

Evolution of the hydrochemical system at Horonobe, Japan: An indication from rock matrix porewater chemistry

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The investigation of the geological environment within a suite of sedimentary formations is currently ongoing at the site of JAEA's Horonobe Underground Research Laboratory in northern Hokkaido, Japan. The main aim is to establish relevant techniques for future repository site characterisations in Japan. One facet of this is one of the few examples worldwide, and the first use in Japan, of rock matrix porewater data, in conjunction with groundwater data, as part of the evaluation of the palaeohydrogeological evolution of the Horonobe area.

More than 100 porewaters have been extracted from cores sampled from the marine sequences of the late Miocene to Pliocene Wakkanai and Koetoi Formations, consisting predominantly of siliceous and diatomaceous mudstones respectively. General trends, *eg* in Cl concentration with depth, indicated by all data, from both the porewater and groundwater datasets, are strikingly consistent. The data indicate the presence of a shallow zone of rapid change in hydrochemistry, followed by more stable conditions below 200–300 mbgl. The deep porewaters are more saline than shallow waters, but are still diluted (Cl = 2,000–15,000 mg/l) and enriched in ¹⁸O ($\delta^{18}\text{O} = 0\text{--}4\text{‰}$) compared to seawater. Although the Horonobe area was not directly glaciated, it is likely that permafrost was present discontinuously during the Last Glacial Maximum and later during the Kenbuchi Stadial (the local equivalent of the Older Dryas) of approximately 11.8 to 12.4 ka BP. The fact that no cold climate and glacial depletion signature is obvious in the porewaters suggests either relatively rapid flushing of the hydrochemical system to remove any evidence of the cold climate or complete sealing of the system by the permafrost against the cold climate signature.

A new analysis of the porewater stable isotope data suggests that the cold climate signature has been effectively removed by mixing with later groundwaters. Tests of this new interpretation against major element data and the M3 mixing model will be presented here.

First principles investigation of the FeOOH-polymorphs under pressure

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Iron-oxyhydroxides (FeOOH) play an important role in nature and technology: they find application in water treatment (e.g. binding heavy metals and arsenic complexes), as inorganic pigments, and in magnetic recording. The high pressure behavior of water containing minerals is fundamental for understanding processes in the Earth's crust and upper mantle.

Using density functional theory (DFT), we investigate the stability, structural, magnetic, and electronic properties of the FeOOH-polymorphs (α -, β -, γ -, and *hp*(ϵ)-FeOOH) under hydrostatic pressure. At ambient conditions goethite (α) is the lowest energy phase consistent with recent calorimetric measurements [1]. Around 9 GPa we predict a transition to the *hp*(ϵ)-phase. Indications for such a phase transition have recently been obtained using x-ray diffraction measurements [2]. This structural transformation is accompanied by a spin-crossover takes place at a much lower pressure than other currently discussed iron-bearing minerals. While the ground-state Fe³⁺-ions are coupled antiferromagnetically, at higher pressure a transition to a ferromagnetic alignment occurs for *hp*(ϵ)-FeOOH within the generalized gradient approximation (GGA). Concerning the electronic properties, including an on-site Coulomb repulsion parameter (LDA/GGA+U method [3]) improves the size of the band gaps at zero pressure substantially.

[1] Laberty and Navrotsky (1998), *Geochimica et Cosmochimica Acta* **62**, 2905-2913. [2] Gleason *et al.* (2008), *American Mineralogist* **93**, 1882-1885. [3] Anisimov *et al.* (1993), *Physical Review B* **48**, 16929.