Microbial mediation of Fe-Mg-Ca carbonates in acidic environments (Rio Tinto): Field studies vs culture experiments

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The influence of microorganisms on mineral precipitation has huge implications for understanding, not only modern carbonate deposits, but also thick carbonate platforms and other sedimentary deposits throughout the geologic record. Carbonate production is thermodynamically inhibited under low-pH conditions. More specifically, in most terrestrial environments, either abiotic or biotic pathways favor the production of carbonates below a pH of ~4.5. However, very recently and for the first time carbonate minerals such as dolomite, ankerite and siderite have been recognized associated to extremely acidic environments of Rio Tinto, Spain [1]. The mentioned carbonates have been found in the subsurface of Rio Tinto suggesting mildly acidic to neutral pH (~ 5-7) and somewhat reducing (Eh < 0) conditions [2]. The acid-sulfate system in Rio Tinto [2] is considered as a process analog from which we can draw lessons for understanding the global evolution of aqueous systems on Mars and Archean oceans.

In order to study the formation for Fe-Mg-Ca carbonates in the acidic environment of Rio Tinto: (1) X-ray diffraction and SEM-EDX analyses of the sediment have been conduted and (2) A set of microareobiosis culture experiments using *Acidiphilium sp.*, a facultative anaerobe bacterium isolated from Rio Tinto, have been performed. This culture experiments have been conducted at different concentration of Fe³⁺, Mg²⁺ and Ca²⁺, pH (3-6) and organic matter (yeast extract) at room temperature.

[1] Fernández-Remolar *et al.* (2008) *Astrobiology* 8, 1023.
[2] Fernández-Remolar *et al.* (2009) *LPSC* 1214.

In situ studies of PVTx properties of aqueous fluids using Brillouin scattering spectroscopy

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Saline-rich aqueous fluids play an important role in metamorphic reaction and chemical transport in a wide range of geological environments. The most important of them are are subduction zones, where fluids expelled from downgoing slabs trigger partial melting in the mantle wedge, and mediate the recycling of elements in the Earth. Despite the the role of high pressure fluids in these processes a number of significant but unaswered questions arise as to their chemical composition, the extent of mass transfer, or the mechanism of element transport from the slab to the mantle wedge. Answer to this questions depends on quantitative thermodynamic modeling of fluid-mineral interactions, that is greatly limited by the lack of thermodynamic data for complex aqueous solutions at high pressure and temperature conditions.

In this contribution, we review recent studies conducted to determine in situ the PVTx properties of aqueous fluids from acoustic velocity measurments in the diamond-anvil cell using Brillouin scattering spectroscopy. Recent results include acoustic velocity and density measurements in H_2O/D_2O fluids and model aqueous systems for subduction zones such as H₂O-NaCl solutions (1-3 m NaCl) and carbonate-bearing fluids up to 400 °C and 5 GPa. Calculated densities for H₂O are in excellent aggrement with predictions from published EoS, showing the reliability of the method. Acoustic velocities determined at low pressure at various temperatures in NaCl-H₂ and carbonate-bearing fluids are also in excellent aggrement with literature data. The PVT data has been parametrized using Modified Redling-Kwong (MRK) -type equations of state (EoS) to facilite their application in geochemcal and petrological calculations. The EoS are used to derive the volumetric (specific and excess volume) and chemical propeties (fugacity, chemical potential) for NaCl-H2O and carbonate-bearing fluids. The results help to builp up an internally consistent dataset for the themodynamical properties of model aqueous systems in subduction zone environments.