Coralline algae as pH-recorders on seasonal to centennial timescales

J. FIETZKE[1*], F. RAGAZZOLA[1,2], J. HALFAR[3], H. DIETZE[1], L.F. FOSTER[2], T.H. HANSTEEN[1], A. EISENHAUER[1]

[1]GEOMAR, Helmholtz Centre for Ocean ResearchKiel, Germany, * jfietzke@geomar.de
[2]Bristol University, Bristol, UK
[3]University of Toronto, Toronto, Canada

Both ocean warming and acidification caused by the antropogenic emission of carbon dioxide (CO_2)are the major challenges to marine ecosystems. In particular marine calcifiers are expecteded to be affected in their ability to produce skeletal hard parts when facing an environment with continuously decreasing calcium carbonate ($CaCO_3$) saturation state.

To evaluate the performance and possible strategies of acclimatisation/adaptation of marine calcifying organisms the reconstruction of ambient seawater pH is essential. This reconstruction is in particular important for the last decades and centuries as it allows for a comparsion of natural and antropogenic pH variability.

Boron stable isotopes ($\delta^{11}B$) revealed from carbonates have been used as a proxy for seawater pH for many years. Using a recently published LA-MC-ICP-MS method [1] we analysed the spatial distribution of boron isotopes in a specimen of *Clathomorphum nereostratum* a long-lived crustose coralline alga that exhibits annual growth increments. Crustose coralline algae have recently been introduced as climate (SST) recorders in high-latitude shallow-water habitats.[2] The particular specimen used in this study was collected alieve off the coast of Attu island (Aleutian Islands) in summer 2004.[2] With an annual growth of 400-500µm the 6cm long profile covers more than the entire 20th century.

Here we present the first high-resolution 2D-images of boron isotopes providing a precision and accuracy close to analytical bulk techniques for a spatial resolution of 100µm. The combination of electron microprobe elemental mappings and LA-MC-ICP-MS isotopic images now allows for a detailed reconstruction of two seawater key parameters: SST from Mg/Ca and pH from $\delta^{11}B$, respectively.

Our data show that long-term pH-decrease is recorded in the skeleton of our sample specimen. Between 1900 and the 1990's boron isotopes indicate a drop of ~0.08(1) pH units which is in accord with the value expected from atmospheric CO_2 time-series data.

A seasonal cycle of pH-variability (up to 0.1 pH units) is recorded too with highest values during late spring/early summer. His is most likely a result of the CO_2 consumption during the spring microalgal bloom. The latter is in agreement with instrumental data from a nearby location. During the spring bloom in May a rapid pH increase of up to 0.15 units was measured.[3]

[1] Fietzke et al. (2010) *J. Anal. Atom. Spectrom.* **25**, 1953-1957.
[2] Halfar et al. (2007) *Geophys. Res. Lett.* **34**, L07702.
[3] Codispoti et al. (1986) *Cont. Shelf Res.***5**, 133-160.

High Pressure and High Temperature Effect on the Smectite Saturated with Lanthanum

V. F. STEFANI[1*], R. V. CONCEIÇÃO[1,2], L. C. CARNIEL[2]

[1]PGCIMAT, UFRGS, Porto Alegre – RS, Brasil
Vicente.stefani@ufrgs.br
[2]Instituto de Geociências, UFRGS, Porto Alegre – RS, Brasil.
rommulo.conceicao@ufrgs.br
larissa.colombo@ufrgs.br

Smectites are phyllosilicates with high cation exchange capacity (CEC) in the interlayers. For these and other features, smectites have been used in various parts of the world as secondary barriers for possible leak of liquids that contain radioactive elements in definitive deposits of nuclear waste disposal [1]. In such case, radioactive cation could be captured by smectite through cationic exchanges. However, very little is known about the stability of smectite under high pressures and high temperatures (HPHT). Preliminary studies developed by our group in dioctahedral calcium smectites showed that the smectite structure is stable, remaining dioctahedric after processing up to 7.7 GPa and at room temperature [2]. This work replaced the calcium of the smectite for La^{+3}, an analogous of the actinide nuclear waste elements, with the difference that those elements are harmless [3]. We submitted this smectite doped with La to different range of pressure (2.5GPa and 7.7GPa) and temperature (400°C, 500ºC, 650°C and 700ºC), using a hydraulic presses with toroidal board, and we obtained a new La-rich muscovite-like structure. Moreover analyses of x-ray diffraction with Rietveld refinement, fourier transform infrared (FTIR) and transmission electron microscopy (TEM) were performed. Image of smectite doped with La from TEM shows layers of smectite with heavier elements due to the contrast of the image (Fig. 1) and also the effect of lattice fringe. Further images will be achieved in the coming days**.**

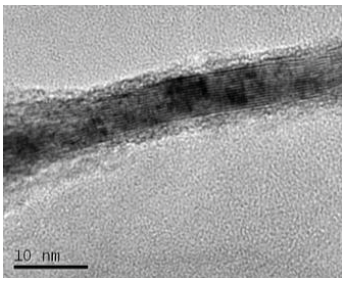

Figure 1: Image of smectite doped with La using TEM

[1] Pusch, R. (1998) *Transport of radionuclides in Smectite Clay*. Environmental Interactions of Clay – Clays and environment. Parker, A., Rae, J.E. Ed. Springer, Berlin.

[2] Alabarse, Frederico Gil. (2009). *Análise da estabilidade estrutural da esmectita sob altas pressões e altas temperaturas.* Master's Thesis – Programa de pós graduação em Ciências dos Materiais. UFRGS. Porto Alegre, Brasil.

[3] Krauskopg, KB (1986) *Thorium and rare-earth metals as analogs for actinide elements.* Chemical Geology, **Vol.** 55, pp. 323-335