Anoxic pyrite oxidation by water radiolysis products — A potential source of biosustaining energy

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ABSTRACT

Radiolysis on rocky planetary bodies provides chemical species across redox gradients that can supply energy for microbial life in subsurface environments. We investigated the oxidation of pyrite to aqueous sulfate (SO_4^{2-}) by water γ-radiolysis products with concomitant production of molecular hydrogen (H_2). The production of H_2, the only gaseous product recovered at the end of pyrite–water irradiation experiments, was found to be dependent on pyrite/water ratios. The yield of radiolytically-produced SO_4^{2-} correlated with the total irradiation dose. The effectiveness of γ-radiation in oxidative dissolution of pyrite is determined by (1) redox reactions between radiolytically-produced oxidants and pyrite, and (2) the interaction between γ-radiation and pyrite's crystalline structure. Radiolytic oxidation of reduced sulfur occurs with the oxidants $HO^{\bullet}$ (hydroxyl radical) and Fe^{3+} (ferric iron) involving two different pathways. The radiolytic production of these two chemical oxidants is self-sustaining in the presence of water and Fe^{2+} in the system. Radiolytic oxidation can produce significant sulfur isotope effects by preferentially bringing ^{34}S into solution as sulfate and leaving a ^{32}S-enriched elemental sulfur layer on the pyrite surface. Experimental abiotic fractionations of sulfur isotopes between original pyrite and its sulfur oxidation products are significant and indicate that isotopically distinct sulfate is being produced during oxidation. Based on measured radiolysis constants for pyrite and radiation dose estimates for continental crust, we show that radiolysis of water coupled to oxidation of metallic sulfides could be a significant source of sulfate in many geological environments. Implications of this work are broad, impacting our assessment of the potential for life to exist in subsurface environments on Earth as well as in extraterrestrial environments.

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1. Introduction

Radiation from the decay of naturally occurring radionuclides interacts with groundwater and triggers important geochemical processes in the subsurface (Vovk, 1982; Vovk, 1987; Dubessy et al., 1988; Savary and Pagel, 1997) yet few experimental studies have assessed the efficiency of radiolysis in the production of oxidizing and reducing species in geological systems (Lin et al., 2005; Lefticariu et al., 2006, Blair et al., 2007). In water-saturated sediments, the radiation emitted by the decay of radioactive elements, such as uranium (^{238}U), thorium (^{232}Th), and potassium (^{40}K), can dissociate water molecules resulting in the formation of highly reactive ionic and excited states (Allen, 1961; Garrett et al., 2005), including oxidizing (e.g., H_2O_2, and $HO^{\bullet}$ radicals) and reducing species (e.g., H_2) (Allen, 1961; Pastina and LaVerne, 2001), and can accelerate water–rock interactions (Savary and Pagel, 1997; Chivian et al., 2008; Bank et al.,

2008). Primarily, the radiolytic production of reactive oxygen species, including $HO^{\bullet}$, $O_2^{\bullet-}$, $HO_2^{\bullet}$ and H_2O_2 (Fig. 1; Table 1), can drive oxidation reactions in otherwise oxygen-limited environments, such as the deep subsurface, where exchange with atmospheric fluids occurs on time scales of 10^5 to 10^7 yrs. (Lin et al., 2006; Onstott et al., 2006; Chivian et al., 2008).

Recent studies have shown that radiolysis coupled to oxidation of sulfide minerals could produce gradients of both H_2 and sulfur species suitable for supporting microbial metabolism (Chivian et al., 2008). Highly diffusive H_2 is essential for life in environments where only trace amounts of organic carbon exist (Pedersen, 2000). In the deep subsurface, lithoautotrophic microbes can be fully independent of solar-driven photosynthesis by acquiring energy from the redox reactions involving H_2 with other electron acceptors (SO_4^{2-}, Fe^{3+}, or CO_2) to synthesize organic compounds. Radiolysis probably plays an underappreciated role in subsurface weathering that is associated with lithotrophic/chemotrophic biological and geological processes.

The recent discovery of sulfate-rich rock outcrops on Mars provides evidence for an oxidizing and acidic (paleo)environment on the surface and/or subsurface of Mars (Gendrin et al., 2005;

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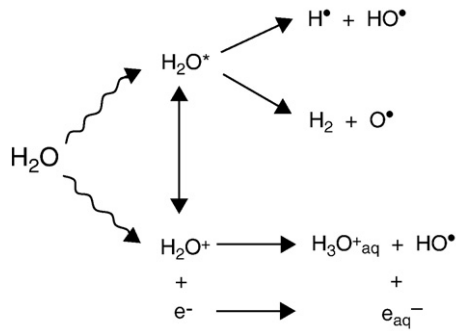E-mail address: Lefticariu@geo.siu.edu (L. Lefticariu).

Fig. 1. Initial processes in the decomposition of water by ionizing radiation (modified after Garrett et al., 2005).

signatures of radiolytic oxidation is particularly important for diagnosis and understanding of biotic and abiotic reaction pathways in environments where the concentration of molecular oxygen is negligible, and for assessing potential sources of chemical energy for microbial metabolism in subsurface environments on Earth as well as in extraterrestrial environments.

2. Methods

2.1. Pyrite preparation and loading

Details of pyrite origin and preparation were described by Lefticariu et al. (2006, 2007). In brief, individual pyrite crystals were hand-picked from massive clusters to limit impurities to ~3 wt. %, as determined by X-ray diffraction and ICP-MS. Experiments used the 100–150 μm grain size fraction of freshly ground pyrite. Washing in deionized water (DI, >18 MΩ cm), deoxygenated 0.1 M HNO_3, and deoxygenated DI was followed by drying under N_2 and weighing of pyrite into pre-annealed 9 mm o.d. silica ampoules. Each loaded ampoule was attached to a vacuum line and evacuated to $<10^{-2}$ Pa pressure, followed by closure of the vacuum connection and injection of deoxygenated DI into the ampoule through a septum. Water was frozen in contact with liquid nitrogen, the vacuum connection was re-established, and the ampoule was sealed off with a torch. Ampoules for blank experiments contained only pyrite or only water.

2.2. Irradiation

Experiments at each irradiation dose were duplicated in parallel sets of ampoules. Radiolysis with γ-rays utilized a Shepherd 109 ^{60}Co source in the Radiation Laboratory at the University of Notre Dame, Indiana.

McLennan et al., 2005) and implies that water has been present during Martian history (Squyres et al., 2004; Elwood Madden et al., 2004), which carries possible implications for Mars' habitability (Knoll et al., 2005; Tosca et al., 2008). On Earth, diverse microbial communities are associated with sulfate-rich, low-pH waters, suggesting that similar extinct or extant life may be present on Mars (Schulze-Makuch and Irwin, 2006; Atreya et al., 2006). Radiolytic processes may potentially play an important role in the formation of sulfates on Mars since radiolytically-produced oxidants could react with sulfides and provided local sources of partially to fully oxidized sulfur species available for microbial metabolism.

This contribution presents the first experimental proof that exposing water and pyrite to a common type of radiation (γ) can produce the necessary chemical ingredients for microbial extraction of energy from reaction of H_2 and sulfate. Recognizing geochemical

Table 1
Reactions in the pyrite–water system during radiolysis and rate constants for individual reactions.

Reaction no.	Reaction	Rate constant ($mol^{-1} s^{-1}$)	Literature source
I. Primary reactions in the radiolysis of pure water			
R1.1	$H_2O \rightarrow e_{aq}^-, H^\bullet, HO^\bullet, H_2, H_2O_2, HO_2^\bullet$		Pastina and LaVerne (2001)
R1.2	$e_{aq}^- + H_3O_{aq}^+ \rightarrow H^\bullet + H_2O$	2.3×10^{10}	Pastina and LaVerne (2001)
R1.3	$H\bullet + OH^- \rightarrow e_{aq}^-$	2.2×10^7	Pastina and LaVerne (2001)
R1.4	$e_{aq}^- + e_{aq}^- \rightarrow H_2 + OH^-$	5.5×10^9	Pastina and LaVerne (2001)
R1.5	$HO^\bullet + HO^\bullet \rightarrow H_2O_2$	3.6×10^9	Pastina and LaVerne (2001)
R1.6	$H^\bullet + OH^\bullet \rightarrow H_2O$	7.0×10^9	Pastina and LaVerne (2001)
II. Reactive oxygen radical reactions			
R2.1	$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O$	2.7×10^7	Pastina and LaVerne (2001)
R2.2	$HO^\bullet + O_2^{\bullet-} \rightarrow OH^- + O_2$	8.2×10^9	Pastina and LaVerne (2001)
R2.3	$O_2^{\bullet-} + H_2O_2 \rightarrow O_2 + \bullet OH + OH^-$	1.3×10^{-1}	Pastina and LaVerne (2001)
R2.4	$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2$	8.9×10^9	Pastina and LaVerne (2001)
R2.5	$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$	7.1×10^5	Pastina and LaVerne (2001)
III. Molecular hydrogen (H_2) formation			
R3.1	$e_{aq}^- + e_{aq}^- (+ 2H_2O) \rightarrow H_2 + 2OH^-$	5.5×10^9	Pastina and LaVerne (2001)
R3.2	$H^\bullet + H^\bullet \rightarrow H_2$	7.8×10^9	Pastina and LaVerne (2001)
IV. Fe^{II} Oxidations			
R4.1	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^-$	5.7×10^2	Rush and Bielski (1985)
R4.2	$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^-$	3.2×10^8	Stuglik and Zagorski (1981)
R4.3	$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^-$	6.6×10^6	Haber and Weiss (1934)
R4.4	$Fe^{2+} + HO^\bullet + H^+ \rightarrow Fe^{3+} + H_2O$	5.6×10^6	Haber and Weiss (1934)
R4.5	$Fe^{2+} + HO_2^\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2$	6.6×10^6	Haber and Weiss (1934)
R4.6	$Fe^{2+} + O_2 \rightarrow O_2^{\bullet-} + Fe^{3+}$	1.2×10^4	King et al. (1995)
R4.7	$Fe^{2+} + O_2^{\bullet-} + 2H^+ \rightarrow Fe^{3+} + H_2O_2$	1×10^7	Rush and Bielski (1985)
V. Fe^{III} Reductions			
R5.1	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+$	2.6×10^{-3}	Kwan and Voelker (2002)
R5.2	$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+$	3.3×10^7	Haber and Weiss (1934)
R5.3	$Fe^{3+} + O_2^{\bullet-} \rightarrow Fe^{2+} + O_2$	1.5×10^8	Rush and Bielski (1985)