Iron speciation and valence in the upper 1 km of fractured crystalline bedrock on the Baltic shield

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The widespread networks of open water-conducting fractures in crystalline bedrock are covered by a variety of Fe-bearing minerals. Quantitative information on Fe mineralogy and valence of these minerals is of great importance not only in constraining the biogeochemical cycle of Fe and other related elements in this largely unexplored space, but also in evaluating the mineralogical capacity to reduce oxygen which is one of the key issues in the risk assessment of nuclear waste repositories.

Here, we studied Fe mineralogy and valence in fracture coatings, fresh rocks and altered rocks in the upper 1 km of fractured crystalline bedrock at two sites (Laxemar and Forsmark areas, Sweden) on the Baltic shield. $Fe^{3+}/\sum Fe$ ratios in these materials were quantified based on the centroid position of the pre-edge feature on Fe XANES spectra, while the speciation of Fe was predicted by reconstructing the sample EXFAS spectra using a linear combination of a large dataset of reference spectra collected previously[1] and in this study. The results were compared with Mössbauer spectra. The fresh and altered rocks showed no systematic difference in $Fe^{3+}/\sum Fe$ ratio, indicating that past hydrothermal activities (red-staining on fracture wall-rock) did not lead to a reduction in reducing capacity within the fracture networks. The fracture coatings from the Forsmark area are of clear hydrothermal character (as indicated by an abundance of hematite, hornblende and muscovite) and have not experienced the same degree of low-T oxidative weathering as the samples from the Laxemar area having frequent and abundant illite and ferrihydrite. However, $Fe^{3+}/\sum Fe$ ratios of the fracture coatings from the two areas showed similar features, including no depth trend and a similar variability from 0.24-0.85 and 0.12-0.71 which are overall larger than the fresh and altered rocks. This suggests that regional geological events can have a significant impact on the speciation of Fe, but not Fe valence.

[1] Yu et al., 2015. *Chem.Geol.* **413**:73-85