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Heterogeneous Oxidation of Ferrous Minerals by Chlorate and Bromate: Effect of Oxyhalogen Brines on Mars

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Ferrous (Fe(II) containing) minerals have been detected on the surface of Mars and in Martian meteorites. Ferrous minerals serve as the primary source of dissolved Fe(II)-ions in the aqueous systems on early Mars. Fe(II) has been shown to be oxidized by chlorate (ClO_3^-) and bromate (BrO_3^-) faster than O_2 and have been proposed to be important oxidants on Mars. Oxidized Fe has been reported to coexist with mineral hosts of Fe(II) at several locations on Mars. Ferrous minerals in contact with oxyhalogen brines could result in direct heterogeneous oxidation, forming Fe(III)-bearing mineral coatings. Here, we investigate the susceptibility of mineral-bound Fe(II) in pyrite (FeS_2) and pyrrhotite (FeS) to be oxidized by chlorate and bromate and the resulting mineral products via laboratory experiments under anoxic conditions in Mars-relevant fluids.

Sealed, Al-foil wrapped reactors containing pyrite and pyrrhotite (~2 g L^{-1}) were aged for ~60 days with ~10 and 100 mmol L^{-1} dissolved sodium chlorate or bromate in magnesium chloride or sulfate fluids at near-neutral to acidic pH at 25°C. The reactors were maintained under static conditions to mimic stagnant lacustrine conditions on Mars. The final fluid and mineral products were analyzed using standard analytical techniques. Pyrite and pyrrhotite showed extensive oxidation in all solutions forming goethite (α-FeOOH) and elemental sulfur. Solutions containing bromate in Mg-chloride fluids at acidic pH experienced faster oxidation than chlorate in Mg-sulfate fluids at near-neutral pH. The extensive oxidation of iron sulfide minerals suggests that oxyhalogen species could be responsible for heterogeneous oxidation of ferrous minerals on Mars. The oxidation of siderite, olivine, and Fe/Mg smectites by oxyhalogens will also be discussed.