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CHARACTERISTICS OF RADIONUCLIDE SORPTION ON FRACTURE-FILLING MINERALS IN THE EYE–DASHWA LAKES PLUTON, ATIKOKAN, ONTARIO†

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ABSTRACT

The Eye–Dashwa Lakes granitic pluton near Atikokan, northwestern Ontario, has been investigated as part of the generic research in the Canadian Nuclear Fuel Waste Management Program. The pluton is characterized by fractures that are filled with a variety of minerals. Fractures will play a dominant role in the transport of radionuclides from a nuclear waste-disposal vault through the host rock, and the filling and other secondary minerals along fracture-flow pathways may impede radionuclide migration through sorption. To compare the sorptive properties of these fracture-filling and other secondary minerals in the rock matrix, radionuclides representing the alkali metals (^{137}Cs). alkaline earths (^{90}Sr), rare-earth elements (^{147}Pm), higher actinides (^{241}Am), and one anionic fission product (^{95m}Tc) were sorbed on thin sections of rock containing fractures. Distributions of the sorbed radionuclides were determined by autoradiography. The results indicate a general enhanced sorption by the secondary minerals compared to that of the primary minerals in the rock matrix. Differences in sorbtive behavior of chemically similar minerals was observed in some instances.

Keywords: nuclear waste disposal, granitic pluton, alteration minerals, sorption, cesium, actinides, fractures, radionuclides, technetium, strontium, Eye-Dashwa Lakes, Ontario.

SOMMAIRE

On a étudié le pluton granitique des lacs Eye-Dashwa, près d'Atikokan, dans le nord-ouest de l'Ontario dans le contexte de la recherche générique du Programme canadien de la gestion des déchets de combustible nucléaire. Ce pluton caractérise par des fractures remplies de minéraux variés. Ces fissures joueraient un rôle dominant dans la migration des radionucléides d'une enceinte d'évacuation de déchets nucléaires à travers la roche-hôte; les minéraux de remplissage et autres se trouvant le long des voies d'écoulement peuvent empêcher la migration des radionucléides par adsorption. Pour comparer les propriétés adsorptives de ces minéraux, on a fait adsorber, sur des lames minces de roche fissurée, des radionucléides représentant les alcalins (^{137}Cs), les alcalino actinides terreux (^{90}Sr), les terres rares (^{147}Pm), les actinides supérieurs (^{241}Am) et un produit de fission anionique (^{95m}Tc). La distribution des radionucléides adsorbés a été déterminée par autoradiographie. Les résultats indiquent une adsorption générale plus grande par les minéraux secondaires par rapport à celle par les minéraux primaires de la gangue de roche. On a pu observer des différences de sorption dans des minéraux de remplissage semblables chimiquement.

Mots-clés: gestion de déchets nucléaires, pluton granitique, minéraux secondaires, sorption, césium, actinides, fissures, radionucléides, technétium, strontium, lacs Eye-Dashwa, Ontario.

INTRODUCTION

The Canadian Nuclear Fuel Waste Management Program involves research into the concept to dispose of nuclear fuel wastes, produced in the generation of electrical power, in cavities mined out of massifs of intrusive rock in the Canadian Shield (Boulton 1978). This disposal concept is based on the use of multiple barriers, one of which is a rock mass 500 to 1000 m thick above the vault.

Should the integrity of the waste containers be breached by groundwater and the radioactive wastes dissolved, interaction of the dissolved radionuclides with geological material may remove them from solution. The interaction may involve mechanisms such as ion exchange, replacement, surface precipitation, and oxidation–reduction followed by ion exchange or precipitation. Although subsequent desorption or redissolution will reintroduce these contaminants back into the groundwater, the overall effect is that the velocity of migration of the contaminant is reduced with respect to that of the groundwater.

Hydrological investigations have shown that the bulk of the movement of groundwater occurs through fracture pathways (Runchal & Maini 1980). These fractures are generally lined with secondary minerals, produced either during hydrothermal activity in the pluton or from long-term interaction of groundwater with the rock mass along the fractures. Radionuclide-sorption studies should, therefore, be carried out on these secondary minerals as well as on the rock matrix. Most sorption work already reported in the literature has been performed on crushed (*e.g.*, Erdal *et al.* 1979, MacLean *et al.* 1978) or machined surfaces of fresh rock (Vandergraaf & Abry 1982, Allard *et al.* 1977). To compare the sorptive behaviors of fracture-filling materials and alteration minerals toward various radionuclides, fresh rock was used from drill cores obtained in an ex-

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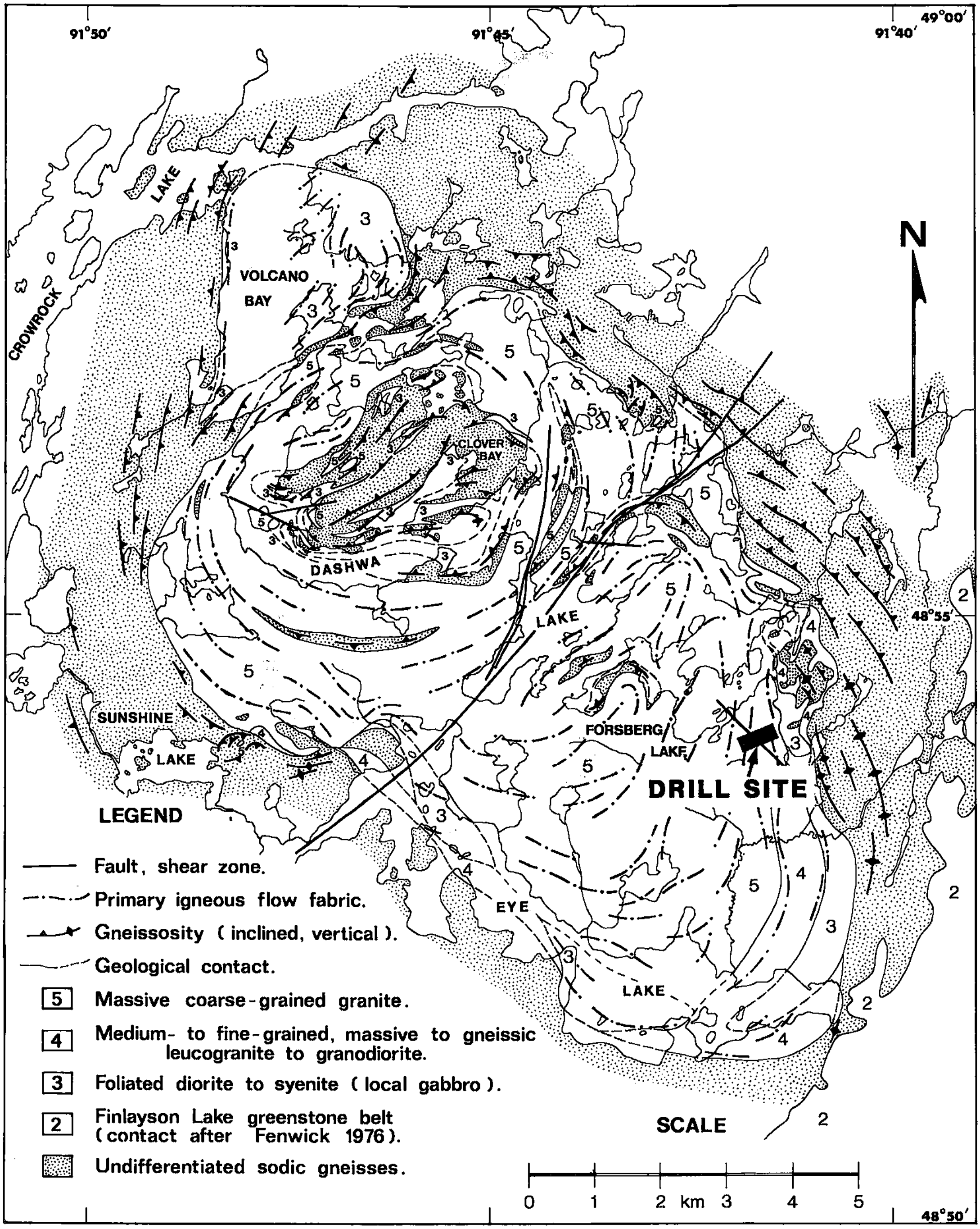

FIG. 1. Map of the Eye–Dashwa Lakes pluton (after Brown *et al.* 1980).

perimental research program carried out in the Eye-Dashwa Lakes pluton near Atikokan, northwestern Ontario.

GEOLOGICAL SETTING

The Eye-Dashwa Lakes pluton near Atikokan, northwestern Ontario, occurs within the Superior structural province of the Canadian Shield. The pluton is of Archean age (2658 ± 50 Ma), as determined by the K–Ar method using hornblende separated from a sample collected on the rim near the drill site (Fig. 1). It intrudes a series of tonalitic gneisses and is located immediately west of the Finlayson Lake greenstone belt (Fenwick 1976). Metamorphic mineral assemblages and foliations present in the surrounding gneisses are absent in the granite. Consequently, the pluton is believed to result from a late syntectonic intrusion related to the Kenoran orogeny (Brown *et al.* 1980). Schwerdtner *et al.* (1979) first identified the pluton, and detailed mapping by Brown *et al.* (1980) revealed its elliptical shape (Fig. 1). Petrographic investigations (Kamineni & Brown 1981) revealed that this pluton has evolved through a sequence of fractional crystallization, with an early phase consisting of quartz monzonite to tonalite, followed by a granodiorite phase and, finally, by a granitic phase that makes up the bulk of the pluton (at the centre).

Fractures and fracture-filling materials

The Eye–Dashwa Lakes pluton is intersected by a series of fractures that are invariably filled, or coated, with mineral matter (Kamineni *et al.* 1980). These fractures can be divided into four groups (Stone & Kamineni 1982), based on their filling minerals: (1) dykes of granitic pegmatite and aplite, (2) epidote-filled fractures, (3) chlorite-filled fractures and (4) fractures filled with low-temperature minerals. According to cross-cutting relations and temperatures of crystallization of filling minerals, these four groups constitute a chronological sequence. The abundance and other characteristics, such as length and orientation, of the four groups of fractures are discussed elsewhere (Stone & Kamineni 1982).

Core samples from boreholes, drilled to depths of 1100 m, on the eastern rim of the pluton (Fig. 1), show a vertical zonal distribution of fracture-filling materials. Aplite and pegmatite dykes occur throughout the pluton, but are more abundant within 500 m of the surface. Fractures intersecting these dykes are usually filled with muscovite. Fractures filled with epidote and dipping at angles of 10–30° are concentrated below 500 m. Above 500 m, steeply dipping fractures, again filled with epidote, are more common, as are chlorite-filled fractures with steep dips (~60°). Fractures filled with low-temperature minerals (group 4) *e.g.*, hematite, carbonate and clay, are concentrated at shallow depths and extend down for 300 m. They also occur at deeper levels and in restricted zones where the fractures are open to flow of water. In addition to the fillings, the fractures contain an alteration halo along their length in the wall rock (Kamineni & Dugal 1982). In the altered rock-matrix, the ferromagnesian minerals biotite and hornblende, are converted to chlorite and epidote, whereas plagioclase is altered to sericite, epidote, carbonate and kaolin.

Since the fractures of the Eye–Dashwa Lakes pluton contain a variety of minerals, and as the drill cores obtained from this pluton had been thoroughly characterized, these cores provided an obvious choice of material to determine the degree of radionuclide sorption on various matrix and fracture-filling minerals, as well as the effect of alteration of the rock matrix on sorption.

SORPTION EXPERIMENTS

Sorption experiments were carried out on thin sections of rock using the procedure described by Vandergraaf *et al.* (1982). Polished sections of about 0.04 mm thickness were used in the sorption experiments. Initially, the sections were ground with 3-μm-sized diamond powder. This was followed by fine polishing, using 0.025-μm-sized diamond powder. The fine polishing provides a smooth section with minimum or no surface damage. A minimum of two polished and one standard thin section were prepared from each core sample investigated. Sections not used in the sorption experiments were used for an analysis of the fracture-filling and other secondary minerals by optical, X-ray, microprobe and scanning-electron-microscope techniques. The areas of the polished thin sections placed in contact with the radionuclide-tagged solutions were delineated with a black, hydrophobic ink. This ink acts as a barrier to keep the solution from spreading beyond the marked area. The surface area of the thin sections ranges from 5 to 7 cm^2.

The thin sections were placed in contact with 1.5 to 2.0 mL of groundwater for two 48-hour periods as suggested in the WISAP (Waste Isolation Safety Assessment Program) procedure (Relyea & Serne 1979). The solutions were removed, and the surface of the thin sections dabbed dry with adsorbent tissue

TABLE 1. COMPOSITION OF SYNTHETIC GROUNDWATERS USED IN SORPTION STUDIES

	GGW	WN-1	SCSSS
Na	3.6×10^{-4}	8.3×10^{-2}	2.2×10^{-1}
K	9.0×10^{-5}	3.6×10^{-4}	1.3×10^{-3}
Mg	1.6×10^{-4}	2.5×10^{-3}	8.2×10^{-3}
Ca	3.2×10^{-4}	5.3×10^{-2}	3.7×10^{-1}
Sr		2.7×10^{-7}	2.3×10^{-4}
Fe		1.0×10^{-5}	
Si			5.4×10^{-4}
HCO_3	9.5×10^{-4}	1.1×10^{-3}	1.6×10^{-4}
Cl	1.4×10^{-4}	1.8×10^{-1}	9.7×10^{-1}
SO_4	9.0×10^{-5}	1.1×10^{-2}	8.2×10^{-3}
NO_3	1.0×10^{-5}	5.3×10^{-4}	8.1×10^{-4}
F	1.0×10^{-5}		
pH	6.5 ± 0.5	7.0 ± 0.5	7.0 ± 0.5

GGW Synthetic Groundwater, WN-1 Saline solution based on groundwater from borehole WN-1, Lac-du-Bonnet pluton, SCSSS Standard Canadian Shield Saline Solution. Concentrations expressed in mol/L.

TABLE 2. INITIAL CONCENTRATION OF RADIONUCLIDES IN SYNTHETIC GROUNDWATER USED IN SORPTION STUDIES

Nuclide	GGW	WN-1	SCSSS
^{90}Sr	1.0×10^{-8}	9.5×10^{-9}	N.D.
^{95m}Tc	1.1×10^{-11}		
^{137}Cs	2.1×10^{-8}	2.2×10^{-8}	2.2×10^{-8}
^{147}Pm	1.7×10^{-9}	1.2×10^{-9}	N.D.
^{241}Am	1.5×10^{-8}	8.8×10^{-9}	1.5×10^{-7}

GGW Synthetic Groundwater, WN-1 Saline solution based on groundwater from borehole WN-1, Lac-du-Bonnet pluton, SCSSS Standard Canadian Shield Saline Solution. Concentrations are expressed in mol/L.

after each contact period, and replaced by 1.5 to 2.0 mL of the appropriate radionuclide-tagged groundwater for ~ 48 hours. The contact time was dictated by loss of solution due to evaporation and subsequent condensation on the inner surface of the tightly closed container.

Synthetic groundwater was used in these studies, because groundwater from the granite pluton was not available in sufficiently large quantities for radionuclide-sorption studies. These synthetic groundwaters contain only the major cations and anions and, hence, are an approximation of the actual groundwater that may be encountered at depth.

Synthetic groundwater, with a composition based on analyses of groundwater from a granitic terrane (White *et al.* 1963, Feth *et al.* 1964), was used to approximate the composition of solutions expected to abound in intrusive bodies of granite.

Because highly saline groundwaters have been found in the Canadian Shield (Frape *et al.* 1981) and also in the Eye–Dashwa Lakes granite below 500 m (Kennedy 1983), some saline solutions were also prepared. The compositions of the solutions used are listed in Table 1. Radionuclides representing various groups of fission products, such as alkali metals (^{137}Cs), alkaline earths (^{90}Sr), rare-earth elements (^{147}Pm), higher actinides (^{241}Am), and one anionic species (^{95m}Tc), were used. These radionuclides were obtained in carrier-free solutions; their initial concentrations in the contact solutions are shown in Table 2.

To check for naturally occurring radionuclides that could interfere with subsequent radiometric analyses, the thin sections were autoradiographed for one week, prior to the radionuclide-sorption step. Kodak Spectrum-analysis glass plates No. 1 (Kodak catalog number 156-7837) were used, as their sensitivity is higher than that of the Ilford plates. After radionuclide sorption, autoradiographs were obtained with Ilford K.5 emulsion-coated glass plates, which have a higher resolution than the Kodak plates. The exposure time varied from 24 h to 7 days. The sections containing sorbed ^{90}Sr were left for 20 days before exposure to allow ^{90}Y (64-h half-life) to grow in and re-establish equilibrium. Finally, both the thin sections and the autoradiographs were photographed with a Wild Heerbrugg 19400 photomicroscope, using transmitted light.

RESULTS

Photomicrographs and autoradiographs of thin sections held in contact with various radionuclide solutions are shown in Figures 2 to 13. The autoradiographs are positives, *i.e.*, the dark areas indicate sorption, and the light areas, little or no sorption.

Sorption of ^{90}Sr

Four typical examples of thin sections containing secondary minerals are presented here: (1) Altered rock-matrix that contains a large crystal of titanite occurring as an accessory mineral (Fig. 2a). (2) Altered rock-matrix (Fig. 3a) adjacent to an epidote-filled fracture. The ferromagnesian minerals horn-

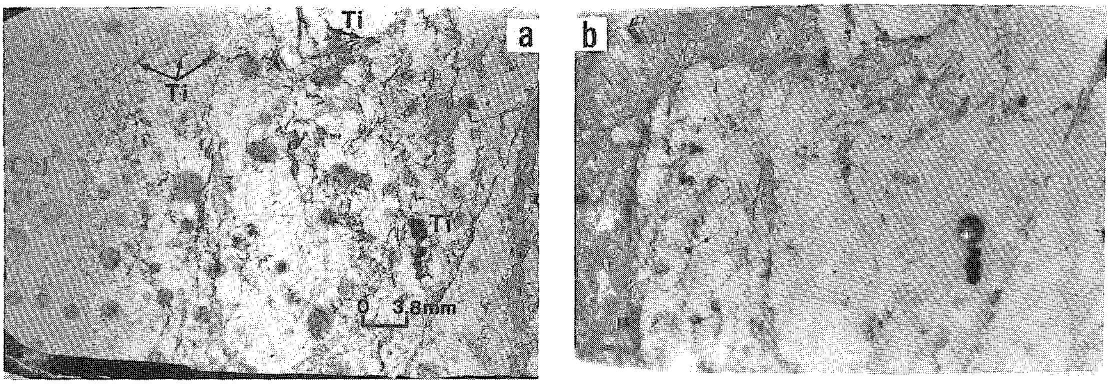

FIG. 2. Photomicrograph (a) and autoradiograph (b) of ^{90}Sr sorbed on a sample of fractured granite (Chl chlorite, Ti titanite). Note strong sorption on the crystal of titanite.

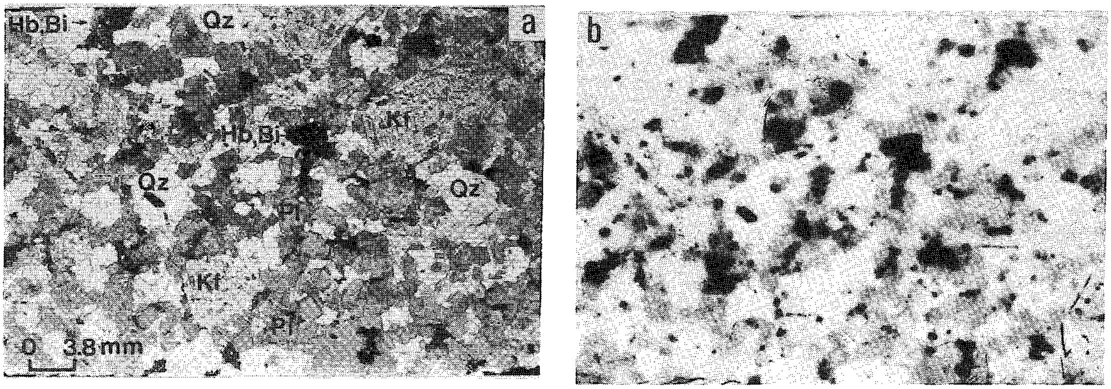

FIG. 3. Photomicrograph (a) and autoradiograph (b) of ^{90}Sr sorbed on a sample of altered granite (Bi biotite, Hb hornblende, Kf microcline, Pl plagioclase, Qz quartz).

blende and biotite are altered to epidote, sericite and carbonate; in general, the grains are masked by a fine product of alteration, possibly kaolin. Titanite, occurring as in the previous case as an accessory mineral, is dispersed throughout the section. (3) A fracture zone showing at least two generations of epidote as inferred from cross-cutting relations (Fig. 4a). A microprobe analysis (Stone & Kamineni 1982) revealed that the two generations of epidote crystals are chemically distinct: the older epidote (FeEp) is relatively rich in iron, and is mixed with titanite, whereas the younger epidote (AlEp) is richer in aluminum and contains little or no titanite. (4) A sample with narrow fractures filled with epidote and titanite and a wide fracture filled with very fine chlorite (Fig. 5a). Somewhat coarser chlorite is distributed as pods throughout the rock matrix.

The dark areas in the autoradiographs (Figs. 2b, 3b, 4b, 5b) indicate sorption on fracture-filling minerals and on other altered grains, such as plagioclase, in the matrix. Some sorption on titanite grains in the matrix is also noted. At this time, the autoradiographs can only be interpreted semiquantitatively. Petrographic investigations show that the densest areas in the autoradiographs correspond to the grains of titanite. Epidote- and chlorite-filled fractures represent the next-most-dense areas. Other minerals present in the matrix (biotite, hornblende, altered and unaltered plagioclase, and microcline) also show some sorption, but not nearly as much as titanite and epidote. In any given species of mineral, sorption of ^{90}Sr appears to be controlled by grain size. For example, areas in the autoradiographs corresponding to the fine chlorite in Figure 5b are much denser than those corresponding to the coarser chlorite, suggesting that the fine chlorite flakes have a higher sorption-capacity than the other grains of chlorite. This can be explained on the basis of sur-

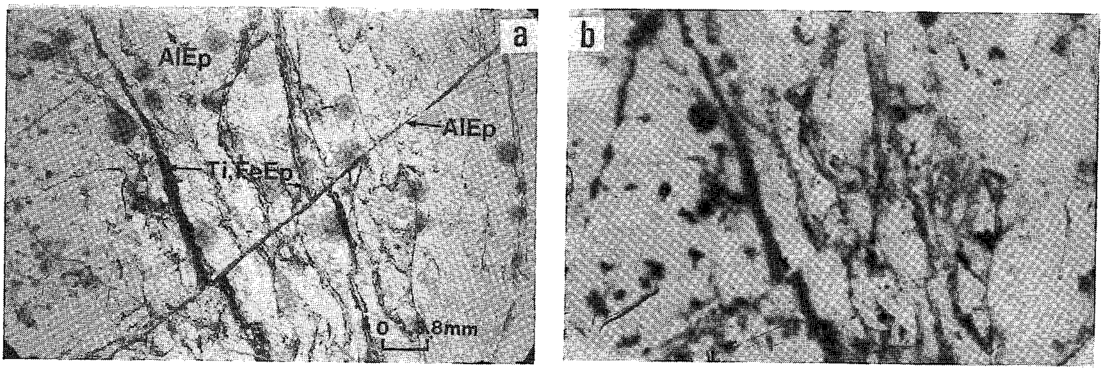

FIG. 4. Photomicrograph (a) and autoradiograph (b) of ^{90}Sr sorbed on a sample of fractured granite. Two generations of epidote-filled fractures are evident through cross-cutting relations (AlEp aluminum epidote, FeEp iron epidote, Ti titanite). Note the relatively low sorption of ^{90}Sr on aluminum epidote.

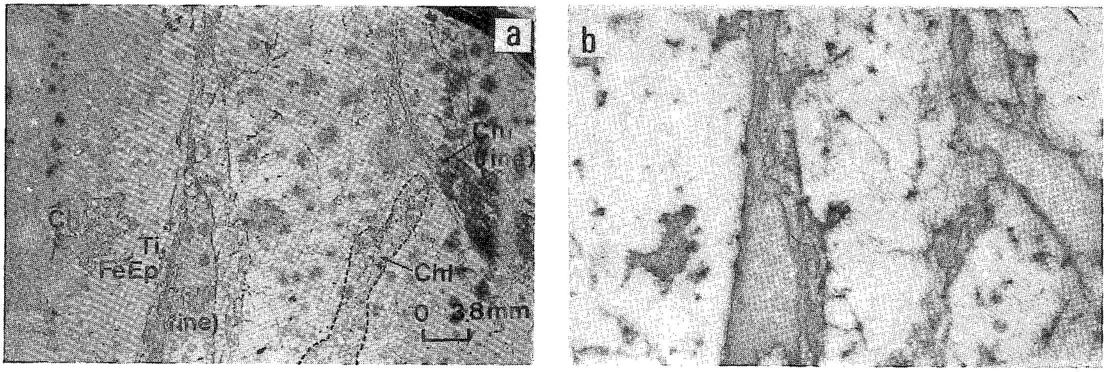

FIG. 5. Photomicrograph (a) and autoradiograph (b) of ^{90}Sr sorbed on a sample of fractured granite (Chl chlorite, Ti titanite, FeEp iron epidote). Note enhanced sorption of ^{90}Sr on the fine-grained chlorite.

face area. Differences in the chemical composition of the two types of epidote are also reflected in their sorption of ^{90}Sr: aluminum-epidote shows little sorption, in contrast to iron-epidote, which sorbs ^{90}Sr strongly (Fig. 4b).

Fracture fillings of carbonate and fluorite show no detectable sorption, and they can be placed in the same category as quartz. Altered hornblende and biotite show higher sorption than the unaltered equivalents, mainly because of the presence of epidote, chlorite and other alteration products in these minerals grains.

From the autoradiographs and petrographic analyses, the following empirical descending sequence can be defined for the sorption capacity of ^{90}Sr: titanite, iron-epidote, chlorite, hornblende and biotite, altered plagioclase, plagioclase, microcline, and carbonate, fluorite, quartz. No sorption of ^{90}Sr from the saline solutions was observed. This is consistent with results obtained for ^{90}Sr sorption from a brine solution containing 175 000 mg/L chlorine (Relyea & Serne 1979). Strontium-90 sorption initially occurs by an ion-exchange mechanism. Large concentrations of cations in solution compete with ^{90}Sr for the sites available for sorption.

Sorption of ^{137}Cs

Photomicrographs of two sections containing microfractures and altered rock-matrix, placed in contact with ^{137}Cs-tagged synthetic groundwater, are shown in Figures 6a and 7a. The fractures in these two samples are filled with epidote, chlorite, hematite and minor titanite. The minerals in the surrounding matrix are altered: the ferromagnesian minerals to chlorite and epidote, and the plagioclase grains to fine sericite and kaolin. Microcline shows little alteration. The autoradiographs (Figs. 6b, 7b) show that the fracture-filling minerals epidote, chlorite and titanite do not sorb appreciable amounts of cesium. On the other hand, the altered plagioclase and biotite do show strong sorption. Sorption on the grains of

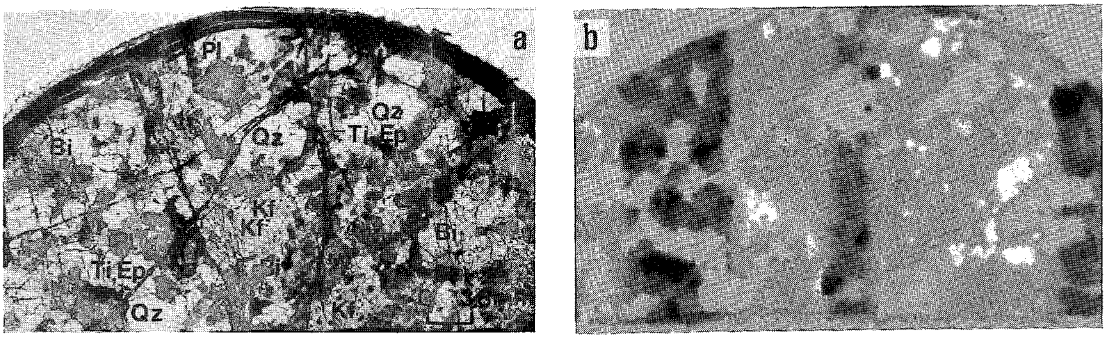

FIG. 6. Photomicrograph (a) and autoradiograph (b) of ^{137}Cs sorbed on a sample of fractured granite. The matrix materials adjacent to the microfractures are altered (Bi biotite, Ep epidote, Kf microcline, Pl plagioclase, Qz quartz, Ti titanite).

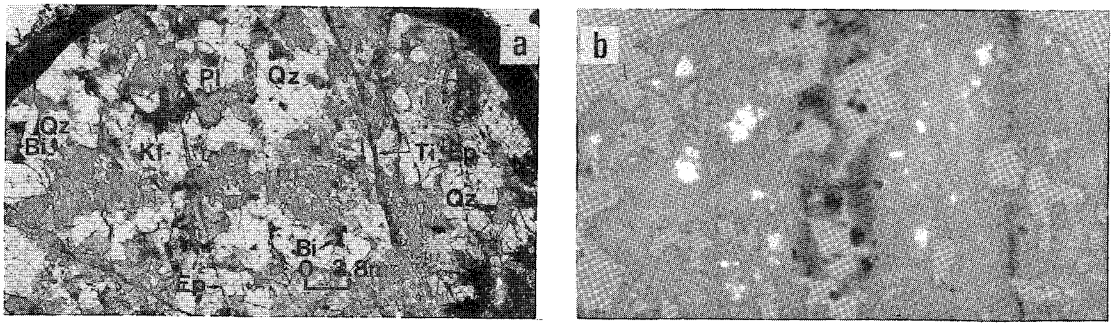

FIG. 7. Photomicrograph (a) and autoradiograph (b) of ^{137}Cs sorbed on a sample of fractured granite. The matrix minerals adjacent to the microfractures are altered (Bi biotite, Ep epidote, Kf microcline, Pl plagioclase, Qz quartz, Ti titanite).

altered feldspar is enhanced when the alteration products are mainly sericite and kaolin. Sorption on these minerals appears to exceed that on biotite flakes. No sorption is observed around the areas where carbonate and epidote occur as alteration products on feldspar grains.

The poor sorption on calcite is consistent with observations made by Failor *et al.* (1982). Cesium-137 is also concentrated in the altered regions of microcline grains. As with ^{90}Sr, no sorption was noted for ^{137}Cs from the two saline solutions. This also agrees with published results (Relyea & Serne 1979).

Sorption of ^{147}Pm

Photomicrographs and autoradiographs of two thin sections, one placed in contact with ^{147}Pm-tagged synthetic groundwater, the other with ^{147}Pm in the highly saline solution, are shown in Figures 8 and 9. In addition, a biotite sample, cut at 45° to the basal plane and containing an apatite inclusion, is shown in Figure 10. The latter was placed in contact with the synthetic groundwater containing ^{147}Pm. The autoradiographs (Figs. 8b, 9b and 10b) show that ^{147}Pm is strongly sorbed on fracture-filling and other secondary minerals in the matrix, from both synthetic groundwater and saline solution. The fracture-filling and secondary minerals consist of epidote, chlorite and titanite. Some grains of titanite, occurring as an accessory mineral, and presumably of primary origin, are present in the matrix. The hematite-filled fractures show no enhanced sorption of ^{147}Pm over that on the feldspars.

Figure 10b clearly shows that ^{147}Pm is strongly sorbed on apatite, more strongly than on biotite. Presumably, this is because the calcium atoms in the apatite are replaced by rare-earth ions or by the precipitation of a very insoluble rare-earth phosphate. Continued replacement of calcium by a rare-earth element could eventually transform apatite into a monazite by the reaction

$$3RE^{3+} + Ca_5(PO_4)_3OH + H^+ \rightarrow 3REPO_4 + 5Ca^{2+} + H_2O.$$

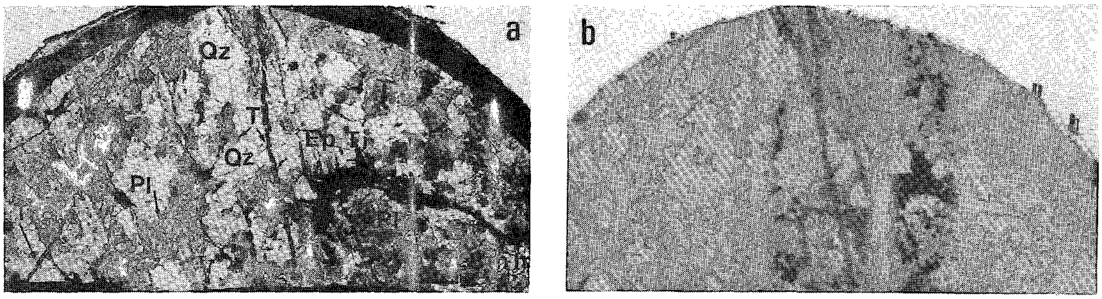

FIG. 8. Photomicrograph (a) and autoradiograph (b) of ^{147}Pm sorbed from granite groundwater onto a sample of fractured granite (Ep epidote, Pl plagioclase, Qz quartz, Ti titanite). Note the preferential sorption of ^{147}Pm on the fracture-filling materials.

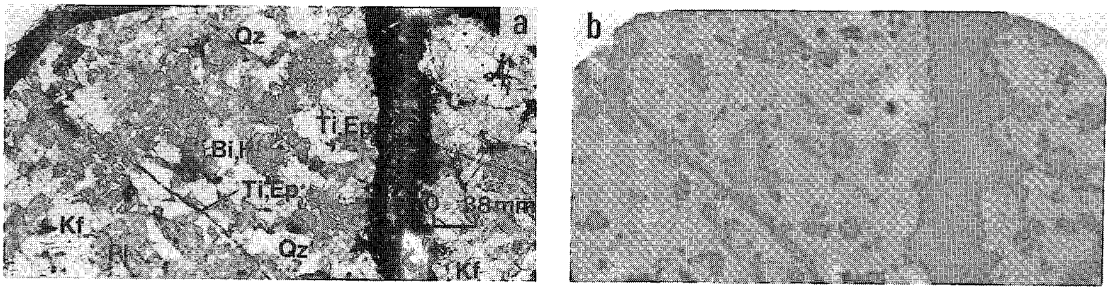

FIG. 9. Photomicrograph (a) and autoradiograph (b) of ^{147}Pm sorbed from a saline solution onto a sample of fractured granite (Bi biotite, Ep epidote, Hb hornblende, Kf microcline, Pl plagioclase, Qz quartz, Ti titanite). Note sorption of ^{147}Pm on fracture-filling materials.

Analytical data on rare-earth-bearing apatite are not plentiful; reports by Deer *et al.* (1963), Le Bas & Handley (1979) and Kamineni *et al.* (1982) suggest that apatite crystals in some geological environments can contain significant amounts of rare-earth elements. Kamineni *et al.* (1982) reported rare-earth-element contents up to 3.1% in apatite crystals from a charnockitic granulite.

Sorption of ^{147}Pm from the highly saline solutions also suggests that the mechanism of sorption does not occur *via* ion exchange, since the high concentration of cations does not inhibit sorption, as was the case for the alkali and alkaline earth ions.

In the Eye–Dashwa Lakes pluton, apatite commonly occurs as inclusions in altered biotite flakes and as a minor constituent in epidote-filled fractures. These apatite grains also show strong sorption of ^{147}Pm.

Sorption of ^{241}Am

Sorption of ^{241}Am is similar to that of ^{147}Pm. Sorption occurs from both synthetic groundwater and highly saline solutions. The samples represent a highly altered rock-matrix with microfractures filled with epidote, chlorite and hematite (Figs. 11a, 12a). Autoradiographs (Figs. 11b, 12b) confirm that ^{241}Am is strongly sorbed on the mafic minerals that are present in both the fractures and the matrix. The dark minerals in the matrix consist of chlorite and epidote, which formed by alteration of biotite and hornblende. Some grains of titanite are also present. Practically no sorption is noted in fractures filled with hematite (Fig. 11b). The dark areas corresponding to the altered plagioclase indicate that ^{241}Am is also concentrated in these regions, but certainly not as much as on the fracture-filling minerals and on the chlorite in the matrix.

The explanation for sorption of americium parallels that for promethium. The fact that large concentrations of cations do not inhibit the sorption of americium hints at processes other than ion exchange. Naturally occurring monazite contains measurable amounts of the actinides, notably

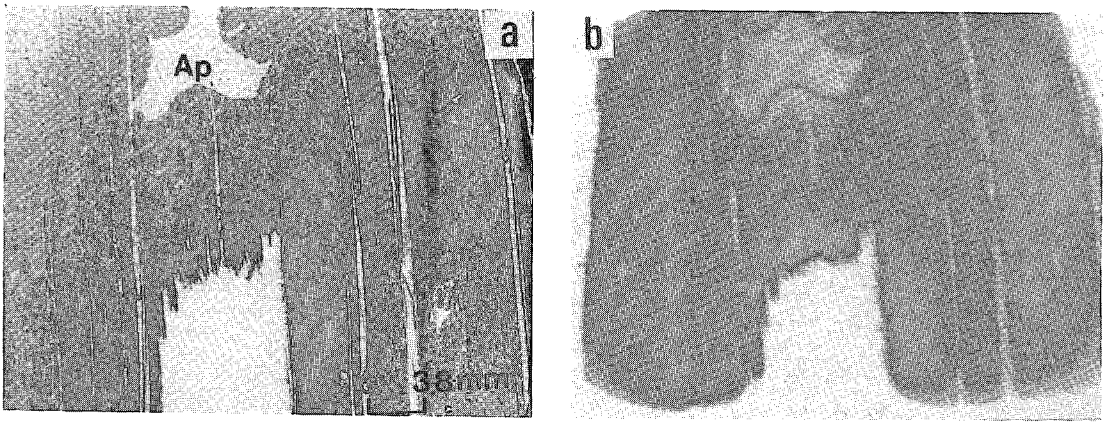

FIG. 10. Photomicrograph (a) and autoradiograph (b) of ^{147}Pm sorbed on a thin section of biotite cut at 45° to the basal plane (Bi biotite, Ap apatite). Note strong sorption on the apatite inclusion.

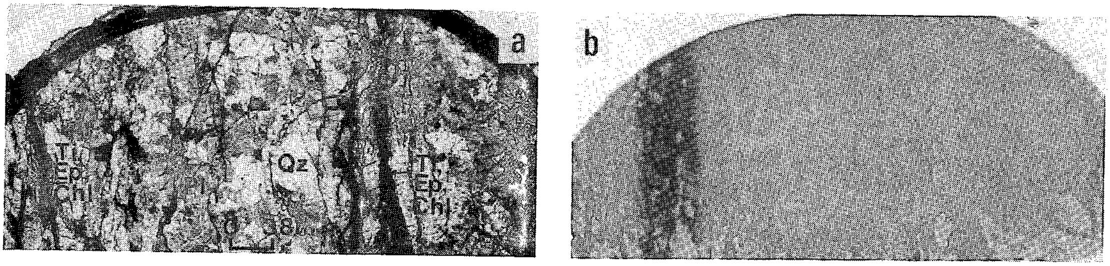

FIG. 11. Photomicrograph (a) and autoradiograph (b) of ^{241}Am sorbed from a granite groundwater on a sample of fractured granite (Chl chlorite, Ep epidote, Qz quartz, Pl plagioclase, Ti titanite). Note enhanced sorption on fracture-filling materials.

thorium. Additional studies have shown that americium, like the rare-earth elements, is indeed very strongly sorbed on apatite inclusions in gabbro and on thin sections of pure apatite.

Sorption of ^{95m}Tc

Technetium is of considerable interest in management studies of nuclear fuel waste. It is a man-made element and does not occur in measurable amounts in intrusive rocks. Under normal laboratory conditions, it exists in the Tc^{7+} state as TcO_4^- and is not sorbed by geological material under these conditions. It has been assumed, therefore, that this radionuclide will not be retarded by sorption, but will behave as a conservative tracer and travel at the same rate as groundwater.

In the absence of oxygen, however, technetium can be reduced by, for example, divalent iron to the 4+ state to form the sparingly soluble TcO_2 (Paquette *et al.* 1980). Bondietti & Francis (1979) have reported the removal of technetium from solution by crushed granite and basalt under anoxic conditions and have attributed this to a reduction of TcO_4^- to insoluble TcO_2, presumably by magnetite in the rock. However, analysis of the granite source-material has shown it to be contaminated with metallic iron (Vandergraaf, unpubl. data). Figure 13 shows a photomicrograph and autoradiograph of a thin section taken from a highly altered zone at the 1070-m level. Sorption indeed occurs on the opaque-filled microfracture and not on other iron-containing minerals such as hornblende and biotite. Other thin sections showed no sorption on secondary minerals such as chlorite and epidote. Recent studies of TcO_4^- with synthetically prepared hematite have shown that this oxide does not sorb technetium under anoxic conditions but that there are sufficient amounts of impurities in naturally occurring hematite and goethite to remove technetium from solution (Vandergraaf *et al.* 1983). Hence, the fracture-filling material in the sample taken from the Eye–Dashwa Lakes pluton cannot be pure hematite, but must contain at least some magnetite, sulfides, or manganese dioxide.

DISCUSSION

The results of this study show that, in many cases, sorption of dissolved radionuclides on secondary (or alteration) minerals and on fracture-filling materials

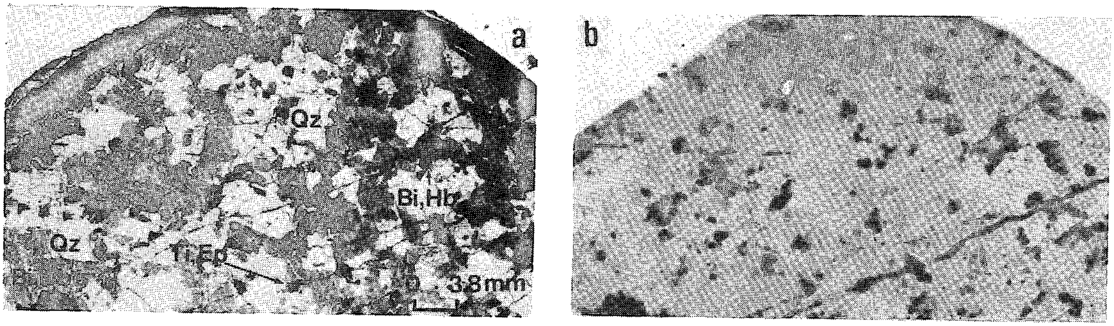

FIG. 12. Photomicrograph (a) and autoradiograph (b) of ^{241}Am sorbed from a saline solution on a sample of fractured granite (Bi biotite, Ep epidote, Hb hornblende, Qz quartz, Ti titanite).

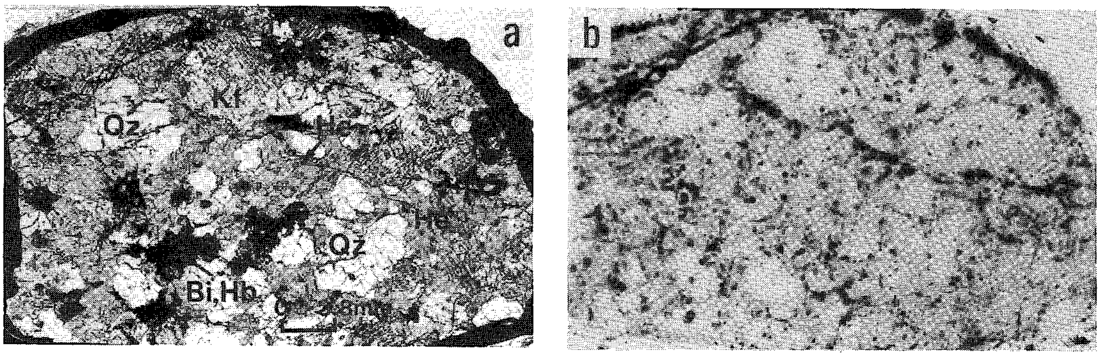

FIG. 13. Photomicrograph (a) and autoradiograph (b) of ^{95m}Tc sorbed on a sample of fractured granite under anaerobic conditions (Bi biotite, Hb hornblende, He iron oxide, Qz quartz, Kf microcline). Note preferential sorption of ^{95m}Tc on iron oxide fracture-filling material.

exceeds that on the minerals that constitute the fresh, unaltered rock. The materials lining the fractures can, thus, be expected to play a major role in retarding radionuclide transport away from a disposal vault of nuclear-fuel waste.

It is evident from this work that a thorough knowledge of the fracture network in the pluton, and of other characteristics of the fractures, such as their length, width, orientation, density and the assemblage of filling minerals, is required before radionuclide migration in crystalline rock can be predicted by the appropriate mathematical models for contaminant transport. In the Eye–Dashwa Lakes pluton, the occurrence of fracture-filling minerals shows some selective distribution in the subsurface. Based on this, some inferences can be made with respect to radionuclide migration from a nuclear fuel waste-disposal vault located at a depth of about 1 km in a pluton such as the Eye–Dashwa Lakes granite.

For example, the rare-earth elements, ^{241}Am and ^{242} Cm can be expected to be sorbed by epidote, titanite and chlorite in fractures and on the adjacent altered rock-matrix at deeper levels (where they are abundant) close to the vault. The same will apply to ^{90}Sr and ^{226}Ra, if the groundwater is not saline. Cesium-137 and cesium-135 will be preferentially sorbed on sericite, which is more abundant in aplite and pegmatite dykes, if the groundwater is not saline. Because these dykes are concentrated above 500 m, cesium can be expected to move farther from the vault if it escapes from the vault. Alternately, preweathered crushed rock introduced into the vault as backfill may contain adequate amounts of sericite to serve as an efficient retainer of cesium. Technetium sorption occurs on opaque minerals (magnetite, sulfides) and, hence, migration of this element can be reduced by adding metallic iron, magnetite, or naturally occurring iron oxides to the buffer-backfill material surrounding the waste containers in the vault.

Radionuclide transport is controlled by sorption on fracture-filling minerals and by the hydraulic conductivity of fracture pathways which, in turn, are governed by the hydraulic head and the aperture of the fracture. The hydraulic conductivities measured in the boreholes (Kennedy 1983) indicate low permeabilities at depth, even in fracture zones. Hydraulic conductivities measured in a deep borehole (ATK–1) in the Eye–Dashwa Lakes pluton show three zones of permeability. Above 250 m, the conductivity ranges from 10^{-9} to 10^{-7} m/s; between 250 m and 400 m, it ranges from 10^{-12} to 10^{-10} m/s, and below 400 m, the values are less than 10^{-12} m/s. The values noted in deep zones are comparable to those for samples of Atikokan granite as reported by Kamineni & Katsube (1982). The generally low conductivities noted in the Eye–Dashwa Lakes pluton, especially at greater depths, support the view that sorption experiments carried out under static conditions are applicable to natural systems in crystalline rocks.

CONCLUSIONS

This study has shown that fracture-filling and other secondary minerals will play a significant role in reducing contaminant transport away from the disposal vault for nuclear fuel wastes, through a geological barrier. The sorption experiments, although qualitative, have shown the selective sorption of radionuclides by different minerals. From the autoradiographs of thin sections placed in contact with the radionuclides, a number of empirical relations can be derived for the sorption by various fracture-filling and other minerals.

(1) Titanite, epidote, chlorite, biotite, hornblende, altered plagioclase, microcline and quartz, in decreas-

ing order, show preferential sorption for ^{90}Sr. Quartz shows no sorption. No sorption occurs from highly saline solutions.

(2) Sericite and altered plagioclase, containing sericite and kaolin, sorb ^{137}Cs strongly. Sorption on biotite is somewhat less significant. Epidote, titanite and other minerals show no appreciable sorption of ^{137}Cs, and sorption from highly saline solution is negligible.

(3) Epidote, titanite and chlorite in the fractures, and biotite, hornblende and altered plagioclase in the matrix, sorb ^{147}Pm better than do microcline and quartz. The same trend is noted for ^{147}Pm in saline solutions. Apatite crystals show the strongest sorption of ^{147}Pm.

(4) Like ^{147}Pm, ^{241}Am also preferentially sorbs on epidote, titanite, chlorite, biotite, hornblende and altered plagioclase. The trend holds for both highly saline solutions and groundwater from granite.

(5) Fractures filled with iron oxides show sorption of ^{95m}Tc. The silicates show no sorption of this element. Sorption also occurs from highly saline solutions.

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