

The oxidation state of sulfur in Apollo samples 71035 and 71055. M. Brounce¹, J. Barnes², J. Boyce³, Z.E. Wilbur², F.M. McCubbin³, C. Crow⁴, J. Mosenfelder⁵, T Zega², and the ANGSA Science Team ¹University of California, Riverside; mbrounce@ucr.edu, ²University of Arizona, ³NASA's Johnson Space Center, ⁴University of Colorado, Boulder, ⁵University of Minnesota, ⁶ list of co-authors includes all members of the ANGSA Science Team (<https://www.lpi.usra.edu/ANGSA/teams/>).

Introduction: The discovery of 100s-1000s ppm sulfur [1-3] was initially puzzling because lunar basalts are thought to form at low oxygen fugacity (fO_2) conditions (including at the time of apatite crystallization) where sulfur exists in its reduced form (S^{2-}), a substitution not previously observed in natural apatite.

Recent S-XANES measurements of apatites and proximal mesostasis in the lunar basalts 12039 and 10044 have shown that sulfur is indeed present as S^{2-} in both the mesostasis glass and apatite when measurements are performed far from cracks or pits in the thin section [4]. This observation is consistent with other mineralogical indications of low fO_2 (IW-1), such as the presence of Fe-metal, ulvöspinel, ilmenite, fayalite, and silica. In the same study, in addition to clear spectral evidence for the dominance of S^{2-} , analyses of apatite grains in both samples that were acquired near cracks or pits in the thin section sometimes revealed non-negligible spectral evidence for the presence of S^{6+} (e.g., $S^{6+}/\Sigma S > 0.03$; [4]). Because S^{6+} was not observed in the mesostasis glass near the apatite grains measured, or in any phase far from cracks or pits in the studied thin sections, it was interpreted as either primary S^{2-} altered to S^{6+} in the thin section, or S^{6+} of secondary origin, deposited in the fractures of the samples [4, 5]. It is unknown whether this alteration is lunar or terrestrial in origin, with implications for lunar petrogenesis if lunar [e.g., 5], or sample handling and curation if terrestrial.

To test between lunar and terrestrial origins for observed S^{6+} in Apollo-era thin sections, we will measure the oxidation state of sulfur in apatite and associated phases in a specially frozen sample from a boulder sampled at Station 1A during the Apollo 17 mission as part of the NASA Apollo Next Generation Sample Analysis (ANGSA) program. Here, we present "control" measurements of samples 71035 and 71055, using Apollo era thin sections of aliquots of these rocks that were processed upon return to Earth and subsequently stored under N_2 atmospheres at room temperature. These will be compared to measurements using newly made thin sections of aliquots of the same rocks (71035 and 71055). In addition, 71036, which has been in cold storage ($-20^\circ C$) since several weeks after the return of the Apollo 17 mission to Earth, has been made available recently through the ANGSA program.

With 71036 we can test the effect of storage temperature on potential oxidation of S^{2-} to S^{6+} in the relatively oxidizing and warm conditions of Earth's surface.

Sample descriptions: 71035 and 71055 are both samples of the same boulder encountered at Station 1a of the Apollo 17 EVAs. Sample 71055 has been dated at 3.64 ± 0.09 Ga [6]. Both 71035 and 71055 are vesicular high titanium basalts with a cosmic ray exposure age of 110 ± 7 Ma [7]. They are olivine-, Ca-pyroxene- and plagioclase-bearing ilmenite basalts with minor amounts of ulvöspinel, troilite, Fe metal, SiO_2 , apatite, and mesostasis glass [8]. In addition to these previously reported phases, detailed examination in the present study also reveals the presence of baddeleyite, tranquillityite, merrillite, and K-feldspar [9] (Fig. 1). Importantly, the presence of ulvöspinel, troilite, Fe-metal, and silica in the mesostasis with apatite fixes fO_2 during apatite crystallization to $\leq IW$.

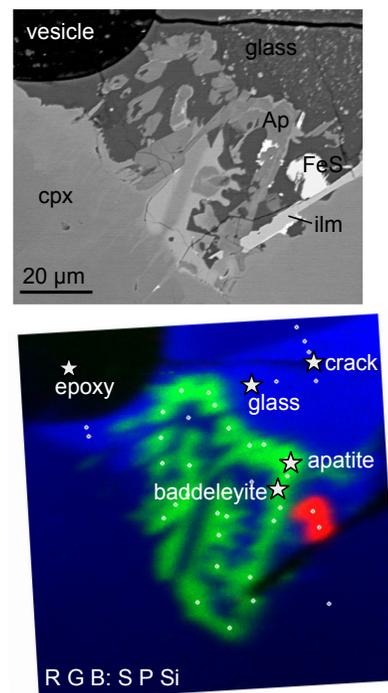


Fig. 1. Top panel: BSE image of a region of interest in thin section 71055, 71. Ap=apatite; ilm=ilmenite; cpx=clinopyroxene. Bottom panel: Synchrotron XRF map of S, P, and Si abundances (RGB). Stars indicate analysis positions, for which spectra are shown in Fig. 2.

Results: Apatite grains far from cracks or pits, or far from intermingled baddeleyite in both 71035, 29 and 71055, 71 contain sulfur present only as sulfide. The proximal mesostasis glass in both thin sections, when present, also contains sulfur only as sulfide (Fig. 2). There is significant sulfur in the epoxy used in both thin sections – 71055, 71 contains sulfur mostly as S^{6+} , while 71035, 29 contains sulfur as a mixture of S^{4+} and S^{6+} (Fig. 2). In all measurements approaching cracks or pits in the measured regions, non-negligible to strong spectral evidence for sulfate is observed (Fig. 2). In measurements of 71055, 71, because the epoxy appears to contain mostly S^{6+} (i.e., indistinguishable from the expectation of spectral forms from apatite or glass containing only S^{6+}), it is not possible to distinguish between measurements containing S^{6+} resulting from contamination by epoxy or S^{6+} dissolved in or precipitated on mineralogical phases in the thin section. In the case of 71035, 29, as in the case of previously examined thin sections 12039, 4 and 10044, 33 [4], the presence of a peak at 2474 eV that is not expected in apatite or other mineralogical phases (Fig. 2, top panel) tentatively assigned to the presence of S^{4+} , allows us to discriminate between S^{6+} present in the epoxy and sulfur dissolved in or precipitated on the phases. In 71035, 29, sulfur which is not only due to the presence of epoxy in the analytical volume appears to be heterogeneously distributed along cracks in the section, and restricted to the cracks and pits themselves.

An additional, sharp and moderate intensity peak ~ 2466 eV is observed in some measurements that are taken in intermixed textures of apatite and baddeleyite (Fig. 1). Because of the strong association between the appearance of this peak and the presence of baddeleyite, it is tentatively interpreted as a contribution from sulfur dissolved in baddeleyite as S^{2-} . Though not observed or commented on widely in studies of natural baddeleyite, synthetic ZrOS has been reported [10], and it may be that S^{2-} partitions into the baddeleyite structure in a substitution for O^{2-} . If true, the very low energy of the peak (i.e., 3-4 eV lower than observed for other S^{2-} species; Fig. 2 bottom panel; [11]) suggests significant covalent character in the Zr-S bond.

Implications: Consistent with measurements of Apollo 11 and Apollo 12 basalts [4], new measurements of two additional thin sections of Apollo 17 basalts reveal the prevalence of sulfide-only apatite and mesostasis glass (Fig. 2). The appearance of significant spectral evidence for sulfate appears restricted to fractured portions of the thin sections. High sulfur contents of some epoxies present significant hurdles for discriminating between epoxy and mineralogical sources of this oxidized sulfur in these Apollo 17 thin sections, though the low sulfur contents and presence of

a peak at 2474 eV in the epoxy used in 71035, 29 suggests that some portion of the oxidized sulfur is mineralogical. Measurement of newly made thin sections from the same samples and of the frozen rock 71036 (sourced from the same boulder) will provide a critical test to determine if storage of rocks and/or thin sections at room temperature contributes to the presence of S^{6+} in lunar thin sections.

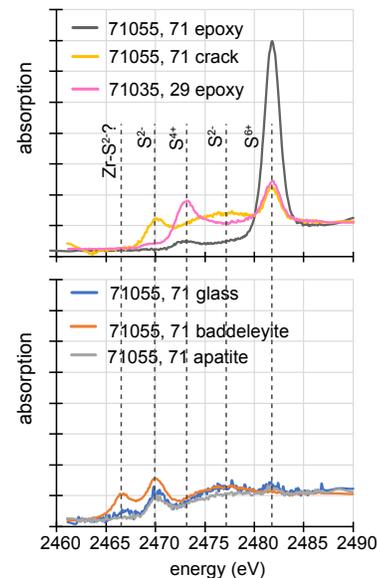


Fig. 2. Representative S-XANES spectra. All spectra from 71055, 71 are marked in Figure 1, bottom panel.

Acknowledgments: This research was performed at GeoSoilEnviroCARS (The University of Chicago, Sector 13), APS ANL. GeoSoilEnviroCARS is supported by the National Science Foundation – Earth Sciences (EAR-1634415) and Department of Energy – Geosciences (DE-FG02-94ER14466). This research used resources of APS, a U.S. Department of Energy (DOE) Office of Science user facility operated for the DOE Office of Science by ANL under Contract No. DE-AC02-06CH1357. Support for this research was provided by NASA ANGSA Grant # 80NSSC19K0803.

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