Experimental approch of carbonate isotopes fractionation related to kinetic effect during travertine growth

L. FLEURENT[1,2*], E. GIBERT-BRUNET[1]
AND F. BARBECOT[2]

[1]UMR 8148-IDES, CNRS-UPS, Université Paris Sud-XI, Orsay, France (*leonora.fleurent@u-psud.fr)
[2]GEOTOP, département des sciences et de l'atmosphère, Université du Québec à Montréal, Montréal, Canada

Travertine are supposed to archive environmental conditions with high temporal resolution up to seasonal, monthly or even daily when finely laminated. It's important to understand the mechanisms of precipitation and the behaviour of isotope and major/trace elements to make environmental reconstruction.

Rate of degassing of CO_2 in rich spring is considered to influence the rate of calcite precipitation and the stable isotope $\delta^{18}O$ and $\delta^{13}C$. Then the isotopic equilibrium is rarely maintained during the deposition of travertine suggesting that the rate of CO_2 degassing may be the main controlling factor of the disequilibrium (1). Combined stable isotope (^{18}O and ^{13}C) measurement on water and on freshly precipitate travertine from rich CO_2 spring under laboratory condition have been developped in order to constrain the non-equilibrium fractionation domain.

In a 80-cm sequence cored in 2008 at the Ours gaseous spring (Massif Central, France), we have observed a disequilibrium between the calculated temperature and corresponding isotopic contents recorded in the laminated travertines, with a apparent shift of 8°C compared to the measured temperature. The main question was thus to understand the precipitation processes that either reflect or not geochemical equilibrium.

In order to understand the processes occuring between rich-CO_2 water, gaz and related travertines such as kinetic of degassing and the geochemical pathways recorded in the carbonates, laboratory tests were conducted. These experimentations allow us to identify the effect on degassing on the behaviour of isotope (fractionation factor) and chemical (partionning) records when precipitation occurs. The isotopic signatures obtained on this core (2) can be thus reinterpreted with a very new geochemical insight of fractionation and interaction processes.

[1] Gonfiantini et al (1968) Earth and Planetary Science Letters pp:55-58. [2] Barbecot et al (2011) Poster Goldschmidt Congress

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Borosilicate glass dissolution driven by magnesium silicate precipitation

B. FLEURY[1*], N. GODON[1], A. AYRAL[2] AND S. GIN[1]

[1]CEA MAR/DEN/DTCD/SECM/LCLT, BP17171, 30207, Bagnols-sur-cèze, France
*correspondence : benjamin.fleury@cea.fr, nicole.godon@cea.fr, stephane.gin@cea.fr)
[2] IEM, Université Montpellier 2, CC 047, Place Eugène Bataillon, 34095, Montpellier Cedex 5, France (andre.ayral@iemm.univ-montp2.fr)

This study deals with the effect of Mg-silicate precipitation on borosilicate glass dissolution mechanisms and dissolution rate. It has been shown that this precipitation is related to the consumption of elements like silicon from the altered glass layers [1]. Investigations are here performed for better understanding of the kinetically limiting mechanisms.

Leaching experiments of SON68 glass, a Mg-free borosilicate glass, were carried out in initial deionized water at 50°C with a glass-surface-area-to-solution-volume ratio of 200 cm^{-1}. After 29 days of alteration magnesium was added in order to trigger the precipitation of Mg-silicate. Additional experiments were also conducted to investigate the importance of other parameters like pH or dissolved silica on the precipitation mechanisms and their consequences on the glass dissolution rate.

Mg-silicate precipitates immediately after magnesium addition. The total amount of altered glass increases with the added amount of magnesium. It is lower when silicon is added to the solution. Increase of pH above 8 strongly accelerates Mg-silicate precipitation. A time lag is observed between magnesium addition and glass alteration resumption because silicon is first provided from partial dissolution of the previously formed alteration gel. It is finally shown that nucleation process does not limit Mg-silicate precipitation.

[1] Frugier *et al* (2008) *J. Nucl. Mater.* **380**, 8-21.

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