CHEMICAL AND ISOTOPIC COMPOSITIONS IN ACID RESIDUES FROM THREE METEORITES

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Abstract: Chemical compositions of acid residues obtained from three types of meteorites, 1) Canyon Diablo (IA), 2) Allende (CV3) and 3) Nuevo Mercurio (H5) were determined. Refractory elements were generally enriched in these acid residues. The results match the features that acid residues contain primary condensates from the cooling solar gas as well as extra-solar grains. In the cases of Allende and Canyon Diablo, the contents of a series of refractory siderophile elements such as W, Re, Os, Ir, Mo, Ru and Pt were determined by INAA and AAS. Particularly, in acid residue of Allende, enrichment factors of these elements relative to CI are generally higher (7–20 times/CI), whereas in the cases of W and Mo, they are slightly depleted compared with those of Canyon Diablo. Since both elements would be the first metals to be oxidized under high oxygen fugacity, acid residue of Allende should contain fractions that were produced under oxidizing conditions. In these samples, the isotopic compositions of Ru have been measured by thermal ionization mass spectrometry. So far, in the measurements of acid residue of Allende, all Ru isotope ratios were found to be indistinguishable from terrestrial values within the experimental errors, though errors were large because of small Ru ion beam intensities.

1. Introduction

Since the discovery of isotopic anomalies of oxygen in calcium-alminum rich inclusions (CAIs) from Allende was made by Clayton *et al.* (1973), isotopic anomalies of many elements in abnormal fractions taken from primitive meteorites have been reported. Most of the isotopic heterogeneities have been attributed to incomplete mixing of the primordial materials in the solar nebula and/or insertion of some materials of diverse nucleosynthetic origins during the condensation stage of the solar system (*e.g.*, Anders, 1981; Begemann, 1980; Rolfs *et al.*, 1987).

Many studies on isotopic compositions of elements, specially noble gases, in acid residues from primitive meteorites have been done, and isotopic anomalies of many elements have been reported (*e.g.*, Lewis *et al.*, 1983; Lugmair *et al.*, 1983; Ott *et al.*,

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Table 1.   Abundances and nucleosynthesis process of each isotopes in Ru and Os. This table is assigned from ANDERS and GREVESSE (1989).

Ru			Os		
Stable nuclide	Natural abundance (atomic percent)	Nucleosynthesis process	Stable nuclide	Natural abundance (atomic percent)	Nucleosynthesis process
Ru–96	5.52	p	Os–184	0.018	p
Ru–98	1.88	p	Os–186	1.58	s
Ru–99	12.7	r, s	Os–187	1.6	s
Ru–100	12.6	s	Os–188	13.3	r, s
Ru–101	17.0	r, s	Os–189	16.1	r
Ru–102	31.6	r, s	Os–190	26.4	r
Ru–104	18.7	r	Os–192	41.0	r

1988; LOSS et al., 1990). Particularly, ZINNER et al. have recently recovered silicon carbide therein, and detected isotopic anomalies of noble gases, C, N, Si, Mg, Ba etc. (e.g., ZINNER et al., 1987, 1989, 1991a, b; AMARI et al., 1992). Therefore, these samples are considered to be of precursor origins which have survived the pre-solar nebula stages. And then, KUMAR and GOEL (1991) recently reported that acid residues of iron meteorite Sikhote Allin (IIB) have isotopically anomalous ratios for ^{190}Os/^{184}Os by using Radiochemical Neutron Activation Analysis (RNAA).

Chemical and isotopic compositions of elements with high condensation temperatures in primordial samples may be especilly good candidates for studies of the pre-history of the solar system.

We are, therefore, planning to carry out systematic investigations on Ru and Os isotopic compositions in acid residues of various meteorites, deep sea iron and chondritic spherules, metal phases from chondrites and so on. The point we aimed at Ru and Os is as follows; Since Ru and Os have not only high condensation temperatures, but also many stable isotopes which would be produced through various processes of nucleosyntheses in active star explosions (Table 1), some grades of isotopic anomalies could be expected to detect in primordial samples caused from imperfect mixing of precursor materials.

However, isotopic analyses of Os with an ionization potential of 8.7 eV cannnot be performed in our mass spectrometer (TIMS; VG 354) using positive thermal ions at present. We are, therefore, measuring Ru isotopic ratios in various samples mentioned above.

In this paper, we present the results of chemical compositions of acid residues from some meteorites determined by instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) and the preliminary results of Ru isotopic ratios obtained by a thermal ionization mass spectrometer (TIMS).

2. Samples and Experimental

2.1. Samples

The meteorites used in our work are; 1) Canyon Diablo (IA) from Arizona, USA, 2) Allende (CV3) from Chihuahua, Mexico, 3) Nuevo Mercurio (H5) from Zacatecas, Mexico. After removing fusion crusts with a ceramics blade grinder, the three types of meteorites were disaggregated by using the freeze-thaw method and were dissolved by repeated alternating treatments with 6N HCl, 10N HF, and aqua regia (6 N HCl + 7 N HNO$_3$) at room temperature. The acid residues were concentrated by centrifuging and then dried up. The weights of the acid residues are listed in Table 2 along with the total weights of the bulk meteorites. One of scanning electron microscopy (SEM) pictures of acid residues from Canyon Diablo are shown in Fig. 1. The constituents look like
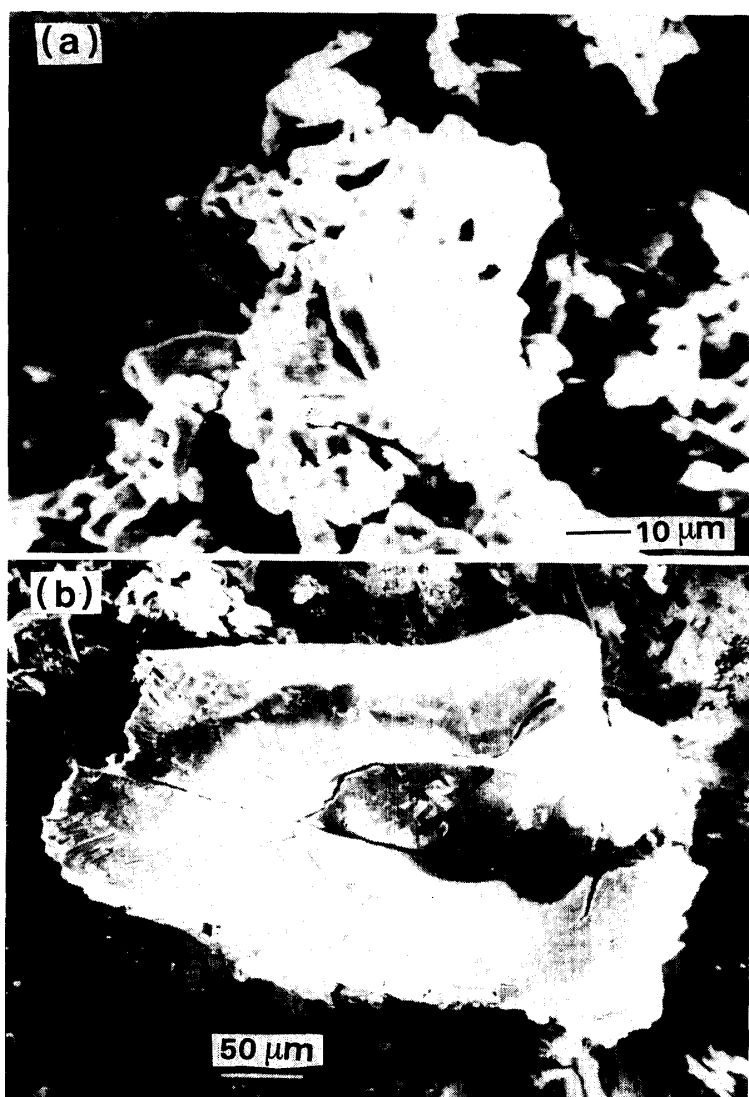

Fig. 1.   Scanning electron microscopy (SEM) pictures of acid residues from Canyon Diablo. The constituents look like aggregates of some grains.
(a): The scale bar is 10 μm, (b): The scale bar is 50 μm.

Table 2.   The weight and fraction % of acid residues.

Sample name	Sample weight (g)	Acid residue weight (g)	Acid residue fraction (wt%)
Canyon Diablo	587.50	3.6425	0.62
Allende	62.379	1.8975	3.04
Nuevo Mercurio	45.104	0.4631	1.03

aggregates of some grains. In Fig. 1a, the size of aggregates is about 100 μm. In Fig. 1b, the size is about 400 μm. Unfortunately, we could not identify what kind of minerals were contained in these acid residues by our SEM (HORIBA EMAX-8000).

2.2.   Elemental analyses

Elemental analyses were carried out mainly by INAA (TRIGAII). Thermal neutron fluxes were 1×10^{12} and 1.4×10^{12} (n/cm²·s) for the pneumatic tube and the long-time irradiation, respectively. Immediately after the pneumatic tube irradiation for 6 min, each sample was measured using an intrinsic Ge gamma ray spectrometer for 4 min. In the cases of long-time irradiations (18–24 hrs), the gamma ray measurements of induced radionuclides were carried out in several hours for each sample on succeeding days after the irradiation.

Reference and standard samples were made of Allende powder for most elements (Kallemeyn and Wasson, 1981; Ebihara et al., 1982; Clarke et al., 1970). The contents of lithophiles were also obtained by the JB-1 glass standard (Nagasawa et al., 1980). The data analyses were carried out using isotopes listed in Table 3. For example, Ru and Os were determined as follows;

Ru contents were determined from 497 keV gammas of ^{103}Ru(39.3d), which was induced through ^{102}Ru[31.6%] (n, γ) reaction.

Os contents were determined from 129 keV gammas of ^{191}Os(15.4d), which was induced through ^{190}Os[26.4%] (n, γ) reaction.

The contents of Mo, Ru and Pt were determined by atomic absorption spectrometer (AAS; Nippon Jarrell-Ash Co., Ltd. AA-890) with a flameless atomizer (FLA-1000) because in the measurements of INAA, these elements are difficultly detected and the estimated errors were large.

The C, N, H and S contents in these samples were analyzed in The Organic Analytical Center (Dep. of Chem., Fac. of Science, Univ. of Tokyo) by combustion method.

2.3.   Isotopic analyses
2.3.1.   Chemistry

The samples of 10–100 mg in weight were decomposed in sealed teflon vessels by a microwave dissolution method with several mixed acids. The solution was transferred to quarz stills and then Ru was separated by distillation with potassium dichromate ($K_2Cr_2O_7$) and strong phosphoric acid (SPA) (Terada et al., 1975). The distillate was transferred to tefron beakers, slowly taken to dryness, and then redissolved in 0.5 N

Meteorite

●Canyon Diablo, [IA]
 Arizona, USA
●Allende, [CV3]
 Chihuahua, Mexico
●Nuevo Mercurio, [H5]
 Zacatecas, Mexico

O removal of fusion crust
 (Ceramic blade grinder)
O disagregation
 (freeze-thaw method)
O decomposition
   HCl, HF, Aqua regia
   ultrasonic cleaning
O centrifuging

acid soluble components	acid residues

O distillation
 of Ru
O cation-exchange
 (removal
  of Ca^{2+}, Sr^{2+})

O microwave
 decomposition
O distillation
 of Ru
O cation-exchange
 (removal
  of Ca^{2+}, Sr^{2+})

Isotopic Analysis	Elemental Analysis	Isotopic Analysis

◆TIMS
 (VG354)

◆Combustion method
  (C,N,H,S)
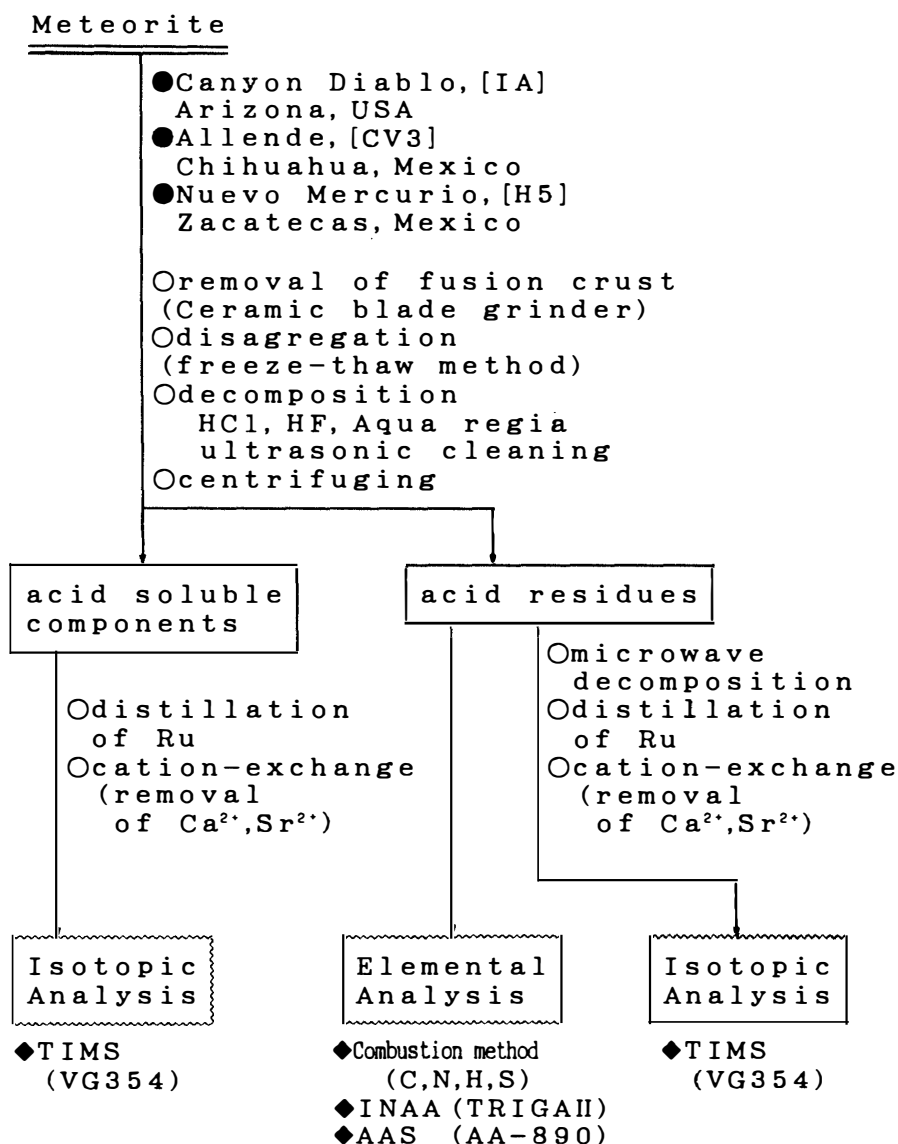◆INAA (TRIGAII)
◆AAS (AA-890)

◆TIMS
 (VG354)

Fig. 2. *Analytical procedure for acid residues of some meteorites.*

HCl. The solution was passed twice through a cation exchange resin column (Biorad AG50W-X8, 200–400 mesh) in order to avoid molecular ions such as $^{40}Ca^{28}Si^{16}O_2$, $^{88}Sr^{16}O$ which disturb Ru ion peaks in mass spectrometry (POTHS *et al.*, 1987; HIDAKA *et al.*, 1991). The total procedural Ru blank was measured by isotope dilution method using ^{104}Ru enriched spike, and only a few ng were detected. All analytical procedures are summarized in Fig. 2.

2.3.2. Mass spectrometry

Ru is one of the elements difficult to analyze by the thermal ionization technique because the metal has a high ionization potential (7.36 eV). Various methods to enhance its ionization efficiency have been proposed (*e.g.*, DEVILLERS *et al.*, 1978 and references therein). In this work, silica-gel combined with phosphoric acid was used as an activator.

Ru isotopic analyses have been performed by TIMS (VG 354). Ru ion beams in

each sample were so faint that they were detected by the Daly photomultiplier detector equipped with an ion counting assembly. In mass spectrometric techniques of Ru, the zone-refined (99.995%) V-shaped Re single filament has been employed. And the filament was outgassed at 5A for at least 1 hour below 3×10^{-7} Torr prior to the measurements in order to reduce isobaric interference of Mo emitted from the filament. Moreover, adequate prebaking was required to reduce the molecular ions derived from phosphoric acid and silica gel. All measurerd ratios of Ru were normalized provisionally to $^{99}Ru/^{102}Ru = 0.4042$, and the mass fractionation was corrected using an exponential law (Hutcheon et al., 1987). The choice of the isotope pair used for normalization is somewhat arbitary, but it was determined to consider nucleosynthesis processes of the individual isotope and to minimize the errors due to the fractionation correction. And Mo ion beam from Re filaments was not negligible as the filament temperature increases, so Mo isobaric interference was corrected by monitoring ^{97}Mo based on recent precise measurements of Mo isotopes (Qilu and Masuda, 1992).

3. Results and Discussion

3.1. Elemental analyses

The results of INAA experiments are expressed in Table 3, along with the isotope used for determination of the contents, half-life and γ-ray energy. The contents of Mo, Ru and Pt determined by AAS are also listed in Table 3. The typical results of elemental analyses are diagramed in Fig. 3. In Fig. 3, the enrichment factors are defined as the ratio of the elemental compositions to those of CI chondrite (Anders and Grevisse, 1989).

In Fig. 3a, the enrichment factors for refractory siderophiles in acid residues from Allende and Canyon Diablo are shown in the order of decreasing condensation temperatures (the order of the presentation was after Sylvester et al., 1990) along with the bulk contents of each meteorite. It was shown that refractory sideophile elements are generally enriched in acid residues of both meteorites, even though the enrichment factors are still low compared with a metal particle in CAI from Allende (10^3–10^4; Palme and Wlotzka, 1976). Particularly, in acid residue of Allende, the enrichment factors of these elements are generally high (7–20 times/CI), but in the cases of W and Mo, they are slightly lower than those of Canyon Diablo. Since both elements would be the first metals to be oxidized under high oxygen fugacity (e.g., Fegley and Palme, 1985; Palme et al., 1982), acid residues of Allende might contain fractions that were produced under oxidizing conditions.

In Fig. 3b, the enrichment factors for moderately volatile siderophiles in acid residues from Allende and Canyon Diablo are plotted in the order of increasing volatility (the order was also after Sylvester et al., 1990). It was shown that these siderophile elements are generally depleted in acid residues except Cr, Au and Sb. However, judging from Fe contents in these acid residues, it could be said that the acid treatments in this work were relatively moderate and/or incomplete.

In Fig. 3c, the enrichment factors for refractory lithophiles in acid residues of Allende and Nuevo Mercurio are plotted. It was shown that these refractory lithophiles are generally enriched in acid residues of both meteorites. This shows that acid residues

Table 3. *Element concentrations in acid residues of some meteorites determined by INAA. Used nuclides and half-life, γ-ray energy of each nuclides are also listed.*

	Allende	Nuevo Mercurio	Canyon Diablo	Isotope	Half-life	Energy (keV)
Al	11.0±0.1 (%)	2.18±0.02 (%)	762±34 (ppm)	^{28}Al	2.25 m	1779
Ca (%)	0.49±0.23	—	—	^{49}Ca	8.72 m	3084
Mg (%)	12.5±1.6	5.7±1.0	—	^{27}Mg	9.45 m	1015
Mn	81±53 (ppm)	0.452±0.030 (%)	—	^{56}Mn	2.58 h	1811
Ti	770±680 (ppm)	0.57±0.10 (%)	—	^{51}Ti	5.76 m	320
V	230±9 (ppm)	0.285±0.009 (%)	3.8±1.8 (ppm)	^{52}V	3.76 m	1434
Fe (%)	1.89±0.02	4.31±0.02	1.05±0.02	^{59}Fe	44.5 d	1099
Ni (ppm)	145±36	—	434±24	^{58}Co	70.9 d	811
Co (ppm)	21.5±0.3	5.68±0.19	60.9±0.4	^{60}Co	5.27 y	1173
Cr	3900±70 (ppm)	1.12±0.03 (%)	15.4±1.2 (ppm)	^{51}Cr	27.7 d	320
Au	1.87±0.02 (ppm)	9.7±1.3 (ppb)	956±8 (ppb)	^{198}Au	2.69 d	412
Sb (ppb)	586±28	13.7±2.0	121±6	^{124}Sb	60.2 d	1691
W	700±170 (ppb)	—	1.91±0.47 (ppm)	^{187}W	23.9 h	686
Re (ppb)	580±74	—	230±19	^{188}Re	16.9 h	155
Os (ppm)	4.15±0.89	—	1.66±0.37	^{191}Os	15.4 d	129
Ir	5.46±0.06 (ppm)	148±5 (ppb)	1.10±0.01 (ppm)	^{192}Ir	73.8 d	468
Mo	*635 (ppb)*	*517 (ppb)*	*2.15 (ppm)*			
Ru	*8.39 (ppm)*	—	*1.97 (ppm)*			
Pt	*7.93 (ppm)*	—	*1.85 (ppm)*			
La (ppb)	225±38	114±20	214±26	^{140}La	1.68 d	1596
Sm (ppb)	113±9	—	13.8±2.2	^{153}Sm	1.93 d	103
Eu (ppb)	85±34	—	10±9	^{152}Eu	13.5 y	122
Yb (ppb)	—	—	66±43	^{175}Yb	4.19 d	396
Sc	77.8±0.3 (ppm)	3.38±0.03 (ppm)	37±11 (ppb)	^{46}Sc	83.8 d	889

—— stands for below detection limit and/or errors are more than 100%. Elements in italics (Mo, Ru, Pt) are determined by ASS and errors can be estimated to be within ±10%. By the way, Ru contents in Canyon Diablo are also determined 1.79±0.72 ppm by INAA (^{103}Ru 39.3 d; 497 keV) which are consistent with the data obtained by AAS.

of both meteorites may contain high temperature condensation minerals such as corundum (Al_2O_3), perovskite ($CaTiO_3$), melilite [$Ca(Al, Mg)(Si, Al)_2O_7$], spinel ($MgAl_2O_4$) and so on, though we could not identify what kind of minerals were in these acid residues.

The C, N, H and S contents in these acid residues analyzed in The Organic Analytical Center in Univ. of Tokyo by combustion method are listed in Table 4.

It is noteworthy that the content of C is more than 40% in acid residue of Canyon Diablo. It probably contains graphite or something although we could not identify minerals this time.

3.2. Isotopic analyses

The Ru isotopic ratios in terrestrial standard (Aldrich RuCl$_3$), the acid soluble components from Canyon Diablo and the acid residue in Allende are shown in Table 5. These results diagramed are also shown in Fig. 4.

In addition to chemical properties of Ru and small sizes of samples, molecular
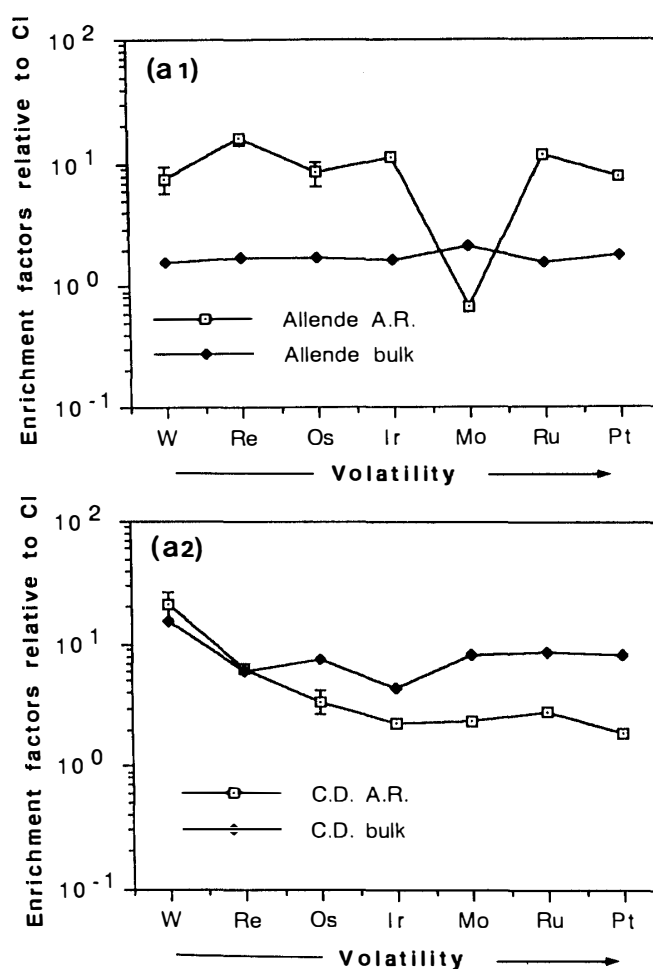
Fig. 3.   Enrichment factors in acid residues relative to CI chondrite. 1 σ error bars are shown when
they are larger than the symbols. A.R. stands for "Acid Residue".

3(a1):   Enrichment factors for refractory siderophiles in acid residues from Allende relative
to CI chondrite, plotted in the order of increasing volatility (decreasing condensation
temperature). The bulk contents of Allende are also shown.

3(a2):   Enrichment factors for refractory siderophiles in acid residues from Canyon Diablo
relative to CI chondrite, plotted in the order of increasing volatility (decreasing condensation
temperature). The bulk contents of Canyon Diablo are also shown. C.D. stands for "Canyon
Daiblo".

Table 4.   Element comcentrations in acid residues (%) (combustion method).

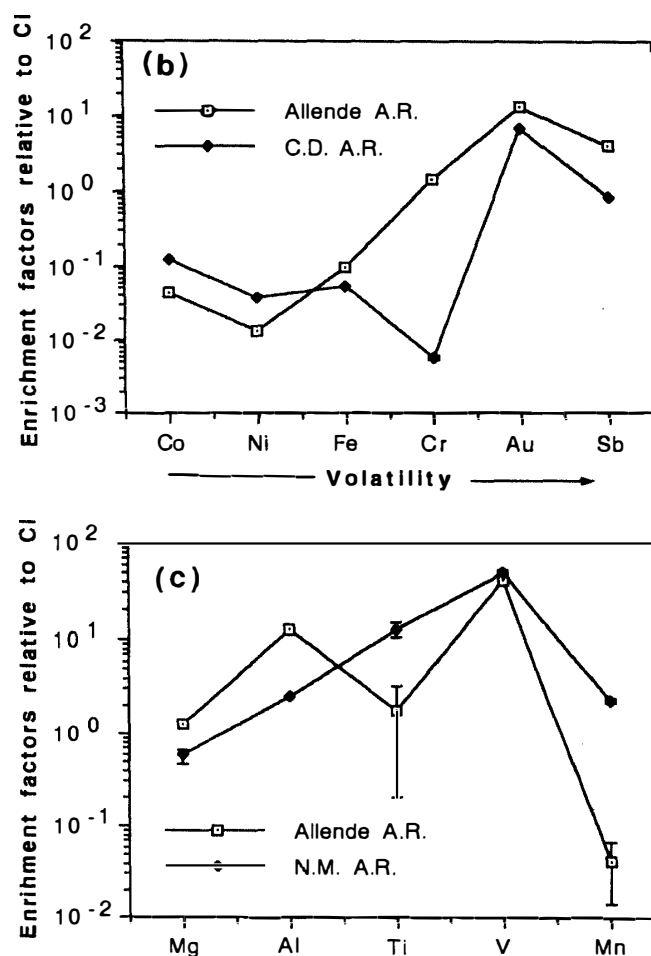|	C	N	H	S
Canyon Diablo	42.86	2.82	2.72	—
Allende	9.70	1.80	0.51	0.60
Nuevo Mercurio	—	0.29	—	2.22

— stands for "not detected".

Fig. 3 (Continued).

3(b): Enrichment factors for moderately volatile siderophiles in acid residues from Allende and Canyon Diablo relative to CI chondrite, plotted in the order of increasing volatility.

3(c): Enrichment factors for refractory lithophiles in acid residues from Allende and Nuevo Mercurio relative to CI chondrite. N.M. stands for "Nuevo Mercurio".

interferences at masses in the range of 96–104 such as $^{40}Ca^{28}Si_2$, $^{40}Ca^{40}Ca^{16}O$, $^{40}Ca^{28}Si^{16}O_2$, $^{88}Sr^{16}O$ gave limitations for precise isotope measurements of Ru. Particularly, molecular interference at mass 100 was not negliable and could be hardly eliminated entirely. And large errors and variousness at mass 96 and 98 were derived mainly from Mo ion beam emitted from Re filament.

In addition to Aldrich reagent, we are measuring regularly acid soluble components from Canyon Diablo as laboratory standards. All Ru isotope ratios in acid soluble components from Canyon Diablo were identical with weighted means of terrestrial values within the experimental errors except a few cases; and even in the cases, the ratios were found to be indistinguishable from the values of one of the Aldrich reagent.

So far, in the measurement of acid residue of Canyon Diablo, accurate data could not be obtained yet. In the measurement of acid residue of Allende, all ratios were not found to be distinguishable clearly from terrestrial values within the experimental errors, though errors were rather large because of small Ru ion beam intensities.
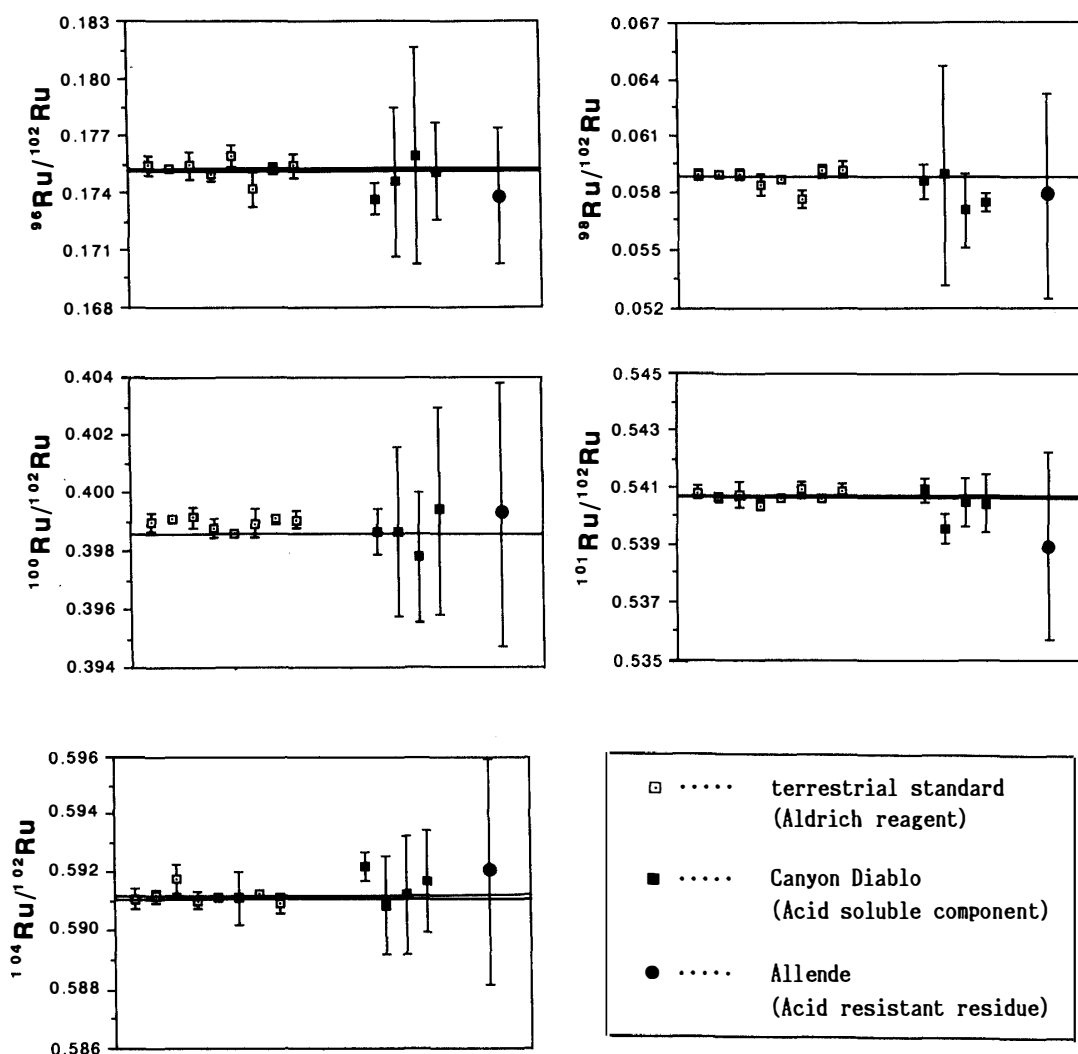
Fig. 4. Preliminary results of Ru isotopic analyses: Isotopic ratios of Ru in terrestial standard (Aldrich $RuCl_3$) and acid soluble components from Canyon Diablo and acid residue of Allende. All isotope ratios are corrected for mass fractionation by normalization to $^{99}Ru/$ $^{102}Ru = 0.4042$ (exponential law). The solid lines represent the range of weight means of each isotopic ratio of Ru in terrestrial standard.

POTHS et al. (1987) also reported that in two aliquants of acid residue of Allende, all isotopic ratios of Ru were indistinguishable from the terrestrial values within the experimental errors.

These results might suggest that even in acid residue of Allende, Ru components are originated mainly from the normal mixtures of the solar materials.

4. Interim Conclusions

This paper is a kind of the progress reports and we cannot state definitive conclusions at the present time. We, therefore, do not point out more than some comments as follows;

Table 5.   Ru isotopic ratios for terrestrial standard, Canyon Diablo (acid soluble component) and Allende (acid residue).

Sample	96/102	98/102	100/102	101/102	104/102
Terrestrial standard	0.17542 ± 52	0.05899 ± 29	0.39898 ± 33	0.54083 ± 24	0.59104 ± 36
(Aldrich reagent)	0.17528 ± 11	0.05894 ± 4	0.39910 ± 8	0.54065 ± 14	0.59114 ± 21
	0.17541 ± 71	0.05897 ± 25	0.39914 ± 34	0.54077 ± 46	0.59171 ± 51
	0.17492 ± 32	0.05839 ± 62	0.39876 ± 33	0.54037 ± 15	0.59099 ± 29
	0.17594 ± 59	0.05865 ± 14	0.39856 ± 3	0.54061 ± 8	0.59111 ± 13
	0.17415 ± 89	0.05763 ± 50	0.39893 ± 47	0.54090 ± 30	0.59110 ± 87
	0.17528 ± 31	0.05912 ± 34	0.39909 ± 16	0.54059 ± 9	0.59121 ± 12
	0.17540 ± 64	0.05920 ± 45	0.39904 ± 30	0.54089 ± 24	0.59092 ± 31
Weighed mean	0.17527 ± 9	0.05892 ± 4	0.39863 ± 3	0.54062 ± 5	0.59114 ± 7
Canyon Diablo	0.1737 ± 9	0.0585 ± 9	0.3987 ± 8	0.5409 ± 4	0.5922 ± 5
(Acid soluble	0.1745 ± 39	0.0589 ± 57	0.3986 ± 29	0.5396 ± 5	0.5909 ± 17
component)	0.1759 ± 57	0.0570 ± 19	0.3978 ± 22	0.5405 ± 9	0.5913 ± 20
	0.1751 ± 25	0.0574 ± 5	0.3994 ± 36	0.5405 ± 10	0.5917 ± 18
Allende	0.1738 ± 36	0.0579 ± 54	0.3993 ± 45	0.5389 ± 33	0.5921 ± 39
(Acid residue)					

All isotope ratios are normalized to $^{99}Ru/^{102}Ru = 0.4042$ by exponential law. Errors are 2σ of the mean.

Our element analyses show that refractory elements are generally enriched in acid residues regardless of the kind of meteorites. It matches the features that acid residues contain primary condensates from the cooling solar gas as well as extra-solar grains. And the considerable diverse chemical compositions of acid residues between these meteorites deserve our attention. The diversity may arise from the difference of generative environmental conditions of these meteorites in space. For example, acid residue of Allende may contain much fractions that were produced under oxidizing conditions.

In addition, the fact that Ru isotopic anomalies have been not yet detected even in the Allende acid residue, which is considered to be the most primordial and exotic sample, suggests the following; Ru components originated from an interstellar medium might be very rare and/or the diffusion of Ru might be unexpectedly rapid due to high temperatures and shock waves or something during the condensation stage of the solar system.

Finally, it is noteworthy that the acid residues we obtained here are not so definite samples. So, the chemical compositions of the acid residues differ with the kinds of acids, and the conditions under acid treatments. That is, the acid residues we used here are, so to say, the samples obtained under "our experimental conditions" (dissolved by repeated alternating treatments with HCl, HF, aqua regia at room temperature).

Unfortunately, we could not identify what kind of minerals were there in these acid residues by our SEM (HORIBA EMAX-8000) this time. We are now preparing to check up these acid residues by transmission electron microscopy (TEM) to identify what kind of minerals are contained there.

And much more precise and reliable isotopic data will be obtained, then more detailed discussions on the prehistory of the solar system, the origins of acid residues could be done, too.

Acknowledgments

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