



Interpreting the dissolution of bio-minerals by irreversible thermodynamics

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It has been recently demonstrated (Takahashi and Nakashima, submitted to Journal of Taphonomy) that the dissolution rate of bio-carbonates strongly varies from one species to another. An evident working hypothesis is that the organic composition of bio-mineral accounts for this discrepancy, not only the organics adsorbed on calcite surface but also those constitutively present inside the crystal (Cuif and Dauphin, 2004). As a matter of fact, the presence of adventitious carbon, even as adsorbed organic compounds, has been found to modify the dissolution processes of calcite (Stipp 2002). *A fortiori*, the composition of "structural organics" should do the same. Therefore, one may expect that the dissolution kinetics is specifically controlled, as many others characteristics of the bio-structures.

The emphasis is here to outline that the mineral fraction is mainly responsible of the capability of one organism to be fossilized. On this account, the capability to resist to the early dissolution is a key feature of the capability of the whole organism to be conserved through time. A method is therefore required to provide us with indications of the mineral losses in a nearly constant environment. Irreversible thermodynamics appears as a relevant tool to define on a comparative way the characteristic time needed for diverse bio-materials to lose a given amount of their mineral components. The key features of this method are:

- Simple sketch of dissolution: (i) a congruent dissolution takes place at the very solid-solution interface, at nearly equilibrium; (ii) there is diffusion of reactant and products through the strongly bound water layer, of nearly constant nano-

metric thickness.

- A key assumption is that there is no coupling among the diffusion processes, which seems reasonable when one deals with mono-mineral systems.
- A quantitative coupling, expressed as a kinetic constant ($\text{mol}^2 \cdot \text{K} / \text{J} \cdot \text{cm}^2 \cdot \text{min}$), is then possible between the export rate of solutes (transport parameter) and the chemical affinity in the bulk (reactional parameter) (Massard, 1977).

The global kinetics thus defined depends only on the composition and the surface of the (bio)mineral, the composition and the flow rate of the solution, and the temperature. Obviously, this approach overlooks the mechanistic processes of the reaction and the nature of the activated complex. In other words, the rate constant here measured does not convey any information on the dissolution microscopic path.

An experimental set-up has been build to carry out a series of flow-through dissolution experiments both on biological calcitic prisms of *Pinna nobilis* (bivalve) and synthetic pure calcite. The results met the assumptions done in the theoretical frame and evidenced the difference in the kinetic behaviour of the inorganic and bio-calcite (Mercury et al., 2004). Further recent experiments tend to indicate that different bio-calcites (*Pinna nobilis*, coral: *Corallium rubrum*, sea urchin: *Paracentrotus lividus*) do kinetically behave in a specific way.

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