PALEOCEANOGRAPHY

Isotopic Tracers of Past Ocean Circulation: Turning Lead to Gold

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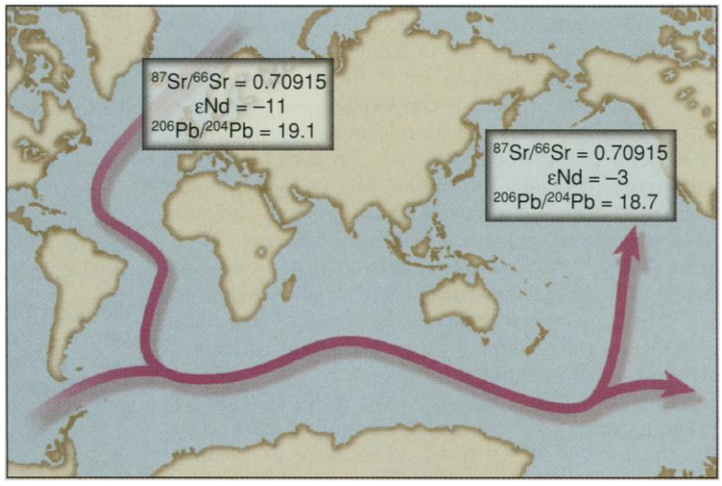
The broad framework of modern ocean circulation is reasonably well understood. Surface water of the Gulf Stream evaporates, cooling the current on its way to the Arctic. When its density increases above that of the underlying Atlantic waters, the surface water sinks and then begins its journey as deep water, first to the south along the east coast of the Americas, then into the circum-Antarctic current, and finally into the Pacific (see figure). A return flow of surface and intermediate waters from the Pacific and Indian oceans replenishes the lost Atlantic deep waters. This "conveyor belt" spins with a period on the order of 1600 years, and because it controls the longitudinal transfer of heat, it is thought to be one of the major factors of climatic modulation. Major issues relative to oceans and climates in the Quaternary and even further back in time hinge on our understanding of how ocean circulation has evolved throughout geological history. On page 913 of this issue, Christensen *et al.* (*1*) take a step forward by using laser mass spectrometry to reveal some surprises about lead isotope variation and past oceanic flow.



The isotope composition of radiogenic isotopes along the conveyor belt of deep seawater. A long residence time keeps the Sr isotope composition constant. In contrast, Nd (reported here in epsilon units, that is, as a relative deviation in parts per ten thousand with respect to the planetary reference) and Pb remain in the ocean only briefly. Their isotopic composition in seawater is therefore variable and can be used to trace exchanges of water between ocean basins.

New trails in paleoceanography are being blazed by groups at Michigan (*1*), Cambridge (*2*), and Mainz (*3*), who are using the geological record of radiogenic isotopes. Variable parent-daughter ratios of such distinct geological units as the continental crust and the mantle foster the diversity in the oceanic sources of radiogenic isotopes. The $^{87}Sr/^{86}Sr$ ratio of carbonates has long been known to reflect the balance between the interaction of seawater with the oceanic crust and the rate of erosion (*4*). Just like all of the major elements of seawater, however, strontium spends several million years in the oceans before being removed by sediments, so that its regional isotopic variability is continuously evened out by ocean circulation. In contrast, neodymium, one of the rare-earth elements, resides in the ocean less than a few hundred years before it is entrained in phosphatic remains or iron-manganese oxide flocs that form nodules and encrustations. Neodymium is therefore not isotopically homogenized by ocean circulation. Although the relative importance of eolian, riverine, and diagenetic sources of Nd in the ocean is still actively being investigated, the $^{143}Nd/^{144}Nd$ ratio offers a promising perspective. Most of the nonradiogenic Nd input to the ocean is derived from the Archean cratons in the Atlantic sector, whereas most radiogenic Nd is contributed by volcanic dust in the Pacific at the other end of the conveyor belt. The global distribution of Nd isotopes in Mn nodules indeed mimics many features of modern bottom-water circulation down to a fine scale such as the northward extension of Antarctic Bottom Water in the Pacific abyssal plains (*5*). The Cambridge group (*2*) has recently analyzed Nd isotopes in successive layers from a ferromanganous crust dated by ^{10}Be by thermal ionization mass spectrometry and found that the closure of the Central America isthmus cut off the Atlantic Ocean from the input of Pacific water and consequently accentuated the nonradiogenic character of the Atlantic Nd. Ferromanganous crusts and nodules, however, typically grow at a rate of only a few millimeters per million years. In order to be able to identify rapid changes or events of climatic relevance that may last 10 to 100 thousand years, it is desirable to analyze samples that are as small as possible. Laser ablation of crust material with a spot size of a few tens of micrometers attached to a high-transmission, high-precision mass spectrometer provides such a high resolution in time. Unfortunately, the precision needed to obtain a meaningful isotopic measurement of Nd, typically less than one part in ten thousand, requires excellent counting statistics incompatible with the amount of material blasted by the laser beam.

For in situ isotope stratigraphy in the successive layers of Fe-Mn crusts, Pb offers a better option than Nd. Lead also resides only briefly in the ocean, typically a few tens of years, before it is scavenged by particles. Consequently, its global distribution in the ocean appears heterogeneous on the 1000-km scale (*3*). The relative isotopic variability of Pb is larger than that of Nd because uranium and thorium have shorter half-lives than samarium. The precision of a fraction of a per mil obtained by Christensen and co-workers at Michigan (*1*) by laser ablation, plasma source mass spectrometry makes it possible to resolve meaningful isotopic differences in Pb from adjacent layers of an encrustation. These authors analyzed Pb isotopes on several tens of spots across two encrustations, each several centimeters thick, dredged from near the Line Islands, Central Pacific, at a depth of 2300 m and near the Marshall Islands, West Pacific, at 1800 m. Each laser spot on which the Pb isotope composition is determined averages 75,000 years of oceanic history. The age of the material blasted by the laser is extrapolated from the ^{10}Be ages of surface layers determined by the Cambridge group.

The Pb isotope compositions differ for identical time slices in the two encrustations, which confirms the heterogeneous distribution of this element and therefore its short residence time in seawater. The obser-

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vation, however, that the rate of change of Pb isotopes with time mimics that of oxygen isotopes in the sedimentary record over the last 50 million years—peak by peak, trough by trough—comes as a major surprise. Oxygen isotopes in foraminifera trace both water temperature and the volume of water sequestered in polar ice caps. Lead isotopes tell us a different story. Efficient removal of this element from the ocean implies that the average oceanic lead must adjust almost instantaneously to the isotopic composition of the riverine and eolian input from the continent.

Causes of lead isotopic variations are twofold, and implications for each of them are far-reaching. A first explanation is that the Pb source (forcing) has varied through time and the consistency of the Pb and the oxygen isotopic record necessitates some form of coupling between climate and the nature of the eroded products. Alternatively, the vigor of exchange between the different domains of the ocean (relaxation) has changed along with thermohaline circulation. Not enough is presently known from the broad-scale distribution of Pb isotopes in the modern and ancient oceans to eliminate this ambiguity, but geochemists are aware of where to focus their upcoming efforts in order to build a major increment of understanding on the dynamics of ancient oceans and atmospheres.

References

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HIGH-PRESSURE PHYSICS

Shocking Matter to Extreme Conditions

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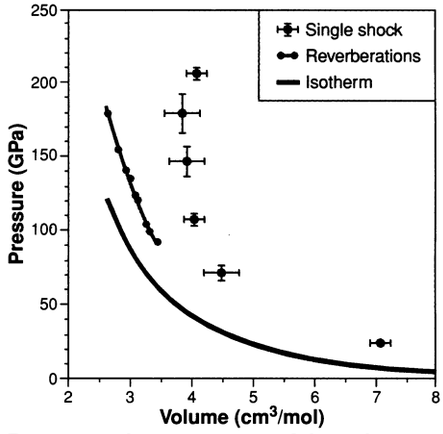
A good understanding of the thermodynamic response of matter at high compression and high energy densities (or temperatures) is important to several areas of physics, including inertial confinement fusion, astrophysics, condensed matter physics, and planetary science. Shock-wave experiments are uniquely suited for obtaining data at extreme conditions because high pressures and temperatures occur naturally in these experiments, and pressure–volume–internal energy (P-V-E) states can be determined directly and accurately in the shocked state through the use of mass, momentum, and energy jump conditions (*1*). Depending on the pressure-temperature (P-T) conditions, shock-compressed matter can be viewed as a condensed system with or without dissociation, or as a strongly coupled plasma.

Although most of the existing high-pressure and high-temperature data have been obtained with the use of gas guns, high explosives, and nuclear detonations (*2*), the development of high-intensity lasers provides a potentially attractive complement to these methods, particularly for equation of state (EOS) studies at high energy densities (*3*). By focusing a short-pulse, intense laser beam on a sample, a rapidly expanding plasma is created, which, in turn, drives a shock wave into the sample; laser-induced shock-wave experiments to obtain high-pressure EOS data (in excess of a megabar) have been carried out for more than a decade (*4*). However, concerns have existed regarding the accuracy of the data owing to the lack of planarity of the shock front, pre-heating of the material ahead of the shock front, difficulty in determining the steadiness of the wave front because of the small sample size, and the absence of absolute P-V-E data. Recent improvements in beam smoothing and other experimental developments have improved the quality of the propagating shock wave (*3*).

The article by Da Silva *et al.* (*5*), published earlier this year, represents an important achievement regarding the use of laser-induced shock waves for EOS studies. In this work, irradiances ranging from 5×10^{12} to 2×10^{14} W/cm^2 were used to generate 8- to 10-ns square pulses in liquid deuterium (D_2). Using a variety of innovative techniques, these authors demonstrated negligible pre-heating of the sample, steady propagation of the shock front, and direct determination of the shock-wave velocity along with particle velocity and density in the shocked state. Because any two of these measurements are sufficient to calculate P, V, and E in the shocked state (*1*), the third measurement provides an internal consistency check. The absolute determination of the thermodynamic variables represents a noteworthy development.

The measurements by Da Silva *et al.* (*5*) along with other recent data on hydrogen and deuterium (*6*, *7*) [there does not appear to be much of an isotopic effect (*7*)] demonstrate that the simplest element in the periodic table is not understood at extreme conditions. Before discussing some of these complexities, we summarize the P-V results on hydrogen and deuterium from several methods (see figure). The points from Weir, Mitchell, and Nellis (*6*) represent the calculated values for their reverberation experiments (quasi-isentropic loading) in which they reported the metallization of hydrogen. The considerable differences observed for the three loading conditions are a consequence of temperature differences and their effects on the internal processes.

The P-V results from Da Silva *et al.* disagree strongly with model predictions that do not include molecular dissociation. Any dissociation of the molecule results in energy absorption, which reduces temperature and makes the material more compressible. The single-shock data for undissociated D_2 would display a considerably steeper response than



Pressure-volume response of deuterium under various conditions. Isotherm from diamond-anvil cell experiments at 300 K (*7*), quasi-isentropic reverberation data of Weir *et al.* (*6*), and single-shock data of Da Silva *et al.* (*5*). Unlike the shock data, the diamond-anvil cell data are for the solid phase.

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