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THE Cr ISOTOPIC COMPOSITION OF PHOSPHATES IN IIIB IRON METEORITES: A SEARCH FOR ^{53}Mn

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The metal phases of iron meteorites contain excess ^{107}Ag most plausibly derived from the *in situ* decay of ^{107}Pd ($\tau_{1/2} = 6.5 \times 10^6\text{y}$) (Kaiser and Wasserburg, 1983; Chen and Wasserburg, 1983). The Ag isotopic data suggest that diverse types of iron meteorites, including the Type IIIABs, usually associated with fractional crystallization and core formation in planetesimals, formed and cooled to $\sim 600^\circ\text{C}$ within $\sim 10^7\text{y}$ of ^{107}Pd production. To obtain improved constraints on the formation and cooling history of iron meteorites and on nucleosynthetic processes we have measured the isotopic composition of Cr in phosphate minerals in the IIIB irons Grant and Bear Creek to search for evidence of ^{53}Mn ($\tau_{1/2} = 3.7 \times 10^6\text{y}$). Mn-rich, Cr-poor phosphates, ideally $(\text{Fe}, \text{Mn})_3(\text{PO}_4)_2$, occur as ellipsoidal blebs up to 1.5 mm in length, enclosed in troilite and occasionally in schreibersite. Clusters of chromites, nearly pure FeCr_2O_4 , are scattered throughout the Grant phosphates enclosed in troilite. The phosphates are chemically inhomogeneous with sizable variations in Mn/Cr and $\text{Fe}/(\text{Fe} + \text{Mn})$ ratios on a 50 μm scale; at least two different phosphate phases, one containing $\sim 5\%$ Na_2O , coexist in Grant.

The Cr isotopic compositions of coexisting chromite and phosphate were measured with the PANURGE ion probe using a mass resolution of ~ 4500 and a primary beam of ~ 0.5 nA. The isotopic ratios are corrected for fractionation by normalizing to $^{50}\text{Cr}/^{52}\text{Cr} = 0.051859$; the contribution from ^{50}Ti was monitored as $^{49}\text{Ti}^+$. The $^{55}\text{Mn}/^{52}\text{Cr}$ ratio was calculated from the measured $^{55}\text{Mn}^+ / ^{52}\text{Cr}^+$ ratio using a sensitivity factor of 0.53 determined by electron probe analyses of a Grant phosphate high in Cr. The data (Table 1) show no significant deviations from normal Cr isotopic composition for samples with the $^{55}\text{Mn}/^{52}\text{Cr}$ ratio ranging from 0.0035 to 610. Excesses of ^{53}Cr greater than 20‰ are excluded by the data and, in contrast to the Pd-Ag system, only a weak correlation between the magnitude of the ^{53}Cr excess and the $^{55}\text{Mn}/^{52}\text{Cr}$ ratio exists. A least squares fit defines a line with slope $^{53}\text{Cr}^*/^{55}\text{Mn} = (7 \pm 4) \times 10^{-7}$ and intercept $\delta^{53}\text{Cr} = 0.4\%$ but with a correlation coefficient of only 0.36. The data clearly show that ^{53}Mn was not abundant (or absent) when the phosphates formed and together with the Pd-Ag data, suggest that ^{53}Mn was far less abundant than other short-lived nuclides ^{129}I , ^{107}Pd , and ^{26}Al . For the rapid cooling rates of the IIIB irons inferred from isotopic and diffusion studies (Kaiser and Wasserburg, 1983; Norayan and Goldstein, 1985), 150 to $500^\circ\text{C}/\text{my}$, the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio must have been less than 3.4 to 1.4×10^{-6} , respectively. The absence of ^{53}Mn has important implications for nucleosynthetic production mechanisms. Both the quasi-equilibrium e-process, a possible source for the ^{48}Ca and ^{50}Ti excesses, and energetic particle irradiation to produce ^{26}Al , typically produce substantial amounts of ^{53}Mn . The new data suggest that a reexamination of (1) the potential contribution of these sources to the nebular isotopic zoo and (2) the nature of ^{53}Mn production is needed. In particular, the irradiation model of Lee (1978), appears untenable in a simple form.

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Table 1

Sample	I($^{52}\text{Cr}^+$)(c/s)	$\delta^{53}\text{Cr}(\text{‰})$	$^{55}\text{Mn}/^{52}\text{Cr}$	Composition
Grant				
Chromite	5×10^5	-0.6 ± 0.7	0.0035	FeCr_2O_4
Phos. A	600	5.2 ± 6.0	462 ± 32	$(\text{Ca}_{44}\text{Fe}_{2.72}\text{Mn}_{32})(\text{P}_{97}\text{O}_4)_2$
1	575	6.8 ± 8.8	70 ± 8	$(\text{Ca}_{44}\text{Fe}_{2.72}\text{Mn}_{33})(\text{P}_{97}\text{O}_4)_2$
2	2×10^4	0.7 ± 1.5	9 ± 1	$(\text{Na}_{.61}\text{Fe}_{2.19}\text{Mn}_{.27}\text{Cr}_{.04})(\text{P}_{.95}\text{O}_4)_2$
3	470	9.8 ± 10.0	610 ± 40	$(\text{Ca}_{.01}\text{Fe}_{2.57}\text{Mn}_{.45}\text{Cr}_{.01})(\text{P}_{.98}\text{O}_4)_2$
Bear Creek				
Phos. 1	1500	5.8 ± 5.0	394 ± 33	
6	175	-7.6 ± 10.0	540 ± 20	

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FURTHER EVIDENCE AGAINST A NEBULAR ORIGIN FOR THE ORDINARY CHONDRITES

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Nebular hypotheses of the formation of the ordinary chondrites require cold accretion of chondrules, metal and "dust," followed by thermal metamorphism (Morgan *et al.*; Rambaldi and Wasson). A nebular origin is required for chondrules. Earlier work (Hutchison and Bevan) is indicative of a planetary origin for chondrules because their compositions appear to have been determined by "geochemistry" rather than cosmochemistry. Furthermore, evidence was cited that is indicative of hot accretion of the ordinary chondrites. Here we present new evidence supporting a planetary origin for Tieschitz and Semarkona.

TIESCHITZ: If the stone accreted hot we could expect evidence of reaction between various components in the interchondrule matrix. An angular fragment of twinned low-Ca pyroxene was found sitting in dark matrix which is surrounded by white matrix. Optically the px has a reaction corona. Microprobe analyses showed the px to be a bronzite (En84) with very low Ca and low MnO. It has a rim of Ca-rich px from 2-10 μm wide which also extends into cracks. Ca enrichment is accompanied by Mn enrichment, the Mn:Fe ratio being about 0.4 (at). Surrounding dark matrix shows concomitant depletion in CaO from 1.8% to 0.3% (wt) in a 30 μm wide zone adjacent to the px. Clearly, reaction between px and dark matrix must have occurred at high temperature when the dark matrix was metal-rich, which is necessary to account for the high Mn:Fe. Thus dark matrix appears to represent a metal-rich assemblage that was oxidized.

SEMARKONA: Optical microscopy and microprobe analyses indicate that the stone suffered hydrothermal alteration. For example, an olivine dendrite enclosed in later crystallized enstatite has been altered by material emanating from the chondrule rim. The hydrated material was found independently of the suggestion of Gooding (Gooding). Hydrated, crystallized glasses abound; many have very low Ca contents (0.3%) coupled with high NaO (2%), suggesting that Ca had been redistributed. Calcite was sought and found. It occurs in veins in dark matrix and in an igneous fragment associated with hydrated glass. In the veins the mineral is optically turbid and microprobe analyses show that crystals have included dark matrix. They grew *in situ*. Semarkona formed under PH₂O and PCO₂ inconsistent with those postulated for a solar nebula. This is the first indication that some ordinary chondrites had a post accretion history like that of CI and CM2 meteorites.