

**Measuring the oxidation state of sulfur in apatites in thin sections of meteorites versus Apollo rocks** M. Brounce<sup>1\*</sup>, J.J. Barnes<sup>2</sup>, C.A. Crow<sup>3</sup>, R. Economos<sup>4</sup>, T. Erickson<sup>5</sup>, J. Boyce<sup>5</sup>, Z.E. Wilbur<sup>2</sup>, F.M. McCubbin<sup>5</sup>, J. Mosenfelder<sup>6</sup>, T.J. Zega<sup>2</sup>, and the ANGSA Science Team<sup>7</sup> <sup>1</sup>University of California, Riverside; mbrounce@ucr.edu, <sup>2</sup>University of Arizona, <sup>3</sup>University of Colorado, Boulder, <sup>4</sup>Southern Methodist University, Texas, <sup>5</sup>NASA's Johnson Space Center, <sup>6</sup>University of Minnesota, <sup>7</sup>list of co-authors includes all members of the ANGSA Science Team (<https://www.lpi.usra.edu/ANGSA/teams/>). \*mbrounce@ucr.edu.

**Introduction:** Sulfur can be present in apatite mineral grains as  $S^{6+}$  [1],  $S^{2-}$  [2], or a mixture of the two [3, 4]. The proportion of  $S^{6+}$  to  $S^{2-}$  present in the apatite is thought to be predominantly controlled by the prevailing oxygen fugacity ( $fO_2$ ) conditions during crystallization (along with temperature, pressure, and major element composition; [2-4]). Measurements of apatites and proximal residual glass in the lunar basalts 12039 and 10044 by X-ray absorption near-edge structure (XANES) spectroscopy show that sulfur occurs as  $S^{2-}$  in both the mesostasis glass and apatite when measurements are performed far from cracks or pits in the thin section [2], consistent with other mineralogical indications of low  $fO_2$  ( $\Delta IW-1$ ) during petrogenesis. However, analyses of apatite grains in both samples that were acquired near cracks or pits in the thin section sometimes revealed minor but non-negligible spectral evidence for the presence of  $S^{6+}$  (e.g.,  $S^{6+}/S > 0.03$ ; [2]). This evidence 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 [2, 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 [e.g., 6].

To test between lunar and terrestrial origins for observed  $S^{6+}$  in thin sections of Apollo rocks made in the years following their return, we will measure the oxidation state of sulfur in apatite and associated phases in an Apollo 17 rock that has been specially curated at -20°C for fifty years. This work is part of the NASA Apollo Next Generation Sample Analysis (ANGSA) program. Here, we present “control” measurements of

samples 71035, 71037, and 71055, using both “previously made” thin sections (i.e., thin sections made in the years following return of the Apollo missions to Earth) and “newly made” thick sections (i.e., made and analyzed within 30 days) of rocks that were stored and processed under  $N_2$  at room temperature while on Earth. In addition, we present measurements of apatite in a moderately weathered, lunar fragmented breccia “find” meteorite, Northwest Africa (NWA) 12593, to compare the fidelity of apatite grains to their primary igneous records in meteorite samples versus those in materials retrieved by sample return missions.

**Sample descriptions:** Apollo samples 71035, 71037, and 71055 are rocks chipped from the same boulder encountered at Station 1A of the first Apollo 17 EVA. Sample 71055 was dated at  $3.56 \pm 0.09$  Ga (after [7], corrected for decay constant). However, results from [8] suggest that 71055 and 71035 both have an older crystallization age of  $\sim 3.85$  Ga. All three samples are high-Ti basalts with a cosmic ray exposure age of  $110 \pm 7$  Ma [9]. They are fine to medium-grained and contain olivine, clinopyroxene, ilmenite, and plagioclase with minor amounts of troilite, baddeleyite, tranquillityite, K-feldspar, merrillite, apatite, and residual glass [10-12]. NWA 12593 is a fragmental breccia composed of basaltic, crystalline impact melt and highlands lithologies embedded in a fine-grained impact melt matrix. The Pb-Pb geochronology of phosphate minerals in NWA 12593 suggest crystallization of most apatites between  $\sim 3.4$ - $3.5$  Ga [13].

**Results:** Apatite grains far from cracks, pits, or far from intermingled baddeleyite in 71035, 29, 71037, 5, and 71055, 71 contain sulfur present only as  $S^{2-}$  (Fig. 1). The proximal residual glass in all thin sections, when present, also contains sulfur only as  $S^{2-}$ . There is significant sulfur in the epoxy used in all “previously made” thin sections – 71055, 71 contains sulfur mostly as  $S^{6+}$ , while 71035, 29 and 71037, 5 contain sulfur as a mixture of  $S^{4+}$  and  $S^{6+}$  (Fig. 1). In all measurements adjacent to cracks or pits in the measured regions, non-negligible to strong spectral evidence for sulfate is observed. However, “newly made” thick sections of the same samples (71035, 50; 71037, 10; 71055, 249) were cut, potted, and prepared according to standard practice except that the sections were left to cure under partial

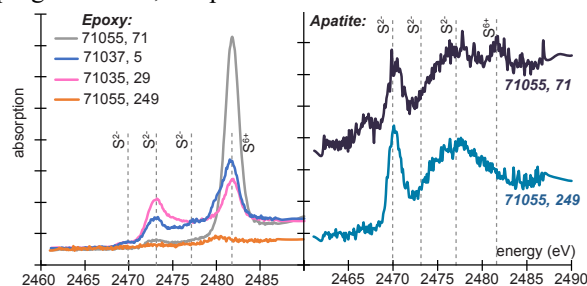


Fig. 1: Normalized S-XANES spectra of epoxy used in Apollo samples (left) and apatite grains from two sections of sample 71055 (right).

vacuum in a warm oven (~16 mm Hg, 55 °C). The resultant epoxy in all three newly made thick sections contain significantly less sulfur, as evident in the degraded signal-to-noise of S-XANES spectra collected directly on epoxy (Fig. 1). Furthermore, there are no  $S^{6+}$  spectral features in any phase (apatite, residual glass) in any portion of the “newly made” thick sections. These data strongly suggest that the epoxy itself and/or interaction between Apollo samples and epoxy at the margins of the cracks and pits of these rocks in Earth’s atmosphere during the epoxy cure is the reason for the presence of  $S^{6+}$  in the otherwise very reduced Apollo rocks studied here, and that curing under partial vacuum eliminates this signal.

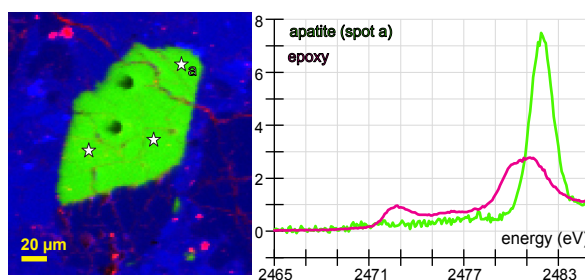


Fig 2: XRF map of apatite grain in NWA 12593 (R G B: S P Si; left) and normalized S-XANES spectra of apatite spot a (marked with a white star on XRF map) and of the epoxy used in the sample.

In contrast to the Apollo samples, apatites in lunar breccia meteorite NWA 12593 contain substantial spectral evidence of  $S^{6+}$  in addition to  $S^{2-}$  (Fig. 2). Though it is possible that some portion of the  $S^{6+}$  signal results from epoxy and/or epoxy interaction, like in the case of the “previously made” thin sections of the Apollo rocks described above, sulfur is clearly and pervasively precipitated in the widespread system of cracks and pits in the meteorite sample. Analysis directly in these fractures reveals the presence of  $S^{6+}$  at higher abundance than in the epoxy used in this thin section (by a factor of ~7) and a narrow  $S^{6+}$  peak shape that distinguishes it from that of the epoxy, which is wider and centered at slightly lower energy (Fig. 2). There is also low abundance but non-negligible  $S^{6+}$  present in the silicate minerals proximal to the measured apatites, in contrast to the Apollo samples (both Apollo-era thin sections and newly made thick sections), where analysis of proximal silicate minerals yield sulfur of any oxidation state below detection (i.e., SNR = 0 in S-XANES spectra). We conclude that significant quantities of  $S^{6+}$  were deposited in the cracks and pits, as well as precipitated in apatite in NWA 12593. Through comparison to Apollo samples 10044 and 12039 [2], and 71035, 71037, 71055 (this study), we tentatively suggest that the observed  $S^{6+}$  is not a primary

feature of any lunar igneous process but reflects secondary processes associated with the impact that ejected NWA 12593 from the lunar surface, its transit in space, and/or exposure to Earth’s atmosphere between the time of entry and impact and procurement for this study.

**Implications:** Consistent with measurements of Apollo 11 and Apollo 12 basalts [2], measurements of three “newly made”, vacuum-cured thick sections of Apollo 17 basalts reveal the prevalence of sulfide-only apatite and residual glass (Fig. 2). The appearance of significant spectral evidence for sulfate in Apollo rocks can be eliminated by curing epoxy under partial vacuum, leading to very low sulfur epoxy. Measurements of the frozen rock 71036 will provide additional tests of handling and preparation procedures, including the effect of storage temperature. New measurements of lunar meteorite NWA 12593 reveal pervasive deposition of  $S^{6+}$  throughout the sample, pointing to important secondary processes specific to meteorite samples that produce an increase in sulfur concentration and oxidation not observed otherwise in samples retrieved directly from the lunar surface. On one hand, this result presents an opportunity to constrain the effects of impact and alteration on the volatile elements present in meteorite samples. On the other hand, it argues strongly in favor of the utility of sample return missions when feasible.

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