ISOTOPE PALEOBIOLOGY AND PALEOECOLOGY: SO WHY *SHOULD* PALEONTOLOGISTS CARE ABOUT GEOCHEMISTRY?

RICHARD M. CORFIELD

Department of Earth Sciences
Oxford University
Parks Road, Oxford OX1 3PR
UK

RICHARD D. NORRIS

Department of Geology and Geophysics
Woods Hole Oceanographic Institute
Woods Hole, MA 02543
USA

INTRODUCTION

Stable isotopic techniques in geology illuminate not only variations in past climates and oceans, but also the life-histories of extinct animals, plants and protistans. This volume focuses on the ways that stable isotopes can be used as tracers of the fossil biology and ecology of long-dead organisms and ecosystems. Here, we introduce relevant aspects of stable isotope systematics and provide a summary of the papers collected in this volume. The nine contributions collected here, from some of the most eminent workers in their respective fields, explore aspects of the ecology, evolution and biology of organisms from planktonic foraminifera to dinosaurs.

The last decade has seen nothing less than an explosion in the use of isotopic techniques to address questions about the biology and ecology of extinct organisms. But until the mid-eighties, most stable isotope research focused on paleoclimatic or what have become known as paleoceanographic issues; that bias reflects the origins of the subject (Urey, 1947). Research began to expand and diversify in the eighties and nineties into the areas of macroinvertebrate and vertebrate palaeontology. There are three principal reasons why this diversification took place. First, it was fuelled by a better understanding of the isotope systems available through dual-inlet analysis (C, N, O, S and H). Secondly, the price of stable isotope measurements decreased markedly in tandem with a growing appreciation of their value in the study of the past. Finally, the development of mass spectrometry techniques that can rapidly measure isotope ratios in organic materials (e.g.

via continuous flow {CF} techniques) has opened whole new vistas of potential application.

Isotopes of a particular element are substances that have exactly the same chemical properties, but differ in their atomic mass due to different numbers of neutrons in the nucleus. Originally, isotopes were recognized as differing in their mode of radioactive decay. However, it was also discovered that the many of the isotopes of a given element were "stable" in that their proportions in the natural environment did not change over time through radioactive processes. For example, carbon occurs both as radioactive isotopes, ^{10}C, ^{11}C, ^{14}C, and as the much more abundant stable isotopes ^{12}C and ^{13}C. Of these stable isotopes, ^{12}C constitutes 98.99% of stable carbon and ^{13}C makes up the remaining 1.11%.

Organism metabolism and many physical processes, like evaporation, discriminate between different isotopes and alter their relative abundances in biological tissues or rain clouds from the gross ratio in the biosphere or hydrosphere. Commonly the lighter isotope, i.e. the one containing fewer neutrons, is more reactive than a heavier isotope of the same element because its bonds are more easily broken. Lighter isotopes, therefore, have a tendency to be more easily evaporated or incorporated in organic tissues than their heavier cousins. For example, clouds tend to be enriched in ^{16}O relative to surface waters because ^{16}O evaporates much more easily than ^{18}O. A consequence of this differential reactivity is that surface waters, rain, snow and ice are greatly enriched in ^{16}O compared to the seawater from which they were originally evaporated. The ratio of these isotopes is traditionally presented in the δ notation:

$$\delta^{18}O = [^{18}O/^{16}O] \text{ sample}/(^{18}O/^{16}O) \text{ standard} - 1] * 1000$$

The unit of measurement is therefore $^{o}/_{oo}$ (per mil).

There are a variety of standards used for different types of isotopic systems, but a common one for analyses of biological carbonates is calcium carbonate from a belemnite in the Pee Dee Formation known as the "Pee Dee Belemnite" or "PDB" (Craig, 1953). The actual belemnite material has long since been consumed, and secondary standards (notably the marble NBS-19) are used in practice. Since the difference between NBS-19 and PDB is accurately known, results continue to be reported relative to the latter. It is, of course, vital to maintain comparability between measurements made at different times and in different laboratories.

The reactivity of oxygen isotopes in particular is affected by temperature. Much of the variability in $\delta^{18}O$ in open marine carbonates (where modification of the isotope ratio by evaporation is small) is due to variation in water temperature that changes the differential susceptibility of ^{16}O and ^{18}O to be taken up during calcification. In calcite, $\delta^{18}O$ becomes more negative as temperature of calcification increases because more ^{16}O relative to ^{18}O is used in calcification at higher temperatures than would be the case at lower temperatures. Consequently, one can use $\delta^{18}O$ variations to assess changes in the temperature at which organisms grew their shells. Since temperature is intimately linked to changes in season of the year, and water depth, we can study many aspects of the life span, depth habitats, and season of growth in marine organisms.

The ratios of isotopes are also modified by biological processes. ^{12}C, for instance, is preferentially taken up during photosynthesis so that most organic carbon fixed by plants or passed from plants through the food chain is greatly enriched in ^{12}C and has a $\delta^{13}C$ ratio of ~-20% compared to inorganic carbon in the ocean. Typically, this ratio increases by a few per mil at every step through the food chain, and may be reflected in the organic carbon produced at each step. Unfortunately, organisms do not always build their shells from respired carbon, so their position in the food chain is not always apparent from the $\delta^{13}C$ of their shells. Still, the strong biological fractionation of many isotopes of carbon, nitrogen, and sulfur, means that these systems can provide much information on the structure of ancient ecosystems and the ecologies of extinct organisms. Consequently stable isotopes are best thought of as tracers, analogous to the radionuclides used in biological and medical research, but whose abundance ideally reflects the biological, physical or chemical conditions under which the organism lived.

The ratios of stable isotopes in the biosphere are not constant over geological time. For example, burial of organic carbon as coal, oil, or gas (all greatly enriched in ^{12}C) removes ^{12}C from the biosphere and increases the $\delta^{13}C$ of carbon available to living organisms. The geologic record is punctuated by periods during which $\delta^{13}C$ of organic carbon and carbonate carbon increased due to burial of carbon somewhere on land or in the oceans. An analogous process has influenced oxygen isotopes whereby the accumulation of large ice sheets on Antarctica and in the Arctic has removed ^{16}O causing the average $\delta^{18}O$ of the biosphere to increase. Paleoclimatologists have long used the episodic increases of $\delta^{18}O$ in marine and non-marine carbonates to identify glacial stages during the Pleistocene when the expansion of glacial ice locked up a greater percentage of ^{16}O than was the case in warmer, more ice-free times. Most of these reservoir changes (changes in the ratio of isotopes due to burial or exhumation) take place on timescales of hundreds to millions of years and so are not significant in many paleoecological studies. However, work on the evolution of clades and ecosystems generally must account for reservoir changes which may mimic long-term changes in temperature preferences or dietary preferences of a clade or the productivity of an ecosystem.

The papers in current volume address a wide spectrum of the modern applications of stable isotopes to geo-biological problems. We summarize them in the following sections according to their main emphasis.

ISOTOPE PALEOBIOLOGY

A great deal of modern isotopic work on biological carbonates has focused on protistans, such as the planktic and benthic foraminifera. These microfossils are an excellent archive of changes in Earth's climate over the last ~100 million years. However,