

Partitioning of divalent elements between calcium carbonates and water: A solid solution model and implications for palaeoenvironmental and palaeoecological reconstructions from biogenic carbonates

B. Reynard

Laboratoire de Sciences de la Terre UMR-CNRS 5570, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon Cedex 07, France

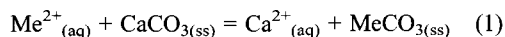
Divalent element incorporation in biogenic calcium carbonates depends on various factors such as the crystal structure (calcite versus aragonite), water temperature, water composition, biological activity (group and genus of the organism, skeleton growth rate)... Thus they are potential tracers of palaeotemperatures, palaeoenvironments, secular seawater composition variations. For instance, the fractionation of Sr between coral aragonitic skeletons and seawater has been extensively used as a proxy to surface seawater temperature and empirically calibrated on living organisms (Weber, 1973). More recently, it has been shown that other divalent elements such as Mg display an even greater temperature dependence of their fractionation between coral aragonite and seawater (Mitsuguchi *et al.*, 1996). In more complex organisms such as bivalves, seasonal variations are observed but are more difficult to relate to temperature variations because of the strong influence of the organism metabolism on the shell compositions. Finally, the mechanisms of incorporation the trace or minor elements determine the fractionation in several ways. Trace metals may be trapped in organism skeletons as adsorbed species on the calcium carbonate surface, in substitution of calcium on crystallographic sites, or in fluid or organic matrix inclusions in the more or less porous matrix. These different sites also determine the resistance of the original geochemical signature of the biogenic carbonate to alteration through geological times.

Thermodynamic modelling of the equilibrium partitioning between calcium carbonates and water can be attempted and compared with empirical calibrations in order to assess the factors governing the actual composition of biogenic shells. We test here a simple elastic model of trace element substitution energies which has been successfully applied to the description of trace element partitioning

between minerals and liquids at high temperature (Blundy and Wood, 1994) to estimate the equilibrium constants for divalent metals between calcite or aragonite and water and compare it with available experimental data and empirical calibrations on various biogenic carbonates in order to decipher the crystal-chemical and biological *sensu lato* controls.

Thermodynamic relationships

We can write the simple chemical equilibrium expressing divalent cation (Me^{2+}) exchange between calcium carbonate and seawater as:



where the subscript (aq) and (ss) refer to the ion in aqueous solution and to the carbonate solid solution, respectively. Assuming an ideal solid solution and similar activity coefficients for the divalent ions in solution, the equilibrium constant for this exchange can be written as:

$$K_{\text{D}(\text{Me}^{2+}/\text{Ca})} = \exp(-(\Delta G_{\text{f}}^0 + \Delta G_{\text{ex}})/RT) \quad (2)$$

where ΔG_{f}^0 is the standard free enthalpy change. The standard free enthalpy change of reaction (1) can be obtained from the standard free enthalpies of formation of end-member carbonates and cations. We estimate the substitution free enthalpy (ΔG_{ex}) of the trace element by considering that this term is the elastic energy due to the deformation of the host crystal lattice around the substituted cation, which can be expressed as (Brice, 1975):

$$\Delta G_{\text{ex}} = 4\pi N_{\text{A}} E \left\{ (r_0/2)(r_1 - r_0)^2 + 1/3(r_1 - r_0)^3 \right\} \quad (3)$$

where N_{A} is the Avogadro number, E the Young's modulus of the crystal, r_0 the ionic radius of the cation normally occupying the site, r_1 the ionic radius of the substituted cation. This expression is valid for isovalent substitutions and at low concentrations

where the substituted cations do not interact, which is the case for Sr and Mg in biogenic aragonites. The substitution free enthalpy can then be calculated using the available elastic data for aragonite and calcite and ionic radii. In the limited temperature range investigated, the substitution energy is assumed to be constant. The calculated values for Sr in aragonite are in very good agreement with experimental data by Plummer and Busenberg (1987). Calculations for Mg in calcite are in good agreement with available thermodynamic measurements on Mg-calcites. The model can thus safely be extended to other divalent cations (e. g. Ba, Mn, Fe, Cu, Zn, Cd ...) for which little information is available.

The equilibrium constants predicted through equations (2) and (3) allow to obtain the compositions of homogeneous solid solutions in equilibrium with water. These show that trace element compositions in coral skeleton are always out of equilibrium. Equilibrium partitioning is approached only in

aragonitic shells of gastropods. Finally, in the nacreous aragonitic layer of bivalves, chemical composition is controlled by extrapallial fluids through an "equilibrium" fractionation that is controlled only by the excess enthalpy term, and not by the solubility product ratio of carbonate end-members. Implications for the use of trace elements in palaeoenvironmental reconstructions are discussed in the light of the present thermodynamic model.

References

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