

THE OXIDATION STATE OF SULFUR IN LUNAR, MARTIAN, AND TERRESTRIAL APATITE. M. Brounce¹, J. Boyce², F.M McCubbin², E. Stolper³, and J. Eiler³, ¹Department of Earth Sciences, University of California, Riverside, CA ²Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX, ³Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA

Introduction: Lunar apatites contain 100s-1000s ppm sulfur. This is puzzling because lunar basalts are thought to form in low oxygen fugacity (fO_2) conditions, including at the point of apatite saturation and crystallization, where sulfur can only exist in its reduced form (S^{2-}), a substitution not previously observed in natural apatite. We present S-XANES and EPMA measurements of the oxidation state and abundance of S in lunar apatites and associated mesostasis glass in order to determine the oxidation state of sulfur in lunar materials. We also present S-XANES and EPMA measurements of the oxidation state and abundance of S in martian apatites, which incorporate both S^{2-} and S^{6+} ; we suggest that the S^{6+}/S^{2-} ratios of apatites containing S of mixed valence might provide a measure of the fO_2 of apatite formation or last equilibration.

Samples: *Lunar:* Sample 12039 is a 3.2 ± 0.05 billion year old, low- TiO_2 basalt [1]. Sample 10044 is a ~ 3.71 - 3.73 billion year old, high- TiO_2 basalt [2, 3]. Apatite can be found in mesostasis pockets in both samples, in contact with mesostasis glass that also contains sulfide blebs, native iron, ulvospinel, fayalite and SiO_2 , among other phases (Fig. 1). Studied apatites in both rocks have equant and skeletal grains with central cavities filled with glass, and are compositionally zoned (Fig. 1); we suggest these are consistent with growth from silicate melt. The coexistence of Fe-metal, ulvospinel, ilmenite, and sometimes fayalite and/or silica in the mesostasis glass constrains fO_2 near the time of apatite crystallization to $\sim IW-1$ [4]. At these fO_2 s, sulfur is expected in melt as S^{2-} [6-8]

Terrestrial: Durango apatite is from volcanogenic deposits near Durango, Mexico and is associated with hematite-after-magnetite in open fractures and gas cavities within sheeted flows and flow breccias from Cerro de Mercado. Halogen-rich gases are thought to have streamed through erupting flows, depositing apatite and oxidizing magnetite to hematite, thus setting the fO_2 conditions under which Durango apatite formed at $>IW+6$ [5]. At these fO_2 s, sulfur is expected in melt as S^{6+} [6-8]

Martian: Nakhla meteorite is a 1.38 ± 0.07 billion year old olivine-bearing clinopyroxenite [9]. Apatite occurs in mesostasis pockets containing glass, plagioclase, pyroxene, and magnetite. Estimates for the fO_2 during Nakhla crystallization range from $\sim IW+3.5$ to $IW+4.5$ [10]. At these fO_2 s, sulfur is expected to be in melt as both S^{6+} and S^{2-} [6-8].

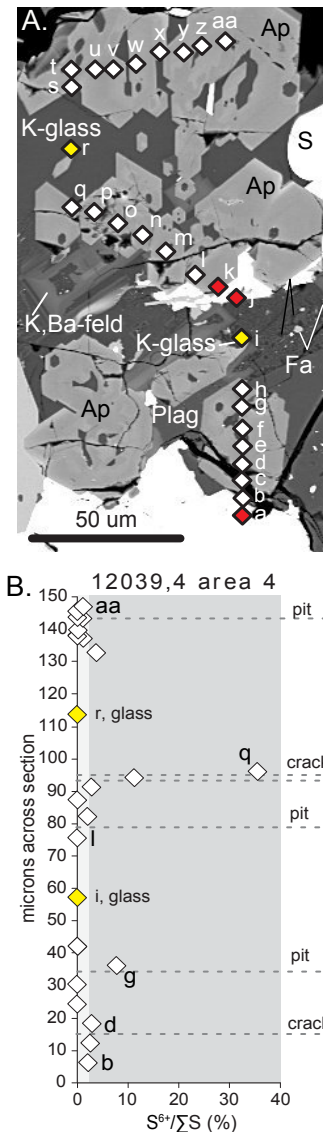


Fig. 1 A) Backscatter electron map showing locations of analyses in thin section 12039.4. Diamonds mark the position of analyses (Ap = apatite; S = sulfide; Fa = fayalite; Plag = plagioclase; K,Ba-feld = K,Ba-feldspar; K-glass = K-rich mesostasis glass). B) Calculated $S^{6+}/\Sigma S$ ratio from spectra at each analysis point from Fig. 1. Locations of cracks and pits near analysis points are marked by gray dashed lines. Dark gray field marks $S^{6+}/\Sigma S > 3\%$. Analytical uncertainties are smaller than symbol size.

Results: The measured apatites in lunar samples have S contents that vary from below the detection limit of our measurements (~ 20 ppm) up to 500 ppm. The $S^{6+}/(S^{6+}+S^{2-})$ (i.e., $S^{6+}/\Sigma S$) ratios of these apatites vary between 0 and 0.45 (Fig 1). The mesostasis glass touching measured apatite in thin section 12039,4 has 69-107 ppm S that is present only as sulfide, i.e., has $S^{6+}/\Sigma S = 0$ (Fig 1). More than half of all measurements on apatite (28 analyses out of 48 total analyses) have $S^{6+}/\Sigma S < 0.03$, which we consider to be indistinguishable from 0 on the basis of the signal-to-noise ratio of S-XANES spectra. This contrasts with our analyses of the terrestrial Durango apatite, all analyses of which have $S^{6+}/\Sigma S = 1$ (i.e., no spectral evidence for sulfide). In apatites from both 12039 and 10044, the locations of analyses that yield $S^{6+}/\Sigma S > 0.03$ are associated with fractures and/or pits (Fig 1). This suggests that the S^{6+} observed in the S-XANES spectra of lunar apatite may not reflect primary sulfur incorporated into the apatite when it crystallized, but rather could be either primary sulfide in the apatite altered to sulfate or sulfur of secondary origin.

In Nakhla meteorite, 32 measured apatites have 82 to 293 ppm total S and $S^{6+}/\Sigma S$ values of 0.05 - 0.99 (Fig 2). Each apatite is ~ 10 -20 μm across in the longest dimension and is enclosed within interstitial glass pools ~ 1 mm across, in which S content varies from below the detection limit up to 185 ppm. The $S^{6+}/\Sigma S$ values of the glass are 0.02 - 0.97, and the measured $S^{6+}/\Sigma S$ values of the enclosing glass correlates positively with the $S^{6+}/\Sigma S$ values of the enclosed apatites. The glass is broadly felsic (normative quartz + plagioclase + orthoclase > 0.90 with molar anorthite/albite ratios of 0.05 - 0.57) and also contains granular sulfides. Glass and apatite pairs within 50 μm of a sulfide grain have the lowest $S^{6+}/\Sigma S$ ratios observed ($S^{6+}/\Sigma S < 0.20$), and glass and apatite pairs > 50 μm from a sulfide grain have the highest $S^{6+}/\Sigma S$ ratios observed ($S^{6+}/\Sigma S > 0.50$).

Implications: We have documented the occurrence of S^{2-} -only apatite in nature. This observation confirms that the S contents of lunar apatites are due to the ability of S^{2-} to partition into the apatite. We have also documented the occurrence of natural apatites that contain both S^{2-} and S^{6+} in the Nakhla martian meteorite (Fig 2).

The $S^{6+}/\Sigma S$ ratios of an individual silicate melt transitions from 0 to 1 over \sim two orders of magnitude in fO_2 . Apatites coexisting with a given melt over the fO_2 range of the transition are anticipated to contain both S^{6+} and S^{2-} and thus could be used to quantify the fO_2 of the system at the time of apatite crystallization, provided that the apatite does not exchange S after

crystallization, and the sulfur can be shown to be primary to the apatite. In detail, the fO_2 dependence of the transition in $S^{6+}/\Sigma S$ for apatites coexisting with melt undergoing the same transition will depend on the individual partition coefficients of S^{2-} and S^{6+} between apatite and melt and the effects of variations in major and minor element composition of the melt and apatite (including the oxidation states of other heterovalent elements and the concentrations of OH^- , F^- , and Cl^-). Thus, development of an oxybarometer based on the $S^{6+}/\Sigma S$ of apatite would require experimental work to determine the individual partition coefficients of S^{2-} and S^{6+} between apatite and melt, and a quantification of the extent to which those partition coefficients vary as a function of pressure, temperature, oxygen fugacity, and melt and apatite composition.

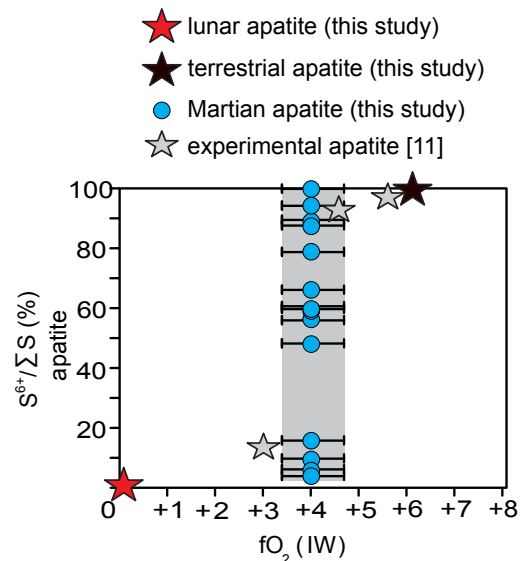


Fig. 2 The relationship between measured $S^{6+}/\Sigma S$ ratios of igneous apatites and inferred fO_2 at the time of apatite crystallization from natural apatites and experimentally grown apatites. Gray box and error bars on blue circles represent the range of accepted fO_2 s for Nakhla meteorite [10].

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