GEOCHEMISTRY

Continental Margins and the Sulfur Cycle

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The transition between land and ocean at the continental margin is one of the most important boundaries on Earth, with marine geochemists often considering the continental margin as a "biogeochemical reactor." On page 2004 in this issue, Turchyn and Schrag (*1*) present exciting new information on the importance of chemical cycling in continental margins, providing a dynamic view of the oceanic sulfur cycle.

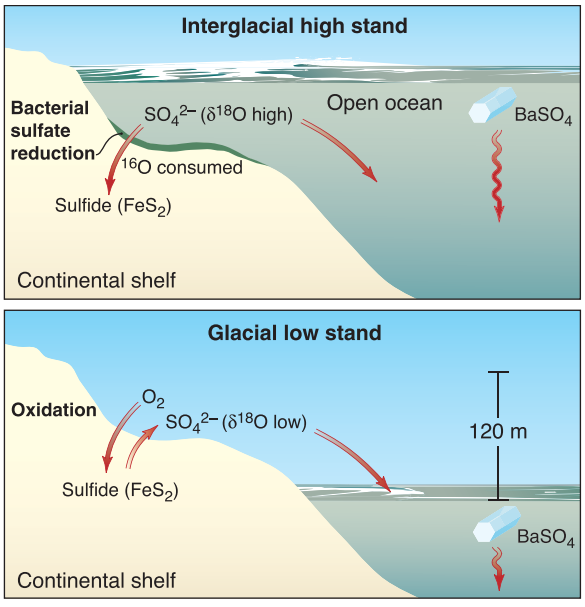
Seawater sulfate is an important oxidant in microbial processes, and helps set the ocean's alkalinity budget. Changes in the ocean's sulfate concentration have generally been regarded as important only on geologically long time scales, because the large oceanic sulfate reservoir, and relatively small river input, results in a long residence time [tens of million years (Ma)] and resistance to rapid change. After chloride, sulfate is the most abundant anion in seawater. It is removed both during formation of evaporite deposits as gypsum, and by reduction to sulfide by microbes in marine muds. Although the energetic yield of carbon metabolism provided by sulfate reduction is low relative to the energetic yield from reduction of either molecular oxygen or nitrate (or even ferric iron), the much greater abundance of dissolved sulfate gives it a major role in sedimentary carbon cycling. In the presence of iron, the sulfide produced by bacterial reduction of sulfate reacts to form pyrite (FeS_2), a common constituent of organic carbon-rich marine sediments and the ultimate source of much of the sulfur released during the combustion of coal.

To probe sulfate cycling in continental margins, Turchyn and Schrag trace the story told by the oxygen in the SO_4^{2-} ion, rather than by the sulfur itself. The three stable isotopes of oxygen (^{16}O constitutes 99.763% of total oxygen; ^{17}O, 0.0375%; and ^{18}O, 0.1995%) are commonly used by geochemists to examine both equilibrium and kinetic processes throughout Earth's history. Turchyn and Schrag exploit the fact that the sulfur-bound oxygens in the SO_4^{2-} ion are tightly held and resistant to isotopic exchange at ambient temperatures. The isotopic composition of the oxygen reflects the source of sulfate: Direct oxidation of sulfides (such as during weathering) produces sulfate with relatively light oxygen, whereas partial reduction of sulfate to give sedimentary sulfide preferentially removes ^{16}O and leaves the residual sulfate "heavy" in oxygen, that is, enriched in ^{18}O. Bacterial oxidation of sedimentary sulfide also yields heavy sulfate, and the picture is further complicated by the fact that the isotopic fractionations during sulfate reduction depend somewhat on the specific pathway. Nevertheless, the oxygen isotopic composition of sulfate produced by oxidative weathering is notably different from that cycled on continental shelves during bacterial metabolism.

How does one trace the oxygen isotopic composition of the SO_4^{2-} ion through time? Here, biogeochemical processes in the ocean come into play. Although the details of the mechanism of its formation remain unresolved (*2*), the highly insoluble mineral barite ($BaSO_4$) forms readily in seawater in association with plankton and organic matter and is incorporated into marine sediments. Because barite forms continuously in the oceans, it provides a convenient and robust archive of sulfate compositions through time (*3*). Turchyn and Schrag analyzed $^{18}O/^{16}O$ variations in barite (expressed as $\delta^{18}O$) from deep-sea marine sediments of Miocene to Holocene age, thus providing a tape recorder–like history of sulfate $\delta^{18}O$ over the past 10 Ma. The $\delta^{18}O$ of barite increases until 3 Ma, and then declines rapidly by ~5%. Neither the magnitude of variation nor the change in slope at 3 Ma can be produced by the smaller, monotonic increase in the $\delta^{18}O$ in ocean water over the same time period but must instead reflect changing sources of dissolved sulfate ion. Before 3 Ma, the sulfate $\delta^{18}O$ data can be plausibly explained by the dominance of bacterial disproportionation reactions as the source of seawater SO_4^{2-}. The rapid decrease in barite $\delta^{18}O$ after 3 Ma requires a shift to sulfate sources dominated by oxidative weathering of sulfides.

The authors modeled a range of solutions, and propose that low Pleistocene sea levels left sulfides on continental shelves vulnerable to oxidation during exposure to the atmosphere. Repeated glacial-interglacial sea-level cycles would have promoted oxidative weathering of sulfides, as shelf sediments deposited during interglacial cycles were exposed to oxidation as a result of erosion during glacial sea-level lows (see the figure). The model results further imply that the overall flux of sulfate to the oceans had to increase beginning at 3 Ma. The authors estimate that the seawater SO_4^{2-} concentration increased by 10 to 20%, and that the direct reoxidation flux of sulfides in shelf sediments also increased. They suggest that this apparently more efficient reoxidation pathway reflects increased dissolved oxygen levels in a colder ocean.

A corollary of the modeled increase in marine sulfate concentration is that it could affect the ocean's alkalinity budget. The ocean's alkalinity sets the total charge that can be con-



A dynamic sulfur cycle: At interglacial high sea level (**upper**), sulfate ion (SO_4^{2-}) is partially removed by bacterial sulfate reduction (BSR) to make sedimentary sulfides. BSR preferentially consumes sulfate with ^{16}O leaving behind sulfate with high ^{18}O (measured as high $\delta^{18}O$), which is transferred to the open ocean where the insoluble mineral barite ($BaSO_4$) is formed. During glacial stages (**lower**), sea level is lowered by ~120 m, and sulfide minerals in shelf sediments can be exposed to oxidation by atmospheric O_2 (dissolved in soil or ground waters). Direct oxidation produces sulfate with low $\delta^{18}O$, which is transferred to the oceans in river runoff.

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tributed by bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, the main forms of dissolved carbon in the oceans, and so changes in alkalinity affect the ocean's capacity to absorb CO_2. Unless chloride levels fell or the concentration of major cations rose proportionally with increased sulfate concentration, seawater alkalinity should have decreased, with important consequences for the carbon cycle. It will be interesting to establish whether any changes in ocean alkalinity occurred during the past 3 Ma, because atmospheric PCO_2 levels are quite sensitive to changes in both the magnitude and vertical distribution of alkalinity in the oceans.

Turchyn and Schrag's conclusion that sea-level change is a major driver of marine SO_4^{2-} chemistry further emphasizes the importance of sea-level change to the operation of the continental margin "biogeochemical reactor." Sea-level change also affected carbon sequestration through the frequent glacial-interglacial climate cycles of the past few 100,000 years, including the Last Glacial Maximum (*4*). It appears that the loss of the continental-margin sink for major nutrients such as phosphorous may have caused a glacial-interglacial redistribution of carbon sequestration between the margin and the deep sea. Thus, the work by Turchyn and Schrag not only demonstrates that the marine sulfur cycle has been more dynamic over the last few million years than we thought, but it further focuses our effort toward understanding the importance of the continental margins in affecting climate change on Earth over all time scales. The next step will be to try and better understand what the interesting implications of the changes in elemental cycling at the continental margins have been.

References

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ASTRONOMY

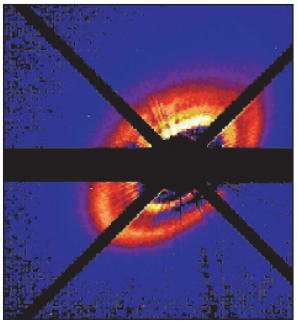
Nearby Planetary Disks

David Mouillet

Understanding the complex process of planetary system formation around a star is one of the major challenges of astronomy today. The conditions required for our own solar system to come into existence, with its stable arrangement of planets and moons, might seem quite unlikely. Study of our solar system alone, however, does not reveal how frequently planetary systems may form around other stars, and which fraction may end up with stable planets likely to support liquid water, possibly favoring the development of life.

During the past decade, the detection of planets around more than 100 bright stars similar to the Sun has clearly demonstrated that planet formation is not an unimportant process. These observations have revived a number of unsolved questions about the size, orbits, and statistics of the discovered planets (*1*, *2*). Another approach is to directly study young systems—circumstellar disks that still contain the material likely to form planets. By sampling systems from a number of evolutionary stages, stellar types, and environments, researchers can draw a comprehensive picture of planetary formation under various conditions. Yet, the detection and imaging of these very faint planetary disks have been successful for only a handful of cases since the discovery of the disk around β Pictoris in the mid-1980s (*3*). On page 1990 of this issue, Kalas *et al.* (*4*) report an interesting image that shows a circumstellar dust disk around AU Microscopii (AU Mic), a sister star to β Pictoris. The young age of the host star and its nearness to us make it very favorable for detailed investigation. Of special interest is the fact that discovery of its very low mass complements previous findings of disks that have only been imaged around more massive stars.

What do we know about the circumstellar disks that harbor planet formation? During the early youth of a star, the infalling material is structured within an accretion disk that is massive, viscous, and opaque, containing more gas than dust. A number of such disks have been detected and/or resolved (*5*). However, the opacity mainly reveals the shape of the disk envelope, or the overall mass content, at far-infrared or millimeter wavelengths. Within a few million years, most of the gas has been either accreted or blown out, while some of the dust has accreted to form larger bodies, up to planetesimals or even planets. At this stage, the small dust grains are no longer protected by the presence of gas that would otherwise reduce their relative velocities and shield the grains from stellar radiation: They are very rapidly destroyed through strong collisions and/or radiation pressure. Consequently, these so-called debris disks are very faint and are difficult to image. The observed disk in visible and near-infrared images consists of short-lived reflecting dust grains produced by collisions among planetesimals (*6*). Such images, possibly with high angular resolution (resolving distances typical of our own solar system's extension around nearby stars), reveal the content and the distribution of this underlying population of planetesimals. Moreover, the distribution of grain sizes, their composition, and asymmetrical structures in the disk tell us about the physical conditions and the dynamics within such active disks (see the figure). This is the basic information needed to understand the physics of the disks when planets are forming or have just been formed.



Young solar system. Debris disk around the 5-million-year-old star HD 141569, located at 100 parsecs (*8*).

During this stage, the influence of the star is crucial in determining the evolution time scale of the disk and the processes that destroy the dust grains. In particular, the impact of the stellar radiation pressure dramatically depends on the star spectrum, and ultimately, on the stellar mass. The disk discovered by Kalas *et al.* surrounds a much less massive star (0.5 solar mass) than those in the previously known systems. The proximity of the star (10 parsecs) will also make it possible to resolve very small structures in the disk, and to investigate its properties close to the star. Such properties are very favorable to further investigations with higher accuracy and will provide an interesting point of comparison for our current models in the case of low-mass stars (which are far more numerous than high-mass stars).

Those questions motivate a number of complementary developments. At long wavelengths (sensitive to the intrinsic emission of the cold circumstellar matter), the Spitzer Space Telescope (operating since 2003 and capable of spatial resolution) will discover much fainter dust disks, thanks to its considerably improved sensitivity (*7*). Later, the ground-based large array of 64 antenna (ALMA, the Atacama Large Millimeter Array) will probe this cold dust and gas with high angular resolution at millimeter and submillimeter wavelengths. In the visible and near-infrared, coronography and adaptive optics on large ground-based telescopes are now leading to improved high contrast and high–angu-

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