

Nickel sorption on chalk and calcite

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Heavy metal retention in aquifers is controlled by sorption on aquifer material. Processes such as precipitation, incorporation and solution complexation also influence retardation, but in all cases, sorption plays a role. At natural or slightly polluted levels, it may be the predominant immobilization process. In several countries, such as those bordering the North Sea, drinking water comes from chalk (>90% calcite, CaCO₃). Nickel contamination can arise from industrial spills, waste disposal leaching, and in some cases [1], from the weathering of pyrite, where Ni is present in solid solution. However, little is known about sorption of Ni or other heavy metals onto chalk as an aquifer material.

We examined sorption on two types of natural chalk and compared it to the behaviour of synthetic calcite. Our purpose was to produce data for safety assessment and more effective remediation strategies. Batch experiments were performed at 25°C with atmospheric CO₂ partial pressure, in calcite equilibrated solutions, in the pH range 7.6 to 8.8.

Nickel sorption on calcite as well as chalk followed the same pattern observed for other divalent cations, namely:

1. At constant pH, Ni sorption was well-described by a Freundlich-type isotherm.

2. Adsorption increases with higher pH in the equilibrium suspension, higher surface area and decreasing adsorbate concentration. This is more consistent with Ni²⁺ exchange on surface sites than with coprecipitation.

Experimentally determined chalk K_d values (L/kg) correlate linearly with pH (as $\log K_d$). Variability over about one order of magnitude disappears when surface area (L/m²) is taken into account: $\log K_d = (1.55 \pm 0.17) \text{pH} - (14.2 \pm 1.3)$. Such behaviour confirms the similarity of sorption properties for chalks and calcite, which is its main constituent.

K_d values can be related to migration velocity (i.e. relative to pore water flow) by the retardation factor R . With this new K_d , a Ni retardation factor for chalk was determined to be $R \sim 130$ and 9 at pH 8 and 7, respectively. This means that sorption onto chalk can significantly decrease Ni mobility, even in aquifers with low clay and organic matter content. Only at pH below 6, where calcite is dissolving, does Ni move substantially in chalk aquifers.

Reference

[1] Larsen F. and Postma D. (1997), *Environ. Sci. Technol.* **31**, 2589-2595.

New evidences for existence of early Archaean terrains within Enderby Land, Antarctica

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Enderby Land is known as the oldest terrain of the Earth with age estimations ≥ 4 Ga (Sobotovitch *et al.*, 1974). Further study of different geological objects at the Enderby Land proved, from one hand, the unique age of this crust segment (DePaolo *et al.*, 1982; Black *et al.*, 1986) and, from the other hand, the unique thermodynamic conditions of accompanying evolution of these rocks ($\geq 1000^\circ\text{C}$) (Sheraton *et al.*, 1987; Harley, Motoyoshi, 2000). As it had been demonstrated in the first studies of zircons from orthogneiss of Sones Mountain (Williams *et al.*, 1984), in such cases we may face very local heterogeneity of zircon grains. It could be caused by their age and complicated reaction of zircon crystalline structure to the condition of ultra-high temperature metamorphism, which is marked twice during the existence of Napier Complex and disturbed all other isotope systems (McCulluch, Black, 1984; Black, 1988). This results in obtaining concordant ages in a rather wide range along U-Pb concordia which may not reflect the real geological events (Harley, Black, 1997).

Zircons from charnockite-enderbite rocks (Aker Peaks, Napier Mountains), which we have dated by SHRIMP-II, were analyzed earlier by conventional multigrain U-Pb ID-TIMS method (Belyatsky *et al.*, 1990), but did not reveal age concordancy and colinearity. Our study demonstrates that the most optimal way to evaluate geologic events is the preliminary complex examination of zircons (CL, BSE, REE composition) and outline of cogenetic groups which allow to use traditional approach to age estimation through discordia construction. This approach has resulted in obtaining, at the first time, the reliable age of magmatic crystallization for enderbites – 3620±30 Ma and the age of primary enderbite's protolith origin – 3950–3970 Ma. While some previously estimated younger ages of 2850–3050 Ma, which are considered as main metamorphic events of granulite facies for the whole Enderby Land (Harley, Black, 1997; Kelly, Harley, 2005), are absent in the studied zircons. At the same time in all dated zircons the metamorphic event of 2450–2480 Ma ago is clearly recorded and it is in agreement with the granulite facies metamorphism described by many authors. It is necessary to note, that zircons also are free of 1000–1200 Ma record in spite the extensive Proterozoic metamorphism dated in the nearby Rayner Complex (Black *et al.*, 1987). These conclusions coincide with Sm-Nd isotope systematics of the enderbites: whole-rock (n=12) isochron corresponds to the age 3660±170 Ma and $\epsilon=+0.7$, with mineral isochrons show age of metamorphic event – 2440–2490 Ma. In general, it evidences to cratonization of the Napier Complex at about 2450–2480 Ma ago.

This study was supported by RFBR grant 07-05-00736a.