

IAS Postgraduate Grant Scheme Report

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Introduction

Under Earth surface conditions, precipitation of magnesium-rich carbonates does not occur spontaneously, due to self-limiting growth inhibition (Land 1998; Davis et al. 2000, Hu et al. 2005, Fenter et al. 2007). It was observed though that in marine sediments high-Mg calcite and dolomite precipitate in the presence of microbes (Vasconcelos et al. 1995; Dupraz et al. 2004). Indeed, it was demonstrated that dolomite precipitates in sulfate reducing bacteria culture experiments (e.g. Warthmann et al. 2000). However the exact process, promoting the incorporation of magnesium into carbonates during organomineralization (Perry et al. 2007) is still subject to discussion.

Dupraz et al. (2004) proposed that the degradation of exopolymeric substances (EPS) is the main process leading to organomineralization of microbial mats and the incorporation of Mg into carbonate. EPS are organic macromolecules, which contain carbohydrates and are secreted by microbes, in order to protect them from environmental impact. They also serve as food source for heterotrophic microbes. EPS contain negatively charged functional groups, such as carboxylic acids, which attract bivalent cations like magnesium and calcium (Decho 2000; Decho et al. 2005). By this EPS decrease the free cations in solution and can inhibit carbonate precipitation. Degradation releases the EPS-bound cations. After degradation and during carbonate precipitation, EPS can act as nucleation site and impact the morphology and mineralogy of the forming crystal (Braissant et al. 2003; Bosak et al. 2003). In addition, EPS degradation may release CaCO_3^0 and MgCO_3^0 (instead of free Mg^{2+} and Ca^{2+}), which could act as nucleation starting points within the EPS (Slaughter and Hill, 1991). This would significantly lower the inhibition of dolomite formation resulting from the large hydration enthalpies of Mg^{2+} and Ca^{2+} .

The proposed laboratory experiment was designed to test whether EPS degradation leads to the formation of magnesium-rich carbonates, when the EPS were saturated with Ca^{2+} and Mg^{2+} prior to degradation. The degradation of EPS will be the result of abiotic reactions in order to control as many parameters as possible during the mineralization process and thus reduce the number of unknowns.

Methodology

Solutions were prepared with dionized water, CaCl_2 and MgCl_2 (both p.a. Acros Organics; solution 1: 8g Ca/L; solution 2: 4g Ca/L and 4g Mg/L solution 3: 1g Ca/L and 7g Mg/L). The solutions were mixed with 0.5% and 1% xanthan (Sigma) respectively. After homogenization, the pH was adjusted with NaOH (0.1N). The solutions (10 ml) were transferred to culture bottles and CO_2 within the solution and the headspace was degassed by N_2 bubbling. The bottles were sealed and then autoclaved. After cooling, 1ml of hydrogen peroxide was gently mixed with the solutions. All solutions reacted 48h

at room temperature. The precipitated minerals were harvested by centrifuging the solution at 8500g for 15 minutes. Afterwards the precipitates were chemically dried in an ethanol bath up to 100%. SEM analyses were conducted using an environmental scanning electron microscope (ESEM), Philips XL30 FEG, equipped with an electron backscattering pattern detector as well as an energy-dispersive X-ray spectrometer (EDS) for chemical analysis.

Preliminary Results

Solution 1:

SEM observations of the precipitates revealed elongated “rod shape” rhombohedra (in 0.5% xanthan), and dumbbell shaped and spherical crystals (in 1% xanthan) in the CaCl_2 treatments (Fig. 1A). EDS analyses show that the crystals are composed of calcium, carbon and oxygen (Fig. 1F).

Solution 2 and 3:

The CaCl_2 / MgCl_2 treatments showed 40 to 200 nm wide spherical accretions of a crystalline phase, embedded in organic material and μm sized rod shaped crystals, often producing twins (Fig. 1B, C).

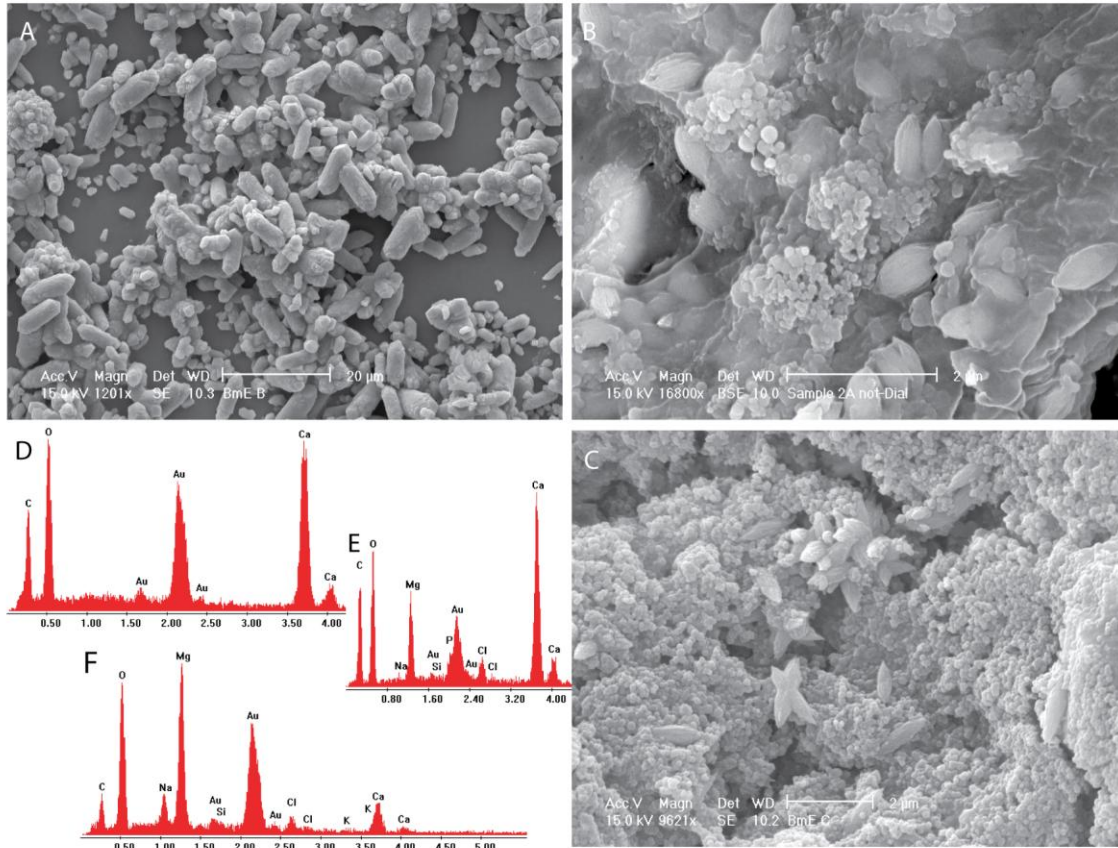
EDS measurements showed high magnesium and oxygen concentrations in the nm sized crystals (Fig. 1F). The calcium peak was higher than the magnesium peak for the μm sized crystals. Peaks of carbon and oxygen were observed as well (Fig 1E).

An increasing MgCl_2 content during the experiment lead to smaller amounts of μm sized crystals and more nanoglobules. A pH rise from 7.5 to 9.5 resulted in reduced precipitation of μm sized crystals versus nanoglobules. The same was detected for increasing xanthan concentrations. Solutions (pH 7.5) containing 0.5% xanthan produced more μm sized crystals than the 1% xanthan solutions (pH 7.5). Nanoglobules precipitated in vast quantities for both xanthan concentrations.

Discussion and Outlook

Our results demonstrate clearly that degradation of xanthan, charged with calcium and magnesium leads to the precipitation of two magnesium rich mineral phases. Due to very high magnesium and very low Ca contents??, the mineralogy of the nanoglobules is unlikely to be carbonates and further microdiffraction analyses are required. However, the rhombohedral nature and the EDS spectra of the μm sized crystals in Fig 1A and 1C indicate that they might be calcite with a varying magnesium content. However, detailed mineralogical investigations have to be carried out in order to identify the minerals and their exact magnesium content. The quantity of each crystal morphology depends on CaCl_2 / MgCl_2 ratio, pH and xanthan concentration. This observation strongly suggests that the reaction kinetics may govern the precipitation of the two distinct crystal phases.

One key result of the performed experiment is that EPS degradation may result in precipitation of a carbonate minerals 1) from organic carbon, 2) exhibiting changes in morphology and 3) containing elevated concentrations of magnesium.



ESEM backscatter images of the produced precipitates from A) solution 1, pH 7.5; B) solution 2, pH 7.5 and C) solution 2, pH 9.5 (0.5% xanthan respectively). Representative EDS spectra are displayed in D) for solution 1; E) for solution 2 2 μm sized crystals and F) for solution 2 nanometer crystals.

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