

IRON MINERAL FINE PARTICLES PRODUCED BY ACIDIC HYDROTHERMAL ALTERATION EXPERIMENTS OF THE SYNTHETIC MARTIAN BASALT. H. Isobe¹ and M. Yoshizawa^{1,2}, ¹Dept. Earth Envi. Sci., Grad. Sch. Sci. Tech., Kumamoto Univ., Kurokami, Kumamoto, 860-8555, Japan, isobe@sci.kumamoto-u.ac.jp ²Present address: JEOL Ltd., 1-2 Musashino 3-chome, Akishima, Tokyo 196-8558, Japan

Introduction: The constituent and its formation process of the Martian surface soil are fundamental problems to understand the current environment of the Mars. Especially, iron minerals should be the key component to characterize surface of “the red planet”. Recently, several probes and rovers provided direct analysis of the Martian surface materials. Martian global compositions with remote sensing data were accumulated by orbiters. Those data show occurrence and distributions of various iron minerals in the Martian global scale (e.g. [1-3]).

The formation processes of the iron minerals on the Martian surface are discussed by several authors with experimental or theoretical studies (e.g. [4-7]). Iron minerals are major alteration and weathering products in the terrestrial environments. The formation and evolution processes of iron minerals are good indicator of the surface environment (e.g. [8-11]) not only in the oxidative terrestrial environment but also in the Martian environment.

The major Martian volcanoes consist of iron-rich basaltic rocks. Volcanic activities of the Martian volcanoes should involve volatiles rich in sulfuric components and CO₂. CO₂ may have more essential role in the alteration processes related to fluids in Martian volcanic activities than that in the terrestrial volcanoes. In this study, hydrothermal alteration experiments are conducted to elucidate the soil formation processes on the Martian surface. We carried out alteration experiments of the synthetic iron-rich basaltic material simulated to the Martian basaltic rock with sulfuric acid and CO₂-bearing hydrothermal fluid. The composition of the synthetic Martian basalt in this work is based on cation component of the averaged surface soil acquired by the Mars Pathfinder rover [1].

Experimental: Experimental temperatures are 100 and 150°C. Acidities of the solutions are pH1.0, 3.0 or 7.0. Run durations are 1, 4, 8 or 16 weeks (100°C) or 1, 3, 6 or 12 weeks (150°C). Approximately 100 or 200 mg of powdered synthetic basaltic rock is sealed in Teflon vessels with 10 or 5 g of reaction fluid to keep 1:50 in rock/fluid ratios, respectively. CO₂ are introduced to the experimental vessels by appropriate mass of dry ice for approximately 1 MPa of CO₂ at the experimental temperature based on the volume of the vessels. Dry ice expelled the air and filled with CO₂ gas inside the vessels before complete sealing of the

vessels to avoid oxidative influence by oxygen in the terrestrial atmosphere. Run products are observed with a powder X-ray diffractometer (XRD) and a scanning electron microscope (SEM) and analyzed with an energy dispersive X-ray spectroscopy (EDS).

Results and Discussion: Run products show characteristic reddish (150°C) or dark brown color (100°C) depending on the acidity and temperature. Major epigenetic phases in the run products identified by XRD are iron oxide/hydroxide minerals. The peaks of hematite (Fe₂O₃) were observed in the run products of 100 and 150°C with pH1.0. The diffraction peaks of goethite (FeOOH) were observed in the run products of 100°C with pH1.0 only less than 56 days run duration. XRD identification of iron minerals and color of the run products are quite concordant. By contrast, with the reaction fluid of less acidic and neutral conditions, pH3.0 and 7.0, iron minerals were not detected by XRD in the same temperature and run durations.

With SEM, occurrence of characteristic petaloidal, radial or spherical iron oxide/hydroxide mineral fine particles were observed in the run products of 100 and 150°C. Especially, iron mineral fine particles produced in 100°C with pH1.0 solution show quite characteristic shape just like “iron mineral snow flakes” (Fig. 1). It should be noted that these iron mineral fine particles can be produced within several days with relatively low temperature hydrothermal conditions. Typical diameter of the iron mineral particles is small enough to be blown up by the Martian winds to cover the

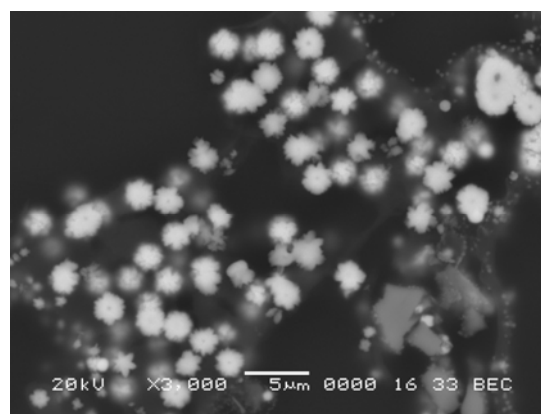


Fig. 1 Iron mineral particles in the run product of 100°C, pH1.0, 7 days. Petaloidal iron mineral particles up to several micron meters in diameter can be seen.

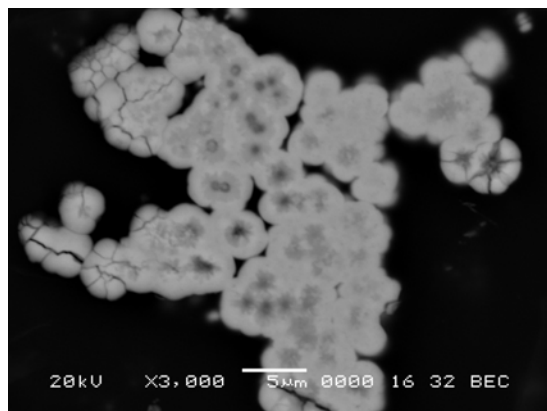


Fig. 2 Iron mineral particles in the run product of 150°C, pH1.0, 21 days. Iron mineral particles are relatively larger and more spherical than those produced in 100°C.

whole Martian surface. By SEM observations, major source of iron to the reaction fluid is iron rich glass phase in the starting materials. Mafic minerals including olivine and pyroxenes are less reactive in these conditions. No iron minerals are observed by SEM in the run products with more neutral fluid conditions as XRD identification. Iron minerals in the run product after 112 days show more crystalline shape but still have diameters less than 5 μm .

The shape of iron minerals produced in 150°C show smoother surface than those of 100°C products (Fig. 2). The dark core of iron mineral particles in 150°C run products may be relict of the precipitated hydrous seed at iron mineral nucleation. At 150°C, flaky hematite crystals can be found after 12 weeks in the run product with spherical particles.

Semi-quantitative EDS analysis of Fe/O ratios of produced iron minerals represented by Fe and O characteristic X-ray intensities were variable depending on the temperature and time (Fig. 3). At 100°C, Fe/O ratios in iron mineral particles distributed in wide range on both side of goethite standard mineral. Precipitation of iron mineral may be initiated in more hydrous and less crystalline phase than goethite, probably ferrhydrite. Hydrous goethite is altered to dehydrated and crystallized phase in more than 4 weeks reaction. At 150°C, iron mineral particles are precipitated as hydrous hematite, approximately identical to composition of the 100°C, 16 weeks run product.

Synthetic Martian basalt reacts with low pH fluid at relatively low temperature hydrothermal fluid even at 100 ~ 150°C. Spherical iron-oxide/hydroxide fine particles are significantly characteristic alteration products. Especially, iron mineral species and morphology strongly depend on temperatures and acidities of the hydrothermal fluid. Morphology of hematite

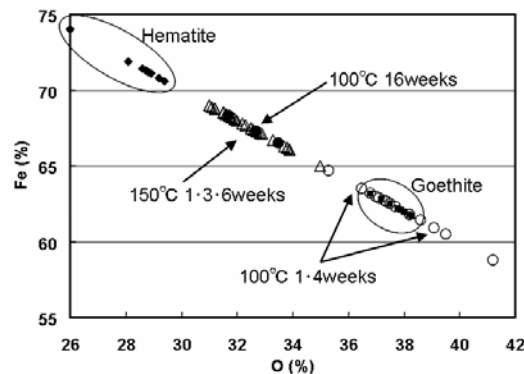


Fig. 3 Semi-quantitative ratios of iron to oxygen represented by Fe and O K α intensities of EDS spectra. \blacklozenge and \blacksquare represent the spectra of standard hematite (Fe_2O_3) and goethite (FeOOH) mineral, respectively.

reproduced by our experiment is quite similar to that of hydrothermal synthesized hematite by Golden et. al. (2008) [7] from synthetic acid-sulfate hydrothermal solutions. However, our experiments suppose only ordinary basaltic rocks and simple volcanic volatiles on the Mars, and do not depend on any specific solutions with iron compound species as starting conditions.

Acidic hydrothermal alteration of the typical iron-rich Martian volcanic rocks may have essential role to form the Martian soil which is rich in iron oxide. The Martian huge basaltic shield volcanoes may be convincing site of the alteration of the iron-rich Martian basaltic rocks with hydrothermal fluid with sulfuric acid. Iron mineral fine particles can spread out into the whole planet from the alteration site in the volcanic provinces by global dust storms. Thin and homogeneous layer of dust containing iron mineral fine particles produced in the Martian volcanoes may be charged with the reddish tone of the Mars. Direct observation of the Martian soil may provide us information on the conditions of hydrothermal alteration related to the Martian volcanic activities.

References: [1] Rieder, R. et. al. (1997) *Science*, 278, 1771-1774. [2] Lane, M. D. et. al. (2008) *Am. Mineral.*, 93, 728-739. [3] Tosca, N. J. and McLennan, S. M. (2006) *EPSL*, 241, 21-31. [4] Bishop, J. L. et. al. (2002) *JGR*, 107, E11, 5097. [5] Christensen, P. R. and Ruff, S. W. (2004) *JGR*, 109, E08003. [6] Barrón, V. et. al. (2006) *EPSL*, 251, 380-385. [7] Golden, D. C. et. al. (2008) *Am. Mineral.*, 93, 1201-1214. [8] Schwertmann, U. and Murad, E. (1983) *Clays Clay Minerals*, 31, 277-284. [9] Waychunas, G. A. (1991) in *Reviews in Mineralogy* Vol.25, 11-68. [10] Isambert, A. et. al. (2006) *EPSL*, 243, 820-827. [11] Davidson, L. E. et. al. (2008) *Am. Mineral.*, 93, 1326-1337.