The hematite-pyrite tandem cell: Avenue to understanding Mars photochemical water oxidation?

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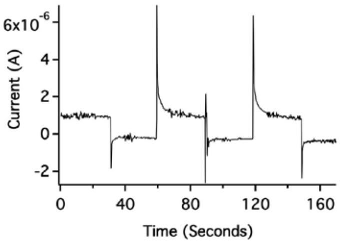
The oxidized Mars surface has been explained as a product of atmospheric photochemistry. Rarely have Mars surface materials been considered a cause of oxidation. For example, hematite must have resulted from oxidation of Fe (II) in Mars rocks. Photooxidation has been invoked in this process. Hematite is under study as a photocatalyst for water oxidation in solar energy research. Thus, once hematite has formed, it may play a role in subsequent water oxidation.

Hematite (bandgap ~ 2.0 eV) absorbs in the visible and UV. While photogenerated valence band holes are highly oxidizing, the conduction band would not be able to reduce H^+ to H_2. However, ferric coatings are an expected part of pyrite oxidation. Pyrite has a smaller bandgap than hematite, and could absorb light transmitted by a hematite coating. Thus, we examined the properties of a hematite-pyrite tandem cell from the point of view of water oxidation on Mars.

Si-doped nanocrystalline hemtite photoanodes were grown on F-doped SnO_2 by atmospheric pressure chemical vapor deposition. Natural pyrite was sliced and used as a photocathode. Current passing from hematite to pyrite was monitored. Various electrolyte solutions were used, including solutions made based on Mars Phoenix lander aqueous chemistry results. Photovoltage was also measured periodically. Experiments were run at Mars-like light intensities as well as higher light intensities using both a Xe lamp as well as a data projector emitting white light. Photocurrents of up to 1 microamp per square centimeter were observed, depending on conditions, as shown in the figure in chopped light and accompanied by substantial photocurrent transients. Given billions of years, such current densities are capable of oxidizing substantial amounts of water and producing both O_2 and H_2. Photooxidation of pyrite would eventually lead to sulfate and perhaps formation of ferric sulfate sediments.



Carbonate clumped isotope thermometry as a tool for paleoceanography

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Carbonate clumped isotope thermometry is based on the temperature-dependent formation of $^{13}C^{18}O^{16}O_2^{-2}$ ion groups in carbonate minerals. Paleotemperatures based on this technique do not depend on the isotopic composition of water from which carbonate grows, and thus can be combined with conventional O isotope analyses to reconstruct the $\delta^{18}O$ of past waters with relatively few assumptions.

At least five laboratories currently make carbonate clumped isotope analyses (Caltech, Harvard, Yale, ETH and Johns Hopkins), all with broadly similar methods and limits of precision. Interlaboratory comparisons of reference carbonates are encouraging but reveal discrepancies that will require coordination to establish a basis for absolute accuracy.

This method has been calibrated for inorganic calcite, diverse biogenic Ca-carbonates, natural and synthetic dolomite, carbonate-bearing bioapatite (Eagle *et al.* this meeting) and inorganic aragonite (Kim *et al.* this meeting). Several of these calibrations conform to a single relationship between T and clumped isotope composition of carbonate ions. However, experimental determinations of this relationship for synthetic calcite and aragonite differ from each other, and only a sub-set of them agree with the relatively uniform calibrations of various biogenic carbonates. These discrepancies are not yet understood and could reflect some combination of interlaboratory analytical artifacts, kinetic isotope effects during experimental carbonate synthesis and/or unrecognized and counter-intuitive vital effects in biogenic carbonates.

The capabilities of this method will be illustrated through three recent applications : reconstruction of the body temperatures of mesozoic land vertebrates; a high-latitude terrestrial Cenezoic climate record; and a determination of the variation in ice volume across the end-Ordovician glaciation and extinction. Finally, we will discuss new insights into the imprint of burial and metamorphic processes on clumped isotope compositions of carbonate-bearing minerals.