	--	--	0	--
2J18 - outer zone	0	--	--	0	--
2J3 - central zone	8.5-57	--	--	22-85	--
3J4 - central zone	7.3-49	--	--	19-73	--
BJ550 - most altered	7.2-48	--	--	19-72	--
Ce [W/R ratios x 10^4]					
2J11 - metavolcanics	0	0	0	0	0
2J21 - outer zone	0.6-4	19	21-84	0.2-1	0-0.04
2J18 - outer zone	0	0	0	0	0
2J3 - central zone	4.3-28	135	147-594	1.7-7.1	0.04-0.3
3J4 - central zone	3.5-23	111	121-490	1.4-5.8	0.04-0.2
BJ550 - most altered	3.6-24	113	122-497	1.4-5.9	0.04-0.2
Sm [W/R ratios x 10^4]					
2J11 - metavolcanics	0	0	0	0	0
2J21 - outer zone	0.1-11	45	40-151	0.3-1.3	0.01-0.03
2J18 - outer zone	0	0	0	0	0
2J3 - central zone	0.4-36	155	138-521	1.1-4.6	0.05-0.09
3J4 - central zone	0.4-33	140	124-469	1.0-4.1	0.04-0.08
BJ550 - most altered	0.4-33	142	126-476	1.0-4.2	0.04-0.08

Notes: W/R = water/rock. Mg seawater composition data (see also Table 3): A = Bischoff and Dickson, 1975; B = Hajash and Chandler, 1981; C = Mitra et al., 1994. REE compositions of

[Notes table 5; continued from page 14] fluids: I = seafloor hydrothermal fluids (Elderfield and Greaves, 1982; James et al., 1995; Mitra et al., 1994); II = ground waters from granitic areas, a = Tibet (Michard and Albarède, 1986), b = Bulgaria (Michard and Albarède, 1986), c = ground waters from Carnmenellis, SW England (Smedley, 1991); III = hydrothermal fluids in the felsic Valles Caldera, New Mexico, USA (Michard, 1989).

DISCUSSION

From the above presentation of different methods for W/R ratio calculation, it must be clear that different methods applied on the same set of samples from the Hjulsjö alteration zones results in a wide range of estimates (Figure 5). Although there is considerable uncertainty inherent in the parameters and assumptions used in the calculations, these are not considered adequate to explain the enormous differences that emerge in the calculated W/R ratios. Thus another explanation for these differences needs to be considered.

The most logical explanation for the observed discrepensies is, that the respective exchange models, used for calculation, reached equilibrium at different stages, such that exchange of the specific parameter (i.e. $\delta^{18}O$, Mg, La, Ce, Sm) between the fluid and the rock also reached a steady state at different times in the alteration process. Subsequent to steady-state, no further modification of that specific parameter occurs in the fluid or rock, and the W/R ratio is effectively "frozen in" at that stage. Thus, all fluid exchanging with the rock after reaching the equilibrium situation, may effect certain parameters, but not others. Considerable amounts of fluid may traverse the rock after equilibration for a given chemical system is reached. Assuming that this is a reasonble explanation, it is concluded that, in the same hydrothermal alteration system, the oxygen isotope exchange system reached equilibrium situation well before the Mg-exchange system, which in turn reached a steady-state long before the REE-leaching system. Because the alteration system comprizes con-centric zones (De Groot and Baker, 1988; De Groot, 1993), where the highest temperature and W/R ratios are expected in the central parts, with decrease towards the outer parts of the alteration zones. With decreased temperature, also the solubilities of elements in the fluids may change, for which no corrections are included in this study, and will result in lower/higher W/R ratios for higher/ lower solubility of REEs in the fluid. The statement that all calculation methods represent lower limits of W/R ratios therefore is a valid one, albeit that some of the results are extremely far from a realistic W/R ratio, and are meaningless for that reason. Even the calculation leading to the highest W/R ratios still is considered as a lower limit for the studied system, although it already represents an extremely high W/R ratio.

Michard (1989) reached a similar conclusion, based on the relatively low REE contents in hydrothermal fluids from the Valles Caldera, New Mexico, and suggested that very high W/ R ratios are needed to change the REE composition of the altered rocks. Michard et al. (1983), concluded, on the basis of REE leaching of < 1% of the seafloor basalt, that W/R ratios are around 1 in sub-seafloor hydrothermal processes. This ratio is supported by Edmond et al. (1979), Albarède et al. (1981), Bowers et al. (1988), and Klinkhammer et al. (1994). The ratio, however, contrast with a later prediction by Michard (1989), as well as the W/R estimates in this work. An important factor, which may explain this discrepency, is the scale of the alteration considered. In sub-seafloor alteration processes the major part of the alteration takes place in channelised zones with very high W/R ratios, while a considerable part of the host rock is only weakly effected, and may lead to a relatively low W/R ratio for the entire system on a larger scale.

Another important factor in W/R calculations is the possible mixture of the hydrothermal fluids with other fluids after fluid-rock exchange, such as during seafloor exhalative processes. This will eventually lead to dilution of the parameter of interest. This prediction could be solved by utilizing "end member" calculations on mixed fluids (James and Elderfield, 1996).

CONCLUSIONS

The objectives of this study were to test whether W/R ratio estimation, in a well-studied early Proterozoic hydrothermally mineralized region, by different methods, will yield consistent and meaningful results. Although a number of assumptions have to be made, it is clear that W/R ratio calculations can be made on ancient mineralized terranes. However, it must also be clear that the wide scatter in W/R ratios by the different methods places severe constraints on the application calculation of estimates which do not account for their reliability and for the specific system in question. This is not only true for ancient, but is also valid for modern alteration systems. Ancient systems generally will show wider ranges of calculated W/R ratios for all methods, because the parameters are less fixed. It is stressed that application of a W/R ratio calculation must be controlled by other methods and must also be in accordance with the chemistry and mineralogy of the alteration system. It is suggested that a major part of published W/R ratios in literature might be unrealistic and may provide very different W/R ratios if other methods are applied on the same alteration systems.

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REFERENCES

Albarède, F., Michard, A., Minster, J.F. and Michard, G., 1981. $^{87}Sr/^{86}Sr$ ratios in hydrothermal waters and deposits from the East Pacific Rise at 21°N. Earth Planet. Sci. Lett., 55: 229-236.

Alderton, D.H.M., Pearce, J.A. and Potts, P.J., 1980. Rare earth element mobility during granite alteration: evidence from southwest England. Earth Planet. Sci. Lett., 49: 149-165.

Allen, R.L., Lundström, I., Ripa, M., Simeonov, A. and Christofferson, H., 1996. Facies analysis of a 1.9 Ga, continental margin, backarc, felsic caldera province with diverse Zn-Pb-Ag-(Cu-Au) sulfide and Fe oxide deposits, Bergslagen region, Sweden. Econ. Geol., 91: 979-1008.

Baker, J.H. and De Groot, P.A., 1983a. Proterozoic seawater-felsic volcanics interaction W. Bergslagen, Sweden. Evidence for high REE mobility and implications for 1.8 Ga seawater compositions. Contrib. Mineral. Petrol., 82: 119-130.

Baker, J.H. and De Groot, P.A., 1983b. Erratum - Proterozoic seawater-felsic volcanics interaction W. Bergslagen, Sweden. Evidence for high REE mobility and implications for 1.8 Ga seawater compositions. Contrib. Mineral. Petrol., 84: 102.

Baker, J.H., 1985a. The petrology and geochemistry of 1.8 - 1.9 Ga granitic magmatism and related sub-seafloor hydrothermal alteration and ore-forming processes, W. Bergslagen, Sweden. Ph.D. thesis, GUA Papers of Geology, University of Amsterdam: pp. 204.

Baker, J.H., 1985b. Rare earth and other trace elements mobility accompanying albitization in a Proterozoic granite, W. Bergslagen, Sweden. Min. Magazine, 49: 107-115.

Baker, J.H., Hellingwerf, R.H. and Oen, I.S., 1988. Structure, stratigraphy and ore-forming processes in Bergslagen: implications for the development of the Svecofennian of the Baltic Shield. Geol. Mijnbouw, 67: 121-138.

Bartley, J.M., 1986. Evaluation of REE mobility in low-grade metabasalts using mass-balance calculations. Norsk Geol. Tidsskr., 66: 145-152.

Bau, M. and Dulski, P., 1995. Comparative study of yttrium and rare-earth element behaviours in fluorine-rich hydrothermal fluids. Contrib. Mineral. Petrol., 119: 213-223.

Bischoff, J.L. and Dickson, F.W., 1975. Seawater-basalt interaction at 200°C and 500 bars: implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry. Earth Planet. Sci. Lett., 25: 385-397.

Boström, K., Rydell, H. and Joensuu, O., 1979. Långban - An exhalative sedimentary deposit? Econ. Geol., 74: 1002-1011.

Boström, K., 1980. Långban - an exhalative sedimentary island arc deposit? Geol. Fören. Stockholm Förh., 102: 185-186.

Bowers, T.S., Campbell, A.C., Measures, C.L., Spivack, A.J., Khadem, M. and Edmond, J.M., 1988. Chemical controls on the composition of vent fluids at 13°-11°N, East pacific Rise. J. Geophys. Res., 93: 4522-4536.

Clayton, R.N. and Mayeda, T.K., 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. Geochim. Cosmochim. Acta, 27: 43-52.

Clayton, R.N., O'Neil, J.R. and Mayeda, T.K., 1972. Oxygen isotope exchange between quartz and water. J. Geophys. Res., 77: 3057-3067.

De Bruin, M., 1983. Instrumental neutron activation analysis - a routine method. PhD thesis, Technical University Delft, Delftse Univ. Pers. Delft: pp. 270.

De Groot, P.A. and Sheppard, S.M.F., 1988. Carbonate rocks from W. Bergslagen, Central sweden: isotopic (C, O, H) evidence for marine deposition and alteration by hydrothermal processes. Geol. Mijnbouw, 67: 177-188.

De Groot, P.A., 1990. A model for the formation of potassic and sodic alteration phases during hydrothermal processes: application of thermodynamic models to natural systems. Geol. Fören. Stockholm Förh., 112: 180-183.

De Groot, P.A. and Baker, J.H., 1992. High element mobility in 1.9-1.86 Ga hydrothermal alteration zones, Bergslagen, central Sweden: relationships with exhalative Fe-ore mineralizations. Precam. Research, 54: 109-130.

De Groot, P.A., 1993. Stable isotope (C, O, H), major- and trace element studies on hydrothermal alteration and related ore mineralization in the volcano-sedimentary belt of Bergslagen, Sweden. PhD thesis, University of Utrecht, Geologica Ultraiectina, No. 98.: pp. 181.

De Groot, P.A., in prep. A stable isotope (O, H) study on the Early Proterozoic Hjulsjö hydrothermal alteration system, W. Bergslagen, central Sweden.

Edmond, J.M., Measures, C., Mangum, B., Grant, B., Sclater, F.R., Collier, R., Hudson, A., Gordon, L.I. and Corliss, J.B., 1979. On the formation of metal-rich deposits at ridge crests. Earth Planet. Sci. Lett., 46: 19-30.

Evensen, N.M., Hamilton, P.J. and O'Nions, R.K., 1978. Rare-earth abundances in chondritic meteorites. Geochim. Cosmochim. Acta, 42: 1199-1212.

Geijer, P. and Magnusson, N.H., 1944. De mellansvenska Järnmalmernas Geologi. Sveriges Geol. Unders., Serie Ca: pp. 654.

Giuliani, G., Cheilletz, A. and Mechiche, M., 1987. Behaviour of REE during thermal metamorphism and hydrothermal infiltration associated with skarn and vein-type tungsten ore bodies in central Morocco. Chem. Geol., 64: 279-294.

Graf, J.L.J., 1977. Rare earth elements as hydrothermal tracers during the formation of massive sulfide deposits in volcanic rocks. Econ. Geol., 72: 527-548.

Hajash, A. and Chandler, G.W., 1981. An experimental investigation of high-temperature interactions between seawater and rhyolite, andesite, basalt and peridotite. Contrib. Mineral. Petrol., 78: 240-254.

Holland, H.D., 1978. The chemistry of the atmosphere and oceans. Wiley & sons: pp. 351.

Holland, H.D., 1984. The chemistry of the earliest atmosphere and oceans. In: H.D. Holland (Editor), The chemical evolution of the atmosphere and oceans. Princeton University Press: 89-127.

Irwin, J.J. and Reynolds, J.H., 1995. Multiple stages of fluid trapping in the Stripa granite indicated by laser microprobe analysis of Cl, Br, I, K, U, and nucleogenic plus radiogenic Ar, Kr, and Xe in fluid inclusions. Geochim. Cosmochem., Acta 59: 355-369.

James, R.H., Elderfield, H. and Palmer, M.R., 1995. The chemistry of hydrothermal fluids from the Broken Spur site, 29°N Mid-Atlantic Ridge. Geochim. Cosmochim. Acta, 59: 651-659.

James, R.H. and Elderfield, H., 1996. Chemistry of ore-forming fluids and mineral formation rates in an active hydrothermal sulfide deposit on the Mid-Atlantic Ridge. Geology, 24: 1147-1150.

Jasinski, A.W., 1988. Activity diagrams for the $MgO-Na_2O-K_2O-SiO_2-Al_2O_3-H_2O-HCl$ system in the temperature range 298-623 K and 1 bar pressure: Application to the 1900 Ma phlogopite-Mg chlorite-sericite schists of W. Bergslagen, Sweden. Geol. Mijnbouw, 67: 379-395.

Kerrich, R. and Fryer, B.J., 1979. Archaean precious-metal hydrothermal systems, Dome Mine, Abitibi greenstone belt. II REE and oxygen isotope relations. Can. J. Earth Sci., 16: 440-458.

Klinkhammer, G.P., Elderfield, H., Edmond, J.M. and Mitra, A., 1994. Geochemical implications of rare earth element patterns in hydrothermal fluids from mid-ocean ridges. Geochim. Cosmochim. Acta, 58: 5105-5113.

Lagerblad, B., 1988. Evolution and tectonic history of the Bergslagen volcano - plutonic complex, central Sweden. Geol. Mijnbouw, 67: 165-176.

Lottermoser, B.G., 1992. Rare earth elements and hydrothermal ore formation processes. Ore Geol. Reviews, 7: 25-41.

Lundström, I., 1987. Lateral variations in supracrustal geology within the Swedish part of the southern Svecokarelian volcanic belt. Precam. Research, 35: 353-365.

Lundström, I., 1988. Regional inter-relationships in the Proterozoic geology of Bergslagen and Southeastern Central Sweden. Geol. Mijnbouw, 67: 157-164.

Magnusson, N.H., 1970. The origin of the iron ores in central Sweden and the history of their alterations. Sveriges Geologiska Undersökning, Serie C, No. 643: pp. 364.

Michard, A., Albarède, F., Michard, G., Minster, J.F. and Charlou, J.L., 1983. Rare-earth elements and uranium in high-temperature solutions from East Pacific Rise hydrothermal vent field (13°N). Nature, 303: 795-797.

Michard, A. and Albarède, F., 1986. The REE content of some hydrothermal fluids. Chem. Geology, 55: 51-60.

Michard, A., 1989. Rare earth element systematics in hydrothermal fluids. Geochim. Cosmochim. Acta, 53: 745-750.

Mitra, A., Elderfield, H. and Greaves, M.J., 1994. Rare earth elements in submarine hydrothermal fluids and plumes from the Mid-Atlantic Ridge., Marine Geol. 46, 217-235.

Muehlenbachs, K., 1986. Alteration of the oceanic crust and the 18O history of seawater. In: J.W. Valley, Taylor, H.P. Jr. and O'Neil, J.R. (Editors), Stable isotopes in high temperature geological processes. Min. Soc. Am., Rev. in Mineralogy, Vol. 16: 425-444.

Muehlenbachs, K., 1987. Oxygen isotope exchange during weathering and low temperature alteration. In: T.K. Kyser (Editor),Stable isotope geochemistry of low temperature fluids. Mineral. Assoc. Canada, Short Course Handbook, Vol. 13: 162-186.

Oen, I.S., Helmers, H., Verschure, R.H. and Wiklander, U., 1982. Ore deposition in a Protero-
zoic incipient rift zone environment: a tentative model for the Filipstad - Grythyttan -
Hjulsjö region, Bergslagen, Sweden. Geol. Rundschau, 71: 182-194.

Oen, I.S., De Maesschalck, A.A. and Lustenhouwer, W.J., 1986. Mid-Proterozoic exhalative-
sedimentary Mn skarns containing possible microbial fossils, Grythyttan, Bergslagen,
Sweden. Econ. Geol., 81: 1533-1543.

Oen, I.S., 1987. Rift-related igneous activity and metallogenesis in SW Bergslagen, Sweden.
Precam. Research, 35: 367-382.

Oen, I.S. and Hellingwerf, R.H., 1988. Textural evidence for seafloor, soft rock hydrothermal
metamorphism in a garnet-scapolite-bearing metatuffite-exhalite-skarn-sphalerite ore
sequence, Nora, Bergslagen, Sweden. Geol. Mijnbouw, 67: 333-348.

Oen, I.S. and Lustenhouwer, W.J., 1992. Cl-rich biotite, Cl-K hornblende, and Cl-rich scapo-
lite in meta-exhalites: Nora, Bergslagen, Sweden. Econ. Geol., 87: 1638-1648.

Parr, J.M., 1988. The metasediments associated with stratabound base metal mineralization,
Ljusnarsberg District, Central Sweden. Geol. Mijnbouw, 67: 189-202.

Poitrasson, F., Pin, Ch. and Duthou, J-L., 1995. Hydrothermal remobilization of rare earth ele-
ments and its effect on Nd isotopes in rhyolite and granite. Earth Planet Sci. Lett., 130:
1-11.

Sheppard, S.M.F., 1986. Characterization and isotopic variations in natural waters. In: J.W.
Valley, Taylor, H.P. Jr. and O'Neil, J.R. (Editors), Stable isotopes in high temperature
geological processes. Min. Soc. Am., Reviews in mineralogy, Vol. 16: 165-183.

Sundius, N.L., 1922. Grythyttefältets Geologi. Sveriges Geol. Unders., Ser C312: 1-354.

Taylor, H.P. Jr., 1979. Oxygen and hydrogen isotope relationships in hydrothermal mineral
deposits. In: H.L. Barnes (Editor), Geochemistry of hydrothermal ore deposits. Wiley &
Sons: 236-277.

Van der Velden, J.W., Baker, J.H., De Maesschalck, A.A. and Van Meerten, Th.G., 1982. Bimo-
dal volcanism in the Grythytte field and associated volcani-plutonic complexes,
Bergslagen, Central Sweden. Geol. Rundschau, 71: 171-181.

ViéleSage, R., Quisefit, J.P., Dejean de la Bâtie, C. and Faucherie, J., 1979. Utilisation du ray-
onnement primaire diffusé par l'enchantillon pour une détermination rapide et précise
des éléments traces dans les roches. X-ray Spectrom., 8: 121-128.

Vivallo, W. and Rickard, D., 1984. Early Proterozoic ensialic spreading-subsidence: evidence
from the Garpenberg enclave, Central Sweden. Precam. Research, 26: 203-221.

Vivallo, W., 1985. Subseafloor hydrothermal alteration during the early Proterozoic at Garpen-
berg, Central Sweden. Mineral. Deposita, 20: 33-42.

Ward, C.D., McArthur, J.M. and Walsh, J.N., 1992. Rare earth element behaviour during evolution and alteration of the Dartmoor granite, SW England. J. Petrology, 33: 785-815.

Wenner, D.B. and Taylor, H.P. Jr., 1971. Temperatures of serpentinization of ultramafic rocks based on $^{18}O/^{16}O$ fractionation between coexisting serpentine and magnetite. Contrib. Mineral. Petrol., 32: 165-185.