# Ion exchange model for reversible sorption of divalent metals on calcite

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### Problematic and objectives

Previous studies dealing with electrokinetic properties of the calcite/water interface have shown that $Ca^{2+}$ and $CO_3^{2-}$ are the main species determining the potential of the calcite surface [1 among others]. This is particular true when systems are in equilibrium with both calcite and a fixed $p_{CO2(g)}$ value, a common case of environment conditions. However, most of the thermodynamic models proposed in literature describing the surface speciation of calcite do not predict a significant contribution of sorbed Ca(II) [2 among others]. Therefore, the aims of this study are (1) to propose a model, based onto the ion exchange theory, able to describe the reversible sorption of Ca(II) at the calcite surface and (2) to apply this model to some divalent metals (*e.g.*, Zn(II), Cd(II) and Pb(II)). Note that aqueous metallic cations presented in natural waters are always in competition with $Ca^{2+}$ and $H^+$ for sorption sites located on mineral surfaces. Therefore, these two latter species should be systematically included in all models predicting sorption of divalent metals on calcite.

### Methodology and main results

Concentrations of Ca(II) sorbed reversibly on the calcite are obtained using a previous methodology based on isotopic measurements [3]. Data are obtained at different pH using solutions saturated with both calcite and a fixed $p_{CO2(g)}$ value (from $10^{-5}$ to $10^{-2}$ atm.). Concentration of sorbed Ca(II) is significant as suggesting by previous electrokinetic data and is practically constant in the [7 - 9.5] pH range to a value close to $1.2\pm0.4\ 10^{-3}$ eq.kg$^{-1}$. Such value is in agreement with total sorption site density calculated by crystallographic considerations. Experiment data are fitted to obtain a selectivity coefficient between $Ca^{2+}$ and $H^+$. Using previous published experimental data [4 among others] fitted metal-protons selectivity coefficients are also proposed for reversible sorption of Zn(II), Cd(II) and Pb(II) on calcite. Finally, the model was used to calculate the contribution of calcite to the sorption of Cd(II) on a natural and complex solid (*e.g.*, calcareous aquifer sand).

[1] Cicerone *et al.* (1992) *J. Colloid Interf. Sci.* **154**, 423-433.
[2] Van Cappellen *et al.* (1993) *Geochim. Cosmochim. Acta* **57**, 3505-3518.
[3] Tertre *et al.* (2010) *J. Colloid Interf. Sci.* **347,** 120-126.
[4] Zachara *et al.* (1991) *Geochim. Cosmochim. Acta* **55**, 1549-1562.

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# Plio-Pleistocene evolution of water mass exchange and erosinal input in the Nordic Seas

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The Arctic Ocean and Norwegian-Greenland Seas (NGS) are presently one of the most important areas for deep water formation in the Northern Atlantic Ocean. Therefore, it is particularly essential to better understand Plio-Pleistocene variations of the circulation in these areas. Significant climatic and oceanographic changes occurred during this period of time including the major intensification of the Northern Hemisphere Glaciation (starting at 2.82 Ma) and the Mid-Pleistocene Transition (1.5 – 0.5 Ma).

To reconstruct erosional input and water mass exchange between the NGS and the Arctic ocean we use the composition of the radiogenic isotopes neodymium (Nd), lead (Pb) and strontium (Sr). For this purpose, we leached the authigenic metal oxide phase on sediments particles [1] of different ODP Sites in the Norwegian-Greenland Seas (Site 911, 986, and 644) and in the North Atlantic Ocean (Site 982).

The first analyses were performed on sediment samples from northernmost ODP site 911 (Leg 151, in 900 m water depth) located on the southeastern slope of the Yermak Plateau in the Fram Strait. Today this location is strongly influenced by the inflow of Atlantic water from the NGS, which is supported by the core top εNd value agreeing well with Atlantic values [2]. Based on these results, downcore samples covering the past 5 million years were analysed.

The record of the Yermak Plateau shows no significant general trend with time, but a very high variability with more radiogenic Nd isotope data during glacial periods at 0.72 Ma, 1.36 Ma, 2.4 Ma, and 2.69 Ma. These shifts indicate major inflow of waters influenced by highly radiogenic source areas, either by the Icelandic basalts in the south or by the Siberian Putorana flood basalts in the hinterland of the Kara/Laptev Sea region. The εNd data suggest that mixing of water masses from the Arctic Ocean and the NGS have controlled the Nd isotope signatures of deep waters on the Yermak Plateau since the onset of the Northern Hemisphere Glaciation (NHG). In contrast, the Pb istotope data of deep waters in the Fram Strait appear to have been dominated by glacial weathering inputs from old continental landmasses, such as Greenland or parts of Svalbard since 2 Ma.

In order to better understand past water mass exchange between the Norwegian-Greenland Seas and the North Atlantic Ocean we will compare these data with isotopic records of ODP Sites 986, 644 (NGS), and 982 (North Atlantic Ocean).

[1] Gutjahr et al. (2007) *Chemical Geology* **242**, 351-370 [2] Lacan, F. and C. Jeandel (2004) *Geochem. Geophy. Geosyst.*, **5**, Q11006