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Isotopic composition of surface-correlated chromium in Apollo 16 lunar soils

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Abstract—We have analyzed by thermal ionization mass spectrometry (TIMS) the isotopic composition of Cr in five progressive etches of size-sorted plagioclase grains separated from lunar soils 60601 and 62281. Aliquots of the etch solutions were spiked for isotopic dilution (ID) analysis of Cr and Ca. The Ca ID data indicate that the initial etch steps represent dissolution of an average 0.1 to 0.2 μm depth from the grain surfaces, the approximate depth expected for implanted solar wind. The Cr/Ca ratio in the initial etches is several fold higher than that expected for bulk plagioclase composition, but in subsequent etches decreases to approach the bulk value. This indicates a source of Cr extrinsic to the plagioclase grains, surface-correlated and resident in the outermost fraction of a μm, which we provisionally identify as solar wind Cr. The surface-correlated Cr is isotopically anomalous and by conventional TIMS data reduction has approximately 1 permil excess ^{54}Cr and half as great excess ^{53}Cr. In successive etches, as the Cr/Ca ratio decreases and approaches the bulk plagioclase value, the magnitude of the apparent anomalies decreases approaching normal composition. If these results do indeed characterize the solar wind, then either the solar wind is enriched in Cr due to spallation in the solar atmosphere, or the Earth and the various parent bodies of the meteorites are isotopically distinct from the Sun and must have formed from slightly different mixes of presolar materials. Alternative interpretations include the possibility that the anomalous Cr is meteoritic rather than solar or that the observed (solar) Cr is normal except for a small admixture of spallation Cr generated on the Moon. We consider these latter possibilities less likely than the solar wind interpretation. However, they cannot be eliminated and remain working hypotheses. *Copyright © 2003 Elsevier Ltd*

1. INTRODUCTION

Most variations in the isotopic composition of geologic and meteoritical materials are due to the natural decay of radionuclides or to known mass-dependent chemical fractionation processes. In the first case, the ratio of the radiogenic daughter isotope to the other isotopes of the element varies over time and from one sample to another because of different parent-daughter elemental ratios in the samples. Understanding these two phenomena, radioactive decay and chemical mass fractionation, has allowed the development of radiometric geochronology and the use of isotopic ratios as tracers in sample provenance studies (e.g., Dickin, 1995). However, specific isotope composition variations exist which cannot be explained by these two processes or by other nuclear effects, such as cosmic-ray induced spallation, that are known to occur in the solar system. These effects are referred to as isotopic anomalies. Such anomalies are believed to represent heterogeneity in the distribution of stellar nucleosynthetic components inherited from the presolar materials from which the solar system formed and which were subsequently preserved through solar system evolutionary processes (e.g., Zinner, 1997). These isotopic anomalies have proven very useful in evaluating models of stellar evolution and nucleosynthesis (e.g., Bernatowicz and Zinner, 1997) and in providing constraints for developing a consistent picture of the formation of the solar system (e.g., Cassen, 1994).

Among terrestrial samples analyzed to date, not including those samples contaminated with meteorite debris (Shukolyukov and Lugmair, 1998), the element Cr is isotopically uniform, reflecting homogenization of presolar components. However, variations exist within and among meteorites and other planetary bodies on physical scales from submicron mineral grains to planetary orbits. Chromium exhibits at least two kinds of isotopic variation, one due to radioactive decay of ^{53}Mn to ^{53}Cr and the other due to isotopic anomalies in ^{54}Cr and possibly also in ^{53}Cr.

The radionuclide ^{53}Mn has a relatively short half-life of 3.7 Ma and is one of a group of several such radionuclides (e.g., Podosek and Nichols, 1997) for which lifetimes are sufficiently short that they are now essentially extinct, but which were present in significant abundance in the early solar system. The presence of ^{53}Mn in particular has been deduced from variations in the relative abundance of the daughter isotope ^{53}Cr which correlate with Mn/Cr ratio in meteoritic minerals (Birck and Allègre, 1985a; Nyquist et al., 1994; Lugmair and Shukolyukov, 1998). The inferred abundance of ^{53}Mn, relative to stable ^{55}Mn, can be used as a sensitive relative chronometer for early solar system isotopic events.

The most prominent isotopic anomaly in Cr is the variation in the relative abundance of ^{54}Cr (Rotaru et al., 1992; Podosek et al., 1997). When undifferentiated chondritic meteorites, particularly CI and CM carbonaceous chondrites, are progressively etched, a consistent pattern emerges. The earliest leachates show a few epsilon (ϵ) units deficiency in ^{54}Cr, whereas some later fractions show enrichments of more than 200 ϵ. (An ϵ-unit

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is defined as a 0.01% departure of a given isotope ratio from a reference "normal" composition. For Cr, normal composition is terrestrial.) Thus, despite a whole-rock Cr isotopic composition that is nearly normal, individual mineral grains are not. The simplest interpretation of these results is that some specific nucleosynthetic component rich in ^{54}Cr resides in an unrecognized phase that was never fully homogenized with the other minerals constituting the meteorite.

Besides the mineral-scale variations in ^{53}Cr abundance, there are variations on a whole-rock scale. These variations are smaller (less than an ϵ-unit) but still are significant and appear to characterize meteoritic parent bodies (Lugmair and Shukolyukov, 1998) such that materials from the Earth and Moon can be distinguished from Mars and Vesta. (This assumes that the various differentiated meteorite subclasses ascribed to Mars and Vesta are indeed from these two planetary bodies.) The variations in ^{53}Cr abundance are approximately of the size that could be explained by the presence or absence of ^{53}Mn at the abundance levels thought to characterize the early solar system. Thus, the present-day variations in the abundance of ^{53}Cr could be interpreted as reflecting a planetary-scale heterogeneity in the distribution of ^{53}Mn. This possibility has attracted much attention because of an apparent simple dependence of ^{53}Mn abundance on heliocentric radius. However, it is also possible that it was Cr, rather than Mn, that was heterogeneous in the early solar system (Lee, 1986). Alternatively, the planetary-scale heterogeneity might be explained by postulating planetary-scale chemical (Mn/Cr) fractionation while ^{53}Mn was still substantially extant, i.e., within the first few Ma of solar system history. This chemical fractionation may have been achieved by nebular processes (Cassen and Woolum, 1997) or planetary differentiation (Birck et al., 1999). The result would be that regions with lower Mn/Cr would show an apparent deficit in ^{53}Cr.

A seemingly parallel effect emerges for ^{54}Cr. The substantial variations in ^{54}Cr abundance seen in stepwise etching of carbonaceous chondrites approximately cancel such that the whole-rock abundances of ^{54}Cr are approximately normal. However, on a finer level, the variations do not quite cancel out and there are differences in ^{54}Cr abundance on a whole-rock (and presumably meteoritic parent body) scale (Shukolyukov and Lugmair, 2001; Podosek et al., 1999). These whole-rock isotopic variations, on the order of one ϵ-unit, are most simply taken to reflect minor variation in the abundance of whatever presolar phase is responsible for the much larger isotopic effects revealed in the stepwise etching. Thus, there are ϵ-level variations in the relative abundances of both ^{53}Cr and ^{54}Cr in different planetary bodies. At least one of these effects, possibly both, is most plausibly attributable to heterogeneous distribution, on a planetary scale, of unknown host materials carrying distinct isotopic components. However, any relationship between these two isotopes is unclear and, quantitatively, these effects do not correlate (Kitts, 2002).

It is often assumed that the isotopic composition of the Sun, and more generally the solar system at large, is represented by the composition of the Earth. Unfortunately, this assumption is questionable for Cr as there are isotopic variations on a planetary scale and there is no compelling reason to favor the Earth over a different planetary body. However, as the Sun itself does provide a representative composition of solar system materials

and will provide a useful background against which to gauge excesses or deficiencies of some specific isotopic component, it is important to determine its actual isotopic composition. Therefore, to do so, we have employed the technique used previously for volatile elements, specifically the analysis of the solar wind in lunar soils. Because the Moon has no atmosphere and its surface is covered by a fine-grained regolith that is well gardened by meteorite impacts, lunar soils contain a high abundance of implanted solar wind that can be analyzed directly. In particular, we have sought to determine the isotopic composition of solar Cr by analyzing the solar wind implanted into plagioclase grains (a mineral with a naturally low abundance of Cr) from Apollo 16 lunar soils. Our primary motivation was to improve understanding of the isotopic variations in Cr, and thereby provide information on the distribution and history of preplanetary materials in the early solar system.

2. EXPERIMENTAL PROCEDURES

As the details of the following procedures are provided elsewhere (Kitts, 2002; Podosek et al., 1997), only a general overview will be presented here.

2.1. Sample Selection

Given that the main goal of this research was to physically isolate and measure the isotopic composition of solar wind Cr, sample selection was governed by the need to minimize contamination by indigenous lunar Cr 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 should contain large amounts of plagioclase, a mineral that contains very little native Cr but is itself quite abundant in the soils. Apollo 16 soils contain the most plagioclase in volume percent of all the Apollo and Luna mission samples and have long exposure ages, as indicated by high maturity indices and noble gas contents (Heiken et al., 1991). Based on this information, initial studies done on 1-gram samples of 60601, 62281, 64421, 65511, and 65701 (Kitts, 2002) and availability of material, we were allocated large 50-g samples of 60601 (splits 62–66) and 62281 (splits 68–72).

2.2. Isolation of Plagioclase Grains

Under clean laboratory conditions, the Apollo 16 lunar soils were weighed and the ultrafines removed by decanting in electronic grade methanol. The remaining grains were size-separated and the nonmagnetic material, primarily plagioclase, was removed from the 150–75 and 75–35 μm grain size fractions via a Frantz magnetic separator. This grain size range responds to the need for a large surface-to-volume ratio but still permits efficient handpicking to eliminate those grains with visible dark inclusions. The yield for clean plagioclase grains in this size range was 1.5–2.0% of the total sample weight.

2.3. Etch Procedure

The plagioclase grains were first rinsed in doubly distilled Millipore purified water and agitated briefly in an ultrasonic bath. The grains were allowed to settle, and the liquid was
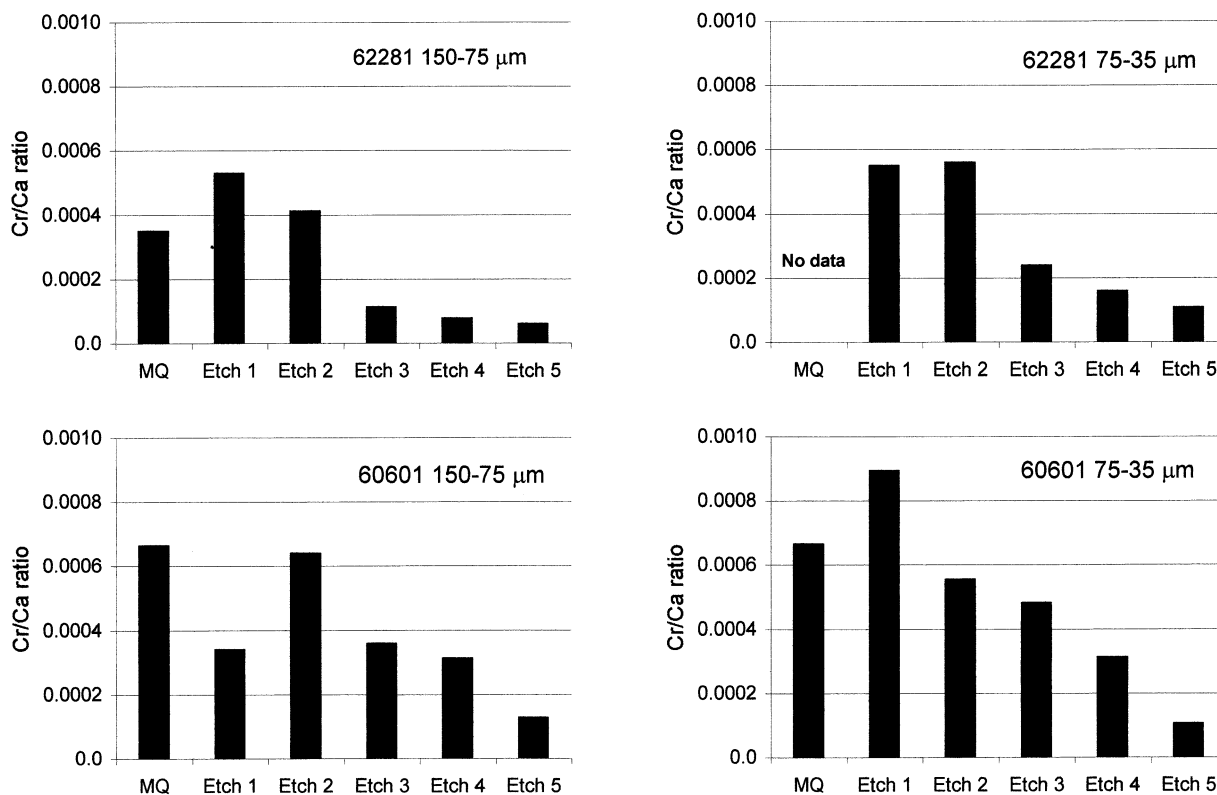
Fig. 1. Cr/Ca ratios from the isotopic dilution analyses of Apollo 16 lunar soils 62281 and 60601. MQ represents the water rinse step described in Section 2.3. Note the highest Cr/Ca ratio corresponding to the implanted solar wind material appears in Etch 1 in three of the four suites and that by Etch 5, the Cr/Ca ratio has returned to the baseline lunar plagioclase Cr/Ca ratio of 0.00007.

pipetted off and centrifuged using a standard Fisher tabletop microcentrifuge. One percent of the liquid was separated out and spiked with ^{54}Cr and ^{42}Ca solutions for isotope dilution. The rest of this material was saved for the isotopic composition analysis. The washed grains were then etched at room temperature in a series of timed steps in purified 0.1 N HCl using the same ultrasonicating and decanting protocol. Figures 1 and 2 display the etch steps and times. As with the wash step, 1% of the acid solution was separated out and spiked for isotope dilution analysis. The rest of this material was saved for the Cr isotopic composition determination. All Teflon beakers used were new and dedicated solely to this project.

2.4. Purification of Cr via Cation Exchange Chromatography

The unspiked Cr was purified chemically by redissolving the dried residues from the etches in dilute HCl, loading them on cation exchange columns, and eluting the Cr. It is important to note the procedure has a 95% yield for Cr 3+ state. This percentage was determined for the columns and procedure used here in a spiked experiment on a Cr standard. It is possible that this incomplete yield could lead to a small mass-dependent fractionation in the analyte, but this would not be distinguishable from instrumental discrimination in the mass spectrometric analysis and it would not impair the identification of any

specific-isotope effects. The spiked aliquots, used to determine Ca and Cr concentrations by isotope dilution, were not passed through cation columns.

2.5. Thermal Ionization Mass Spectrometry (TIMS) Analysis

The dried samples were dissolved in 1 N HCl and loaded on a Re filament with silica gel and saturated boric acid, which is used as an activator for Cr ionization. The spiked samples were analyzed on a VG 354 thermal ionization mass spectrometer using a Daly detector (in pulse-counting mode). These spiked samples were loaded directly on filaments and analyzed first for Cr at a relatively lower temperature (i.e., filament current) followed by the Ca measurements at a higher temperature.

The unspiked Cr aliquots were analyzed on a Micromass Sector 54 instrument by single-collector Daly detection in pulse-counting mode. After the Daly detector analyses were completed, those samples with sufficient Cr remaining were analyzed again in a dynamic multi-collector Faraday mode at a higher beam current. No Cr spike of any kind has ever been introduced into the Sector 54 machine.

For all analyses, the normalizing ratio for correction of instrumental isotopic discrimination was ^{50}Cr/^{52}Cr = 0.051859 (Shields et al., 1966) with the mass dependence assumed to follow the exponential law described by Russell et al. (1978).
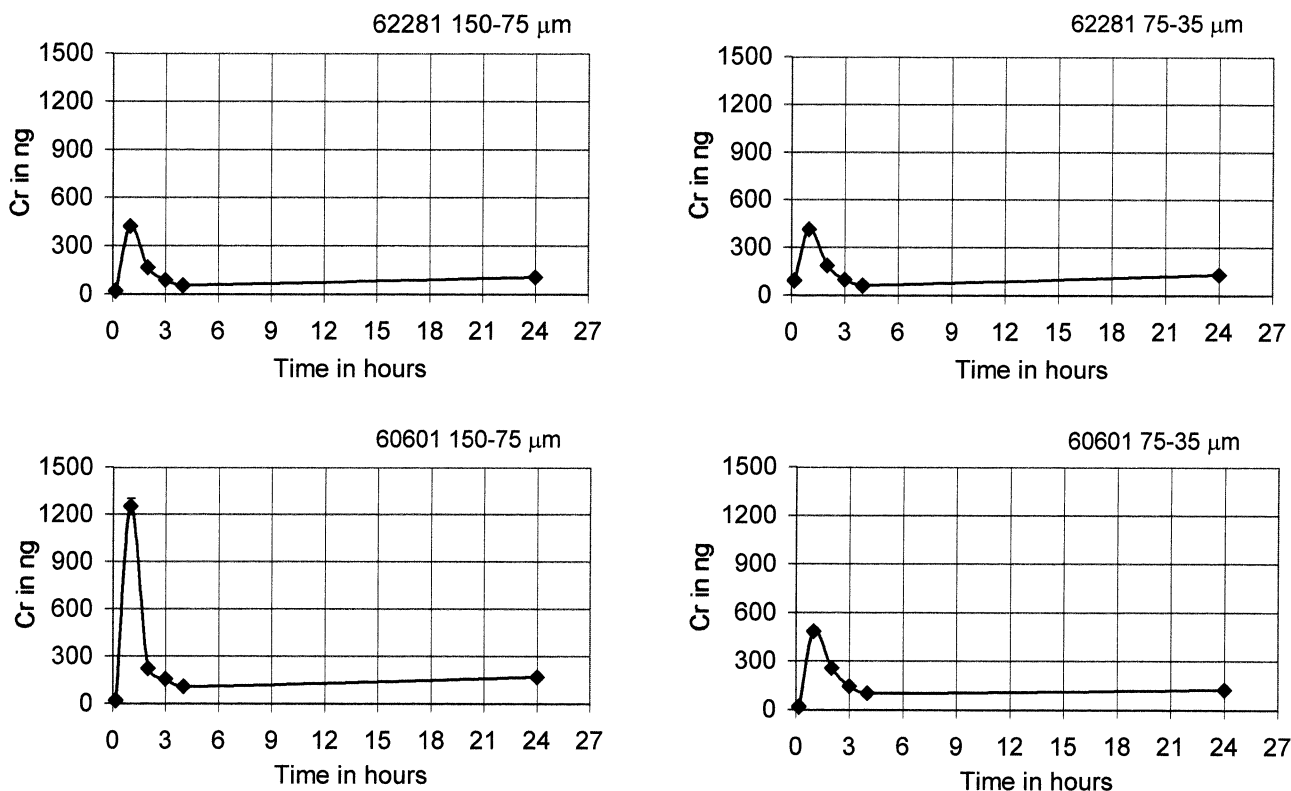
Fig. 2. Chromium isotopic dilution analyses for Apollo lunar soils 62281 and 60601. Note that the Cr abundance peak is associated with Etch 1 in all four sample suites. Etch 1 corresponds to the purported implanted solar wind fraction.

Calibration suites of terrestrial standard Cr were performed for each type of detection procedure and beam intensity used in the isotopic composition sample analyses (Kitts, 2002; Podosek et al., 1997). Sample analytical results are cited as fractional deviations in ϵ-units from the mean of the standard calibrations.

2.6. Procedural Blanks

Procedural blank measurements were made in parallel with the lunar samples during each phase. The blanks for the isotope dilution procedure were spiked for Cr and Ca, whereas the blanks for the isotopic composition procedure were spiked for Cr only. The blanks for the isotope dilution were 0.060 ng for Cr and 4.7 ng for Ca. The isotopic composition procedure included the Cr purification step which used six different cation columns. These procedural blanks, including the column blanks, ranged between 0.13 and 0.70 ng Cr. All blanks were insignificant when compared to the samples which appear in Tables 1–3. For example, the Cr and Ca blanks for the 62281 150–75 μm sample amounted to less than 0.01%.

3. RESULTS

3.1. Isotope Dilution Analysis of Cr and Ca

A summary of the isotope dilution analysis data for the Apollo 16 lunar soils 62281 and 60601 appears in Table 1. The purpose of obtaining these data was to monitor the etching procedure and to provide leverage to distinguish the sources of Cr.

The dissolved plagioclase quantities (Table 1) can be translated into an effective etch depth by assuming an average grain size for each fraction. The etch-depth calculations appear in Table 2. In most cases, 40 min in 0.1 N HCl results in an effective etch depth of approximately 0.1 to 0.2 μm. For comparison, the solar wind implantation depth inferred for noble gases is <0.2 μm (Jull and Pillinger, 1977), thus the etch depth is comparable to solar wind depth.

Table 1 includes the Cr/Ca ratio and the total quantity of Cr in each step. These results are also illustrated in Figures 1 and 2, respectively. Table 1 also lists the effective Cr concentration in the material dissolved in each step (assuming stoichiometric An_{95} plagioclase). For comparison, we will estimate that the intrinsic Cr concentration in Apollo 16 soil plagioclase is 10 ppm (Kitts, 2002). Again assuming stoichiometric Ca in An_{95}, the corresponding Cr/Ca ratio of the lunar plagioclase is 0.00007 by weight. By examining either the Cr concentration or the Cr/Ca ratio, it is evident that there is much more Cr in the early etches than is expected from the amount of feldspar dissolved alone, and that with progressive etching the amount of Cr decreases until approaching the intrinsic lunar value in the final etch. We conclude that in the earliest etches there is a source of Cr, extrinsic to the lunar plagioclase, which is concentrated near the grain surfaces at depths less than 1 μm.

The intrinsic lunar plagioclase Cr/Ca ratio, taken to be 0.00007, is very much lower than the solar (cosmic) ratio of 0.22 (Anders and Grevesse, 1989). If we assume a two-com-

Table 1. Isotope dilution data for Apollo 16 lunar plagioclases.[a]

Sample size/weight	Solvent 0.1 N HCl	Dissolved Ca in μg	Dissolved[b] Plag in μg	Dissolved Cr in μg	Cr[c] in ppm	Cr/Ca[sd] ratio
62281.68–72	Water	51	371	0.018	48	0.00035
150–75 μm	Etch 1	789	5765	0.419	73	0.00053
0.83168 g	Etch 2	393	2868	0.162	56	0.00041
	Etch 3	763	5575	0.086	15	0.00011
	Etch 4	668	4884	0.052	11	0.00008
	Etch 5	1732	12654	0.105	8	0.00006
62281.68–72	Water	no data	no data	no data	no data	no data
75–35 μm	Etch 1	744	5435	0.410	75	0.00055
0.46835 g	Etch 2	325	2375	0.182	77	0.00056
	Etch 3	401	2926	0.096	33	0.00024
	Etch 4	385	2816	0.062	22	0.00016
	Etch 5	1161	8482	0.127	15	0.00011
60601.62–66	Water	28	207	0.019	91	0.00066
150–75 μm	Etch 1	3674	26845	1.248	46	0.00034
0.62225 g	Etch 2	342	2497	0.219	88	0.00064
	Etch 3	426	3109	0.153	49	0.00036
	Etch 4	334	2441	0.105	43	0.00031
	Etch 5	1305	9534	0.166	17	0.00013
60601.62–66	Water	29	210	0.019	91	0.00067
75–35 μm	Etch 1	540	3942	0.482	122	0.00089
0.33367 g	Etch 2	459	3354	0.255	76	0.00056
	Etch 3	297	2167	0.143	66	0.00048
	Etch 4	319	2328	0.100	43	0.00031
	Etch 5	1117	8164	0.120	15	0.00011

[a] Uncertainties are taken as 4% based on the delivery variance of the micropipetter used to deliver the spike and not the sample variance which is lower.
[b] The amount of dissolved plagioclase is calculated assuming a stoichiometric anorthite Ca value of 14% and a lunar An of 95.
[c] The Cr abundance is calculated using the data from columns 4 and 5.
[d] The Cr/Ca ratios are calculated from columns 3 and 5.

ponent system, with intrinsic and extrinsic components having Cr/Ca ratios of these lunar (plagioclase) and solar values, the observed Cr/Ca ratio provides the leverage necessary to resolve the two contributions. We calculate that in all fractions in Table 1, the Ca is mostly (>99%) intrinsic (lunar) but that in the first one or two etches of each sample the Cr is mostly (>90%) from the extrinsic component. Because of the more than three orders of magnitude difference between the end-member Cr/Ca ratios, these calculated percentages are quite insensitive to the exact values of the assumed compositions. Therefore, we infer that the extrinsic (assumed solar wind) Cr component has been successfully isolated from the intrinsic lunar Cr to the degree necessary to permit isotopic characterization.

3.2. Chromium Isotopic Composition Results and Characterization

Table 3 compiles the isotopic composition data for both size fractions of 62281 and one size fraction of 60601. (The 60601

75–35 μm samples have been reserved for future work.) The data from the two size fractions of 62281 are consistent within errors, and it is reasonable to combine these values. Thus, data identified below or in figures as "average 62281" are the weighted means of the data for analysis of both size fractions, as also presented in Table 3.

Most of the etch data in Table 3 indicate apparent isotopic

Table 3. Isotopic composition of Apollo 16 soils 62281 and 60601.

Sample	Etch	ε53	$\pm2\sigma$	ε54	$\pm2\sigma$
62281 75–35 μm	1	4.0	1.0	8.4	1.4
	2	2.3	0.6	5.8	1.0
	3	2.3	7.0	3.1	10
	4	1.6	1.0	5.3	2.0
	5	−1.0	6.6	0.4	14
62281 150–75 μm	1	3.6	0.8	8.8	2.6
	2	2.8	0.4	6.4	1.8
	3	1.8	0.4	3.3	0.8
	4	1.6	10	3.3	12
	5	0.0	0.8	0.3	1.2
62281 Combined	1	3.9	0.8	8.5	2.4
	2	2.3	0.4	5.8	0.9
	3	2.0	0.4	3.2	1.2
	4	1.6	1.2	4.3	2.4
	5	−0.3	1.5	0.3	2.8
60601 150–75 μm	1	4.5	0.2	15.0	0.6
	2	3.4	0.2	3.2	1.6
	3	0.7	3.8	1.6	7.4
	4	0.7	10	0.6	12
	5	0.2	0.8	0.6	0.8

Table 2. Etch depth calculation from Ca ID data for 62281 and 60601.

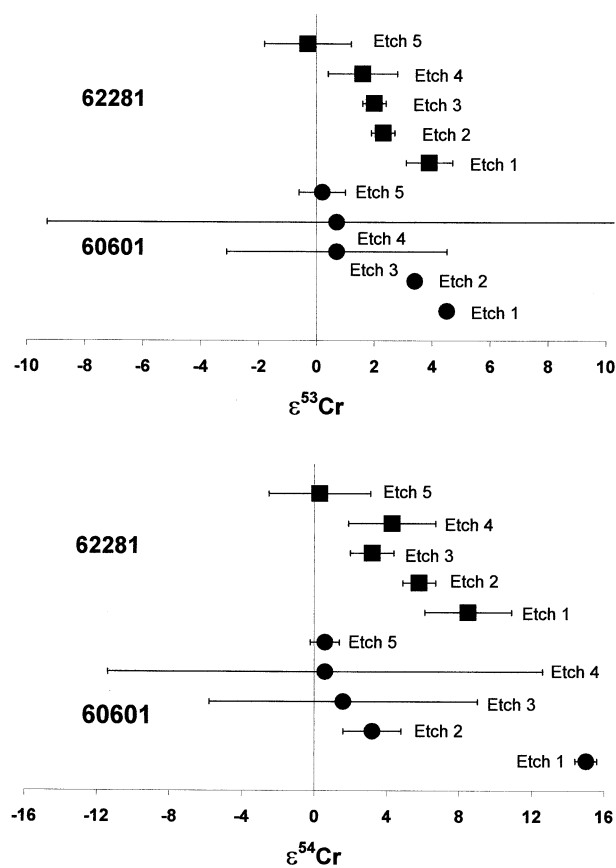| Etch depth in μm	62281 150–75 μm	62281 75–35 μm	60601 150–75 μm	60601 75–35 μm
Etch 1	0.13	0.11	0.81	0.11
Etch 2	0.07	0.05	0.08	0.09
Etch 3	0.13	0.06	0.10	0.06
Etch 4	0.11	0.06	0.08	0.07
Etch 5	0.29	0.17	0.30	0.23

Fig. 3. Chromium isotopic composition of all etches for average
62281 and 60601 150–75 microns 2σ uncertainty.

anomalies of as much as several ε-units. It is noteworthy that
the fractional anomalies for ^{53}Cr are approximately half of
those for ^{54}Cr. (A fit to the 62281 data yields $\epsilon_{53}/\epsilon_{54} = 0.46$.)
Figure 3 illustrates these data as a function of etch sequence,
and Figures 4 and 5 show the relationship between the results
for ^{53}Cr and ^{54}Cr. The overall pattern is that the largest anom-
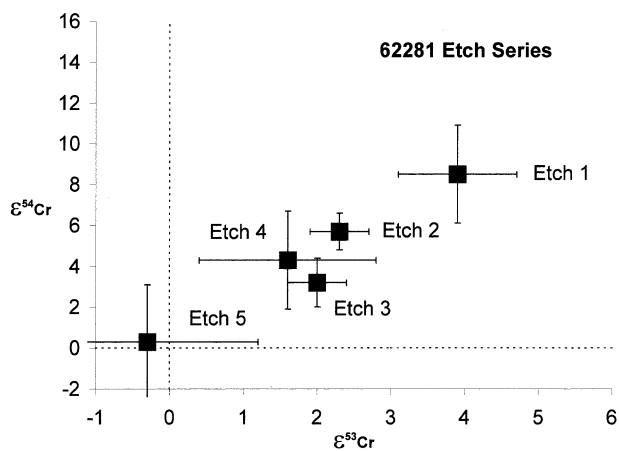
Fig. 4. Chromium isotopic composition of the combined 62281 etch
series 2σ uncertainty. Data are from Table 3.
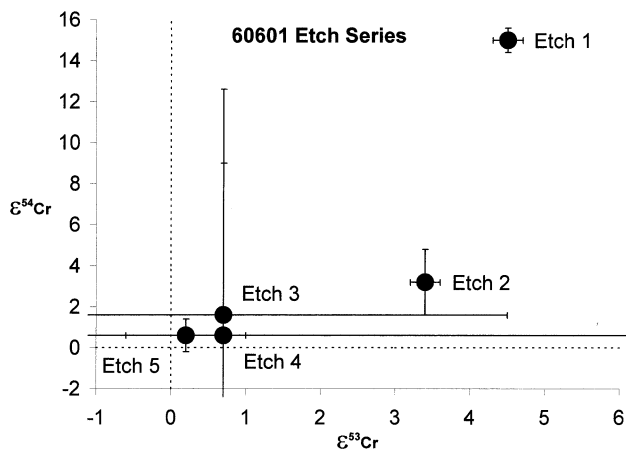
Fig. 5. Chromium isotopic composition of the 150–75 μm size
fraction of 60601 2σ uncertainty. Data are from Table 3.

alies are observed in the earliest etches, and the anomalies
decrease as etching progresses. For all samples, the data for
Etch 5 are normal within errors.

The lunar background Cr signature has been measured in
whole rock basalts by Birck and Allègre (1988) and Harper and
Wiesmann (1992), who found the composition to be normal
within errors. In addition, Lugmair and Shukolyukov (1998)
measured the Cr isotopic composition of lunar mineral sepa-
rates and also found normal Cr. Our present results are consis-
tent with the conclusion that *lunar* Cr is normal. Specifically,
the anomalies decrease as the inferred proportion of intrinsic
lunar Cr increases and the final etches contain mostly intrinsic
lunar Cr as from the chemical (isotope dilution) data.

The customary data reduction procedure for TIMS analysis
assumes that for one specific isotope ratio, the "normalization"
ratio, the difference between the measured value and a known
true value is due solely to instrumental discrimination, and the
other measured ratios are corrected accordingly. We have ap-
plied this procedure making the conventional choice of ^{50}Cr/
^{52}Cr for the normalization ratio. This choice is arbitrary. In
general, a different choice of normalization ratio with the same
raw data would result in apparently anomalous ^{50}Cr/^{52}Cr. From
the measured data, it is possible to infer that the isotopic
composition is anomalous but it is not possible to localize
unambiguously the anomaly to one or two ratios nor to infer
that *any* isotope ratio is indeed normal.

A separate issue, but also one related to this normalization
scheme, is the possibility of isobaric interferences. In particu-
lar, with this normalization scheme, an undiagnosed interfer-
ence at mass 50 or 52 would be manifested as apparent anom-
alies at ^{53}Cr and ^{54}Cr. If a mass interference is present, it seems
more likely to be a single interference on mass 50 or 52 than
two independent interferences at masses 53 and 54, which
remain in nearly constant proportion even as they vary in
magnitude. An undiagnosed interference at mass 52 would
result in apparent anomalies at 53 and 54 in a 3:4 ratio. This is
not what we observe and is, therefore, unlikely. However, of
greater concern is an undiagnosed interference at 50 amu which
would produce apparent anomalies in a 1:2 ratio. This is con-
sistent with the observed results. Indeed, Nyquist et al. (2001)

proposed that there might be a possible interference at mass 50 produced from the boric acid used as an activator for Cr ionization. However, they could find no such interference and neither did we. In addition, despite monitoring masses 49 and 51 for each sample run to look for potential interferences from isobars ^{50}Ti and ^{50}V, we never detected any significant signals attributable to Ti or V. As molecular interferences might also be a concern, we explicitly investigated the possibility of hydrocarbon interferences by taking high-resolution field scans capable of identifying any significant interfering molecule that contains more than one H atom. We detected no such signal.

There are also two circumstantial arguments against significant interference. The first argument is the obvious correlation between apparent anomaly and etch sequence (Fig. 3). It becomes difficult to explain how and why an interference would correlate with etch sequence. The second argument is that most of the lunar samples were analyzed in both Daly-detector and multiple-Faraday-collector modes which showed the same anomalies despite a 40-fold difference in beam intensity. Thus, any hypothesized interference would have to behave identically to Cr during the spectrometry.

Given the rather surprising nature of the isotopic composition (i.e., positive and fairly large anomalies), it becomes especially important to consider the possibility that these results have a more mundane explanation. For example, these results might represent an artifact, such as contamination, or some mass-dependent chemical isotopic fractionation process.

The possible sources of contamination are terrestrial, lunar, and spike. As was described previously, blanks were run in parallel with the lunar samples through all procedures. All blanks were quantitatively insignificant compared to the samples. Moreover, both the expected blank and any unforeseen and unnoticed gross contamination, terrestrial or even lunar, would presumably have normal composition, and so serve only to dilute anomalies, not produce them. We conclude that contamination cannot be responsible for the reported anomalies.

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 different mass spectrometers, and Cr spike has never been introduced into the Micromass Sector 54 instrument used for the isotopic composition analyses. More importantly, the Cr spike is nearly pure ^{54}Cr and any inadvertent spike contamination could not account for the 1:2 ratio of the calculated ^{53}Cr and ^{54}Cr anomalies.

There is ample evidence of significant mass-dependent isotopic fractionation in several elements, arguably due to sputtering, evaporation, or diffusion, in the near-surface regions of lunar soil grains (Epstein and Taylor, 1971; Rees and Thode, 1972; Garner et al., 1975; Clayton et al., 1974; Russell et al., 1977, 1978; Humayun and Clayton, 1995). The 1:2 ratio of ϵ_{53} and ϵ_{54} may seem suggestive of fractionation, but it should be noted that any such suggestion is misleading. Because of the standard TIMS data reduction procedure employed, the effects of mass-dependent fractionation will be removed (to first order). Indeed, we would not be able to distinguish between natural fractionation and instrumental discrimination. The reported anomalies cannot be attributed to isotopic-mass-dependent fractionation.

To summarize this section, we cannot conclusively rule out

the possibility that the reported Cr anomalies reflect only an artifact, but we have given this issue considerable attention without finding any specific evidence to support this possibility, and much evidence to oppose it. Therefore, we will proceed on the premise that the anomalies are real. Nominally, the anomalies are reported as excesses of both ^{53}Cr and ^{54}Cr, but they could equally well be understood as excess ^{50}Cr.

4. DISCUSSION

The data presented here show that Apollo 16 feldspar grains host a distinct, surface-correlated Cr component which is extrinsic to the grains and is isotopically anomalous. The anomalies are large (on the order of 1 permil), unexpected, and difficult to explain. In this section, we will evaluate the proposed identification of this anomalous Cr as solar wind derived, pursue the ramifications of anomalous solar Cr, and assess the plausibility of alternative hypotheses as explanations for this anomalous surface-correlated Cr component.

4.1. Evaluation of Anomalous Cr as Implanted Solar Wind

In light of the results reported in Section 3 that the supply of anomalous Cr is clearly extrinsic to the lunar feldspar grains and is concentrated near grain surfaces ($<1~\mu$m), we have provisionally assigned these etch data to solar wind Cr. However, there is one other potential source of Cr in these samples, a meteoritic component. Such meteoritic material impacting the moon and being mixed into the lunar regolith would also be clearly extrinsic and presumably surface-correlated. One way to evaluate the source and nature of the apparently anomalous Cr is to consider whether the total quantities of Cr observed here are plausibly attributable to solar wind implantation alone or whether an additional source is required.

Because native lunar surface materials are nearly devoid of volatiles, the presence of solar wind may be inferred by the existence of trapped noble gases. Unfortunately, there are no noble gas measurements of grain-size separated samples of either 60601 or 62281. However, there are grain-size data for other mature lunar soils (Hintenberger and Weber, 1973). These data are variable, but it is reasonable to generalize that for the grain sizes of interest here (35–75 μm and 75–150 μm) the concentration of noble gas, specifically of ^{36}Ar, is some 10–30% of the parent bulk soil concentration. We further assume that the concentrations in the specific mineral plagioclase will be the same as in the mixed-mineral assemblage of a natural soil. The concentrations of ^{36}Ar in bulk soils 60601 and 62281 are reported to be in the range 4–5×10^{-4} cm^{3}STP/g (Walton et al., 1973; Hintenberger and Weber, 1973). Therefore, we estimate that the concentration of solar wind ^{36}Ar in our samples is $\sim 1 \times 10^{-4}$ cm^{3}STP/g.

For this concentration of solar wind ^{36}Ar, assuming cosmic proportions (Anders and Grevesse, 1989), the predicted concentration of solar wind Cr in our samples is approximately 35 ppb. This is much less than the 10 ppm (Kitts, 2002) we take to represent indigenous lunar Cr in the feldspar. Thus, quantitative evaluation is sensitive to how we distinguish between intrinsic and extrinsic Cr. If we interpret the high Cr concentrations in the early etch steps, i.e., the outermost parts of the grains, to

reflect the extrinsic source (Table 1), then the total quantity of extrinsic Cr is found to be a factor of 30 more than what is expected from the solar wind on the basis of this estimated ^{36}Ar concentration. Although this calculation suggests we should consider other sources of Cr besides the solar wind, there are mitigating factors which strongly qualify this comparison.

One such factor is that in lunar soils the noble gases themselves typically do not occur in cosmic proportion, the heavier gases being progressively more abundant. It is often thought that this characteristic pattern reflects the greater ease with which lighter gases may diffuse to and be lost from the surface. By this logic, solar wind Ar has been greatly depleted from the soils and is not the best scale by which to predict solar wind Cr. For example, Jull and Pillinger (1977) concluded that all the noble gases in several Apollo soils were greatly depleted relative to cosmic proportions normalized to N, Ar by more than an order of magnitude and even Xe by a factor of 3.7. They attributed the difference to diffusive loss of the noble gases. If this is the case, the high abundance of Cr relative to noble gases may be irrelevant. However, it is important to note that Wieler et al. (1999) have proposed that most of the N in lunar soils is not actually of solar wind origin and this could affect Jull and Pillinger's assertions.

Another mitigating factor is that the elemental composition of the solar wind is not necessarily the same as the elemental composition of the solar photosphere (which is in turn equated with cosmic composition). Elemental abundances in the outer solar atmosphere differ from bulk solar values as a function of the first ionization potential (FIP) or a related parameter, the first ionization time (FIT) (Bochsler, 2000 and references therein). This fractionation is usually represented as a step function with elements having an FIP ≤ 10 eV being 4–5 times overabundant in the solar wind or in solar flares when normalized to their abundances in the photosphere. Cr has a relatively low first ionization potential (FIP) of 7 eV, and is expected to be in the low-FIP group that is enhanced relative to other elements with higher FIP, notably including Ar. It may be that this FIP/FIT-based elemental fractionation is sufficient to account for the noble gas elemental fractionations observed in lunar soils (Wieler and Baur, 1995), without the need to invoke any diffusive losses. Indeed, it may be that changes due to losses from soil grains are superimposed upon those generated in the formation of the solar wind.

To summarize this section, we find that the quantities of extrinsic surface-correlated Cr in our sample are greater, by more than an order of magnitude, than what would be predicted by assuming cosmic composition normalized to the solar wind Ar. Much of this apparent discrepancy can be accounted for by lunar regolith processes, such as diffusive loss, which can be expected to affect Ar more than Cr, and/or elemental fractionation processes in the generation of the solar wind, which enhance Cr relative to Ar. Therefore, it may be that Ar concentration is not an appropriate analog for solar wind Cr abundance.

4.2. Sources of Anomalous Cr: Cosmic-ray Induced Spallation on the Moon?

Lunar soil materials exposed to the solar wind will also be exposed to cosmic rays at and near the surface. In this section, we consider whether cosmic-ray-induced nuclear reactions (broadly, "spallation") can account for the effects observed in Cr isotopic composition, i.e., whether the observed effects can be interpreted as isotopically normal Cr plus spallation Cr. First, we will consider the *compositional* effect of adding a spallation component to normal Cr and then whether lunar spallation can produce the quantity of Cr required to account for these results.

Spallation will contribute to all four isotopes, but the data reduction procedure applied to TIMS data (Section 3.2), which involves the assumption that ^{50}Cr/^{52}Cr is normal, will generate apparent anomalies only for ^{53}Cr and ^{54}Cr. For the often-assumed spallation component proportions of 1:1:1:1 (for the isobars 50, 52, 53, and 54 respectively), and terrestrial proportions of 4.3:83.8:9.5:2.4, the apparent anomaly ratio $\epsilon_{53}/\epsilon_{54}$ will be 0.32. Using instead the proportions 0.2:1:1:1 reported by Shima and Honda (1966), the calculated $\epsilon_{53}/\epsilon_{54}$ is 0.25. The ratio of reported anomalies in our data is 0.46, which is distinct from either of these ratios, but not radically so. It is not clear how much uncertainty should be attached to the spallation compositions cited above, but it would seem difficult to base a definitive conclusion about a spallation interpretation of the present data solely on the basis of composition.

To calculate the quantity of Cr produced from lunar spallation, we will assume again that the intrinsic (interior) Cr composition of Apollo 16 feldspar is 10 ppm (Kitts, 2002). The principal target for the production of spallation Cr is Fe (Nishiizumi et al., 1976), which we take to have an intrinsic concentration of 0.12% ([FeO] = 0.15%; Kitts, 2002). Using a ^{53}Cr production rate of 2.9×10^{11} atoms/g(Fe)/Ma (Birck and Allègre, 1985b; Leya et al., 2000), and a (cosmogenic ^{21}Ne) exposure age of 230 Ma for 62281 (Walton et al., 1973), the resultant calculated anomalies are $\epsilon_{53} = 0.1$ and $\epsilon_{54} = 0.3$ (for the Shima and Honda, 1966, composition). This could indeed be the composition of Cr in the interiors of the Apollo 16 feldspar as our error limits for these latter fractions are not low enough to resolve such a small a deviation from normal. However, it is clear that this level of spallation Cr contribution cannot account for the much higher apparent anomalies found in the earlier etches (Table 3).

The next question is whether spallation can make a greater compositional effect in the outer parts of the grains where the concentration of target Fe is expected to be higher due to solar wind implantation itself. It can be expected that the Cr/Fe ratio in the outer parts of the grains will be somewhere between the intrinsic ratio in grain interiors (Cr = 10 ppm, Fe = 0.12% or Cr/Fe = 0.008 by weight) and the cosmic ratio (0.015; Anders and Grevesse, 1989). Additionally, however, the solar wind is also entraining Cr, and its concentration will be higher as well in the outer portion of the grains. Accordingly, we expect that in the outer parts of the grains the Cr/Fe ratio will be higher than in the interiors, and thus the apparent anomalies arising from spallation will be *less* than what is calculated above for the interiors. Therefore, we conclude that the observed apparent anomalies cannot be attributed to in situ spallation.

We must also consider the possible effect of spallation recoil (Nyquist et al., 1973) from outside the feldspar grains to inside, specifically from neighboring grains containing much greater concentrations of the Fe target into the plagioclases. Some of the spallation Cr produced on these external Fe targets will

recoil into the grains. Because the Fe concentration outside is higher than Fe concentration inside, the result will be apparent anomalies higher than those calculated above based on the lower intrinsic concentrations. A quantitatively adequate evaluation of this effect would require complex modeling. Such modeling would necessitate knowing the distribution of Fe outside the grains, the distribution of solar wind Fe and Cr inside the grains, and the spatial distribution of the material dissolved in each etch step. Such information is not available. However, we can make some plausible semiquantitative evaluations.

One approach to this evaluation is to note that at the boundary between target-rich and target-poor half-spaces, recoil will result in a spallation product density half of the value in the interior of the target-rich medium. If we assume that feldspar grains are surrounded by material with Fe concentration of 3.9% by weight (the average Apollo 16 soil Fe concentration; Heiken et al., 1991), and otherwise adopt the parameters cited above, then right at the boundary, the apparent anomaly caused by recoil of spallation Cr would be $\epsilon_{54} = 5.0$. This is nearly as high as the range observed in our early etch data. However, the similarity is misleading because in these same etch data the inferred Cr concentration is typically several fold higher than the background 10 ppm used above. For early etch Cr concentrations 5 to 10 times greater than the background 10 ppm (see Table 1), the apparent anomalies due to recoil at the boundary with Fe-rich surroundings will be less than an ϵ-unit and thus inadequate to explain our results.

Another approach is to consider the total inventory of spallation Cr recoiled into the grains. Turner and Cadogan (1974) modeled the penetration of recoiling atoms from target-rich into target-poor regions. (Turner and Cadogan were concerned with recoil of ^{39}Ar in the ^{40}Ar-^{39}Ar dating technique, but it is the same problem.) They found the empirical expression

$$c = 1/2c_o e^{-z/h} \qquad (1)$$

to be an adequate representation of their numerical integrations. Here c_o is the concentration of product species in the target-rich region far from the boundary, c is the concentration in the target-poor region of recoiling atoms at depth z from the boundary, and h is the mean recoil length. Integrating over depth, the inventory of spallation atoms which will be recoiled into grains of radius r (r >> h) becomes

$$s = 3/2[Fe]P\,T\,(\rho_o/\rho)\,h/r \qquad (2)$$

where s is the inventory (expressed as atoms/g) of recoiling atoms, [Fe] is the weight concentration of Fe in the surrounding material, P is production rate, T is exposure age, and ρ_o and ρ are the densities of the surrounding materials and of the grains, respectively. As an example, for [Fe], P and T as above, equal densities, r of 50 μm and, as illustration, h = 1 μm, the inventory of recoiled atoms is 0.8×10^{11} atoms/g. For comparison, if we interpret the data for Etch 1 of the 62281 75–150 μm fraction as normal Cr plus a spallation component, the number of spallation ^{54}Cr atoms needed to generate that large an apparent anomaly (Table 3) in that much Cr (Table 1) is 1.2×10^{11} atoms/g. By this calculation, recoiled spallation products are only marginally inadequate to account for the effects seen in this one etch. When allowance is made for the apparent

anomalies in the other etch fractions, however, the quantitative shortfall is about a factor of two.

The key to the inventory assessment is the mean recoil length h. The mean recoil length for Cr (h = 1 μm) in material of density ~2.6 g/cm^3 was computed using the Stopping and Range of Ions in Matter (SRIM) code (Zeigler, 2003). The recoil energy used in the computation was estimated from the linear relationship between recoil energy and fractional mass difference between the target and product (Ott and Begemann, 2000). Additionally, there are a few cases where spallation recoil length seems greater than expected (Ott and Begemann, 2000) and to our knowledge, there are no experiments, analyses of natural materials, or detailed modeling of the production of spallation Cr that would support a firm statement that the mean recoil length is much less than 1 μm. However, our own data do provide a plausibility argument. If the apparent anomalies in the etch data were really due to spallation, with characteristic recoil depth as much as 1 μm, the recoiled spallation Cr would actually be buried deeper than most of our etches. We would then expect that with progressive etching, and decrease in the concentration of total Cr in the material dissolved, the apparent anomalies would increase. Instead, the anomalies decrease, undermining the hypothesis of recoil to such depths.

To summarize this section, we have considered the possibility that the isotopic effects we observe can be interpreted in terms of normal Cr (lunar or solar wind) plus Cr produced by cosmic-ray-induced spallation in the lunar regolith. We do not have the information that would be needed for detailed modeling, but we can make plausible quantitative evaluations which lead us to the conclusion that the observed effects cannot be attributed to spallation. Spallation is about an order of magnitude too small an effect in this context. We consider this conclusion robust as long as the input parameters used in these considerations are correct. However, if future research indicates that any of these parameters are substantially incorrect, the issue of spallation Cr should be revisited.

4.3. Sources of Anomalous Cr: Spallation on the Sun?

In the prior section, we considered the possibility that the observed isotopic effects might be interpreted in terms of normal Cr composition in the solar wind with a small addition of spallation Cr generated on the Moon. Here, we consider the possibility of normal Cr with a small addition of spallation Cr produced on the Sun itself, which is entrained in the solar wind. We know from γ-ray measurements of the solar atmosphere that nuclear reactions occur between energetic protons and the ambient gas at various depths (Hua et al., 1989). Spallation on the Sun has also been inferred by the presence in the solar wind of the radionuclides ^{14}C, ^{10}Be, and excess stable ^{7}Li (Jull et al., 1995; Nishiizumi and Caffee, 2001; Chaussidon and Robert, 1999). As in our previous argument, we will first consider the composition of spallation Cr likely to be produced in nuclear reactions in the solar atmosphere.

Predicting quantitative yields of a given isotope is a difficult problem which requires integration of the product of cross section with energy spectrum. However, if the cross sections are not too complicated in the energy region of peak production, the ratio of two spallation product isotopes is not sensitively dependent on the details of the energy spectrum and the
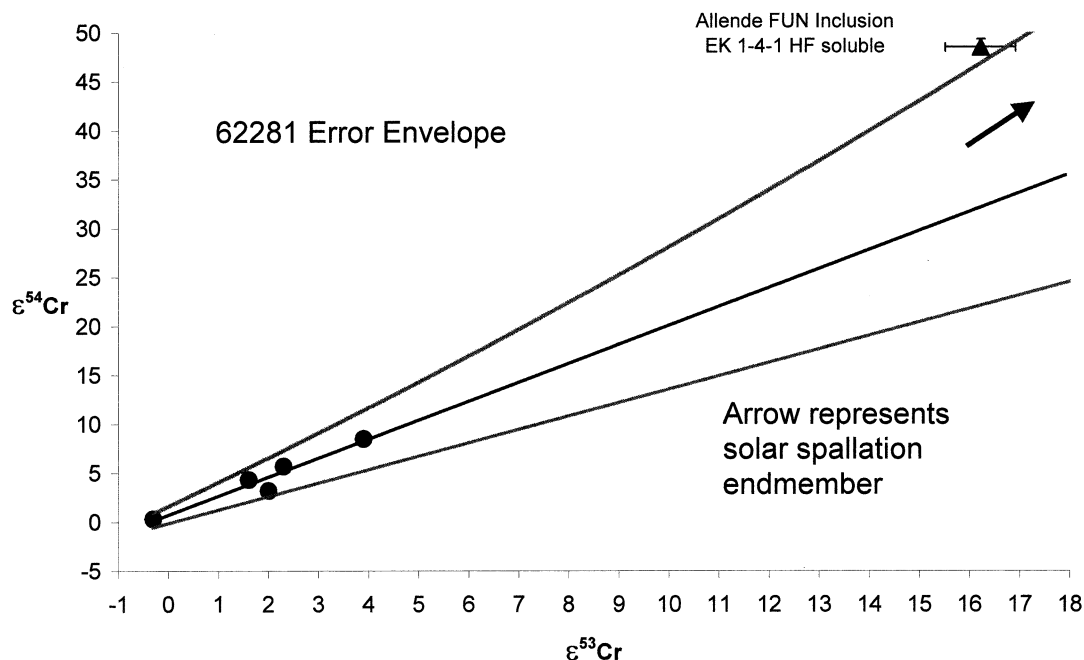
Fig. 6. Linear extrapolation and error envelope for the 62281 etch series. Note that the Allende FUN inclusion EK 1-4-1 HF soluble fraction point lies on the upper extreme of the envelope. This point also lies within the error envelope for the 60601 series (not shown). The arrow shows where the solar spallation end-member composition would fall if the scale of the graph were extended.

ratio of product isotopes can be approximated by the ratio of representative cross sections. This approach accounts reasonably well (5–25%) for the production of ^{53}Mn and ^{54}Mn from Fe (Nishiizumi et al., 1983). Here we apply it to direct production of Cr plus production of Mn isobars by primary proton spallation on Fe targets. The combined cross sections from Reedy and Arnold (1972) and Webber et al. (1998) are 26, 60, 60, and 42.5 mb, for ^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr, respectively. These then yield spallation composition ^{50}Cr/^{52}Cr = 0.43, ^{53}Cr/^{52}Cr = 1.00, and ^{54}Cr/^{52}Cr = 0.71. When Cr of this composition is added to normal Cr, and the resultant composition subjected to the TIMS data reduction procedure (Section 3.2), the result is apparent anomalies at ^{53}Cr and ^{54}Cr in the ratio $\epsilon_{53}/\epsilon_{54} = 0.37$. This ratio is higher than the ratio calculated for spallation on the Moon. (These results differ because of the importance of production by secondary neutrons in rocky targets.) It is also interesting to note that this composition is within the error envelope for the linear extrapolation of the etch data. This calculated solar spallation end-member is represented by the arrow in Figure 6. Thus, based on these assumptions, solar spallation could produce the necessary isotopic composition of the Cr data presented here.

For a quantitative evaluation, an admixture of approximately 20 ppm of this spallation Cr mixed in with normal Cr would be required to produce the apparent anomalies in the 62281 Cr data, for example. Given the cross sections cited above, an energetic proton flux of 3×10^6 particles/cm^2/s (Lang, 2001), and cosmic proportions of Cr and Fe relative to H, the production rate of spallation Cr will be 1.5×10^{-23} atoms/s per atom of target H. This figure is comparable to those calculated for C, Be, and Li (Jull et al., 1995; Nishiizumi and Caffee, 2001;

Chaussidon and Robert, 1999). At this rate, the nominal 20 ppm spallation Cr contribution would be produced in ~25 ka. This is about a factor of 100 to 200 greater than the time required for the C, Be, and Li. However, given the fact that ions might be effectively trapped by magnetic field lines in the corona, especially in flare loops (Nishiizumi and Caffee, 2001), it is unknown whether this amount of time is reasonable or not.

To summarize this section, there is evidence that energetic-proton-induced spallation reactions producing C, Be, and Li occur in the atmosphere of the Sun above the photosphere. Spallation reactions will also produce Cr. As best we can evaluate, the composition of the spallation Cr added to normal Cr would be consistent with the effects we observe. However, given the uncertainties about residence times, an evaluation of the quantity of solar spallation Cr is problematic.

4.4. Sources of Anomalous Cr: A Meteoritic Component?

In this section we consider the possibility that the anomalous Cr reflects a source extrinsic to the Moon itself but not originating in the solar wind. Instead, it may represent infall of meteoritical material from elsewhere in the solar system. As discussed in Section 4.1, it may not be *required* that there is an important source besides the solar wind for the bulk of the extrinsic, surface-correlated Cr we observe, but it is certainly *permitted* to exist.

Lunar soils contain more of some elements than can plausibly be attributed to lunar rock sources, particularly siderophile elements, and these excesses have been attributed to meteorite infall (Ganapathy et al., 1970). For Apollo 16 in particular, the models of Korotev (1987) indicate a meteoritic component of

0.7% to 1.7%. Therefore, we will adopt a nominal level of 1% for the sake of illustrative calculations. Chondritic meteorites characteristically have Cr concentrations in the range 2000 to 3000 ppm. Thus, if the meteoritic component in Apollo 16 soils is not radically different from chondritic composition, it can be expected that meteoritic infall will contribute on the order of 20 ppm or more Cr to bulk Apollo 16 soils.

How this nominal 20 ppm compares to the total contribution of the solar wind is unknown because of uncertainty in how solar wind Cr scales to solar wind noble gases such as Ar, the usual quantitative measure of solar wind accumulation (see Section 4.1). Depending on the elemental composition of the solar wind, and on the extent to which noble gases may have been lost from the soil, the meteoritic component may be comparable to the solar wind component or it may overshadow the solar wind contribution by more than an order of magnitude. It is worth noting that prior studies of solar wind species in lunar soils have focused on volatile elements (e.g., noble gases) which are strongly depleted in meteorites relative to cosmic proportions, so that unlike the present case for Cr, the meteoritic contribution is small compared to the solar wind contribution. This may or may not hold true for Cr.

Given the expectation that there is as much or more meteoritic Cr in Apollo 16 soil than there is solar wind Cr, the issue of how relevant this is to the present study hinges on how the meteoritic Cr is distributed. Unfortunately, this distribution is not well constrained. It might be expected that most meteoritic Cr would be in agglutinates or in particles of size much smaller than those analyzed here and thus the meteoritic Cr would not interfere with identification and characterization of solar wind Cr in our samples. Unfortunately, we have no basis for a quantitative evaluation of the distribution of any possible meteoritical Cr. However, we do expect that most of the infalling meteoritic material will be vaporized on impact. Thus, this material will be deposited from a vapor phase onto soil grain surfaces. This implies that most of the meteoritic Cr would be surface-correlated, just like solar wind Cr, and even more superficially sited. We know that lunar soil grains are characteristically rimmed with a thin (100–200 nm) amorphous layer (Dran et al., 1970; Bibring et al., 1974; Borg et al.,1982) commonly ascribed to radiation damage accompanying solar wind implantation. Even though these layers have the composition of the underlying mineral (Bernatowicz et al., 1994), there is evidence in some cases for vapor deposition or splash deposits (Keller and McKay, 1993, 1997). It is unclear how to translate such observations into quantitative prediction of how meteoritic Cr deposits compare to solar wind Cr.

In evaluating the plausibility of a meteoritical source for the observed anomalous Cr, it is important to realize that Cr of the necessary composition is essentially absent from our meteorite collections. A literature search reveals that there is exactly one observation of meteoritic Cr, an HF-etch fraction of the FUN inclusion EK 1-4-1 (Papanastassiou, 1986), which could be a suitable end-member to account for the present observations (see Fig. 6). However, this is not a representative sample. From all whole-rock meteorite data to date (e.g., Birck and Allègre, 1988; Lugmair and Shukolyukov, 1998; Nyquist et al., 2001; Podosek et al., 2003), bulk meteoritic Cr is normal within an ϵ-unit or less. The hypothesis that our results reflect meteoritic infall on the Moon would have to be accompanied by a further assumption that the bulk of the meteoritic material impacting the Moon is unlike anything in our meteorite collections (or that a minor fraction of the infall is extremely anomalous).

Thus, the hypothesis that the anomalous Cr measured here may be due to meteoritical infall on the Moon is entirely speculative. However, it is not entirely impossible or absurd. Our present meteorite collection is biased in at least two ways that the Moon is not. First, the collections lack fragile materials that are destroyed upon entry into the atmosphere, and second, the collections lack all but the most recent (on a geologic time scale) infall. Therefore, it is possible that, over the long term, the meteorite infall on the Moon is anomalous in Cr. Potential support for this speculation may be found in the studies of Loss et al. (1994) on Vigarano Calcium Aluminum Inclusions (CAIs). They found an inclusion with essentially identical isotopic anomalies to that of the FUN inclusions in Allende but with significantly distinct major and trace element contents. They suggested that this provided convincing evidence for the presence of isotopically distinct reservoirs in the early solar system practically unsampled in the current collection.

4.5. Sources of Anomalous Cr: An Anomalous Sun?

In this section, we consider the interpretation that the anomalous Cr is actually characteristic of the solar wind, that this composition reflects the overall and original composition of the Sun and not a secondary modification of primordial composition by spallation or other processes as discussed in Section 4.3.

We consider the principal argument against this interpretation to be that it defies the conventional wisdom that the Sun and at least the terrestrial planets, if not also the Jovian planets, were all originally made from the same material. If the terrestrial planets are isotopically distinct from the Sun, models for the formation and evolution of the solar nebula and the planets are constrained to account for the difference. This type of isotopic distinction might arise in a variety of ways such as spatial or temporal heterogeneity in the interstellar cloud from which the solar system formed, "cosmic chemical memory" on a planetary scale, or significant local nucleosynthesis in the vicinity of the protosun. We will not attempt to elaborate on potential astrophysical scenarios here, but note that the expectation that the Sun and planets should have the same initial isotopic compositions seems largely based on the current paradigm for the formation of the Sun and the planetary system (Shu et al., 1987). We note also that empirical observations relevant to the similarity of isotopic compositions in the Sun and planets permit differences which are small in absolute terms.

For example, there are well known, and in some cases, large differences between solar wind and planetary isotopic compositions in the light elements H, He, Li, C, and (arguably) N. However, these are understood in terms of solar nuclear processes or mass-dependent fractionation which do not address the possibility of small differences in primordial isotopic compositions. Among the heavier elements with three or more isotopes, for which it is possible to distinguish between specific isotope variations and mass-dependent fractionation and for which it would be less easy to ascribe specific-isotope effects to solar nuclear reactions, it has been observed that solar wind Si and Mg compositions are the same as terrestrial compositions

(Kucharek et al., 1998; Wimmer-Schweingruber et al., 1998, 1999), although only within error limits greater than the size of the effects found here in Cr. The isotopic differences among solar wind, terrestrial and meteoritic noble gases Ne and Xe are well known, and although they may ultimately be explained in terms of planetary histories and the unique cosmochemical features of noble gases, they certainly do not demand original isotopic uniformity among Sun and planets. Even given the other two noble gases, Ar and Kr, for which there may be no significant primordial isotopic differences between Sun and planets (except possibly for fractionation), analytical error limits do not support similarity of solar and planetary compositions below the magnitude indicated for Cr, i.e., 1 to 2 permil.

Altogether, as far as we are aware, there are no empirical observations which require solar and planetary isotopic compositions to be identical, at a level less than 1 to 2 permil, for any element. Analogy with other elements thus provides no argument against the possibility that solar and planetary Cr are different at this level. Indeed, a possibly more relevant comparison is with the isotopic composition of O, which displays permil-scale mass-independent variations among diverse classes of planetary materials (Clayton, 1993). On the scale of interest here, the composition of the Sun is not yet known, nor in effect, is the basic mechanism for the origin of the O variation. Thus, it is not possible to judge whether such effects in O reflect similar processes in Cr.

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