Verde had to answer two key questions: Is the MV-II occupation really archaeological and, if so, is it really that old? That is, does the site meet the modern version of the apparently eternal criteria first forged by Lyell? Reading this volume leaves no doubt that the answer is "yes." This was also the decision reached by an interdisciplinary team (of which I was a member) that examined the Monte Verde collections and visited the site in 1997 (*5*).

Intriguingly, there is more to the Monte Verde site than the MV-II findings. Dillehay has discovered other apparent archaeological material, called MV-I, at the base of glacial outwash deposits some 2.1 meters beneath the present ground surface and some 80 meters distant from the MV-II deposits. Associated radiocarbon dates fall at 33,370 ± 530 and >33,020 years BP; these are fully consistent with dates of ~25,000 years BP from higher in the stratigraphic sequence, and of >42,100 years BP from lower in that sequence. Dillehay is cautious about this material, but having seen some of the objects and the context from which they came, it is quite clear that at least some of it is artifactual (for example, the basalt core from which flakes were removed, illustrated in figure 14.70 in this volume).

It is hard to overemphasize the importance of the discoveries described in this book. We now have a New World archaeological site some 16,000 kilometers south of the Bering Land Bridge that predates Clovis by more than 1000 radiocarbon years (MV-II), and that might even contain a much earlier occupation (MV-I). As a result, archaeologists must rethink their ideas about the peopling of the New World, a process that has already begun (*6*). But in doing so, it would be good to remember what has happened in similar situations in the past after convincing breakthroughs. Criteria for evaluating potentially ancient archaeological sites have been relaxed and invalid sites interpreted as authentic, only to be rejected after virtually identical criteria were redeveloped to evaluate them. Then, one or more sites met the new criteria, and the process began again. That Monte Verde is quite clearly a pre-Clovis archaeological site does not mean that it is time to relax our skepticism about other sites—and there are many—that may or may not be archaeological and that may or may not be old.

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SCIENCE'S COMPASS • PERSPECTIVES

PERSPECTIVES: PALEOCLIMATE

The Sulfur Cycle and Atmospheric Oxygen

Robert A. Berner and Steven T. Petsch

The isotopic composition of carbon and sulfur in rocks and sediments provides an important record of global change over geologic time. Changes in the ratios of $^{13}C/^{12}C$ and $^{34}S/^{32}S$ of the oceans largely reflect changes in global biological processes that cause fractionation of these isotopes. The biological processes include photosynthesis, which brings about the depletion of ^{13}C (compared with its abundance in seawater) in sedimentary organic matter, and bacterial sulfate reduction, which brings about the depletion of ^{34}S in sedimentary pyrite (FeS_2). Because organic matter and pyrite burial in sediments, along with their weathering on the continents, constitute the four major processes affecting atmospheric oxygen, study of the rates of these processes is important, not only for the evolution of the carbon and sulfur cycles but also for the history of atmospheric oxygen (*1–3*) (see figure).

The record of $^{34}S/^{32}S$ of the oceans over geologic time (*4*, *5*) has heretofore been based on the analysis of calcium sulfate minerals precipitated from seawater through intense evaporation in restricted portions of the sea. However, there are problems with the use of evaporites for obtaining isotopic data because of their infrequent occurrence and their location at marine margins, which can lead to initial water compositions different from that of the open ocean (*6*). The alternate use of another sulfate mineral, formed from the open ocean at normal salinity, allows one to obtain a much more complete isotopic record and to avoid the pitfalls presented by marginal marine environments. As reported on page 1459 of this issue, this has now been done by Paytan *et al.* (*7*) for the Cenozoic era (the past 65 million years) by analyzing barite ($BaSO_4$), a common minor component of deep-sea sediments. The excellent correlation between different localities and the finding of the modern ocean $^{34}S/^{32}S$ ratio for barite in very young sediments show that this barite data set is reliable and provides the best record to date of the evolution of oceanic sulfur.

The processes that affect the evolution of oceanic sulfur over geologic time include (*8*) (i) river input from the weathering of pyrite and calcium sulfate minerals on the continents; (ii) removal of sulfur from seawater through bacterial sulfate reduction to hydrogen sulfide followed by the reaction of H_2S to form sedimentary pyrite plus minor organic sulfur compounds; (iii) removal from seawater through the precipitation of calcium sulfate in evaporite basins; and (iv) the exchange of sulfur through the interaction of basalt with seawater at midoceanic ridges.

Sedimentary pyrite formation and calcium sulfate precipitation constitute the two major processes of sulfur removal from seawater. By comparison, net removal of sulfur through thermally induced sulfate reduction at midocean ridges has been shown to be minor. This is based on both sulfur isotopic mass balance (*9*) and the inability to balance the oxygen cycle if this process were quantitatively important (*10*). Also, the permanent removal of sulfate as $CaSO_4$ at ridges can be shown to be minor from the study of sea-floor basalts (*9*). The addition of reduced sulfur to Earth's surface from the mantle may occur episodically; however, massive maintained sulfur fluxes have been shown to be quantitatively unimportant on the basis of both isotopic and oxygen mass balance considerations (*11*).

The sulfur that is removed from seawater as sedimentary pyrite involves considerable isotopic fractionation (*12*) and is highly depleted in heavy sulfur (low $^{34}S/^{32}S$), whereas calcium sulfate precipitation involves negligible isotopic fractionation. Input to the oceans from continental

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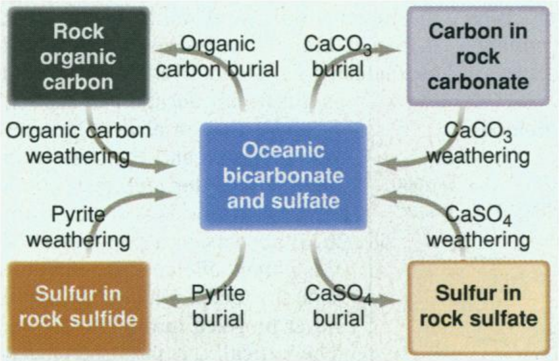
weathering represents a mixture of light sulfate from pyrite oxidation and heavy sulfate from calcium sulfate dissolution. Changes in the sulfur content and isotopic composition of the oceans over geologic time represent a balance between these burial and weathering processes. It is the job of global cycle modeling to try to discern which of these processes have dominated in the geologic past.

Because sulfur and carbon each exist in both oxidized ($CaSO_4$ and $CaCO_3$) and reduced (FeS_2 and organic C) states in rocks and because they are the dominant elements involved in surficial redox cycling (*2*, *13*), the global conversion between oxidation states for one element, if not perfectly balanced by a reciprocal conversion for the other, ultimately involves changes in the concentration of atmospheric oxygen (*1*). Calculation of the effect of change in the global carbon and sulfur cycles over geologic time on atmospheric oxygen has been attempted through the use of isotope mass balance models (*2*, *3*, *14*–*16*). A major problem with those models that try to calculate actual O_2 concentrations (*5*, *16*) is the extreme sensitivity of the mass of atmospheric O_2 to very small relative changes in the much larger masses of oxidized and reduced carbon and sulfur as calculated from isotopic data.



Elemental flow chart. The cycles of carbon and sulfur as they affect atmospheric oxygen. Prolonged shifts of each element from the reduced to the oxidized form ultimately require an opposite shift in the other element to prevent excessive fluctuations of atmospheric oxygen. Deep burial and thermal decomposition of the various forms of carbon and sulfur can occur, leading to the emission of gases to Earth's surface. This degassing, along with the air oxidation of any accompanying reduced gases, is included here under the term "weathering." Also, reduced organic sulfur compounds are lumped together with pyrite.

Major shifts in the isotopic composition of sulfur and carbon in seawater are due to shifts in the amount of reduced versus oxidized S and C being buried in sediments or supplied to the oceans from weathering and to variability in isotopic fractionation during the formation of FeS_2 or organic carbon. The simplest model assigns all isotope shift to variations in burial, for example, correlating a rise in the ^{34}S content of seawater to an increase in pyrite burial. A more elegant approach allows for variations in continental weathering, so that an increase in sediment mass results in an increase in weathering. However, this mass-dependent approach does not account for tectonic events such as the India-Asia collision and the rise of the Himalayas. The initial stages of this orogeny uplifted and eroded much light organic C- and pyrite-rich shelf sediment (*17*). However, as pointed out by Paytan *et al.* (*7*), 40 million years of post-collision history has generated very little change in the sulfur isotope record and, by implication, the global sulfur cycle. The effects of specific tectonic events on the C-S-O system have not been incorporated into an O_2 model and should be included in future efforts.

Variations in the isotopic composition of pyrite and organic carbon buried in sediments are strongly influenced by changes in isotope fractionation. For example, the fractionation of sulfur isotopes during sedimentary pyrite formation can vary considerably depending on rates of sulfate reduction (*12*) and the degree of openness of the sediment to sulfate in the overlying seawater (*5*). Also, carbon isotope fractionation is sensitive to the availability of CO_2 (*18*). Models of the C-S-O system can accommodate this variability by explicitly using the isotope ratio difference between oxidized and reduced phases, instead of what is often done, applying a constant fractionation.

Feedbacks are normally invoked in geochemical cycle models to return to geologically reasonable conditions after a perturbation. For C-S-O cycle models driven by the isotope records, however, feedbacks required to stabilize atmospheric O_2 are very problematic. Because the models require carbon, sulfur, and oxygen mass balance, processes that act as negative feedbacks with respect to oxygen may behave as positive feedbacks with respect to sulfur and carbon. These include both rapid recycling (*15*) and O_2-sensitive weathering and burial (*15*, *16*, *19*). For example, a rise in seawater $^{34}S/^{32}S$ may be modeled as an increase in the burial of sedimentary pyrite, which results in a rise in atmospheric O_2. If the weathering of pyrite is increased to return O_2 to normal concentrations (the negative feedback), the input of isotopically light sulfur to the oceans will rise. To maintain isotope mass balance, a even larger mass of pyrite must be buried, which leads to positive feedback. Although negative feedbacks are very useful in dynamic models of geochemical cycles, to date no negative feedback involving atmospheric O_2 has been identified that is well-behaved in an isotope-driven model. One way to escape these problems is to avoid the use of isotopes altogether by using rock abundances and their organic carbon and pyrite sulfur contents (*20*). Nevertheless, there is still a need to find a way to accomplish O_2 stabilization in isotope mass balance models, especially as new and better data such as those of Paytan *et al.* (*7*) become available.

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