

EXTRATERRESTRIAL CHROMIUM IN THE PERMIAN-TRIASSIC BOUNDARY AT GRAPHITE

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The cause of the catastrophic mass extinction at the end of the Permian has been the focus of considerable debate. Becker et al. [1,2] and others [3-5] have presented evidence that a major impact was associated with the destruction of > 90% of marine taxa. The evidence includes fullerenes with extraterrestrial helium and argon [1, 6], Fe-Ni-Si "metamorphosed grains" of probable meteoritic origin [3], Fe-Ni metals with impact spherules [4,5] and shocked quartz [7,8]. The implication of these findings is that the P/T mass extinction may have been associated with a meteorite impact.

It was shown earlier [9] that most meteorite classes are characterized by a variable excess of ⁵³Cr relative to terrestrial samples. This reflects an early Mn/Cr fractionation and/or a heterogeneous distribution of the now-extinct parent radionuclide ⁵³Mn (T_{1/2} = 3.7 Ma). The observed difference in ⁵³Cr/⁵²Cr ratios between Earth and meteorites permits to unequivocally demonstrate the existence of an extraterrestrial component in geological samples on Earth that contain a significant proportion of meteoritic Cr. Through the measurement of the Cr isotopic composition evidence for an extraterrestrial component was obtained in the K/T-boundary layer [10], in Late Archean spherule beds [11], and in a series of impact melt samples [12]. The isotopic variations are measured as the deviations of the ⁵³Cr/⁵²Cr ratios from the standard terrestrial value. These are expressed in ε-units (1 ε is 1 part in 10⁴), where, by definition, the standard terrestrial ⁵³Cr/⁵²Cr ≡ 0 ε. The ordinary chondrites reveal an excess of ~0.48 ε [9], the enstatite chondrites show a smaller excess of ~0.17 ε [10], the different types of carbonaceous chondrites show varying ⁵³Cr excesses and, in contrast to most of the meteorite classes, are characterized by an excess of ⁵⁴Cr due to the presence of a pre-solar component [e.g. 10,13]. In order to obtain high precision we use a second order mass fractionation correction using the ⁵⁴Cr/⁵²Cr ratio [9], which, for this purpose, is assumed to be normal. Therefore, an elevated ⁵⁴Cr/⁵²Cr ratio in carbonaceous chondrites translates into apparent *deficit* in ⁵³Cr. Thus, in some cases it is not only possible to demonstrate the presence of an extraterrestrial component but also to identify the type of the projectile.

Here we applied the Cr isotope method for the detection of an extraterrestrial component in the P/T boundary at Graphite Peak in Antarctica. This well-

studied sequence of paleosols has measurements of Ir, δ¹³C organic carbon, shocked quartz, biostratigraphy, grain size and mineralogy [7,14]).

The initial sample size (#2060) was 50 g of clay-rich material containing substantial amounts of sand-sized minerals and polycrystalline aggregates, which were pre-sorted to a 2 gm fraction. Magnetic grains from this material were separated with an approximate yield of 0.05% of mostly opaque and silicate fragments. Three types of opaques, including Fe-rich metal nuggets, less abundant Fe, Ni, P, S-bearing oxides, and rare Fe-Ni sulfides, were identified. In addition, these magnetic fractions also yielded several particles enriched in silicate minerals. Electron microprobe studies of these particles revealed chemical compositions of forsterite and clinoenstatite indicative of an extraterrestrial origin [15]. The Fe/Mg and Mn/Fe ratios in olivine and pyroxene and the chemistry of Fe-, Ni-, P-, and S-bearing oxides in the meteorite fragments are typical of CM-type chondritic meteorites.

We studied the Cr isotopic composition in the bulk magnetic fines (MF) and in two separate phases. The bulk MF sample was treated with an HF/HNO₃ mixture at room temperature. This dissolution left behind a tiny acid-resistant residue highly enriched in Cr, most likely a chromite-spinel phase. This residue was dissolved in a bomb at 180°C. The element concentrations were analyzed using ICP-AES. The chemical and mass spectrometric procedures were similar to those described in [9].

The concentrations of major and minor elements in the bulk MF are surprisingly similar to chondritic (except Ca) (Table 1). This most likely indicates that MF represents essentially pure cosmic material. The least altered carbonaceous chondrites (CI, CM, Tagish Lake) show the best match to the MF element concentrations.

The Cr isotopic compositions in bulk MF, the soluble phase and the residue are given in Table 2. For comparison we also present recent data on the Cr isotopic composition for some carbonaceous chondrites [13,16]. The most striking feature is the presence of a large excess of ⁵⁴Cr in the MF residue: +8.10±0.78 ε (ε(54)_{raw} in Table 2). ⁵⁴Cr excesses of a comparable magnitude were found in the acid resistant residues of CI and CM chondrites ([16] and Table 2). ε(54)_{raw} in

the MF residue is intermediate between values in Ivuna ($+13.2 \pm 0.20 \epsilon$) and Murchison ($+5.35 \pm 0.29 \epsilon$). The soluble phases of MF and Ivuna also indicate a similarity between Cr isotopic compositions: $\epsilon(53)_{\text{raw}}$ and $\epsilon(54)_{\text{raw}}$ in MF and Ivuna show moderate excesses in ^{53}Cr ($+0.29 \pm 0.14 \epsilon$ and $+0.57 \pm 0.18 \epsilon$, respectively) and moderate deficits in ^{54}Cr ($-0.85 \pm 0.25 \epsilon$ and $-0.66 \pm 0.32 \epsilon$, respectively). The $\epsilon(53)_{\text{corr}}$, calculated using the second order fractionation correction (see above), are much more precise. Although these values do not represent the actual Cr isotopic composition, they permit better resolution. $\epsilon(53)_{\text{corr}}$ in the MF residue are also intermediate between those in the Ivuna and Murchison residues. Bulk MF reveals a clearly non-terrestrial Cr isotopic signature: $\epsilon(53)_{\text{corr}} = -0.13 \pm 0.04 \epsilon$. However, this value falls outside the range of those in the studied carbonaceous chondrites (~ -0.3 - $\sim -0.4 \epsilon$). Therefore, the Cr data could imply that the MF material represents another type of carbonaceous chondrite.

Finally, the results presented here clearly demonstrate the presence of carbonaceous chondrite material in the P/T boundary bed. However, more measurements of samples above and below the boundary at Graphite Peak and in other P/T locations worldwide is

needed to establish a large impact event at the end-Permian.

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Table 1. Element concentrations in the magnetic fines from the P/T boundary at Graphite Peak and in chondrites.

	Magnetic fines	CI*	CM*	Tagish Lake [§]	CV*	H*	I*
Fe, %	20.1	18.2	21.0	19.8	23.5	27.5	21.5
Mg, %	10.2	9.7	11.7	10.7	14.5	14.0	14.9
Al, %	1.04	0.86	1.18	1.06	1.75	1.13	1.22
Ca, %	0.73	1.83	1.27	1.13	1.90	1.25	1.31
Ni, %	1.11	1.07	1.20	1.20	1.34	1.60	1.20
Co, ppm	550	508	575	550	655	810	590
Cr, ppm	2750	2650	3050	2840	3600	3660	3880
Mn, ppm	1570	1900	1700	1610	1450	2320	2570
Ti, ppm	610	420	580	560	980	600	630
V, ppm	~70	55	75	~60	96	74	77
K, ppm	~570	560	400	~650	310	780	825

* - after [17], [§] - after [18]

Table 2. Cr isotopic compositions in the magnetic fines (MF) and carbonaceous chondrites.

	MF Bulk	MF Soluble phases	MF Residue	CI- Ivuna Bulk	CI- Ivuna Soluble phases	CI- Ivuna Residue	CM- Murray Bulk	CM- Murchison Residue
$\epsilon(53)_{\text{corr}}$	-0.13 ± 0.04	0.71 ± 0.03	-4.69 ± 0.03	-0.44 ± 0.03	1.12 ± 0.03	-7.95 ± 0.02	-0.31 ± 0.03	-3.23 ± 0.03
$\epsilon(53)_{\text{raw}}$	nd	0.29 ± 0.14	-0.37 ± 0.40	0.41 ± 0.11	0.57 ± 0.18	-0.90 ± 0.09	0.27 ± 0.09	-0.34 ± 0.17
$\epsilon(54)_{\text{raw}}$	nd	-0.85 ± 0.25	8.10 ± 0.78	1.59 ± 0.24	-0.66 ± 0.32	13.2 ± 0.20	1.13 ± 0.21	5.35 ± 0.29

The presented uncertainties are $2 \sigma_{\text{mean}}$. nd – not determined. ‘raw’ – raw ratios, ‘corr.’ – second order corrected.