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of bacterial and mammalian methyltransferases show little structural or sequence similarity. In bacterial enzymes, this region specifically contacts the CG dinucleotides located in the DNA strand that is complementary to the strand that contains the CG methylation target. It may be that in mammalian enzymes the TRD plays a similar role and that the presence of the CXXC domain not only helps position the autoinhibitory linker in the active site, but also precludes TRD interaction with DNA. Biochemical assays show that mutant enzymes lacking the CXXC domain, or the autoinhibitory linker, or amino acids that interact specifically with the CG dinucleotide region have increased methylation activity, thus supporting the structural observations and the model for autoinhibition.

The proposed mechanism of substrate selection by DNMT1 reflects recurring themes in enzyme regulation: the recruitment of structural domains to provide additional interactions, and the use of mobile

polypeptide loops that block the active site, as has been observed, for example, in some kinases that phosphorylate protein substrates. Furthermore, the structures confirm expected similarities in the methyltransferase domains of DNMT1 and DNMT3A.

The work by Song *et al.* prompts several questions about the structure of DNMT1 in complex with its preferred substrate, hemimethylated DNA. In this case, it may be possible to determine the structure of a productive complex with DNA and discover the position of the CXXC domain and the autoinhibitor linker by using azacitidine-derived cytosine bases to stabilize the complex for crystallization. A structure of full-length DNMT1, which includes the amino-terminal protein interaction domains, may also reveal the functional relationships of all the domains within this complex enzyme.

Cysteine-rich domains in DNMT3A, DNMT3B, and DNMT3L [a nonfunctional regulatory partner of DNMT3A and

DNMT3B (7)] differ from the CXXC domain in DNMT1, suggesting that they may have divergent functions, such as facilitating de novo methylation of unmethylated substrates. By contrast, the structural similarity between the CXXC domains in DNMT1 and MLL (8), a histone methyltransferase, may provide functional information about this domain in unrelated enzymes that modify chromatin to regulate gene expression.

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GEOCHEMISTRY

Sulfur Surprises in Deep Geological Fluids

Craig E. Manning

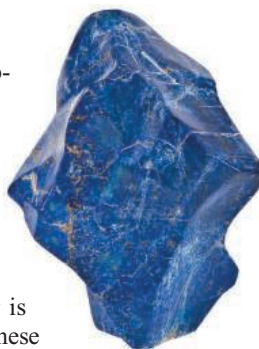
Priced for their deep-blue color, the mineral lazurite and the rock it dominates, lapis lazuli, have been quarried for millennia in a few localities such as the Sar-e-Sang mines in Badakhshan province, Afghanistan. The ultramarine stones have contributed to jewelry boxes and pigment bases from before King Tut's reign to modern times. Their remarkable coloration originates from charge transfer between groups of the trisulfur anion, S_3^- (1, 2). It is so striking a hue that French postmodernist Yves Klein famously created his own version of this pigment to coat his friends and his sculptures in blue, foreshadowing today's Blue Man Group. On page 1052, Pokrovski and Dubrovinsky (3) provide new evidence that S_3^- may be far more common than previously realized.

Sulfur plays a critical role in biology, atmospheric and ocean chemistry, and multiple interior processes (4), so it is important to know what forms it takes in different geo-

chemical settings. Sulfur is distributed throughout the mantle and crust mainly in sulfide (S^{2-}) and sulfate (SO_4^{2+}) minerals, and it finds its way into deep geologic fluids when these mineral reservoirs are perturbed by tectonic processes. For example, when rocks melt deep in Earth, sulfur is drawn into the molten magma. As these liquids rise to the surface, they cool and decompress, and some of the material crystallizes. These processes expel dissolved gases (mainly H_2O and CO_2), which can then form a separate liquid or vapor that can serve as a reservoir for sulfur. Similarly, tectonic burial of surface rocks causes constituent hydrous crystals to react and form new minerals that contain less water, creating a fluid phase rich in water. The accompanying sulfur-bearing minerals partly dissolve, likewise transferring sulfur to the fluid.

Studies of sulfur dissolved in fluids have focused on sulfide and sulfate forms chiefly because they predominate in sulfur-bearing minerals, glasses quenched from magmas, and fluids included in tiny bubbles within

Sulfur in hot, high-pressure water exists in an unexpected form, S_3^- , that changes our understanding of processes as varied as ore formation and volcano degassing.



Even sulfur gets the blues. Lapis lazuli gets its distinctive blue color from the mineral lazurite, $(Na,Ca)_8Al_6Si_6O_{24}(SO_4,S,Cl)_2$, when light excites charge transfer between groups of the trisulfur anion S_3^- . This anion was thought to be relatively scarce, but the results of Pokrovski and Dubrovinsky suggest that it may be the dominant state of sulfur in fluids deep within Earth.

minerals. Dissolved sulfide and sulfate mediate geochemical processes through formation of aqueous complexes with metals. For example, gold is normally unreactive, but valuable deposits of gold are found in ore veins that precipitated from hot geologic fluids. The transport agent that is often invoked is sulfur because it forms stable bisulfide (HS^-) complexes (5). Through a complicated series of physical and chemical steps, sulfur complexes extract and transport gold to its eventual site of precipitation in such settings as magmatic hydrothermal systems (6). The very different oxidation states of sulfate ($6+$) and sulfide ($2-$) mean that the changes

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between these two forms lead to transfers of many electrons, which can drive oxidation or reduction reactions of the host rocks. Large tracts of deep crustal rocks exhibit evidence for in situ oxidation that may have been influenced by sulfur redox chemistry (7).

The assumption that sulfur in deep fluids exists chiefly as sulfide or sulfate is based on these species being the most common forms in surface waters, but they could also be products of rapid reactions of other sulfur compounds in deep fluids as they rise to the surface. Pokrovski and Dubrovinsky used a hydrothermal diamond-anvil cell and Raman spectroscopy to look for other sulfur species dissolved in water at high pressures and temperatures. They found that S_3^- is favored as temperature and pressure are increased, and predominates above $\sim 300^\circ\text{C}$ at all pressures investigated and over a wide pH range.

The results offer intriguing possibilities for rethinking processes in deep geofluids. They support additional pathways for gold transport and deposition in hydrothermal systems (8). They also require a new assessment of sulfur's history before it reaches the atmosphere in some volcanic eruptions. Sulfur-rich volcanic systems are associated with convergent plate boundaries—for example, the Pacific “Ring of Fire”—and may emit large volumes of SO_2 gas. So much stratospheric SO_2 was liberated during the 1991 eruption of Mount Pinatubo that average surface temperatures dropped globally by $\sim 0.5^\circ\text{C}$ for several years (9). Interestingly, more sulfur was degassed in that event than could be accounted for in the magma parent, and the simplest explanation is that a sulfur-rich vapor phase released deep below the volcano was carried upward with the rising magma and into the eruption plume (10). If Pokrovski and Dubrovinsky are correct, much of the SO_2 that caused temporary global cooling could have formed from precursory aqueous S_3^- .

If S_3^- is to predominate in fluids at depth, it must be stable in both acidic and alkaline solutions at high pressures and temperatures. As pressure and temperature increase, acids such as HCl and H_2SO_4 become much weaker and water dissociates more extensively to H^+ and OH^- . (Neutral pH in pure water at the pressures and temperatures encountered 15 km beneath an active mountain belt such as the Himalayas is about 4, rather than 7.) Elevated pressure also enhances the solubility of the minerals lining the fracture and cavity walls that allow fluids to migrate (11). Acids would have less capacity to neutralize alkaline solutions that are produced by a wide range of mineral-water reactions. Thus, it is noteworthy that the S_3^- anion was found to

be stable over a wide range of pH.

However, Pokrovski and Dubrovinsky provide only part of the story. In magmas and ore-forming fluids, iron content can influence the behavior of sulfur and its oxidation state, but only iron-free fluids were investigated. Pokrovski and Dubrovinsky suggest that the similarity of the 103°S-S-S bond angle in S_3^- to that of H-O-H might make it more easily accommodated into the tetrahedral hydrogen-bonded network of the aqueous solvent. However, other groups, also using in situ Raman spectroscopy, detected no evidence for hydrogen bonding in water above $\sim 400^\circ\text{C}$ (12, 13); such results imply that this familiar and chemically important feature of water diminishes with temperature.

If we could shine light on deep geologic fluids, the apparent prevalence of S_3^- means that they should be ultramarine blue in color (14). Pokrovski and Dubrovinsky have now done for deep fluids what others have done for silicate glasses and precursors to volcanic gases (15, 16) by revealing a form of sulfur with an intermediate redox state (relative to sulfide and sulfate) whose geochemical consequences must now be explored. Their findings continue a tradition of surprises in sulfur

geochemistry that extends even to the source of color in ultramarine pigment, which could involve S_2^- in addition to S_3^- (17).

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ECOLOGY

Functional Extinctions of Bird Pollinators Cause Plant Declines

Cagan H. Sekercioglu

Researchers have documented how the loss of pollinating birds affects a plant that depends on them.

The world's approximately 10,000 bird species are key “mobile links” (1) in most major ecosystems, from tropical rainforests to the depths of the Antarctic Ocean. Birds provide crucial ecosystem services, including seed dispersal, pollination, predation, scavenging, nutrient deposition, and ecosystem engineering (2–4). Countless plant species depend on mutualistic relationships with birds for their survival (5–7). However, threats such as habitat loss, introduced species, and exploitation (7–9), exacerbated by the growing impact of climate change (10, 11), are causing large population declines and extinctions among birds (see the photo). As a result, hundreds of species now contribute negligibly to ecosystem function

and are “functionally extinct” (8). Researchers have speculated that these losses could lead to declines in dependent plants (12–14), but experimental proof has been scarce (4, 7, 12). On page 1068 of this issue, however, Anderson *et al.* (6) show that the functional extinction of three kinds of pollinating birds on an island in New Zealand has reduced pollination, seed production, and plant density in a dependent shrub.

Although research on bird-plant mutualisms tends to focus on seed dispersal rather than on pollination (5), researchers have documented about 2000 bird species visiting flowers; more than 900 species pollinate about 500 of the 13,500 genera of vascular plants (7, 15, 16). Anderson *et al.* studied three species of birds known to pollinate the shrub *Rhabdothermus solandri*. They compared shrub populations at sites on the North

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