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Volatile loss following cooling and accretion of the Moon revealed by chromium isotopes

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Terrestrial and lunar rocks share chemical and isotopic similarities in refractory elements, suggestive of a common precursor. By contrast, the marked depletion of volatile elements in lunar rocks together with their enrichment in heavy isotopes compared with Earth’s mantle suggests that the Moon underwent evaporative loss of volatiles. However, whether equilibrium prevailed during evaporation and, if so, at what conditions (temperature, pressure, and oxygen fugacity) remain unconstrained. Chromium may shed light on this question, as it has several thermodynamically stable, oxidized gas species that can distinguish between kinetic and equilibrium regimes. Here, we present high-precision Cr isotope measurements in terrestrial and lunar rocks that reveal an enrichment in the lighter isotopes of Cr in the Moon compared with Earth’s mantle by 100 ± 40 ppm per atomic mass unit. This observation is consistent with Cr partitioning into an oxygen-rich vapor phase in equilibrium with the proto-Moon, thereby stabilizing the CrO2 species that is isotopically heavy compared with CrO in a lunar melt. Temperatures of 1,600–1,800 K and oxygen fugacities near the fayalite–magnetite–quartz buffer are required to explain the elemental and isotopic difference of Cr between Earth’s mantle and the Moon. These temperatures are far lower than modeled in the aftermath of a giant impact, implying that volatile loss did not occur contemporaneously with impact but following cooling and accretion of the Moon.

Moon | chromium | evaporation | low temperature | equilibrium

The volatile-depleted nature of the Moon was recognized upon analysis of the first lunar samples returned by the Apollo missions (1), yet it remains one of its most enigmatic characteristics (2, 3). The gross depletions in volatile elements in the lunar mantle relative to Earth’s stand in contrast to the chemical and isotopic similarity observed for refractory elements (4–6). Although some models account for this accord by a giant impact in which the impactor had an isotopic composition identical to that of Earth (7), this explanation cannot account for the impoverishment of Cr, Mn, and V in the lunar mantle. The depletion in these elements in both the lunar and terrestrial mantles relative to other solar system bodies uniquely resulted from the high pressure under which Earth’s core formed (8–10) and constitutes strong evidence for the derivation of the Moon from Earth’s mantle (4).

Within this genetic framework, however, the thermochemical conditions that could engender similarity in refractory lithophile element abundances yet strong volatile element depletion in the Moon remain poorly understood. Based on the observation that lunar mare basalts are depleted only in elements more volatile than Li (e.g., ref. 11), temperatures of ~1,100 K for lunar volatile loss have been proposed (2, 12), reflecting the nebular half-condensation temperature of Li. However, this conclusion is contingent upon the assumption that element volatility during condensation temperature of Li. However, this conclusion is contingent upon the assumption that element volatility during evaporation of lunar silicates. Equilibrium thermodynamic calculations provide grounds to reject this assumption, as the vapor calculated to be in equilibrium with a model lunar mantle composition has oxygen fugacities orders of magnitude higher (13, 14) than in the solar nebula. These thermodynamic variables affect element volatility, and new dynamical simulations invoke higher temperatures (~2,500 K) to simultaneously reproduce lunar volatile depletion in the Earth–Moon disk and equilibrate refractory elements between the two bodies (14, 15).

Stable isotopes can shed light on these discrepant temperature estimates because, at equilibrium, their fractionation between two phases (e.g., liquid and gas) is proportional to 1/T2. The enrichment in the heavier isotopes of Zn, K, Ga, and Cl in lunar rocks relative to Earth’s mantle attests to their evaporation and subsequent escape from the Moon (16–21). Whether this loss occurred during local magmatic degassing (20, 22), a magma ocean phase (17, 23, 24), or following a giant impact (1, 16) remains debated. Determining the conditions of volatile depletion, therefore, has the potential to distinguish between these scenarios. However, it has been hitherto impossible to quantify evaporation temperatures by using the isotope compositions of Zn, K, Ga, and Rb, because their vapor species are monatomic gases (e.g., Zn0) (25), which favor the lighter isotopes with respect to the condensed phase (e.g., ZnO) (26). As such, the direction of isotopic fractionation is the same, be it at equilibrium or during kinetic vapor loss into a vacuum, for which the fractionation factor is temperature-independent. Chromium represents a special case: although CrO2(g) is stable in the solar nebula, unlike the aforementioned elements, it also has several oxidized gas species, namely, CrO4(g), Cr2O3(g), and CrO2(g) (27). Therefore, under the more oxidized conditions that typify evaporation of planetary mantles (13), Cr becomes more volatile, whereas other moderately volatile elements (e.g., Rb and Zn) become

Significance

With the exception of volatile elements, which are strongly depleted and isotopically fractionated, the Moon has chemical and isotopic signatures that are indistinguishable from Earth’s mantle. Reconciliation of these properties with Moon formation in a high-energy giant impact invokes evaporative loss of volatile elements, but at conditions that are poorly known. Chromium isotopic fractionation is sensitive to temperature variations and liquid–gas equilibration during evaporation. We measure an isotopic difference between Earth’s mantle and the Moon, consistent with the loss of a Cr-bearing, oxidized vapor phase in equilibrium with the proto-Moon. Temperatures of vapor loss required are much lower than predicted by recent models, implying that volatile elements were removed from the Moon following cooling rather than during a giant impact.

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less so. As such, evaporative loss of Cr is possible under these conditions (11) and could engender light isotope enrichment in the residue.

To evaluate whether there are any Cr isotope differences between Earth and the Moon, 17 spinifex-textured komatiites, whose compositions approximate those of liquids, were sourced from five different cratons (28). These samples constitute records of Earth’s mantle composition in the Archean, and together with three modern peridotites, they are used to estimate its Cr isotope composition through time and space. Estimates of the Moon’s composition were garnered by analysis of six Mg-Suite samples, a set of cogenetic cumulate rocks that record the early stages of the Moon’s differentiation (29), in addition to five lunar mare basalts and lunar green glass. The Cr isotope data are reported as δ53Cr, the per-mille deviation of the 53Cr/52Cr ratio of the sample from the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) 979 standard, together with its associated 2SD uncertainty.

Table 1. Chromium isotopic composition, chromium content, and MgO content of samples

| Sample | Rock type | δ53Cr, ‰ | 2xSD n Cr, ppm | MgO, wt% |
|--------|-----------|-----------|----------------|---------|
| Earth  |           |           |                |         |
| 49J    | Komatiite | –0.065    | 0.041 3       | 3,190   | 32.16 |
| 88J    | Komatiite | –0.155    | 0.035 3       | 2,650   | 27.72 |
| 179/751| Komatiite | –0.122    | 0.066 3       | 3,240   | 23.54 |
| 176/723| Komatiite | –0.122    | 0.048 3       | 2,450   | 31.13 |
| 7SD/554.5| Komatiite | –0.121    | 0.017 2       | 3,050   | 25.72 |
| 331/783| Komatiite | –0.082    | 0.039 3       | 2,894   | 26.69 |
| 331/777A| Komatiite | –0.114    | 0.012 2       | 2,717   | 26.26 |
| 422/94 | Komatiite | –0.147    | 0.035 2       | 3,464   | 22.41 |
| 422/95 | Komatiite | –0.168    | 0.059 2       | 3,260   | 23.60 |
| 422/84 | Komatiite | –0.112    | 0.004 2       | 2,902   | 30.32 |
| RL-12-1Kom. basalt | –0.111    | 0.010 2     | 1,351   | 13.68 |
| 331/98 | Pp. cumulate | –0.132   | 0.006 2    | 3,371   | 16.05 |
| 422/96 | Komatiite | –0.097    | 0.001 2      | 3,060   | 28.71 |
| 7SD/400| Komatiite | –0.098    | 0.004 2      | 2,428   | 27.99 |
| 422/96a| Komatiite | –0.085    | 0.001 2      | 3,060   | 28.71 |
| 331/948| Komatiite | –0.104    | 0.004 2      | 2,915   | 23.54 |
| 331/779| Komatiite | –0.097    | 0.004 2      | 2,706   | 26.76 |
| DTS-1  | Dunite    | –0.127    | 0.007 2      | 3,990   | 49.59 |
| PCC-1  | Harzburgite | –0.083   | 0.004 2         | 2,730   | 43.43 |
| DTS-1a | Dunite    | –0.123    | 0.003 2      | 3,990   | 49.59 |

| Moon   |           |           |                |         |
| 15445  | Norite    | –0.082    | 0.007 2       | 1,635   | 10.20 |
| 15455  | Norite    | –0.116    | 0.009 2       | 810     | 10.90 |
| 76535  | Troctolite| –0.253    | 0.005 2      | 753     | 19.09 |
| 78235  | Norite    | –0.140    | 0.003 2       | 1,500   | 11.76 |
| 78328  | Norite    | –0.138    | 0.006 2       | 1,500   | 11.76 |
| 72415  | Dunite    | –0.297    | 0.011 2       | 2,414   | 43.61 |
| 15555  | Low Ti    | –0.283    | 0.004 2       | 4,290   | 11.10 |
| 12002  | Low Ti    | –0.234    | 0.009 2       | 5,949   | 14.82 |
| 15426  | Green glass | –0.186   | 0.009 2        | 3,557   | 17.50 |
| 10003  | High Ti   | –0.307    | 0.007 2       | 1,583   | 7.10  |
| 70135  | High Ti   | –0.196    | 0.012 2       | 3,921   | 9.30  |
| 10010  | High Ti   | –0.243    | 0.002 2       | 2,303   | 7.60  |

n denotes the number of replicates on the MC-ICP-MS. Kom., komatiitic; Pp., pyroxene.

Mechanics of Cr Isotope Fractionation During Magmatic Processes

Chromium isotope fractionation arises from the decoupling of Cr2+ and Cr3+ in magmatic phases. Their relative abundance in silicate liquids is dependent on oxygen fugacity, fO2, according to the homogeneous equilibrium:

$$\text{CrO}_2 = \text{Cr} + \frac{1}{2} \text{O}_2$$  \[1\]

The positive entropy change of reaction (Eq. 1) stabilizes chromic oxide to high temperatures (32). Terrestrial and lunar magmas have fO2 near the fayalite–magnetite–quartz (FMQ) and ~1 log unit below the iron–wüstite (IW) buffers, respectively (33). Under these conditions with logKCrO2 ~ 1.9 at 1,400 °C, Cr2+/(Cr2+ + Cr3+) is 0.32 and 0.91 for terrestrial and lunar magmatic liquids, respectively (34).

In (ultra)mafic magmas, olivine, pyroxene, and chromite can leverage Cr isotope fractionation in the liquid from which they crystallize. The precipitation of chromite, (Fe,Mg)Cr3O4, is favored by increasing fO2 and falling temperature that increase aCrO2 in the liquid (Eq. 1, ref. 35). Although chromite saturation occurs with olivine in some komatiitic magmas, its effect on the Cr isotope composition of the samples measured is negligible, owing to (i) the high temperatures, >1,450 °C (36); (ii) the fact that they represent quenched liquids and have not undergone chromite accumulation or fractionation; and (iii) the high fO2 and hence Cr2+ content of terrestrial melts.

Conversely, the Cr isotope variation observed in lunar magmas is larger, up to 0.22‰. Lunar mare basalt parent magmas have Mg# ~ 0.45, constrained by fO2 and aKCrO2 = 0.3 (37). These magmas have 1 bar liquidus temperatures of ~1,200–1,250 °C, at which point olivine and chromite crystallize in tandem (38). The Cr isotope fractionation between Cr2+–bearing chromite and a lunar silicate melt (assuming it is equivalent to Cr3+–bearing forsterite) with Cr2+/(Cr2+ + Cr3+) = 0.91 is +0.35 × 106/T (39), and Δ53Crchromite-melt = +0.16‰ at 1,200 °C, which is identical to that empirically determined by ref. 31.

The cumulative samples of the Mg Suite, whose compositions are complementary to those of liquids, have a more magnesium parent magma (~15 wt% MgO; refs. 40 and 41) than those of mare basalts, with a higher liquids (1,300 °C), at which only olivine is stable. Indeed, the Cr budget in 72415 dunite and 76535 troctolite was entirely hosted in olivine (41), into which both Cr2+ and Cr3+ are incorporated subequally. Thus, minimal isotopic fractionation occurs during crystallization of 72415 and 76535, meaning that their Cr isotope composition reflects that of the Mg-Suite parent magma. Relative to Cr2+–trivalent Cr is ~10 times more compatible in orthopyroxene (35), such that even a lunar melt with ~10% Cr2+ will crystallize orthopyroxene with Cr2+/(Cr2+ + Cr3+) ~ 0.45. Adopting Δ53Crchromite-melt = +0.35 × 106/T (39), weighted for the difference in Cr2+/(Cr2+ + Cr3+) between orthopyroxene and melt, predicts Δ53Crorth-melt = +0.10‰ at 1,200 °C.
(SI Appendix, Fig. S1). This results in orthopyroxene-plagioclase cumulates, represented by norites 78235/8 and the more evolved 15455, with δ53Cr 0.10‰ heavier than the Mg-Suite parent magma (−0.25‰), in agreement with the measured values (Table 1). Norite 15445 is mineralogically similar to 15455, except that it has twice the amount of Cr (1,635 vs. 810 ppm) and a correspondingly heavier δ53Cr (−0.08 ± 0.01‰ vs. −0.12 ± 0.01‰), consistent with 0.25% chromite accumulation.

Composition of the BSE and Moon

Owing to the potential for chromite to engender isotopic fractionation, especially in lunar magmas where the disparity in valence state of Cr in the melt (Cr2⁺) and in chromite (Cr3⁺) is large, quenched liquids or direct mantle samples are the best indicators of mantle composition.

In determining the Cr isotope composition of the BSE, data for ultramafic rocks from this study and the literature (30, 42, 43) were filtered for (i) lithologies that represent mantle-derived rocks (excluding cumulates such as wehrlites and hornblendites) and (ii) fertile, unmetasomatized peridotites with Cr contents of 2,520 ± 630 ppm, Mg# [molar Mg/(Mg + Fe)] between 0.885 and 0.910, and >2 wt% Al2O3. The remaining 42 samples with mean δ53Cr = −0.11 ± 0.11‰ were then filtered for statistical outliers at the 95% confidence level using Grubbs’ test, leaving 36 samples with δ53Cr = −0.01 ± 0.06‰, whose population is normally distributed (SI Appendix, Table S9) and has a 2SE of ±0.02‰.

To quantify the degree of mineral accumulation in lunar mare basalts, bulk rock Mg# was compared with that expected for a liquid in equilibrium with the highest Mg# olivine (or orthopyroxene in olivine-free basalts) in the sample, given KFe = Mg3/[Mg+Fe] ~ 0.3 (44). Samples were rejected from the derivation of the bulk silicate Moon value if they had experienced (i) significant (>0.1) olivine accumulation or fractionation (0.4 < Mg# < 0.5 were kept) and (ii) chromite accumulation (high Cr and δ53Cr) or fractionation (low Cr and δ53Cr). This exercise left 17 measurements of 15 lunar samples from ref. 31 and this study, with average δ53Cr = −0.21 ± 0.06‰ and 2SE of ±0.03‰ (SI Appendix, Table S11; no outliers were found).

A two-tailed Student’s t test yielded a t statistic of 13.36 relative to a critical value of 2.00, illustrating that the δ53Cr of the Earth (−0.11 ± 0.02‰, 2SE, n = 36) and Moon (−0.21 ± 0.03‰, 2SE, n = 17) are clearly statistically resolvable at δ53CrMoon-Earth = −0.10 ± 0.04‰.

Estimates for the Cr content of the lunar mantles, based on Fe/Cr and on Cr/V correlations in lunar rocks give 2,200 and 2,500 ppm (8), respectively. The latter estimate is a maximum because it assumes V is refractory, despite the fact that Al/V ratios increase from 159 in CI chondrites to 182 in CV chondrites (9). If V is slightly depleted in the Moon (by a factor of 159/182), then its Cr content decreases to 2,180 ppm. A value of 2,000 ppm is calculated by combining the ~3,500 ppm Cr in lunar green glass beads with chromium partitioning during partial melting of an olivine-dominated lunar mantle source (9). An average of these estimates gives 2,125 ± 110 ppm Cr in the Moon, which is therefore depleted with respect to the Earth’s mantle (2,520 ± 250 ppm) by 16 ± 10%.

Isotopic Fractionation of Chromium During Planetary Formation

By adopting the Earth’s mantle as the Moon’s progenitor (4, 40), either core formation or volatile loss can simultaneously decrease Cr abundance and shift its isotopic composition.

Geophysical results from the Gravity Recovery and Interior Laboratory mission have shown that the core comprises 1% of the Moon’s mass (45). At 55 kbar, the pressure at its center, the partition coefficient of Cr into Fe–Ni metal is very near unity at IW-2 (10), and, as such, the lunar core would only contribute to a minor (~1%) depletion of Cr, attested to by the paucity of solutions in lunar core formation models that fit observed Cr depletion (46). Furthermore, ab initio calculations show that the isotopic composition of metallic Cr is slightly lighter than Cr2O3 in the M sites of olivine (39), meaning that metal segregation would result in isotopically heavy silicates, contrary to observations. It is therefore unlikely that core formation can account for the Cr depletion or its light isotopic composition in the lunar mantle.

Vaporization of silicate material of a bulk lunar composition gives rise to fO2 of IW+2.5 at 1,800 K (13). The relatively oxidizing vapor, near the FMQ buffer, evolved upon vaporization of silicate material, be it at high temperature (1,827–1,970 K, olivine; ref. 47) or low temperature (1,396–1,499 K, lunar mare basalt 12002; ref. 48) is evidenced by experimental Knudsen effusion mass spectrometry studies. Gas-phase equilibria among the four Cr oxide species (ref. 27 and SI Appendix, Fig. S2) show that CrO2(g) is stable for all fO2 > IW. Considering the predominance of Cr2O3 in a lunar silicate liquid (34), the appropriate evaporation equation is:

\[
CrO(l) + \frac{1}{2} O_2(g) = CrO_2(g) \tag{2}
\]

Increasing oxygen fugacity increases the volatility of Cr (Eq. 2), in contrast to Zn, Rb, Ga, or K (25). The partial pressure of CrO2(g) is calculated in a vapor in equilibrium with a BSE-like silicate melt composition (13) as a function of temperature and fO2 (Fig. 2). Given an ideal gas, significant (~1%) Cr in the vapor occurs only above 1,500 K (Fig. 2), assuming a CrO activity coefficient in silicate melts of ~3 (34).
Cr depletion in the lunar mantle. Solving Eq. \( \beta \) bearing gas phase can be calculated by mass balance, in which:

\[
\delta^{53} \text{Cr} = \text{substitution in the diatomic molecule CrO(g) in the harmonic}
\]

drive the condensed phase to isotopically light compositions re-

we calculated the reduced partition function ratio of \( ^{53}\text{Cr}/^{52}\text{Cr} \) values of \( f_C \) are calculated from Eq. 2 and depend on temperature, pressure, and \( f_{O_2} \), where the total pressure is that in the gas above a BSE composition (13). Values of \( \delta^{53} \text{Cr}_{\text{Moon-earth}} \) are given by Eq. 4. The dark gray field demarcates the permissible range of \( f_C \) and \( \delta^{53} \text{Cr}_{\text{Moon-earth}} \) defined by sample data; curves passing through this field satisfy both constraints.

Whether gas–liquid exchange between \( \text{CrO}_2(g) \) and \( \text{CrO}(l) \) can drive the condensed phase to isotopically light compositions requires knowledge of the force difference between the Moon and BSE, \( \Delta^{53}\text{Cr}_{\text{Moon-earth}} \). The curves correspond to values of \( f_C \) and \( \Delta^{53}\text{Cr}_{\text{Moon-earth}} \) calculated by liquid–vapor equilibrium between \( \text{CrO}_2(g) \) and \( \text{CrO}(l) \) at various temperatures (1,500 K, blue; 1,600 K, green; 1,700 K, yellow; and 1,800 K, red) and oxygen fugacities (dashed lines, \( \Delta \text{FMQ}+1 \), \( \Delta \text{FMQ} \), and \( \Delta \text{FMQ}-1 \)). Values of \( f_C \) may be written:

\[
\begin{align*}
\Delta^{53}\text{Cr}_{\text{CrO}_2(l)-\text{CrO}(g)} &= -0.31 \pm 0.16 \times 10^6 |\text{T}|^{-1} (\% \text{oo}) \text{.} \\
\end{align*}
\]

The composition of the lunar mantle in equilibrium with a \( \text{CrO}_2 \)-bearing gas phase can be calculated by mass balance, in which:

\[
\delta^{53} \text{Cr}_{\text{vap}} = \delta^{53} \text{Cr}_{\text{system}} - \delta^{53} \text{Cr}_{\text{silicate moon}} f_{\text{silicate moon}} (1 - f_{\text{silicate moon}}) \text{.} \]

The \( \delta^{53} \text{Cr}_{\text{system}} \) is Earth’s mantle \((-0.11 \pm 0.02 \% \text{oo})\), \( \delta^{53} \text{Cr}_{\text{silicate moon}} \) is \(-0.21 \pm 0.03 \% \text{oo}\), and \( f_{\text{silicate moon}} \) is \( 0.84 \pm 0.10 \), yielding \( \delta^{53} \text{Cr}_{\text{vap}} = +0.41 \pm 0.33 \% \text{oo} \) or \((+2.00/-0.45) \% \text{oo}\), considering uncertainty in the \( \text{Cr} \) depletion in the lunar mantle. Solving Eq. 3 for temperature and propagating uncertainties yields \( \sim 700 (+1,100/−300) \text{ K} \). Importantly, both thermodynamic and isotopic constraints converge at temperatures between 1,600 and 1,800 K and \( f_{O_2} \) between FMQ and \( \text{FMQ}+1 \) (Fig. 2).

**Implications for the Origin of the Moon**

Relative to terrestrial ultramafic rocks, the uniformly light \( \text{Cr} \) isotope composition of samples most representative of the lunar mantle, independent of whether they are extrusive (e.g., green glass) or intrusive (Mg Suite) supports a global-scale vapor-loss event, manifest in the depletion of moderately volatile elements (2, 4, 11). In contrast with recent numerical giant impact models that predict temperatures >4,000 K (15, 52), the temperature of volatile loss must have been <1,800 K to produce measurable equilibrium isotope fractionation of \( \text{Cr} \) (Fig. 2). Moreover, \( \text{Zn}, \text{Ga}, \text{and Cl} \) exhibit variable isotopic compositions in different lithologies, suggesting that lunar volatile loss occurred during magma ocean crystallization, at temperatures not higher than the silicate liquidus (23, 24). If volatile depletion did occur as a direct result of the impact, evaporation at the highest temperatures did not leave any stable isotopic trace. Instead, isotopic fractionation and loss must have occurred after the Earth–Moon system had fallen from its peak temperatures.

This is difficult to reconcile with the supposition that loss of a volatile-laden atmosphere is facilitated by higher temperatures \( (T) \), which impart higher velocities on its constituent particles \( (v_{th}) \) of mass \( m \), such that more exceed the escape velocity of a body \( (v_{esc}) \), a condition that is quantified by the escape parameter \( (S) \):

\[
\lambda_{esc} = \frac{m v_{esc}^2}{2 |k_B | T} \text{.} \]

where a value of approximately three marks the transition between the Jeans (greater than three) and Hydrodynamic (less than three) escape regimes. Given that the temperature of the atmosphere decays over time, \( t_{1/2} \sim 100 \text{ y} \) (54, 55), the likelihood of gas escape should be highest immediately after the giant impact (Eq. 5). However, the \( v_{esc} \) of a body is proportional to its mass. Before the accretion of the Moon, the bulk of the material lies within the Roche limit (Fig. 3 A and ref. 56), where the combined masses of the Earth and Moon result in high \( v_{esc} \) (11.2 km/s), thereby rendering volatile escape difficult, especially in the presence of an \( \text{O}_2 \)–\( \text{SO}_2 \)-dominated atmosphere (57). Indeed, at 4,000 K, 99.99% of molecules \( m = 0.052 \text{ kg/mol} \) in the vapor have \( v_{th} < 3.8 \text{ km/s} \). However, as the disk cools, material migrates beyond the Roche limit by viscous spreading and begins to form the proto-Moon within 1,000 y of the initial collision (Fig. 3 B and ref. 55). Over this time, the disk has cooled sufficiently to temperatures (54) that are consistent with estimates based on \( \text{Cr} \) isotopes (1,600–1,800 K; Fig. 3 C). The formation of the Moon facilitates volatile escape due to the decrease in escape velocity compared with that of Earth. A particle is lost from the Moon’s atmosphere when it is trapped by the gravity field of Earth, at a boundary called the Hill sphere, and is:

\[
V_{esc, \text{Moon} (Hill)} = \sqrt{\frac{2 G M_{\text{Moon}}}{r_H}} \left( \frac{1}{v_{th}} - 1 \right) \text{,} \]

where \( G \) is the gravitational constant, \( M \) and \( r \) are the Moon’s mass and radius, and \( r_H \) is the Hill sphere radius \( (r_H = a(M/M_\oplus) 1/3) \), where \( a \) is the distance between \( M_M \) and \( M_{\oplus} \) (taken to be the Roche limit, \( 3R_\oplus \)). Gaseous molecules in the atmosphere surrounding the Moon have a Maxwell–Boltzmann distribution of velocities for which 2% (1,600 K) to 4% (1,800 K) exceed the Hill escape velocity of the Moon. In this scenario, \( \lambda_{esc} \sim 4–5 \), meaning that loss of \( \text{Cr} \) from the lunar atmosphere is expected to occur via Jeans escape. Continued outward migration of the Moon beyond \( 3R_\oplus \) increases \( v_{esc} \) (Eq. 6) and hence \( \lambda_{esc} \). If Jeans escape controlled the lunar abundances and stable isotope compositions of the
moderately volatile elements, their fractionation should depend on \( m/m_2 \), causing them to be isotopically heavy in the Moon. This is difficult to uniquely assess for elements like Zn or K (17, 18) because a combination of both equipment and kinetic isotope fractionation induced by Jeans escape could have produced the heavy isotopic compositions observed. Conversely, that Cr isotopes are lighter in the Moon relative to Earth implies that volatile loss via Jeans escape was either unimportant (i.e., loss was driven by another process) or went to completion, resulting in quantitative loss of the Cr (and lighter elements) present in the lunar atmosphere over the timescales for cooling of the Moon.

Materials and Methods

Chromium Double Spike. A \(^{50}\)Cr-\(^{54}\)Cr double spike was prepared from enriched \(^{50}\)Cr (96.5%; oxide form) and \(^{54}\)Cr (95.5%; metal form), purchased from CortecNet. The single spikes were separately digested in 6 M HCl at \( \sim 120°C \) on a hotplate (\(^{50}\)Cr) and in 15 M HNO\(_3\) in a Parr Bomb at \(-160°C \) for several days \((T_{\text{Cr}})\), respectively. After digestion, the \(^{50}\)Cr was evaporated and redissolved in 15 M HNO\(_3\). The optimal spike composition (i.e., 0.580.42 \(^{50}\)Cr-\(^{54}\)Cr) was calculated by using the double spike toolbox (SB). The two digested single spikes were mixed accordingly, and the double spike was further diluted with 2 M HNO\(_3\) to a concentration of \( \sim 38 \text{ mg/mL} \). The \(^{50}\)Cr-\(^{54}\)Cr double spike was calibrated relative to the reference material NIST SRM 979 for spike/sample mixing ratios of 0.13:0.87 to 0.39:0.61. The optimal mixing ratio according to ref. 58 is 0.28:0.72.

Sample Preparation and Purification. Approximately 30 mg of sample powder was dissolved in a concentrated HCl-HF-HNO\(_3\) mixture (1, 0.5, and 0.2 mL, respectively) at 130°C for 48 h and afterward evaporated. Subsequently, the samples were redissolved in concentrated HNO\(_3\)-HF (2 and 0.2 mL, respectively) and placed in Parr Bombs under pressurized steel jackets at 190°C in an oven for 72 h to dissolve refractory chromite. No residues were observed upon visual inspection of the digested samples. An adequate amount of \(^{50}\)Cr-\(^{54}\)Cr double spike was added to the samples following dissolution, and sample and double spike were allowed to equilibrate in closed pressure-alkoxy (PFA) Teflon sample vials at \(-120°C \) overnight.

Chemical separation of Cr from matrix elements (e.g., Mg, Ca, and Fe), and particularly from elements causing isotopic interferences on the Cr masses during mass spectrometry (i.e., Fe, Ti, and V), was achieved by using a two-step chromatography procedure with AG50W-X8 (200-400 mesh) cation exchange resin, adapted from ref. 59. The first cation-exchange column, custom-made from heat-shrinkable Teflon, accommodated 1.1 mL of resin and was conditioned with 0.5 M HCl. Evaporated samples were redissolved and loaded in 1.1 mL of 0.55 M HCl, and Cr was collected immediately upon sample loading. Further elution of Cr was achieved in 4 mL of 1 M HCl. Major matrix elements, such as Mg, Ca, and Fe, remained sorbed to the resin, quantitatively removing them from the Cr-bearing eluate during this step. As minor amounts of Al, Ti, and V coelute with Cr, a second cation-exchange column was used to further purify the samples. The evaporated Cr fraction was redissolved in 2.1 mL of 0.8 M HNO\(_3\) and loaded onto custom-made Teflon microcolumns, accommodating 300 \( \mu \)L of cation-exchange resin, which was conditioned with MilliQ deionized H\(_2\)O. Matrix elements were removed with 2.5 mL of 0.8 M H\(_2\)O and 6 mL of 1 M HCl before Cr was collected in 3 mL of 6 M HCl.

Recovery of Cr from this procedure was between 60% and 90%. Although stable isotope fractionation is caused by incomplete elution of Cr (42), this, along with other sources of mass bias during analysis, was corrected for by the double spike reduction. Following chromatographic purification, the samples were evaporated under concentrated HNO\(_3\) diluted to a concentration of 1 ppm Cr, and dissolved in 2% (vol/vol) (0.317 M) H\(_2\)O for isotopic analysis.

Mass Spectrometry and Data Reduction. The purified Cr samples were introduced via a Cyclopic-Scott Double Pass spray chamber into a Thermo Scientific Neptune Plus multicollector inductively coupled plasma mass spectrometer housed at the Institut de Physique du Globe de Paris. Medium-resolution mode, which permits resolution of polyatomic interferences (e.g., \( ^{54}\)Ar-\(^{56}\)Ar on \(^{52}\)Cr and \(^{40}\)Ar-\(^{40}\)Ar on \(^{56}\)Fe) was employed, and analyses were performed on peak shoulders. Isobaric interferences from \(^{56}\)Fe on \(^{54}\)Cr and \(^{50}\)Ti on \(^{56}\)Cr were monitored on \(^{56}\)Fe, \(^{40}\)Ti, and \(^{51}\)V, respectively, and corrected for using the exponential mass fractionation law. Samples were bracketed by the NIST SRM 979 reference material (standard-sample-sample-standard) and analyzed two or three times each, with each analysis consisting of 100 cycles of 4,194-s integration time. Instrumental mass bias was corrected for by the \(^{50}\)Cr-\(^{54}\)Cr double spike, following the iterative solution of ref. 60, assuming exponential instead of linear fractionation. The isotopic ratio is reported in delta notation:

\[
\delta^{53}\text{Cr}(‰) = \left( \frac{^{53}\text{Cr}}{^{50}\text{Cr}} \right)_{\text{sample}} / \left( \frac{^{53}\text{Cr}}{^{50}\text{Cr}} \right)_{\text{NIST SRM 979}} - 1 \times 1,000.
\]

The intermediate measurement precision was estimated by calculating the pooled SD (\( s_p \)) of the sample dataset:

\[
s_p = \sqrt{\frac{\sum_{i=1}^{n} (s_i - \bar{s})^2}{n - 1}}
\]

where \( n \) is the number of repeated measurements of each sample and \( s_i \) its variance. The resulting 2\( s_p \) of \(-0.03\% \) (\( k = 3 \)) is identical to the 2SD of repeated analyses of the US Geological Survey geological reference material BHVO-2 (\(-0.104 ± 0.03\% ; n = 4 \)). The \( ^{53}\text{Cr} \) value of the BHVO-2 is further in agreement with literature data (61–63), assuring accuracy of the analyses.

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