

# Transformation of Precursor Iron(III) Minerals in Diagenetic Fluids: Potential Origin of Gray Hematite at Vera Rubin Ridge

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## Key Points:

- Jarosite transforms to gray hematite at 200 °C in both sulfate- and chloride-rich fluids.
- Other iron(III) minerals (goethite, akaganeite, ferrihydrite, schwertmannite, and red hematite) do not convert to gray hematite.
- Jarosite may be a viable precursor mineral to the gray hematite found at Vera Rubin ridge, Gale crater, Mars.

**21 Abstract**

22 Coarse-grained ( $> 3\text{-}5\ \mu\text{m}$ ) gray hematite particles occur at Vera Rubin ridge (VRR)  
23 within Gale crater, Mars. VRR has likely undergone multiple episodes of diagenesis, at least one  
24 of which resulted in the formation of gray hematite. The precursor mineralogy and nature of the  
25 diagenetic fluids that produced coarse-grained hematite remain unknown. Analog laboratory  
26 experiments were performed on a variety of iron(III) minerals to assess the potential fluid  
27 conditions and precursor mineralogy that form coarse-grained hematite. Gray hematite formed  
28 from the transformation of jarosite after 20 days at  $200\ \text{°C}$ . Conversion was complete in chloride-  
29 rich fluids but substantial jarosite remained in sulfate-rich fluids; no transformations of jarosite  
30 occurred when aged at  $98\ \text{°C}$ . All other precursor minerals (akageneite, ferrihydrite, goethite, and  
31 schwertmannite) did not transform or produced only red, fine-grained hematite under all  
32 conditions assessed. In addition, seeding precursor iron(III) phases with red hematite and  
33 coarsening pre-existing red hematite both failed to produce gray hematite. These results suggest  
34 that jarosite was the precursor of gray hematite at VRR and the diagenetic fluids were low in  
35 sulfate and potentially chloride-rich. Jarosite produces gray hematite because the acidic  
36 conditions it generates yield both a low degree of hematite supersaturation, producing few  
37 nuclei, and high dissolved iron concentrations, enabling rapid hematite growth. Gray hematite  
38 readily forms under oxic conditions and its occurrence at VRR is not a marker for a redox  
39 interface. The associated diagenetic event was thus unlikely to have generated substantial new  
40 chemical energy for life.

41

42 **Plain Language Summary**

43 Hematite is often formed from other pre-existing iron-bearing minerals in water-rich  
44 environments. Depending on its grain size, hematite can be either red (fine-grained) or gray  
45 (coarse-grained) and these grain sizes likely indicate distinct past conditions. Gray hematite has  
46 been observed at Vera Rubin ridge (VRR) in Gale crater, Mars but how it formed is currently  
47 unknown. Laboratory experiments in this study demonstrate that jarosite, an iron- and sulfur-  
48 bearing mineral, converts to gray hematite in chloride-rich and sulfate-poor fluid conditions at  
49 elevated temperatures. Other iron(III)-bearing minerals (akageneite, ferrihydrite, goethite,  
50 schwertmannite, and fine-grained hematite) did not transform to gray hematite under any  
51 experimental conditions studied. The gray hematite at VRR likely formed by conversion from  
52 jarosite during alteration after the sediments in Gale crater had already formed. This event did  
53 not require reducing conditions and thus did not provide any new chemical energy for life.

54

55 **Key words**

56 Hematite, Jarosite, Vera Rubin ridge, Diagenesis, Gale crater, Mars

57

## 58 **1 Introduction**

59 Vera Rubin ridge (VRR) is a topographically-distinct sedimentary unit exposed on the  
60 northwestern slope of Aeolis Mons, the 5-km-tall central peak within Gale crater, Mars (Edgar et  
61 al., 2020). Also known as “hematite ridge,” VRR has been identified as a hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)-  
62 bearing unit based on the strong ferric absorptions (attributed to the presence of crystalline  
63 hematite) throughout the ridge by both the Compact Reconnaissance Imaging Spectrometer for  
64 Mars (CRISM) onboard the Mars Reconnaissance Orbiter (MRO) and the Mars Science  
65 Laboratory (MSL) Curiosity rover (Fraeman et al., 2013; Fraeman et al., 2016; Fraeman, Johnson,  
66 et al., 2020; Johnson et al., 2016). Notably, within VRR are two separate particle sizes of hematite,  
67 each with distinct spectral characteristics (Fraeman, Johnson, et al., 2020; Horgan et al., 2020).  
68 Fine-grained hematite, also called “pigmentary hematite,” is distinctly red in color but transitions  
69 to gray-colored, coarse-grained hematite at a particle size around 3-5  $\mu$ m (Catling & Moore, 2003;  
70 Kerker et al., 1979; Lane et al., 2002; Morris et al., 2020). In addition to the widespread  
71 occurrences within VRR (Horgan et al., 2020), gray hematite has also been observed on Earth,  
72 such as in basaltic sediments at Maunakea volcano in Hawaii (Morris et al., 2020), Proterozoic  
73 banded iron formations (BIFs) (Fallacaro & Calvin, 2006), and sandstone injectites (Jensen et al.,  
74 2018), as well as on Mars at Meridiani Planum, Aram Chaos, and Valles Marineris (Christensen  
75 et al., 2001).

76 The formation of well-crystalline gray hematite rather than the more common fine-grained,  
77 red hematite in localized regions of VRR and other locations on Earth and Mars may be the result  
78 of distinct formation conditions that, in the case of VRR, are likely diagenetic (Bennett et al.,  
79 2021). VRR is composed of two hematite-bearing members of the Murray formation: the  
80 Pettegrove Point member and the Jura member (Edgar et al., 2020). Red hematite is found  
81 throughout both members, but gray hematite is primarily observed within the Jura member,

82 crosscutting the surrounding strata, which further supports its diagenetic origin (Horgan et al.,  
83 2020). VRR is primarily composed of thinly-laminated mudstones with distinctive diagenetic  
84 sedimentary features, including nodules, Ca sulfate veins, crystal molds, and cross-cutting color  
85 variations (Edgar et al., 2020) that are often associated with coarser-grained rock targets (Bennett  
86 et al., 2021). The mineralogy and geochemistry of VRR also provide further evidence for multiple  
87 stages of diagenetic fluid events in the past (McAdam et al., 2020; Thomas et al., 2020). The  
88 hydrogen content in samples from VRR is variable, which indicates rocks at Gale crater were  
89 possibly exposed to other aqueous activity besides that associated with a paleolake (Thomas et al.,  
90 2020). Additionally, the highest hydrogen content was frequently associated with larger grain sizes  
91 within VRR sediments which supports the argument for the formation of gray, coarse-grained  
92 hematite from fluid interactions (Thomas et al., 2020).

93         Compared to the recessive strata below it, VRR is also particularly resistant to weathering  
94 and maintains a distinct topographic profile, which may be the result of diagenesis (Edgar et al.,  
95 2020). Whether this increased resiliency of VRR mudstone units is due to cementation,  
96 mineralogy, or coarser grain sizes is yet to be determined. Despite substantial evidence for several  
97 past episodes of aqueous diagenesis in Gale crater (Edgar et al., 2020; Fraeman, Edgar, et al., 2020;  
98 Frydenvang et al., 2017; Horgan et al., 2020; Stack et al., 2014; Thomson et al., 2011), the origin  
99 and nature of the permeating fluids, as well as the precursor mineralogy, remain unclear.  
100 Diagenetic fluid temperatures, acidities, salinities, and compositions are not well-constrained for  
101 VRR. Identifying candidate minerals and the range of possible fluid conditions that generate gray  
102 hematite provides insight into past diagenetic events and the potential for ancient habitable  
103 conditions at Gale crater.

104           The purpose of this study is to investigate the transformation products of iron(III) minerals  
105 subjected to simulated diagenetic fluid conditions and identify potential pathways to gray hematite.  
106 Iron(III) minerals were aged in a variety of Mars-relevant fluids to assess the impact of variable  
107 initial pH values, background salts, and temperatures on the reaction products formed. Mineralogy  
108 and crystallinity of the solid transformation products were determined, including identification via  
109 grain size-dependent spectral features in the visible wavelengths. This study provides a broad  
110 assessment of potential precursors to well-crystalline hematite that are either directly observed on  
111 Mars or expected to occur given its geologic history.

## 112 **2 Methods**

### 113 **2.1 Precursor mineral synthesis**

114           Akaganeite ( $\beta\text{-FeO}_{1-x}(\text{OH})_{1+x}\text{Cl}_x$ ), ferrihydrite ( $\sim\text{Fe}_{10}\text{O}_{14}(\text{OH})_2\cdot n\text{H}_2\text{O}$ ), goethite ( $\alpha\text{-}$   
115  $\text{FeOOH}$ ),  $\sim 60$  nm red hematite,  $\sim 10$  nm red hematite, schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_8\cdot$   
116  $x(\text{SO}_4)_x\cdot n\text{H}_2\text{O}$ ), and potassium jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) were synthesized according to standard  
117 laboratory techniques (see supporting information for full details). It was necessary to produce  
118 multiple batches for some experiments due to constraints on the mass of mineral produced in each  
119 synthesis. Each synthesized mineral was washed, dried in a convection oven at  $\sim 40$  °C (ferrihydrite  
120 was dried in a desiccator instead of by heating because of its instability at elevated temperatures),  
121 and ground to a powder in a mortar and pestle. The mineralogical purity of each synthesis product  
122 was evaluated via powder X-ray diffraction (XRD).

123

### 124 **2.2 Simulated diagenesis experiments**

125           Laboratory experiments were performed to approximate potential conditions under which  
126 precursor iron(III) minerals (akaganeite, ferrihydrite, goethite, red hematite, jarosite, and

127 schwertmannite) may transform (or coarsen) diagenetically to gray, coarse-grained hematite in an  
128 aqueous setting. For each initial mineral, ~1.6 to 2 g were suspended in ultrapure water and added  
129 to a salt solution containing either magnesium chloride or magnesium sulfate to create a 20 mL  
130 mineral suspension; chloride and sulfate salts have been observed throughout VRR via Sample  
131 Analysis at Mars (SAM) and Chemistry and Mineralogy (CheMin) analyses (Clark et al., 2020;  
132 McAdam et al., 2020; Rampe et al., 2020). Total salt concentrations in final solutions were set to  
133 1 mol L<sup>-1</sup>. Additional experiments on goethite and ferrihydrite were conducted with small amounts  
134 of ~60 nm hematite added to seed the transformations. A 1:9 molar ratio of hematite to goethite or  
135 ferrihydrite was added, assuming chemical formulas of  $\alpha$ -FeOOH and Fe<sub>10</sub>O<sub>14</sub>(OH)<sub>2</sub> for goethite  
136 and ferrihydrite, respectively. Each 20 mL mineral suspension was adjusted to a pH value of either  
137 3 or 7 via dropwise additions of 1 mol L<sup>-1</sup> hydrochloric acid and 1 mol L<sup>-1</sup> sodium hydroxide. Since  
138 jarosite has the ability to generate substantial acidity through the release of H<sup>+</sup> as it dissolves and  
139 reacts quickly with added base, the solution pH was set before adding this mineral and the pH then  
140 freely evolved during reaction. Additional jarosite experiments used 0.1 mol L<sup>-1</sup> salt concentrations  
141 to investigate the impact of different anion concentrations. The resulting mineral suspensions were  
142 heated in a digital convection oven for 20 days at 98 °C in polypropylene tubes sealed with PTFE  
143 thread seal tape or 200 °C in PTFE-lined bombs (Parr Instrument Co.) to minimize fluid  
144 vaporization; the 98°C experiments resulted in ~20-30% evaporative loss of the solution.

145

### 146 **2.3 Mineral and fluid characterization**

147 After aging for 20 days at elevated temperatures, the experiments were ended and the  
148 sample products were cooled to room temperature. The resulting suspensions were passed through  
149 0.22  $\mu$ m mixed cellulose ester (MCE) filters via syringe filtration to isolate the fluids from the

150 solid product. The final pH values of the fluids were measured, and final dissolved iron (as well  
151 as potassium and sulfur for experiments involving jarosite) concentrations were determined via  
152 inductively-coupled plasma optical emission spectrometry (ICP-OES) using a Thermo iCap 7400  
153 Duo instrument. Each fluid sample was measured 3 times, and the raw counts were averaged. The  
154 uncertainties in the slope and intercept of the calibration curves, obtained by linear regression,  
155 were propagated with the standard deviations of the measurements reported by the instrument to  
156 obtain concentration errors.

157         The solid products were washed with ultrapure water either via syringe filtration, vacuum  
158 filtration, or centrifugation to remove residual salts, dried in a convection oven, and ground with  
159 a mortar and pestle. The powdered mineral products were then analyzed via powder XRD and  
160 visible to near infrared (VNIR) reflectance spectroscopy. VNIR spectroscopy was performed on  
161 the solid transformation products using an Analytical Spectral Devices (ASDs) portable VNIR  
162 spectroradiometer to identify key absorption features. The resulting spectra were splice-corrected  
163 to reduce the offsets at ~1000 and ~1825 nm between each of the three built-in detectors. Powder  
164 XRD was performed using a Bruker d8 Advance powder X-ray diffractometer, Cu X-ray source  
165 (40 kV and 40 mA), step size of 0.02° per step, and counting time of 0.5 seconds per step for each  
166 measurement. A LynxEye XE energy-dispersive strip detector was used for data collection. Each  
167 of the 192 detector strips separately measures a given  $2\theta$  value for the stated counting time, giving  
168 a total integration time per point of 96 s. Final mineral abundances and coherent scattering domain  
169 sizes were determined using Profex to perform Rietveld refinement on the XRD patterns (Doebelin  
170 & Kleeberg, 2015).

171         For samples with a coherent scattering domain (CSD) size greater than ~100 to 200 nm,  
172 the peak width is determined by instrumental broadening rather than the actual domain size.

173 Therefore, select samples with large CSD sizes were imaged with a Thermofisher Quattro S  
174 Scanning Electron Microscope (SEM) to examine both the morphology and particle size of the  
175 solid products. CSD size indicates the size within an individual crystallite where atomic structure  
176 is uniform and X-rays are scattered coherently, whereas particle size refers to the visual size of  
177 discreet grains, which may be agglomerates of smaller crystals. When particles are single crystals  
178 and not aggregates, the CSD size is equal to the particle size. The SEM images were analyzed  
179 using ImageJ (Schneider et al., 2012) to measure individual particle sizes. The measured particle  
180 sizes taken from the SEM images may be biased toward grains that are larger, intact, and  
181 unobscured by other surrounding particles because they are more visible in an image.

182

### 183 **3 Results**

#### 184 **3.1 Characterization of precursor minerals**

185 All synthesized precursor minerals were free of other phases and generally showed  
186 consistent particle sizes among different batches (Table S1). The two batches of goethite used in  
187 the single-mineral experiments resulted in multi-domainic acicular needles generally about 2 to 4  
188  $\mu\text{m}$  long and 0.1 to 0.4  $\mu\text{m}$  wide (Table S1; Figures S1 and S2). The third batch of goethite,  
189 synthesized for the two-mineral experiments, had a slightly smaller coherent domain size based on  
190 refinement of its diffraction pattern (Table S1; Figure S3). Synthesized akaganeite (Figure S4)  
191 resulted in a CSD size of  $15 \pm 1$  nm based on refinement of its XRD pattern (Table S1; Figure S5).  
192 Two batches of ferrihydrite were synthesized for the single-mineral and two-mineral experiments.  
193 Both batches had two broad diffraction peaks (Figures S6 and S7), indicative of two-line  
194 ferrihydrite, which typically consists of crystallites 2 to 3 nm in size (Janney et al., 2000; Michel  
195 et al., 2007). Note that crystallite size cannot be determined using XRD patterns for particles  
196 smaller  $\sim 10$  nm because of the lack of long-range periodicity (Egami & Billinge, 2012). The initial

197 schwertmannite produced a diffraction pattern with broad peaks (Figure S8), consistent with a  
198 particle size of < 10 nm. Two batches of red hematite with ~60 nm CSD sizes were synthesized,  
199 one for the single-mineral experiments and one for the two-mineral experiments where goethite  
200 and ferrihydrite were seeded with hematite (Table S1; Figure S9). A final batch of red hematite  
201 with ~10 nm CSD size was synthesized for the single-mineral experiments to explore the impact  
202 of the initial hematite particle size on the transformation products (Table S1; Figure S10). The  
203 jarosite synthesized had an initial crystallite size of  $89 \pm 4$  nm (Table S1).

204

## 205 **3.2 Transformation of individual precursor minerals**

### 206 **3.2.1 Product mineralogy**

207 The transformation products of experiments performed on individual precursor minerals  
208 were identified via XRD. Hematite was the most common reaction product from the iron(III)  
209 minerals assessed (Table 1). Diffraction patterns indicate that hematite (both ~10 nm and ~60 nm),  
210 akaganeite, ferrihydrite, and schwertmannite fully converted to (or remained) crystalline hematite  
211 in experiments performed at 200 °C (Figure 1; Table 1; Figures S5, S6, and S8-S10). However,  
212 goethite and jarosite resulted in more variable reaction products (Tables 1 and 2; Figures 1 and 2;  
213 see Figure S2 for all goethite patterns). Goethite transformed to red hematite at a higher  
214 temperature under acidic conditions but resulted in a mixture of red hematite and goethite at pH 7  
215 and 200 °C (Table 1; Figure 2; Figure S2). Experiments on jarosite at high temperatures (200 °C)  
216 yielded mixtures of hematite and jarosite in sulfate fluids and 0.1 mol L<sup>-1</sup> chloride fluids, while  
217 complete transformation to crystalline hematite occurred in 1 mol L<sup>-1</sup> chloride fluids (Table 2;  
218 Figures 1 and 2). Diffraction patterns indicate that hematite (both ~10 nm and ~60 nm), akaganeite,  
219 and ferrihydrite typically transformed completely to or remained crystalline hematite in  
220 experiments performed at 98 °C (Table 1; see Figures S5, S6, S9, and S10 for all patterns). Goethite

221 and jarosite did not show evidence of transformation at 98 °C (Tables 1 and 2; Figures 1 and 2),  
222 but schwertmannite completely converted to goethite at this temperature (Figure S8).

223

224 **Table 1.** Final mineral abundances, crystallite sizes, and particle sizes of the solid products of experiments on the transformation of  
 225 akaganeite, ferrihydrite (seeded and unseeded), goethite (seeded and unseeded), hematite (~10 nm and ~60 nm), and schwertmannite  
 226 in simulated diagenetic fluids.

227

Initial Mineral	Temperature (°C)	Salt	Initial pH	Final Mineral Abundances (wt. %)		Crystallite Size (nm)		Particle Size (nm)
				<i>Hematite</i>	<i>Akaganeite</i>	<i>Hematite</i>	<i>Akaganeite</i>	<i>Hematite</i>
akaganeite	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	35 ± 1	-	-
			7	100	-	45 ± 2	-	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	-	16.7 ± 0.5	-	-
			7	70 ± 2	30 ± 2	24 ± 1	3.6 ± 0.4	-
	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	66 ± 2	-	600 ± 200
			7	100	-	63 ± 2	-	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	-	60 ± 2	-	-
			7	100	-	64 ± 2	-	-
ferrihydrite	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	87 ± 2	-	-
			7	100	-	73 ± 2	-	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	-	62 ± 2	-	-
			7	100	-	77 ± 2	-	-
	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	79 ± 3	-	90 ± 20
			7	100	-	72 ± 2	-	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	-	65 ± 2	-	-
			7	100	-	57 ± 1	-	-
goethite	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	-	100	-	47 ± 1	-
			7	-	100	-	46 ± 1	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	-	100	-	47 ± 1	-
			7	-	100	-	48 ± 1	-
	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	240 ± 7	-	1000 ± 500
			7	1.9 ± 0.5	98.1 ± 0.5	68 ± 40	52 ± 1	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	97.2 ± 0.5	2.8 ± 0.5	220 ± 7	60 ± 10	-
			7	43.7 ± 0.6	56.3 ± 0.6	206 ± 9	62 ± 2	-
hematite (~10 nm)	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	22.5 ± 0.6	-	-
			7	100	-	22.7 ± 0.7	-	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	-	20.1 ± 0.5	-	-
			7	100	-	19.6 ± 0.5	-	-
	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	37 ± 1	-	50 ± 20

		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	7	100	32.8 ± 0.9	-	
			3	100	35 ± 1	-	
			7	100	34.6 ± 1.0	-	
				<i>Hematite</i>	<i>Hematite</i>		
hematite (~60 nm)	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	58 ± 1	-	
			7	100	57 ± 1	-	
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	56 ± 1	-	
			7	100	55 ± 1	-	
	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	64 ± 2	90 ± 20	
			7	100	60 ± 2	-	
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	64 ± 2	-	
			7	100	63 ± 1	-	
				<i>Hematite</i>	<i>Goethite</i>	<i>Hematite</i>	<i>Goethite</i>
schwertmannite	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	-	100	-	13.1 ± 0.4
			7	-	100	-	13.5 ± 0.5
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	-	100	-	14 ± 1
			7	-	100	-	14.7 ± 0.4
	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	133 ± 4	-
			7	100	-	109 ± 4	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	-	97 ± 4	-
			7	100	-	81 ± 5	-
				<i>Hematite</i>	<i>Hematite</i>		
	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	93 ± 2	-	
			7	100	68 ± 2	-	
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	45 ± 2	-	
			7	100	70 ± 2	-	
ferrihydrite seeded with hematite	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	99 ± 2	120 ± 30	
			7	100	65 ± 2	-	
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	83 ± 2	-	
			7	100	61 ± 1	-	
				<i>Hematite</i>	<i>Goethite</i>	<i>Hematite</i>	<i>Goethite</i>
	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	18.0 ± 0.9	82.0 ± 0.9	64 ± 6	37 ± 1
			7	15.5 ± 0.8	84.5 ± 0.8	64 ± 7	27.5 ± 0.7
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	12 ± 1	88 ± 1	50 ± 10	26.4 ± 0.9
			7	17.9 ± 0.7	82.1 ± 0.7	57 ± 5	32.2 ± 0.8
goethite seeded with hematite	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100	-	158 ± 4	-
			7	15 ± 1	85 ± 1	58 ± 9	32 ± 1
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	100	-	143 ± 4	-
			7	32.3 ± 0.8	67.7 ± 0.8	80 ± 4	35.7 ± 1.0

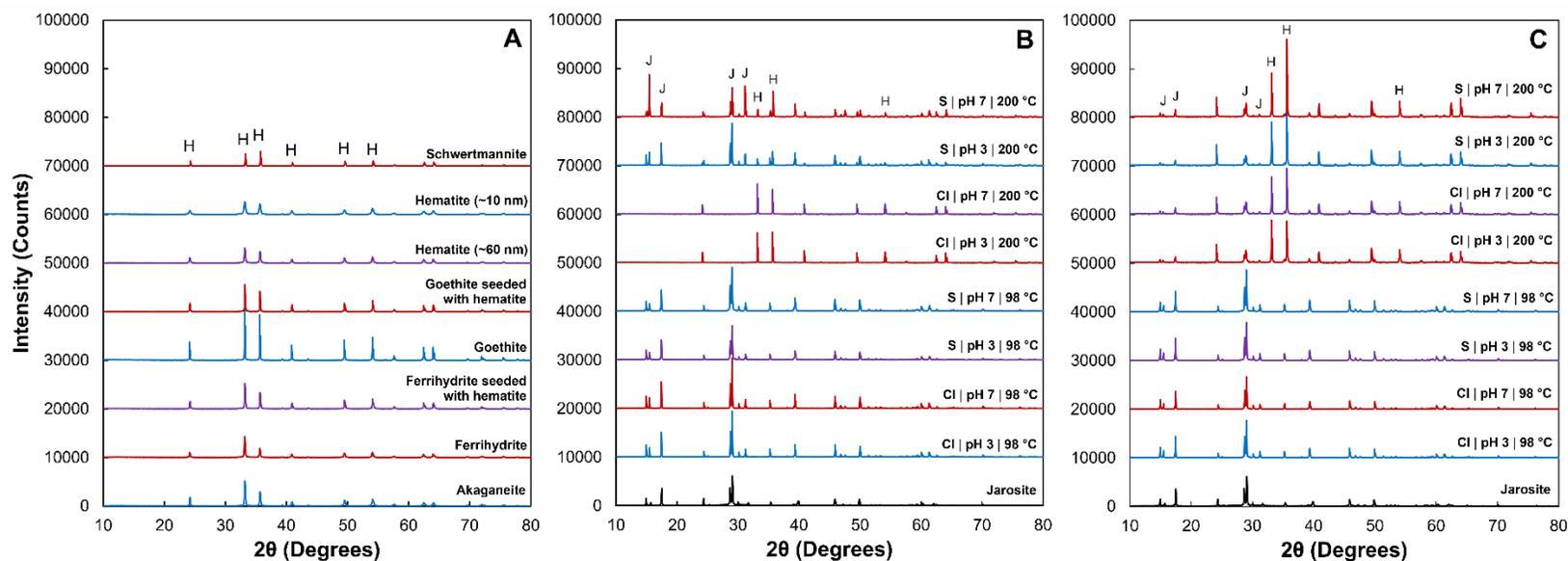
228 **Table 2.** Final mineral abundances, crystallite sizes, and particle sizes of the solid products of experiments on the transformation of  
 229 jarosite in simulated diagenetic fluids.

230

Initial Mineral	Temperature (°C)	Salt	Initial pH	Final Mineral Abundances (wt. %)		Crystallite Size (nm)		Particle Size (nm)
				<i>Hematite</i>	<i>Jarosite</i>	<i>Hematite</i>	<i>Jarosite</i>	<i>Hematite</i>
jarosite	98	0.1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	-	100	-	163 ± 5	-
			7	-	100	-	148 ± 5	-
		0.1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	-	100	-	128 ± 4	-
			7	-	100	-	119 ± 3	-
	200	0.1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	67.1 ± 0.7	32.9 ± 0.7	128 ± 5	55 ± 3	6000 ± 1000
			7	64.4 ± 0.7	35.6 ± 0.7	150 ± 5	58 ± 3	-
		0.1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	72.9 ± 0.7	27.1 ± 0.7	181 ± 7	67 ± 4	6000 ± 1000
			7	70.9 ± 0.6	29.1 ± 0.6	223 ± 9	92 ± 5	-
	98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	-	100	-	220 ± 8	-
			7	-	100	-	210 ± 7	-
		1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	-	100	-	106 ± 3	-
			7	-	100	-	104 ± 3	-
	200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	100.00	-	290 ± 20	-	14000 ± 4000
			7	100.00	-	300 ± 10	-	-
1 mol L <sup>-1</sup> MgSO <sub>4</sub>		3	12.3 ± 0.5	87.8 ± 0.5	340 ± 50	210 ± 10	2000 ± 1000	
		7	19 ± 1	81 ± 1	270 ± 60	120 ± 10	-	

231

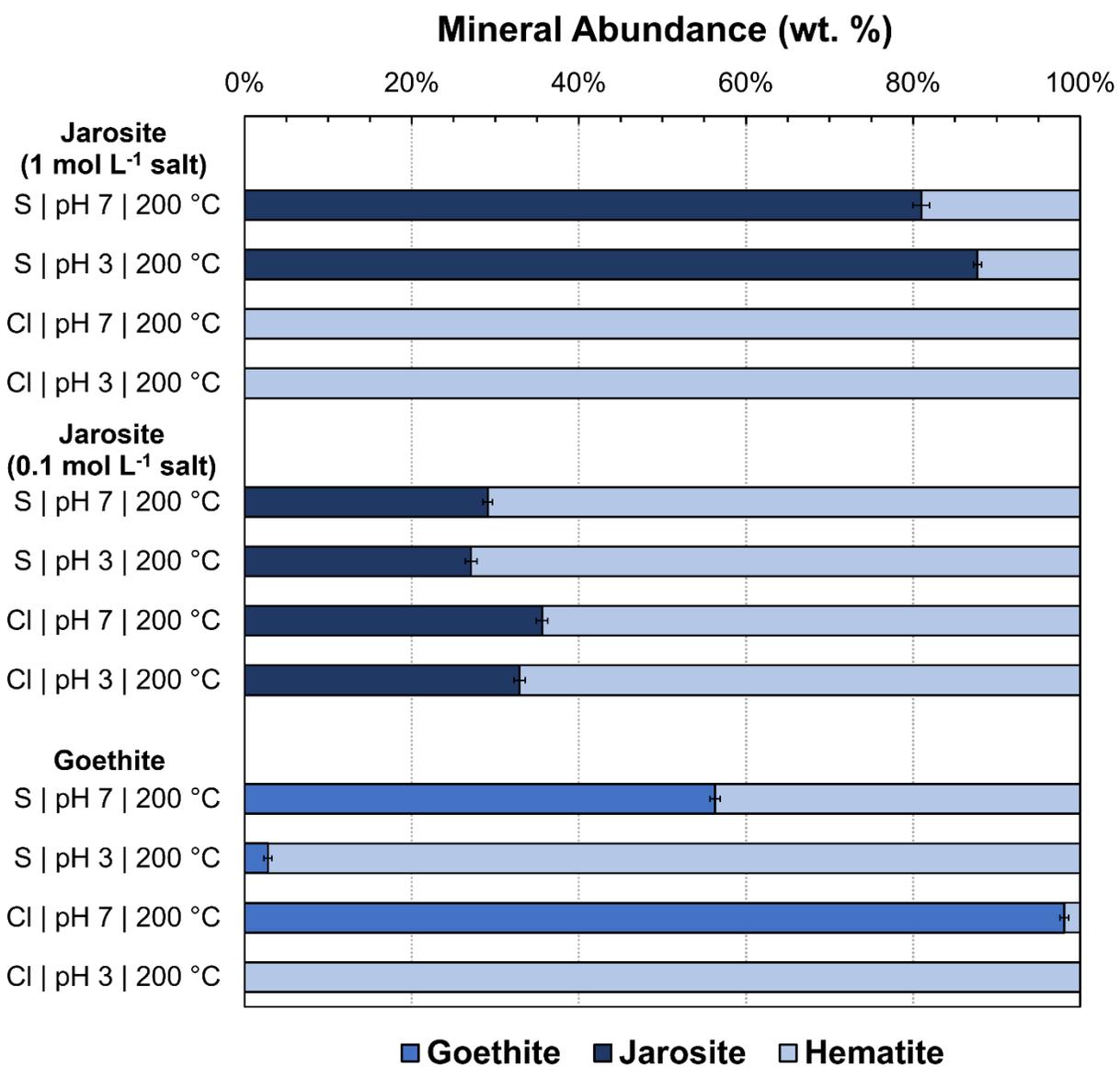
232



233

234 **Figure 1.** XRD patterns of (a) the red hematite transformation products of synthesized minerals subjected to pH 3, 1 mol L<sup>-1</sup> MgCl<sub>2</sub>  
 235 200 °C fluid conditions for 20 days, (b) synthesized jarosite and its transformation products in various 1 mol L<sup>-1</sup> fluid conditions, and  
 236 (c) synthesized jarosite and its transformation products in various 0.1 mol L<sup>-1</sup> fluid conditions. Cl and S indicate MgCl<sub>2</sub> and MgSO<sub>4</sub>  
 237 background salts, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and experimental temperature (98 °C  
 238 or 200 °C) are indicated for each sample. Characteristic jarosite (“J”) and hematite (“H”) peaks are labeled. Patterns offset in intervals  
 239 of 10000 and patterns from experiments on jarosite in 200 °C fluids with 0.1 mol L<sup>-1</sup> salt vertically exaggerated by a factor of 2 for  
 240 clarity.

241



242

243 **Figure 2.** Final mineralogy (wt.%) of reaction products of jarosite and goethite experiments. Cl  
 244 and S indicate background salts of MgCl<sub>2</sub> and MgSO<sub>4</sub>, respectively, in the transformation fluids.  
 245 Initial fluid pH value (pH 3 or pH 7) and experimental temperature (200 °C) are provided for  
 246 each sample.

### 247 **3.2.2 Fluid composition**

248           In general, experiments on akageneite, ferrihydrite, schwertmannite, ~10 nm red hematite,  
249 and jarosite produced substantial (> 1 pH unit) decreases in pH value (Table 3; Table S2). The  
250 final pH values of ~60 nm hematite and goethite fluids remained relatively unchanged from the  
251 initial value in comparison. Across all experiments, final pH values tended to be higher for sulfate-  
252 rich samples and lower for chloride-rich samples (Table 3; Table S2). We attribute the decrease in  
253 pH to fluid evaporation and grain coarsening. The latter process decreases total surface area in the  
254 system, releasing  $H^+$  as anions desorb and surface sites are overgrown. Schwertmannite,  
255 akaganeite, and jarosite also generate  $H^+$  as they transform to hematite.

256           Jarosite experiments displayed final dissolved concentrations of iron, potassium, and sulfur  
257 that were non-stoichiometric with respect to the chemical formula of potassium jarosite (Table 3).  
258 Jarosite partially dissolved when aged at 98 °C (Table 3) but no new phases were precipitated  
259 (Table 2; Figures 1 and 2). The final fluid compositions in these samples are therefore only  
260 controlled by the dissolution of jarosite. In the samples where jarosite was the sole mineral phase  
261 present at the end of the experiment, iron was substantially depleted in the final fluid composition  
262 relative to both sulfur and potassium, while potassium was enriched slightly relative to sulfur. In  
263 addition, elevated chloride concentrations increased the ratio of iron to sulfur and decreased the  
264 ratio of iron to potassium in the final fluid (Table 3).

265 **Table 3.** Final fluid compositions (pH values, dissolved ion concentrations, and molar ratios) of experiments on the transformation of  
 266 jarosite in simulated diagenetic fluids.

267

Temperature (°C)	Salt	Initial pH	Final pH	Fe (mmol/kg)	K (mmol/kg)	S (mmol/kg)	K:S	K:Fe
98	0.1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	1.46	0.338 ± 0.004	52.6 ± 0.6	66 ± 3	0.79 ± 0.04	156 ± 3
		7	1.48	0.36 ± 0.004	60.1 ± 0.4	72 ± 3	0.84 ± 0.04	167 ± 2
	0.1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	1.75	0.109 ± 0.002	35.7 ± 0.6	-	-	326 ± 9
		7	1.47	0.095 ± 0.002	39.4 ± 0.4	-	-	415 ± 10
200	0.1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	1.12	2.2 ± 0.04	147.9 ± 0.8	260 ± 4	0.568 ± 0.008	67 ± 1
		7	1.11	2.2 ± 0.04	176.3 ± 0.9	275 ± 5	0.64 ± 0.01	80 ± 1
	0.1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	0.78	0.71 ± 0.03	136 ± 1	-	-	193 ± 10
		7	0.72	0.96 ± 0.03	185.5 ± 0.9	-	-	194 ± 7
98	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	0.84	11.97 ± 0.09	66.3 ± 0.4	93 ± 3	0.71 ± 0.02	5.54 ± 0.06
		7	0.90	12.4 ± 0.1	58.3 ± 0.4	91 ± 3	0.64 ± 0.02	4.70 ± 0.05
	1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	1.87	0.232 ± 0.003	38.3 ± 0.4	-	-	165 ± 3
		7	1.55	0.109 ± 0.002	39 ± 0.4	-	-	359 ± 8
200	1 mol L <sup>-1</sup> MgCl <sub>2</sub>	3	0.52	60.9 ± 0.6	213 ± 2	353 ± 4	0.603 ± 0.008	3.50 ± 0.04
		7	0.43	75 ± 2	180 ± 1	393 ± 4	0.459 ± 0.006	2.40 ± 0.08
	1 mol L <sup>-1</sup> MgSO <sub>4</sub>	3	1.01	0.203 ± 0.003	83.2 ± 0.8	-	-	410 ± 7
		7	0.89	0.314 ± 0.004	133 ± 1	-	-	423 ± 6

268

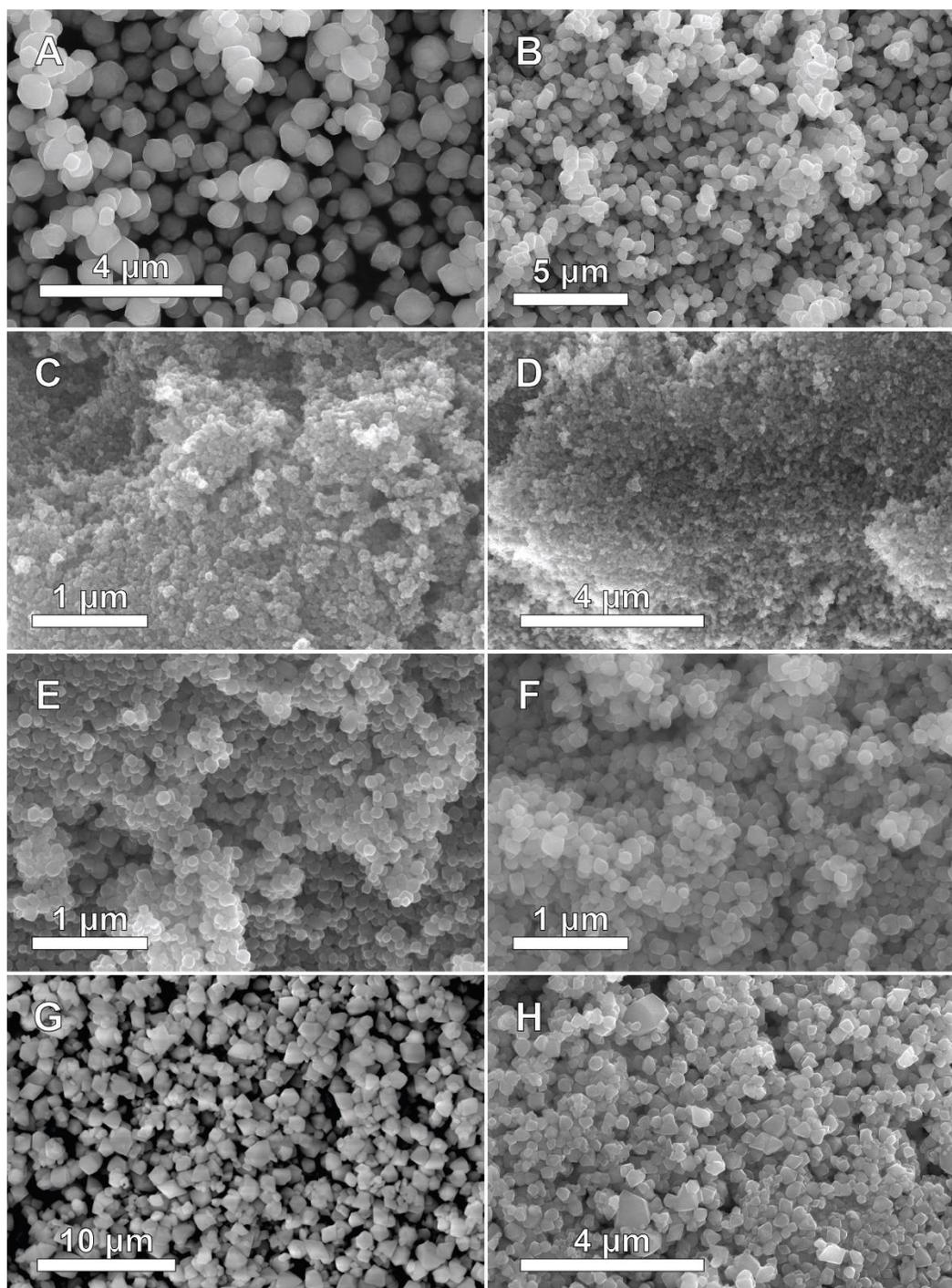
269

### 270 **3.2.3 Particle and crystallite sizes**

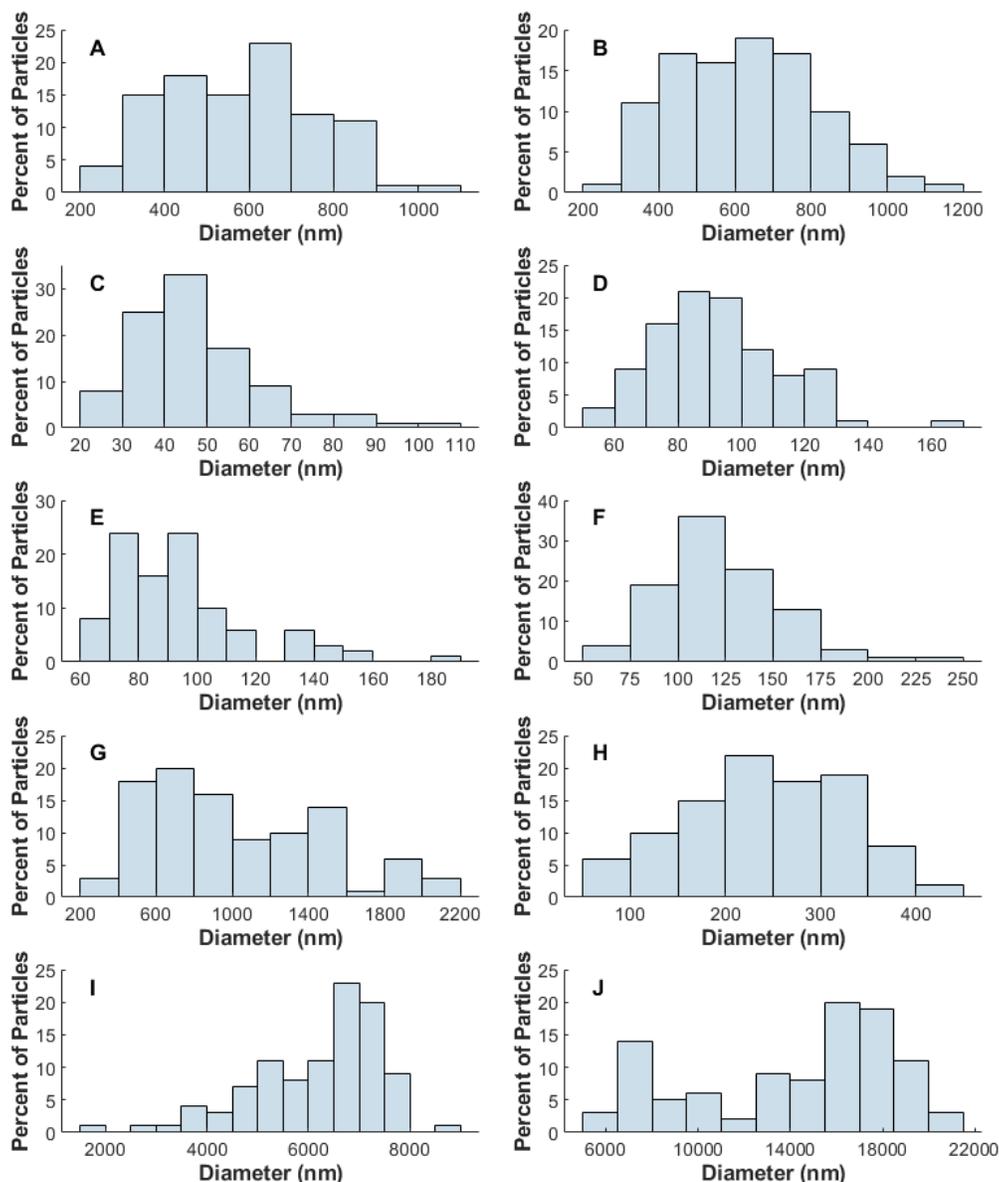
271 Generally, high temperature (200 °C), chloride-rich, acidic conditions produced the largest  
272 final CSD sizes of hematite for most minerals. Refinement of diffraction patterns for the hematite  
273 reaction products of ~10 nm red hematite, ~60 nm red hematite, akaganeite, ferrihydrite, and  
274 schwertmannite resulted in CSD sizes generally less than 150 nm (Table 1), indicative of red  
275 hematite. Initial hematite with a smaller, ~10 nm initial CSD size experienced a greater relative  
276 increase in size compared to larger, ~60 nm initial hematite but its final particle size was still  
277 smaller than that of the ~60 nm hematite. The XRD-derived CSD sizes of the hematite produced  
278 from precursor akaganeite were < 70 nm; however, SEM images show  $0.6 \pm 0.2 \mu\text{m}$  particles,  
279 suggesting that these particles were aggregates of multiple individual crystals (Figures 3 and 4).

280 In contrast, goethite and jarosite generally resulted in more crystalline hematite reaction  
281 products with crystallite sizes that exceeded the upper limit of quantification from XRD patterns  
282 (Tables 1 and 2). SEM images revealed that goethite in acidic, high temperature (200 °C) fluids  
283 converted to hematite with a particle size of ~1  $\mu\text{m}$  (Figures 3 and 4). SEM images of the hematite  
284 produced from jarosite show that in chloride-rich, 200 °C fluids, hematite ranged in length from  
285 ~5-20  $\mu\text{m}$  (Figures 4 and 5). In fluids with lower ( $0.1 \text{ mol L}^{-1}$ ) chloride concentrations and fluids  
286 with sulfate, the hematite product of jarosite was smaller (< 10  $\mu\text{m}$ ) but still notably coarse (Figures  
287 4 and 5). The morphology of the hematite product varied with grain size (Figures 3 and 5; Figure  
288 S11). Small (~1  $\mu\text{m}$ ) particles were rhombohedral, while larger (~14  $\mu\text{m}$  long) particles were  
289 elongated and somewhat “spindle-shaped,” with distinct crystal faces.

290

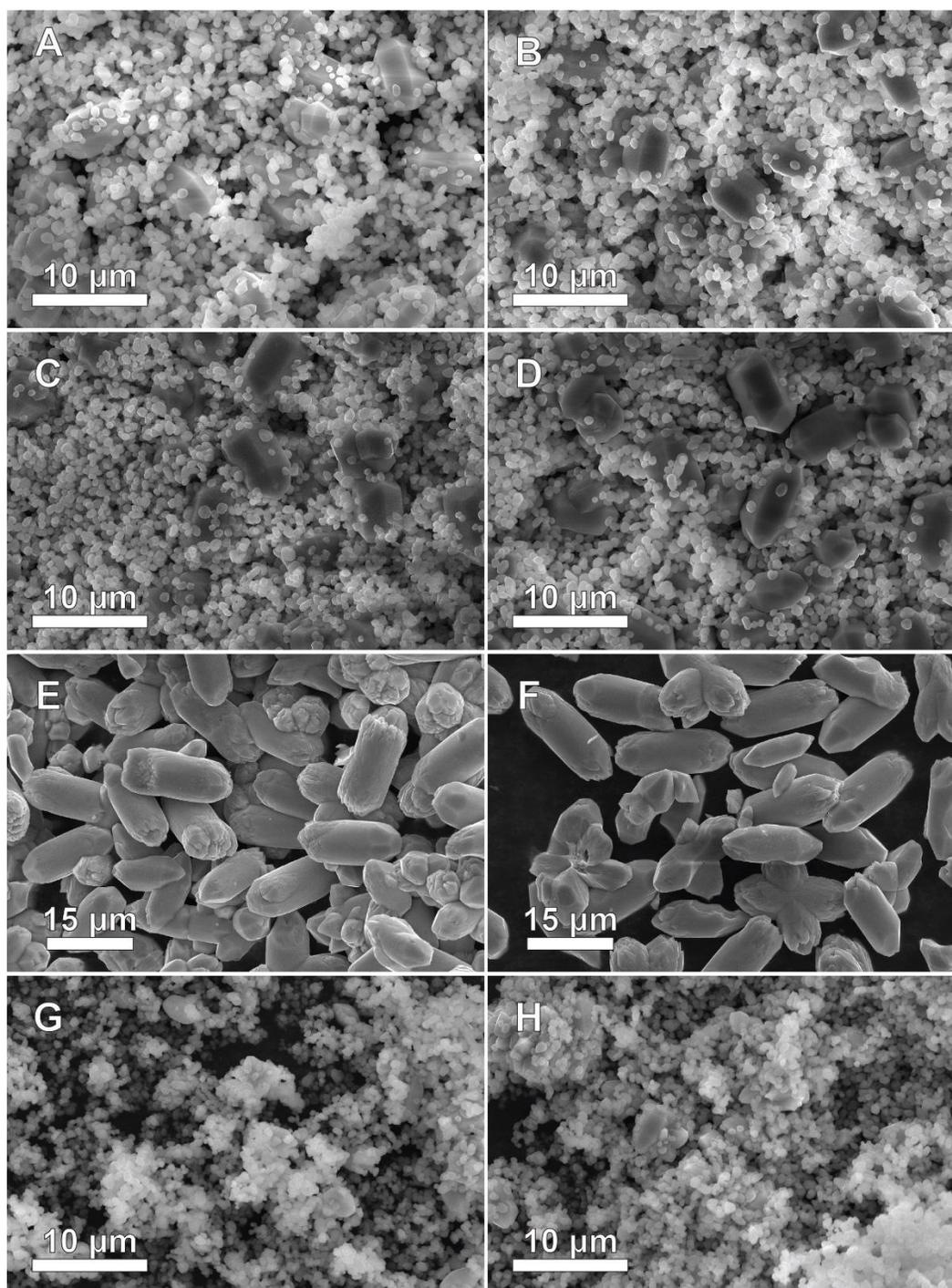


291  
292 **Figure 3.** SEM images of the red hematite transformation products of synthesized minerals  
293 subjected to 1 mol L<sup>-1</sup> MgCl<sub>2</sub>, pH 3, 200 °C fluids for 20 days. Initial mineralogy: (a) akageneite,  
294 (b) schwertmannite, (c) hematite batch 3 (~10 nm), (d) hematite batch 1 (~60 nm), (e) ferrihydrite  
295 batch 1, (f) ferrihydrite batch 2 seeded with hematite batch 2, (g) goethite batch 2, (h) goethite  
296 batch 3 seeded with hematite batch 2.



297 **Figure 4.** Measured final particle sizes of the hematite transformation products  
 298 of (a) akageneite, (b) schwertmannite, (c) hematite batch 3 (~10 nm), (d) hematite batch 1 (~60  
 299 nm), (e) ferrihydrite batch 1, (f) ferrihydrite batch 2 seeded with hematite batch 2, (g) goethite  
 300 batch 2, and (h) goethite batch 3 seeded with hematite batch 2 subjected to pH 3, 1 mol L<sup>-1</sup>  
 301 MgCl<sub>2</sub>, 200 °C fluids for 20 days. Measured final particle sizes of the hematite transformation  
 302 products of jarosite subjected to (i) 0.1 mol L<sup>-1</sup> MgCl<sub>2</sub> and (j) 1 mol L<sup>-1</sup> MgCl<sub>2</sub> fluids set to pH 3  
 303 and heated to 200 °C for 20 days.

304



305

306 **Figure 5.** SEM images of the transformation products of jarosite subjected to various 200 °C  
307 fluids for 20 days. Fluid characteristics: (a) pH 3, 0.1 mol L<sup>-1</sup> MgCl<sub>2</sub> (b) pH 7, 0.1 mol L<sup>-1</sup> MgCl<sub>2</sub>,  
308 (c) pH 3, 0.1 mol L<sup>-1</sup> MgSO<sub>4</sub>, (d) pH 7, 0.1 mol L<sup>-1</sup> MgSO<sub>4</sub>, (e) pH 3, 1 mol L<sup>-1</sup> MgCl<sub>2</sub>, (f) pH 7,  
309 1 mol L<sup>-1</sup> MgCl<sub>2</sub>, (g) pH 3, 1 mol L<sup>-1</sup> MgSO<sub>4</sub>, (h) pH 7, 1 mol L<sup>-1</sup> MgSO<sub>4</sub>.

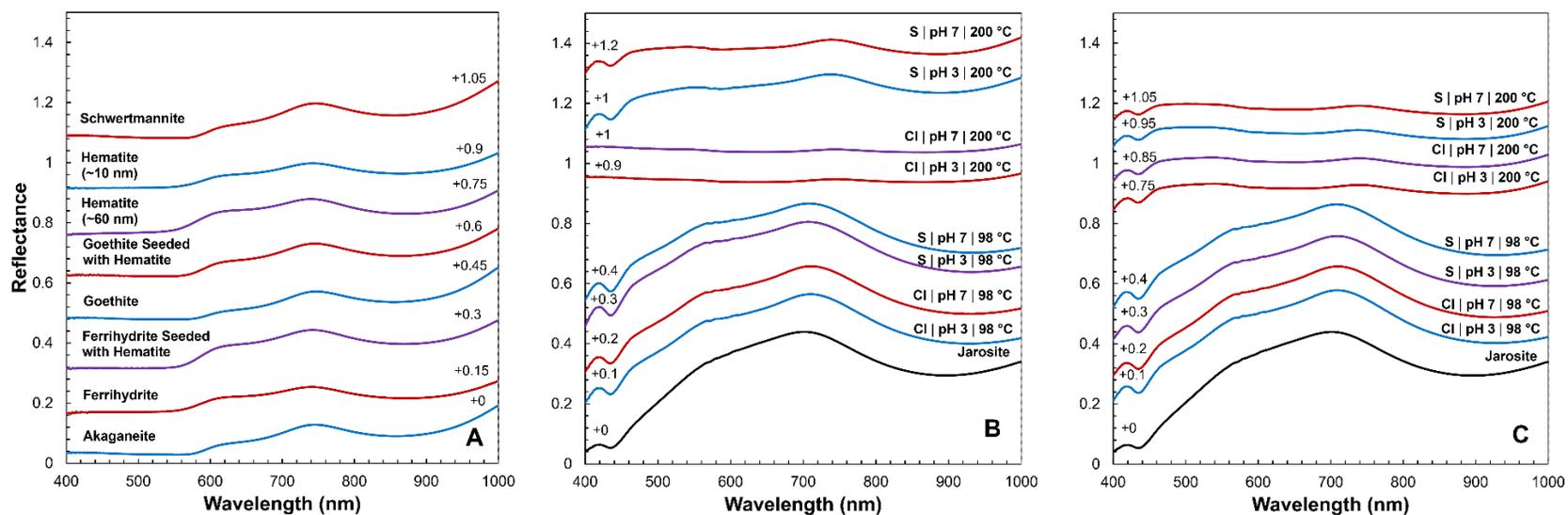
### 310 **3.2.4 Reflectance spectroscopy**

311 Hematite and other iron (oxyhydr)oxides are identifiable via visible to near-infrared  
312 (VNIR) reflectance spectroscopy due to four electronic absorption features occurring between 400  
313 and 1000 nm (Sherman, 1985). These electronic absorptions are visible when the iron  
314 (oxyhydr)oxide is both crystalline and maintains a small enough particle size that it retains a strong  
315 positive reflectance slope in the red portion of the visible spectrum (Lane et al., 2002).  
316 Distinguishing between different iron (oxyhydr)oxides can be challenging because the key  
317 absorption features often overlap (Catling & Moore, 2003; Morris et al., 2000). However, red,  
318 fine-grained hematite and gray, coarse-grained hematite can be distinguished easily from each  
319 other and from other iron (oxyhydr)oxides. Fine-grained hematite has a strong 860 nm absorption  
320 feature similar to other ferric minerals but exhibits a sharper inflection at 535 nm (Fraeman,  
321 Johnson, et al., 2020; Lane et al., 2002; Morris et al., 2000; Sherman & Waite, 1985). Coarse-  
322 grained hematite has strong absorption at all visible wavelengths, eliminating the 535 nm inflection  
323 and 860 nm ferric absorption edge from its visible spectrum and producing a “flat” or neutral  
324 reflectance spectrum at all visible wavelengths (Lane et al., 2002; Morris et al., 2020).

325 Transformation products of most minerals exhibited the 860 nm electronic absorption  
326 feature as well as the spectral inflection at 535 nm characteristic of red crystalline hematite with  
327 VNIR spectroscopy (Figure 6; Figures S12-S18). The large grain size of the hematite particles  
328 produced from interaction of jarosite with chloride-rich, 200 °C fluids is supported by the VNIR  
329 spectra (Figure 6; Figures S19 and S20). These spectra exhibit decreased reflectance in the red  
330 portion of the visible spectrum, causing them to be more spectrally neutral, a characteristic of gray  
331 hematite. Reaction products that contain mixtures of hematite and jarosite (e.g., sulfate-rich  
332 samples) exhibit jarosite absorption features at ~435 nm and have “flatter” slopes and less

333 reflectance in the visible portion of the spectrum compared to that of pure jarosite (Figure 6;  
334 Figures S19 and S20).

335



336

337 **Figure 6.** VNIR reflectance spectra of (a) red hematite transformation products of synthesized minerals subjected to pH 3, 1 mol L<sup>-1</sup>  
 338 MgCl<sub>2</sub>, 200 °C fluid conditions for 20 days, (b) synthesized jarosite and its transformation products in various 1 mol L<sup>-1</sup> fluid  
 339 conditions and (c) synthesized jarosite and its transformation products in various 0.1 mol L<sup>-1</sup> fluid conditions. Cl and S indicate  
 340 background salts of MgCl<sub>2</sub> and MgSO<sub>4</sub>, respectively, in the transformation fluids. Initial fluid pH value (pH 3 or pH 7) and  
 341 experimental temperature (98 °C or 200 °C) are provided for each sample. Spectra offset for clarity as indicated.

342

### 343 **3.3 Effect of hematite seeds on precursor mineral transformations**

344 Additional experiments involving goethite or ferrihydrite seeded with hematite produced  
345 similar results as the experiments which investigated goethite or ferrihydrite alone. Complete  
346 conversion of the goethite mineral mixture to hematite resulted from high temperature, acidic  
347 conditions (Figure 1; Figure S3), whereas ferrihydrite seeded with hematite completely converted  
348 to hematite in all conditions (Figure 1; Figure S7). Final hematite particle sizes for all experiments  
349 seeded with hematite were substantially smaller than the 3 to 5  $\mu\text{m}$  minimum size of gray hematite  
350 (Table 1; Figures 3 and 4; Figures S3 and S7) and produced spectra consistent with red hematite  
351 (Figures S21 and S22).

352

## 353 **4 Discussion**

### 354 **4.1 Impacts of precursor mineralogy on hematite transformation products**

#### 355 **4.1.1 Jarosite**

356 Jarosite was the only initial mineral to yield gray, crystalline hematite in the transformation  
357 products of any experimental conditions. Prior studies (e.g., Golden et al. (2008)) have produced  
358  $\mu\text{m}$ -scale rounded hematite particles from hydronium jarosite, which further emphasizes that  
359 crystalline hematite can be formed from jarosite. Similar to all other initial minerals, experiments  
360 on jarosite in chloride-rich, high temperature (200 °C), acidic fluid conditions generally resulted  
361 in the largest average hematite grain size post-transformation. The detection of tridymite at Gale  
362 crater implies the past existence of hydrothermal fluids in the crater (Yen et al., 2021), which  
363 would have promoted the formation of larger hematite. Jarosite proved to be more stable in sulfate-  
364 rich fluids than in chloride-rich fluids, as anticipated, due to the common ion effect. Increased

365 stability of jarosite in sulfate solutions resulted in only partial transformation to hematite in most  
366 higher temperature (200 °C) experiments for both 1 mol L<sup>-1</sup> and 0.1 mol L<sup>-1</sup> sulfate concentrations.

367         Diffraction patterns of the final solid products of experiments on jarosite at 98 °C indicated  
368 that no secondary iron-bearing phases precipitated, yet final dissolved Fe, K, and S concentrations  
369 measured in the fluids were non-stoichiometric. The Fe:K and Fe:S molar ratios were several  
370 orders of magnitude lower than stoichiometric ratios based on the chemical formula of jarosite,  
371 similar to observations made by Welch et al. (2008). This suggests that jarosite dissolution  
372 involved preferential removal of potassium and sulfate over iron, similar to observations of non-  
373 stoichiometric jarosite dissolution via laboratory experiments and computational modeling  
374 (Becker & Gasharova, 2001; Smith et al., 2006). Smith et al. (2006) observed a goethite residue  
375 on the surface of jarosite grains after removal of surface K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, but no crystalline secondary  
376 iron phases were observed via XRD or VNIR analyses and nanocrystalline or amorphous iron  
377 minerals, like ferrihydrite, are unstable at the temperatures of our experiments (Cornell &  
378 Schwertmann, 2003). However, the positions of many of the jarosite XRD peaks in the 98 °C and  
379 200 °C (Figure 1; Figures S23 and S24) were shifted to different angles compared to the peak  
380 positions produced by the initial synthesized jarosite. These shifts better align with the expected  
381 diffraction pattern for potassium jarosite and is inconsistent with partial incorporation of H<sub>3</sub>O<sup>+</sup>  
382 (Basciano & Peterson, 2007; Basciano & Peterson, 2008). Jarosites often contain iron vacancies,  
383 leading to an excess of potassium and sulfate in the structure (Scarlett et al., 2010). Heating may  
384 have promoted recrystallization that annealed these vacancies, releasing excess K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> to  
385 solution.

386

#### 387 **4.1.2 Coarsening of fine-grained, red hematite**

388           The coarsening of finer-grained hematite was minor and did not result in gray hematite.  
389   The ~10 nm hematite resulted in a greater relative increase in particle size compared to ~60 nm  
390   hematite, which remained largely unchanged in size after 20 days. The increased solubility of  
391   smaller particles due to their greater surface area may favor more rapid dissolution and subsequent  
392   crystal growth compared to an initially well-crystalline mineral. However, little to no grain size  
393   increase was observed for red hematite, regardless of initial crystallite size, suggesting that the  
394   coarsening of fine-grained iron oxides alone may not be a viable pathway to gray hematite  
395   formation. Minor observed increases in particle size were likely achieved through Ostwald  
396   ripening, in which smaller particles are dissolved and reprecipitated as growth onto larger particles  
397   (Ostwald, 1897; Steefel & Van Cappellen, 1990). Given unrestricted time in an aqueous  
398   environment, finer-grained hematite may eventually coarsen substantially. However, on Mars the  
399   duration of aqueous alteration is restricted temporally due to the persistence of diagenetically-  
400   juvenile deposits, such as opaline silica and smectites, on the surface (Tosca & Knoll, 2009).

401

#### 402 **4.1.3 Ferrihydrite and goethite**

403           Ferrihydrite subjected to the same fluid conditions as ~10 nm hematite produced larger  
404   grain sizes across all comparable samples despite having a smaller starting crystallite size. The  
405   transformation from ferrihydrite to hematite proceeds through the aggregation of smaller particles  
406   of ferrihydrite that crystallize to hematite, potentially via a mechanism such as oriented attachment  
407   (Freitas et al., 2015; Schwertmann et al., 1999; Soltis et al., 2016; Wang et al., 2022; Zhu & De  
408   Yoreo, 2022). Such aggregation-based growth provides a mechanism through which conversion  
409   from ferrihydrite generates larger final particles than coarsening of existing ~10 nm hematite. This

410 further highlights the ineffectiveness of Ostwald ripening for generating gray hematite from pre-  
411 existing fine-grained hematite.

412 In contrast to the complete conversion of ferrihydrite to hematite, goethite-to-hematite  
413 transformation rates were exceedingly slow at 98 °C, with no hematite formed after 20 days of  
414 aging at this temperature. For experiments conducted at 200 °C, the initial pH of the system  
415 dictated the degree of transformation. Acidic systems yield total or near-total transformation of  
416 goethite to hematite while 56 to 98% of the goethite remained after aging at pH 7. The relationship  
417 between stability at elevated temperature and pH aligns with previous observations (Das et al.,  
418 2011; Schwertmann & Carlson, 2005; Smith & Kidd, 1949). Goethite generally produced  
419 relatively large (0.2 to 1  $\mu\text{m}$ ) particles (Figure 3; Figure S1), but still red hematite except at  
420 circumneutral sulfate-rich fluids where little transformation occurred. Consistent with previous  
421 observations (Davidson et al., 2008; De Grave et al., 1999; González et al., 2000; Lin et al., 2014),  
422 hematite did not retain the acicular form of the precursor goethite. Notably, the bipyramidal  
423 morphology of the hematite products (Figure 3; Figure S1) matches that of the hematite formed  
424 via epitaxial growth on goethite in hydrothermal systems (Lin et al., 2014), suggesting a  
425 dissolution and reprecipitation transformation mechanism.

426 Additional experiments investigating the effects of seeding goethite and ferrihydrite with  
427 red, fine-grained hematite to remove possible nucleation barriers resulted in no substantial changes  
428 to the transformation products. Seeding also did not affect the final particle sizes of the  
429 transformation products. The nucleation rate of hematite therefore does seem to impose a limit on  
430 these transformation processes. Particularly with respect to goethite, the inhibition of  
431 transformation to hematite under neutral pH conditions at high temperature and all low temperature  
432 conditions is not due to a nucleation barrier.

433

#### 434 **4.1.4 Akaganeite and schwertmannite**

435 Unlike jarosite, akaganeite and schwertmannite showed no impact from the common ion  
436 effect on their transformations despite containing background salt anions. Akaganeite has been  
437 observed to transform to hematite via dissolution and reprecipitation (Bailey et al., 1993; Cornell  
438 & Giovanoli, 1990; Goñi-Elizalde et al., 1987; Peterson et al., 2018). The hematite products in this  
439 study do not reflect the rod-like morphology of the precursor akaganeite and instead appear similar  
440 to akaganeite transformation products analyzed by Bailey et al. (1993) that formed via dissolution  
441 and reprecipitation. This suggests that akaganeite in this study transformed to red hematite through  
442 a similar mechanism.

443 Schwertmannite displayed a temperature-dependence in its transformation products,  
444 forming goethite at 98 °C but red hematite at 200 °C. This is consistent with observations made in  
445 prior studies (Barham, 1997; Davidson et al., 2008). These transformations may occur via a  
446 ferrihydrite precursor (Davidson et al., 2008), although this cannot be evaluated by our data since  
447 no ferrihydrite was detected in the final aging products. Hematite particle sizes (Table 1; Figure 3)  
448 were generally larger when produced by a schwertmannite precursor (80 to 130 nm) than for a  
449 ferrihydrite precursor (60 to 90 nm). This may reflect the impact of sulfate released during  
450 transformation of schwertmannite, differences in pH at the onset of hematite nucleation from a  
451 ferrihydrite intermediate, or larger aggregates of ferrihydrite forming in the schwertmannite  
452 experiments before crystallization to hematite.

453

#### 454 **4.2 Impacts of initial fluid composition on iron (oxyhydr)oxide transformation products**

455 While each mineral system had variable reaction products and final particle sizes, some  
456 general trends were evident across most samples that indicate a specific role of fluid composition.

457 Experiments in sulfate-rich systems generally resulted in higher final pH values, smaller final  
458 particle sizes, and occasionally less complete transformation to hematite. Sulfate commonly  
459 adsorbs onto iron oxides as binuclear surface complexes (Hug, 1997; Paul et al., 2005; Wang et  
460 al., 2018), which may inhibit the transformation of precursor iron(III) oxides as well as the growth  
461 of hematite crystals. Sulfate tends to form binuclear complexes at the surfaces of iron oxides,  
462 whereas chloride may bond more weakly (Boily & Shchukarev, 2010; Shchukarev & Boily, 2008;  
463 Shchukarev et al., 2007; Shchukarev & Sjöberg, 2005). In contrast, samples in chloride-rich fluids  
464 often resulted in complete transformation to hematite, larger final particle sizes, lower final pH  
465 values, and higher dissolved iron concentrations. Chloride shows weaker adsorption to iron oxide  
466 surfaces than sulfate (Boily & Shchukarev, 2010; Shchukarev & Boily, 2008; Shchukarev et al.,  
467 2007; Shchukarev & Sjöberg, 2005) but may promote more rapid dissolution of the precursor  
468 phases (Pritchett et al., 2012; Virtanen et al., 1997), potentially increasing the rate of mass transfer  
469 to growing hematite crystals. In addition, chloride complexes iron in solution, especially at  
470 elevated temperature (Gammons & Allin, 2022; Liu et al., 2006; Stefánsson et al., 2019),  
471 increasing the solubility of iron and its availability for hematite growth. The initial pH value also  
472 impacts the final fluid composition and reaction products. Experiments initially set to acidic  
473 conditions (pH 3) generally resulted in larger final particle sizes, lower final pH values, and more  
474 complete transformation to hematite as well, suggesting that acidic conditions may be more  
475 favorable to the formation of coarser-grained hematite.

476

#### 477 **4.3 Jarosite as a potential precursor mineral to gray hematite**

478 Of all the precursor minerals investigated, only jarosite forms hematite of sufficient grain  
479 size to be spectrally gray. We hypothesize that this system was uniquely able to maintain both a  
480 slow nucleation rate and rapid growth of hematite. Nucleation rate is controlled by the degree of

481 supersaturation of hematite (De Yoreo & Vekilov, 2003), which depends on the dissolved iron  
482 concentration and pH. While jarosite dissolution creates elevated dissolved iron concentrations, it  
483 also generates substantial acidity. This apparently prevents the system from reaching high degrees  
484 of supersaturation with respect to hematite, creating few nuclei. However, the elevated dissolved  
485 iron concentrations enable rapid growth of the small number of nuclei that form, creating large  
486 hematite crystallites. The transformation of jarosite to hematite further acidifies the system,  
487 creating a positive feedback that drives further jarosite dissolution and hematite growth. Validation  
488 of our hypothesized mechanism requires a reactor design that would enable sampling the fluid  
489 phase at 200 °C to track the time evolution of dissolved iron and pH.

490        Incomplete transformation of jarosite to hematite in sulfate-rich fluids may reflect  
491 conditions where the phases are in equilibrium. Complete jarosite transformation was only  
492 observed in the presence of high dissolve chloride concentration ( $1 \text{ mol L}^{-1}$ ), which resulted in  
493 over an order of magnitude greater dissolved iron concentration at 200 °C compared to other  
494 conditions (Table 3). Complexation of iron(III) sites on the surface of jarosite by chloride may  
495 maintain charge balance of the system as sulfate is released and accelerate its dissolution (Pritchett  
496 et al., 2012). High concentrations of chloride also form aqueous iron complexes (e.g.,  $\text{FeCl}_4^-$ ) at  
497 elevated temperature (Gammons & Allin, 2022; Liu et al., 2006; Stefánsson et al., 2019),  
498 increasing the total concentration of iron in solution. The presence of elevated dissolved chloride  
499 in jarosite-bearing systems thus enhances the formation of gray hematite.

500        In contrast, akaganeite, ferrihydrite, goethite, and schwertmannite may transform through  
501 solid-state processes and aggregation of small particles, providing a distinct nucleation route, or  
502 generate high degrees of supersaturation while maintaining low dissolved iron concentrations  
503 because of the high pH conditions. Further, the iron octahedra in jarosite are corner-sharing (Kato

504 & Miúra, 1977), but the iron octahedra in hematite are edge and face sharing (Blake et al., 1966;  
505 Pauling & Hendricks, 1925). This may slow the initial nucleation of hematite in systems initially  
506 containing jarosite. Other iron(III) minerals investigated in this study have edge-sharing octahedra,  
507 which may instead facilitate the nucleation of hematite and result in many smaller final hematite  
508 particles. Goethite came the closest to generating gray hematite, forming particle at or near 1  $\mu\text{m}$   
509 at 200 °C. These larger hematite particles may form from goethite via solid-state transformation if  
510 its long acicular needles aggregate.

511         Although this study explores mineral transformations in 98 °C and 200 °C fluids, these  
512 temperatures were primarily chosen to accelerate the rate of reaction to enable investigation within  
513 laboratory time scales. Tosca & Knoll (2009) examined the integration of the temperature and time  
514 required to diagenetically transform a given sediment via kinetic formulations. Their models  
515 exemplify how mineral transformations have a time-temperature integral threshold that can be met  
516 in multiple ways; transformations occurring at lower temperatures over longer periods of time may  
517 also occur at higher temperatures much more rapidly. Time-temperature integral thresholds exist  
518 for each of the transformations observed in this study; therefore, the results obtained at high (98  
519 °C and 200 °C) temperatures over 20 days in this study might also be observed in lower, ambient-  
520 temperature aqueous systems over substantially longer time scales. Additionally, while  
521 temperature alters chemical equilibria, hematite remains the thermodynamically-stable iron(III)  
522 phase at ambient temperatures and above as well as at low water activities (Navrotsky et al., 2008),  
523 so this relative stability was not altered by the higher temperatures used.

524

#### 525 **4.4 Implications for diagenetic hematite at Vera Rubin ridge**

526         Comparison of the results of this investigation with observations by MSL Curiosity  
527 provides new insight into the formation conditions of gray, coarse-grained hematite at VRR.

528 Deposition of VRR and other Murray formation sediments occurred in lacustrine environments  
529 (Edgar et al., 2020; Fraeman, Edgar, et al., 2020; Thompson et al., 2020). Much of VRR is red in  
530 color, with the isolated gray portions cross-cut strata and laminations indicating a diagenetic origin  
531 (Fraeman, Edgar, et al., 2020). Evidence for isochemical alteration at VRR (Bedford et al., 2019)  
532 implies that iron in gray, crystalline hematite in the Jura member is derived from pre-existing iron  
533 sources in the rocks, such as jarosite. The drill sample Highfield in the gray portion of the Jura  
534 member at VRR contained no akaganeite or jarosite while the neighboring drill sites in the red  
535 portions of the ridge (Stoer and Rock Hall) contained 1.0 to 2.3 wt.% jarosite and 1.2 to 6.0 wt.%  
536 akaganeite (Rampe et al., 2020). The conspicuous absence of jarosite in Highfield is consistent  
537 with it having converted to gray hematite via diagenetic alteration. Chloride salts have been  
538 confirmed at VRR by evolved gas analyses (EGA) performed by SAM (McAdam et al., 2020),  
539 supporting the possibility that chloride-rich fluids were present during diagenesis. While sulfate  
540 salts also occur, the presence of calcium sulfate minerals indicate that sulfate solubility would be  
541 relatively limited compared to the concentrations used in the present study (0.1 and 1 mol L<sup>-1</sup>).  
542 Calcium sulfate precipitation provides a mechanism to maintain the lower sulfate concentrations  
543 that promote jarosite transformation to gray hematite, while similar mechanisms to remove  
544 chloride from solution are lacking.

545         The relative lack of iron in the X-ray amorphous component of VRR sediments compared  
546 to the iron content of Duluth (the drill sample in the Blunts Point member just below VRR) may  
547 be the result of such phases crystallizing to form iron(III) (oxyhydr)oxides and sulfates such as  
548 jarosite, akaganeite, and hematite (McAdam et al., 2020; Rampe et al., 2020). However, it remains  
549 unclear whether the amorphous component of VRR sediments could have directly converted to  
550 gray, crystalline hematite without first forming an intermediate phase. Jarosite elsewhere in the

551 Murray formation may be as young as the Amazonian (Martin et al., 2017). If this precursor of  
552 gray hematite formed from amorphous material via a prior diagenetic event, then this would  
553 indicate multiple periods of aqueous activity that substantially post-dates primary sediment  
554 deposition at Gale crater.

555 The observations of this study further support the formation of gray hematite at VRR as  
556 occurring under non-reducing conditions. The isochemical nature of alteration of VRR noted  
557 above precludes the formation of gray hematite from Fe(II)-bearing groundwaters because these  
558 would have increased the total iron content. Our results provide a formation mechanism for gray  
559 hematite that occurs under oxidizing conditions: diagenetic transformation of jarosite. The  
560 diagenetic event that produced gray hematite is thus unlikely to have produced a redox gradient  
561 that would generate chemical energy to support life at VRR.

562

## 563 **5 Conclusions**

564 Jarosite is the first iron(III) mineral known to occur on Mars demonstrated to serve as a  
565 diagenetic precursor for gray hematite. Transformation to coarse-grained hematite is aided by  
566 acidic conditions generated by jarosite dissolution. This creates low degrees of hematite  
567 supersaturation, and thus few initial nuclei, while also maintaining elevated dissolved iron  
568 concentrations, leading to fairly rapid particle growth. Chloride-rich fluids, particularly when  
569 combined with acidic conditions, appear to play an active role in the dissolution of iron(III)  
570 minerals, including jarosite, by increasing precursor mineral dissolution rates and solubilizing iron  
571 via aqueous complexation, thereby promoting larger final hematite particle sizes. The gray  
572 hematite found throughout VRR may have formed from chloride-rich fluids dissolving jarosite  
573 and reprecipitating the iron as hematite. Other minerals investigated (akaganeite, ferrihydrite,  
574 goethite, schwertmannite, and fine-grained hematite) are not promising precursor minerals to the

575 gray hematite at VRR. The distinct behavior of jarosite may be due to differences in transformation  
576 mechanisms (dissolution and reprecipitation versus solid-state transformation) or slow rates of  
577 initial hematite nucleation due to the absence of edge-sharing iron octahedra.

578

### 579 **Acknowledgements**

580 This research was funded by Washington University. A.L.K. was supported by the NASA  
581 Mars Data Analysis Program through Award No. 80NSSC20K0939. K.M. was supported by the  
582 NASA Science Mission Directorate Future Investigators in NASA Earth and Space Science and  
583 Technology (FINESST) program through Award No. 80NSSC19K1521. J.G.C. was supported by  
584 the NASA Exobiology program through Award No. 80NSSC18K1292. Raymond Arvidson, Paul  
585 Carpenter, and Elaine Flynn are thanked for their assistance with sample characterization. The  
586 authors acknowledge support from the Institute of Materials Science and Engineering for the use  
587 of laboratory instruments and staff assistance.

588

### 589 **Open Research**

590 All data used in the manuscript are available in the supporting information or in  
591 Washington University in St. Louis Research Data via <https://doi.org/10.7936/6rxs-103632> with  
592 Creative Commons Attribution (CC BY) 4.0 International (Knight et al., 2023). Profex version 5  
593 used for refinement of X-ray diffraction patterns is preserved at <https://www.profex-xrd.org/>  
594 (Doebelin & Kleeberg, 2015). ImageJ version 1.53k used for grain size analyses is preserved at  
595 <https://imagej.nih.gov/ij/download.html> (Schneider et al., 2012).

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