

Continuum model for diffusive transport in the electrical double layer and clay interlamellæ

J.M. GALINDEZ^{1*}, C.I. STEEFEL¹ AND U. MAEDER²

¹Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720, USA

(*correspondence: JMGalindez@lbl.gov)

²Universität Bern, Switzerland (urs.maeder@geo.unibe.ch)

A continuum model for diffusive transport in the electrical double layer and the interlamellar space in clays is presented. The model makes use of a Donnan equilibrium assumption to calculate explicitly the composition of the diffuse double layer given an arbitrary bulk solution composition. In this approach, rather than solving the Poisson-Boltzmann equation explicitly, an average electrostatic potential corresponding to the double layer is computed. In the model, the double layer balances the charge of the mineral surface, which may be fixed charge (as in the case of ion exchange) or dynamically computed charge using a surface complexation model. In the case of clay interlamellæ, the charge of the clay is fixed and the ions occupying the space are treated as part of a double layer that may or may not be overlapping. Diffusive transport is handled with the Nernst-Planck equation, with accounting for the local immobile charge of the mineral surface. The approach allows for modeling of anion exclusion in clay-rich materials, as well as ion exchange within clay interlamellæ and edges.

Based on the same theoretical foundations as the single-type porosity model developed by Birgersson and Karnland [1], this continuum model provides identical predictions as long as the entire pore space is assumed to be occupied by the electrical double diffuse layer as, e.g., in highly compacted clays. These predictions were in turn validated by comparison with diffusion experiments conducted by Van Loon *et al.* [2]. The present work also explores the limitations of a discrete two-type porosity model in reproducing the actual continuous distribution of ion concentrations over the pore space as obtained with analytical expressions for very simple cases involving a pore space confined between two parallel electrically charged walls and saturated with a binary salt.

[1] Birgersson & Karnland (2009) *Geochim. Cosmochim. Acta* **73**, 1908-1923. [2] Van Loon, Glaus & Müller (2007) *Appl. Geochem.* **22**, 2356-2552.

Geochemistry of nickel isotopes in ferromanganese crusts

L.GALL^{1*}, H.M. WILLIAMS², C. SIEBERT¹ AND A.N. HALLIDAY¹

¹Department of Earth Sciences, University of Oxford, Oxford, OX1 3AN, UK

(*correspondence: louiseg@earth.ox.ac.uk)

²Department of Earth Sciences, University of Durham, Durham, DH1 3LE, UK

The stable isotope behavior of nickel (Ni) has not been studied as intensively as those of other transition metals (e.g. Fe and Mo), even though Ni is ubiquitous in many geological environments and a bioessential trace metal, for example in the production of methane by methanogens [1]. In this study we have measured the mass-dependent isotope composition of Ni ($\delta^{60/58}\text{Ni}$, relative to Ni SRM 986) in a variety of terrestrial samples by MC-ICPMS [2].

Our results demonstrate that there are significant variations in $\delta^{60/58}\text{Ni}$ in nature (-0.5 – 2.5‰). The Ni isotopic composition of 8 samples of igneous and mantle rocks is effectively homogeneous, with only small variations (<0.2‰) between different rock types. In contrast we find that ferromanganese crusts are much heavier. We analysed surface scrapings from 20 hydrogenetic crusts, including samples from all major ocean basins. The average $\delta^{60/58}\text{Ni}$ value for these crusts is +1.65‰ with a variation of $\pm 0.4\%$.

There is no systematic variation with geographical position, water depth, or Ni concentration. However, given the residence time of Ni in the oceans (10,000 yr [3]), Ni isotope variations in ferromanganese crusts might reflect extreme local effects, such as differences in isotopic composition of source materials, input from hydrothermal vents, and fractionation during removal of Ni from seawater and adsorption. Further studies are needed to identify the specific processes. However, our data clearly demonstrate mass dependent fractionation of Ni isotopes in the marine environment.

[1] Cameron *et al.* (2009) *PNAS* **106**, 10944-10948. [2] Gall, Williams, Siebert, and Halliday (2011, *in prep*). [3] Sclater *et al.* (1976) *Earth Planet. Sci. Lett.* **31**, 119-128.