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David B. Senn and Harold F. Hemond
Science 296, 2373 (2002);
DOI: 10.1126/science.1072402

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The observation of vibrational mode-selectivity in the conformational isomerization of a molecule of this size is an unexpected result. Many previous studies on much smaller molecules have concluded that vibrationally mode-specific behavior is increasingly unlikely as the size of the molecule increases (12, 13). Intramolecular vibrational redistribution, or vibrational state mixing, increases with increasing molecular size because the density of vibrational states at a given energy rises quickly with increasing molecular size, washing out mode-specific excitation by diluting the make-up of the state carrying the oscillator strength with an increasing number of background levels at that energy.

However, the present experiment probes conformational isomerization rather than bond breaking, with barriers separating the conformational minima of about 20 kJ/mol, total excitation energies of only about 40 kJ/mol, and fast cooling in the expansion (with the first cooling collision on the 10^{-10}s time scale). Such conditions could limit the extent to which energy can redistribute throughout the molecule before trapping behind a barrier to isomerization. If the molecule is large enough, the parts of the molecule far from the point of excitation should play little role in the dynamics that follow IR excitation. In this sense, vibrational mode-selectivity may be more readily achieved in very large molecules than in small ones, if selective excitation can be achieved. In addition, the cooling collisions may participate in changing the conformational populations rather than simply quenching them. Thus, in the presence of competing deactivation, the kinds of conformational change that can be induced by IR excitation may have a characteristic length scale that the present experiment could be beginning to explore, pointing to the need for further experiments of this kind, supported by theory.

References and Notes
5. D. Evans, D. J. Wales, personal communication.
10. These measurements are equivalent to a photochemical quantum yield measurement. Photoexcitation of conformer I produces a certain population of excited molecules. The quantum yield \( \phi_0 \) is then the fraction of this excited population of conformer I that ends up as conformer J.
11. On the basis of preliminary results from N-acetyltryptophan amide and melatonin.
14. We acknowledge the National Science Foundation and the Petroleum Research Fund for support of this research (grant CHE-9728636). A.L. acknowledges the MCYT for his postdoctoral fellowship.

Nitrate Controls on Iron and Arsenic in an Urban Lake

David B. Senn*† and Harold F. Hemond

Aquatic ecosystems are often contaminated by multiple substances. Nitrate, a common aquatic pollutant, strongly influenced the cycling of arsenic (As) under anoxic conditions in urban Upper Mystic Lake (Massachusetts, USA) by oxidizing ferrous iron ([Fe(II)]) to produce As-sorbing particulate hydrous ferric oxides and causing the more oxidized As(V), which is more particle-reactive than As(III) under these conditions, to dominate. This process is likely to be important in many natural waters.

Arsenic cycling in aquatic systems is strongly influenced by redox processes. For example, oxidized [arsenate, \( \text{H}_3\text{AsO}_4^- \)] and reduced [arsenite, \( \text{H}_2\text{AsO}_3^- \)] forms of inorganic As can differ both in their tendency to form soluble or insoluble complexes (1–3) and in their toxicity to humans and aquatic communities (4). Moreover, because surface complexation of As by solid hydrous ferric oxide (HFO; Fe in the +III oxidation state) often plays a dominant role in immobilizing As (2, 3), redox processes that affect Fe speciation can also have a strong indirect effect on As (4). Thus, redox-active pollutants (oxidants or reductants) could have the potential to affect As mobility. Nitrogen (N) pollution, arising from activities such as agricultural fertilization and fuel combustion, is generally of concern for its roles in eutrophication and fuel combustion, and its toxicity to humans and aquatic communities (4). However, because surface complexation of As by solid hydrous ferric oxide (HFO; Fe in the +III oxidation state) often plays a dominant role in immobilizing As (2, 3), redox processes that affect Fe speciation can also have a strong indirect effect on As (4). Thus, redox-active pollutants (oxidants or reductants) could have the potential to affect As mobility.

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Field observations confirm nitrate’s control over Fe chemistry in UML. NO$_3^-$ did not become fully depleted in 1997, and as predicted, Fe(II) levels remained low. By contrast, in 1999, NO$_3^-$ depletion occurred in the deepest waters by late October, and resulting Fe(II) accumulation was highly coincident, spatially and temporally, with the NO$_3^-$-depleted region (Fig. 3A). An HFO peak developed at the NO$_3^-$-rich NO$_3^-$-depleted interface, analogous to the peak observed at the oxic-anoxic interface in systems in which O$_2$ controls Fe cycling (19).

Mass balance at depths of 21 to 24 m indicated that NO$_3^-$, rather than other oxidants, was responsible for oxidizing most Fe(II) during anoxic, NO$_3^-$-rich periods (21). In 1997, O$_2$ and Mn$^{IV}$O$_2$ accounted for at most 25% of NO$_3^-$ consumption [total Fe(II) oxidation = 60,000 ± 18,000 mol = 60,000 e$^{-}$ equivalents], whereas only 40% of the NO$_3^-$ consumption was required (total NO$_3^-$ consumption = 29,000 mol = 145,000 e$^{-}$ equivalents, assuming N$_2$ to be the product). The remaining NO$_3^-$ consumption likely occurred through conventional denitrification. Mass balances for Fe(II) oxidation in 1998 and 1999 yielded similar results (20).

Although abiotic Fe(II) oxidation by NO$_3^-$ proceeds at insignificant rates under conditions typical of UML (22), microcosm experiments using anoxic surface-sediment slurries spiked with NO$_3^-$ (21) demonstrated the feasibility of biologically mediated Fe(II) oxidation by NO$_3^-$ in this system (Fig. 3B). NO$_3^-$ consumption (~1 mM, or 5 meq e$^{-}$ liter$^{-1}$ when NO$_3^-$ reduction to N$_2$ is considered) was sufficient to explain the observed oxidation of both Fe(II) (1.2 meq e$^{-}$ liter$^{-1}$) and Si(II) [2.1 meq e$^{-}$ liter$^{-1}$ (20)], whereas negligible Fe (or sulfitide) oxidation was observed in controls killed with azide or formaldehyde. These observations are consistent with culture-based studies demonstrating the existence of bacteria that can mediate Fe(II) oxidation through reduction of NO$_3^-$, primarily to N$_2$ (and some N$_2$O) (6–8).

The presence or absence of NO$_3^-$ also dictated As redox chemistry (Figs. 1B and 3C). Contrary to conventional expectation (19), As(V), rather than As(III), accumulated during anoxic but NO$_3^-$-rich periods. In that As is simply masked by concurrent oxidation of Fe(III) or Mn$^{IV}$O$_2$ (21), whereas negligible Fe (or sulfitide) oxidation was observed in controls killed with azide or formaldehyde. These observations are consistent with culture-based studies demonstrating the existence of bacteria that can mediate Fe(II) oxidation through reduction of NO$_3^-$, primarily to N$_2$ (and some N$_2$O) (6–8).

Despite the presence of NO$_3^-$, As(III) remained considerably lower than As(V) concentrations, primarily to N$_2$ (and some N$_2$O) (6–8).

An important consequence of NO$_3^-$ leading to the dominance of HFO and As(V) is that most As should form particulate HFO complexes. To confirm this hypothesis, we designed an N$_2$-purgd in situ serial filtration system to measure size distributions of Fe and As in anoxic water when NO$_3^-$ was present (20). This device rigorously excludes O$_2$ and filters...
at low velocities (~0.02 cm min⁻¹), minimizing possible artefacts such as Fe(II) oxidation and accelerated coagulation. During 1997, ~95% of As was associated with particles (including colloids) at 22 m (representative hypolimnetic depth) throughout the period of anoxia (fig. 15). Similar observations were made at 20 and 22 m during fall 1996. Using surface complexation modeling (21, 23) of As sorption by HFO, we predicted (typically within ±15%) the measured distribution of As between particulate and dissolved (i.e., smaller than 0.05 μm) phases. Although the presence of other sorbing surfaces cannot be ruled out, none is needed to explain the observations. We calculate that >90% of As was complexed by HFO in late November 1997 in the bottom 4 m of the lake. Had As been present entirely as As(III), less [only ~60%] calculated using sorption constants of (3)] would have been complexed by HFO. Over the entire season, mass balance estimates indicate that settling resulted in a 40% decrease in net As remobilization to the water column.

N pollution may thus have direct effects on the cycling of As in numerous other systems and may indirectly alter the cycling of other particle-reactive substances (e.g., PO₄³⁻, Pb, Hg, Cd) through the Fe cycle. These effects may not necessarily be adverse; in some instances, lowered metal toxicity could result owing to sorption by HFO. NO₃⁻ levels greater than 50 μM are common in lakes across the United States and Europe (table S1). Elevated NO₃⁻ is at least partly responsible for many coastal eutrophic “dead zones” (24) (table S1) and may influence Fe and trace metal geochemistry there. Many groundwaters in the United States contain elevated NO₃⁻ (25) (table S1). Postma et al. (26) provide evidence for oxidation of reduced Fe (as pyrite) in a NO₃⁻-contaminated aquifer, and biologically mediated Fe(II) oxidation by NO₃⁻ has recently been demonstrated in laboratory studies of anoxic paddy soils (27). Elevated NO₃⁻ has also been measured in some Bangladeshi groundwaters (28, 29) (table S1), which commonly contain elevated As. Although these As concentrations are often much greater than those in UML, and multiple solid phases are present, the few available data (i.e., in which both NO₃⁻ and As have been measured) suggest that As tends to decrease at high NO₃⁻ levels (28, 29).

References and Notes
19. Classical Fe and As cycling in lakes: Fe(II) (10) and As(III) (18) are expected to dominate in anoxic waters. In oxic, circumneutral-pH sediments, Fe(III) typically occurs as insoluble and highly sorptive HFO solids, which can be reduced to soluble Fe锈 when O₂ is depleted, as commonly happens beneath a lake’s thermocline during the summer (10). When this occurs, both Fe(II) and substances previously sorbed by HFO are released from the

Fig. 3. Impact of NO₃⁻ on Fe and As redox chemistry. (A) During 1999, particulate HFO initially accumulated in anoxic, NO₃⁻-rich waters, but was replaced by dissolved Fe(II) at NO₃⁻-depleted depths. (B) Fe(II) oxidation by NO₃⁻ in anaerobic sediment-slurry. In live bottles, slurry color changed from black to orange-brown as Fe(II) levels decreased, suggesting that Fe(II), likely as Fe₃S₄, was oxidized to HFOs. The concomitant accumulation of sulfate (data not shown) is consistent with this interpretation. Nitrite (NO₂⁻) did occur occasionally in bottles (maximum of 0.2 mM) but decreased to less than 0.01 mM before most Fe(II) oxidation occurred. In addition, NO₃⁻ was observed in the formaldehyde controls (up to 0.13 mM by day 32) in which no Fe(II) oxidation was observed, suggesting that abiotic Fe(II) oxidation by NO₃⁻ was not important under these conditions. (C) As(V) accumulated in the water column during summer and early fall of 1999 when NO₃⁻ was present, but As(III) replaced As(V) at NO₃⁻-depleted depths. O₂ concentrations were below detection limits (less than ~5 μM) in waters deeper than those denoted by the dashed line. HFO was calculated as the difference between total Fe and Fe(II). As(V) was calculated as the difference between total As and As(III).
REPORTS

50 Million Years of Genomic Stasis in Endosymbiotic Bacteria

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Comparison of two fully sequenced genomes of Buchnera aphidicola, the obligate endosymbionts of aphids, reveals the most extreme genome stability to date: no chromosome rearrangements or gene acquisitions have occurred in the past 50 to 70 million years, despite substantial sequence evolution and the inactivation and loss of individual genes. In contrast, the genomes of their closest free-living relatives, Escherichia coli and Salmonella spp., are more than 2000-fold more labile in content and gene order. The genomic stasis of B. aphidicola, likely attributable to the loss of phages, repeated sequences, and recA, indicates that B. aphidicola is no longer a source of ecological innovation for its hosts.

The availability of genome sequences for related bacteria is providing exciting insights into evolution, but one limitation has been the lack of identifiable bacterial fossils to provide a time frame for these studies. We have quantified total rates of genomic evolution for Buchnera aphidicola, an obligate mutualistic symbiont of aphids, by sequencing the genome of the B. aphidicola symbiont of Schizaphis graminum (Sg) (1) and analyzing its divergence from the published sequence of the B. aphidicola symbiont of Acrystosiphon pismum (Ap) (2).

This case allows genome evolution to be calibrated reliably with respect to time. Because the symbiont phylogeny mirrors that of its aphid hosts, indicating synchronous diversification, divergence dates reconstructed for ancestral aphids can be extended to the corresponding B. aphidicola ancestors. This approach has been used to infer that this endosymbiosis was established at least 150 million years ago (Ma) and that the lineages represented by B. aphidicola (Sg) and B. aphidicola (Ap) diverged 50 to 70 Ma (3, 4) (Fig. 1A). These are the only fully sequenced organisms that have eliminated recA, which is expected to lower the incidence of recombination events (5).

The genomes of B. aphidicola (Sg) and B. aphidicola (Ap) are similar in size (0.64 megabases (Mb)) and are among the smallest of bacterial genomes. Their gene content is also very similar, with 526 genes shared of the 564 and 545 intact genes present in B. aphidicola (Ap) and B. aphidicola (Sg), respectively (Table 1). A comparison of the aligned genome sequences (1) confirms a high degree of divergence at the nucleotide sequence level. On the basis of a divergence date of 50 million years (My), average rates of sequence evolution were estimated at 9.0 \times 10^{-9} synonymous substitutions per site per year and 1.65 \times 10^{-8} nonsynonymous substitutions per site per year. The observed divergence at synonymous sites shows low variance among genes (1), suggesting that the synonymous divergence level corresponds to the mutation rate of B. aphidicola, which is similar to or slightly higher than the rate estimated in E. coli and Salmonella typhimurium (4, 6, 7).

Despite high levels of sequence divergence, the two B. aphidicola genomes show complete conservation of genomic architecture (Fig. 1B). No inversions, translocations, duplications, or gene acquisitions have occurred in either lineage since their divergence. Of the 564 protein-coding genes originally annotated in B. aphidicola (Ap), only four (ybaI to yba4) were reported not to have orthologs in E. coli (2), a closely related free-living species (Fig. 2A). Our analyses suggest that even these genes were present before the establishment of the symbiosis (1), providing even stronger evidence that the symbiotic life-style did not in-

Table 1. Comparison of genome features for B. aphidicola (Sg) and B. aphidicola (Ap).

<table>
<thead>
<tr>
<th>Feature</th>
<th>B. aphidicola (Sg)</th>
<th>B. aphidicola (Ap)</th>
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<tbody>
<tr>
<td>Genome size (bp)</td>
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<td>640,681</td>
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<tr>
<td>Genic G + C content (%)</td>
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<td>26.3</td>
</tr>
<tr>
<td>Intergenic G + C content (%)</td>
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<td>16.1</td>
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<td>Protein coding genes (no.)</td>
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<td>564</td>
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<tr>
<td>Pseudogenes (no.)</td>
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<td>13</td>
</tr>
<tr>
<td>Avg. gene length (bp)</td>
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<td>985</td>
</tr>
<tr>
<td>Avg. intergenic length (bp)</td>
<td>118</td>
<td>127</td>
</tr>
</tbody>
</table>

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