

Characterisation of iron oxides in fractured granite

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Iron(III) (hydr)oxides, henceforth termed Fe-oxides, may act as a sink for contaminant compounds, including radioactive elements where extremely small amounts are dangerous to the health. Incorporation of such elements in the crystal lattice of Fe-oxides may be of great importance to the environment, should nuclear waste repositories leak. The lanthanides (the rare earth elements – REE) can be used as a model for the actinides because they behave in the same way as a result of similar electron structure. In addition to providing information about the likely behaviour of the actinides, better understanding of the trace element uptake behaviour at various temperatures might reveal one or more indicators for determining the source or the history of the Fe-oxide components.

In several northern countries, repositories are being planned in granitic rocks that are assumed to be geologically stable. In a particular example, in Sweden, radioactive waste is to be stored in copper canisters that are highly durable under reductive conditions. However, it has been proposed that a future glaciation may change the groundwater flow pattern radically, leading to oxidising conditions at the level of the repository. Because such change in redox conditions would facilitate precipitation of Fe-oxides that differs in chemical signature from the hydrothermal precipitate, characterising the trace element composition of the Fe-oxide may reveal evidence of oxid low-temperature environments in the past.

Fe-oxide-bearing fracture material has been collected at various depths from a rock core near Äspö, Sweden. X-ray diffraction (XRD) of the fracture material shows a diverse mineralogical composition that includes hematite, feldspar, quartz and clay. The chemical composition of the Fe-oxides has been characterised through selective dissolution procedure where the REE concentration of the Fe-oxides was determined with ICP-MS analysis of supernatant from the dissolution experiments and the trace element concentration was estimated by comparing TOF-SIMS and XPS analysis of whole samples with analyses of the residual material after dissolution.

Precipitation of aragonite by membrane diffusion of gaseous CO₂ and the coprecipitation of Sr²⁺ and Ba²⁺ (10° to 50°C)

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In the present study aragonite is crystallized by a new precipitation technique from a calcium - magnesium - chloride solution between 10° and 50°C. The dissolved inorganic carbon (DIC) is transferred from a solution containing dissolved CO₂ to another solution containing Mg²⁺ and Ca²⁺ by diffusion of gaseous CO₂ through a polyethylene membrane. The experiments simulate situations where only gaseous CO₂ and no dissolved components may be transferred through natural or anthropogenic types of membranes. The results show that significant amounts of DIC may be mobilized by the diffusion of gaseous CO₂ through such a membrane. The rate of aragonite precipitation depends strongly on the gradient of partial pressure of CO₂ and on the temperature.

The coprecipitation experiments show that the distribution coefficients of Ba²⁺ and Sr²⁺ into aragonite decrease from 10° to 50°C according to the equations

$$D_{Ba,a} = 2.31 - 0.03455 \cdot T(^{\circ}C) \text{ and}$$

$$D_{Sr,a} = 1.27 - 0.005212 \cdot T(^{\circ}C), \text{ respectively.}$$

In the case of Ba²⁺ the temperature dependence for the incorporation of barium into aragonite is unique. Nevertheless, the range of D_{Ba,a} values given by Kitano et al. (1971) for incorporation of barium into aragonite for 20°C coincide with the results of the present study. The effect of the temperature on the D_{Sr,a}-value is similar to the results obtained by Kinsman and Holland (1969). In their experiments the precipitation of aragonite was carried out by the addition of a diluted sodium carbonate solution into sea water. The present experimental solutions contain low concentrations of Cl⁻ and no SO₄²⁻. Thus, incorporation of Sr²⁺ into aragonite is constant within the range of chemical composition of the present solution and the sea water up to 50°C. The incorporation of Sr²⁺ into aragonite is different if the precipitation is induced by bionic processes (e.g. Beck et al., 1992). Nevertheless, the variation of D_{Sr,a} with temperature is similar to that for inorganic precipitation of aragonite.

References

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