

FE-SULFATES ON MARS: CONSIDERATIONS FOR MARTIAN ENVIRONMENTAL CONDITIONS, MARS SAMPLE RETURN AND HAZARDS. P. L. King^{1,2}, M. D. Lane³, B. C. Hyde², M. D. Dyar⁴, and J. L. Bishop⁵, ¹Inst. Meteoritics, Univ. New Mexico, Albuquerque, NM 87131 USA. ²Dept. Earth Science, Univ. Western Ontario, London, ON Canada, ³Planetary Science Institute, Tucson, AZ USA. ⁴Mount Holyoke College, South Hadley, MA USA. ⁵SETI Institute/NASA-Ames Research Center, Mountain View, CA USA.

Introduction: Iron sulfates have been identified in martian meteorites and also in discrete locations on Mars [e.g., 1-4]. Most observations and calculations favor sulfates dominated by Fe³⁺ [Table; 5-7]. Whether significant mass of Fe-sulfates are found in samples returned from Mars will depend on the sampling site.

Fe-sulfates as sensitive indicators of environmental conditions: King and McSween [6] examined Fe-sulfates on Mars and discussed how they may form via either interaction of SO₂ with rocks or from alteration of Fe-sulfides (pyrrhotite). On Earth, Fe³⁺-sulfate assemblages are most common where pyrite or pyrrhotite are oxidized, for example, in ore deposits and acid-mine drainage sites [7]. Fe-sulfate assemblages are sensitive indicators of pH, water activity (*a*H₂O or relative humidity, RH), oxygen activity (*a*O₂), sulfate activity (*a*SO₄) and iron activity (*a*Fe) [6]. Preservation of Fe-sulfates requires a water-limited environment (e.g., cryogenic or arid) like on Mars [6].

To obtain information on environmental variables, it is critical to identify specific *Fe-sulfate suites* (multiple minerals, found together) on Mars. Using visible/near-IR (VNIR-with two data processing methods), thermal IR (TIR), Mössbauer (MB) and alpha-particle X-ray (APX) spectroscopies, Fe-sulfate suites in Gusev Crater were identified as ferricopiapite (ID by 5 methods), coquimbite and fibroferrite (ID with 4 methods), and possibly parabutlerite and rhomboclase (ID with 3 methods) (Table). To constrain the environmental conditions of these minerals on Mars, it is useful to examine ferricopiapite/copiapite stability (Figs. 1-3).

Bulk chemistry of the precipitating solution. Figure 1 shows that solutions in equilibrium with ferricopiapite-coquimbite have F_e2O₃:H₂O:SO₃ = 8-20:52-60:25-32, or if ferricopiapite coexists with coquimbite the solution ratio is 17:54:29.

log_aO₂-log_aH₂O conditions. Figure 2 shows that copiapite is stable over log_aO₂ = -42.4 to -38 and RH ~45 to 80%. Ferricopiapite may co-exist with copiapite at relatively high log_aO₂ and RH (near ii in Fig. 2). Other Fe-sulfates may also co-exist (i and iii in Fig. 2).

pH-p_e conditions. Figure 3 shows that ferricopiapite is stable at extremely low pH (0-1) and oxidizing conditions. The pH limits will change dependent on the co-existing phases (iv and v in Fig. 3).

Containment issues for sample return: Because of their phase relations, to preserve Fe-sulfate minerals it is best to store many of them under controlled condi-

tions, away from oxidizing agents (e.g., air) and high (or low) RH that may cause hydration (or dehydration). For a sample return mission, an economical approach is to seal Fe-sulfate-bearing materials in an airtight, waterproof container on Mars, preferably with an RH/*a*O₂/temperature data logger. If such containment is not possible, then any present Fe-sulfates may form acids that may corrode the sample/holder, or form Fe (oxy)-(hydr)-oxides that may stain the sample/holder.

Hazards of Fe-sulfates: It is not expected that Fe-sulfates will be in sufficient volume to be hazardous; however, precautions should be taken with regard to ingesting, inhaling and handling Fe-sulfates. Most of the hazards associated with Fe-sulfates are related to their high Fe content and capability for acid-production. It is doubtful that sufficient Fe would be ingested to be hazardous [lethal doses are 180-300 mg/kg body weight; 8] and an upper safety limit of 50 mg Fe/day helps limit gastrointestinal irritation (e.g., nausea, vomiting, heartburn, diarrhea, epigastric discomfort) [8]. A more likely hazard is acid production from ingested Fe-sulfates resulting in oral, esophageal, and stomach burns and possible metabolic acidosis [9]. Dermal contact with Fe-sulfates produces irritation and some minerals (e.g. rhomboclase) may cause acid burns to the skin, eyes, and mucous membranes. Inhalation may cause pulmonary dysfunction, likely due to acid burns, and pulmonary fibrosis may occur [9].

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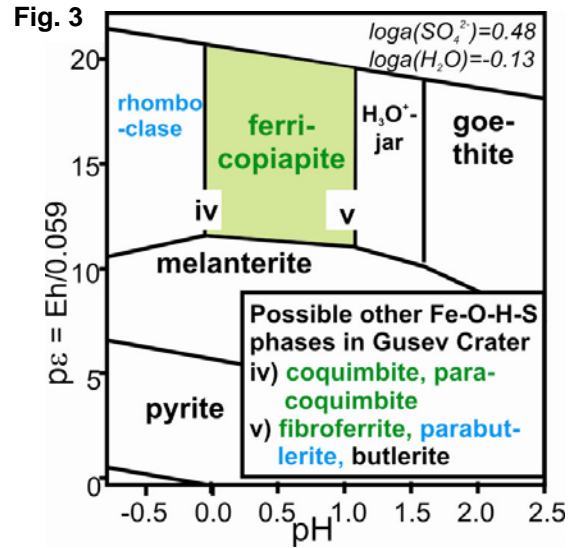
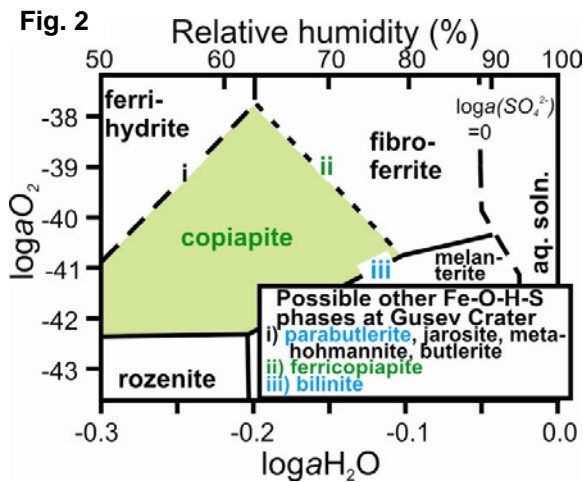
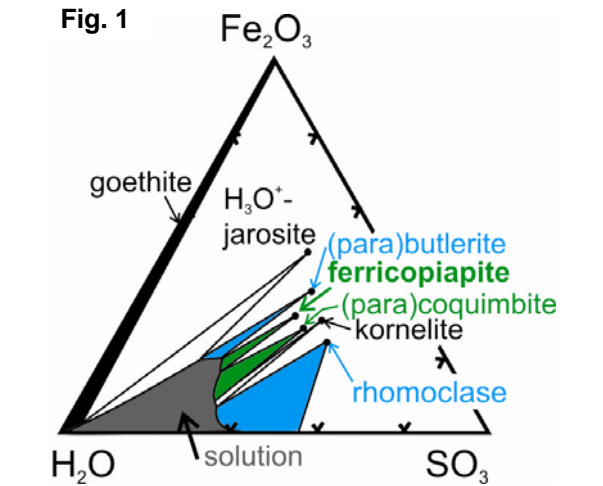


Figure 1: Fe₂O₃-H₂O-SO₃ diagram [modified after 11] showing the stability of different Fe³⁺-sulfates, goethite and solution.

Figure 2: log_aO₂ versus log_aH₂O (or relative humidity) diagram showing the stability ranges of certain Fe-sulfate and Fe-hydroxide minerals and solution [modified after 12]. Other minerals identified with spectroscopic methods may have stability boundaries as postulated (i, ii, iii), but their exact locations have not been calculated yet.

Figure 3: pE versus pH diagram for various Fe-sulfates, pyrite and goethite [modified after 13]. Other minerals identified with spectroscopic methods may have stability boundaries as postulated (iv, v), but their exact locations have not been calculated yet.

Table: Fe-sulfates identified at Gusev Crater, Mars.

Mineral	Ideal Formula	Lane et al. [1] examined PR soil# with APX plus:			Johnson et al. [2] used VNIR† on samples at several Gusev localities	Found on Earth with fcop*
		VNIR†	TIR	MB		
Fe-sulfates identified using at least 4 methods						
Ferricopiapite	Fe ³⁺ _{4.6} (SO ₄) ₆ (OH) ₂ ·20H ₂ O	Y	Y	Y	Yell. Tyrone	Y
Coquimbite	Fe ³⁺ ₂ (SO ₄) ₃ ·9H ₂ O	Y	Y	N	W. PR	Y
Paracoquimbite	Fe ³⁺ ₂ (SO ₄) ₃ ·9H ₂ O	Y	Y	N	W. Tyrone, PR	Y
Fibroferrite	Fe ³⁺ SO ₄ (OH)·5H ₂ O	Y	N	Y	Yell. Tyrone, Arad, PR	Y
Fe-sulfates identified using at least 3 methods						
Parabutlerite	Fe ³⁺ (SO ₄)(OH)·2H ₂ O	n.a.	Y	Y	n.a.	Y
Rhomboclase	(H ₃ O)Fe ³⁺ (SO ₄) ₂ ·3H ₂ O	Y	N	N	Yell. Tyrone, W. Arad	Y
Fe-sulfates identified by at least 1 method						
H ₃ O ⁺ jarosite	H ₃ O ⁺ Fe ³⁺ ₆ (SO ₄) ₄ (OH) ₁₂	n.a.	n.a.	n.a.	Yell. Tyrone, Arad	Y
Bilinite	Fe ²⁺ Fe ³⁺ ₂ (SO ₄) ₄ ·22H ₂ O	n.a.	Y	N	n.a.	Y
Butlerite	Fe ³⁺ (SO ₄)(OH)·2H ₂ O	n.a.	n.a.	Y	n.a.	Y
Metahohmannite	Fe ³⁺ ₂ (SO ₄) ₂ O·4H ₂ O	N	N	Y	n.a.	N

#Fe-phosphate also identified in Paso Robles (PR) soil. †VNIR [1] used a pattern-matching technique and VNIR [2] used a spectral database deconvolution technique. *Data on mineral assemblages found with fcop (ferricopiapite) from [8]. Note: Fcop may also be associated with other Fe²⁺-sulfates (e.g., melanterite, szomolnokite, rozenite), Fe³⁺-Fe²⁺-sulfates (e.g., romerite, voltaite), and Fe³⁺-sulfates (e.g., ferrinatrite, hohmannite, metavoltine, quenstedtite), but these have not been identified at Gusev Crater. Y- definite identification, N- not identified; n.a.- measurement not made; Yell. Tyrone- yellow Tyrone soil; W. PR- white Paso Robles soil; W. Tyrone- white Tyrone soil; W. Arad- white Arad soil, Arad- white and yellow Arad soils.