Speciation of Mg in biogenic Calcium Carbonates

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Abstract. A selection of marine biominerals, mostly aragonitic coral skeletons were probed at the Mg K-edge by XANES spectroscopy coupled to μXRF methods and compared to an extensive set of relevant model compounds (silicates, carbonates, oxides and organic). Extensive methodologies are required to better describe the speciation of Mg in those minerals. A combination of *ab-initio* XANES calculations for defective clusters around Mg in aragonite together with wavelets analyzes of the XANES region are required to robustly interpret the spectra. When using those methodologies, the speciation of Mg ranges from a magnesite-type environment in some scleractinian corals to an organic-type environment. In all environments, the Mg-domains probed appear to be less than 1 nm in size.

1. Introduction

Mg has a strong impact on the crystal properties of aragonite, calcite and dolomite [1-3] and is used by a wide variety of organisms to actively control skeletal morphology at the micrometer scale. Furthermore, paleo-climatic reconstructions from e.g. coral skeletons are often based on observations that skeletal trace-element abundances (e.g., Sr and Mg) vary in response to changes in water temperature. However, a number of recent micro-analytical studies of e.g. coral skeletons (including reef-building and deep-sea species) have uncovered large amplitude chemical variations in Mg that cannot be ascribed to external environmental variability [2-4]. Magnesium exhibits dramatic variability in the layered fibrous aragonite that are unexplainable by changes in environmental parameters, such as sea-surface temperature and more likely is the result of direct biological control over the biomineralization process. However, very little is known about the speciation of Mg in marine biocarbonates in general. It has been proposed that Mg is known to play a key role in the formation of a transiently stable carbonate precursor phase, often referred to as amorphous calcium carbonate (ACC) [4]. In order to provide data that might help answer some of these questions, we present a μXRF-μXANES study of Mg in various bio-aragonites thanks to the recent availability of the LUCIA beamline [5].
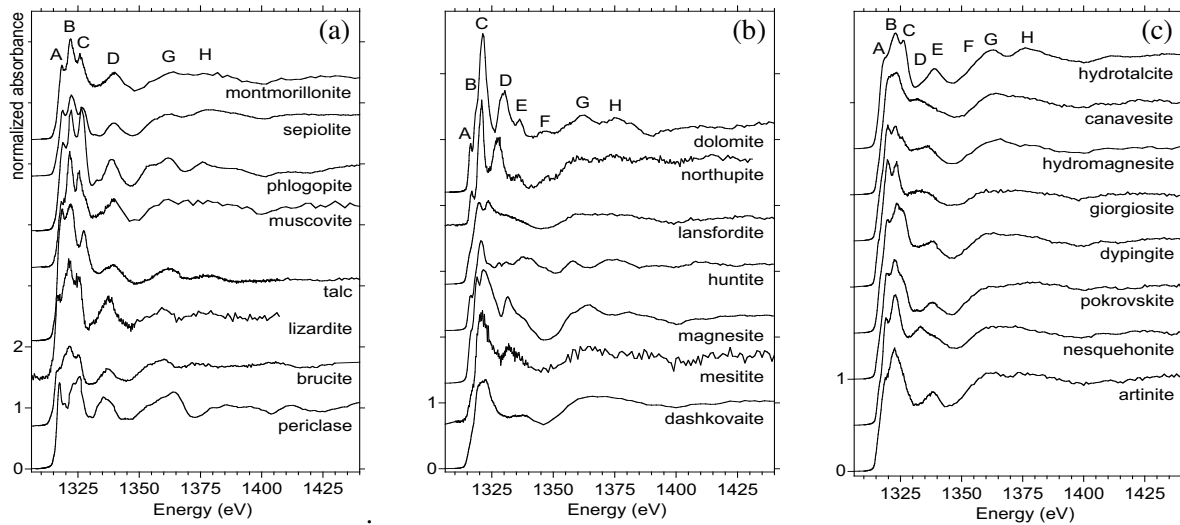
Figure 1 — Mg K-edge bulk XANES spectra for relevant model compounds of Mg: (left, a) silicates and oxides, (center, b) simple carbonates and organic and (right, c) complex carbonates.

2. Experimental

μXRF and μXANES spectra were collected in 2007 at the Mg K-edge using the LUCIA beamline (SOLEIL) [5] hosted at the SLS (Switzerland), operating at 2.4 GeV and 400 mA currents. Harmonics were rejected using Ti-coated mirrors. Flux on the sample is 2×10^{12} ph/s at 400 mA injected currents and 2 keV. We used a beryl (10-10) double crystal monochromator and K-B mirrors. Energic and lateral resolution are ca. 0.5 eV and 10 μm, respectively. Samples were polished and set into a vacuum chamber while the K-α fluorescence of Mg was collected using a Si-drift SDD detector.
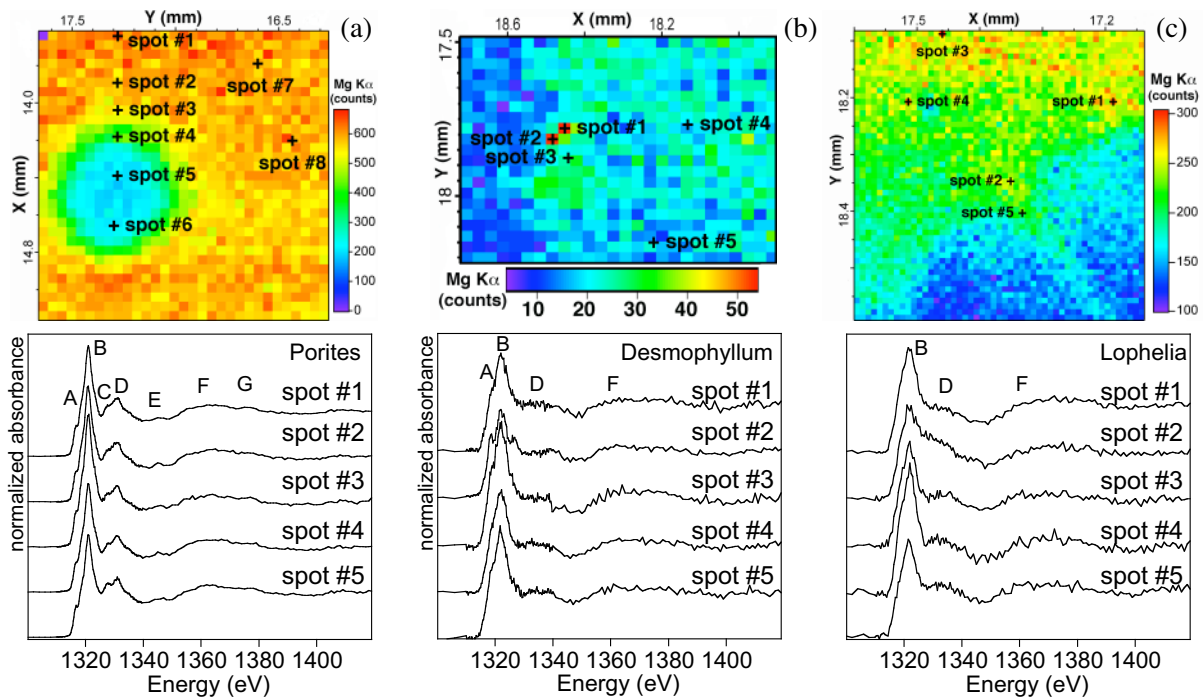

Figure 2 — Mg Kα XRF map (top) and Mg K-edge XANES spectra (bottom) for the spot probed on the Mg-map for *Porites (*left*), Desmophyllum (*center*) and Lophelia (*right*).

Energetic and lateral resolution are ca. 0.5 eV and 10 μm, respectively. Samples were polished and set into a vacuum chamber while the K-α fluorescence of Mg was collected using a Si-drift detector. μXRF maps were collected (1 sec/pixel) while μXANES spectra were collected every 0.2 eV (2 s/point). Model compounds include carbonates, silicates, oxides and a formate (dashkovaite, from the type locality in Russia), among many others (see Figures 1-3). Mg K-edge spectra were normalized following standard procedures using the XAFS3 package [6].

3. Results

Figure 1 shows Mg K-edge bulk XANES spectra collected for a selection of model compounds. Much other Mg-carbonates were run, including biogenic compounds such as landsfordite (from an Arizona saguaro cactus). Figures 2 and 3 show mapping and spectroscopic information for a selection of 4 scleractinian corals, a gorgonian coral and a bivalve shell. Due to their low Mg contents (usually around a few thousand ppm) and the presence of an intense Na Kα fluorescence, the XANES were averaged (2-10 scans). However, in some cases, the XANES remained rather noisy. We then decided to collect spectra for 3-10 spots for each sample to observe the homogeneity of speciation.
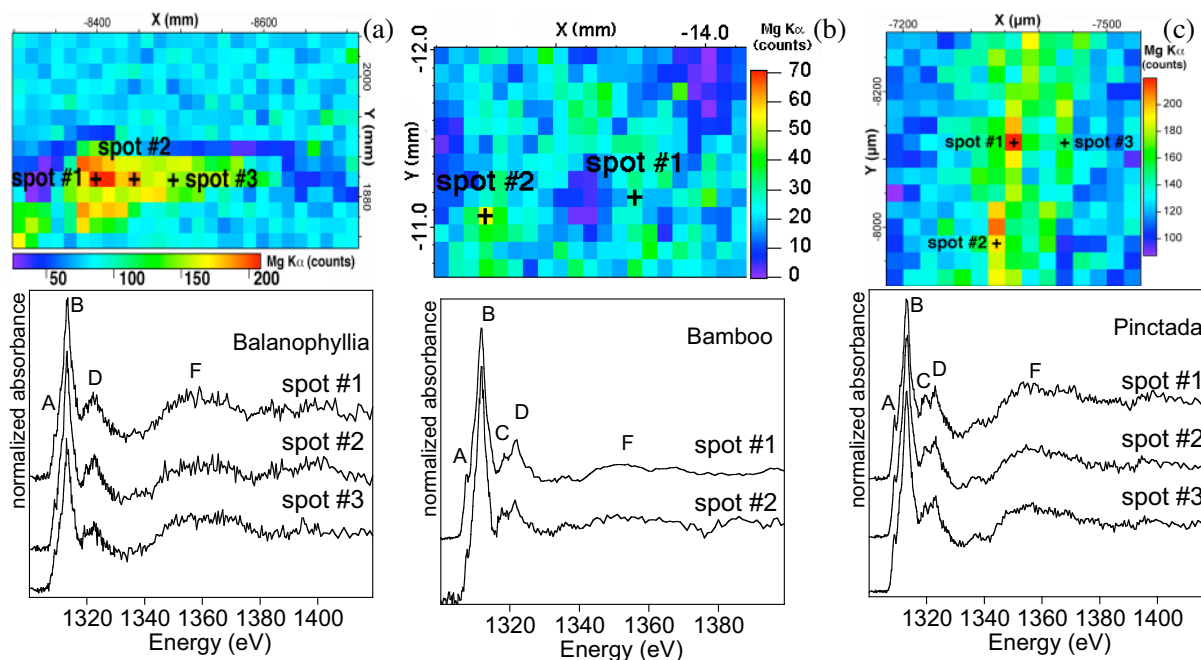

Figure 3 — Mg Kα μXRF and Mg K-edge μXANES spectra for (a) the Balanophyllia coral (scleractinian), (b) Bamboo coral (gorgonian) and (c) Pinctada margaritifera (bivalve shell).

4. Discussion

Large variation in distribution and speciation are observed among the samples studied. *Desmophyllum*, *Lophelia* and *Balanophyllia*. scleractinian corals show less featured XANES spectra whereas scleractinian *Porites* and gorgonian Bamboo (*Keratoisis profunda*) corals are more structured, as is the shell bivalve *Pinctada margaritifera*. For each sample studied, the speciation of Mg is relatively homogeneous. Exceptions are spot #3 for *Desmophyllum and Lophelia*, which show more features (A and D), as in brucite. Other XANES spectra are lesser structured and were interpreted to indicate that Mg is bond to organic matter [7] but it can also be that of Mg in poorly crystallized inorganic environments (amorphous, colloidal etc).

Then, a*b-initio* XANES calculations [8] were computed with FEFF8.4 for dashkovaite and magnesite (Figure 4). The obtained spectra are consistent with the experiment (Figure 1). Based on this, we refined a 3D atomic model for Mg in aragonite, which is the main host of those biominerals.

The computation of the Mg K-edge XANES spectra is tricky as Mg cannot substitute for Ca because of their enormous difference in ionic radii. However, Mg can form in aragonite a locally defective substitution [9], keeping its average Mg-O bonds near 2.10 Å [7] but expanding its medium-range to adapt to its host. Earlier studies did not envision this model. But, based on the defective substitution model or not (Figure 5), both simulations provided spectra that are inconsistent with any experiment.
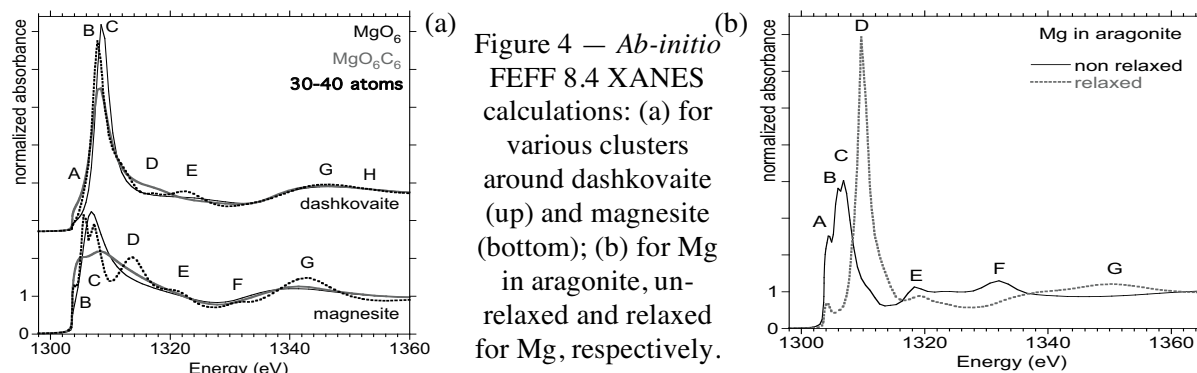

Figure 4 — *Ab-initio* FEFF 8.4 XANES calculations: (a) for various clusters around dashkovaite (up) and magnesite (bottom); (b) for Mg in aragonite, un-relaxed and relaxed for Mg, respectively.

Alternatively, wavelet analyzes of the XANES spectra [10] were computed (Figure 5) for 2 selected model compounds (dashkovaite and magnesite). Both minerals possess MgO_6 moieties but in a well different C-rich medium-range environment (organic vs. carbonate). Dashkovaite show a less structured XANES (no signals above 3.5 Å around Mg) as compared to magnesite (with features up to 5.5 Å). Figure 5 shows that the local structure around Mg in *Desmophyllum* is close to that in dashkovaite while that for *Porites* is closer to that in magnesite. As a conclusion, in the above biominerals, Mg does not form Mg-rich clusters inside aragonite, but either organic-type or rhomboedric-carbonate-type environments that are (based on Figure 5) at least 5 Å in average radius.
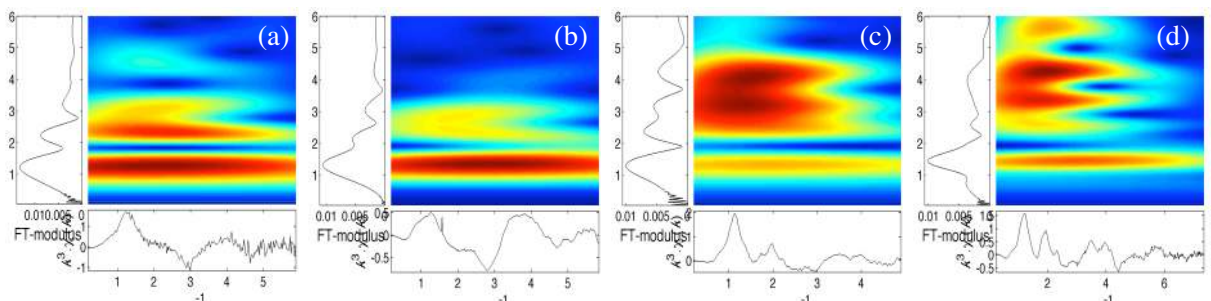

Figure 5 — Wavelets of the XANES spectra for *Desmophyllum*, dashkovaite, *Porites* and magnesite.

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