Redox front formation in fractured crystalline rock: an analogue of matrix diffusion in an oxidizing front along water-conducting fractures

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ABSTRACT: Redox fronts may be formed in the geological environment surrounding shallow underground radioactive waste repositories (such as in the low-level radioactive waste (LLW) repository planned at Rokkasho, NE Japan). Additionally, various mechanisms associated with vitrified high-level waste (HLW) and spent fuel (SF) such as groundwater radiolysis by the highly active waste (see Hofmann 1999; JNC 2000, for detailed discussions) could also produce redox fronts between the waste and the reducing geological environment surrounding a repository. In both instances, radionuclide retardation in the geo-sphere is likely to be influenced by: changes in speciation due to changing redox potential; uptake/sorption on secondary iron phases; potential production of colloids at the redox front and buffering of radiolytically-produced oxidants within the rock matrix; and effects of matrix diffusion (for example, reduction of matrix porosity due to the development of secondary oxyhydroxide phases).

In this paper, the focus is on matrix diffusion processes in the vicinity of redox fronts, including an assessment of the nature of changes to the matrix porosity by the secondary phases and some limited assessment of matrix buffering capacity. Matrix diffusion is considered to be an important retardation process in the context of a repository performance assessment in that the volume of rock in contact with contaminants migrating in a water-conducting feature will be greatly increased from just the fracture surface to a larger portion of the bulk rock behind the surface (e.g. Grisak & Pickens 1980; Neretnieks 1980). This will obviously increase the retardation of sorbing radionuclides but will also have a significant effect on non-sorbing contaminants (such as ¹²⁹I) due to dilution in the matrix pore space.

Such characterization studies on the process of matrix diffusion in fractured rocks have been carried out as a part of natural analogue studies (e.g. Alexander et al. 1990; Valkiainen 1992) and in laboratory experiments (e.g. Bradbury & Stephen 1986; Yoshida et al. 2002). However, the natural processes of matrix diffusion in relation to redox reaction and/or oxidizing area formed along water-conducting fractures have only rarely been studied for repository host rock environments (e.g. Baertschi et al. 1991; Mazurek et al. 1996; Yoshida et al. 2003). Here, data concerning matrix diffusion processes around an oxidizing front that might occur in the geological environment surrounding an underground disposal site are presented. In particular, the possibility of nuclide release in an oxidizing fluid flowing through a groundwater-conducting feature is presented together with information on how the oxidizing part reacts with contaminants during matrix diffusion.

INTRODUCTION

Formation of redox fronts along shallow, water-conducting fractures due to the infiltration of oxidizing surface water is to be expected under most conditions. This will influence elemental migration within the near-surface geological environment surrounding shallow underground radioactive waste repositories (such as in the low-level radioactive waste (LLW) repository planned at Rokkasho, NE Japan). Additionally, various mechanisms associated with vitrified high-level waste (HLW) and spent fuel (SF) such as groundwater radiolysis by the highly active waste (see Hofmann 1999; JNC 2000, for detailed discussions) could also produce redox fronts between the waste and the reducing geological environment surrounding a repository. In both instances, radionuclide retardation in the geosphere is likely to be influenced by: changes in speciation due to changing redox potential; uptake/sorption on secondary iron phases; potential production of colloids at the redox front and buffering of radiolytically-produced oxidants within the rock matrix; and effects of matrix diffusion (for example, reduction of matrix porosity due to the development of secondary oxyhydroxide phases).

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SAMPLE AND METHODS

The present study focused on a redox front formed along fractures in the Cretaceous Naegi granite (c.60–75 Ma; Shibata et al. 1962; Kawano & Ueda 1966; Hayase & Ishizaka 1967; Suzuki et al. 1994) in an open quarry in Gifu Prefecture, central Japan. The studied redox front was formed along a single, almost vertically developed, fracture in the host rock body and reaches up to several tens of metres deep from the ground.
The redox front has been formed almost symmetrically about the fracture plane and all fronts examined display reddish-brown coloured secondary ‘iron oxyhydroxide’ that penetrates from the fracture surface into the rock matrices (Fig. 1). In the oxidizing zone, the major rock-forming minerals, such as feldspar and biotite, seem to be quite fresh and almost no alteration feature can be seen in hand specimens.

In order to exclude the influence of weathering effects, a block sample of redox front was carefully collected at a fresh quarry face at c. 20 m depth from the surface. The sample was cut into 28 pieces in parallel to the fracture plane and each sample was crushed to less than 115-mesh (0.124 mm) by an agate ball-mill. Major and trace element compositions were then determined by X-ray fluorescence (XRF; SXF-1200 equipped with Rh X-ray tube, 40 kV, 70 mA), and rare earth elements (REE; La–Lu) were determined by inductively coupled plasma–mass spectrometry (ICP-MS; HP4500) at Nagoya University.

In the analysis, glass beads were prepared by fusing mixtures of 0.7 g of powdered sample with 6.0 g of lithium tetraborate for the major elements, and by fusing mixtures of 2.0 g of powdered sample with 4.0 g of lithium tetraborate for the trace elements. The calibration has been carried out using standard rock samples issued by the Geological Survey of Japan and the composite standards prepared by Yamamoto & Morishita (1997) for the major and trace elements, respectively. In the measurements, Fe(II) was determined by KMnO4 titration and Fe(III) was calculated by subtracting Fe(II) from total Fe. In the REE analysis, about 50 mg of powdered sample was digested with 0.5 ml HClO4 and 1 ml HF on a hot plate at 160 °C, and subsequently digested again with 0.5 ml mixed acid (HF:HClO4 = 2:1) on the hot plate at c. 160 °C. Subsequently, the residue was dissolved in 1.7 N HCl and centrifuged at 12 000 rpm. The supernatant after centrifugation was transferred to another 10 ml Teflon beaker. In order to recover REE in the acid digestion residue deposited in the centrifugation tube, the residue was transferred to a 2 ml Pt crucible and dried.
at a temperature of c. 60 °C. After adding c. 50 mg of Na₂CO₃–H₃BO₃ (3:1 by weight), the crucible was heated at 880 °C for 20 minutes to fuse the mixture. The fused cake was dissolved using 1.7 NHCl with mild heating and the solution was centrifuged at 12 000 rpm. In most cases, no residue was recognized after centrifugation. The 1.7 NHCl solutions prepared after HF–HClO₄ digestion and Na₂CO₃–H₃BO₃ fusion were mixed and applied to the cation chromatographic separation of REE from major elements and Ba, which interfere with the REE analyses by ICP-MS. Finally, the sample solution was dissolved in c. 20 ml of 2% HNO₃ for ICP-MS analyses. Mixed standard solutions made from individual REE oxides were used as external calibration standards and, in the case of both In and Bi, were used as internal standards. The levels of oxide formations of light REE were determined individually by analyses of the 20 ppb solutions of each REE. Analytical precision was estimated to be better than 1% for Si, 3% for other major elements, 10% for trace elements and 3% for REE through the analyses of rock reference samples issued by the Geological Survey of Japan (Sugisaki et al. 1977; Yamamoto et al. 2005).

Loss on ignition (LOI) of the sample was measured by gravimetric analysis in order to assess the degree of hydration during the elemental matrix diffusion. Elemental distribution was examined by electron probe microanalysis (EPMA; JOEL JXA-8800R) and an alpha-track method (Basham 1981) was applied to identify the specific location of U in the matrices. A scanning electron microscope (SEM; JOEL JSM-6100) was used to examine sample morphological features.

**RESULTS**

**Elemental distribution across the front**

Distribution profiles of major elements across the front, from the fracture surface to the rock matrix, are shown in Figures 2 and 3. Apart from Fe, most of the major element concentrations do not change in the oxidation zone, although a small CaO depletion is present around the fracture plane. LOI (Fig. 2), and total-Fe₂O₃ peak together behind the redox front. Profiles of Fe₂O₃ and FeO show that ferric iron in the oxidation zone is generally about two times higher (and up to six to eight times higher) at the front part compared to the background level, and ferrous iron in the oxidation zone is c. 30% lower than those of the parent rocks (Fig. 3). The
migration depth of Mn is limited to the vicinity of the fracture surface. Distribution profiles of the trace elements are also shown in Figures 4 and 5. Ba, Pb and Rb are highly concentrated near the fracture surface and display concentration profiles which are similar to that of Mn (Fig. 4). The profiles of the REE (apart from Eu), Y and CaO have a similar pattern across the front (Fig. 5). These features suggest that REE and Y have been depleted mainly at the vicinity of the fracture plane. However, the detailed analysis of REE profiles show that heavy REEs are slightly accumulated at the front part in the oxidized zone (Fig. 6).

Uranium and Cs (Fig. 7) appear to have migrated from the fracture surface to the redox front and are highly concentrated at the front edge. Concentration patterns suggest that U and Cs have high correlation with Mn and Fe concentrations. The highest U concentration peak (up to 17 ppm) was formed at a slightly different point from the peak of Cs and Fe (ferric iron) concentrations, and the U concentration decreases rapidly to the background level (c. 8 ppm) thereafter.

Microscopic morphological features

Microscopic observations with an optical microscope reveal that ferric iron is concentrated at the grain boundary and/or micro-pores among rock-forming minerals (Fig. 8a). Iron oxyhydroxides (identified by relatively high Fe(III)/Fe(II) ratios in the oxidizing zone and the translucent reddish-brown colour observed under the optical microscope; Scheinost & Schwertmann 1999) were also identified in the mineral cleavages of feldspar and biotite. Manganese oxide was also formed at grain boundaries, but the distribution is limited to immediately around the fracture surface as shown in the elemental profile (Fig. 3).

Detailed observation of the Fe oxyhydroxide by SEM reveals that small (c. 10 µm in diameter (Fig. 8b)) spherical grains and associated aggregates have been formed in the grain boundaries and/or on the pore walls. These are almost clogging the porosity and presumably reduce accessible pore space for fluid migration. The spherical particles display a zoning structure probably formed during the grain growth. EPMA mapping shows that these grains are composed mainly of Si and Fe, with Si concentrated mainly in the crust of the grain, while Fe is relatively evenly distributed across the whole grain (Fig. 9a, b).

Alpha-track examination reveals that U has formed concentration spots within the oxidizing zone. The distribution features of alpha-track particles (Fig. 10a, b) show that U has been specifically and almost homogeneously concentrated where the Fe oxyhydroxides have accumulated at the grain boundaries and in the mineral cleavages. This could be taken as evidence that U has migrated and intimately mixed into it when the oxidizing zone was formed because of the relatively high mobility of U under oxidizing environment (Langmuir 1978).

![Fig. 7. Concentration profiles of U and Cs across the front. Both elements migrate through the oxidized zone and accumulate, closely associating with Fe and Mn oxides, respectively. In particular, U has a high concentration peak at the front edge, presumably caused by the redox change.](image)

![Fig. 8. Photographs by optical microscope (open) and SEM. (a) Spherical iron oxide aggregations forming in the grain boundaries and/or mineral cleavages: Qz, quartz; Pl, plagioclase. (b) SEM photo of a grain of spherical iron oxide formed in the pore space.](image)
DISCUSSION

Formation of the redox front

Geochemical analyses and direct observations of the redox front reveal that the front is characterized by the secondary accumulation of ferric iron (Fe-oxyhydroxide). This suggests that Fe-oxyhydroxide has been formed by oxidation of ferrous Fe in the pore water by in-diffusion of oxygen from the groundwater. Although the granitic host rock contains significant redox buffer capacity in the main mineral phases, it is often the case that such capacity is difficult to access because Fe is trapped in the crystal structure and therefore induces a kinetic effect on the buffering rate. This would allow some penetration of the oxygen before precipitation. Alternatively, assuming a fast reaction, the current position of the precipitated Fe-oxyhydroxide suggests that the reducing capacity of the host rock has been exhausted by the oxidizing fluids up to the zone where ferric iron has now precipitated. Such an effect has been observed at the Poços de Caldos U mine in Brazil where the redox front has been observed to be migrating downwards, into the reduced host rock, at a rate of ~10 m per million years (Chapman et al. 1991; Cross et al. 1991), presumably being driven by the erosion of the host rock which is at about the same rate, based on independent measurements.

The precipitation and concentration of Mn oxide along the fracture surface shows that the vicinity of fracture surface has been more strongly oxidized than the rock matrix where ferric iron accumulated. The fact that the Mn front forms nearer the fracture is in agreement with the fracture supplying oxidizing water. Standard models of redox front development (e.g. Froelich et al. 1979) show that Mn reduction occurs at higher oxygen levels than does Fe reduction. By assuming an initially reduced host rock, dissolved Mn in the pore water would be oxidized by the incoming redox front nearer to the fracture. This is a well-documented effect in soils and marine and freshwater sediments (e.g. Upstill-Goddard et al. 1989) but has also been observed in other rock matrices such as Liassic indurated clays (Opalinus Clay; Mazurek et al. 1996) and crystalline rocks (Grimsel granodiorite; Baertschi et al. 1991). This assumption, however, still may not be able to explain why the high concentration peak of ferric iron exists at the front in the rock matrix of the oxidized zone. If the redox front formed only by the supply of oxygen dissolved in the ground-water from the fracture and met the reducing pore water in the host rock, then the concentration profile of ferric iron should be like the profile of Mn oxide, which has a high concentration peak closer to the fracture plane. If the ferrous iron is provided from the granitic rock and meets the oxygen from the fracture to form the ferric iron precipitations, the concentration gradient of ferrous iron in pore water will be reduced near to the fracture plane and more ferrous iron can be supplied from the granitic rock. Due to the continuous supply of oxygen, more high concentration peaks of ferric iron along the fracture can be identified.

Akagawa et al. (2005) also showed that the concentration of total Fe in biotite shows no significant changes between the oxidized and reduced rock. This suggests that at least the biotite may not be a major source of ferrous iron to the pore water in the granite itself and, presumably, some of the ferrous iron may be ‘fossil’, having been added from reducing groundwater when the granite was previously more deeply buried. In that case, dissolved NO₃⁻ in the pore water (Iwatsuki & Yoshida 1999) infiltrated from the fracture is probably a possible oxidant supplied to the rock matrix. Another possibility for ferrous iron oxidation in a reducing environment is by microbial activity. Yoshida et al. (2003, 2005) reported evidence that the ferric iron in a sedimentary rock matrix was produced by the concerted activity of iron reducing and oxidizing bacteria to form Fe-oxyhydroxide.

Trace element migration

REE, U and Cs have been studied as chemical analogues of HLW material in the geological environment (see Miller et al. 2000, for examples). First, in order to discuss the REE distribution pattern in the oxidizing zone and across the front, the averaged REE composition of eight host samples (nos 21–28) was used instead of a chondritic-normalized composition (as this makes the REE mobility during oxidized zone formation much clearer) and the results are shown in Figure 12.

The degree of Ce anomaly was expressed mathematically by Ce/Ce*=Ce/Ce*(La₈×Pr₈)¹/² and, similarly, the degree of Eu...
anomaly was expressed by \( \text{Eu}_{\text{obs}} = \text{Eu}_{\text{obs}}^* \times (\text{Sm}_{\text{n}} \times \text{Gd}_{\text{n}})^{1/2} \)

where subscript \( n \) indicates normalization by the fresh granite. This formalization has been commonly used for the pattern analysis of REE (e.g., Takahashi et al. 2000). The REE patterns across the front are similar to those of the main host rock apart for Ce and Eu. REE concentrations, however, decrease to levels of approximately 20% of the host rock, particularly around the fracture plane (Fig. 11). As a specific feature of the REE patterns, the concentrations of light rare earth elements (LREE) are more depleted than heavy rare earth elements (HREE). Suzuki et al. (1990) reported that approximately 45% of the whole rock La and 35% of the Nd had accumulated at the grain boundaries of constituent minerals of the fresh Naegi granitic rock. Detailed EPMA analysis across a boundary between quartz crystals suggests that the LREE have been specifically concentrated within the first few micrometres of the crystal boundary. Although the form of the REEs is currently unknown, the near-surface accumulation in the crystals may have allowed preferential leaching by infiltrating oxidizing groundwaters. Such an effect would presumably be magnified by the presence of the secondary Fe-oxyhydroxide via sorption, particularly for the LREE (Sharma & Rajamani 2000). This combination of LREE specific processes could explain the slightly different concentration pattern existing between HREE and LREE across the front.

A strong positive Ce anomaly is evident in the sample closest to the fracture plane. The Ce anomalies of other samples in the oxidized zone are mostly negative but minor (Fig. 6). The geochemical behaviour of Ce is generally different from those of other REE as Ce(III) can be converted into Ce(IV) in oxidizing conditions and, because the solubility of Ce(IV) is much lower than that of Ce(III), this difference of redox-dependent solubility can result in Ce anomalies found in the sample along the fracture plane. As one of the possible explanations for the Ce enrichment at the fracture surface, Ce in the rock matrix was leached under a reducing environment and the dissolved Ce was then oxidized along the fracture surface. Secondary Mn oxide, which acts as a catalyst for Ce oxidation (Ohia & Kawabe 2001), in the vicinity of the fracture surface can also accentuate the Ce positive anomaly due to the co-precipitation and/or the sorption onto the Mn oxide surface (De Carlo & McMurtry 1992). Concentration profiles of Pb, Rb and Ba suggest that these trace elements may also be adsorbed on the Mn oxide during and/or after forming the redox front.

A positive Eu anomaly is also observed in the oxidized zone (Fig. 6), although it changes from positive to negative across the front. It is generally believed that Eu is predominantly incorporated into plagioclase (Phinney & Morrison 1990). This, in turn, suggests that REE in crystal boundaries show negative Eu anomalies because of selective incorporation of Eu into plagioclase. The changes of REE concentrations from the
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fracture surface to the front are also very similar to that of the Ca concentration (Fig. 5). It can be seen that there is a positive correlation between Ca and all REE except Ce (and Eu in the oxidized zone). In the granite, plagioclase is a Ca-rich major mineral and simultaneous leaching of REE and Ca from the plagioclase is a possible process to explain this correlation.

Uranyl and Cs concentrations across the front suggest that U–VI has diffused into the matrix from the oxidizing groundwater (Fig. 7) and has accumulated at the redox front where the redox potential changes. There is also a suggestion that U in the granite has been leached by the oxidizing water penetration (Fig. 7). Uranium has been concentrated at Fe-oxhydroxide spots, presumably in a manner similar to that reported in other U deposits (e.g. Edgill 1991). Caesium shows a positive correlation with both Fe and Mn concentrations and is presumed to indicate Cs accumulation on these secondary oxides (although no evidence is currently available to propose a mechanism).

CONCLUSION

Detailed characterization of the redox front formed along a discrete single fracture in a granitic rock has been carried out and revealed that ferric iron defines the visible redox front via an accumulation of micro-spherical Fe-oxhydroxide aggregations at crystal boundaries, pore surfaces and mineral cleavages. Geochemical analyses show that some trace elements are concentrated in the vicinity of the fracture surface associated with Mn oxide, while REEs, Cs and U are concentrated at the redox front. In particular, U has been highly concentrated at the edge of the redox front and retained by secondary Fe oxyhydroxides behind the front, in the oxidized zone.

Such oxidation fronts could be formed in the deep geological environment surrounding a HLW/SF repository due to radiolysis of the groundwater by the waste (although this is unlikely to be the case where the canister is steel; see Alexander & McKinley 1999) or around shallower repositories for LLW due to the incursion of near-surface oxidized groundwaters. These findings suggest that, despite changes to the near-fracture matrix due to oxidation effects (e.g. secondary mineral formation), the matrix is still accessible to contaminant diffusion and that the redox front interface around an oxidized rock can be an effective site of contaminant retardation. These data are useful for supporting the conceptual models of radionuclide retardation in a repository host rock but, as noted by Hofmann (1999), much more work needs to be carried out on features such as these to ascertain quantitatively the likely efficiency of such ‘contaminant traps’ before the data can be integrated into a repository performance assessment.

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