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RARE-EARTH ABUNDANCES IN HOST GRANITIC ROCKS AND FRACTURE-FILLING GYPSUM ASSOCIATED WITH SALINE GROUNDWATERS FROM A DEEP BOREHOLE, ATIKOKAN, ONTARIO

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ABSTRACT

Data are presented on the concentration of the rare-earth elements (*REE*) in the granitic host-rock and associated fracture-filling gypsum from a borehole located 30 km northwest of Atikokan, Ontario, within the Archean Eye-Dashwa lakes pluton. The granite is relatively homogeneous and has a steep light-*REE*-enriched pattern. It is irregularly altered; epidote and associated secondary minerals are developed. In addition, some fractures are filled with coarse-grained low-temperature gypsum that appears to be spatially associated with highly saline groundwater. The gypsum samples are also characterized by steep light-*REE* enrichment and, in some cases, *REE* concentrations greatly exceeding those of the adjacent granite. The data suggest that the *REE* content of the gypsum is a product of effective partitioning from the parental brines, which in turn reflects the *REE* distributions of the host granite acquired during long-term rock–water interaction.

Keywords: rare-earth elements, gypsum, fracture fillings, saline groundwaters, plutonic rocks, Atikokan, Ontario, water–rock interaction.

SOMMAIRE

On présente des données sur les concentrations des terres rares dans un granite hôte et du gypse qui en tapisse les fissures; les échantillons proviennent d'un trou de forage situé à 30 km au nord-ouest d'Atikokan, dans le pluton archéen des lacs Eye et Dashwa (Ontario). C'est un granite relativement homogène qui montre un enrichissement marqué en terres rares légères. Il est altéré de façon non homogène, à une association d'épidote et autres minéraux secondaires. Certaines fissures ont été remplies à basse température de cristaux grossiers de gypse qui montreraient une association spatiale à une saumure souterraine. Ce gypse montre aussi l'enrichissement marqué en terres rares légères; dans certains cas, le facteur d'enrichissement surpasse même celui du granite hôte. Les concentrations des terres rares dans le gypse résulteraient d'une répartition efficace de ces éléments à partir des saumures, dont la composition en terres rares reflète la répartition de ces éléments au cours d'une interaction prolongée impliquant granite hôte et saumure.

(Traduit par la Rédaction)

Mots-clés: terres rares, gypse, remplissage de fissures, saumures, roches plutoniques, Atikokan, Ontario, interaction roche - eau.

INTRODUCTION

Saline groundwaters with very high loads of dissolved salts are now known to be widely distributed in the ancient shield areas of the world (Pinneker & Lomonosov 1964, Fritz *et al.* 1979, Korotkov *et al.* 1980, Frape *et al.* 1984). These waters occur in faults and shear zones at depths in excess of 650 metres, and have a range of isotopic and chemical compositions distinct from seawater, meteoric water and brines in sedimentary basins. The origin of these waters is unknown.

We report here some preliminary results of a study of the rare-earth-element (*REE*) chemistry of eight samples of granitic host-rock and nine samples of associated fracture-filling gypsum from a borehole on the Canadian Shield that is also a source of very saline groundwater. The *REE*s in the rock and mineral samples were determined by instrumental neutron-activation procedures in order to throw light on any relationship between the composition of the host rocks and that of the secondary minerals and the saline groundwater.

The geochemical relationship between groundwater and fracture-filling minerals may have important implications to the transport, adsorption and desorption of important ions within such fracture systems. This aspect, in turn, is important in the program of storage of nuclear fuel waste.

GEOLOGY OF THE EYE-DASHWA LAKES PLUTON, ONTARIO

The zoned Eye–Dashwa granodiorite–granite pluton, which is of Archean age, occurs within the Superior Province of the Canadian Shield, and is located about 30 km northwest of Atikokan, Ontario. The 14×9 km pluton is being studied in detail as part of an Atomic Energy of Canada Limited program on the suitability of granitic plutons for the disposal of nuclear fuel waste. Geological studies have included work on the petrology, fractures, and fracture fillings (Kamineni & Brown 1981, Stone & Kamineni 1982), rock alteration (Kamineni & Dugal 1982) and geochronology (Kamineni & Stone 1983).

The granite is coarse grained and affected by alteration, which is concentrated near fracture zones (Kamineni & Dugal 1982). Alteration of the feldspars is indicated by irregular discoloration to shades of pink and green from their original grey and by the development of epidote, carbonate, sericite, chlorite and, occasionally, kaolinite. Fractures and minor shear-zones are very common throughout the rock mass, and many are considered (Stone & Kamineni 1982) to have been sealed during the closing stages of pluton emplacement and cooling.

Much of the alteration is considered to be of the same age. However, some fractures cutting the pluton are predominantly filled with coarse-grained gypsum, which is assumed to be of low-temperature origin and much younger in age (Kamineni 1983). Our project focused on these gypsum-bearing fractures.

Five boreholes (ATK1 – ATK5) were drilled in a small study-area in the southwestern part of the pluton. A core from one of the deepest of these, ATK1, was chosen for study, and from this a representative suite of fresh granite samples and gypsum fracture-fillings was collected. In addition, three samples of saline groundwater from different depths in the hole were sampled by Atomic Energy of Canada Limited for analysis.

Methods and Results

The whole-rock samples were analyzed by Dr. John Ludden, Université de Montréal, using instrumental neutron-activation procedures (Gordon *et al.* 1968, Gibson & Jagam 1980). The samples were activated for four hours in a flux of 1×10^{12} neutron $cm^{-2}s^{-1}$. Counting was performed using a Li(Ge) detector, with a resolution of 1.6 keV at 122 keV.

Specimens of the fracture-filling minerals were hand-separated under a binocular microscope and identified optically and by X-ray diffractometry. They were subsequently crushed in an agate mortar until no particles were distinguishable with the naked eye. The mineral separates were analyzed by the same procedures and counted using a low-energy photon detector, with a resolution of 0.65 keV at 122 keV.

The results for the rock and mineral samples are shown in Tables 1 and 2. In Table 2, results for La were not included as there were analytical difficulties in counting. The precision for the *REE* data for both the rock and mineral samples is better than ±10% (2σ) for all elements.

Discussion

Host-rock geochemistry

The *REE* data for the unaltered material from the ATK1 borehole indicate that the granite was originally quite homogeneous over the 600 m sampled. The only anomalous sample was taken at 1024.6 m. The high *REE* concentrations of this sample may indicate an unusually high modal content of a *REE*-bearing minor phase. The mean *REE* content of the samples (excluding 1024.6) is plotted in Figure 1. The granite has the steep light-rare-earth-enriched pattern typical of granitic rocks of the Precambrian Shield (Ronov *et al.* 1967, Hanson 1980).

REE concentrations in the gypsum

The *REE* contents of nine samples of fracture-filling gypsum from drill hole ATK1 are shown in Figure 2. The gypsum is associated with other secondary minerals, including chlorite and fluorapophyllite $[KCa_4Si_8O_{20}(F, OH) \cdot 8H_2O]$. However, no *REE*-rich secondary phases were observed as fracture fillings, and no correlation is apparent between the amount of chlorite and apophyllite and the *REE* content of the gypsum. X-ray and microscopic examinations suggest that the gypsum is free of inclusions of such *REE*-rich phases as apatite and zircon. We contend that the rare-earth elements are present in the structure of the gypsum, substituting for calcium.

Three features of the gypsum results are important: (a) the dissimilarity between the *REE* patterns of hydrothermal anhydrite of Morgan & Wandless (1980) and those of the gypsum from Atikokan; (b) the extreme light-rare-earth enrichment in some of the gypsum samples, with values of the chondrite-normalized Ce/Yb ratio of over 1000; and (c) the

TABLE 1. REE CONCENTRATIONS IN GRANITE SAMPLES FROM ATK1

Depth(m)	La	Ce	Nd	Sm	Eu	Tb	Ho	Tm	Yb	Lu
443.9	58.4	113.	47.2	7.1	1.85	0.56	0.45	0.27	1.05	0.11
526.4	50.3	95.	39.5	5.6	1.34	0.39	0.57	0.09	0.99	0.16
778.5	61.0	107.	39.8	5.3	1.25	0.33	0.75	0.18	0.97	0.17
888.7	56.1	101.	38.6	5.2	1.28	0.26	0.19	0.03	0.82	0.14
917.5	52.0	100.	41.0	6.0	1.38	0.46	0.25	0.05	1.04	0.15
1013.9	63.1	114.	42.9	5.9	1.40	0.50	0.27	0.15	0.95	0.10
1024.6	77.9	138.	61.8	11.2	3.27	1.01	1.27	0.38	1.63	0.22
1042.9	55.1	100.	43.4	6.0	1.37	0.39	0.33	–	0.81	0.14
Mean*	56.6	104.	41.7	5.9	1.41	0.41	0.40	0.12	0.95	0.14
CV%*+	8.17	6.9	7.1	10.8	14.3	24.8	50.0	70.1	10.2	18.4

* calculated excluding sample 1024.6. Data in ppm.
\+ coefficient of variation.

TABLE 2. REE CONCENTRATIONS IN GYPSUM FROM FRACTURES CUTTING ATK1

Depth (m)	Ce	Nd	Sm	Eu	Gd	Tb	Yb
562.8	70.2	24.1	2.95	.62	–	.17	–
563.3	49.8	12.6	.90	.20	–	.04	.10
752.7	7.77	2.22	.19	.06	–	.05	.04
837.1	.77	.29	–	.01	–	.004	.007
927.7	573.	169.	11.1	1.19	–	.21	.17
927.7	613.	180.	7.25	1.22	2.75	.20	.16
960.6	57.8	16.1	1.65	.32	–	.12	.22
1093.2	84.4	35.2	3.39	.72	1.57	.15	.10
1103.6	5.41	1.52	.13	.03	–	–	–
1129.8	12.5	3.93	.42	.12	–	.02	.04

Data in ppm.

pattern of variation in the Ce/Yb ratio (chondrite-normalized values) of the gypsum with depth in the borehole.

There is very little published information on the *REE* contents of either gypsum or anhydrite; however, Morgan & Wandless (1980) presented data on two samples of hydrothermal anhydrite (Fig. 2).

The different crystal-structures of $CaSO_4{\bullet}2H_2O$ and $CaSO_4$ invalidate a direct comparison of the *REE* concentrations of the two minerals. However, if the gypsum presently found in the fractures is the hydrated equivalent of hydrothermal anhydrite, the *REE* contents might remain unchanged. The dissimilarities of the plots for anhydrite and gypsum indicate that this has not occurred, or else the anhydrite re-equilibrated with groundwater during the hydration. It seems more likely that the observed patterns refer to gypsum formed in equilibrium with low-temperature groundwater.

The steepness of some of the gypsum patterns is of interest because it indicates either *REE* fractionation during precipitation of gypsum or precipitation from *LREE*-enriched parental solutions. It is noted above that the host rock of the fracture-filling material is granitic, and that it has a steep, *LREE*-enriched pattern. Waters in equilibrium with such rocks would inherit *REE* characteristics controlled by the mineralogy of the host rock, the prevailing pressure–temperature conditions, and the appropriate distribution-coefficients. Fractionation of the *REE* would certainly be possible (Nesbitt 1979, Duddy 1980) but is not required, and we assume that waters in equilibrium with the granites were *LREE*-enriched. Unfortunately, it is difficult to demonstrate this by analyzing the samples of water from the borehole, as the rare-earth elements appear to partition very effectively into the secondary gypsum precipitate; observed concentrations of the *REE* in the saline waters are very low (see below). We are not aware of any partition-coefficient data that would allow

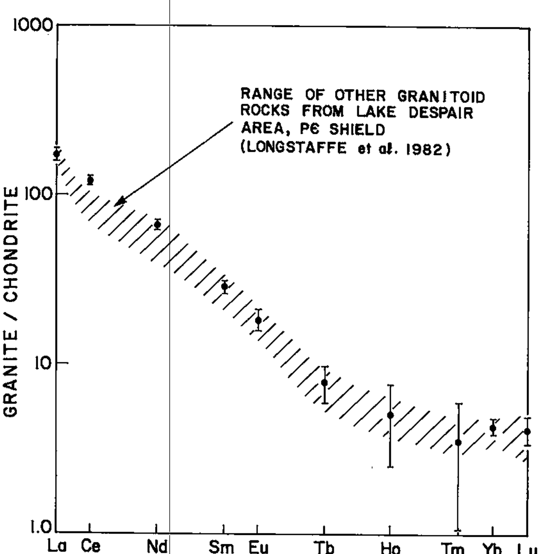

FIG. 1. Mean chondrite-normalized abundances of the rare-earth elements in fresh granite samples from borehole ATK1, Eye–Dashwa lakes pluton. Bars indicate coefficient of variation.

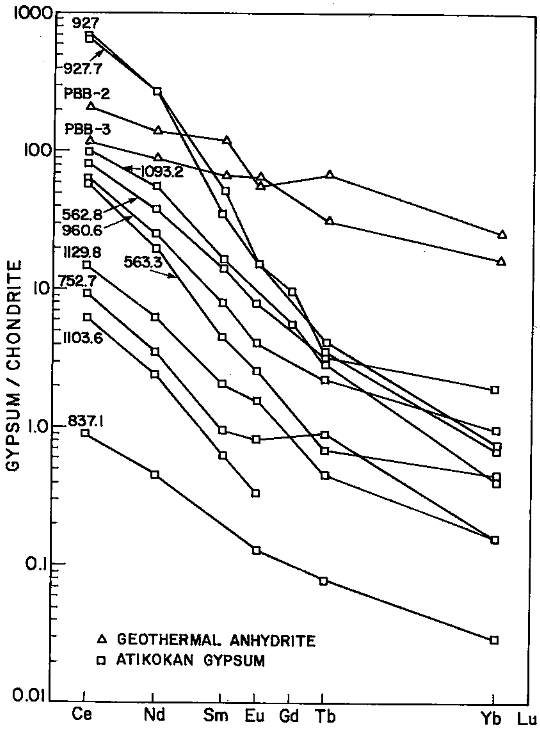

FIG. 2. Chondrite-normalized abundances of the rare-earth elements in gypsum from borehole ATK1, together with data for some examples of hydrothermal anhydrite from Morgan & Wandless (1980). Note: (a) the similarities of the *REE* abundances in the gypsum and granite host (Fig. 1), (b) the strong dissimilarities in *REE* abundances between hydrothermal anhydrite and low-temperature gypsum, and (c) the extreme *LREE* enrichment in both samples of gypsum from 927.7 m, which suggests that these gypsum samples differ in their origin from others collected from the core.

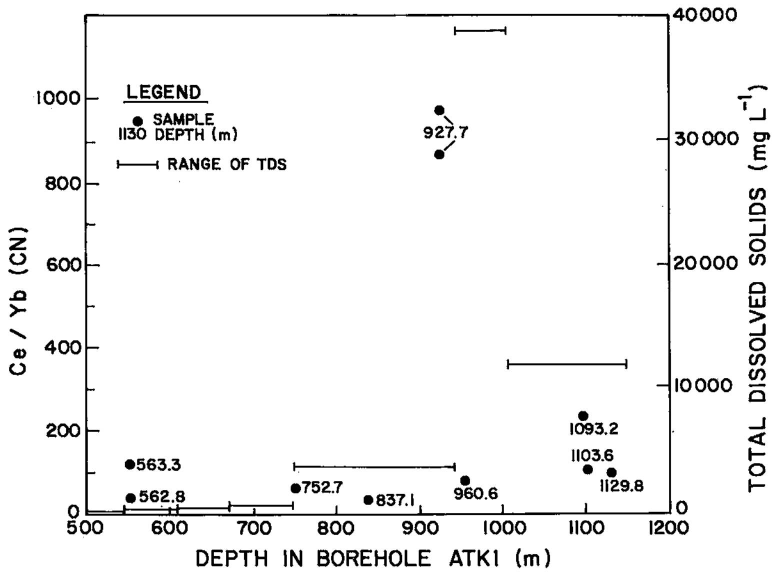

FIG. 3. Chondrite-normalized Ce/Yb ratio in fracture-filling gypsum and groundwater salinity *versus* depth in borehole ATK1. Note the gradual increase in both Ce/Yb ratio and salinity with depth and the anomalous nature of the gypsum samples from 927.7 m, close to the narrow zone of saline waters encountered between 950 and 1000 m.

theoretical calculation of the *REE* abundances of Ca–Na–Cl brines in equilibrium with gypsum.

Other considerations also suggest that fluids in equilibrium with the granite of the Eye–Dashwa pluton are likely to be enriched in the light rare-earths. Kamineni (1985) has demonstrated that increasing intensity of alteration of the Eye–Dashwa granite is associated with decreasing abundances of the *REE*, particularly of the light rare-earths. If these data are interpreted as an indication of an absolute loss of the rare earths from the granite, the fluids instrumental in that loss must also have been enriched in the light rare-earths.

A further point concerning the gypsum data is illustrated in Figure 3. Although there are exceptions, the salinity of the groundwaters gradually increases with depth in the sampled section, with little change in the value of the Ce/Yb ratio for the associated gypsum. However, a sample of strongly saline water was collected from 950 to 1000 m. This may have resulted from the injection of a brine of deep origin along a fracture into a regime of brackish water. Solubility data for $CaCl_2$ (Runnels 1969) suggest that the injection of brackish water saturated with respect to sulfate (Frape *et al.* 1984) would result in the rapid precipitation of large volumes of gypsum in the zone of mixing. Whereas gypsum from within this zone (at 960 m) appears normal, samples from above this zone at 927 m have an anomalously high value of Ce/Yb and high absolute concentrations of *REE*. This coincidence of the depth of anomalous features in both *REE* chemistry and groundwater salinity in this particular case is taken as evidence of a genetic relationship between the gypsum and the highly saline groundwater.

Rare-earth geochemistry of the $CaCl_2$ brines

Attempts were made at the University of Waterloo to determine the *REE* concentrations of the three Atikokan water samples supplied by AECL. However, it was only possible to determine that the concentrations of the *REE* elements are below the detection limit for the instrumental neutron-activation procedure employed. These detection limits are approximately: 0.2 mg/L Ce, 0.02 mg/L Eu, 0.04 mg/L Tb and 0.2 mg/L Yb. These low abundances may be the result of partitioning of the *REE* into gypsum.

CONCLUSIONS

1. The gypsum in the Atikokan borehole is characterized by steep *LREE*-enriched chondrite-normalized patterns.

2. The observed *REE* concentrations in the Atikokan brines are low (less than 2 mg/L total *REE*) and may be the result of effective partitioning of the *REE* into gypsum precipitated from the brines.

3. Two samples of gypsum from a single fracture

show high values of the Ce/Yb ratio. This fracture is associated with a zone of high-salinity groundwater. The gypsum may have been precipitated as a result of mixing of highly saline brine with brackish groundwater.

4. Long-term rock–water interaction at the Atikokan site would produce a water with a steep light-rare-earth-enriched pattern inherited from the host granite. This pattern may be subject to modification, but is considered the primary control of the steep *LREE* enrichment observed in the gypsum.

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