Microfossils Reveal the Workings of a Water Planet

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Knowing past changes in surface ocean salinity would provide a powerful tracer of the hydrologic cycle, yielding climatic information such as the amount of water vapor in the atmosphere or meridional shifts in moisture sources. Water vapor itself is a potent greenhouse gas, with the potential to further heat an already warm atmosphere. Its equator-to-pole distribution on the globe affects Earth’s geographic climate zones, ranging from deserts to rainforests, with obvious implications for world populations. Holbourn et al. (2010, p. 783 in this issue of Geology) show how geochemical records of surface ocean–dwelling foraminifera can be used to reconstruct changes in one aspect of the hydrologic cycle, the tropical-subtropical rain belt during the middle Miocene. By combining different tracers preserved by the same zooplankton microfossil, Holbourn et al. are able to determine elusive aspects of the hydrologic cycle such as surface water salinity.

Tracking past changes in the hydrologic cycle is a difficult task because evaporation versus precipitation patterns (or simply put, surface ocean salinity) do not leave a unique trace in the geologic record. We can, however, indirectly assess large-scale changes in the hydrologic cycle, such as the amount of fresh water locked up in polar ice sheets, using the oxygen isotopic composition of the calcium carbonate tests of foraminifera. Polar ice sheets concentrate water molecules with the lighter of the oxygen isotopes, $^{16}$O, and their growth and decay brings about changes in the oxygen isotopic composition of seawater. The effect is ultimately due to a slight tendency of water molecules tagged with $^{18}$O to evaporate, and a slight tendency of water molecules containing the heavier oxygen isotope, $^{16}$O, to precipitate. On its poleward path, water vapor becomes progressively depleted in $^{16}$O, leading to $^{16}$O-depleted polar ice. The growth and decay of these ice sheets thus leads to global changes in the oxygen isotopic composition of seawater. At the same time, the regional balance of evaporation versus precipitation, or salinity, determines the oxygen isotopic composition of the surface ocean, and affects the oxygen isotopic composition of planktic foraminiferal tests calcifying in it.

It is difficult, however, to interpret a planktic foraminiferal $\delta^{18}$O record ($\delta^{18}$O values are the $^{18}$O/$^{16}$O ratios of the tests, expressed as a per mil deviation from a universal standard) with respect to changes in surface ocean salinity, even if assumptions regarding the magnitude of the so-called ice volume signal can be made. This is because the amount of $^{18}$O entering the carbonate during calcification is also a function of the water temperature (Urey, 1947). If, however, this temperature effect can be constrained using an independent paleothermometer, and the ice volume contribution can be assessed, then the residual signal is one that can be interpreted with respect to paleosalinity and the hydrologic cycle.

This is the approach of Holbourn et al., who have generated an ~3 m.y. long record of planktic foraminiferal $\delta^{18}$O values and Mg/Ca ratios from the northwestern subtropical Pacific. The Mg/Ca ratios provide the proxy for paleotemperatures, which in conjunction with corresponding $\delta^{18}$O values can be used to derive relative changes in surface water salinity and hence the (tropical) hydrologic cycle.

Foraminiferal Mg/Ca ratios are a relatively recent proxy for paleotemperatures. The Mg$^{2+}$ cation substitutes for the Ca$^{2+}$ cation in the calcium carbonate crystal lattice. The amount of Mg entering the carbonate is governed by a partition coefficient, which is as function of temperature, and the Mg/Ca ratios of seawater at the time of calcification. If it can be assumed that these ratios are invariant on the time scale under consideration, then foraminiferal Mg/Ca ratios provide a quantitative paleothermometer (see reviews by Lear, 2007; Billups and Scheiderich, 2009). Such is the case on the relatively short time scales of the Quaternary, when secular changes in seawater Mg and Ca concentrations are not as important because of the long residence times of these cations (~13 m.y. and 1 m.y., respectively; Broecker and Peng, 1982). Species-specific calibrations exist (Anand, et al., 2003; Lear et al., 2002), and foraminiferal Mg/Ca ratios have become a fairly common tool to reconstruct water temperatures.

The Mg/Ca paleotemperature proxy is not without complications. Foraminiferal calcite is susceptible to dissolution, diagenesis, and seawater carbon chemistry potentially obscuring the original temperature signal. Because the Mg cation destabilizes the crystal lattice, dissolution lowers the Mg/Ca ratio of some species (Dekens et al., 2002). Recrystallization of carbonate in the sediments, on the other hand, may add inorganic calcite, which has a higher partition coefficient than biotic calcite and may add Mg-rich carbonate to a test (Morse and Bender, 1990). Recrystallization of carbonate in the sediments, on the other hand, may add inorganic calcite, which has a higher partition coefficient than biotic calcite and may add Mg-rich carbonate to a test (Morse and Bender, 1990). Recrystallization of carbonate in the sediments, on the other hand, may add inorganic calcite, which has a higher partition coefficient than biotic calcite and may add Mg-rich carbonate to a test (Morse and Bender, 1990). Recrystallization of carbonate in the sediments, on the other hand, may add inorganic calcite, which has a higher partition coefficient than biotic calcite and may add Mg-rich carbonate to a test (Morse and Bender, 1990).

Proper cleaning of foraminiferal tests for Mg/Ca analysis is critical. The presence of aluminosilicate clays, which are high in Mg, yields abnormally high Mg/Ca ratios (Barker et al., 2003). Rosenthal et al. (2004) illustrated that the cleaning protocol may determine how effectively contaminants such as clays and manganese crusts are removed from the tests. Holbourn et al. follow the cleaning procedure of Martin and Lea (2002), which includes a number of chemical cleaning steps to remove detrital clays, oxide coatings, and organic matter from the tests.

On time scales longer than the residence time of Mg and Ca in the ocean, a caveat arises from uncertainties in changes in seawater Mg/Ca ratios through time. Tyrrell and Zeebe (2004) review the evolution of seawater Mg/Ca ratios through time, based on geochemical models, measurements of fluid inclusions, and pore fluids. Fortunately, the average time period that Mg and Ca cations spend in seawater from their time of input until uptake is relatively long, and thus the majority of studies have focused on temperature reconstructions on Quaternary time scales. Comparatively few studies have extended this proxy into the Tertiary (Lear, 2007; Billups and Scheiderich, 2009).

The significance of combining $\delta^{18}$O values with Mg/Ca ratios lies in its power to resolve the relationship between the temperature of seawater and its oxygen isotopic composition, leading to insights into the mechanisms of climate change on many time scales. For example, over the Eocene to Oligocene boundary, ~33 m.y. ago, the first major step occurred...
in Antarctic ice sheet expansion (e.g., Zachos et al., 2001). We now know from Mg/Ca ratios that a 2.5 °C cooling of deep water temperatures and a 2.5 °C cooling of tropical sea-surface temperatures preceded ice sheet growth (Katz et al., 2008; Lear et al., 2008). The degree of cooling is important to numerical climate models that test the role of greenhouse gas forcing during this major climate transition (DeConto and Pollard, 2003). During the second phase of major Antarctic ice sheet growth, the middle Miocene, geochemical records resolved at orbital scales show that surface water temperatures in the Southern Ocean also cooled before ice volume increased, pointing to ocean circulation changes as a major player in climatic cooling at that time (Shenvell et al., 2004). During the late Pliocene when Northern Hemisphere ice sheets first began to reach mid latitudes, and throughout the glacial interglacial cycles of the Pleistocene, Mg/Ca-derived temperatures responded several thousands of years before ice volume (Sosdian and Rosenthal, 2009; Medina-Elizalde and Lea, 2005).

Few studies have attempted to interpret the δ18O values of seawater calculated from foraminiferal δ18O and Mg/Ca with respect to changes in surface ocean salinity. This is because in most regions of the ocean, the uncertainties related to the geochemical analyses and the quantification of global ice volume changes are likely to introduce an error that is nearing the change in the δ18O of surface water expected from changes in salinity. In addition to making an assumption about the magnitude of the ice volume, a regionally defined relationship between surface water salinity and the δ18O of the modern surface ocean is needed to convert δ18O of surface seawater to salinity, with the implicit assumption that this relationship remains constant through geologic time (e.g., Rohling and Bigg, 1998). Holbourn et al. do not quantify salinity from their data set, rather they argue that surface water freshening is the most cogent way to interpret a stepwise decrease in the δ18O of seawater during the middle Miocene period of Antarctic ice sheet development.

Much progress has been made over the past ten years in developing foraminiferal Mg/Ca ratios as a paleothermometer. As this method is further developed, new uncertainties and limitations are sure to be recognized. This effort is important because these data provide quantitative constraints on numerical climate models that test the sensitivity of climate to factors such as greenhouse gas levels.

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