

Calcium isotope systematics of low temperature alteration carbonates in the ocean crust

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During low temperature alteration (LTA) of the ocean crust CaCO₃ precipitation in veins and vesicles causes a calcium flux from seawater into the basaltic crust that represents about 10% of the total calcium output flux from the oceans [1]. Thus, LTA carbonates may represent a significant factor in the global ocean calcium isotope budget.

We analyzed Sr/Ca, Mg/Ca, δ¹⁸O, δ¹³C, ⁸⁷Sr/⁸⁶Sr, and δ^{44/40}Ca of CaCO₃ from basement samples of DSDP and ODP drill cores from the Atlantic and Pacific Oceans. Most ⁸⁷Sr/⁸⁶Sr ratios point to seawater as the major source for Sr. This interpretation is corroborated by the generally low δ¹⁸O temperatures, close to bottom water values, and by normal marine δ¹³C values.

Calcium isotope values show large variations with δ^{44/40}Ca ranging from -0.7 ‰ to 1.8 ‰ (NIST SRM 915a). In good agreement with previous studies [2,3] δ^{44/40}Ca differs between aragonite (-0.2 to +0.3 ‰) and calcite (+0.9 to +1.8 ‰). A negative correlation of δ^{44/40}Ca and Sr/Ca ratios can be explained by precipitation rates varying between <10⁻² to 10² μmol/m²/h [4]. The calcites with the highest δ^{44/40}Ca and lowest Sr/Ca values probably formed close to isotopic equilibrium [5]. The δ^{44/40}Ca of LTA calcites is very high compared to biogenic carbonates: 1.6 ‰ for Cenozoic LTA calcite compared to 0.6 ‰ for average modern biogenic carbonates [5]. Therefore LTA carbonates represent a sink for heavy Ca isotopes, both with respect to the land-ocean calcium cycle and to the crust-mantle Ca exchange.

[1] Alt & Teagle (1999) *Geochim. Cosmochim. Acta* **63**, 1527-1535. [2] Amini *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 4107-4122. [3] Gussone *et al.* (2005) *Geochim. Cosmochim. Acta* **69**, 4485-4494. [4] Tang *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 3733-3745. [5] Fantle & DePaolo (2007) *Geochim. Cosmochim. Acta* **71**, 2524-2546.

Electrolyte adsorption at the hematite/water interface: A cryogenic XPS study

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Electrolyte ions play a commanding role on the structure and reactivity of the mineral/water interface, yet their adsorption reactions are poorly tractable. X-ray Photoelectron Spectroscopy (XPS) on frozen (-170°C) centrifuged/filtered wet mineral pastes can however be used to circumvent these shortcomings as the hydration environments of electrolytes and mineral surfaces can be preserved under those conditions.

In this study we report Cl⁻ and Na⁺ adsorption edges on colloidal hematite spheroids. We show that Cl (Cl 2p, Cl 2s) and Na (Na 1s, Na KLL) lines are highly sensitive to adsorbed electrolyte ions but also to residual supernatant in the wet paste. The contributions of the latter are greatest at the isoelectric point but negligible under conditions of high surface charge and can be explained in terms of differences in electric field strengths at the mineral/water interface. Effective strategies aimed at removing these contributions are presented. We also demonstrate a relationship between surface charge arising from H⁺/OH⁻ adsorption and surface-bound electrolyte ions that can further be used in the calibration of thermodynamic adsorption models.