

Low-Temperature Mobility of Rare Earth Elements (REE), U, and Th at the Olkiluoto Site, SW Finland

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ABSTRACT

This work is a first effort to link hydrogeological measurements to structural modeling by using the mobility of rare earth element (REE), U, and Th at the Olkiluoto site. REE, U and Th concentrations were measured in 5 groundwater samples located at depths varying between 132 and 446 m in three drill holes at the Olkiluoto site. The pH of groundwater samples are all about 8 and Eh(Pt) varies from -50 to -200 mV. Also the REE, U and Th concentrations of rock samples collected from core sections in the vicinity of water conducting fractures were measured to examine rock-water interactions in the system. The rock samples were cut into slices parallel to the fracture surface. An aliquot of each slice was leached with 0.5 N acid nitric to examine the readily leachable REE, U and Th fraction of each slice. The groundwater samples were normalized to each of the analyzed rock samples. Although the REE concentrations of the water samples are overall depleted in all the REEs compared to the rocks and leachates, and whole REE spectra could not be obtained for any of the groundwater samples, enrichment in the intermediate REE (IREE) with respect to the light REE (LREE) is observed.

An increasing loss of REE and U from rock matrix towards fracture surface is observed in samples at depths of 141, 159, and 466 m. Loss of U is also observed in a sample at about 246 m depth. Loss of Th is only observed at the depths of 159 and 246 m. The loss of U (readily leachable fraction) in the rock samples was found to be linked to the hydraulic conductivity in the related water-conducting fractures.

INTRODUCTION

REEs are considered as useful chemical analogues for trivalent actinides, and U and Th can be used as analogues for Pu (e.g., 1, 2). This study aims to get information on the behavior of REE, U and Th in a still relatively undisturbed system by linking hydrological measurements to structural modeling. Olkiluoto in Eurajoki (SW Finland) has been selected as the final disposal site for the spent nuclear fuel repository and it is intend to host an Underground Rock Characterization Facility for further investigations [3]. The application of the mobility of the elements to structural and paleohydrological issues is also considered. Background geological and geochemical site information in [4] and references therein are used as a starting point for this study.

EXPERIMENTAL

The rock samples used in this study were collected from cores from the depth intervals in Table I. Each core section was cut longitudinally. One half was used to prepare petrographic thin sections and the other was used for chemical analysis as indicated in Figure 1. Each section (T ≡ transverse section for whole rock analysis) and slice (S ≡ leachates) was crushed and then powdered with a tungsten carbide mill to a particle-mesh size less than 100 μm. The transverse section (T) was analyzed by ICP-MS to get the concentration of REE in bulk.

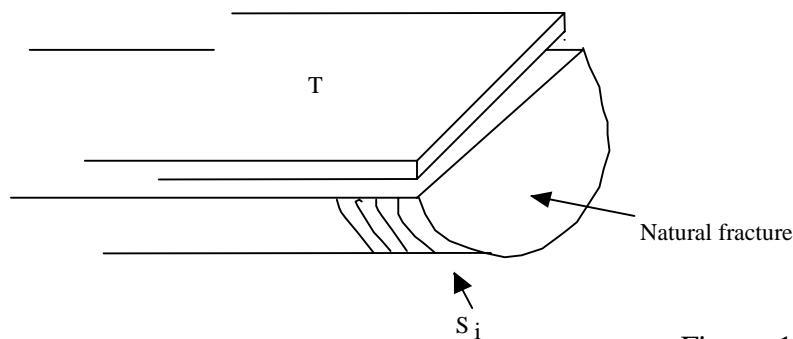


Figure 1. Transverse section (T) and slices (S_i) from the bisected drill core.

Table I. Position of the rock samples in the boreholes.

Borehole	Depth interval (m)	Sample Code
OL-KR3	158.95 - 159	OL3/6T ¹⁾
	183.83 - 183.88	OL3/6KT ²⁾
	256.47 - 246.52	OL3/5T ¹⁾
OL-KR4	141.55 - 141.60	OL4/5T ¹⁾
OL-KR5	210.70 - 210.76	OL5/5T ³⁾
	408.90 - 408.95	OL5/2T ¹⁾
	466.12 - 466.2	OL5/1T ²⁾

- 1) Migmatite; 2) Granite-pegmatite;
 3) Migmatite, fracture surface coated with calcite.

Table II. Water samples

Borehole/Packer $SO_4^{2-}; Cl^-$ in mg/l.	Depth interval (m)	Sample Code
OL-KR3/T6 218;2800	141 - 231	R3/T6
OL-KR3/T5 2.5;2700	231 - 261	R3/T5
OL-KR4/T5 500;4500	132 - 192	R4/T5
OL-KR5/T2 75;4700	376 - 446	R5/T2
OL-KR5/T5 440;4300	191 - 261	R5/T5

The distribution of REE as a function of distance from a natural fracture was obtained from the leachates of slices (S_1 being closest to fracture) parallel to the fracture surface. The readily leachable REE fraction of each slice was examined by reacting 0.5N ultrapure HNO_3 solution with each crushed slice. The method is similar to that described by [5] except that the rock-acid mixtures were allowed to react for 1 min (15 min with 1 N HNO_3 in [5]), as the interest is in whether readily exchangeable REEs from the fractured bedrock can contribute to the REE signatures of the groundwater samples. Approximately 50 to 100 mg of crushed rock for each of the slices of the rock samples was weighed and placed in previously cleaned (acid-washed with 1 N HNO_3) HDPE bottles. The bottles were then filled with 0.5N ultrapure HNO_3 solution up to form 10 ml rock-acid mixture. The bottles were subsequently sealed and the rock-acid mixtures allowed to react for 1 min while being constantly agitated. The resultant supernatant was filtered through 0.45 μm acid-washed membrane (Autovial[®]) filters. These leach solutions were then analyzed for the REEs using ICP-MS. The water samples in Table II were selected for this study. There were only five available water samples (in 100 ml bottles) that corresponded to core samples. Water samples were also analyzed for the REEs, U and Th using ICP-MS. All the ICP-MS analyses were performed at the Geological Survey of Finland.

RESULTS

The analytical results for REE, U and Th of whole-rock samples and leachates are shown in Table III. The data for groundwater samples is presented in Table IV.

REE patterns

Chondrite-normalized REE patterns for each of the rock samples are presented in Fig. 2. The chondrite values employed are those of [6]. In general, all REE patterns of these samples exhibit similar overall shapes that are enriched in the LREEs compared to the heavy REEs (HREE). With the exception of sample OL4/5T, all REE patterns of migmatite samples display negative Eu anomalies. The REE patterns of granite pegmatite samples exhibit positive Eu anomalies mainly due to the occurrence of abundant plagioclase in these samples. Plagioclase is known to be enriched in Eu, as this mineral selectively uptakes Eu during the crystallization of the rock [7]. The REE concentrations of groundwater samples are overall depleted in all the REEs compared to the rocks (Fig. 3), but enrichment in IREEs over LREEs is observed.

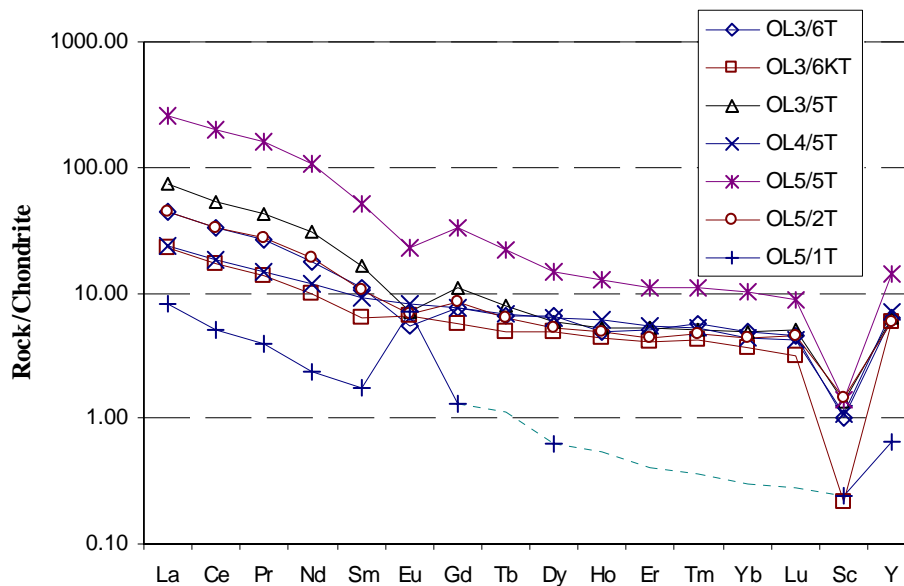


Figure 2. Chondrite-normalized REE profiles for whole-rock samples. Dashed line for sample OL5/1T = elements below detection limits.

The shape of the rock-normalized (RN) leachate patterns resembles each other for the same sample, i.e., all the leachates patterns of sample OL3/6T show the same shape when normalized to rock. For the sake of clarity only a few leachate samples are shown in Figure 4.

Table III. REE, U and Th concentration data ($\mu\text{g/g}$) for rock samples (T) and leachates (S).
 (- = below detection limits). D = distance from fracture surface in mm.

Sample	D	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y	U	Th
OL3/6T		16	31.3	3.68	12.4	2.53	0.48	2.35	0.38	2.47	0.41	1.26	0.2	1.22	0.17	8.86	14.4	7.79	4.61
OL3/6S₁	0	1.6	3.06	0.40	1.61	0.40	0.16	0.42	0.07	0.37	0.06	0.16	0.02	0.13	0.02	0.07	1.93	0.85	0.28
OL3/6S₂	4.3	2.04	3.8	0.47	1.77	0.42	0.20	0.45	0.07	0.45	0.08	0.22	0.03	0.18	0.02	0.25	2.60	1.27	0.57
OL3/6S₃	8.6	1.75	3.22	0.40	1.57	0.35	0.15	0.36	0.06	0.36	0.06	0.17	0.03	0.15	0.02	0.10	1.89	1.10	0.24
OL3/6KT		8.29	16.3	1.87	6.89	1.48	0.58	1.72	0.28	1.85	0.37	1.01	0.15	0.92	0.12	1.85	13.1	32.2	2.51
OL3/6KS₁	0	2.42	4.69	0.58	2.23	0.52	0.09	0.56	0.10	0.58	0.24	0.24	0.03	0.20	0.02	0.03	2.71	0.92	0.11
OL3/6KS₂	6	0.82	1.55	0.18	0.72	0.18	0.13	0.22	0.04	0.25	0.12	0.12	0.02	0.09	0.01	0.08	1.41	0.97	0.12
OL3/6KS₃	12	0.41	0.78	0.09	0.37	0.09	0.06	0.11	0.02	0.11	0.06	0.06	0.01	0.05	0.01	0.03	0.70	0.33	0.04
OL3/5T		27.1	50.9	5.88	21.4	3.77	0.62	3.38	0.46	2.24	0.45	1.3	0.18	1.22	0.19	11.7	14.4	4.36	11.7
OL3/5S₁	0	11.92	23.80	2.84	10.6	2.30	0.16	2.38	0.37	1.99	0.34	0.90	0.12	0.85	0.11	1.01	9.68	0.22	0.72
OL3/5S₂	2.6	9.46	17.29	2.03	7.63	1.28	0.15	1.17	0.13	0.64	0.10	0.26	0.03	0.21	0.03	0.50	2.93	0.47	1.20
OL3/5S₃	7.7	7.72	14.18	1.69	6.33	1.09	0.23	0.98	0.11	0.52	0.08	0.21	0.02	0.15	0.02	0.40	2.28	0.46	1.33
OL4/5T		8.8	17.8	2.02	8.48	2.12	0.71	2.35	0.39	2.38	0.52	1.35	0.19	1.09	0.16	9.32	15.9	5.7	7.28
OL4/5S₁	0	4.11	7.51	0.87	3.15	0.60	0.04	0.61	0.08	0.43	0.07	0.20	0.03	0.18	0.02	0.2	2.30	0.20	0.50
OL4/5S₂	5	6.80	12.56	1.49	5.44	0.97	0.18	0.97	0.11	0.51	0.07	0.17	0.02	0.10	0.01	0.46	2.21	0.35	0.47
OL4/5S₃	12	6.43	11.93	1.42	5.50	1.03	0.14	1.04	0.13	0.66	0.10	0.24	0.03	0.15	0.02	0.4	2.96	0.64	0.94
OL5/5T		95.5	189	21.6	76.7	12	1.96	10.2	1.26	5.53	1.07	2.75	0.39	2.49	0.33	12.1	31.9	4.55	10.2
OL5/5S₁	0	23.14	49.43	5.79	21.4	5.34	0.54	5.57	0.93	5.14	0.89	2.36	0.3	1.96	0.25	0.91	23.8	0.21	0.21
OL5/5S₂	5	1.09	2.67	0.39	1.8	0.54	0.11	0.62	0.11	0.68	0.13	0.37	0.05	0.29	0.03	0.18	3.54	0.1	0.1
OL5/5S₃	12.5	1.02	2.51	0.37	1.69	0.52	0.12	0.59	0.11	0.66	0.13	0.34	0.05	0.27	0.03	0.11	3.31	0.11	0.08
OL5/2T		16.2	31.3	3.72	13.7	2.47	0.6	2.61	0.36	2.04	0.42	1.11	0.17	1.08	0.17	12.7	13.1	2.35	6.3
OL5/2S₁	0	0.68	1.38	0.18	0.78	0.21	0.05	0.24	0.04	0.25	0.05	0.12	0.02	0.10	0.01	0.28	1.24	0.55	1.44
OL5/2S₂	6	0.53	1.16	0.16	0.74	0.23	0.08	0.27	0.05	0.28	0.05	0.13	0.02	0.10	0.01	0.21	1.36	0.50	1.23
OL5/2S₃	12.9	0.39	0.84	0.12	0.57	0.18	0.08	0.22	0.04	0.20	0.04	0.09	0.01	0.07	0.01	0.05	0.99	0.49	0.82
OL5/1T		3.01	4.94	0.53	1.64	0.41	0.62	0.4	-	0.24	-	-	-	-	-	2.07	1.47	0.56	0.72
OL5/1S₁	0	0.58	1.28	0.18	0.72	0.18	0.08	0.19	0.03	0.13	0.02	0.06	0.01	0.05	0.01	0.06	0.83	0.03	0.15
OL5/1S₂	3	2.43	4.70	0.55	2.01	0.42	0.21	0.44	0.06	0.25	0.04	0.09	0.01	0.05	0.01	0.07	1.07	0.05	0.18
OL5/1S₃	11	1.56	2.76	0.31	1.12	0.21	0.17	0.22	0.03	0.14	0.02	0.06	0.01	0.05	0.01	0.04	0.72	0.13	0.18

Table IV. Data for groundwater analyses in ppb ($\mu\text{g/l}$). (Pr, Tb, Ho, Tm, Lu and Sc concentrations below detection limits (-) for ICP-MS).

	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Y	U	Th
R3/T5	0.01	0.01	-	-	-	-	0.01	-	-	0.01	0.07	0.04
R4/T5	0.01	0.02	0.01	-	-	0.01	0.01	-	-	0.03	1.68	0.05
R5/T5	0.01	0.01	0.01	0.01	0.01	-	0.01	-	0.01	0.07	0.46	0.04
R5/T2	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.01	0.01	0.06	0.14	0.05
R3/T6	0.01	0.01	-	0.01	-	-	0.01	-	-	0.01	0.2	0.03

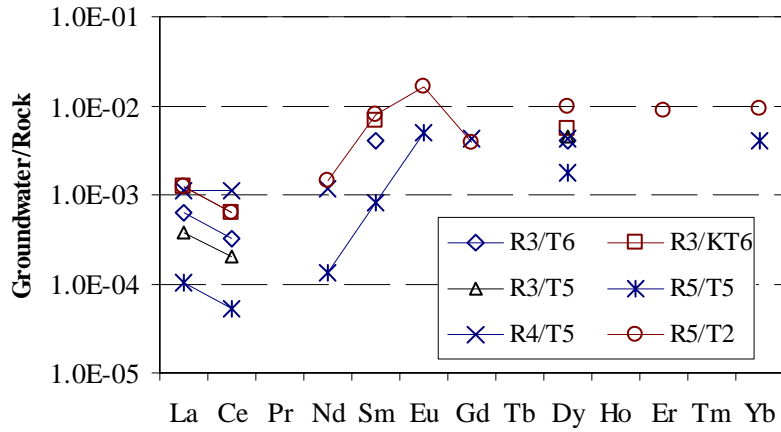


Figure 3. Groundwater concentrations normalized to the REE concentrations of the corresponding whole-rock samples.

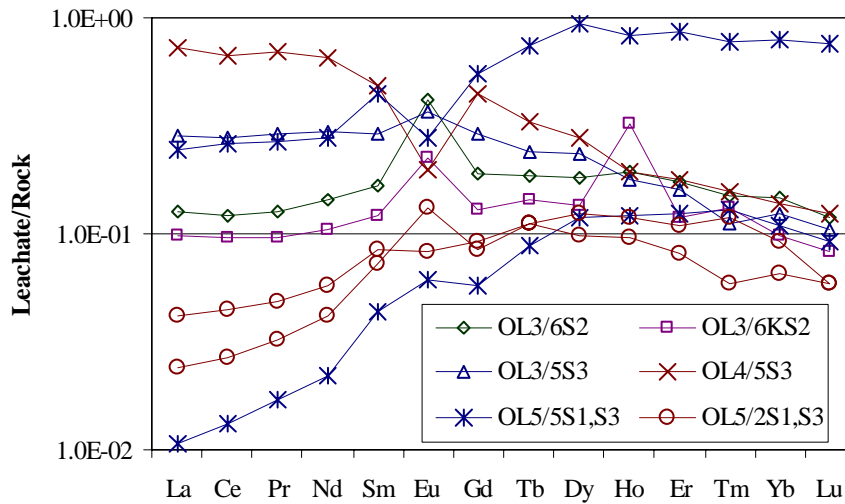


Figure 4. REE concentrations of leachate solutions normalized to the REE concentrations in the corresponding rocks.

The rock-normalized leachate patterns (Fig. 4) indicate that the only acid leachable fraction of the rock that closely resembles the whole-rock pattern is that of sample OL4/5T. The RN leachate pattern of sample OL3/5T shows a moderate LREEs enrichment slightly resembling the whole-rock pattern. The leachates exhibiting IREE enrichments (Fig. 4) compared to the rocks contain mineral phases from which the IREEs are preferentially leached. For these rocks (OL3/6T, OL3/6KT, OL5/5T, OL5/2T), the readily leachable IREE enriched phases do not control the whole-rock REE concentrations (compare Figs. 2 and 4).

Loss of elements

The results of element concentration profiles are summarized in Table V. The hydraulic conductivity (K) of the depth intervals of groundwater samples [8] is included as it is intended to associate element mobility to groundwater flow and water-rock interactions.

Table V. Increased loss of elements from rock matrix towards fracture surface marked with X. M = Minor loss, - = no loss, FC = fracture surface coating, and Cc = Calcite.

K (m/s) [8]	Sample	LREE	IREE	HREE	U	Th	Y	FC
1.1E-07	OL4/5T	X	X	-	X	-	-	Partially, kaolinite
1.0E-10	OL3/6T	X	X	X	X	X	X	Clean
1.0E-10	OL3/6KT	-	(Eu) -	-	M	-	-	Partially, kaolinite
3.0E-06	OL5/5T	-	-	-	-	-	-	Totally, 1mm thick Cc
8.4E-08	OL3/5T	-	-	-	X	X	-	Partially, Cc, Pyrite
3.0E-08	OL5/2T	-	X	-	-	-	X	Clean
2.0E-08	OL5/1T	X	X	X	X	M	X	Clean

The distribution of U and Th in groundwater (UW, ThW) with respect to the readily leachable U and Th fraction in the slices closest (US1, ThS1) to fracture (and hence, to groundwater flow) was plotted against hydraulic conductivity in Figure 5. A positive trend can be observed, independent of depth, in the preferential release of U and Th in fractures where hydraulic conductivity exceeds 1E-8 m/s.

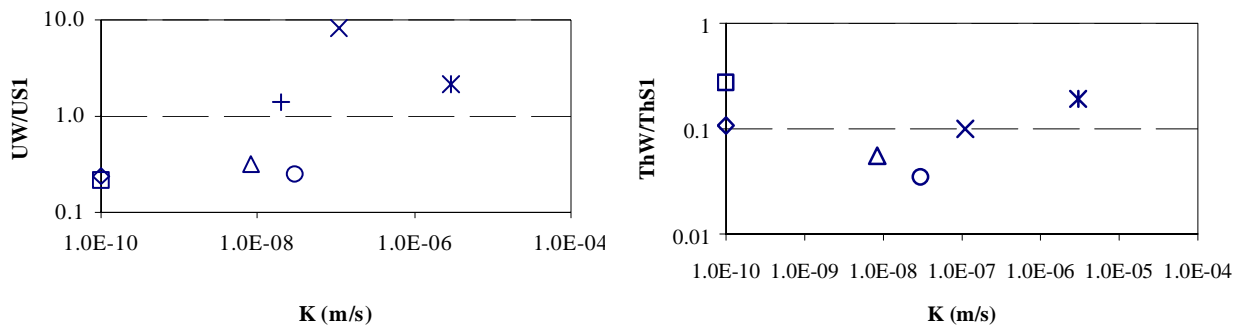


Figure 5. Distribution of U and Th in groundwater (UW, ThW) with respect to the easily leachable U and Th fraction in the slice closest (US1, US1) to fracture (and hence, to groundwater flow) versus K. (Symbols: □ OL3/6K, O OL5/2, Δ OL3/5, ◇ OL3/6, x OL4/5, + OL5/1, * OL5/5).

DISCUSSION AND CONCLUSIONS

In previous investigations it has been found that groundwaters typically exhibit REE signatures that closely resemble the rocks through which they have flowed (e.g., [9,10]), but Figure 3 clearly indicates that groundwaters are enriched in the IREEs compared to the LREEs with respect to bulk REE compositions of all of the rock samples collected from the cores in the vicinity of water conducting fractures. That is, fractionation has occurred during water-rock interaction. Although the origin of IREE enriched patterns in waters is not clearly understood at present (e.g., [11]) these patterns are often interpreted as the signature of REE from some specific mineralogy undergoing weathering in acidic conditions. This and the resemblances between the REE patterns for the leachates (Fig. 4) and groundwaters suggest that the enrichment is most possible due to past intrusions of acidic waters in the system. In fact, at the Olkiluoto site glacial melt water is an important component of groundwater between depths of 100 to 500 m [4]. The imprint of the process (acidic water intrusion) can still be seen in spite of the present groundwater conditions not being acidic due to the high chloride content of the groundwater. Chloride and, to some extent, sulfate preferentially complexes IREEs [12] in acidic conditions. In increasing the pH (above 6.8) carbonate species became predominant [13], but carbonate concentration in these groundwater samples is close to zero and bicarbonate concentration remains well below 110 mg/l [4]. That is, in the absence of other competitive effects, it became apparent that chloride and sulfate complexes remain as the dominating REE speciation even at pH about 8. This is possible because of the high chloride and sulfate concentrations in the groundwater samples (Table II).

The RN leachates of samples OL4/5T and OL3/5T do not display IREE enrichments, as do the respective groundwater samples. This is due to the mineralogy of the samples. They represent the paleosome or dark-coloured part of the migmatite, rich in biotite. Biotite is a mineral slightly enriched in LREE [14] and the acid leaching of this dominant mineral in the samples obscures the IREE enrichment that would otherwise be as in the other samples.

The activity or functional character of the fractures with respect to groundwater flow is examined from a geochemical point of view. The functioning of the fracture is seen as an increasing loss of elements from rock matrix towards fracture surface. This is best reflected in samples OL3/6T and OL3/6KT. Both belong to the same depth interval with respect to groundwater sample R3/T6, but the behavior of elements is different. The loss of elements in sample OL3/6T suggests that groundwater could be flowing at higher rates in the fracture in the vicinity of this sample. And certainly, in a recent report by [15] at the depth of sample OL3/6T, a flow rate of about 10^3 ml/h was measured in comparison to a flow rate of 10 ml/h at the depth of sample OL3/6KT. Previous hydrological investigations [16] have suggested that the matrix permeability is lower at depth, but the activity of the fractures is not. There was a trend, independent of depth, in the preferential release of U and Th in fractures where the hydraulic conductivity is over $1E-8$ m/s (Fig. 5). The apertures (A) of the fractures considered in this work vary from about 0.5 to 2 mm. Unfortunately no correlation data exist between A and K to date.

Although there is a trend in the release of Th from the host rock to groundwater as K increases, the greatest ThW/ThS1 value corresponds to a minimum in K. It has been reported before [17] that Th concentration in groundwater increases preferentially as a result of groundwater-rock interactions in a system where groundwater is not flowing. This enhanced Th leaching in static groundwater systems may be due either to the occurrence of Th in readily

leachable mineral phases or to the long water-rock interaction time in the system, which enhances both alteration of the rock and the remove of Th from it.

This study illustrates that the relative mobility of the actinides U and Th and REE can be used to address the hydrological functional character of the fractures, at least qualitatively. It could be observed that loss (migration) of elements is higher in drill cores presenting clean fracture surfaces than in drill cores with partially or totally covered fracture surface. This finding agrees with a view that clean fracture surfaces also indicate interaction with reactive waters [18]. Evidence of possible intrusion of acidic waters is important because the properties of some radionuclides are different under acidic groundwaters. Acidic groundwaters could contain dissolved oxygen as well, but whether oxidizing conditions were encountered in the past could not be deciphered in this study. The nature and timing of past intrusion(s) could be revealed using U-series disequilibria studies.

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