

Cr ISOTOPIC ANOMALIES IN Cr-RICH MURCHISON SPINELS

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We have determined the Cr isotopic composition of individual Cr-rich spinel inclusions from the Murchison meteorite. A "direct-loading" technique was developed which enabled the measurement of Cr isotope ratios without resorting to chemical separation. Isotopic anomalies in Cr have been previously documented [1,2]. The observed isotopic pattern in Cr is similar to that determined for Ca and Ti: The largest effects occur at the neutron rich isotopes ⁴⁸Ca, ⁵⁰Ti and ⁵⁴Cr [2,3,4]. A further general property associates the magnitude of the anomalies with inclusion type. Ordinary inclusions have small anomalies; FUN-inclusions, which have the distinguishing property of mass fractionated Mg, Si and Oxygen isotopes, display 5 to 10 times larger effects; highly refractory hibonite inclusions exhibit even larger (an order of magnitude larger than FUN types) anomalies in ⁴⁸Ca and ⁵⁰Ti. No Cr isotopic studies have been undertaken in hibonite inclusions partly due to the lack of significant Cr concentration. However, there have been reports of Cr-rich spinel grains separated from the Murchison meteorite as well as a possible association between spinel and hibonite inclusions [5,6,7]. The purpose of the present study was to determine whether large ⁵⁴Cr anomalies were present in the Cr-rich spinels.

The Murchison spinel grains were hand-picked from the dense fraction of material following crushing. Cr-rich spinels were visually identified on the basis of their pink to red colours. Suitable candidates, ranging in size from 50 to 200 μm , were mounted without polishing for EPMA analysis. Seven Cr-rich spinel grains were identified with Cr₂O₃ content ranging from 3 wt.% to 21 wt.%. Individual grains were directly loaded on Re-dimple filaments (dimple diameter \sim 500 μm) filled with spectroscopic purity Re-powder (Johnson, Matthey & Co.) and wetted with boric acid. Filament temperatures during runs ranged from 1150 to 1200°C. No hydrocarbon interferences were observed; the measured backgrounds near each peak were of similar magnitude to those with no beam present. The amount of Cr on the filament, estimated from crystal dimensions, ranged from 60 to 280 ng. The Cr ionization efficiency (Cr⁺/Cr) was about 2×10^{-4} . Significantly larger ($> \times 3$) ionization efficiency could be obtained by using a mixture of Si-gel and boric acid. However, for the present experiments, the Si-gel method could not be used due to the presence of ⁵⁴Fe⁺ interference. A small ($\sim 10^{-13}$ A) ⁵⁶Fe beam was present during the early stage of the runs with Re-powder at about 900°C. However, as the Cr running temperatures were reached the ⁵⁶Fe beam was exhausted. The FeO content of Murchison spinels ranged from 0.1 to 6 wt.%. Terrestrial Fe- and Cr-rich spinels from Mt. Isa (Queensland) used as standards, had significantly higher FeO contents (\sim 20 wt.%). No ⁵⁶Fe⁺ interference was detectable at the Cr-running temperatures. The contribution of the ⁵⁴Fe beam to ⁵⁴Cr, estimated as twice the level of the measured background at the position of ⁵⁶Fe peak, is less than 5×10^{-4} and is negligible. No V⁺ or Ti⁺ beams were observed. The measurements were undertaken on the triple-collector ANU 61 cm mass spectrometer. During the first half of the experiments (⁵³Cr run), as the Cr⁺ intensity increased ⁵⁰Cr, ⁵²Cr and ⁵³Cr were measured. Typically 1000 ratios of 1.28 sec integration time were accumulated. During the second half of the experiment (⁵⁴Cr run), ⁵⁰Cr, ⁵²Cr and ⁵⁴Cr were measured. Typical ⁵⁴Cr intensity ranged from (10-15) $\times 10^{-14}$ A. The ⁵³Cr and ⁵⁴Cr runs were analysed separately. The ⁵⁰Cr/⁵²Cr ratio and the power law were used for normalization to the NBS ⁵⁰Cr/⁵²Cr value [8]. Due to small samples and consequent low precision of the data any differences between various fractionation laws [9] could not be discerned; the power law normalization procedure was found to be adequate.

The data are shown in the Table and in the Figure. The last entry in the table, X3 consisted of a combination of three small crystals which individually did not have sufficient Cr for analysis. The 2 σ precision obtained for normalized ⁵³Cr/⁵²Cr was about 0.6 ‰. Due to its lower abundance the uncertainty in ⁵⁴Cr/⁵²Cr ranged from 1.1 to 2.6 ‰. The data show statistically significant excesses in ⁵³Cr/⁵²Cr and ⁵⁴Cr/⁵²Cr. Sample B2 has an excess of 3.2 ‰ in ⁵³Cr, this is about a factor of two larger than that recorded for the FUN sample EK-1-4-1 [2]. The upper limit for the ⁵⁵Mn/⁵²Cr ratio in inclusion B2, as determined from electron probe analyses is 0.07. If the excess ⁵³Cr in B2 is attributed to ⁵³Mn decay ($\tau_{1/2} \sim 3.8 \times 10^6$ yr.) then the initial ⁵³Mn/⁵⁵Mn ratio is larger than 5×10^{-3} . This ratio is about 13x larger than that inferred from

FUN inclusion EK 1-4-1 [2]. However, given the anomalies in ^{54}Cr and the isotopic pattern for Ca and Ti the ^{53}Cr anomalies are more suggestive of a heterogeneous Cr distribution than ^{53}Mn decay. The excesses in ^{54}Cr (Figure), within errors, are of similar magnitude as those in EK1-4-1, however, they are an order of magnitude larger than those for non-FUN inclusions. These data confirm the highly anomalous nature of the Cr isotopes in the Murchison spinels in accord with the large Ti and Ca anomalies, established by ion-probes, in hibonites [10]. The possibility of even larger Cr anomalies in the more refractory hibonite inclusions remains open.

The correlated excesses in the neutron-rich isotopes of ^{48}Ca , ^{50}Ti and ^{54}Cr have been generally attributed to neutron-rich equilibrium nucleosynthesis within multiple zones characterized by variable n-excesses which can be adjusted to reproduce the observed anomalies [11]. The present ^{53}Cr anomalies are of the same order of magnitude as the ^{54}Cr anomalies and would require a significant contribution from an additional low n-excess process.

References:

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Cr Isotopic Composition of Murchison Cr-rich Spinel

Sample	Cr-content (ng) ^a	$\delta(^{53}/^{52})\text{‰}^b$	$\delta(^{54}/^{52})\text{‰}^b$
A4	240	1.0±0.6	1.2±1.1
F5	280	0.0±0.6	4.0±1.1
G5	60	2.1±0.7	5.5±2.6
B2	120	3.2±0.6	2.9±2.4
X3	170	0.3±0.6	-1.5±1.1

a Cr-content estimated from EPMA analyses and measured crystal dimensions.

b Deviation in per mil of Cr isotope ratios from terrestrial Cr. The quoted uncertainties are 2 σ mean. The power law was used to normalize the data with $^{50}\text{Cr}/^{52}\text{Cr} = 0.051859$ [8] as the index ratio. The mean values for six terrestrial standards are $^{53}\text{Cr}/^{52}\text{Cr} = 0.11421 \pm 0.00006$, $^{54}\text{Cr}/^{52}\text{Cr} = 0.02856 \pm 0.00002$.

