

LONG-TERM MODELING OF OXIDATION REACTIONS IN ANOXIC GEOCHEMICAL ENVIRONMENTS: THE CASE OF MARS.

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Introduction: Growing information on Mars, based on spectroscopic data from rovers, has allowed find out important clues about the presence of stable water masses in early Mars [1] and drawing up the main lines of its geochemical evolution. One of most challenging questions about Mars geochemical conditions in the past, concerns the possible redox mechanisms that were able to transform the initial reducing environments and to sequentially induce the precipitation of oxides and sulfates.

Recent investigations about this topic have shown that mineral surfaces of sulfides and silicates can act as catalysts for the formation of highly reactive oxygen species (ROS) and high-valent iron species when reacted with water in strictly anoxic conditions, thus being potentially capable of transform anoxic environments to oxic ones in the long term [2].

The aim of this work is twofold: beginning with an alkaline scenario, derived from the interaction of basalt-bearing minerals with water, to explore the coeval evolution of both acid-base and redox states in an ocean approaching circumneutral pH, i.e., the actual steady state of Earth's oceans, through kinetically controlled geochemical calculations, including transitional halogen species (ClO^- , HClO) and iron superoxides ($\text{FeO}_4^{=}$, $\text{Fe}^{4+}=\text{O}_2^-$). Second, performing micro and nanostructural analysis of the resulting solid phases, through laboratory analogs. Silica garden structures built from iron salts, were used as an instantaneous mixing device for acidic iron-rich and alkaline silica-rich regions and were employed as a laboratory analogous of precipitation at the silica-iron interfaces in a dual acidic to basic environment.

Methods: Geochemical modeling was performed by starting from alkaline ($\text{pH}=12-14$) and oxidant ($\text{pe}=10-13$) conditions, thus placing the system within the stability field of iron (VI)-ferrate, as the stable phase, and Fe(V), Fe(IV) as possible transient species. For the modeling purposes a dissolution representative of the weathering of basaltic glass was used as initial solution. In such case, fast dissolution of basalt releases OH^- and causes the rise of pH to alkaline values. Oxidation was induced through volcanic outgassing, namely $\text{SO}_2(\text{g})$, $\text{H}_2\text{S}(\text{g})$, $\text{Cl}_2(\text{g})$, as source of volatile species. In such a situation iron oxidation takes place as an stepwise process, first inducing the formation of Fe^{+3} species, fol-

lowed by the rapid transformation to iron (IV), iron (V), and iron (VI), catalyzed by highly reactive chlorine species.

Acidification in the system was induced by varying $\text{CO}_2(\text{g})$ partial pressure. Additionally, in the case of Mars models, the geochemical evolution of both, aqueous species and solid phases was controlled by inducing evaporation/sublimation of water and volatils through time.

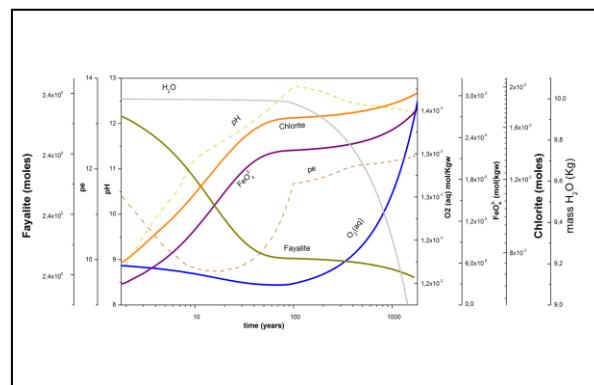
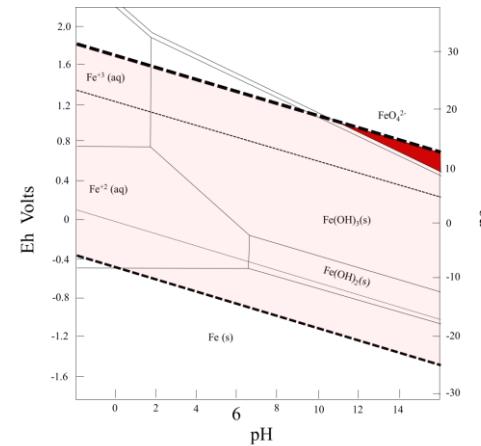


Figure 1: (a) Pourbaix diagram showing the starting conditions of the models and iron speciation. (b) dissolution of olivine from basalt allowing the generation of iron(VI) at very alkaline and oxidizing conditions.

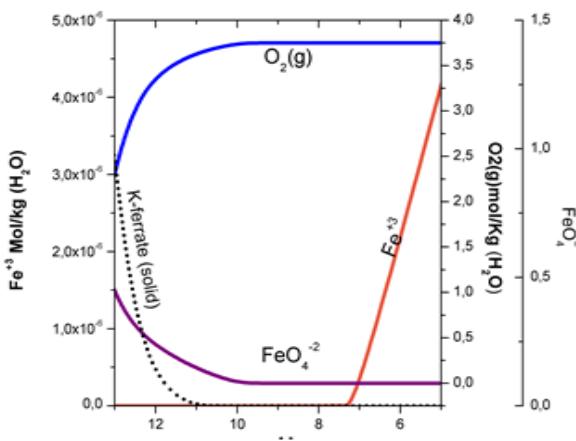


Figure 2: Evolutions of species during destabilization of iron(VI) when the pH reaches neutral values inducing precipitation of Fe^{+3} solid-phases and the formation of oxygen as a byproduct.

All geochemical calculations were carried out with PHREEQC software that was employed to determine the equilibrium concentration of chemical species and saturation indices. In addition, the kinetic evolution of solid phases was followed by using rate expressions based on the Transition State Theory.

We used silica gardens (SG) as laboratory models for *in situ* mixing of acidic-alkaline species. SG were made by reacting, either Melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) or Molybdate (FeCl_3) with sodium metasilicate, respectively as iron and silica sources. Experiments were performed on both, oxic and anoxic conditions. In the latter case, Na-dithionite was used to stabilize iron in the form of Fe^{+2} . Redox evolution of the process inside SG and across the silica membrane was followed in real time by cyclic voltammetry using Pt and Ag/AgCl electrodes.

Resulting textures, solid phases and species forming at the acidic-alkaline interface, on both, oxic and anoxic conditions, were analyzed by UV-VIS, HREM and optical microscopy.

Results: Geochemical modeling show that Fe-superoxides are formed transitionally along the evolution from alkaline-oxidant conditions to neutral pH values. Its further destabilization when the pH reaches neutral values causes the simultaneous precipitation of iron oxides and oxyhydroxides giving rise to the formation of oxygen as a byproduct. microstructural analysis conducted by using silica gardens also indicates that the precipitation takes place in the form of self-organized patterns, resulting in textures similar to the eutectic textures, with organization at different scales. HREM microstructural analysis shows that this organization is also extended to the molecular level, figure 3(b) inducing some incipient organization in the form of layered silicates.

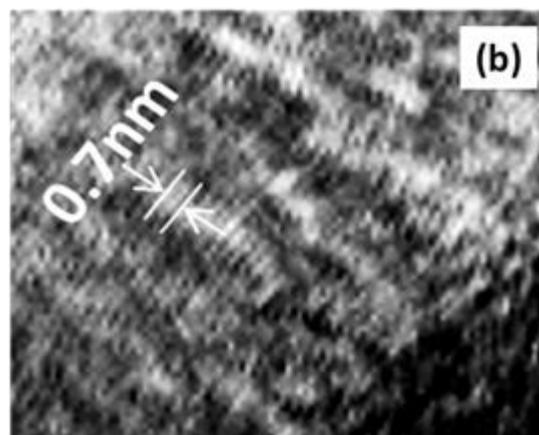


Figure 3: (a) SG microstructure formed by alternate Fe-Si bands. (b) hydrated silicates formed at SG showing layered nanostructures.

Conclusions: Both, laboratory analogous and geochemical models show the mixed precipitation of iron salts together with hydrated silicates when pH drops to neutral values as result of their dual pH stability behavior. Significantly, the model demonstrates that, although Fe-species are not soluble in alkaline conditions -the main argument against an Early soda ocean-iron superoxides, like FeO_4^{+2} are. Their destabilization near neutral pH conditions may induce the precipitation of Fe^{+3} solid phases, together with the generation of $\text{O}_2(\text{g})$ as a byproduct. This process also induces the formation of Fe-Si composites, selforganized as layered structures.

References:

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- [2] Dávila A.F. et al. (2008) Earth and Planetary Science Letters, 272, 456-463.

This work is supported by the Spanish Ministry of Science, MICINN, Project CGL2011-30079 .