Modelling trace metal partitioning into calcium carbonate from solution

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Calcium carbonates are well known to contain significant concentrations of trace metals; Manganese for example is incorporated into calcite via dissolution-recrystallization processes, where the maximum solubility of Mn is controlled by its reaction with calcite and the mixing thermodynamics of the $(Mn,Ca)CO_3$ solid solutions.

Sr and Mg found in coral fossils are used as proxies for the reconstruction of past climates, based on correlations found between the Sr/Ca or Mg/Ca ratios and the sea surface temperature (SST) during biomineralization. Magnesium is always present in corals but with typical Mg/Ca ratios well below the ratio of in seawater. The variation found for the Mg/Ca ratio with SST is about four times that of the Sr/Ca ratio, thus promising higher resolution in climate change reconstructions. However, although it was initially thought that the Mg in corals occupies lattice positions in aragonite, recent experimental data seem to suggest otherwise.

We have used a combination of molecular dynamics simululations and grand-canonical statistical mechanics to investigate the mixing thermodynamics of Ca, Mn, Sr and Mg in carbonate solid solutions. Our results show a small degree of Ca/Mn ordering in calcite-structured minerals, in agreement with recent experiment, whereas most aragonite-structured Ca/Sr solid solutions are metastable with respect to separation into a Ca-rich and Sr-rich phase. However, the concentration of Sr in coral aragonites lies in the miscibility region of the phase diagram and formation of separated Sr-rich phases in coral aragonites is therefore thermo-dynamically unfavourable.

We have also calculated the equilibrium partitioning of Mg between aqueous solution and the bulk and surfaces of aragonite, including the effect of the different Mg and Ca chemical potentials. Results show that the total Mg content in the aragonite particles was found to be highly surface-dependent but too small to account for the measured Mg/Ca ratios in corals. It is therefore likely that most Mg in corals is either highly metastable in the aragonite lattice or located outside the aragonite phase of the coral skeleton, which has clear implications for its use as a proxy in paleothermometry.

Mesoarchean Tectonic Evolution of the Carajás Domain, Carajás Province, PA, Brazil.

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The Carajás Province represents an Archean block located in the southeastern part of Amazon Craton, in the north of Brazil. The province is subdivided into two domains (1) Carajás at north and (2) Rio Maria at south.

The Carajás Domain is composed of Mesoarchean basement represented by orthogranulitic rocks and migmatites of tonalitic to granodioritic composition and several intrusive and tectonically imbricated calc-alkaline granites [1][2][3][4][5]. The Mesoarchean evolution of the Carajás Domain occurred between 3.0 and 2.83 Ga [5]. Tonalitic to granodioritic crust with high La/Yb was formed between 3.0 and 2.92 Ga. It was followed by events of high-grade metamorphism, migmatization and emplacement of calc-alkaline I-type tonalites, monzogranites, and granites with volcanic arc signature between 2.87 and 2.83 Ga [2][3][4]. The basement is covered by ca. 2.76-2.73 Ga metavolcano-sedimentary units of the Carajás Basin and crosscut by 2.74 Ga granites and grabbronorites and 1.88 Ga A-type granites [5][6].

The geochemical and geochronological date suggest that the development of a subduction zone related to an arc setting may be responsible for formation of the most ancient rocks of the Carajás Domain. The youngest Mesoarchean rocks may have formed in an event of crustal reworking associated with the final subduction stage, as indicated by metamorphic, structural and geochemical evidences.

The relationship of these events with the juxtaposition of the two tectonic domains of the Carajás Province is still uncertain. However, Neoarchean magmatic and tectonic events have been recorded only in the Carajás Domain.

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