By growing precise structures incorporating an external gate, the interface can be statically and dynamically tuned over many orders of magnitude. At the high end, the doping levels should allow access to phase transitions that have not been previously reachable. These phase transitions can be precisely traversed and studied, as demonstrated by Thiel *et al.* Control of the interface electronic structure is central to the function and improvement of virtually all existing oxide device characteristics—similar considerations have already played a role in enhancing magnetic tunnel junctions, as an example (*11*). These and other advances are rapidly opening a new frontier in the science and technology of oxide heterostructures.

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GEOCHEMISTRY

Manganese Redox Chemistry Revisited

Manganese in natural oxygen-poor waters can persist in a +3 oxidation state, a state previously seen only in the lab, necessitating a major revision of the current understanding of manganese aqueous geochemistry.

Kenneth S. Johnson

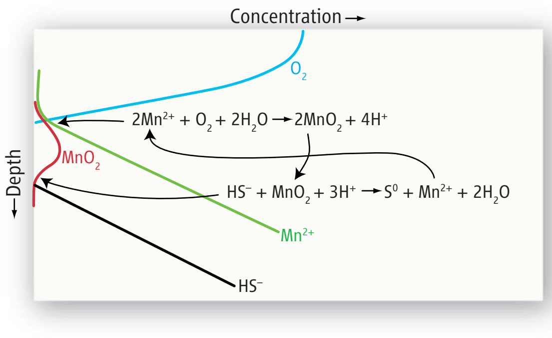
Manganese is an important component of some marine reduction-oxidation cycles. It is usually assumed that only the Mn(II) and Mn(IV) oxidation states play an important role in these cycles. But recently, Webb *et al.* (*1*) suggested that during the oxidation of Mn(II) by bacteria, Mn(III) is formed as an intermediate. Large concentrations of Mn(III) would then accumulate and leak into the environment. On page 1955 of this issue, Trouwborst *et al.* (*2*) show that in regions of the Black Sea and Chesapeake Bay where the concentration of molecular oxygen is extremely low (suboxic regions), much of the dissolved manganese is indeed present as Mn(III). This discovery will alter the paradigm on which our understanding of manganese aqueous geochemistry is based.

Manganese acts as a catalyst that shapes chemical gradients in the oxygen-deficient zones found throughout the coastal ocean and marginal seas. It can perform this role because it exists in multiple oxidation states and is recycled rapidly between these states by bacterial processes. These transformations serve as an electron-transfer system for other chemical cycles. For example, oxidized manganese consumes upwelling hydrogen sulfide in the Black Sea, which contains the world's largest mass of anoxic water (*3*). The reduced manganese produced during oxidation then diffuses upward, where it consumes downwelling oxygen (see the figure). This reaction resupplies the pool of oxidized manganese, thereby creating a catalytic cycle and a suboxic zone in which molecular oxygen and sulfide concentrations are very low.

Our understanding of how manganese mediates chemistry in these suboxic areas has been based on the paradigm that there are two predominant forms of manganese in the environment: dissolved, reduced Mn(II) and particulate, oxidized MnO_x [where x is near 2 and most of the manganese is in the +4 oxidation state, although particulate Mn(III) also exists]. The vertical or lateral gradients in dissolved or particulate manganese set limits on the rates of reaction that can occur. These gradients, multiplied by the appropriate diffusion coefficient or, in the case of particulate MnO_x, the appropriate settling velocity, define the flux of electron donors and acceptors available for reaction.

Dissolved Mn(III) has been largely ignored, because it is both a very strong oxidant and reductant that is expected to rapidly disproportionate to Mn(II) and MnO_2. The Mn(III) detected by Trouwborst *et al.* persists because it is stabilized by dissolved ligands, perhaps pyrophosphate. The authors measured the Mn(III) concentration by using desferrioxamine-B (DEF-B), an Fe^{3+}-binding ligand that is produced by bacteria. DEF-B also strongly binds Mn(III) and can outcompete natural ligands to sequester all of the dissolved Mn(III) in a filtered sample. The concentration of the DEF-B–Mn(III) complex can then be determined electrochemically.

In the Black Sea, water below a depth of about 100 m is permanently anoxic. The Chesapeake Bay is much shallower (~20 m), and anoxic zones form below ~15 m in the summer in response to nutrient-stimulated inputs of decaying phytoplankton. These two environments represent the extremes in anoxic conditions found in natural waters, one permanent and the other temporary. Dissolved Mn(III) was observed in both loca-



How manganese catalyzes chemical cycles in the Black Sea. In subsurface waters, Mn(II) reacts with oxygen, depleting its concentration and forming manganese oxide (MnO_2) particles. The particles sink into deeper waters, where they react with upwelling hydrogen sulfide, resulting in the regeneration of Mn(II). Trouwborst *et al.* report that much of the dissolved manganese in the suboxic zone is Mn(III), rather than Mn(II). This finding will require a reevaluation of how such cycles operate.

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tions in the suboxic zones, where both molecular oxygen and sulfide are nearly absent. In some cases, all of the dissolved manganese in the suboxic zone was in the +3 oxidation state, reaching concentrations of up to 4 μM.

Thermodynamic considerations indicate that manganese may play a dominant role as a catalyst in chemical cycles other than the HS^-/O_2 cycle shown in the figure. For example, the reduction of nitrate by Mn(II) and the oxidation of ammonia by MnO_2 are thermodynamically favorable in suboxic marine environments (*4*). Oxygen and Mn(II) concentrations do not seem to overlap in many sediment profiles, providing indirect evidence for the oxidation of Mn(II) in the absence of O_2. However, these reactions have been difficult to demonstrate with direct measurements in environmental samples (*5*).

The analytical tools used in these studies are based on the assumption that the dissolved manganese is all in the reduced form. If Mn(II) is oxidized in a one-electron step to Mn(III), then the concentration of dissolved Mn [which is the sum of Mn(II) and Mn(III) in most analytical methods] will not change. The classical paradigm would indicate that no reaction had taken place. This situation resembles our understanding of anaerobic methane oxidation a decade ago. At that time, field data suggested that a reaction consuming methane occurred, but the mechanism became clear only when new methodologies were developed (*6*). The work of Trouwborst *et al.* is a crucial step in moving us beyond the stalemate in our understanding of manganese cycling.

The discovery of substantial amounts of Mn(III) may also have implications for regions of the ocean that are not suboxic. The concentration of dissolved manganese decays smoothly in the deep (~3000 m) waters that flow along the oceanic conveyor from the North Atlantic into the Pacific. After several hundred radiocarbon years, manganese reaches a uniform concentration of 0.15 nM in these waters (*7*). In the case of Fe^{3+}, ligands such as DEF-B ("siderophores") act as a control that drives iron concentrations in the deep ocean toward uniform values (*8*). There has been little plausible evidence for similar processes involving dissolved manganese, because Mn(II) interacts with organic ligands much more weakly than does Fe^{3+}. The evidence for substantial production of Mn(III) and its capability to interact strongly with siderophores introduces a new mechanism for sustaining uniform manganese concentrations in the deep ocean.

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GENOMICS

Genomics and the Tree of Life

The wealth of genome sequences—from more than 400 organisms to date—has enriched the evolutionary tree, but has also presented new challenges.

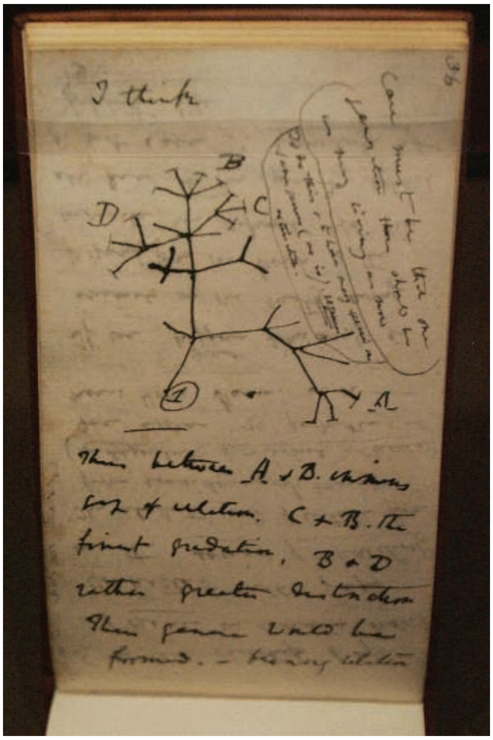
Antonis Rokas

Only a decade has elapsed since the first prokaryote and eukaryote genomes were decoded. More than 400 genomes have been completed, some 1600 additional genomes are currently in progress, and genome-scale data sets (e.g., expressed sequence tags) are being generated at an unprecedented rate. Among the many fields feeling the impact of this genomic avalanche is phylogenetics, the discipline concerned with discovering the evolutionary interrelationships among all living organisms, an effort frequently visualized in the form of the Tree of Life (see the figure) (*1*). The wealth of genomic data has allowed the discovery of new molecular markers for phylogenetic reconstruction, such as rare genomic changes, but it has also presented new challenges for theoretical phylogenetic research.

The dramatic increase in data set sizes has led, in many cases, to increased confidence in the inference of evolutionary relationships (*2*, *3*). Data sets with small gene numbers can generate inaccurate phylogenies because of sampling error or simply the lack of sufficient amounts of data (*3*). Although typical genome-scale phylogenetic studies have been rich in sequence data and thin in species number (*3*), as the number of sequenced genomes increases, genome-scale phylogenetic analyses are beginning to feature much larger numbers of species (*4*).

But further increases in data set sizes present challenges as well. Analyzing many thousands of nucleotides for hundreds or thousands of species requires substantial computational power to efficiently search among all possible trees (*5*). More sophisticated statistical algorithms are also needed for discovering the trees best supported by the data (*6*). Several clades of the Tree of Life, including the one of Metazoa, are proving difficult to resolve too (*7*). Most parameters of sequence evolution vary across lineages. Slight biases—amplified by the sheer volume of data—can potentially mislead phylogenetic algorithms and provide high support for the wrong trees.

Whereas the linear information in genome sequences may not always suffice, other rare features in the genomes' contents, such as sequence rearrangements or integrations of



A lovely tree. Charles Darwin's famous notebook B containing the first known sketch of an evolutionary tree.

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Editor's Summary