

## Modeling of Zn sorption onto clayey sediments using a multi-site and multi-component ion-exchange model

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In literature, many sorption models have been proposed to interpret experimental sorption data onto complex mineralogical assemblages, such as sediments and soils. Nevertheless, these models are often empirical and can not interpret data obtained in a wide range of physico-chemical conditions (pH, ionic strength, initial trace element concentration, solid/solution ratio...).

The aim of this study is (1) to elaborate a model of multi-site and multi-component cation exchange capable to describe the retention of transition metal on pure clay-minerals (2) to test the ability of this approach to reproduce the retention of these elements on natural material (soils/ sediments) in various chemical conditions.

This study is focused on the behaviour of Zn in presence of clayey sediments. Considering that clay-minerals behave as a multi-site cation exchanger, it is possible to describe the retention of metals as well as the competitor cations, including the protons, by ion-exchange equilibria with the surface minerals. This approach was applied with success to interpret the experimental data obtained by Bradbury and Baeyens (1997) in the Zn-Na-montmorillonite system. Behaviour of Na, K, Ca and Mg versus pH was already studied in previous studies on pure montmorillonite (Gorgeon, 1994; Nolin, 1997) and permit us to elaborate a thermodynamic data base including the exchange site concentrations associated to the montmorillonite and the selectivity coefficients of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, and Zn<sup>++</sup> versus H<sup>+</sup>.

Sorption isotherms of Zn were carried out onto two different sediments in batch reactors at different pH and ionic strengths, and using NaCl and CaSO<sub>4</sub> as electrolytes. CEC measurements of both sediments were performed by cation displacement using CsCl solution.

Modelling of Zn retention onto sediments was carried out for the different experimental conditions, using the data base obtained previously upon montmorillonite. Assuming that clay minerals are the main ion-exchanging phases, site concentrations can be expressed in function of fractional weight content of the clayey minerals constituting of the sediments. Whatever the physico-chemical conditions tested, we observe a relatively good agreement between experimental and simulated Kd's.

### References

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## Isotopic record of Hadean crust in Western Australia

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Application of the <sup>147</sup>Sm-<sup>143</sup>Nd and <sup>146</sup>Sm-<sup>142</sup>Nd chronometers suggests that mantle depletion and related crust extraction had started during the first hundred million years of Earth history (Caro *et al.*, 2006), but there is limited evidence for the presence of an enriched silicate reservoir before 4.0 Ga (Harrison *et al.*, 2006). Here, we report new <sup>147</sup>Sm-<sup>143</sup>Nd data from low-grade metamorphosed Paleoproterozoic volcanic and sedimentary rocks of the Warrawoona Group, Pilbara Craton, Western Australia. A Sm-Nd isochron age of 3.48 ± 0.09 Ga is in an agreement with the U-Pb zircon age from intercalated volcanoclastic rocks and indicates the preservation of their Sm-Nd isotope signature since the Archean. The initial ε<sub>Nd</sub> value of -3.3 ± 0.5 is out of the range (+1 < ε<sub>Nd</sub> < +3) established for the Archean cratons based on whole-rock Sm-Nd isochrons with ages agreeing with independent chronological constraints. This data is best explained by the assimilation of older continental crust, as shown by significant Ta-Nb depletion associated with LILE, Th, U and LREE enrichment (Green *et al.*, 2000). Geochemical modeling suggests the assimilation of 10% to 20% of crustal material that may be either Archean granites, shales, or average upper continental crust (Condie, 1993). Assimilation of this crustal material with ε<sub>Nd</sub> values of -6 (granite), -8 (shales) and/or -10 (upper CC) by a mantle-derived melt accounts for the observed Nd isotope composition of basalts. This crustal component, with <sup>147</sup>Sm/<sup>144</sup>Nd ratios of 0.09–0.12, would have been isolated from the depleted mantle at 4.0–4.4 Ga, which is consistent with the Nd model ages derived from the studied rocks. Our observations, albeit indirect, clearly show the existence of an Hadean crustal reservoir. Its presence is confirmed by negative ε<sub>Nd</sub> of Archean seawater, inferred from carbonate rocks with seawater-like REE patterns. The presence of a crustal basement involved in plume magmatism indicates eruption of flood basalts onto a submerged continental platform, analogous with the Phanerozoic Kerguelen plateau (Van Kranendonk and Pirajno, 2004). This could have been an important mode of crustal production in the Archean.

### References

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