



## Magnesium incorporation in calcite in the presence of organic ligands

Vasileios Mavromatis, Andre Baldermann, Bettina Purgstaller, and Martin Dietzel

Technical University of Graz, Institute of Applied Geosciences, Austria

The formation of authigenic Mg-calcites in marine early diagenetic environments is commonly driven by a bio-induced process, the anaerobic oxidation of methane (AOM), which provides inorganic carbon required for the precipitation of such authigenic carbonates. In such settings the availability of major and/or trace divalent metal cations ( $\text{Me}^{2+}$ ) incorporated in calcite and their aqueous speciation are controlled by the presence of aqueous organic molecules that are produced either as (by-)products of biological activity (i.e. exopolymeric substances) or during degradation of allochthonous organic matter in the sediments. Despite the fact that the presence of aqueous organic ligands strongly affects the growth rates and the mineralogy of precipitating  $\text{CaCO}_3$  polymorphs, till now no study addresses the role of  $\text{Me}^{2+}$ -ligand aqueous complexes on the extent of Mg and/or other trace element content of Mg-calcites. In order to shed light on this process, relevant to authigenic calcite formation in organic-rich marine sediments and continental soils, we precipitated calcite in the presence of aqueous Mg and a variety of low molecular weight carboxylic- and aminoacids. Our experimental data indicate that the presence of organic ligands augments significantly the saturation state of calcite in the parent fluid during its precipitation. Moreover, they suggest that the higher the ligand concentration, the higher the obtained distribution coefficient of Mg in calcite. The latter is directly proportional to the ratio of  $\text{Mg}^{2+}/\text{Ca}^{2+}$  aqueous ions for all ligands used. Hydrogeochemical modelling of the aqueous fluids indicate that the observed correlation can be explained by the stronger complexation of  $\text{Ca}^{2+}$  with organic ligands compared to  $\text{Mg}^{2+}$ , which results in higher availability of  $\text{Mg}^{2+}$  vs.  $\text{Ca}^{2+}$  aqueous ions. Overall the obtained results suggest that the higher the organic ligand aqueous concentration the higher the Mg content of calcite forming from this fluid. These findings are of great importance for the understanding of the mechanisms controlling impurities and trace element incorporation in carbonates forming in marine diagenetic and soil environments.