Reactive oxygen species at the oxide/water interface: Formation mechanisms and implications for prebiotic chemistry and the origin of life

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ABSTRACT

The goal of our study is to identify free radical formation pathways on mineral surfaces. Organic molecules on early Earth might have been modified or decomposed by such pathways, thus affecting the total organic inventory for prebiotic synthesis reactions. Specifically, we evaluated several common oxide minerals under a range of environmental conditions and combinations of conditions (pH, O_2 level, UV-wavelength, and particle loading), for formation of highly reactive oxygen species (ROS) at the oxide surfaces by quantifying the generated $[OH^{\bullet}]$ and $[H_2O_2]$. We identified anatase/rutile (β-TiO$_2$/α-TiO$_2$) and hematite (α-Fe$_2$O$_3$) as active in ROS production and, importantly, found different dominant pathways for ROS formation on anatase/rutile versus hematite. Hydroxyl radicals ($OH^{\bullet}$) in anatase and rutile suspensions were generated mainly through the oxidation of OH^- by photo-generated holes and H_2O_2 was generated through the combination of an $OH^{\bullet}$ radical with an OH^- and a hole. This pathway for the TiO$_2$ phases did not require the presence of O_2, and was not shut down under anaerobic conditions. In contrast, formation of H_2O_2 and $OH^{\bullet}$ in hematite suspensions involved reduction of O_2 by electrons, which was inhibited under anaerobic conditions. The surface ROS as well as free radicals formed by reactions with other gases on early Earth atmosphere were capable of destroying molecules such as lipids and pre-RNA or RNA essential to assembly of protocells and survival of the earliest cells. At the same time, surface associated ROS and other free radicals may also have promoted aminoamide formation. Thus, the surface ROS would have affected prebiotic organic compound inventory and protocell/early life evolution.

1. Introduction

1.1. Geochemical environments for occurrence of mineral surface-associated radicals

Mineral surfaces can induce the formation of radical species involving reactions with H_2O, O_2, NO_x, CO_2, and SO_2, etc., in atmospheric, aqueous and solid rock or soil environments when exposed to ultraviolet radiation, impact shocks, or mechanical grinding (Yen et al., 2000; Schoonen et al., 2004). The radicals formed are highly reactive and capable of oxidizing organic molecules in close proximity. For example, hydroxyl radical ($OH^{\bullet}$) – the most studied radical species because of its prevalence in biological and environmental systems – reacts rapidly with carbohydrates, fatty acids, RNA, DNA, nucleic acids and other biological molecules (Aruoma and Halliwell, 1991; Djordjevic, 2004; Cohn et al., 2006), leading to alteration or decomposition of these molecules. Reactive oxygen species (ROS) associated with mineral surfaces are well documented in biomedical studies (Schoonen et al., 2006; Fubini et al., 1995; Fenoglio et al., 2001; Fubini and Hubbard, 2003; Elias et al., 2000; Donaldson et al., 2001; Li et al., 2003; Rimal et al., 2005). Inhalation of particulate quartz, cristobalite, crocidolite, and iron oxide dusts, for example, initiates formation of H_2O_2, $NO^{\bullet}$, and $OH^{\bullet}$ in vivo, leading to acute inflammation of lungs and pulmonary fibrosis over long-term exposure. On the molecular level, silica, pyrite, and iron oxides

can cause severe damage of RNA and nucleic acids in vitro (Gutteridge and Halliwell, 1982; Cohn et al., 2004), and peroxidize phospholipids both in vitro and in vivo (Gutteridge and Halliwell, 1990; Maness et al., 1999). UV-illuminated titanium oxides exhibit bactericidal effect toward *Escherichia coli* and *Pseudomonas aeruginosa* cells by breaking down the cell walls also via surface-bound OH$^\bullet$ (Sunada et al., 1998; Cho et al., 2004; Xu et al., 2012). In general, the ability of minerals to produce ROS represents their potential to degrade biomolecules by oxidation, which may have had a direct or indirect impact on early life by affecting the organic inventory available for prebiotic synthesis and/or by affecting the stability of "protocell" amphiphilic membranes in contact with these mineral surfaces. Thus, ROS, in addition to other mineral properties such as hydrophilicity, hydrophobicity, surface-charge and Hamaker constants (Sahai, 2002; Oleson and Sahai, 2008, 2010; Xu et al., 2009; Oleson et al., 2010, 2012), etc. may have influenced evolution of life on Earth and other solid terrestrial worlds.

Beyond the oxides and asbestiform minerals, reactive radicals and intermediates including superoxide, peroxide, hydroxyl, and carbonyl have recently been identified on a wide range of minerals present in simulated or natural geochemical settings. For example, large quantities of H_2O_2 have been detected on pyrite surfaces over a range of pH conditions (Schoonen et al., 2010), and both O_2^- and H_2O_2 were detected on Mars-analog minerals including feldspar, olivine, and diopside when exposed to UV radiation under simulated Martian atmospheres (Klein, 1977; Hurowitz et al., 2007; Zent et al., 2008; Shkrob et al., 2010). These findings reveal the potential impact of mineral-associated free radicals in the biogeochemical context.

The role of mineral aerosol surfaces in catalyzing redox reactions of absorbed gaseous species in the Earth's atmosphere is also being recognized. Based on samples from East Asia and the Sahara Desert, these aerosols usually consist of insoluble cores of silica and alumina, with soluble solid shells of carbonate and trace metals, where the metals are the centers for ROS generation. The presence of dense mineral aerosols and sand dusts can influence tropospheric chemistry in terms of the types and concentrations of reactive (radical) species, and the total redox capacity (Zhang and Carmichael, 1999; Zhou et al., 2003). These kinds of aerosols may affect the stability of organic molecules, if present, in other planetary atmospheres.

1.2. Aims of present study

The specific ROS species and their concentrations on mineral surfaces depend on many factors, from physical–chemical mineral properties such as electronic structure, particle size, point of zero charge (PZC), and excitation energy, to environmental conditions such as solution pH, presence of O_2, and illumination wavelengths. The broad goals of the present study are to identify the formation pathways of ROS on oxide minerals in aqueous suspensions by investigating the effects of several major environmental factors, and to establish a geochemical context relevant to early Earth for studies of mineral-induced ROS.

We focus on the mechanisms for generation of ROS at common model oxide minerals, by examining some of the key environmental conditions and combinations of these conditions. Oxyhydroxides are ubiquitous in geochemical settings and they are relatively insoluble at circum-neutral pH. Specifically, we choose amorphous silica, quartz (α-SiO$_2$), rutile (α-TiO$_2$), anatase (β-TiO$_2$), hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$), and alumina (γ-Al$_2$O$_3$), to represent a spectrum of mineral surface properties and crystallinity (Table 1). The generated ROS are detected using a recently developed probe, 3′-(p-aminophenyl) fluorescein (APF), which is able to capture the presence of OH$^\bullet$ radicals with precision and sensitivity (Setsukinai et al., 2003). Cohn et al.

Table 1
Physicochemical properties of the oxide particles used in the ROS experiments.

	Particle size[a] (nm)	Specific surface area[b] (m^{2}g^{-1})	pH$_{PZC}$[c]	Band gap energy[d] (eV)
Amorphous silica	50, 275	47.18	1.8	8.9
Quartz	100–500, 1369	6.04	2.9	
γ-Alumina	43, 270	26.91	7.8–9	9.5
Maghemite	100, 1280	57.46	6.5	
Anatase	50, 241	8.79	4.8	3.2
Rutile	100–500, 977	3.26	5.8	3
Hematite	50–200, 537	14.51	8.5	2.1

[a] Primary particle size (left) reported by the manufacturer and confirmed here by transmission electron microscopy characterization, and secondary particle size (right) in buffer solutions of pH 7. The secondary particle sizes were Z-averages calculated based on intensity-size distribution charts by dynamic light scattering.
[b] Measured using N$_2$ multi-point BET adsorption isotherms.
[c] pH of the point of zero charge, from references Schoonen (1994), Sahai and Sverjensky (1997) and Eggleston and Jordan (1998).
[d] From references Xu and Ching (1991), Xu and Schoonen (2000) and Gratzel (2001).

(2009) developed a protocol for the use of this probe in mineral slurries, which can also be used to determine H_2O_2 concentrations by adding horseradish peroxidase to the mineral slurry. Previous investigations into the mechanisms of ROS formation on oxides, especially titania and hematite, have explored a limited range of solution conditions resulting in conflicting inferred pathways. By comparing a wide range of environmental conditions, we are able to determine two distinct pathways for ROS generation on rutile/anatase versus hematite.

Before proceeding we provide below a brief background for the formation mechanisms of reactive radicals and intermediates in biogeochemical systems.

1.3. Potential mechanisms for formation of mineral surface-associated radicals and other reactive species

Radical formation at mineral surfaces involves photocatalysis, or reactions via soluble metals released through mineral dissolution, insoluble metals exposed at mineral surfaces, and mineral surface defects, both intrinsic to the crystal lattice and mechanically formed (Schoonen et al., 2006). The efficiency of photocatalysis in generating radicals and intermediates in minerals depends on the wavelength of the incident photons and on the electronic structure of the mineral. In particular, the electronic properties of relevance are the band gap energy (difference between conduction and valence band energies) and the absolute positions of band edges. Supra-band gap irradiation promotes electron transfer from the valence band (VB) to the conduction band (CB) at the mineral surface, leaving an electron vacancy (a hole) in the VB (Kiwi and Gratzel, 1979; Kraeutler et al., 1978; Xu and Schoonen, 2000). Depending on the specific band edge positions (i.e., their energy level) with respect to the highest occupied molecular orbital in the adsorbate, these holes may be capable of oxidizing a variety of surface-sorbed molecules including H_2O, O_2, CO, NH$_3$, and organic compounds, thus generating reactive radicals or intermediate species (Fig. 1). Photocatalysis in semiconductor colloids and thin-film systems, such as TiO$_2$, has been studied intensively since the 1980s, with a major focus on applications to waste-water treatment and energy conversion (Draper and Fox, 1989; Hagfeldt et al., 1994; Linsebigler et al., 1995; Ishibashi et al., 2000; Gratzel, 2001; Chen et al., 2002).