

Calcium isotope fractionation during dolomite formation

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Dolomite is an important component of the global calcium cycle, being a source of Ca to the oceans [1]. Calcium released to the oceans by dolomitization of chalk and limestones can potentially be quantified using marine Ca isotope records [2]. However, little is known about Ca isotope fractionation and the Ca isotopic composition of dolomitic rocks. Theoretical calculations point to a -2 ‰ depletion in $\delta^{44/40}\text{Ca}$ of dolomite relative to calcite at 25°C [3]. Ordovician dolostones interbedded with limestones were reported to be depleted in $\delta^{44/40}\text{Ca}$ by -0.6 ‰ relative to the limestones [4].

We have investigated dolomites from an ODP core (Site 183-1140) drilled at the Northern Kerguelen Plateau (46.3°S 68.5°E, 2394 mbsl). The core penetrated 235 m of nannofossil ooze and chalk of early Oligocene to middle Miocene age, and 88 m of pillow basalts forming the basement for the sediments. The basalts erupted at about 34 Ma (latest Eocene) [5]. An interbedded chalk layer was found in the basalt, about 40 m below the top of the basement. The chalk was partly dolomitized at the contact with the basalt.

We measured oxygen, carbon, calcium and radiogenic strontium isotopes of bulk chalk and dolomite samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicate an age of dolomitization of about 10 Ma (late Miocene). Dolomitization obviously occurred about 20 Ma after eruption of the basalts, in a deep burial setting. Oxygen isotope values of chalk and dolomite demonstrate that dolomitization occurred at slightly elevated temperatures (10-20°C). The calcium isotopes of the dolomite are enriched in $\delta^{44/40}\text{Ca}$ by about +0.5 ‰ compared to the chalk. This is in contrast to the depletion of $\delta^{44/40}\text{Ca}$ in dolomite reported in the literature. On the other hand, dolomite veins in ocean crust basalts (DSDP/ODP Sites 37-332 and 129-801) are depleted in $\delta^{44/40}\text{Ca}$ compared to calcite veins of similar age. Fluid composition, diagenetic history and kinetic isotope fractionation have to be considered when interpreting Ca isotope values of dolomite.

[1] Berner, (2004) *Amer. J. Sci.*, **304**, 438-453. [2] Heuser *et al.*, (2005), *Paleoceanography*, **20**, doi:10.1029/2004PA001048. [3] Rustad *et al.*, (2010), *GCA*, **74**, 6301-6323. [4] Holmden, (2009), *Chem. Geol.*, **268**, 180-188. [5] Frey *et al.*, (2003) *Proc. ODP Sci. Res.*, **183**

Hydroxyl group reactivity at FeOOH/gas and FeOOH/water interfaces

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Reactions involving mineral surfaces and their surrounding environments play important roles in atmospheric and geochemical processes. Knowledge of the types, distributions and orientations of reaction centers on minerals with different surface structures is notably essential for molecular-scale resolution of mineral/gas and mineral/water interactions.

This work is focused on properties of hydroxyl functional groups of important crystal planes of FeOOH minerals exposed to vacuum, gaseous as well as liquid water. Molecular dynamics simulations were carried out to identify hydrogen bonding patterns and calculate their properties in these different systems. These efforts formed the basis of an interpretative framework to our Fourier transform infrared measurements of α -, β -, and γ -FeOOH particles (Fig. 1). These measurements, which were limited to gaseous systems, were used to extract spectroscopic signatures for distinct isolate and hydrogen-bonded hydroxyl groups.

Our combined computational and experimental efforts are helping categorize different crystallographic terminations of FeOOH minerals on the basis of their site distributions, hydrogen bonding patterns and reactivity towards water.

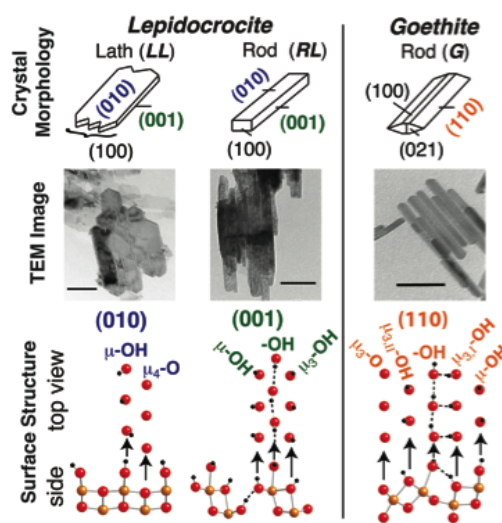


Figure 1: Morphology, TEM imaging (scale bar = 50 nm) and surface structures in three types of particle used for this work.