

ANOMALOUS Cr ISOTOPE FRACTIONATION IN TERRESTRIAL SPINELS FOLLOWING HIGH TEMPERATURE DISTILLATION

Tezer M. Esat. Research School of Earth Sciences, The Australian National University, Canberra 2601, Australia.

Recently there have been reports of Cr isotope anomalies in inclusions from Allende (labelled PSI = Ψ)[1] and in individual Cr-rich spinel inclusions from the Murchison meteorite[2]. The Cr anomalies in these materials are distinguished by the relatively large magnitude of effects in ^{53}Cr and ^{54}Cr and are accompanied by significant mass dependent fractionation. In an accompanying paper[3] we confirm the previous tentative assignment of Cr isotope fractionation in the Murchison Cr-rich spinels. The Murchison spinels are characterized by excesses in ^{53}Cr and ^{54}Cr and are enriched in the heavy Cr isotopes[2]. The PSI are also enriched in the heavier Cr isotopes but in contrast have deficits in ^{54}Cr . Analysis of Allende group II inclusions reveal enrichments in the lighter Cr isotopes and excesses in ^{53}Cr and ^{54}Cr [3].

The complimentary isotopic pattern of Mg isotopes in coarse- and fine-grained inclusions from Allende have been documented previously[4]. The coarse-grained inclusions are enriched in the heavier Mg isotopes and the fine-grained inclusions in the lighter Mg isotopes. This isotopic pattern can be duplicated in the laboratory by distillation of Mg bearing silicates at high temperature. The vaporized material is enriched in the lighter isotopes and the residue in the heavier isotopes[4]. This is the expected pattern for a convecting molten reservoir at constant temperature as the lighter isotopes have higher velocities and a better chance of overcoming surface forces.

We have undertaken high-temperature distillation experiments using terrestrial Cr-spinels to determine the nature and magnitude of any resultant isotope effects in Cr. This is made possible, in part, by the availability of a sensitive technique for distinguishing intrinsic Cr fractionation from instrumental effects[1]. Instrumental fractionation for dissolved samples, run with Si-gel and boric acid, can be controlled to within ± 1 ‰ per mass unit. Terrestrial Cr-rich spinel fragments (20 to 60 mg in weight) were placed in a carbon crucible in vacuum (5×10^{-6} torr) and heated with an RF-coil. The vaporized material (condensate) was collected on teflon beakers placed directly above the carbon boat at a height of about 8 cm. The deposited thin film was dissolved with HF and HNO_3 . The only significant isotopic interference in the mass spectrometer is from ^{54}Fe . Fe was chemically removed from the samples using the procedures described by Kelly, Tera and Wasserburg[5]. No V or Ti interference was observed. The residues are highly refractory and difficult to dissolve. We have analyzed the residues by direct loading. However, directly loaded solid samples tend to fractionate during a run and only limits on intrinsic mass fractionation can be obtained. In addition ^{54}Cr cannot be determined due to ^{54}Fe interference.

A batch of 7 samples were subjected to distillation for times ranging from 1 to 10 seconds at about 2100 °C. Samples at this temperature coalesce into small, rapidly rotating, balls and the vaporized material can be observed as a deposit on the teflon cup. For the residues the original colour of the sample changes from black, to dark grey, to white as vaporization proceeds. Examination of the broken fragments of the residues showed that the Cr and Fe had segregated and coalesced into a Cr-Fe-rich region (dark red) as opposed to the main, Cr-Fe-depleted (pale white) bulk of the sample. Chemical analyses of the starting material and the Cr-rich and Cr-poor parts of the residue are shown in Table 1. In these experiments only a minimal amount of Cr was volatilized in the hope of maximizing the fractionation effects in the vaporized material. The vaporized material is expected to be *depleted* in the heavy Cr isotopes.

The data for these samples (1 through 7) are listed in Table 2. All samples have either zero or negative values for the raw $^{50}\text{Cr}/^{52}\text{Cr}$ ratio relative to standards. The negative values indicate *enrichment* in the heavier Cr isotopes. This result is contrary to expectation and previous experience in Mg for similar experiments[3]. The next two samples in Table 2 (8 and 9) provide an explanation for this anomalous behaviour. Sample 8 is a piece from the Cr-Fe-depleted region of the residue left over from experiment 2. Sample 9 is from the corresponding Cr-Fe-rich region. These samples were analyzed by direct loading and only a range in intrinsic fractionation can be provided. Nevertheless, it is clear from the data that the two samples are fractionated in a complementary fashion. The Cr-rich portion is enriched in the light Cr isotopes as opposed to the

Cr-poor portion which is enriched in the heavy Cr isotopes. This provides an explanation for the observed heavy isotope enrichment in the condensates in samples 1 through 7. The material contributing to the condensates must be predominantly originating from the Cr-depleted areas of the vaporizing sample which is dominated by heavy-Cr isotopes. As expected the magnitude of fractionation in the Cr-poor part (sample 8) is significantly larger than that observed for the condensate 2 (Table 2). If vaporization is continued until most of the Cr in the original sample is depleted, the vaporized material is dominated by the heavy-Cr isotopes as shown in Table 2 for sample 10.

These experiments demonstrate the complex nature of isotope fractionation processes that could have occurred in the early solar nebula. The major constituents of spinel, the oxides of Al and Mg are much more refractory than the oxides of Fe and Cr. During a heating event Fe and Cr are preferentially volatilized relative to Al and Mg. The present experiments reveal that an intermediate step prior to the volatilization of Cr and Fe causes these elements to partially segregate from the bulk of the sample. This process (diffusion or possibly chemical bond-breaking?) appears to be responsible for the large isotope fractionation in Cr between the Cr-Fe-rich and the Cr-Fe-poor reservoirs within the solid. It is likely that Fe isotopes behave in a similar fashion. It will also be of interest to determine the oxygen isotopic composition of the two reservoirs.

In addition to mass dependent fractionation the data also show small residual anomalies, after correcting for fractionation, in both ^{53}Cr and ^{54}Cr . The data was corrected for fractionation using the power law and the NBS $^{50}\text{Cr}/^{52}\text{Cr}$ value [6]. The use of the exponential law does not significantly alter the results. The power law was used in preference to the exponential law as it provided a better fit to the data. At present the data base for these effects is too small to reveal any systematic trends as was observed for Mg [4]. Distillation using Cr-bearing silicates, as opposed to oxides, may provide better constraints on any non-mass dependent effects.

References:

- [1] D.A. Papanastassiou and C.A. Brigham LPSC XIX (1988) 899. [2] T.M. Esat and T.R. Ireland LPSC XIX (1988) 305; to be published EPSL. [3] T.M. Esat and S.R. Taylor (abstract, this volume). [4] T.M. Esat GCA 52 (1988) 1409. [5] R. Kelly, F. Tera and G.J. Wasserburg Anal. Chem. 50 (1978) 1279. [6] W.R. Shields, T.J. Murphy, E.J. Cantanzaro and E.L. Garner J. Res. NBS 70A (1966) 193.

Table 2 Cr isotopic composition of vaporized terrestrial spinels

Sample [‡]	Fractionation [§] $\Delta(^{50}\text{Cr}/^{52}\text{Cr})\% \text{AMU}^{-1}$	$\delta(^{53}\text{Cr}/^{52}\text{Cr})\% \text{‰}^*$ $\pm 2 \text{ s.d.}$	$\delta(^{54}\text{Cr}/^{52}\text{Cr})\% \text{‰}^*$ $\pm 2 \text{ s.d.}$
1	-2.5	-0.5 \pm 0.1	-0.5 \pm 0.2
2	-3.6	-0.4 \pm 0.1	-0.9 \pm 0.1
3	-1.6	-0.3 \pm 0.1	-1.0 \pm 0.1
4	-2.4	0.1 \pm 0.1	0.3 \pm 0.2
5	-1.0	-0.2 \pm 0.1	0.2 \pm 0.2
6	-1.0	0.3 \pm 0.2	0.0 \pm 0.3
7	-1.7	-0.2 \pm 0.1	0.4 \pm 0.2
8 [†]	-5 to -8	-0.5 \pm 0.2	-
9 [†]	+4 to +3	0.0 \pm 0.1	-
10	+4.5	0.4 \pm 0.3	-

[‡] Samples 1 through 7 and sample 10 are vaporized material.

[§] $\Delta(^{50}\text{Cr}/^{52}\text{Cr}) = [(^{50}\text{Cr}/^{52}\text{Cr})_{\text{meas}} / (^{50}\text{Cr}/^{52}\text{Cr})_s - 1] \times 1000 / 2$ per amu, where s denotes the raw grand mean value for standards: $^{50}\text{Cr}/^{52}\text{Cr} = 0.05254$. The range of instrumental fractionation is within $\pm 1\%$ per amu.

* Deviation in per mil of Cr isotope ratios from Cr standards (BCS Grecian Cr-Ore #308). The mean normalized values for 7 standards are $^{53}\text{Cr}/^{52}\text{Cr} = 0.11429 \pm 0.00001$ and $^{54}\text{Cr}/^{52}\text{Cr} = 0.028532 \pm 0.000006$.

[†] Directly loaded residues.

Table 1 Electron-microprobe analyses of vaporized spinel residues

	Original	Residue-7	Cr-poor	Cr-Rich
SiO ₂	0.1	<0.1	<0.1	<0.1
TiO ₂	<0.1	0.2	<0.1	0.1
Al ₂ O ₃	56.8	80.5	84.1	76.7
V ₂ O ₃	0.1	<0.1	<0.1	<0.1
Cr ₂ O ₃	15.9	1.7	0.7	1.3
FeO	5.8	1.0	0.2	0.7
MnO	<0.1	<0.1	<0.1	<0.1
MgO	20.6	17.1	15.0	13.5
CaO	<0.1	<0.1	<0.1	<0.1
Total	99.3	100.5	99.3	92.3

Wavelength-dispersive analyses in weight per cent on rough surfaces. The original Cr-spinels are from Mt. Isa Queensland.