

**CHROMIUM ISOTOPIC COMPOSITION OF IMPLANTED SOLAR WIND FROM APOLLO 16 LUNAR SOILS.** K. Kitts, F. A. Podosek, R. H. Nichols, Jr., J. C. Brannon, J. Ramezani, R. Korotev and B. Joliff Earth and Planetary Science Dept. Washington University, St. Louis, MO 63130, USA. Correspondence to: kitts@levee.wustl.edu.

**Introduction:** Stepwise leaching/dissolution analyses of whole rock carbonaceous chondrites and at least one ordinary chondrite reveal several  $\epsilon$ -units (one  $\epsilon$ -unit is 0.01%) anomalies of both signs in  $^{54}\text{Cr}$  [1-4]. This indicates preservation (non-homogenization) of presolar components rich in Cr. In addition, there are variations in the relative whole-rock isotopic composition of both  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  in diverse meteorites [e.g. 5]. These variations are more modest, on the order of one  $\epsilon$ -unit, and appear to be systematic with meteorite type. This suggests that the isotopically distinct Cr is distributed inhomogeneously on a planetary scale and not simply preserved on the microscopic scale of individual grains in a meteorite. It is unclear whether the variations in  $^{53}\text{Cr}$  represent an anomaly generated by inhomogeneity of a Cr carrier or by inhomogeneity in the distribution of the short-lived radioactive precursor  $^{53}\text{Mn}$ . In either case, it has been proposed that the distribution of the anomaly within the early solar system may be dependent on heliocentric radius [6]. It is not known whether there is any relationship between the  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  anomalies.

Interpretation of these anomalies and pattern of heterogeneity is made more difficult because the apparent planetary scale variations call into question the concept of "normal composition" as derived from terrestrial measurements. Therefore, in order to investigate this issue, we seek to determine the isotopic composition of solar Cr using the same approach for noble gas measurements, specifically the analysis of the solar wind trapped in lunar soil.

**Sample Selection and Methods:** Determination of solar wind Cr isotopic composition is technically more difficult than for noble gases due to the presence of substantial indigenous lunar Cr. Therefore, in order to minimize the contribution of lunar Cr, plagioclase grains, which naturally contain very low abundances of Cr, were separated from the lunar samples and only the surfaces of these grains (i.e. the solar wind implantation zone) were sampled by etching. Specifically, large 50 gram allotments of 62281 and 60601 were separately sieved, the plagioclase removed with a Frantz magnetic separator and then handpicked removing all grains with visible dark inclusions. Two size fractions of each soil, 35-75 and 75-150  $\mu\text{m}$ , were selected for further processing on the basis of total mass of the fraction and surface-to-volume ratio. The grains were then etched in a series of timed steps in 0.1N HCl and finally totally dissolved in an HF/HNO<sub>3</sub> acid solution. Small aliquots of each etch were removed for spiking with Cr and Ca for isotope dilution. By spiking for Ca, it is possible to measure the amount of plagioclase removed in each etch and to monitor the Cr/Ca ratio

which acts as a proxy for solar wind content. The Cr samples were purified by cation exchange chromatography. The spiked samples were analyzed on a VG 354 thermal ionization mass spectrometer using a Daly detector in pulse-counting mode and the unspiked fractions were analyzed on a Micromass Sector 54 in the same manner.

**Results:** For present purposes, we will take the average Cr concentration in lunar plagioclase to be 16 ppm as measured by INAA in handpicked grains of 65511. Using this number and a stoichiometric anorthite Ca value of 22%, the Cr/Ca ratio of lunar plagioclase is 0.00007 by weight. This is much lower than the photospheric ratio of 0.27 [7] verifying that the Cr/Ca ratio is diagnostic of solar wind contribution.

Figure 1 plots the Cr/Ca ratio for water-wash and etch steps of the 75-35  $\mu\text{m}$  size fraction of 60601. This pattern is characteristic of both size fractions of 60601 and 62281. In the first few etch steps the Cr/Ca ratio is much higher than the intrinsic ratio, indicating that the Cr is extrinsic to the plagioclase. (However, the Ca is inferred to be almost entirely derived from the dissolved grains.) By measuring the Ca, it is possible to calculate the amount of plagioclase dissolved and translate that into an average depth. Forty minutes in 0.1N HCl results in an etch depth of 0.13  $\mu\text{m}$  and corresponds to Etch 1. For comparison, the solar wind implantation depth inferred for noble gases is on the order of 0.2  $\mu\text{m}$  [8]. It is therefore reasonable to interpret the pattern seen in Figure 1 as indicating that solar wind is present most prominently in the first acid etch, falling off to mostly intrinsic Cr with progressive etching.

Isotopic analyses of the Cr are in progress and the presently available data appear in Table 1. The implanted solar wind fraction (Etch 1) appears to have an excess of  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  of  $3.9 \pm 0.5$  and  $8.5 \pm 0.7$   $\epsilon$ -units respectively. These have been obtained by replicate TIMS analyses as described above. We have followed the common procedure of correcting for instrumental discrimination by assuming normal  $^{50}\text{Cr}/^{52}\text{Cr}$ .

**Discussion:** Given that the etch depth for Etch 1 is 0.13  $\mu\text{m}$ , that the Cr/Ca ratios indicate the presence of a solar wind component and reach a maximum in Etch 1, we infer that we have successfully isolated the implanted solar wind component from the background lunar signature. The data shown in Table 1 nominally indicate, that relative to the implanted solar wind, the earth and other solar system materials are either deficient in  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$ , or, equivalently, that the implanted solar wind has significant excesses of these isotopes. These isotopic results are quite surprising. Thus, it is prudent to consider the possibility that these re-

sults represent an artifact or are otherwise misleading. A careful examination of possible sources of contamination, spallation and isobaric interferences is warranted.

The possible sources of contamination are terrestrial, spike and meteoritical. Blanks were run in parallel with the lunar samples through the entire procedure then spiked and analyzed. All blanks were insignificant when compared to the samples. In addition, terrestrial contamination would drive the isotopic signature towards normal and is counterindicated. Spike contamination is unlikely in that all labware was kept separate and parallel heavy-isotope excesses do not appear in the blanks. Additionally, the spiked and unspiked samples were analyzed in separate mass spectrometers, and no spike has been introduced into the instrument used for the unspiked lunar samples. More importantly, the spike used is nearly pure  $^{54}\text{Cr}$  and could not produce the  $^{53}\text{Cr}$  excesses seen in Table 1. As for meteoritical contamination, to date no meteoritical components have been found that can account for both the  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  excess pattern displayed here.

Cosmic-ray induced spallation (on the Moon) could produce Cr isotopes in roughly equal proportions, which would lead to apparent excesses of  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$ , but this is quantitatively inadequate to explain the present effects. Plagioclase has a very low natural abundance of Fe which acts as the principal target for the production of Cr via spallation. Using a production rate of  $2.9 \times 10^{11}$  atoms/gram of Fe/Ma [9], an Fe abundance of 0.15 weight percent (INAA data for 65511, this work) and a nominal exposure age of 100 Ma, the spallation Cr production is only 4 ppt of either isotope. Even assuming that all the spallation Cr produced by all the Fe in the soil magically came to rest in the plagioclase grains, the  $^{54}\text{Cr}/^{52}\text{Cr}$  ratio would change by only 0.38  $\epsilon$ -units and cannot account for the observed data.

A potential undiagnosed interference in the mass spectrometry is always a concern. However, we are unaware of any interference which could produce such results. If interference is significant, it seems more likely to be an interference at mass 50 than separate interferences at both masses 53 and 54. Because of the standard procedure for TIMS mass discrimination correction, an interference at mass 50 would actually appear as excesses of  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  in a 1:2 ratio (in  $\epsilon$ -values), close to what is observed. Indeed, Nyquist et al. [10] have proposed an interference at mass 50 produced from the boric acid used as an activator for Cr, but they find no direct evidence to support this suggestion. We also find no such evidence in careful mass scans of the Cr mass range, with or without sample Cr in the load.

If these results can be accepted as accurately characterizing the solar wind, within their errors, it is unclear how to interpret them. It may be that solar wind Cr is fractionated, but that would not explain the present results. Some unanticipated nuclear processes in the sun, or an unexpectedly large and complicated heterogeneity in the distribution of presolar components, would be required. None of these pos-

sibilities seem very palatable, so any of these interpretations must be considered only tentative or speculative.

**References:** [1] M. Rotaru et al. (1992) *Nature*, 358, 465-70. [2] F. Podosek et al. (1997) *MAPS*, 32, 617-27. [3] J. Dougherty et al. (1999) *LPSC*, 30, 1451-2. [4] C. Alexander et al. (2001) *LPSC*, 32, 2191. [5] A. Shukolyukov et al. (2000) *MAPS*, 35, A146-7. [6] G. Lugmair and A. Shukolyukov. (1998) *GCA*, 62, 2863-86. [7] K. Lodders and B. Fegley (1998) *The Planetary Scientist's Companion*, Oxford, 99. [8] P. Eberhardt et al. (1970) *Proc. Apollo 11 LPSC*, 1037-70. [9] J. Birck and C. Allègre (1985) *Isotopic Ratios in the Solar System*, Cepadues-Editions, 21-5. [10] L. Nyquist et al. (2001) *MAPS*, 36, 911-38.

**Table 1. Isotopic Composition of Solar Wind Implanted Cr.**

62281 75-35 $\mu\text{m}$	$\epsilon^{53}\text{Cr}$	$\epsilon^{54}\text{Cr}$
Etch 1 (Solar Wind)	$3.9 \pm 0.5$	$8.5 \pm 0.7$
Etch 2	$1.7 \pm 0.7$	$6.1 \pm 1.3$
Etch 4	$1.6 \pm 0.5$	$5.3 \pm 1.0$

$$\epsilon = 0.01\% \text{ or } 1 \text{ in } 10^4$$

**Figure 1. Cr/Ca ratio of 60601 75-35  $\mu\text{m}$  size fraction.**

