Abiotic O_2 availability on an Early alkaline ocean through halogen-induced superoxide species

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Whether Early Earth oceans were acidic or alkaline and, if so what such a difference would imply in the further evolution of atmosphere and life, has been -and still is- a subject of great controversy. Because of the primitive ocean was in equilibrium with an atmosphere mainly composed of CO_2 it has been assumed the Hadean ocean was probably acidic. Alternatively, it has been suggested that reactions between sodium-rich silicates and atmospheric CO_2, leading to the formation of Na_2CO_3, may have produced an early soda ocean [1]. Both hypotheses are mainly supported by mass-balance calculations performed under the assumption of equilibrium conditions, while neglecting kinetic effects as well as simultaneous redox evolution resulting from reaction with volatiles other than CO_2.

The aim of this work is twofold: beginning with the 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. This was done through kinetically controlled geochemical calculations including transitional halogen species (ClO^-, $HClO$) and iron superoxides ($FeO_4^=$, $Fe^{4+}=O^{2-}$). Second, perform micro and nanostructural analysis through laboratory. Silica garden structures (SG), built from iron salts, were used as an instantaneous mixing device for acidic iron-rich and alkaline silica-rich regions and were used as a laboratory analogous. 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 of geochemical modeling show that Fe-superoxides are formed transitionally along the evolution from alkaline-oxidant conditions to neutral pH values. Significantly, the model demonstrates that, although Fe-species are not soluble in alkaline conditions -the main argument against an Early soda ocean- superoxides are. Their desestabilization near neutral pH conditions may induce precipitation of Fe^{+3} solid phases, together with $O_2(g)$ as a byproduct and gives rise to the formation of Fe-Si composites, selforganized as layered structures.

[1] Kempe and Degens (1985) *Chem. Geol.*, **53,** 95-108.

Thermodynamics of hydration of MX80 smectite derived from hydration isotherms

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Hydration energies contribute significantly to the stability of hydrated clay minerals. However, thermodynamic data of hydration for clay minerals are still poorly known. The present study aims to improve our comprehension of the hydration processes of sodic smectite MX80, and to implement a new methodology for extracting thermodynamic data of hydration of the smectite.

A first approach consists in applying a global hydration model to extract the thermodynamic data of total adsorbed water (G, H and S) from adsorption/desorption isotherms at 25°C and 45°C. The results are in good agreement with calorimetric data at 84 and 91% RH, from [1]. As capillary water, which is present in the intergranular porosity of the clay sample, does not contribute to the thermodynamic stability of the hydrated clay mineral, a refined calculation method has been implemented to discriminate hydration water from capillary water in the total adsorbed water. The so called "hydration water" refers to interlayer water and surface recovering water of the smectite. Contrary to capillary water, the amount of hydration water depends on the nature of the smectite (nature of interlayer cations, layer charge and location of the charge). The thermodynamic properties of capillary water are calculated according to [2]. The present method allows (i) to estimate the respective amounts of hydration and capillary waters and (ii) calculate the energies of formation of the hydration water.

This work is to be extended to other hydrated clay minerals in order to refine the solid solution model from [3] and to finally provide a global predictive model for clay mineral hydration energies.

[1] Gailhanou *et al* (2012) GCA **89**, 279-301. [2] Lassin *et al* (2005) GCA **69**, 5187-5201. [3] Vieillard *et al* (2011). GCA **75**, 5664-5685.