

ALTERATION OF METEORITE-DERIVED KAMACITE IN MARTIAN REGOLITH: A NEW INSIGHT OF CHEMICAL PROCESSES IN MARTIAN SOILS. G. Berger, Université Paul Sabatier; CNRS; IRAP, 14 Av. E. Belin, 31400 Toulouse, France.

Introduction: The alteration processes that have occurred billions year ago on the surface of Mars are not fully understood. Phyllosilicates and sulfate minerals discovered in several places on the Mars surface are the most visible secondary minerals and are used, besides the classical geomorphologic observations, to constrain the water history. Phyllosilicates are generally observed from orbit in old Noachian terrain [1], and more recently trioctahedral smectites were even characterized in drilled samples by the *Curiosity* rover at Gale [2]. For sulfate, many different minerals have been detected on the surface of Mars in the Burns Formation, at the *Phoenix* landing site, in Endeavour Crater, in North Polar dunes and are reviewed in [3].

More recent observations by *Curiosity* also evidenced the occurrence of akaganéite [3], a chlorine-bearing Fe(III) hydroxide (β -FeO(OH)Cl), also suspected in several other location by orbital detection [4]. This chloro-hydroxide, also used as electron acceptor in biomileralization experiments [5], occurs on the Earth in restricted conditions. When formed by a low temperature process, it is often associated with corrosion of metallic phases induced by chloride ions such as the atmospheric corrosion of carbon steel in marine environments [6] or as a corrosion products of native Fe,Ni metal grains of meteorites [7]. On Mars, [8] envisaged the possibility that crystalline hematite was derived from iron oxyhydroxide precursor minerals but the question of the origin of akaganeite was not specifically investigated.

We developed here the idea that the old martian regolith, which is assumed to be contaminated by meteoritic inputs, may have contained kamacite (Fe-Ni), a metallic phase from common in meteorites. The reaction of an iron based metal offers new perspectives for the alteration mechanisms. In particular, the redox potential of kamacite associated with protons-donnors like HCl-SO₃ issued from volcanic gas have an huge reactional potential. This potential is illustrated with simple batch experiments using kamacite or iron, JSC-Mars1 simulant and various HCl-H₂SO₄ acidic fluid.

Methodology: We carried out experimental interactions of H₂SO₄ and HCl brines with a material commonly used as a simulant of the Martian regolith, the JSC-Mars1, mixed with 10% of kamacite as slabs or iron as fine powder, between -17 and +25°C. JSC-Mars1 is the <1 mm fraction of weathered volcanic ash from Pu'u Nene, Hawaii. It is considered as a Martian regolith analogue [9] and its texture is presented in

Fig.1. The originality of these experiments is multiple : the use of a natural material previously altered and containing allophanes, mixed with a metallic phase, and under negative temperatures (in Celsius). The acid brines (0.01 to 1 molal) modelled a volcanic influence. Given the low water/rock ratio used (2.5), the high reactivity of metal with protons and the exchange capacity of allophanes, the primary acidity was quickly neutralized and the precipitation of secondary phases proceed under near-neutral pH.

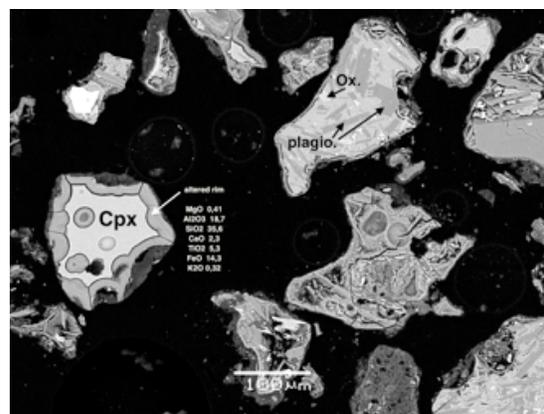


Fig. 1: Polished section of the JSC-Mars1 simulant.

Mineralogical transformation: The secondary phases were characterized by X-ray diffraction and scanning electronic microscopy (SEM). Two kinds of reactions were identified. In SO₄ dominated brines, gypsum formed at the surface or within the grains of the simulant. The lower temperatures promoted the larger crystals (Fig.2). In HCl dominated brine, akaganeite formed at the surface of the kamacite slabs (Fig.3). When Fe is supplied by iron powder, the high surface area and the high reactivity of the powder led a significant electron exchange between the solution and iron: H₂ bubbles are visible when opening of the experimental reactors (Fig.4).

Discussion and Conclusions : Combined with the chemical analyses of the reacted solutions, two main mineralogical reactions may be identified:

- 1) H⁺/cation exchange with the silicate fraction (most likely the allophanes) releasing Ca⁺⁺, as well as Al⁺⁺⁺ and Fe⁺⁺⁺ at low pH. The most visible mineral by-product is gypsum in concentrated sulfate solutions.
- 2) Electron exchanges between the metallic phase and H⁺ or H₂O. This reaction produces H₂ and promotes the formation of akaganeite at the metal surface in concentrated chloride solutions.

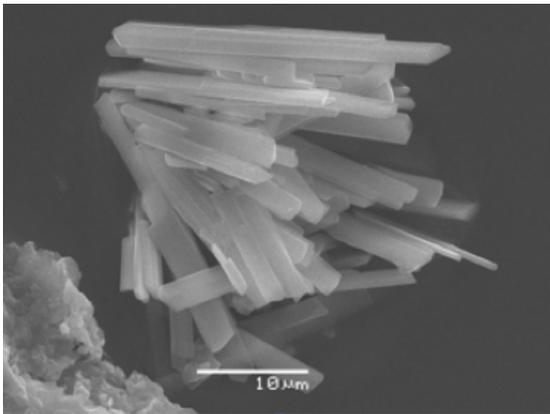


Fig. 2: Gypsum crystals produced at -17°C at the surface of the JSC-Mars1 reacted for 12 days with $1\text{m H}_2\text{SO}_4$.

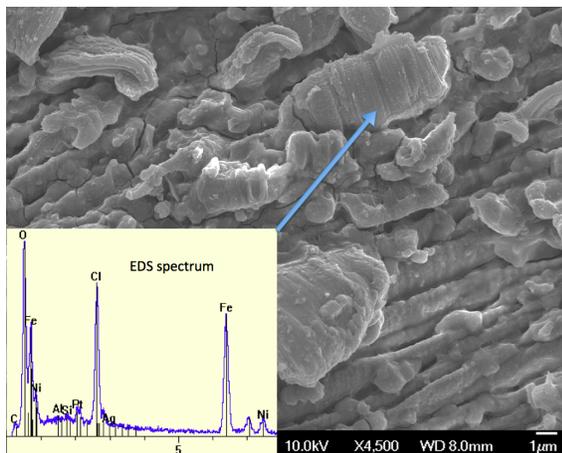


Fig. 3: Akaganeite coating a kamacite slab, after 12 days of reaction of kamacite-JSC-Mars1 mixture with $1\text{m H}_2\text{SO}_4$.



Fig. 4: Hydrogen bubbles at the opening of an experiment using iron powder.

The reaction 2) is also known to produce hydrogen free radical (H°) at the metallic surface. This highly reactive form of hydrogen, even if transitory, is able to reduce polyanions such as SO_4^{--} and NO_3^{--} reputed stable at low temperature ([10], [11]). So another expected mineral by-product of reaction 2) is the reduction of aqueous sulfate or pyrite (FeS_2 , an igneous sulphide) in troilite, pyrrhotite or mackinawite (FeS , the most reduced form of sulphide). In this perspective, it is interesting to note that pyrrhotite was also detected in the drilled samples by the *Curiosity* rover at Gale [2], in association with akaganeite.

References: [1] Ehlmann et al. 2013, *Space Sci. Reviews* 174, 329-364. [2] Vaniman et al., 2013, *Science*, doi:10.1126/science.1243480. [3] Gaillard et al., 2013, *Space Sci. Reviews* 174, 251-300. [4] Carter et al. 2014, *LPS Conf XXXV*, 2364. [5] Roh et al. 2003, *Clays & Clay Min.* 51, 83-95. [6] Cook et al., 1998, *Hyperfine Interact.* 113, 319-329. [7] Glotch et al., 2008, *Phys. Chem. Minerals*, 569-581. [8] Lee et al., 2004, *Geochim. Cosmochim. Acta* 68, 893-916. [9] Morris et al. (2001), *JGR* 106, 5057-5083. [10] Truche et al. 2013, *Applied Geochem.* 28, 155-163. [11] Truche et al. 2010, *Geochim. Cosmochim. Acta* 74, 2894-2914.

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