Temperature-dependent oxygen isotope fractionation factor for dolomite: Constraints based on bacterial culture experiments

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The origin of dolomite has long been an area of controversy, as it has proven extremely difficult to precipitate it in the laboratory under Earth's surface conditions. As a result, the experimental temperature-dependent dolomite-water oxygen isotope fractionation factor has remained undefined. Different approaches were taken, however, to establish the relationship among $\delta^{18}O_{dolomite}$, $\delta^{18}O_{water}$ and precipitation temperature. For example, extrapolations from high temperature experiments or indirect measurements from Holocene examples of co-existing calcite and dolomite, without any control on the time of precipitation, were used. These extrapolations and assumptions led to inconsistent results and the stable isotope geochemistry of dolomite continued to be one of the most enigmatic and complex in sedimentary geochemistry.

A new line of research indicates that dolomite precipitates in the laboratory at low temperatures mediated by microbial metabolism under anoxic conditions (Vasconcelos et al., 1995; Warthmann et al., 2000). The results of our microbial experiments, using specific strains of sulfate-reducing bacteria, show that, at 25 and 30 °C, a mixture of high Mg-calcite and Ca-dolomite formed, whereas, at 40 and 45 °C, pure stoichiometric dolomite was obtained. Using a dolomite-phosphoric acid fractionation factor of 1.0093 for the reaction temperature of 90 °C (Rosenbaum and Sheppard, 1986), the dolomite-water fractionation is described by the equation: $1000\ln\alpha = 2.734 * 10^6 T^{-2} + 0.26$. This equation indicates that, at equilibrium, the oxygen isotope composition of dolomite would be approximately 2.2 ‰ more positive than that of the co-existing calcite. Based on this equation, we are now able to better evaluate the environmental or diagenetic conditions under which ancient dolomites precipitated. Further, we propose to reinterpret previously reported isotope fractionation data, which were used to assess the mechanism(s) of dolomite formation.

References

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Fluoride Sorption and Associated Al Release in Iron Oxide Rich Soils

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Introduction. Anion-soil interactions play an important role in determining soil weathering, nutrient availability, and contaminant fate and transport. Sorption of anions, particularly fluoride (F^-), is often a precursor to Al dissolution: the electronegative F^- replaces –OH/H_2O groups bound to surficial Al atoms (ligand exchange), loosens other Al-OH bonds and facilitates the dissolution of Al from the surface [1-2]. Our understanding of anion interactions in soils of temperate regions is relatively well advanced. In comparison, our knowledge of anion behaviour in variable charged soils, such as the prominent iron oxide rich soil orders (Ultisols and Oxisols), is limited.

Goals. This study is aimed at understanding F^- sorption and related Al release in Ultisols as a function of soil depth, composition and physical-chemical properties and evaluating potential mechanisms of fluoride-surface interactions. This study also addresses a related question: Is the extent of fluoride-facilitated Al release a useful measure of soil susceptibility to ligand (anion) promoted dissolution?

Methods. A total of ten samples representing A, B and BC horizons of a Georgeville soil and A, E, and B horizons of an Appling soil were obtained from freshly dug pits in Durham County, NC, USA. Following extensive characterization of the soils, fluoride sorption was measured in batch experiments over a wide aqueous F^- concentration range (0-15 mM) at soil pH and at an initial pH of 3.5. The Langmuir equation was used to derive the maximum extent of fluoride sorption (F_{max}) under each pH condition. Al and OH- release was monitored in experiments conducted at soil pH.

Findings. We find that fluoride sorption is strongly correlated with soil Fe and Al oxide content, anion and cation exchange capacities, and maximum phosphate sorption capacity. Although fluoride complexation to surficial Fe and Al ions is the dominant sorption mechanism, we find indirect evidence that implies fluoride precipitation in patches. For the Appling series, we find that Al release to soil solution is proportional to the extent of fluoride sorption and soil Al and Fe content. However, the Georgeville series exhibit low Al release despite possessing a high capacity for fluoride sorption and a high Al content. In this case, it is likely that the soil mineralogy protects against Al dissolution and/or fluoride sorption to surficial Fe is preferred over sorption to surficial Al ions. Measures of fluoride facilitated Al release may be a useful surrogate for soil susceptibility to ligand promoted dissolution.

References.

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