Hydrothermal activity on Earth’s Moon recorded by sulfur-in-apatite. Brian A. Konecke¹, Adrian Fiege²,³ and Adam C. Simon¹; ¹Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA. ²Department of Earth and Planetary Sciences American Museum of Natural History, New York, New York 10024-5192, USA.

Introduction: It has been hypothesized that H-rich lunar apatite rims reflect an increase of H/F in coexisting silicate melts during fractional crystallization due to the preferential major element incorporation of F over Cl and OH into the apatite structure [1]. This scenario contrasts the elevated H₂O-content in lunar magmas suggested elsewhere in the literature [e.g., 2], which suggests that fractional crystallization alone is probably incapable of explaining the volatile signatures in lunar apatite [2]. In this study, we report resemblances between the fluid-induced S-signatures of terrestrial apatites from a magmatic-hydrothermal iron oxide–apatite (IOA) ore deposit (Mina Carmen, Chile) [4] and the S-signatures of lunar apatites [1, 3] (Figure 1). Notably, sulfur (S) is incorporated into apatite—Ca₅(PO₄)₃O(F, Cl, OH)—as a trace element (e.g., up to 430 ppm S in lunar apatite rims [1, 3]), justifying the use of Nernst-type partitioning coefficients (D_{S²⁸⁻⁰⁶}²⁶) [5] to estimate the S-content in the apatite and the S-content in the coexisting melt that it crystallized from (and vice versa).

Experimental approach and analysis: Apatite crystallization experiments were conducted in internally heated pressure vessels (IHHPV) at Leibniz University Hannover (LUH). Hydrous mafic and felsic compositions were heated to 1000°C, pressurized to 300 MPa and run for 3-5 days at the fayalite-magnetite-quartz oxygen fugacity (fO₂) buffer (ΔFMQ+0). The experimental conditions were chosen to investigate end-member, best-case scenarios for lunar magmatic systems (i.e., to determine highest D_{S²⁸⁻⁰⁶}²⁶ values). Here, temperature, fO₂ and the S-content in the melt impose the strongest control on the D_{S²⁸⁻⁰⁶}²⁶ [5]; e.g., D_{S²⁸⁻⁰⁶}²⁶ decreases with (a) increasing temperature and (b) increases when fO₂ of the system is >> ΔFMQ+0, whereas (c) D_{S²⁸⁻⁰⁶}²⁶ remains constant at fO₂ ≤ ΔFMQ+0. The experimental products (e.g., apatite and glass) were analyzed for major and trace elements via electron microprobe.

Thermodynamic modeling: The thermodynamic software package MELTS [6] was applied to estimate the liquidus temperature for the evolved residual glass and Apollo 12 mare basalt 12039 (from [1, 3, 7]; T_{liqui.} = 1090±40°C and T_{liqui.} = 1189±40°C, respectively). The T_{liqui.} were used for the S-content at sulfide saturation (SCSS) model [8], which constrains the maximum S-content in lunar melts, considering that the Apollo 12 lunar melt (12039) is primary sulfide undersaturated [7]. At the low oxygen fugacity fO₂ predicted for lunar magmatism (near the ΔIW: iron-wüstite fO₂ buffer; cf., [9]) and reduced terrestrial magmas (near ΔFMQ; cf., [10]), the H₂O content of the melt has the strongest effect on the SCSS. Here, SCSS was modeled using 1-10,000 μg/g and 1-100 μg/g dissolved H₂O for evolved felsic and primitive mafic melts, respectively, in order to achieve the highest S-content in melt before reaching sulfide-saturation while considering conditions reasonable for lunar magmatism (e.g., <100 μg/g in the mafic melt; [11]).

Figure 1: Sulfur zonation in lunar (sample 12039,42 grain 12 from [1, 3]) and terrestrial (this study) apatites. Both samples show a systematic (diffusion-like) increase in S from core to rim (lunar) and proximity to volatile-bearing cavities (terrestrial). The square symbols represent the terrestrial Mina Carmen apatite (IOA deposit, Chile; [4]) data and the circles the lunar apatite data. The open circles represent the data excluded by [1] and were described as being a cross-axial heterogeneity effect. Errors bars are 2σ standard deviation and are smaller than the symbol size (Mina Carmenapatite analysis, this study).
**Discussion and conclusion:** Using new experimentally determined $D_S^{\text{apatite}}$ values and thermodynamic modeling, continued fractional crystallization of lunar silicate melts (e.g., ~90 to 100% crystallization [1]) would crystallize apatite cores and rims containing orders of magnitude lower S-concentrations than measured in lunar apatite [1, 3], contradicting the fractional crystallization hypothesis proposed by [1]. Based on the experimental and modeled dataset, we propose that lunar apatite was subjected to metasomatic alteration by a S-rich aqueous phase, producing the observed S zonation reported by [1].