

CHROMIUM ISOTOPIC COMPOSITION OF SOME CHONDRITIC METEORITES

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Abstract: The Cr isotopic composition of primitive meteorites (acid-residue fractions) was studied. Five chondrites were analyzed in this work [Allende (CV3), Murchison (CM2), Nuevo Mercurio (H5), La Criolla (L6), Qingzhen (EH3)]. Although in most samples, no isotopic anomalies beyond the experimental errors could be detected, an elevated $^{54}\text{Cr}/^{52}\text{Cr}$ ratio was found in the acid-soluble fraction from Qingzhen. Moreover, $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ show an inverse correlation among the meteorites analyzed in this study, and the acid residues have larger $\epsilon^{54}\text{Cr}$ and smaller $\epsilon^{53}\text{Cr}$ values than do the acid-soluble fractions in Allende and Murchison. The enrichment of ^{54}Cr in the Qingzhen sample suggests that the ^{54}Cr heterogeneity due to stellar nucleosynthesis has remained in enstatite chondrite as well as carbonaceous chondrite. In addition, the inverse correlation of $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ detected in acid residue samples indicates that the high-temperature condensate contained more exotic ^{54}Cr . It is also suggested that the homogenization of Cr isotopes proceeded with time, and terminated within a relatively short time scale of less than 2–3 Ma.

1. Introduction

Since BIRCK and ALLEGRE (1984, 1985) first found a small excess of ^{54}Cr as well as a variation of ^{53}Cr correlated with the Mn/Cr ratio in Ca-Al-rich inclusions (CAIs) in Allende, Cr isotopic analysis in meteorites has received considerable attention.

Cr has four stable isotopes. According to the standard scenario of nucleosynthesis (*e.g.*, WOOSLEY, 1986), ^{54}Cr is synthesized in a neutron-rich nuclear statistical equilibrium, whereas $^{50,52,53}\text{Cr}$ is produced in explosive oxygen and/or silicon burning. ^{53}Cr is formed as the daughter of ^{53}Mn ($T_{1/2} = 3.7 \times 10^6 \text{yr}$). The meteoritic Cr isotopic compositions are interesting for the following reasons.

Firstly, ^{54}Cr variations are due to an incomplete mixing of several major nucleosynthetic components. Indeed, isotopic anomalies of ^{54}Cr have been found in refractory materials of primitive meteorites, such as Allende inclusions and Murchison spinels (*e.g.*, PAPANASTASSIOU, 1986a; PAPANASTASSIOU and BRIGHAM, 1989; ESAT and IRELAND, 1989; SIMON *et al.*, 1994). In addition, it was found that these anomalies accompanies neutron-rich isotopes of other iron-peak elements (^{48}Ca , ^{50}Ti , ^{58}Fe and

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Passed away on January 15th in 1995.

^{64}Ni), and the extent of anomalies are roughly correlated with each other (e.g., NIEDERER *et al.*, 1985; PAPANASTASSIOU, 1986b; HINTON *et al.*, 1987; BIRCK and LUGMAIR, 1988). Later, ROTARU *et al.* (1992) found that positive ^{54}Cr anomalies exist in some C1 to C4 carbonaceous chondrites with each maximum value decreasing with increasing petrographic type. This has been believed to indicate that the ^{54}Cr isotopic anomalies were lost according to a secondary alteration in the meteorite parent body.

Secondly, the ^{53}Cr variations are due to the decay of the extinct radioactive nuclide, ^{53}Mn . BIRCK and ALLEGRE (1988) carried out Cr isotopic analyses of enstatite chondrite Indarch (E4) and stony-iron meteorite Eagle Station (pallasite), as well as Allende (CV3), and found that ^{53}Cr isotopic variations arose from the in situ decay of ^{53}Mn . LUGMAIR *et al.* (1992, 1994a, b) investigated the timescales of early differentiation based on a Mn-Cr isotopic evolution by analyzing differentiated meteorites, such as angrites (LEW86010, Angra dos Reis) and eucrites (Chervony Kut [CK], Juvinas [JUV]). HUTCHEON *et al.* (1992) found that the IIIAB iron meteorite has positive ^{53}Cr values, and that they are linearly correlated with the Mn/Cr ratios. NYQUIST *et al.* (1994) studied the Mn-Cr isotopic composition of LEW86010 (angrite) in order to establish a precise time interval between the condensation of the first solids in the nebula and the formation of angrites. As mentioned above, it was suggested that the isotopic variations of ^{53}Cr were closely correlated with the Mn/Cr ratios, and that ^{53}Mn - ^{53}Cr isotopic systematics are a valuable chronometer for establishing time scales for the formation of meteorites.

In the present study, we focused on acid-residue samples, because they are often considered the least effected portion of the meteorite from metamorphism due to secondary heating and shock. From this viewpoint, and also to clarify the characteristics of high-temperature condensates in the early solar system, we have continued a detailed analysis of primitive meteorites. In our previous work, we have described the elemental analysis of acid residues from Allende (CV3), Nuevo Mercurio (H5) and Canyon Diablo (IA) (KANO *et al.*, 1993).

Since acid-residue samples have low Mn contents, the effects of ^{53}Mn decay to ^{53}Cr are very low. Thus, we regard acid-residue samples to be very suitable for surveying $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ correlations; $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ are defined as follows:

$$\begin{aligned}\epsilon^{53}\text{Cr} &= [(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{53}\text{Cr}/^{52}\text{Cr})_{\text{std}} - 1] \times 10^4, \\ \epsilon^{54}\text{Cr} &= [(^{54}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{54}\text{Cr}/^{52}\text{Cr})_{\text{std}} - 1] \times 10^4.\end{aligned}$$

Here, we present Cr isotopic data for some chondritic meteorites, and discuss the implications of these data from the viewpoint of the evolution of the solar system.

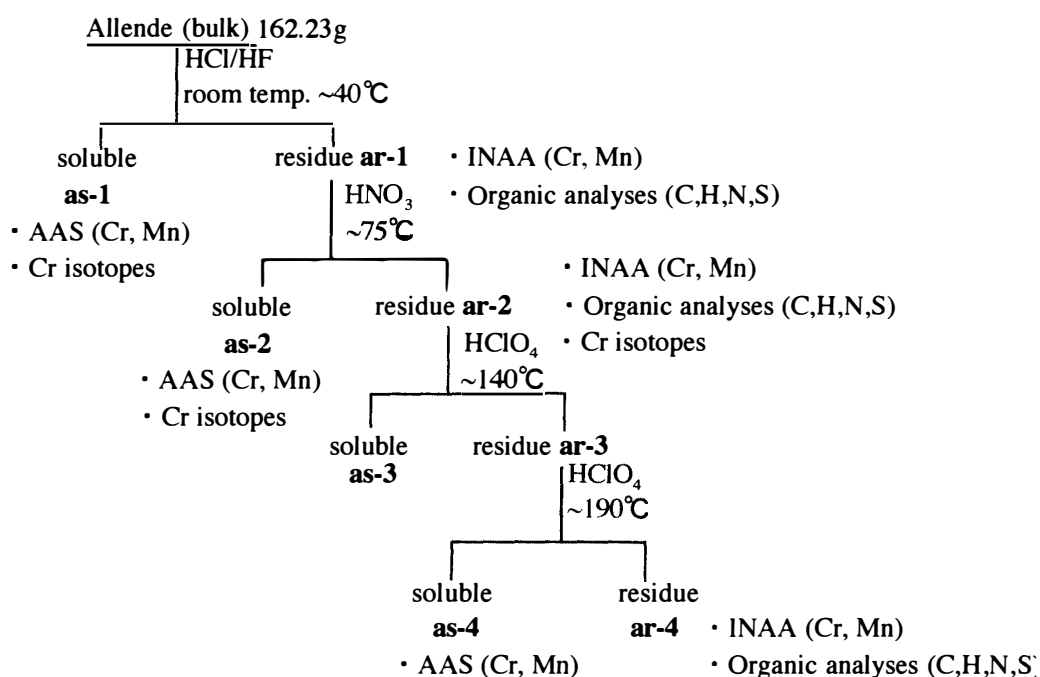
2. Experimental

2.1. Samples

The chondritic meteorites used in this work were (1) Allende (CV3), (2) Murchison (CM2), (3) Nuevo Mercurio (H5), (4) La Criolla (L6), (5) Qingzhen (EH3). After removing the fusion crusts with a ceramic blade, these chondrites were disaggregated using the freeze-thaw method with liquid nitrogen. They were dissolved by alternating treatments with several acids, such as 6N HCl and 10N HF. An outline of

the acid treatment used in this work is shown in Fig. 1. The acid-residues were concentrated by centrifuging (3000 rpm), washed with distilled H₂O and acetone, and then dried. The determination of C, H, N, and S concentrations was carried out in order to characterize the acid residues. The fractions of each acid residue are given in Table 1 along with the contents of C, H, N and S.

a) Allende (CV3)



b) Murchison (CM2)

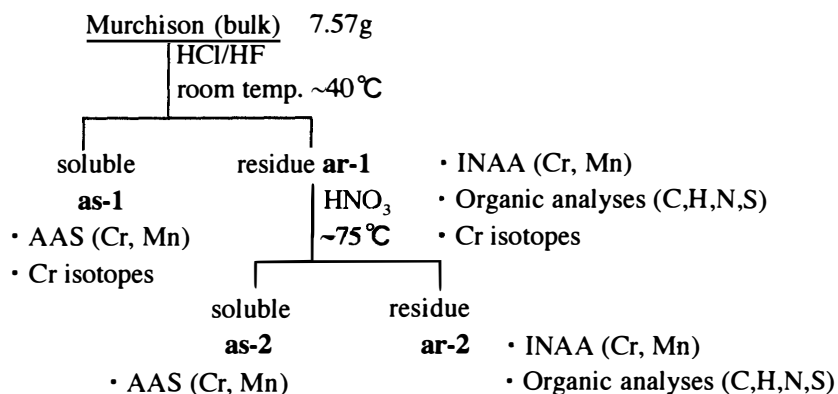


Fig. 1. Acid treatment of chondritic meteorites in this work [(a) Allende (CV3), (b) Murchison (CM2), (c) Qingzhen (EH3), (d) Nuevo Mercurio (H5), (e) La Criolla (L6)].

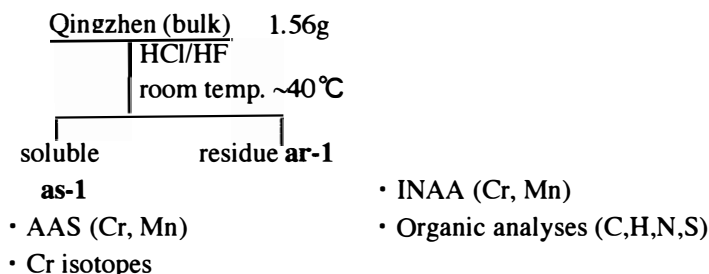
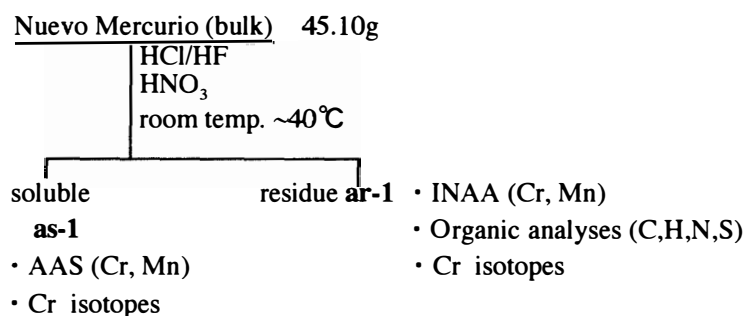
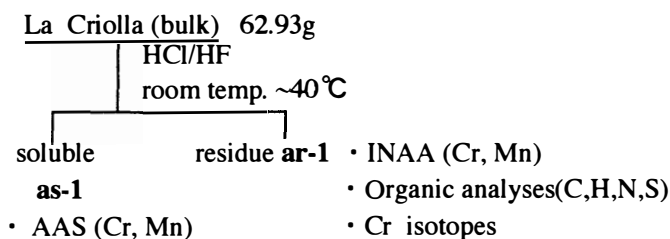
c) **Qingzhen (EH3)**d) **Nuevo Mercurio (H5)**e) **La Criolla (L6)**

Fig. 1 (Continued).

2.2. *Sample preparation*

The acid-residue samples were decomposed in sealed poly-tetrafluoroethylene (PTFE) vessels (Fig. 2) by a microwave dissolution method with a mixture of acids. The typical decomposition procedures, conditions and used acids are as follows.

A weighed sample powder (④ in Fig. 2) was placed in an innermost vessel made of Teflon (DV-7: ③ in Fig. 2; expressed as Teflon inner vessel hereafter) with 2.0 ml of conc. nitric acid, 0.3 ml of 60% perchloric acid, 0.15 ml of 6 M hydrochloric acid, and 0.15 ml of conc. hydrofluoric acid. After dispersing the powdered sample fully into these mixed acids by rotating the vessel, the Teflon inner vessel was tightly fastened and put into a Teflon vessel (PT-25: ② in Fig. 2) with 1.5 ml of water.

Table 1. C, H, N, S contents of acid residues from chondritic meteorites.

Acid residues fraction (wt%)				Contents (wt%)*			
				C	H	N	S
Allende (CV3)							
HCl/HF	residue (ar-1)	2.78	8.13	1.39	–	24.5	
HCl/HF-HNO ₃	(ar-2)	1.64	20.4	0.74	0.73	42.6	
HCl/HF-HNO ₃ -HClO ₄	(ar-4)	0.68	33.7	0.93	–	34.4	
Murchison (CM2)							
HCl/HF	residue (ar-1)	3.12	34.6	2.10	1.48	46.5	
HCl/HF-HNO ₃	(ar-2)	1.30	29.5	1.71	2.56	27.5	
Qingzhen (EH3)							
HCl/HF	residue (ar-1)	0.85	6.26	2.05	0.71	7.27	
Nuevo Mercurio (H5)							
HCl/HF-HNO ₃	residue (ar-1)	1.03	–	0.29	–	2.22	
La Criolla (L6)							
HCl/HF	residue (ar-1)	0.83	1.20	0.16	–	12.8	

*C, H, N, S contents of acid residues from meteorites were analyzed by T. SEKI of Tokyo University by combustion method.

Subsequently, this vessel (PT-25) was put into a polypropylene tube (PP-25: ① in Fig. 2), and tightened and sealed. This polypropylene tube (PP-25) was then put into a microwave oven with a 100 ml beaker, which contained more than 50 ml of water, and heated at 200 W for 3 min. After removing only the beaker from the microwave oven, the polypropylene tube was heated again at 200 W for 3 min. Next, the polypropylene tube was removed from the microwave oven, cooled for 3 min and slowly opened. Subsequently, the Teflon inner vessel was removed from the Teflon vessel and opened. When the samples were not fully dissolved, the heating procedure in the microwave oven was repeated. The Teflon inner vessel was slowly heated with

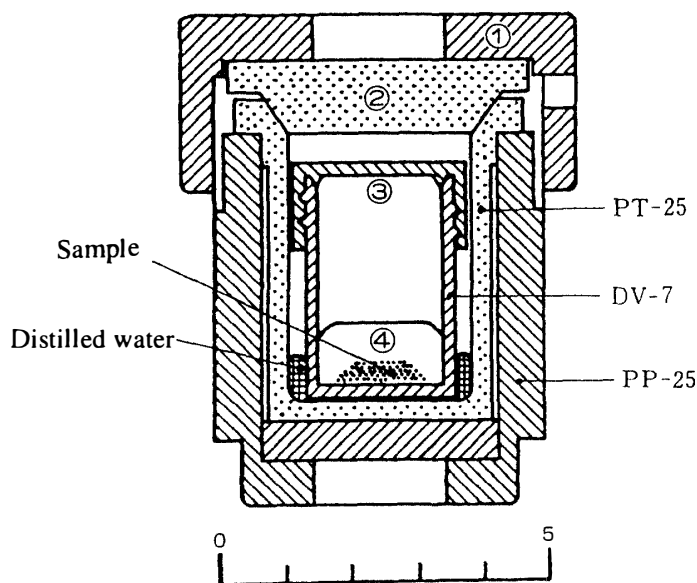


Fig. 2. Scheme of vessels for microwave sample decomposition.

an infrared lamp. After evaporating the contents to dryness on a hotplate while using an infrared lamp simultaneously, 1 ml of 0.1 M perchloric acid was added to dissolve the contents. Finally, the total weight of the inner vessel was measured and the weight of the sample solution was calculated. According to the contents of the measuring elements, the sample solution was diluted.

From these residues, as well as from the acid-soluble fraction, Cr was separated by precipitation as $\text{Cr}(\text{OH})_3$, and then passed twice through a column packed with an anion-exchange resin (Biorad AG1 \times 8). The separation procedure, which is slightly modified from LEE and TERA (1986), is shown in Fig. 3.

2.3. Determination of Mn and Cr contents

To supplement the Cr isotopic analysis, the contents of Mn and Cr in the samples used in this work were determined by atomic-absorption spectrometry (AAS; Nippon Jarrell-Ash Co., Ltd. AA-890) and instrumental neutron-activation analysis (INAA). Neutron irradiations (the pneumatic tube irradiation for Mn and the long-time irradiation for Cr) for INAA were carried out by using the TRIGAII reactor at Rikkyo University. The thermal-neutron fluxes were 1×10^{12} and 1.4×10^{12} ($\text{n}/\text{cm}^2 \cdot \text{s}$) for the pneumatic tube and the long-time irradiation, respectively. The standard materials used in this work were the same as those used in our previous work (KANO *et al.*, 1993). The analytical method used (*i.e.*, AAS, INAA) for each sample is also shown in Fig. 1.

2.4. Mass spectrometry

Cr isotopic analyses were performed using a VG 354 thermal-ionization mass spectrometer (TIMS) with a single Faraday collector. The samples were loaded on a zone-refined (99.995%) outgassed V-shaped Re single filament with silica gel and boric acid used as an activator. The filament was outgassed at 5A for at least 1 hour below 3×10^{-7} torr; adequate prebaking was required to reduce the interference from molecular ions. Isotopes from possible interfering elements (Ti, V and Fe) were monitored at ^{49}Ti , ^{51}V and ^{57}Fe . No Ti or V interferences have been detected. However, small Fe signals were not negligible along with an increase in the filament temperature. We therefore corrected the measured data for the isobaric interference using $^{50}\text{Ti}/^{49}\text{Ti} = 0.969150$, $^{50}\text{V}/^{51}\text{V} = 0.002406$ and $^{54}\text{Fe}/^{57}\text{Fe} = 2.622222$.

Isotopic measurements were carried out in the peak jumping mode. The isotope ratios were normalized to $^{50}\text{Cr}/^{52}\text{Cr} = 0.051859$ (SHIELDS *et al.*, 1966), and the mass fractionation was corrected using an exponential law (*e.g.*, HUTCHEON *et al.*, 1987).

3. Results

3.1. Standards

The Cr isotopic compositions of the terrestrial standards from the reagent ($\text{K}_2\text{Cr}_2\text{O}_7$, KANTO Co.) and the Cr separated from JB-1 were measured regularly during these experiments (Table 2). The Cr reagent was dissolved in a 0.01M HNO_3 solution, and the chemical form was $\text{Cr}(\text{NO}_3)_3$ on the filament. JB-1 is one of the silicate rock reference materials (alkali basalt) supplied from the Geological Survey of Japan

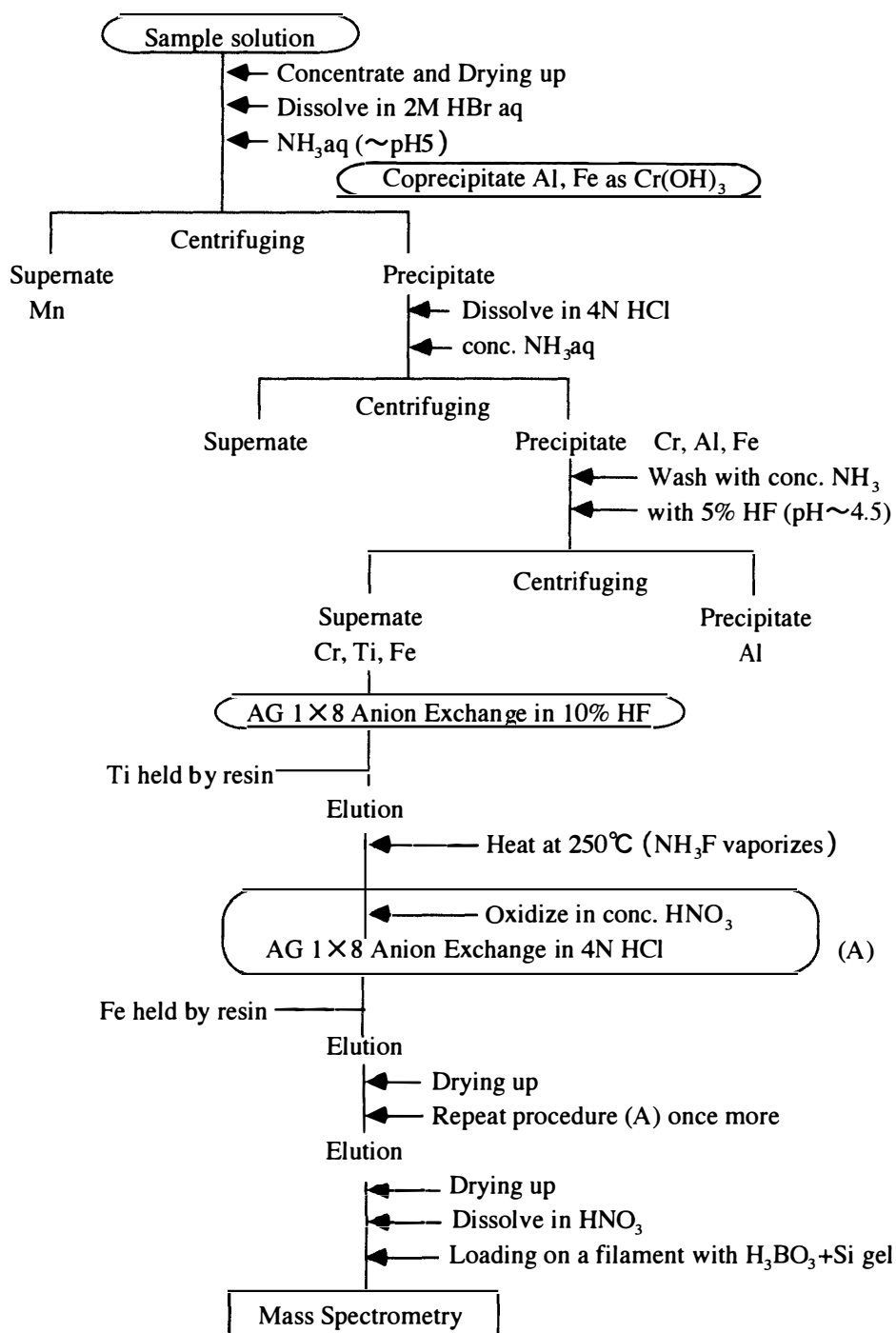


Fig. 3. Chemical scheme for extraction and purification of Cr.

Table 2. Cr isotopic ratios of terrestrial standards*.

	$^{53}\text{Cr}/^{52}\text{Cr}$	$^{54}\text{Cr}/^{52}\text{Cr}$	Date	
Cr reagent	0.113449 ±24	0.028214 ±28	1993.01.18	
	0.113452 ±24	0.028207 ±48	01.19	
	0.113458 ±18	0.028210 ±36	03.29	
	0.113465 ±34	0.028217 ±38	04.08	
	0.113474 ±32	0.028226 ±34	05.10	
	0.113431 ±18	0.028239 ±24	07.16	
	0.113422 ±30	0.028224 ±16	11.02	
	0.113459 ±24	0.028253 ±52	1994.01.07	
	0.113414 ±36	0.028229 ±22	03.05	
	0.113446 ±22	0.028206 ±42	05.26	
	0.113454 ±24	0.028208 ±36	05.30	
	0.113460 ±38	0.028217 ±26	07.04	
	JB-1	0.113478 ±36	0.028238 ±46	1994.01.09
		0.113454 ±76	0.028231 ±38	05.29
0.113446 ±38		0.028224 ±38	07.07	
Weighed mean [#]	0.113449 ± 9	0.028224 ± 7		

* All isotopic ratios are corrected for mass fractionation by normalization to $^{50}\text{Cr}/^{52}\text{Cr}=0.051859$ (SHIELDS *et al.*, 1966) by exponential law. Errors given are two standard deviations of the mean.

[#] The uncertainties of weighed means are the external reproducibility, estimated at 95% confidence limits for 15 separate analyses.

(GSJ).

The measured ratios were grouped as data sets of 10–15 cycles, and the mean $^{50}\text{Cr}/^{52}\text{Cr}$ isotope ratios were normalized to $^{50}\text{Cr}/^{52}\text{Cr}=0.051859$ (SHIELDS *et al.*, 1966). The mean $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ for each data set were corrected for the mass fractionation using an exponential law. Usually, 20–40 data sets were collected. After removing those highly unstable and exceeding $\pm 2\sigma$ data, the mean values were recalculated.

The weighed mean of the measured $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ ratios (12 for reagents and 3 for JB-1) corrected for fractionation were 0.113449 ± 9 and 0.028224 ± 7 , respectively; the uncertainties of the weighed means represent the external error estimated at the 95% confidence limits for 15 separate analyses. These “standard” values of $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ used in this work were identical with those of previously published work (Table 3). The distribution of $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ ratios in each analysis relative to our overall average are displayed in histograms (Fig. 4).

3.2. Samples

The Cr isotopic compositions of the chondritic meteorites measured in this work are shown in Table 4. These results are also plotted in Fig. 5 as deviations from the means of the standards.

Although no significant isotopic anomalies beyond the experimental errors were detected in most cases, one noticeable result is that an enrichment of the $^{54}\text{Cr}/^{52}\text{Cr}$ ratio relative to the terrestrial standard value was detected in the Qingzhen acid-soluble fraction; though in the case of the acid residues of Qingzhen, no reliable data were

Table 3. Comparison of the normalized Cr isotopic ratio for the terrestrial standard*.

	$^{53}\text{Cr}/^{52}\text{Cr}$	$^{54}\text{Cr}/^{52}\text{Cr}$
BIRCK and ALLEGRE (1984)	0.113446 ± 19	0.0282065 ± 11 (power law)
	0.113436 ± 19	0.0281994 ± 11 (exponential law)
LEE and TERA (1986)	0.113487 ± 15	0.028229 ± 9 (power law)
PAPANASTASSIOU (1986a)	0.113459 ± 5	0.0282129 ± 15 (exponential law)
BIRCK and ALLEGRE (1988)	0.1134569 ± 10	0.0282108 ± 5 (exponential law)
ROTARU <i>et al.</i> (1992)	0.1134556 ± 5	0.0282116 ± 2 (exponential law)
SIMON <i>et al.</i> (1994)	0.113474 ± 9	0.028228 ± 4 (exponential law)
NYQUIST <i>et al.</i> (1994)	0.113450 ± 5	0.028212 ± 3 (Oct. 1991)
	0.113450 ± 4	0.028211 ± 4 (Mar. 1992)
	0.113452 ± 5	0.028211 ± 2 (Mar. 1992)
	0.113458 ± 6	0.028209 ± 4 (Oct. 1993)
This work	0.113449 ± 9	0.028224 ± 7

* All isotopic ratios are corrected for mass fractionation by normalization to $^{50}\text{Cr}/^{52}\text{Cr}=0.051859$ (SHIELDS *et al.*, 1966).

obtained. Moreover, $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ are inversely correlated as a whole, and, in Allende and Murchison, the acid residues show more $\epsilon^{54}\text{Cr}$ and less $\epsilon^{53}\text{Cr}$ values than the acid-soluble fractions. In the Qingzhen acid-soluble fraction, which showed some excess of $^{54}\text{Cr}/^{52}\text{Cr}$, a slight deficit of $^{53}\text{Cr}/^{52}\text{Cr}$ relative to the terrestrial standard value was also observed. On the other hand, in the acid residues of equilibrated ordinary chon-

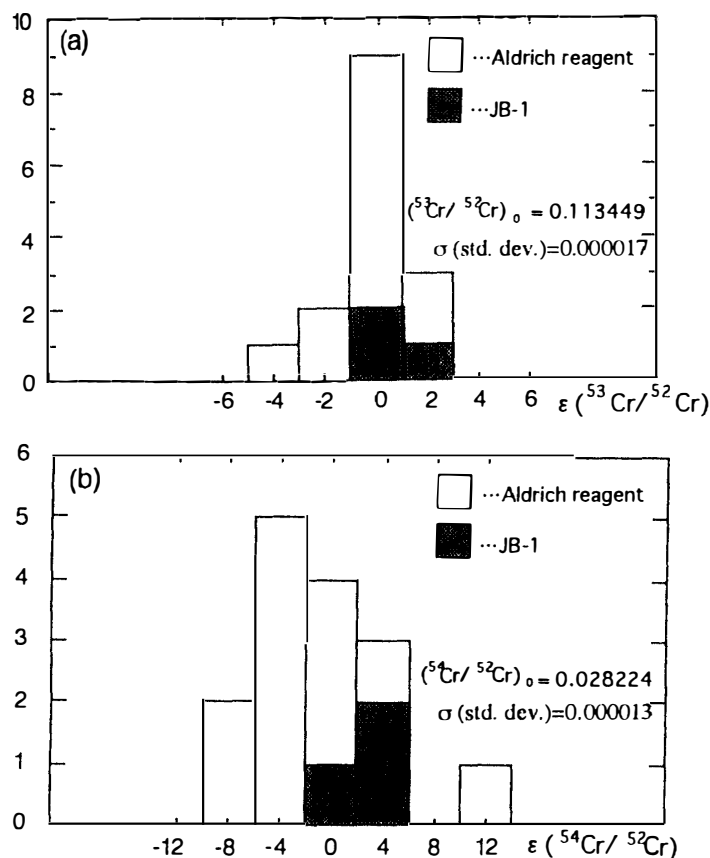


Fig. 4. The histograms of 15 terrestrial standard (12 Aldrich reagents and 3 JB-1) runs for $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ normalized to $^{50}\text{Cr}/^{52}\text{Cr}=0.051859$ by exponential law.

Table 4. Cr isotopic ratio for some chondrite meteoritic samples*.

	$^{53}\text{Cr}/^{52}\text{Cr}$	$^{54}\text{Cr}/^{52}\text{Cr}$	Number of data blocks
Allende (CV3)			
HCl/HF soluble	0.113445 ±20	0.028230 ±28	27
HCl/HF residue			
-HNO ₃ soluble	0.113441 ±24	0.028240 ±18	26
-HNO ₃ residue	0.113442 ±26	0.028248 ±22	25
Murchison (CM2)			
CH ₃ COOH soluble	0.113464 ±72	0.028209 ±68	14
HCl/HF soluble	0.113453 ±38	0.028232 ±56	17
HCl/HF residue	0.113424 ±22	0.028274 ±48	15
Qingzhen (EH3)			
HCl/HF soluble	0.113409 ±20	0.028266 ±12	38
	0.113430 ±22	0.028247 ±24	24
Nuevo Mercurio (H5)			
HCl/HF-HNO ₃ soluble	0.113454 ±22	0.028232 ±32	25
HCl/HF-HNO ₃ residue	0.113447 ±18	0.028219 ±24	36
	0.113463 ±40	0.028226 ±34	20
La Criolla (L6)			
HCl/HF residue	0.113451 ±24	0.028234 ±28	32
Normal (N=15)	0.112449 ±17	0.028224 ±13	

*All isotopic ratios are normalized to $^{50}\text{Cr}/^{52}\text{Cr}=0.051859$ (SHIELDS *et al.*, 1966).

Errors given are two standard deviations of the mean.

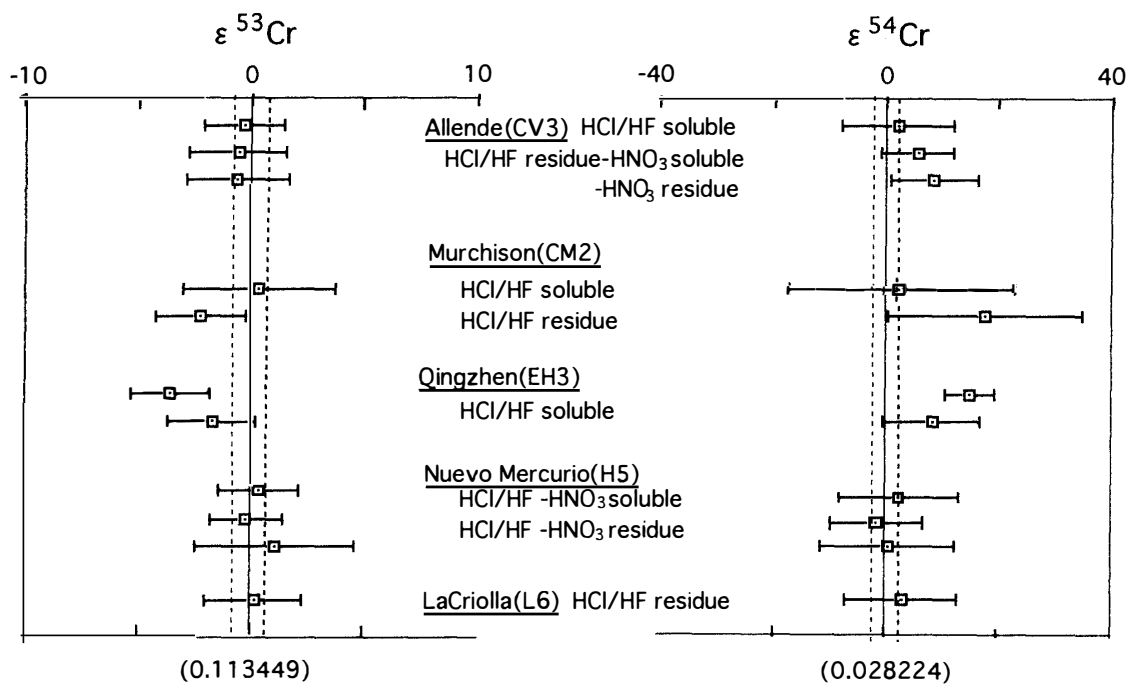


Fig. 5. Cr isotopic compositions of some chondrite samples.

All isotopic ratios are corrected for mass fractionation by normalization to $^{50}\text{Cr}/^{52}\text{Cr}=0.051859$ (SHIELDS *et al.*, 1966). Errors given are two standard errors of the mean. Dotted lines indicate the range of uncertainties for "Normals" (terrestrial) at the 95% confidence limit.

Table 5. Mn - Cr isotopic data for some chondrite meteoritic samples.

Sample	*Mn	*Cr	⁵⁵ Mn/ ⁵² Cr	ε ⁵³ Cr
Allende (CV3)				
HCl/HF soluble (as-1)	0.138%	0.232%	0.710	-0.35 ± 1.76
HCl/HF residue (ar-1)				
-HNO ₃ soluble (as-2)	210 ppm	0.266%	0.0942	-0.71 ± 2.12
-HNO ₃ residue (ar-2)	124 ppm	4.53%	0.00327	-0.62 ± 2.29
Murchison (CM2)				
HCl/HF soluble (as-1)	0.166%	0.256%	0.799	0.35 ± 3.35
HCl/HF residue (ar-1)	780 ppm	1.14%	0.0820	-2.20 ± 1.94
Qingzhen (EH3)				
HCl/HF soluble (as-1)	0.195%	0.274%	1.04	-3.53 ± 1.76
				-1.67 ± 1.94
HCl/HF residue (ar-1)	673 ppm	0.409%	-	-
Nuevo Mercurio (H5)				
HCl/HF-HNO ₃ soluble (as-1)	0.234%	0.218%	1.28	0.44 ± 1.94
HCl/HF-HNO ₃ residue (ar-1)	0.203%	4.03%	0.0601	-0.18 ± 1.59
				1.23 ± 3.53
La Criolla (L6)				
HCl/HF soluble (as-1)	0.210%	680 ppm	-	-
HCl/HF residue (ar-1)	0.361%	35.6%	0.0121	0.18 ± 2.12

* Errors of Mn, Cr contents in these samples are within ±10%.

drites, such as La Criolla and Nuevo Mercurio, no significant isotopic anomalies beyond the experimental errors were detected.

3.3. Mn and Cr contents

The Mn and Cr contents in a series of samples are given in Table 5.

It is evident that the acid-residual fractions have a lower Mn/Cr ratio in each meteorite, and that Cr is relatively concentrated in the acid-soluble fraction of Qingzhen compared to other meteorites.

In Table 5, the ⁵⁵Mn/⁵²Cr and ε⁵³Cr values of each sample are also given based on the data from Cr isotopic compositions and Mn, Cr contents.

4. Discussion

4.1. ε⁵³Cr-ε⁵⁴Cr plot

An ε⁵³Cr-ε⁵⁴Cr correlation plot of the samples analyzed in this work is shown in Fig. 6.

In general, ε⁵³Cr and ε⁵⁴Cr are inversely correlated, and the acid residues have larger ε⁵⁴Cr and smaller ε⁵³Cr values than do the acid soluble fractions in Allende and Murchison. In the Qingzhen acid-soluble fraction, some excess of ⁵⁴Cr/⁵²Cr and a slight deficit of ⁵³Cr/⁵²Cr relative to the terrestrial standard value were also observed.

4.2. Cr isotopic studies in previous published work

BIRCK and ALLEGRE (1984) observed a slight deficit in ⁵³Cr in CAIs. Furthermore, they reported that the isotopic variation of ⁵³Cr was closely correlated with the Mn/Cr

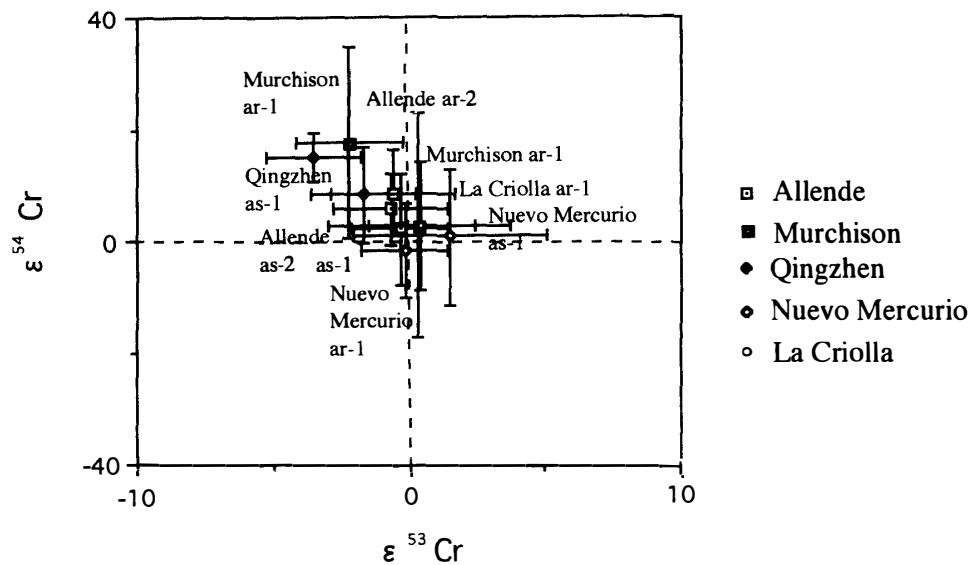


Fig. 6. $\epsilon^{53}\text{Cr}$ versus $\epsilon^{54}\text{Cr}$ plots of chondrite samples presented in this work.

ratio (BIRCK and ALLEGRE, 1985). From the mean values of these samples, the initial $^{53}\text{Mn}/^{55}\text{Mn}$ for Allende inclusions was estimated to be $(4.4 \pm 1.0) \times 10^{-5}$ (BIRCK and ALLEGRE, 1985, 1988). However, it was pointed out that these values cannot be accounted for unless the initial Cr isotopic heterogeneity and/or Mn-Cr fractionation is also considered (e.g., LEE, 1986; HARPER and WIESMANN, 1992).

Later, C1 to C4 carbonaceous chondrites were analyzed by stepwise dissolution (BIRCK *et al.*, 1990; ROTARU *et al.*, 1992). BIRCK *et al.* (1990) reported values of the initial $^{53}\text{Mn}/^{55}\text{Mn}$ for Orgueil (CI1) of 2×10^{-5} , Murchison and Murray (CM2) of 1.2×10^{-5} , and Karoonda (CK4) of $(0.6-3.5) \times 10^{-6}$. ROTARU *et al.* (1992) measured nine carbonaceous chondrites. Here, we give their results converted to $\epsilon^{53}\text{Cr}-\epsilon^{54}\text{Cr}$ values in Fig. 7. Although positive anomalies of ^{54}Cr exist in C1 to C4 type all around, each maximum value decreases with increasing petrographic type, such as Orgueil (CI1) $\sim 100\epsilon$, Murchison and Murray (CM2) $\sim 27\epsilon$, and Felix (CO3) and Coolidge (CV4) $\sim 2.8\epsilon$. They considered this to be due to a secondary alteration in the meteoritic parent body. It is remarked that the excess of ^{54}Cr is larger in the silicate phases than in the refractory phases such as spinels for CI1 chondrite. On the other hand, it is largest in the refractory phases for CM2 chondrite.

Inverse correlations of $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ are also found in Allende and Vigarano inclusions (PAPANASTASSIOU, 1986a; PAPANASTASSIOU and BRIGHAM, 1989; BIRCK and ALLEGRE, 1988; LOSS *et al.*, 1994), though it has not been clearly pointed out in the literature.

4.3. Cr isotopic ratios in Qingzhen and high-temperature condensate in E chondrite

Here, we consider the ^{54}Cr excess detected in the Qingzhen acid-soluble sample. As mentioned above, since only ^{54}Cr is synthesized in a neutron-rich nuclear statistical equilibrium (e.g., HARTMANN *et al.*, 1985), Cr isotopic inhomogeneities at the stage of nucleosynthesis in stars may remain in an E chondrite, such as Qingzhen (which was formed in the reducing environment of the solar system).

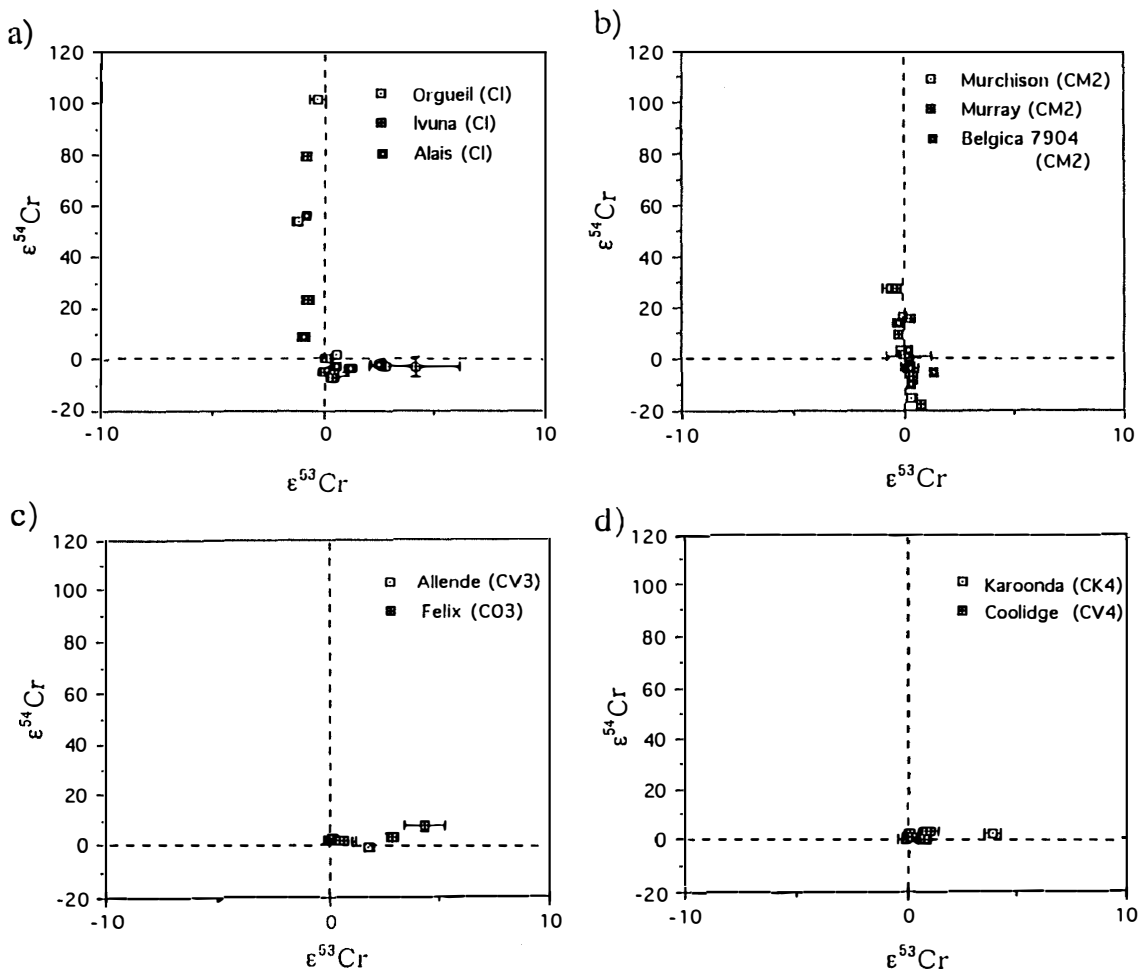


Fig. 7. $\epsilon^{53}\text{Cr}$ versus $\epsilon^{54}\text{Cr}$ plots of some carbonaceous chondrites [(a) CI, (b) CM2, (c) C3, (d) C4] based on the data of ROTARU *et al.* (1992).

The acid-soluble samples in which ^{54}Cr excess was so far detected are silicate phases in CI meteorites, such as Orgueil, Ivuna and Alais (ROTARU *et al.*, 1992). Our Qingzhen data are shown in Fig. 8 along with Orgueil, Ivuna and Alais data of ROTARU *et al.* (1992). One possibility of the endmember of ^{54}Cr excess in the Qingzhen acid soluble is the silicate phases (fraction 4) of Orgueil, though the error for $\epsilon^{53}\text{Cr}$ in the Qingzhen sample is rather high. In other words, the ^{54}Cr -enriched host phase which caused the ^{54}Cr excess in Orgueil may be included in the Qingzhen sample.

The ^{54}Cr -enriched phase in Qingzhen could be attributed to acid-soluble minerals containing isotopically anomalous Cr, which are characteristic of E chondrites formed in regions of reducing environments.

LATTIMER *et al.* (1978) suggested that enstatite chondrites, which formed in regions of the solar nebula in which $\text{C/O} > 1$, could contain presolar grains of TiC, C, SiC, Fe_3C , AlN and CaS. Of these minerals, CaS is an acid-soluble mineral, and is thought to be the high-temperature counterparts of the more oxidized minerals found in CAI inclusions in carbonaceous chondrites (*e.g.*, LARIMER and GANAPATHY, 1987; LUNDBERG *et al.*, 1992). Thus, CaS may be one of the candidates of Cr carriers for the Qingzhen

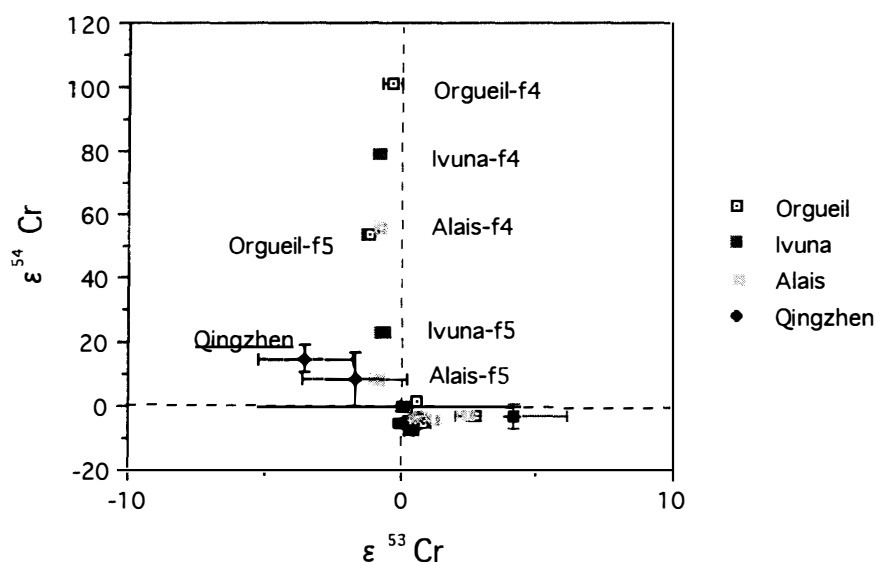


Fig. 8. $\epsilon^{53}\text{Cr}$ versus $\epsilon^{54}\text{Cr}$ plots of Qingzhen in this work and CI chondrites (Orgueil, Ivuna, Alais) based on the data of ROTARU *et al.* (1992). In case of CI chondrites, -f4 stand for silicate phases and -f5 stand for refractory phases [cf. ROTARU *et al.* (1992)].

acid-soluble fraction.

The only other study of the Cr isotopic composition measured by a thermal ionization mass spectrometer (TIMS) for an enstatite chondrite was the BIRCK and ALLEGRE (1988)'s work for Indarch (EH4), which shows that all of the Cr isotope ratios were close to the normal ratios.

The difference between our result and that of BIRCK and ALLEGRE (1988) may be due to the carriers of the Cr component. Indeed, it is pointed out that there are many differences in the mineral compositions between EH3 and EH4, 5 (KALLEMEYN and WASSON, 1986), and much diversity in the Cr concentrations in each phase between them. According to the differences in the parent body and/or the regions in the solar nebula, the Cr host phase may differ, and the components which show anomalous Cr isotopic compositions are considered to be heterogeneously distributed.

4.4. Possibility of the effect of *s*-process nucleosynthesis

The Qingzhen $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ data can also be interpreted as representing a *s*-process nucleosynthesis component.

Isotopic anomalies of noble gases, C, N, Si have been reported in silicon carbide (SiC) extracted from primitive carbonaceous chondrites, such as Murchison (*e.g.*, ANDERS and ZINNER, 1993), and these anomalies have been attributed to *s*-process nucleosynthesis in AGB (Asymptotic Giant Branch) stars (*e.g.*, LEWIS *et al.*, 1990, 1994).

We now consider the fluctuations of the early high-temperature condensate relative to the standard solar system material in *s*-process nucleosynthesis. When we transcribe the excess neutron fluence ($\Delta\tau$), neutron-capture cross section of each Cr isotope (mass number = A) (σ_A), and the abundance of the *s*-nuclide of atomic mass number (A) (N_A), the variation in $^{50}\text{Cr}/^{52}\text{Cr}$ (*i.e.* $\epsilon^{50}\text{Cr}$) can be written as follows:

$$\varepsilon^{50}\text{Cr} = -\left(\sigma_{50} - \sigma_{52} + \sigma_{51} \cdot \frac{N_{51}}{N_{52}}\right)\Delta\tau \left(\equiv -\eta \cdot \Delta\tau\right).$$

The coefficient for normalization to the standard solar $^{50}\text{Cr}/^{52}\text{Cr}$ value is $1 + 1/2\varepsilon^{50}\text{Cr}$ for $^{53}\text{Cr}/^{52}\text{Cr}$, and $1 + \varepsilon^{50}\text{Cr}$ for $^{54}\text{Cr}/^{52}\text{Cr}$.

Thus, the variations in $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ [*i.e.*, $\varepsilon^{53}\text{Cr}$ and $\varepsilon^{54}\text{Cr}$], considering the effect of normalization to $^{50}\text{Cr}/^{52}\text{Cr}$, are approximately expressed as follows:

$$\begin{aligned} \varepsilon^{53}\text{Cr} &= \left[\left(\sigma_{52} \cdot \frac{N_{52}}{N_{53}} - \sigma_{53} \right) - \left(\sigma_{51} \cdot \frac{N_{51}}{N_{52}} - \sigma_{52} \right) - \frac{1}{2} \eta \right] \Delta\tau, \\ \varepsilon^{54}\text{Cr} &= \left[\left(\sigma_{53} \cdot \frac{N_{53}}{N_{54}} - \sigma_{54} \right) - \left(\sigma_{51} \cdot \frac{N_{51}}{N_{52}} - \sigma_{52} \right) - \eta \right] \Delta\tau. \end{aligned} \quad (*)$$

The present subject is concerned with neutron capture in the s-process in stars. The neutron-capture cross section (σ) is often represented as corresponding to $kT=30$ keV ($T=3.48 \times 10^8$ K) under this circumstance. On the other hand, the $^{13}\text{C}(\alpha, n)^{16}\text{O}$ reaction, which contributes to producing neutrons for s-process nucleosynthesis in an AGB star, is known to be most efficient at about 1.5×10^8 K (TAKAHASHI, 1994).

The neutron-capture cross sections (σ_A) and the solar-system abundances (N_A) of four Cr stable isotopes and ^{51}V at various temperatures (kT) are given in Table 6. By substituting these values in eq. (*), we obtain the variations of $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ at each temperature as the ratios of $\varepsilon^{53}\text{Cr}/\varepsilon^{54}\text{Cr}$ (Fig. 9).

The $\varepsilon^{53}\text{Cr}/\varepsilon^{54}\text{Cr}$ ratio observed in the Qingzhen sample in this work corresponds to the neutron irradiation at $kT=14$ keV–19 keV. The value of kT should be larger if small variations of $\varepsilon^{53}\text{Cr}$ due to ^{53}Mn decay are considered. In contrast, the Cr isotopic results of the silicate phases in CI meteorites (Orgueil, Ivuna, Alais) measured by ROTARU *et al.* (1992) correspond to the neutron irradiation at about $kT=30$ keV.

The maximum positive value of $\varepsilon^{54}\text{Cr}$ for Qingzhen is about 20×10^{-4} . The extent of the variation of the neutron flux influenced on Qingzhen sample ($\Delta\tau$) is estimated from eq. (*), assuming $kT=15$ keV:

$$\Delta\tau = 5.2 \times 10^{21}/\text{cm}^2.$$

The variation of the neutron flux in an AGB star ($\Delta\tau_{\text{AGB}}$) can be written as follows using a time-scale of the s-process duration time of $t=10\sim 10^2$ yr, a neutron den-

Table 6. Neutron cross sections for Cr stable isotopes and ^{51}V .

	Abundances of		Neutron cross sections #			
	the solar system *		σ (mb)			
	(Atoms/ 10^6Si)	$E_n=15$ keV	20 keV	25 keV	30 keV	40 keV
^{50}Cr	587	94.14	73.22	60.67	52.30	41.84
^{51}V	292	87.87	64.22	50.62	42.00	32.16
^{52}Cr	11310	9.140	9.070	8.930	8.790	8.470
^{53}Cr	1283	120.8	88.43	70.36	58.00	44.69
^{54}Cr	319	10.82	7.988	7.215	6.700	6.185

* From ANDERS and GREVESSE (1989).

From BEER *et al.* (1992).

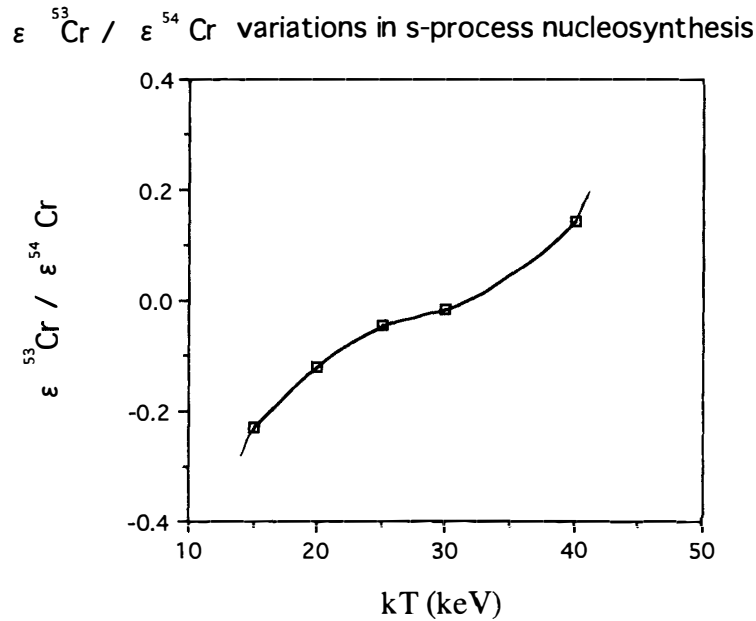


Fig. 9. Temperature dependent $\epsilon^{53}\text{Cr}/\epsilon^{54}\text{Cr}$ variations in s-process nucleosynthesis from AGB stars (kT = thermal energy). k : Boltzmann constant; T : temperature (K).

sity (n_n) of $10^8/\text{cm}^3$ and neutron velocity ($V_{15\text{keV}}$) of $1.7 \times 10^8 \text{cm/s}$:

$$\Delta\tau_{\text{AGB}} = n_n \cdot V_{15\text{keV}} \cdot t = (0.5\sim 5) \times 10^{25}/\text{cm}^2.$$

The Qingzhen sample in this work possibly contained $1/10^3 \sim 1/10^4$ of the material which underwent the effect of neutron capture in the He-burning shell in an AGB star.

4.5. Inverse correlation of $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ in acid residue samples

Since the Mn contents in acid-residue samples are very low, and the effects of ^{53}Mn decay to ^{53}Cr (i.e., $\epsilon^{53}\text{Cr}$ values) are very low ($< 0.3\epsilon$), these samples are suitable for surveying the $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ correlations during their formation stage. The Cr isotopic compositions of the acid-residue samples in this work are shown in Fig. 10 along with the literature data. This figure also represents the relative time scale for Cr isotopic homogenization, that is, the relative condensation age of each sample, assuming that chromium condenses within high-temperature minerals from a homogeneous nebula. Here, the $\epsilon^{53}\text{Cr}$ value after the complete decay of ^{53}Mn is taken as $\epsilon^{53}\text{Cr} = 0.385$, the mean value for bulk CI chondrites (Orgueil, Ivuna) measured by ROTARU *et al.* (1992).

The acid-residue samples generally have a negative $\epsilon^{53}\text{Cr}$ and a positive $\epsilon^{54}\text{Cr}$. However, the degree of the deficit in $\epsilon^{53}\text{Cr}$ and the excess in $\epsilon^{54}\text{Cr}$ is larger in the acid residues of primitive carbonaceous chondrites, such as Murchison and Allende, than in acid residues of equilibrated ordinary chondrites, such as La Criolla and Nuevo Mercurio. In the acid residues of La Criolla and Nuevo Mercurio, the $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ values are close to that of bulk meteorites. The Cr isotopic characteristics of acid residues in Fig. 10 shows that a high condensate, which was formed during an earli-

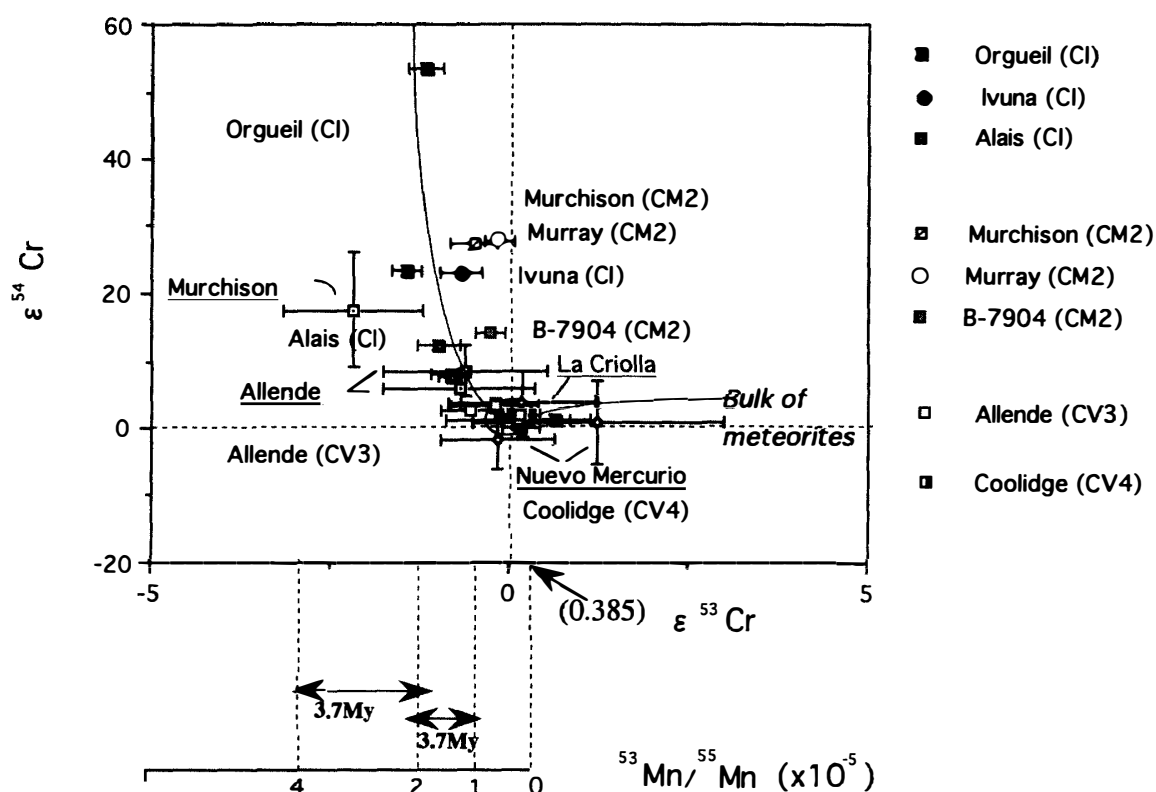


Fig. 10. $\epsilon^{53}\text{Cr}$ versus $\epsilon^{54}\text{Cr}$ plots of acid (HCl/HF) residue samples in this work and fraction 5 (refractory phases) of some carbonaceous chondrites based on the data of ROTARU *et al.* (1992) and BIRCK and ALLEGRE (1988). And, for reference, $^{53}\text{Mn}/^{55}\text{Mn}$ ratio assuming solar abundances of the elements is shown and it also represents the relative time scale for the evolution of high-temperature condensate.

er stage, contained more exotic ^{54}Cr , assuming that the variations in ^{53}Cr are due to the decay of ^{53}Mn in nebula.

4.6. Evolution of Mn-Cr and the time scale of Cr isotopic homogenization

In Allende, Murchison and Nuevo Mercurio, Cr isotopic analyses were carried out in more than 2 different phases (Table 4); it was found that the phase which had a larger value of Mn/Cr had a larger $\epsilon^{53}\text{Cr}$ value in these meteorites, though the experiment errors were rather large (Table 5). These results support the correlation of $^{53}\text{Cr}/^{52}\text{Cr}$ and Mn/Cr, which show the existence of the extinct radioactive nuclide ^{53}Mn .

Here, we discuss the evolution of Mn-Cr based on only the acid residues. A schematic diagram for the Mn-Cr isotopic evolution is shown in Fig. 11.

The $^{53}\text{Mn}/^{55}\text{Mn}$ ratios during the condensation stage of the acid-residue samples were estimated by calculating the slope P_1S_2 in Fig. 11.

From Fig. 11, the present $^{53}\text{Cr}/^{52}\text{Cr}$ ratios for a sample and the whole solar system may be written in terms of its initial ratios ($^{53}\text{Cr}/^{52}\text{Cr}$)₀, ($^{53}\text{Mn}/^{55}\text{Mn}$) and $^{55}\text{Mn}/^{52}\text{Cr}$ as the following equation:

$$(^{53}\text{Cr}/^{52}\text{Cr})_i = (^{53}\text{Cr}/^{52}\text{Cr})_0 + (^{53}\text{Mn}/^{55}\text{Mn}) \times (^{55}\text{Mn}/^{52}\text{Cr})_i,$$

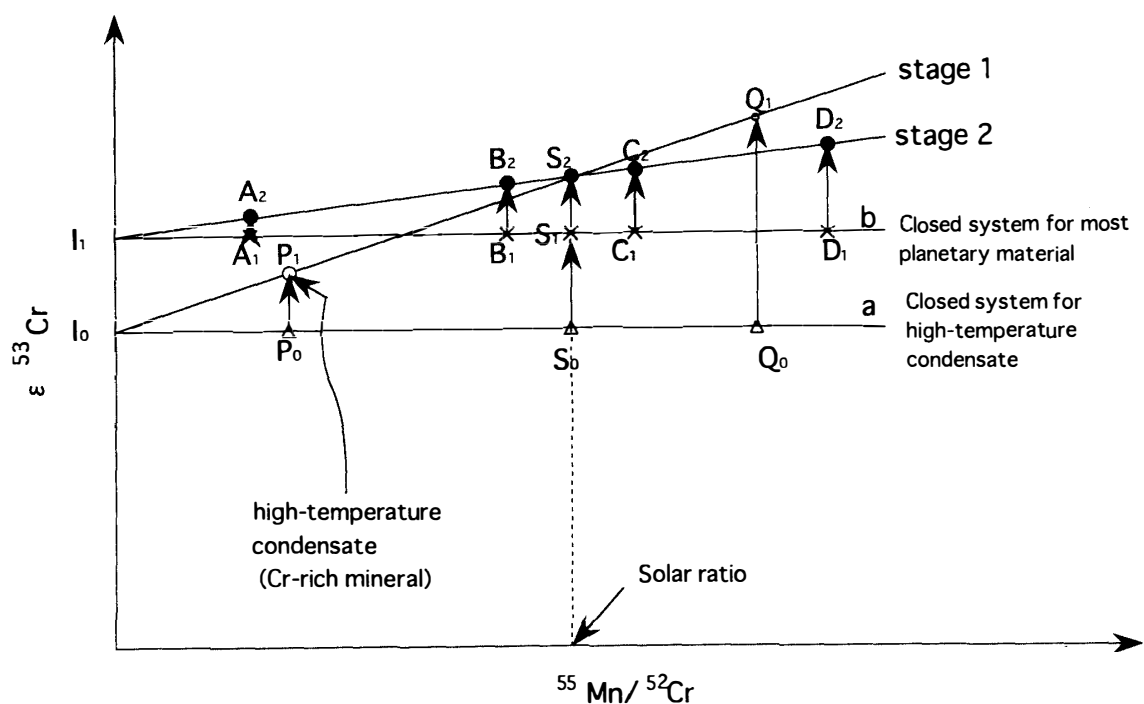


Fig. 11. Schematic diagram for the isotopic evolution of Cr.

A solid line "a" represents the time when high-temperature condensate become closed system in relation to Mn and Cr. A solid line "b" represents the time when most minerals containing Mn and Cr become closed system in relation to Mn and Cr.

Standard solar-system material (mean value) evolves $S_0 \rightarrow S_1 \rightarrow S_2$ with time (i.e. with the decay of ^{53}Mn). Cr-rich high-temperature minerals (e.g. chromite) proceed from P_0 to P_1 (stage 1). (If Mn-rich high-temperature minerals should exist, they would proceed from Q_0 to Q_1 .) Most planetary materials evolve in a way such as $A_1 \rightarrow A_2$, $B_1 \rightarrow B_2$, $C_1 \rightarrow C_2$, $D_1 \rightarrow D_2$ (stage 2). For example, A_2 (Mn/Cr ratio is small) is a secondary Cr-rich mineral.

$^{53}\text{Mn}/^{55}\text{Mn}$ ratios at the condensation stage of acid residue samples are estimated by calculating slope P_1S_2 . On the other hand, $^{53}\text{Mn}/^{55}\text{Mn}$ ratios at the time when almost minerals are solidified is evaluated by calculating slope $A_2B_2C_2D_2$ (internal isochron method).

where suffix i represents sample (S) or solar value (\odot).

Using

$$\epsilon^{53}\text{Cr} = [({}^{53}\text{Cr}/{}^{52}\text{Cr})_s / ({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\odot} - 1] \times 10^4,$$

we obtain

$$({}^{53}\text{Mn}/{}^{55}\text{Mn}) [({}^{55}\text{Mn}/{}^{52}\text{Cr})_s - ({}^{55}\text{Mn}/{}^{52}\text{Cr})_{\odot}] = [\epsilon^{53}\text{Cr}/10^4] \times ({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\odot}.$$

By using $({}^{55}\text{Mn}/{}^{52}\text{Cr})_s$ and $\epsilon^{53}\text{Cr}$ (shown in Table 5) as P_1 in Fig. 11 and $({}^{55}\text{Mn}/{}^{52}\text{Cr})_{\odot} = 0.893$, $({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\odot} = 0.113$ of the whole solar system as S_2 in Fig. 11, we can derive $({}^{53}\text{Mn}/{}^{55}\text{Mn})$ at the formation stage of each acid-residue sample. These values are given in Table 7 along with each $\epsilon^{54}\text{Cr}$. For a comparison, the reported $^{53}\text{Mn}/{}^{55}\text{Mn}$ and $\epsilon^{54}\text{Cr}$ values, obtained by internal isochron method (corresponding to the slope $A_2B_2C_2D_2$ in Fig. 11), are also shown in this table.

In addition, we can obtain information about the relative formation ages from the $^{53}\text{Mn}/{}^{55}\text{Mn}$ ratio during the formation stage of each acid-residue sample, $({}^{53}\text{Mn}/{}^{55}\text{Mn})_s$.

Table 7. $^{53}\text{Mn}/^{55}\text{Mn}$ ratios and $\epsilon^{54}\text{Cr}$ for acid residues from chondritic meteorites.

	$^{53}\text{Mn}/^{55}\text{Mn}$	$\epsilon^{54}\text{Cr}$
Allende (CV3) ar-1		
as-2	$(1.0 \pm 3.0) \times 10^{-5}$	5.7 ± 6.4
ar-2	$(0.8 \pm 2.9) \times 10^{-5}$	8.5 ± 7.8
Murchison (CM2)		
ar-1	$(3.1 \pm 2.7) \times 10^{-5}$	17.6 ± 17.0
Nuevo Mercurio (H5)		
ar-1	$(0.2 \pm 2.2) \times 10^{-5}$	-1.8 ± 8.5
La Criolla (L6)		
ar-1	$(-0.2 \pm 2.7) \times 10^{-5}$	3.5 ± 9.9
Orgueil (CI) *	2×10^{-5}	$12.4-53.6$
Murchison (CM2) *	1.2×10^{-5}	27.4
Murray (CM2) *	1.2×10^{-5}	27.6
Allende (CV3) #	$(4.4 \pm 1.0) \times 10^{-5}$	$2.6-3.4$

For a comparison, the reported $^{53}\text{Mn}/^{55}\text{Mn}$ data obtained by the internal isochron method and $\epsilon^{54}\text{Cr}$ of the acid-residue fractions of some carbonaceous chondrites are also given.

* $^{53}\text{Mn}/^{55}\text{Mn}$ data are taken from BIRCK *et al.* (1990) and $\epsilon^{54}\text{Cr}$ data are from ROTARU *et al.* (1992).

$^{53}\text{Mn}/^{55}\text{Mn}$ and $\epsilon^{54}\text{Cr}$ data are taken from BIRCK and ALLEGRE (1988). This $^{53}\text{Mn}/^{55}\text{Mn}$ value is not unambiguous. See text for details.

The formation age of each sample relative to standard sample can be estimated on the basis of the following equation:

$$\Delta t = 1/\lambda \{ \ln(^{53}\text{Mn}/^{55}\text{Mn})_o - \ln(^{53}\text{Mn}/^{55}\text{Mn})_s \},$$

where $(^{53}\text{Mn}/^{55}\text{Mn})_o$ denotes the $^{53}\text{Mn}/^{55}\text{Mn}$ ratio during the formation stage of the standard sample.

The acid-residue sample with a larger degree of ^{54}Cr excess also shows the larger $(^{53}\text{Mn}/^{55}\text{Mn})_s$ values. From the above discussion and in Fig. 10, it is suggested that the high-temperature condensate which was formed during an earlier stage contained more exotic ^{54}Cr , and that the homogenization of Cr isotopes proceeded with time and terminated within a relatively short time scale as less than 2–3 Ma.

5. Conclusion

1) A ^{54}Cr excess beyond the experimental error was detected in a specimen of the Qingzhen (EH3) acid-soluble fraction. It is therefore suggested that the ^{54}Cr heterogeneity from nucleosynthesis has been preserved in enstatite chondrites, which formed in the reducing environment of the solar system.

It is premature, however, to say that the Qingzhen sample has anomalous Cr at this point only from these data.

2) Since the Mn contents in the acid-residue samples are very low, and, hence, the effects of ^{53}Mn decay to ^{53}Cr (*i.e.*, $\epsilon^{53}\text{Cr}$ values) are very low, these samples are suitable for surveying the $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ correlations during their formation stage.

An inverse correlation between $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ was clearly shown from these

acid-residue data, in agreement with the literature data. By interpreting the ^{53}Cr variations as the result of ^{53}Mn decay in the primitive solar nebula, an acid-residue sample in which a large ^{54}Cr excess is detected has a larger $^{53}\text{Mn}/^{55}\text{Mn}$ value. This suggests that the high-temperature condensate which was formed during an earlier stage contained more exotic ^{54}Cr . In addition, the homogenization of Cr isotopes proceeded with time, and terminated within a relatively short time scale of less than 2–3 Ma.

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References

- ANDERS, E. and GREVESSE, N. (1989): Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta*, **53**, 197–214.
- ANDERS, E. and ZINNER, E. (1993): Interstellar grains in primitive meteorites, diamond, silicon carbide, and graphite. *Meteoritics*, **28**, 490–514.
- BEER, H., VOSS, F. and WINTERS, R. R. (1992): On the calculation of Maxwellian-averaged capture cross sections. *Astrophys. J. Suppl.*, **80**, 403–424.
- BIRCK, J. L. and ALLEGRE C. J. (1984): Chromium isotopic anomalies in Allende refractory inclusions. *Geophys. Res. Lett.*, **11**, 943–946.
- BIRCK, J. L. and ALLEGRE C. J. (1985): Evidence for the presence of ^{53}Mn in the early solar system. *Geophys. Res. Lett.*, **12**, 745–748.
- BIRCK, J. L. and ALLEGRE C. J. (1988): Clues to early solar history from chromium isotopes in carbonaceous chondrites. *Nature*, **331**, 465–470.
- BIRCK, J. L. and LUGMAIR G. W. (1988): Nickel and chromium isotopes in Allende inclusions. *Earth Planet. Sci. Lett.*, **90**, 131–143.
- BIRCK, J. L., ROTARU, M. and ALLEGRE, C. J. (1990): ^{53}Mn in carbonaceous chondrites. *Meteoritics*, **25**, 349–350.
- ESAT, T. M. and IRELAND, T. R. (1989): Chromium isotopic anomalies in the Murchison meteorite. *Earth Planet. Sci. Lett.*, **92**, 1–6.
- HARPER, C. L., Jr. and WIESMANN, H. (1992): High precision investigations on the ^{53}Mn - ^{53}Cr systematics. I. Bulk carbonaceous chondrites, planetary reservoirs and the moon. *Lunar and Planetary Science XXIII*. Houston, Lunar Planet. Inst., 489–490.
- HARTMANN, D., WOOSLEY, S. E. and EL EID, M. F. (1985): Nucleosynthesis in neutron-rich supernova ejecta. *Astrophys. J.*, **297**, 837–845.
- HINTON, R. W., DAVIS, A. M. and SCATENA-WACHEL, D. E. (1987): Large negative ^{50}Ti anomalies in refractory inclusions from the Murchison carbonaceous chondrite: Evidence for incomplete mixing of neutron-rich supernova ejecta into the solar system. *Astrophys. J.*, **313**, 420–428.
- HUTCHEON, I. D., ARMSTRONG, J. T. and WASSERBURG, G. J. (1987): Isotopic studies of Mg, Fe, Mo, Ru and W in Fremdling from Allende refractory inclusions. *Geochim. Cosmochim. Acta*, **51**, 3175–3192.
- HUTCHEON, I. D., OLSEN, E., ZIPFEL, J. and WASSERBURG, G. J. (1992): Cr isotopes in differentiated meteorites: evidence for ^{53}Mn . *Lunar and Planetary Science XXIII*. Houston, Lunar Planet. Inst., 565–566.
- KALLEMEYN, G. W. and WASSON, J. T. (1986): Compositions of enstatite (EH3, EH4,5 and EL6) chon-

- drites: Implications regarding their formation. *Geochim. Cosmochim. Acta*, **50**, 2153–2164.
- KANO, N., YAMAKOSHI, K., MATSUZAKI, H. and NOGAMI, K. (1993): Chemical and isotopic compositions in acid residues from three meteorites. *Proc. NIPR Symp. Antarct. Meteorites*, **6**, 325–337.
- LARIMER, J. W. and GANAPATHY, R. (1987): The trace element chemistry of CaS in enstatite chondrites and some implications regarding its origin. *Earth Planet. Sci. Lett.*, **84**, 123–134.
- LATTIMER, J. M., SCHRAMM, D. N. and GROSSMAN, L. (1978): Condensation in supernova ejecta and isotopic anomalies in meteorites. *Astrophys. J.*, **219**, 230–249.
- LEE, T. (1986): Inferences on the evidence for radioactive ^{53}Mn in the early solar system. *Nature*, **324**, 352–354.
- LEE, T. and TERA, F. (1986): The meteoritic chromium isotopic composition and limits for radioactive ^{53}Mn in the early solar system. *Geochim. Cosmochim. Acta*, **50**, 199–206.
- LEWIS, R. S., AMARI, S. and ANDERS, E. (1990): Meteoritic silicon carbide: pristine material from carbon stars. *Nature*, **348**, 293–298.
- LEWIS, R. S., AMARI, S. and ANDERS, E. (1994): Interstellar grains in meteorites. II, SiC and its noble gases. *Geochim. Cosmochim. Acta*, **58**, 471–494.
- LOSS, R. D., LUGMAIR, G. W., DAVIS, A. M. and MACPHERSON, G. J. (1994): Isotopically distinct reservoirs in the solar nebula: isotope anomalies in Vigarano meteorite inclusions with isotope anomalies. *Astrophys. J.*, **338**, L37–L40.
- LUGMAIR, G. W., MACISAAC, C. and SHUKOLYUKOV, A. (1992): The ^{53}Mn - ^{53}Cr isotope system and early planetary evolution. *Lunar and Planetary Science XXIII*. Houston, Lunar Planet. Inst., 823–824.
- LUGMAIR, G. W., MACISAAC, C. and SHUKOLYUKOV, A. (1994a): Small time differences in differentiated meteorites recorded by the ^{53}Mn - ^{53}Cr chronometer. *Lunar and Planetary Science XXIII*. Houston, Lunar Planet. Inst., 813–814.
- LUGMAIR, G. W., MACISAAC, C. and SHUKOLYUKOV, A. (1994b): Small time differences recorded in differentiated meteorites. *Meteoritics*, **29**, 493–494.
- LUNDBERG, L. L., CROZAZ, G. and ZINNER, E. (1992): Ca and S isotopic compositions and REE concentrations in oldhamite of five unequilibrated enstatite chondrites. *Lunar and Planetary Science XXIII*. Houston, Lunar Planet. Inst., 835–836.
- NIEDERER, F. R., PAPANASTASSIOU, D. A. and WASSERBURG, G. J. (1985): Absolute isotopic abundances of Ti in meteorites. *Geochim. Cosmochim. Acta*, **49**, 835–851.
- NYQUIST, L. E., BANSAL, B., WIESMANN, H. and SHIH, C. Y. (1994): Neodymium, strontium and chromium isotopic studies of the LEW86010 and Angra dos Reis meteorites and the chronology of the angrite parent body. *Meteoritics*, **29**, 872–885.
- PAPANASTASSIOU, D. A. (1986a): Chromium isotopic anomalies in the Allende meteorite. *Astrophys. J. Lett.*, **308**, L27–L30.
- PAPANASTASSIOU, D. A. (1986b): Correlated isotopic effects near the Fe abundance peak. *Advances in Nuclear Astrophysics*, ed. by E. VANGIONI-FILM *et al.* Paris, Institute Astrophysics, 449–459.
- PAPANASTASSIOU, D. A. and BRIGHAM, C. A. (1989): The identification of meteorite inclusions with isotope anomalies. *Astrophys. J. Lett.*, **338**, L37–L40.
- ROTARU, M., BIRCK, J. L. and ALLEGRE, C. J. (1992): Clues to early solar system history from chromium isotopes in carbonaceous chondrites. *Nature*, **358**, 465–470.
- SHIELDS, W. R., MURPHY, T. J., CATANZARO, E. J. and GARNER, E. L. (1966): Absolute isotopic abundance ratios and the atomic weight of a reference sample of chromium. *J. Res. Nat. Bur. Standards (U.S.)*, **70A**, 193–197.
- SIMON, S. B., PODOSEK, F. A., ZINNER, E. and PROMBO, C. A. (1994): Petrography, compositions, and origin of large, chromian spinels from the Murchison meteorite. *Geochim. Cosmochim. Acta*, **58**, 1313–1334.
- TAKAHASHI, K. (1994): Neutron capture origins for the heavy elements. *Proceedings of International Conference on Neutrons and Their Applications*, ed. by G. VOURVOPOULOS and T. PARADELLIS. SPIE-The International Society for Optical Engineering, Vol. **2339**, 20–37.
- WOOSLEY, S. E. (1986): Nucleosynthesis and stellar evolution. *Nucleosynthesis and Chemical Evolution*, ed. by B. HAUCK *et al.* Sauverny, Geneva Observatory, 1–195.

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