

ABUNDANCE AND CHARGE STATE OF IMPLANTED SOLAR WIND TRANSITION METALS IN INDIVIDUAL APOLLO 16 AND 17 LUNAR SOIL PLAGIOCLASE GRAINS DETERMINED IN SITU USING SYNCHROTRON X-RAY FLUORESCENCE. K. Kitts¹, S. Sutton^{2,3} and M. Newville³, ¹Department of Geology & Environ. Geosciences, Northern Illinois University (Davis Hall 312, Normal Rd, DeKalb, IL 60115; kkitts@niu.edu), ²Department of Geophysical Sciences and ³Center for Advanced Radiation Sources (University of Chicago, Chicago, IL 60637).

Introduction: By virtue of its mass alone, the Sun provides a representative composition of the solar system and can be used as a background against which to gauge excesses or deficiencies of specific components. One way of sampling the Sun is by measuring solar wind implanted ions in lunar soil grains. Such measurements are valuable because of their long exposure ages which compliment shorter time scale collections, such as those obtained by the Genesis spacecraft.

Kitts et al. [1] sought to determine the isotopic composition of solar Cr by analyzing the solar wind implanted into plagioclase grains from Apollo 16 lunar soils. The isotopic composition of the solar wind bearing fraction was anomalous and did not match any other known Cr isotopic signature. This could only be explained by either (1) an enrichment in the solar wind of heavy Cr due to spallation in the solar atmosphere or (2) that the Earth and the various parent bodies of the meteorites are distinct from the Sun and must have formed from slightly different mixes of presolar materials.

To help resolve this issue, we have developed a wholly independent method for determining the relative abundances of transition metals in the solar wind implanted in individual lunar soil grains. This method is based on *in situ* abundance measurements by microbeam x-ray fluorescence [2] in both the implantation zone and bulk grains using the synchrotron x-ray microprobe at the Advanced Photon Source (GSECARS sector 13) at Argonne National Laboratory. Here, we report results for Apollo 16 and 17 plagioclase grains. Additionally, a micro-XANES technique [3] was used to determine charge states of the implanted Cr, Mn, Fe and Ni.

Materials and Methods: Sample selection was governed by the need to minimize the background of indigenous lunar transition metals and to maximize the total abundance of implanted solar wind by using materials with long exposure ages and large surface-to-volume ratios. Thus, the most suitable samples were soils containing large amounts of plagioclase, a mineral that contains very little native Ti through Ni but is itself quite abundant in lunar soils. Apollo 16 soils contain the highest volume percent plagioclase of all the Apollo and Luna samples and have long exposure ages, as indicated by high maturity indices and noble gas contents [4].

However, in order to verify that the results obtained truly represent implanted solar wind and not some peculiar artifact in Apollo 16 plagioclases, plagioclases

from a different petrogenic source were required (i.e. not a product of highlands anorthosite). Therefore, two additional soil samples from Apollo 17 were analyzed as the majority of these plagioclase grains derive from brecciated basalts [4] and [5].

Under clean lab conditions, plagioclase grains from five soils (62281, 64421, 60601, 75081 and 70181) were hand-picked as described in [1], mounted on an acrylic rod and placed in the x-ray beam. The majority of the grains selected were free of visible inclusions and had large flat crystal faces. A wide range of grain size was used (35 to 525 μm) to avoid any possible size sorting effects. Six to eight measurements were made on each grain. Additionally, a few grains containing visible inclusions or metal "splashes" were analyzed for comparison. Due to the small size and high x-ray flux of the beam (3 x 3 μm containing $\sim 10^{12}$ photons/sec), these contaminants could be avoided or targeted.

XRF analyses were obtained in (1) a grazing incidence geometry (solar wind plus bulk plagioclase) and (2) a 45 deg geometry (bulk plagioclase dominated). The bulk contribution was subsequently subtracted off in order to obtain the solar wind signature. The method is described in detail in an accompanying abstract [2].

For the grazing incidence measurement, the crystal face was aligned to be at as small of an angle to the x-ray beam as possible to enhance the signal from the implanted solar wind (~ 200 nm peak depth; [6]). In practice, this angle was ~ 0.5 deg (8 mrad). Alignment of each individual crystal in the grazing incidence orientation was achieved by scanning the crystal through the beam and measuring the derivative of the transmitted intensity. The XRF and XANES measurements were obtained at the crystal angle where this derivative profile was sharpest and most intense.

Results and Discussion: Twenty-two of the 96 grains mounted for analysis had both high quality crystal faces and proper orientation to allow the requisite analyses in both grazing incidence (implantation zone) and large angle (bulk) geometries. Crystal face quality was determined by visual flatness and the presence of a solar wind signal. Due to the fragility of the grains, picking and mounting occasionally exposed a fresh surface which lacked a solar wind component.

A student's T test analysis showed no statistical difference in the means of the Fe normalized data among all five Apollo 16 and 17 soils. Therefore, combining all grain data to determine an average solar

wind implantation signature is justified. These Fe normalized concentrations appear in Figure 1.

The blue diamonds represent CI [7]. The red box shows the Cr abundance as determined by thermal ionization mass spectrometry (TIMS) [1]. The black triangles represent the average Apollo 16 and 17 solar wind implantation zone abundances and the green circles the bulk signature.

Clearly, there is a signature difference between the bulk grain and the implantation zone. Cr, Mn and Ni are 5x lower, 4x higher and 10x lower in the bulk crystals, respectively. The Fe-normalized Cr and Mn abundances determined here are both within one sigma of CI. The Ni is 2x higher and corresponds to the model Ni concentration produced by the data in [8].

The Fe-normalized Cr abundance matches that of Kitts et al. [1] and is distinct from the bulk pattern. Because this pattern has been replicated using two very different techniques (XRF and TIMS) and five different soils representing two different petrogenic processes (i.e. anorthositic vs. basaltic petrogenesis and subsequent brecciation), it is most likely attributable to implanted solar wind. This signature difference can be considered robust and used as an independent measure of transition metal abundances to that of the Genesis collector shards.

MicroXANES spectra collected in grazing incidence and 45 deg geometries show the oxidation states were Cr^{3+} , Mn^{2+} and mixed $\text{Fe}^{3+}/\text{Fe}^{2+}$. Since lunar melts are expected to have abundant divalent Cr, the observation of trivalent Cr here suggests a crystal chemical preference similar to that observed for lunar pyroxene [9]. The observation of Mn^{2+} is consistent with the generally reduced Mn on the Moon. Ferric/ferrous iron ratios were 0.5 – 2.0, showing generally equal proportions of the two states, except for one surface analysis with a reduced ratio of 0.2. Thus, the Fe oxidation state is somewhat more oxidized than the dominant ferrous iron in lunar mafic minerals but is consistent with the generally mixed iron oxidation states observed in planetary feldspars including those from the Moon [10].

We observed no significant difference between the oxidations states of the implanted and bulk metal ions in these grains. This suggests that if the solar wind ions have oxidation states different from those in the bulk plagioclase, the implantation process effectively removes these differences during incorporation into the feldspar. For example, if solar wind Cr ions become highly charged during ejection, these ions become reduced to 3+ during implantation.

Surface and bulk Ni was found to be oxidized (presumably 2+) except for “splashes” on surfaces. Such splashes were readily identified by their very high Ni

content and their microXANES spectra showing a predominately metallic spectrum.

Conclusions: The results reported here demonstrate a new direct method for the determination of solar wind abundances and oxidations states on individual lunar plagioclase grains. In this initial work, we find the Fe-normalized abundances of Cr and Mn to be consistent with CI values. Ni results are about a factor of two lower than CI but are consistent with previous estimates from models based on the Cr data in [8].

References: [1] Kitts et al., (2003) *Geochim. et Cosmochim. Acta*, **67**, 4881-4893. [2] Kitts et al., (2007) this volume. [3] Sutton et al., (2005) *Geochim. et Cosmochim. Acta*, **69**, 2333-2348. [4] Heiken et al. Eds., (1991) Cambridge University Press, 736 pp. [5] CAPTEM <http://curator.jsc.nasa.gov/lunar/compendium.cfm>. [6] Jull and Pillinger, (1977) *Proc. Lunar Sci. Conf.* **8**, 3817–3833. [7] Anders and Grevesse (1989) *Geochim. et Cosmochim. Acta*, **53**, 197-214. [8] Kitts (2002) Ph.D. thesis, 129 pp.. [9] Sutton et al. (1993) *Geochim. et Cosmochim. Acta*, **57**, 461-468. [10] Dyar et al. (2001) *LPS XXXII*, 1065.

Acknowledgements: We thank the Curatorial Staff at Johnson Space Center for providing the Apollo 16 and 17 soils, Dr. Frank Podosek and Dr. Joyce Brannon for the use of their clean lab facilities and Dr. Randy Korotev for valuable advice on the selection of the Apollo 17 soils. GeoSoilEnviroCARS is supported by NSF-Earth Sciences (EAR-0622171) and DOE-Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

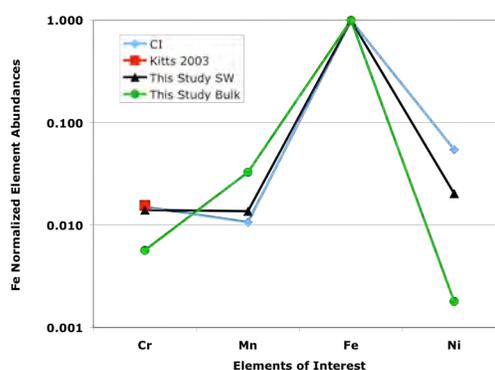


Figure 1: Fe normalized Cr, Mn and Ni bulk and implantation zone (SW) concentrations of averaged Apollo 16 and 17 plagioclase grains.