

Transformation of jarosite to hematite in simulated Martian brines

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Abstract

The presence of jarosite – a hydrous iron sulfate – at Meridiani Planum supports the past existence of water on Mars surface. Thermodynamic calculations suggest that jarosite should transform to ferric oxyhydroxides in aqueous media. Here we show that jarosite can transform directly to hematite – the iron oxide identified at Meridiani Planum – in simulated Martian brines. Our results are consistent with a short aqueous history, but also indicate that jarosite can persist in highly saline Martian brines. The formation of goethite, a common iron oxyhydroxide on Earth, is prevented by the low water activity and/or high phosphate concentration of Martian brines.

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1. Introduction

Formation of jarosite on Mars has been attributed to (i) precipitation in acidic briny water bodies after evaporation [1], (ii) weathering by “acid fog” [2], (iii) aqueous oxidation of iron-sulfide mineral deposits [3,4], (iv) percolating acidic water interacting with basaltic materials [5], (v) deposition of volcanic ash followed by reaction with condensed SO₂– and water-bearing vapours emitted from fumaroles [6], and (vi) oxidative weathering of sulfides and acid sulfate formation in water films within deposits from turbulent flows of rock fragments, sulfides and brines caused by meteorite impact [7]. Irrespective of its formation conditions, equilibrium thermodynamic simulations indicate that jarosite can persist

over geologic timescales only in arid (i.e. low water activity) environments on Mars [8]. Jarosite is predicted to be stable under present Martian atmospheric conditions [9], allowing for the preservation of jarosite in the ancient Meridiani outcrops for several billion years [1].

Jarosite and hematite are suggested to be the main iron-bearing minerals from Mössbauer analyses of outcrop rocks at Meridiani Planum [10]. Both minerals are closely associated, as they are found in all analyses of outcrop rocks in Eagle Crater by the Opportunity Mössbauer spectrometer, which has an ~1.5 cm diameter target area and 0.2–3 mm sampling depth [10]. The exact textural relationships between jarosite and hematite have not been properly elucidated, but the hematite spherules likely do not contain jarosite [11]. Non-spherule hematite is also found dispersed throughout the outcrop matrix, as is jarosite [11]. Equilibrium calculations for simulated Martian fluids predict the disappearance of jarosite in

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favour of a $\text{Fe}(\text{OH})_3$ phase for $\text{pH} > 4$ [8]. Detailed geochemical modelling of acidic evaporative processes at Meridiani Planum, predicts jarosite to transform to goethite during fluid recharge events [12]. This prompted us to investigate the nature of the possible transformation pathways of jarosite to hematite and the environmental factors controlling such transformation. To this end, we synthesized jarosite in the laboratory and examined its transformation in simulated Martian brines of different composition.

2. Materials and methods

2.1. Jarosite synthesis and properties

Jarosite was prepared by adding a concentrated solution of KOH to 160 ml of a brine containing 0.1 mol of $\text{Fe}_2(\text{SO}_4)_3$, 0.4 mol MgSO_4 , 0.04 mol of AlCl_3 , 0.06 mol of Na_2SO_4 , 0.002 mol of CaCl_2 , 0.004 mol of MnSO_4 and two amounts (0 or 0.004 mol) of KH_2PO_4 until pH was 2. [The relative atomic proportions of the cations in this brine were similar to those of the soils analyzed at Meridiani Planum by the Alpha Particle X-ray Spectrometer [13] with the exception of Al, Mn and Ca. These were added in smaller proportion to prevent precipitation at higher pH (Al, Mn) or by sulfate (Ca) in some of the experiments described below. The relative proportion of sulfate and chloride ($\sim 6:1$) was also similar to that of S:Cl in the Meridiani Planum soils. In summary, the composition of this solution attempts to simulate a brine derived from the weathering of rocks on the Mars surface]. The ~ 220 -ml resulting suspension was then gently, magnetically stirred at 298 K for 14 days. At that time, the solids consisted exclusively of jarosite, which was analyzed by the methods described below. Its structural formula was $(\text{K})_{0.57}(\text{Na})_{0.01}(\text{H}_3\text{O})_{0.42}(\text{Fe})_{2.28}(\text{SO}_4)_2(\text{OH})_{3.84}(\text{H}_2\text{O})_{2.16}$ and Munsell dry colour 4.8Y 8.4/3.1. The structural parameters resulting from the Rietveld analysis were $a = 0.731$ nm and $c = 1.710$ nm, consistent with a K- H_3O jarosite with a minor Na component (ICDP-PDF File No. 22-0827). The room temperature Mössbauer spectrum with an isomer shift of 0.39 mm s^{-1} and a quadrupole splitting of 1.16 mm s^{-1} also indicated a nearly Na-free jarosite [14]. Its specific surface area by the BET method with N_2 adsorption was 15 m² g⁻¹ and micropore surface 6 m² g⁻¹.

2.2. Ageing experiment

Portions of the jarosite suspensions prepared with or without PO_4 (first factor) were mixed with saline solutions of the same ionic composition as the one used in

the synthesis [except for the presence of Fe(III) and PO_4], deionized water and diluted KOH at different proportions so that the resulting ionic strength (I) of the suspension solution (second factor) was either 0.01, 0.25 and 2.2 M and the pH (third factor) was either 4, 6 or 8. The suspensions were aged for 180 days at a temperature (fourth factor) of either 303 or 333 K. During ageing, pH and salt concentration were periodically adjusted to the target values. After ageing, the suspension was centrifuged and the sediment washed with deionized water until free of salts (electrical conductivity of the equilibrium solution < 0.01 dS m⁻¹) and freeze dried.

2.3. Chemical and mineralogical analyses

The concentrations of Fe, K and Na in the initial jarosite were determined after dissolving 25 mg of the product in 1 ml of cold 11 M HCl. Then, Fe in solution was determined by the *o*-phenathroline method [15] and K and Na by flame emission photometry. From these data, the formula was calculated according to Drouet and Navrotsky [16]. The powder X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer equipped with $\text{CoK}\alpha$ radiation and a graphite monochromator at a step size of $0.05^\circ 2\theta$ and a counting time of 25 s. Unit cell parameters were calculated through Rietveld refinement using the PowderCell software [17]. Mixtures of external standards of hematite, goethite, ferrihydrite, lepidocrocite, and the initial jarosite were used to semiquantitatively estimate the proportions of these minerals in the products, except for samples containing $< 6\%$ hematite. The reflectance (R) spectrum of the solids was acquired at intervals of 0.5 nm in the range 380–710 nm range with a UV-Vis-NIR Spectrophotometer Cary 5000 equipped with a diffuse reflectance attachment and converted to tristimulus values (X, Y, Z) according to the CIE colour-matching spectral energy distribution weighted for CIE Source C [18] and then to the Munsell hue, value and chroma using the method given by the Munsell conversion program (www.munsell.com). The characteristic jarosite band at ~ 435 nm [19] and hematite band at ~ 535 nm [20] were used to estimate semiquantitatively the proportion of hematite in the jarosite/hematite that contained $< 6\%$ hematite. As a proxy for the true band intensity we used the difference in ordinate between the minimum (that indicates the band position) and the next maximum in the second derivative of the Kubelka-Munk function $[(1-R)^2/2R]$ spectrum (SDKM spectrum). We prepared different mixtures of jarosite and hematite and plotted the hematite/jarosite band intensity ratio (obtained from

the SDKM spectra) against the proportion of hematite. An excellent linear relationship ($R^2=0.997$) up to 6% hematite was found, so the corresponding regression line was used to estimate the hematite content in jarosite/hematite mixtures. For the calibration we used the same jarosite used in our ageing experiments and hematite that was prepared by ageing such jarosite in water at pH 7 and at 373 K for 30 days.

Mössbauer spectra were collected at room temperature with an EG and G constant accelerator spectrometer in transmission mode. The source of nominal activity (10 mCi) was ^{57}Co in an Rh matrix. The velocity scale was calibrated from the magnetic sextet of a high purity iron foil absorber. Experimental data were fitted to Lorentzian lines by using a least square-based method. The goodness of the fit was controlled by the χ^2 test. The isomer shift is given relative to the centre of the $\alpha\text{-Fe}$ spectrum at room temperature.

Scanning electron microscopy (SEM) of gold-coated particles deposited on muscovite flakes were examined on a SIRION FEG microscope. Transmission electron micrographs (TEM) were acquired with a JEOL JEM-2010 equipment after dispersing small portions of the powder in water and depositing small drops of the suspension onto a carbon copper grid.

3. Results and discussion

As can be seen from Fig. 1 (products after 180 days of ageing), the degree of transformation of jarosite to hematite and/or other Fe (hydr)oxides (ferrihydrite, goethite and lepidocrocite) was greater at 333 than at 303 K, but temperature did not affect the overall mineralogy of the products. In the two suspensions where the transformation product consisted exclusively of hematite and goethite (low I , no PO_4 , pH 6), the hematite/goethite ratio was higher at 333 than at 303 K, consistent with thermodynamic calculations [21]. With increasing pH, the degree of transformation increased, so more hematite and/or goethite was formed at pH 6 than at pH 4 and complete conversion into Fe (hydr)oxides occurred after ageing at pH 8 for all experiments. The increase in I (i.e., decrease in water activity) resulted, at pH 4 and 6, in significant decrease in the degree of, or no transformation, and, at pH 8, in less formation of hematite and/or lepidocrocite relative to ferrihydrite. The effects of adding PO_4 were to (i) suppress the formation of goethite (that in the absence of PO_4 was formed at only pH 6 and low I), (ii) hinder jarosite transformation at pH 4 and 6, and (iii) favour the formation of lepidocrocite at pH 8 and $I=0.25$ M.

At pH 8, 2 days were sufficient for complete transformation of jarosite to ferrihydrite (data not shown),

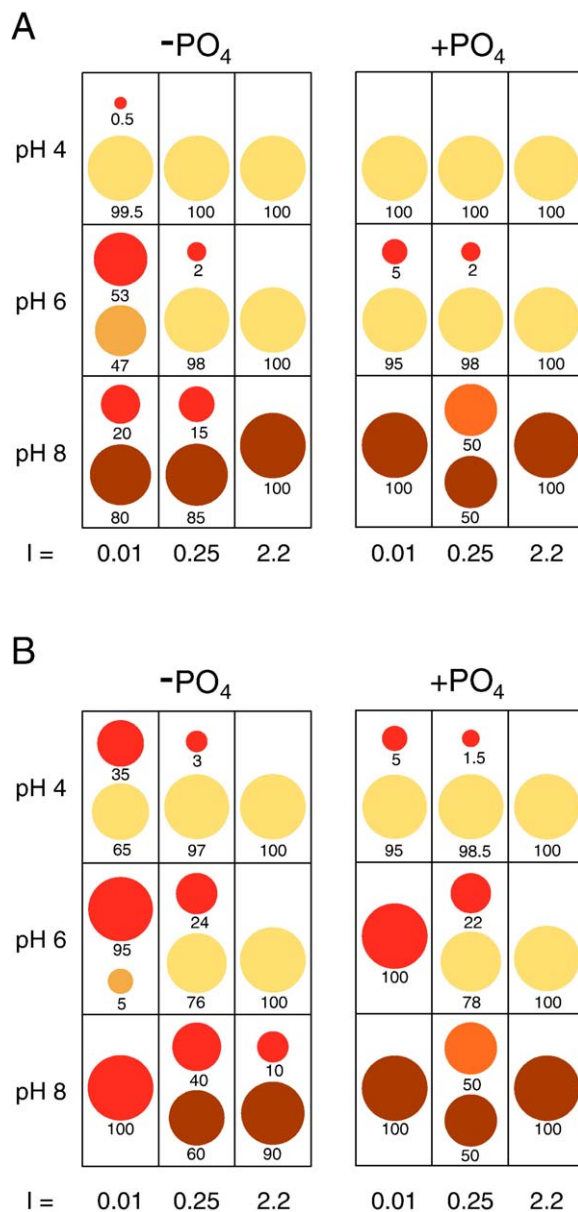


Fig. 1. The products of transformation of jarosite aged in solutions of different ionic strength ($I=0.01$ M, 0.25 M, and 2.2 M) and pH, and containing phosphate or not (+ PO_4 , - PO_4). (A) Ageing at 303 K; (B) ageing at 333 K. The circles are pale yellow for jarosite, red for hematite, brownish yellow for goethite, dark reddish brown for ferrihydrite, and orange for lepidocrocite. The percentage of each component in the different boxes is indicated below the corresponding circle. To help reader's eye, the diameter of each circle is proportional to the corresponding percentage raised to 1/3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

which gradually evolved to hematite or lepidocrocite. The transformation of jarosite to hematite or hematite/goethite that took place at pH 4 or 6 was slower and

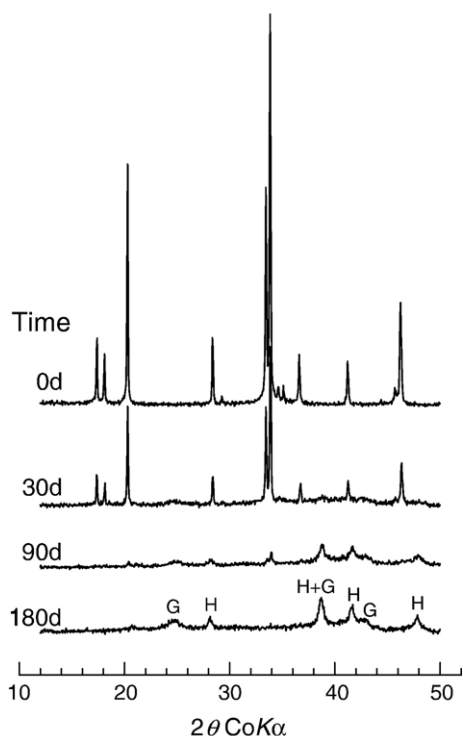


Fig. 2. Powder X-ray diffraction patterns of the products of transformation of jarosite aged at 303 K for 0, 30, 90, and 180 days in a phosphate-free solution of pH 6 and ionic strength 0.01 M.

occurred without the appearance of intermediate phases, as illustrated by the XRD patterns for the transformation products at pH 6 and $I=0.01$ M (Fig. 2). The corresponding SE micrographs (Fig. 3) show the fresh jarosite to consist of 200–1000 nm subspherical particles exhibiting irregular surface cracks. On ageing, the particles became slightly smaller and the surface cracks widened, so that the particles adopted framboidal morphology (Fig. 3D). The TE micrographs (Fig. 3E) showed this product to consist of ~ 50 nm aggregates, with some individual particles exhibiting typical goethite habits (hexagonal twins, short laths), consistent with the semiquantitative XRD estimations (47% goethite, 53% hematite). Neither the XRD patterns nor the microscopic images provided any indication of the presence of other mineral phases during ageing.

In our experiments, high ionic strength and/or presence of PO_4 prevent the formation of goethite, but only hinder the formation of hematite from jarosite. These results are in line with experiments on the crystallization of ferrihydrite, which demonstrated the pro-hematitic/anti-goethitic effect of high I [22] and PO_4 [23]. We suggest that these environmental conditions may determine the apparent absence of goethite at Meridiani

Planum landing site. The Meridiani Planum rocks are rich in phosphorus (~ 1 wt.% P_2O_5 [13]), as are a number of rocks at Gusev Crater [24]. Acidic weathering should release substantial amounts of PO_4 into solution due to high solubilities and dissolution rates of apatite minerals in low pH fluids [25,26]. According to our results, high concentrations of dissolved phosphate prevent the jarosite to goethite transformation, irrespective of the ionic strength. On the contrary, in waters with low concentrations of salts and PO_4 , as is the case with the

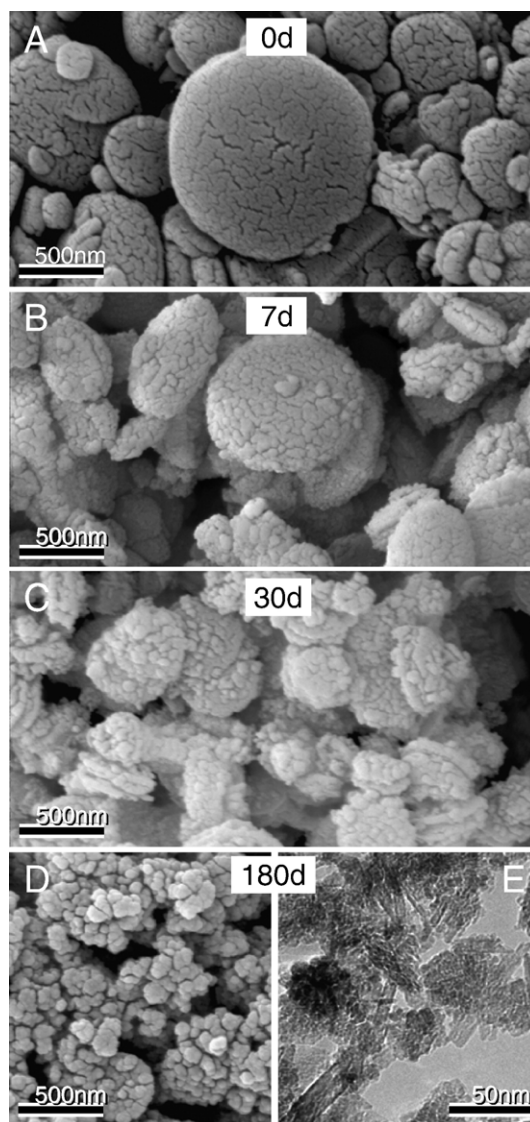


Fig. 3. Scanning electron (SE) and transmission electron (TE) micrographs of the transformation products of jarosite aged at 303 K in a phosphate-free solution of pH 6 and ionic strength 0.01 M. (A)–(D), SE micrographs at 0, 7, 30, and 180 days, respectively. (E) TE micrograph at 180 days.

Rio Tinto in the wet season, jarosite is hydrolyzed to nanophase goethite but not hematite [27]. Our results also indicate that goethite and hematite are direct products of the hydrolysis of jarosite. The alternative hypothesis that hematite is formed by dehydration of poorly crystalline goethite [12,27] may not hold true despite thermodynamic calculations indicating that poorly crystalline goethite is unstable relative to coarse grained hematite [12,28]. Indeed, the solid phase transformation of goethite to hematite in low-temperature terrestrial surface environments has never been substantiated [21].

Our results also suggest that the hydrolysis of jarosite in hypothetical Martian alkaline brines is unlikely to result in formation of goethite probably because (i) jarosite first hydrolyzes to ferrihydrite, and (ii) the formation of goethite from ferrihydrite has been found to be hindered at slightly alkaline pH [21], suppressed at high ionic strength [22], and retarded in the presence of PO_4 [23]. The high phosphate content of Martian rocks would seem a crucial factor for the formation of hematite via other proposed pathways, since weathering of these phosphate-rich rocks could lead to high phosphate concentration in Martian fluids, and phosphate has been shown to be important in the formation of hematite, maghemite and lepidocrocite [29,30].

Because of the relatively rapid jarosite to hematite transformation, the identification of both jarosite and hematite in sulfate-rich outcrop rocks at Meridiani Planum suggests that the disappearance of an aqueous phase may have been abrupt at this site. Alternatively, we can speculate that jarosite was not completely transformed to hematite because the aqueous phase became highly saline due to evaporation and remained so for an unspecified period. If jarosite and hematite are genetically unrelated and were precipitated from different solutions that varied both chemically and temporally at the Meridiani landing site, our experimental results of the rapid hydrolysis of jarosite to ferric oxide or oxyhydroxide phases would suggest that any fluid recharge events after jarosite formation must have been short in duration (though a persistent highly saline fluid cannot be ruled out at this time).

In summary, our results suggest that direct transformation of jarosite to hematite can occur under acidic conditions at low temperature, without intermediate ferric oxyhydroxide phases. The presence of high dissolved phosphate can suppress the jarosite to goethite transition, and leads to direct transformation of jarosite to hematite under circum-neutral pH conditions. The prolonged diagenetic history proposed for the Burns formation [11] suggests that jarosite may have been a relatively late precipitate, rather than an early-forming

mineral. Jarosite mineralization could even be a much later feature of the Burns formation, such as during transient aqueous activity due to extreme obliquity cycles [31]. The rapid kinetics of the jarosite–hematite transformation suggests a relatively transient period of liquid water at Meridiani Planum. The transient nature of water at the site would not seem conducive to the evolution of Martian biota at this site.

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