

A COMPREHENSIVE SIMS STUDY OF HYDROGEN, FLUORINE, AND CHLORINE IN NOMINALLY ANHYDROUS MINERALS FROM 15 LUNAR SAMPLES. J. L. Mosenfelder, J. R. Caseres, and M. M. Hirschmann, Department of Earth Sciences, University of Minnesota, 310 Pillsbury Dr. SE, Minneapolis, MN, 55455 (jmosenfe@umn.edu).

Introduction: The role of volatile elements in the origin and differentiation of the Moon remains controversial [e.g., 1,2,3], despite a burgeoning number of recent studies on lunar materials using modern, low detection limit analytical techniques. One of the most surprising findings is the FTIR measurement by Hui et al. [4] of trace amounts of H in plagioclase (Pl) from three Apollo samples: one troctolite (76535) and two ferroan anorthosites (15415 and 60015). This H was inferred to have been partitioned from the lunar magma ocean (LMO) and then preserved throughout an ~4.4 billion year history including cooling of the LMO and surface processes such as cataclasis and shock from impact events. However, preliminary data we presented at *LPS XXXXVII* [5] and new results herein challenge details of this hypothesis.

Using ultra-low blank SIMS, we obtained ~250 new analyses of H and F in 15 Apollo samples, including the three studied by [4,6]. Cl was also analyzed in selected samples. Although we focused on Pl from the ferroan anorthosite suite (FAN; 13 samples total), we also investigated a norite (77215) and troctolite (76535) from the Mg-suite.

Methods: SIMS was performed on the Cameca 7f-GEO at Caltech using previously outlined methodology [7] enabling us to achieve limits of detection (LOD) for H₂O and F of ~1 ppmw and 0.1 ppmw, respectively. The effective LOD for H₂O in anorthitic Pl varied from 1.5 to 2 ppmw, owing to differences in calibration between anorthite and more Na-rich feldspars [7] and slightly worse vacuum conditions compared to analyses reported in [5]. Cl was under the LOD with the exception of some analyses of 60015 (see below). Particular attention was paid to screening analyses for organic surface contamination resulting from sample preparation, owing to extremely low inherent H concentrations. We also examined SIMS craters after the session using BSE imaging and EDS mapping in order to assess possible contamination from cracks and confirm phase identifications where necessary (Fig. 1).

Samples: The FAN samples for which we obtained uncontaminated analyses of anorthitic Pl are: 15415, 60015, 60618, 60619, 60639, 62237, 65315, 65325, 65326, 67635, 67746, 68515, and the "big white" anorthosite clast from 73255, 251 [8]. Some of these FAN exhibit high degrees of shock (e.g., 60015), were contained within impact melt (e.g., 60618), or have granoblastic textures (60619, 67746) suggesting protracted cooling histories after crystallization, allowing us to

test the effects of these secondary processes on H and F retention.

From the Mg-suite, we measured newly polished Pl and Ol grains from troctolite 76535 [cf. 5] as well as Pl and Opx from noritic breccia 77215 (Fig. 1).

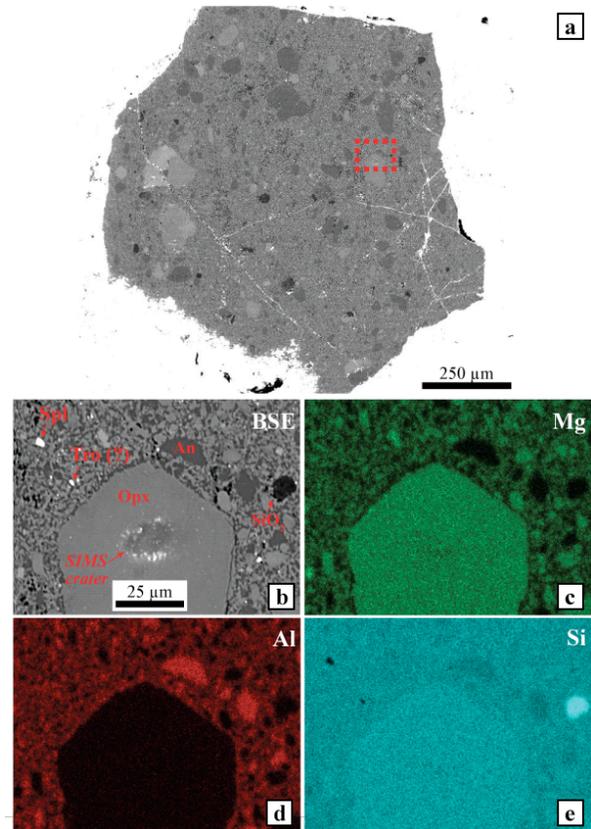


Figure 1. a. BSE image of chip from cataclastic norite 77215 studied by SIMS. The breccia is composed primarily of anorthitic Pl (dark grey) and Opx (light grey), with larger clasts embedded in a fine-grained matrix, as previously described [9]. Red rectangle outlines area shown at higher magnification in BSE (b) and selected EDS maps (c-e) showing location of a SIMS analysis in an Opx clast that yielded 5.4 ppmw F. Smaller clasts of opx, Pl, SiO₂, spinel, and troilite (?) are also visible in this image, as labeled. We also measured 3.0-5.6 ppmw F in Opx separates from this sample.

Results: *FAN studied by Hui et al.* Hui et al. [4] reported 0.5-5 ppmw H₂O in four Pl single crystals from 15415. We acquired 24 analyses from five Pl crystals from this sample; 23 analyses are below the LOD for H₂O with only one being above it (at 2 ppmw). In contrast to this potentially anomalous result,

F contents in 15415 are consistently elevated above the LOD, ranging up to 0.6 ppmw; a graphical example demonstrating our low LOD is depicted in Fig 2.

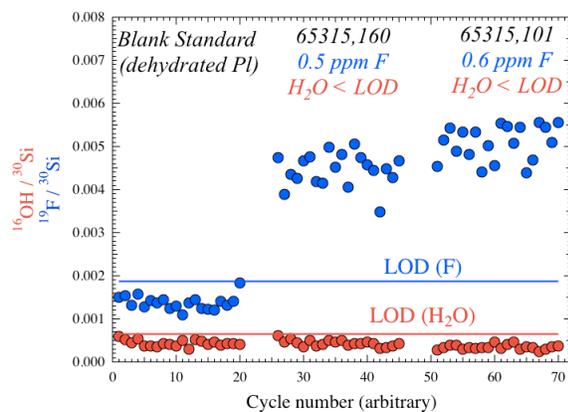


Figure 2. Sequential SIMS analyses of the blank and two anorthite single crystals from two different splits of FAN 65315 demonstrating low limit of detection (LOD) for fluorine. $^{16}\text{O}^1\text{H}$ is below LOD in the analyses of 65315 but ^{19}F is well above LOD, with concentrations calculated based on F-bearing basalt glass standards. 17 analyses of 6 single crystals from 65315 yielded 0.5 to 1 ppmw F.

Following up on our initial results presented on two Pl crystals from 60015 [5], we acquired 28 new analyses on 4 additional Pl crystals. In contrast to our previous estimate of 2 ± 1 ppmw H_2O in this sample, our new measurements are characterized by highly varying amounts of H_2O (from below LOD up to 28 ppmw) and F (2.6 to 45 ppmw, compared to 6 ± 4 ppmw F reported previously), with no obvious systematic spatial variation. Furthermore, some measurements yield significant Cl (up to 20 ppmw); we have not detected Cl in any other terrestrial or lunar feldspar and would not expect to see it, because of the large ionic radius of Cl. The high variability in H_2O , F and Cl supports a previously unconsidered hypothesis that the volatiles reside primarily or entirely in melt inclusions (MI), which are known to be present in 60015 and inferred to be shock induced [10]. Further work is needed to assess the distribution of MI in the Pl we measured in both of our SIMS sessions.

Additional FAN samples. We failed to find H above the LOD in Pl from the other 11 FAN samples we measured. On the other hand, F in Pl in 9 of these FAN is consistently above the LOD, ranging from 0.3 to 1.1 ppmw (Fig. 2). F was below LOD in 60619 and ranged from below LOD to just above it (0.2 ppmw) in 67746. Notably, these two samples differ from the others in having granoblastic textures indicative of subsolidus recrystallization; protracted cooling and/or reheating events may have resulted in volatile loss.

Mg-suite. We analyzed 4 additional Pl and 3 Ol single crystals from troctolite 76535 and once again failed to reproduce the results of [4,6] on this sample, finding no H or F in Pl above the LOD. Our previously reported value of 2 ppmw H_2O in one Ol analysis from this sample appears to be a singular anomaly.

Investigation of noritic breccia 77215 proved to be much more enlightening. Two Opx single crystal separates yielded 3 to 5.6 ppmw F, with H_2O below the LOD; this result was confirmed by analysis of a polycrystalline slab (Fig. 1) containing Opx and Pl clasts.

Discussion: Our results call into question the interpretation of [4] that original H has been preserved in FAN and troctolite 76535. Our hypothesis that the volatiles in 60015 are partly or wholly contained in MI bears further study and raises further questions about the impactor and impact process. Nevertheless, even if the original estimate of 6.4 ppmw by [4] is considered to be robust, the calculated H_2O concentration of the melt in equilibrium with the Pl is reduced by an order of magnitude, from 1600 ppm to 160 ppm. This results from two factors: a revision of the FTIR calibration for H in plagioclase [7] that reduces the 6.4 ppmw estimate to 3.3 ppmw, and our preliminary, experimentally determined anorthite-melt partition coefficient of ~ 0.02 , presented by Caseres et al. at this meeting [11].

Our measurements of up to 1.1 ppmw F in a large number of FAN also allow us to place constraints on F in the FAN parent melt; using a preliminary F partition coefficient of 0.02 [11] we calculate 50 ppmw in the melt, and application of a simple fractional crystallization model with the bulk partition coefficient from [12] yields 15 ppmw F in the LMO, which is in the range of previous estimates for F in the bulk silicate moon [1,2]. The higher F concentrations measured in 77215 are consistent with crystallization of this Mg-suite rock from an incompatible element enriched magma [13].

References: [1] McCubbin F.M. et al. (2015) *Am. Mineral.*, 100, 1668–1707. [2] Hauri E.H. et al. (2015) *EPSL*, 409, 252–264. [3] Lin Y. et al. (2017) *Nat. Geosci.*, 10, 14–19. [4] Hui H. et al. (2013) *Nat. Geosci.*, 6, 177–180. [5] Mosenfelder J.L. and Hirschmann M.M. (2016) *LPS XXXVII*, Abstract #1716. [6] Hui H. et al. (2015) *LPS XXXVI*, Abstract #1927. [7] Mosenfelder J.L. et al. (2015) *Am. Mineral.*, 100, 1209–1221. [8] Blanchard D.P. and Budahn J.R. (1979) *Proc. 10th Lunar Sci. Conf.*, 803–816. [9] Chao, E.C.T. et al. (1976) *Proc. 7th Lunar Sci. Conf.*, 2287–2308. [10] Sclar, C.B. and Bauer J.F. (1974) *Proc. 5th Lunar Sci. Conf.*, 319–336. [11] Caseres et al. (2017) *LPS XXXVIII*, Abstract #2303. [12] Rosenthal A. et al. (2015) *EPSL*, 412, 77–87. [13] James O.B. and Flohr M.K. (1983) *JGR*, 88, A603–A614.