Interfacial Phenomena Possibly Affecting Trace-Element and Isotope Ratios in Biogenic Carbonates

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Viewed from a materials science perspective, biogenic carbonates have at least two things in common with many other substances: 1) they are polycrystalline; and 2) they grow from a saturated solution containing "impurity" ions. These two characteristics suggest possible roles for interfaces in determining the trace element (and possibly isotopic) composition of the bulk carbonate.

Effects arising solely from the polycrystalline nature of the carbonate are easy to describe but difficult to quantify due to lack of relevant data. In brief, the grain boundary region of a polycrystalline material can be thought of as a second phase that is in partitioning equilibrium with the crystal interiors, and whose relaxed (possibly chaotic) structure accommodates cation impurities that might be relatively incompatible in the crystal lattice. In biogenic carbonates, a plausible result of this grain-boundary enrichment would be a positive correlation between bulk impurity abundance (e.g., of Sr^{2+}) and grain size, because fine-grained materials have a higher proportion of grain-boundary volume. If grain size depends on growth rate (say, of a coral skeleton), then bulk Sr/Ca might appear to correlate with growth rate as well.

Like the grain-boundary effect just described, enrichment of impurities at the *crystal/fluid* interface is also an equilibrium phenomenon, but it is one whose effects can be recorded in the composition of the crystal interior when certain kinetic criteria are met [1,2]. Advancement of the growth surface into the fluid amounts to continuous "burial" of the enriched surface layer. Once buried within the crystal, this layer will attempt to rid itself of impurities by outward diffusion through the lattice. Preservation of surface-enriched impurities within the crystal volume (growth "entrapment") thus depends upon the competition between the growth rate, V, of the crystal and the diffusivity, D, of the impurity in the crystal lattice. The extent of surface enrichment and the width, x, of the enriched surface layer also enter in, but the outcome of the growth/diffusion competition can be described in terms of a simple dimensionless number $(V\cdot x)/D$. Values >0.1 result in some growth entrapment. Values >10 lead to highly efficient entrapment, effectively preserving the surface concentration within the crystal lattice. Data on biogenic carbonate growth rates and Sr diffusion suggest a possible role for this mechanism in determining Sr/Ca ratios [1,3]. There is reason to believe that $^{18}O/^{16}O$ could also be affected, because the diffusivities of the two isotopes must be slightly different.

References

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Hydropyrolysis of the organic macromolecular material in the Murchison meteorite

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Carbonaceous chondrites are the most primitive chondrites having escaped much of the geological recycling endured by other solar system bodies and contain several percent indigenous carbon, the majority of which is organic in nature. Less than 25% of this organic component is attributed to the presence of free, readily solvent extractable species. The remainder is present as a predominantly aromatic macromolecular network, this fraction has been relatively poorly characterised. From past studies it is evident that there is a significant interstellar component.

Hydropyrolysis refers to pyrolysis assisted by continuous flow high pressure hydrogen in the presence of a catalyst. This technique has been successfully used in the past to liberate high yields of GC amenable hydrocarbons from a variety of organic macromolecules, while retaining their structures and stereochemistries. This study is the first time this hydropyrolysis method has been applied to extraterrestrial material. Relatively high molecular weight polycyclic aromatic moieties (characterised by GC-MS) were released from the macromolecule. These included phenanthrene, carbazole, flouranthrene, pyrene, chrysene, perylene, benzoperylene and coronene with varying amounts of alkylation. Aromatic isomers are dominated by the most stable configuration. Comparison with hydrous pyrolysis indicated that hydropyrolysis is more efficient at releasing fragments from the condensed organic macromolecule.

Figure 1: Partially reconstructed mass chromatogram displaying hydropyrolysis products from Murchison macromolecule.