

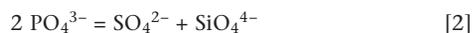
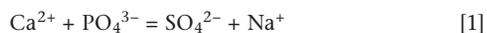
# SULFUR IN THE APOLLO LUNAR BASALTS AND IMPLICATIONS FOR FUTURE SAMPLE-RETURN MISSIONS

Maryjo Brounce<sup>1</sup>, Jeremy W. Boyce<sup>2</sup>, Jessica Barnes<sup>3</sup>, and Francis M. McCubbin<sup>2</sup>

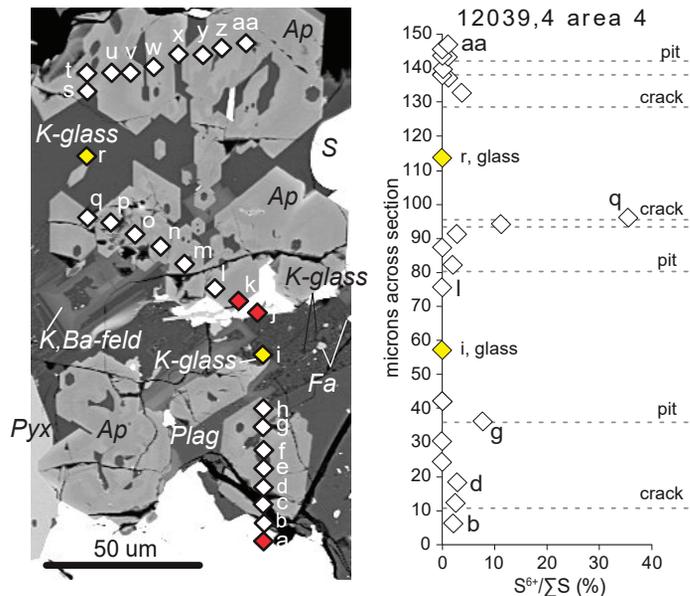
Between 1969 and 1972, Apollo mission astronauts explored the lunar surface, collecting geologic materials and returning them to Earth for careful study. After consideration of many lines of evidence, one of the many major results of studying the Apollo rocks is the broad scientific consensus that the Moon formed from the debris of a giant impact of a large body with the proto-Earth (e.g., Stevenson 1987). This left the Moon depleted in highly volatile elements such as hydrogen, relative to Earth. So it was thought.

In situ analytical techniques have advanced significantly since the Apollo era. This now allows scientists to measure the composition of the Apollo rocks far more precisely, which has been done in relation to element abundance, isotopic composition, and speciation of the highly volatile elements of carbon, hydrogen, sulfur, and chlorine. Furthermore, these measurements are now routinely performed at the spatial scale of a few microns, which is necessary for measuring the phases found in the Apollo materials that are likely to contain these volatile elements. The phases in question are the volcanic glass beads found in lunar soils and regolith samples; glassy melt inclusions trapped in the olivines and pyroxenes that comprise the glass beads and the igneous rocks; and volatile-bearing accessory mineral phases, such as apatite [Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, F, Cl)]. Through advanced in situ measurements, it has become apparent that these phases contain higher concentrations of carbon, hydrogen, sulfur, and chlorine than previously thought, and, in some cases, perhaps in concentrations similar to those observed in materials from Earth (e.g., Saal et al. 2008; Wetzel et al. 2015; Boyce et al. 2010). This observation has led to a significant revival of interest in examining models for the giant impact hypothesis for the formation of the Moon.

One particularly puzzling aspect of the volatile chemistry of the Apollo lunar rocks is the observation of hundreds to thousands of parts per million of sulfur dissolved in the phosphate mineral apatite (Boyce et al. 2010). Rocks from Earth, where apatite is common, are sufficiently oxidized to contain sulfur dissolved as sulfate (SO<sub>4</sub><sup>2-</sup>, where the oxidation state of sulfur is S<sup>6+</sup>). When apatite crystallizes from such a magma, sulfate substitutes into the apatite mineral structure for the phosphate anionic group in a charge coupled substitution with SiO<sub>4</sub><sup>4-</sup> or Na<sup>+</sup> (Fleet et al. 2005); see EQUATIONS 1 and 2 below:



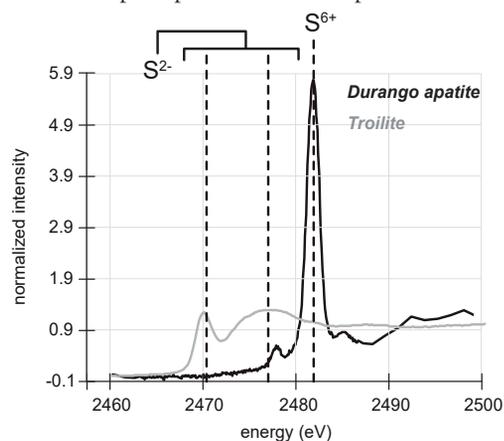
However, the Apollo lunar rocks are much more reduced than rocks from Earth—apparent in thin section from the presence of iron metal and other phases—and should contain sulfur dissolved as sulfide (S<sup>2-</sup>), which was not known to partition into natural apatite the way sulfate does. Why then, does lunar apatite contain so much sulfur? This question had been difficult to answer, in part because the lunar apatites are very small: they are on the order of 1–20 μm (rarely 100 μm) in longest dimension (Fig. 1). The hundreds to thousands of parts



**FIGURE 1** (LEFT) Backscatter electron image of thin section 12039,4 (thin section number 4 from lunar rock specimen 12039, a pigeonite basalt collected during NASA's Apollo 12 mission). Phases labeled as follows: Ap = apatite; S = sulfide; Fa = fayalite; Plag = plagioclase; Pyx = pyroxene; K,Ba-feld = K-Ba-feldspar; K-glass = K-rich mesostasis glass. Sulfur X-ray absorption near-edge structure (S-XANES) analysis positions marked in diamonds: red = sulfide measurement; white = apatite measurement; yellow = glass measurement. (RIGHT) The proportion of S<sup>6+</sup> and S<sup>2-</sup> present determined via S-XANES expressed as the percentage of S<sup>6+</sup>: sulfide-only has S<sup>6+</sup>/ΣS = 0; sulfate-only has S<sup>6+</sup>/ΣS = 100. The position of cracks and pits in the thin section are marked with horizontal dashed gray lines.

per million sulfur discovered in these apatites is much higher than expected, yet it is still below the detection limit of many available analytical techniques.

Synchrotron-source sulfur X-ray absorption near-edge spectroscopy (S-XANES) can readily distinguish between the K-alpha peak shapes of electronic transitions in sulfide from those peaks in sulfate (Fig. 2). At beamlines of sufficiently brilliant light sources, such as that of the GSECARS (GeoSoilEnviro Center for Advanced Radiation Sources) beamline 13IDE at the Advanced Photon Source at the Argonne National Laboratory (Illinois, USA), this can be done at ~5 μm spatial scales on samples with ≥w100 parts per million sulfur present as sulfate or sulfide,



**FIGURE 2** Sulfur X-ray absorption near-edge structure (S-XANES) spectra of S<sup>6+</sup>-bearing apatite from Earth (Durango apatite standard, black curve) and the S<sup>2-</sup> mineral troilite (FeS, gray curve), demonstrating the ability of S-XANES to distinguish between S<sup>6+</sup> (Durango) and S<sup>2-</sup> (troilite).

1 Department of Earth and Planetary Sciences  
University of California Riverside  
Riverside CA 92592 USA  
E-mail: mbrounce@ucr.edu

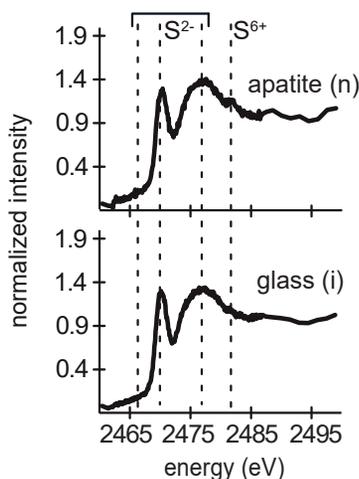
2 Astromaterials Research and Exploration Science  
NASA Johnson Space Center  
Houston TX 77058 USA  
E-mail: jeremy.w.boyce@nasa.gov, francis.m.mccubbin@nasa.gov

3 Lunar and Planetary Laboratory  
University of Arizona  
Tucson AZ 85721 USA  
E-mail: jibarnes@arizona.edu

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or as a mixture of the two. This cutting-edge analytical technique is ideally suited to answering the question, “Why is there sulfur dissolved in lunar apatite?”

To answer this question, two Apollo-era lunar rocks were examined—Apollo 11 rock sample 10044, a high-Ti ~3.7 billion-year-old basalt; Apollo 12 rock sample 12039, a ~3.2 billion-year-old low-Ti basalt. Both are slightly vesiculated and contain pyroxene, plagioclase, and ilmenite phenocrysts. Apatite occurs as an accessory phase in both samples, sometimes in contact with a glassy groundmass (known as a “mesostasis”), which also contains sulfide blebs, iron metal, and a variety of phases that indicates crystallization under very reducing conditions. When the oxidation state of sulfur in the apatite was measured using S-XANES, the answer was immediately obvious—the sulfur was present in the apatite as sulfide (FIG. 3) (Brounce et al. 2019). Sulfur in the glassy groundmass was also present as sulfide. Both observations confirmed that lunar rocks are very reduced, consistent with the presence of Fe metal in the same rocks. This is exciting, because it is the first measurement of a natural sulfide-bearing apatite, and confirms recent hypotheses about sulfide substitution into apatite made on the basis of ab initio computations and experimental work (Kim et al. 2017; Konecke et al. 2017a). Those hypotheses suggest that, if possible, sulfide substitutes for  $\text{OH}^-$ ,  $\text{Cl}^-$ , and/or  $\text{F}^-$  on the column site of the apatite mineral structure. The discovery of sulfide-bearing apatite suggests that the stoichiometry of the column site in apatites from sufficiently reduced systems should be  $\text{S}^{2-} + \text{OH}^- + \text{F}^- + \text{Cl}^- = 1$ , and that the presence of sulfide in the apatite will impact studies seeking to estimate the water content of a magma from measurements of  $\text{OH}^-$  in apatite.



**FIGURE 3** Sulfur X-ray absorption near-edge structure (S-XANES) spectra of an apatite grain (spot n on FIGURE 1) and the K-rich glass (spot i on FIGURE 1) in thin section 12039,4 (pigeonite basalt from the Apollo 12 mission). The energy positions of peaks for sulfide ( $\text{S}^{2-}$ ) and sulfate ( $\text{S}^{6+}$ ) are marked with vertical dashed lines.

Upon closer examination of the lunar rocks, another surprising observation was made. In addition to the sulfide present in the glassy groundmass and apatite grains, there was sulfate present in the cracks and pits of the polished thin section surface (FIG. 1) (Brounce et al. 2019). And this sulfate is heterogeneously distributed: not every crack or pit has sulfate, suggesting that it is not from the epoxy that the Apollo

collection curators had used to make the thin section. This sulfur is not thought to be dissolved in mineral structures but precipitated on top of them within the cracks as a secondary mineral phase. It is not known whether this secondary sulfur was precipitated in the rock on the lunar surface (revealing important details of hydrothermal or space weathering processes, e.g., Konecke et al. 2017b) or whether it was precipitated in the rock once it had been brought back to the relatively hydrous, oxidizing conditions of Earth’s surface, so presenting important implications for how we store, process, and protect planetary samples in our laboratories (all of the pristine Apollo samples are currently curated under dry gaseous  $\text{N}_2$ ).

To test between a lunar and a terrestrial origin for the secondary sulfur in Apollo-era thin sections, we will measure the oxidation state of sulfur in rocks from the Apollo 17 mission as part of the NASA Apollo Next Generation Sample Analysis (NASA ANGSA) program under Project Investigator Jessica Barnes (assistant professor, University of Arizona, USA). Some of these rocks were frozen a few weeks after their return to Earth and kept that way until now, in anticipation of then-unimagined innovations in analytical techniques and with foresight for answering the question, “What effect does Earth’s relatively warm surface temperatures have on the lunar rocks?” In celebration of the 50<sup>th</sup> anniversary of the landing on the Moon by the Apollo 11 mission, the NASA ANGSA teams will apply cutting-edge analytical techniques, including synchrotron S-XANES, to these specially frozen rocks to learn about lunar processes and to best prepare for future sample-return missions. Our team will determine the extent to which Earth’s relatively warm surface temperatures have altered the volatile composition of the Apollo rocks (concentrations, isotopes, and speciation) and make specific recommendations for the curation teams of future sample-return missions.

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