

SULFUR MINERALOGY AT THE MARS PHOENIX LANDING SITE. D. C. Golden¹, D. W. Ming², B. Sutter¹, B. C. Clark³, R. V. Morris², W. V. Boynton⁴, M. H. Hecht⁵, and S. P. Kounaves⁶; ¹ESCG-JE23, Houston TX, ²NASA-JSC, Houston, TX, ³Space Science Institute, Boulder, CO, ⁴LPL, University of Arizona, Tucson, AZ; ⁵JPL, Pasadena, CA. and ⁶Dept of Chemistry, Tufts University, MA.

Introduction. The Mars Phoenix Scout mission landed at the northernmost location (~68°N) of any lander or rover on the martian surface. This paper compares the S mineralogy at the Phoenix landing site with S mineralogy of soils studied by previous Mars landers. S-bearing phases were not directly detected by the payload onboard the Phoenix spacecraft. Our objective is to derive the possible mineralogy of S-bearing phases at the Phoenix landing site based upon Phoenix measurements in combination with orbital measurements, terrestrial analog and Martian meteorite studies, and telescopic observations.

Sulfur mineralogy on Mars. Sulfur and chlorine (typically 5-10 wt. % as SO₃; 0.4-1.0 wt. % as Cl) are ubiquitous global volatiles in Martian soil and dust so they likely occur in the dust and soils at the Phoenix landing site. Sulfur also occurs locally in much higher concentrations in Gusev Crater (e.g., Paso Robles class soils, 29.6 class ave. wt. % as SO₃, 0.5 class ave. wt. % as Cl, [1]) and Burns Outcrop in Meridiani Planum (21.7 ave. wt. % as SO₃ and 1.2 ave. wt. % as Cl, from [2]). Sulfur mineralogy at the Phoenix landing site was derived first by assuming a suite of Martian minerals (observed) and Mars S-bearing oxidants (hypothetical) as potential Martian minerals based upon mineralogy determined by landed, orbital and telescopic observations, and martian meteorite and terrestrial analog studies (e.g., [3]). Next, the suite of possible candidates were refined using (1) evolved gas mineralogy determined by Phoenix's Thermal and Evolved Gas Analyzer (TEGA), (2) soil solution chemical properties (i.e., redox, pH, EC, ionic compositions) obtained by Phoenix's Wet Chemistry Laboratory (WCL); and (3) orbital observations of the northern Polar Region by the Mars Reconnaissance Orbiter and Mars Express.

The starting suite of possible S-bearing phases based on spacecraft remote sensing, robotic rovers, Mars meteorite analysis, and laboratory analog studies are Mg-sulfates (e.g., kieserite), Ca-rich sulfates (e.g., anhydrite, gypsum), Fe-rich sulfates; (e.g., jarosite, ferric sulfate), sulfides (e.g., pyrite, pyrrhotite), sulfites (e.g., hannebachite), thiosulfates, (e.g., sidpietersite), and highly oxidized peroxy monosulfates and peroxydisulfates (these strong oxidants have no known natural terrestrial occurrences).

Phoenix TEGA and WCL results. The TEGA evolved gas analysis (EGA) of a surface sample dubbed "Baby Bear" evolved CO₂ (two major releases

from 200-600°C and 700-1000°C), H₂O (two releases from 325-500°C and 700-1000°C), and a mass 32 species (325-625°C) [4, 5, 6]. No SO₂ or other S-containing gas species were identified by TEGA during heating of Phoenix soils up to 1000°C. The mass 32 species is likely O₂ evolved from the thermal decomposition of a perchlorate salt [6] although S and hydrazine also have a mass of 32 and cannot be totally ruled out.

The soil pH was 8.3±0.5 [7] and in combination with the thermal and evolved gas properties of soils at the Phoenix landing site suggest the presence of a Ca-carbonate [4]. Calibrations are still underway to determine if there is soluble SO₄ in the Phoenix soils. The Wet Chemistry Laboratory (WCL) data have important implications on the S-phases that may be present in soils (see below).

Absence of SO₂ (No mass 64 fragment). Most sulfates evolve SO₂ in the range of 25-1000°C; however, sulfates of alkali metals (i.e., Na, K), and Ca do not evolve SO₂ in this region [8]. The absence of SO₂ indicates that either there is no sulfate in the soils at the Phoenix landing site or that the sulfate is in a thermally stable form to 1000°C (i.e., Na-, K-, and/or Ca-sulfate, see Fig.1). The TEGA results eliminate the possibility of Mg- and Fe-sulfates occurring in the soils at the Phoenix landing site because these sulfates breakdown well below 1000°C and evolve SO₂ [e.g., 8; 9]. The possibility of no S-bearing components in soils cannot be ruled out; however, the presence of Cl (in the form of perchlorate) and the well-known correlation of Cl and S in martian global dust and soils strongly suggests that S is present in the soils at the Phoenix landing site. Alkali sulfates, which are relatively soluble, may be S-containing phases because WCL did measure appreciable activities for Na in addition to Ca [7]. The most likely candidate for a sulfate mineral phase is a Ca-sulfate (e.g., gypsum, bassanite, anhydrite). Ca-rich sulfates (gypsum) have been identified in the longitudinal dunes of Olympia Planitia region near the north pole [10]; however, no distinct water release was detected by TEGA that would indicate the dehydration of gypsum or bassanite (i.e., H₂O releases around 120°C). The evidence favors anhydrite if a Ca-sulfate phase is present in Phoenix soils.

Evolution of O₂. Oxygen evolution between 325-625°C in combination with the WCL ion selective electrode measurements strongly suggest the presence of a perchlorate salt in the Phoenix soils [6]. Perchlor-

rates are powerful oxidants generating O_2 when heated that may react with any reduced S forms. Therefore, reduced S forms such as sulfides and thiosulfates will likely be oxidized and evolve SO_2 , which was not detected by TEGA. Sulfites on the other hand will be oxidized to sulfate in the presence of perchlorate (i.e., O_2 released during thermal decomposition) and for all practical purposes will act like sulfates. The lack of SO_2 detection suggests that S is not in the form of sulfides and thiosulfates in the Phoenix soils; however, some sulfites (i.e., Na, K, Ca) cannot be ruled out because they may form thermally stable sulfates (stable between 25-1000°C) during the evolution of O_2 from the thermal decomposition of perchlorate salts.

Persulfates are also a possible oxidant and even if they were present they would release O_2 (mass 32) and leave behind a sulfate byproduct. Persulfates however decompose at temperatures lower than 365°C and hence are not likely candidates for S-bearing phases at the Phoenix landing site.

Conclusion. The most likely S-bearing phase at Phoenix site is anhydrite based on the TEGA, WCL, and orbital datasets. Sodium- and K-sulfates are relatively soluble and the low concentrations of K in solution suggest that K-sulfates are not a primary S-bearing phase at the Phoenix landing site. Additional refinement of the TEGA and WCL datasets should provide further constraints (e.g., redox measurements, ionic activities) on the S-bearing mineralogy at the Phoenix landing site (e.g., constraints on Ca- vs. Na-sulfates). There is the remote possibility that the soils around the Phoenix landing site are void of S, which would indicate a very different soil material than observed at all five other landing sites around the planet. The presence (or not) of S at the Phoenix site has important implications to the aqueous history of the Martian polar regions. Anhydrite, for example, may have formed from interaction of a Ca-rich minerals (e.g., calcite, anorthite) with sulfuric acid waters or fog under warm temperatures (e.g., $>40^\circ C$ or mild hydrothermal conditions). Alternatively, gypsum may have formed under wet and warm periods and dehydrated over time to anhydrite.

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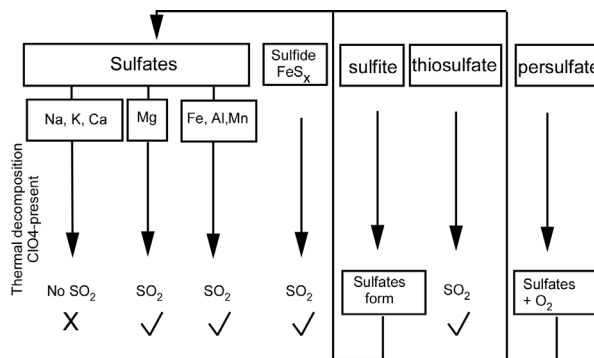


Figure 1: Thermal and evolved gas behaviors for candidate S-bearing phase with the presence of perchlorate salts. No SO_2 evolved from soils that were heated in TEGA at the Phoenix landing site. Anhydrous Na-, K-, and Ca-sulfates as possible candidates that do not evolve SO_2 upon heating to 1000°C. Sulfates are probable formation products during the thermal decomposition of sulfites and persulfates. The flow (arrow) from the sulfite and persulfate columns to the sulfates column suggests that the sulfates that form during the thermal decomposition of sulfites and persulfates have thermal properties similar to the sulfates listed in this column [X = no SO_2 evolved; ✓ = SO_2 evolved].