Origin of siderite in anoxic and ferruginous lake Pavin: clues from C and O isotope compositions

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The chemical and isotopic compositions of carbonates are widely used as a proxy of ancient seawater and paleo-environmental conditions. Siderite (Fe-carbonate, $FeCO_3$) in Archean and Paleoproterozoic sedimentary rocks has been proposed as a mineralogical evidence that, at that time, the oceans were anoxic, enriched in dissolved Fe(II), and in equilibrium with a CO_2-rich atmosphere. The possibility of a CO_2-rich atmosphere has been strongly debated since recent studies based on chemical and isotopic analyses of ancient sedimentary rocks suggest that siderite reflects diagenetic microbial reactions, and thus local conditions, rather than the global ocean equilibrated with the atmosphere.

Lake Pavin is a unique stratified aquatic system characterized by permanent anoxic and ferruginous deep water, topped by oxic shallow water, and can thus be regarded as a modern analog for Archean and Paleoproterozoic oceans. In the present work, we determined C and O isotope compositions of siderite contained in lake Pavin sediments in order to provide constraints on siderite formation mechanism. $\delta^{13}C$ and $\delta^{18}O$ values expressed relative to PDB range from -0.78 to +11.96‰, and -13,06 to -4,53‰, respectively. Sediment siderite content (up to 18wt%), and $\delta^{13}C$ and $\delta^{18}O$ values are positively correlated. The comparison of these data with $\delta^{13}C$ of dissolved inorganic carbon and $\delta^{18}O_{H2O}$ of the water column analyzed in a previous study (Assayag *et al*., 2008), demonstrates that siderite was formed in the sediment during diagenetic reactions and does not record water column composition. The range of $\delta^{13}C$ values observed in lake Pavin siderite is interpreted as reflecting a mixing between dissimilatory iron reduction and methanogenesis imprint, both representing organic matter degradation processes. The positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values indicates that O isotope signature is also impacted by microbial processes, and that siderite is not equilibrated with local porewater.

Assayag *et al*. (2008) Applied Geochemistry 23, 2800-2816.