Isotopic and elemental tracers in calcium carbonate fossils

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Calcareous fossils are used for an incredible variety of purposes in paleoceanographic research: elemental and isotopic temporal variability in the ocean and geochronology. Apart from the major components themselves – calcium, carbon and oxygen, the latter two of which provide opportunities for stable isotope studies – all of these tracers are incorporated into calcareous fossils as minor elements substituting for calcium or carbonate ion. The basic structural principles of minor element incorporation into calcite and aragonite are well known to most of us and the basic relations between crystal structure and ionic radius featured prominently in Goldschmidt's treatment of geochemistry (Indeed, he discussed the incorporation of cadmium into calcium carbonate; perhaps there is nothing new under the sun). Similarly, the basic thermodynamic principles governing the free energy relationships between calcium carbonate and seawater are known (although significant controversies remain concerning the actual values of thermodynamic constants). Finally, significant analytical information is available on the incorporation of Sr, Cd, and Ba into calcitic fossils, and of Sr, Ba, U, Cd into aragonitic fossils; other elements are being actively studied and of course much is known about Sr isotope variability.

These elements fall into a variety of classes concerning the site into which they are incorporated. We may rest assured that Sr is dominantly incorporated into the cation sites substituting for calcium, although it's slightly larger ionic radius favors some discrimination against this element. Similarly, as Goldschmidt noted, it makes eminent sense that Cd, whose otavite end-member forms a continuous solid solution series with calcite and whose ionic radius is all but identical to that of calcium, should find it natural to substitute into the Ca site particularly in calcite but probably with as much facility in aragonite. Barium and lead are similar to strontium in some respects but their larger ionic radii creates more strain for each substitution for calcium, although this strain may be a negligible factor at part-per-million levels, and is a lesser factor in the larger aragonite Ca^{++}

site. Other elements – such as the tiny Mg ion or the large U ion – are more problematical, and incorporation of univalent ions such as Na^+ or F^- into Ca^{++} or CO_3^{2-} sites raises issues of how the charge balance is maintained. For these elements, and perhaps even for Sr, Ba, and Cd, it is possible that heterogeneous distributions occur, with higher concentrations at defects and grain boundaries. Frustratingly, the ability to determine the chemical environment at the atomic level simply does not exist for elements present at low concentrations, and we can only investigate issues of elemental heterogeneity through indirect and rather blunt tools.

At earth-surface temperatures in a seawater medium, calcium carbonate recrystallizes only very slowly, with pinhead-size calcium carbonate organisms retaining much of their original chemical composition for many tens of millions of years. This property is a blessing because it means that signals incorporated contemporaneously with the formation of the crystals are retained in the geological record for considerable time and open the doors for paleoceanographic research. But this slow recrystallization is also a curse because it means that it is all but impossible to confidently establish thermodynamic equilibrium relationships in the laboratory. People have even questioned whether we know the true equilibrium oxygen isotopic ratio at low temperatures! A perhaps even more fundamental problem is that most calcium carbonate is precipitated by organisms at high crystal growth rates, opening the question of whether equilibrium thermodynamics has anything to do with natural carbonates, save perhaps for its *influence* on disequilibrium biologically-driven kinetic processes. While there is empirical evidence for a relationship between seawater composition and biogenic carbonate composition for several elements – Li, Sr, Cd, Ba, Pb, and U, as well as a few others – for most of these elements we know little more than that they are perhaps within an order of magnitude of what we would expect from equilibrium thermodynamics. Particularly suspicious is the near-unity partition coefficients [D_p =

$(X/Ca)_{CaCO_3}/(X/Ca)_{seawater}$ where X is the minor element] for many dissimilar elements in coralline aragonite (Sr, Ba, Cd, Pb, U for examples). One almost gets the impression that corals throw seawater at a wall and make it stick there! Similarly discomforting are the depth-dependence of Cd uptake by calcitic benthic foraminifera (Boyle, 1992; but not aragonitic benthic foraminifera) and the extensional-rate effect on coralline Sr incorporation (DeVilliers *et al.*, 1994). These uncertainties mean that those who would use minor elemental composition of natural calcites to infer seawater composition *must* continuously scrutinize the incorporation mechanisms to be sure that some unsuspected variable is at play, particularly because we don't understand the mechanisms creating these artifacts.

If biogenic carbonates are heterogeneous at some scale – be it at the atomic level (lattice substitution sites or edge/defect sites) or simply through a broader-scale compositional zoning – there is a possibility that dissolution artifacts may compromise sedimentary data. For example, planktonic foraminifera are known to deposit their calcite over a depth range where temperatures and seawater composition vary, and it is known that within a single organism these calcites differ in their mechanical structure. Hence if dissolution occurs, it may preferentially dissolve one type of calcite at the expense of the other and hence alter the composition of the residual organism depending on the extent of dissolution. Similarly, even benthic foraminifera may have some zoning due to kinetic factors during calcite precipiation. For example, J. Erez (personal communication) has proposed that foraminifera precipitate their calcite from a reservoir 'pool' via a fractional crystallization with the composition of the pool and the precipitating solid evolving if the partition coefficient differs from unity. Hence even benthic foraminifera could display dissolution artifacts. At present there is clear evidence that more heavily dissolved planktonic foraminifera have lower Mg/Ca, F/Ca (Rosenthal and Boyle, 1993) and U/Ca (Russell *et al.*, 1994) than less dissolved specimens. Recently, I have obtained evidence from cores in the deep Pacific that the apparent partition coefficient of Cd decreases by a factor of two with strong dissolution (i.e., greater

depth), as have also McCorkle et al. (manuscript in review).

In spite of all of these problems, there are ways to overcome them. The most important method – where an extraneous factor such as extensional rate, uptake depth, or dissolution can be identified – is to control for these variables or eliminate samples for which the effect is substantial (e.g., it is possible to identify heavily-dissolved samples and eliminate these from consideration). The second most important method is redundancy; i.e., we simply don't believe a single tracer until it is confirmed by other methods (e.g., believe those elements of deepwater paleoceanography where Cd and $\delta^{13}C$ agree, and disbelieve those where they do not). Similarly, concerns over depth-dependent calcitic benthic foraminiferal Cd uptake and heavy dissolution on foraminifera Cd can be overcome by comparing to non-depth dependent aragonitic benthic foraminifera. The similarity of the aragonitic and calcitic based estimates also lays to rest fears concerning the effect of dissolution on the Cd record at some sites. The final method – if it can be called such – is simply to never accept any paleoceanographic finding as final and absolute; they all have problems and require continuous testing and comparison with new techniques.

Employing these techniques to control for artifcts, it has been possible to learn much about chemical distributions in ancient oceans through ice age cycles, and the talk will close with a few examples of these applications.

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