

Trace element analysis of ureilites: New constraints on their petrogenesis

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Abstract—Six ureilites (ALHA77257, ALHA81101, ALH82130, PCA82506, Kenna, and Novo Urei) were analyzed using neutron activation analysis for Ca, Sc, Cr, Mn, Fe, Co, Ni, Zn, Ga, REE, W, Re, Os, Ir, and Au. We examined bulk samples as well as acid-treated samples. In the bulk samples the refractory siderophiles' concentrations range from approximately 0.1 to 1.0 times CI chondrites while the volatile siderophiles range from about 0.07 to 0.3 times CI chondrites. Rare earth elements (REEs) in ureilites are quite depleted and display light and heavy rare earth enrichments. The Antarctic meteorites display either much less pronounced v-shaped patterns or no enrichment in the light rare earths at all.

In terms of the new trace-element results, ureilites do not fall into the coherent groups that other workers have defined by chemical or petrographic characteristics. Trace elements do provide additional constraints on the models for the petrogenesis of ureilites. In particular, the siderophile element abundances call for simplified models of chemical processing rather than the complex, multistage processing called for in silicate fractionation models. REE concentrations, on the other hand, imply multistage processing to produce the ureilites. None of the ureilite petrogenesis models extant account for the trace element data. These new data and the considerations of them with respect to the proposed ureilite petrogenesis models indicate that the direction of modelling should be toward contemplation of mixtures and how the components we observe in ureilites behave under such conditions.

INTRODUCTION

UREILITE METEORITES are ultramafic rocks consisting of coarse grains of olivine, low-Ca pyroxene, \pm high-Ca pyroxene, and fine-grained carbon-rich areas. The latter contain graphite, diamond, and amorphous carbon in varying amounts, as well as metal, sulfides, silicates, and possibly unidentified phases (VDOVYKIN, 1970; GÖBEL et al., 1978; BERKLEY et al., 1980). Recent modelling based on Ca/Al ratios, siderophile-element, and rare earth element (REE) data (GOODRICH et al., 1987a,b; SPITZ and GOODRICH, 1987) has promoted the idea that the ureilites are cumulates resulting from a complex, multistage igneous processing. Workers presenting new data on oxygen isotopic composition (CLAYTON and MAYEDA, 1988), however, suggest that ureilites are primitive objects and cannot be related by mass dependent fractionation from a homogeneous reservoir. This observation indicates a heterogeneous source area for the rocks—either multiple parent bodies or a heterogeneous single parent body which has not experienced much igneous processing (CLAYTON and MAYEDA, 1988). The dilemma is to reconcile the major and minor element data with the oxygen isotopic data in order to explain the formation of these meteorites.

In order to further characterize this class of meteorites, to illuminate the origin of the components of the ureilites, and to clarify the apparent paradoxes of the available data, we report results of our trace element study of six ureilites, several of which have not been analyzed previously. This work was reported in preliminary form in SPITZ and BOYNTON (1986, 1988). Our emphasis is on the determination of siderophile and REE data. We have collected trace element data on Kenna, Novo Urei, Allan Hills A77257, Allan Hills A81101, Allan Hills 82130, and Pecora Escarpment A82506 (hereafter Allan Hills will be designated as ALH and Pecora Escarpment

as PCA) using instrumental neutron activation analysis (INAA) and radiochemical neutron activation analysis (RNAA). The non-Antarctic meteorites, Kenna and Novo Urei, have been analysed previously for trace elements (BOYNTON et al., 1976; WASSON et al., 1976; HIGUCHI et al., 1976; JANSSENS et al., 1987) and therefore serve as a control for our data. The Antarctic meteorites, ALHA77257, ALHA81101, ALH82130, and PCA82506 had not been analysed for trace elements prior to the commencement of this work. Results for ALHA77257, ALHA81101, ALH82130, LEW85328, LEW85440, META78008, Y791538, and Y8448 appear in SPITZ and BOYNTON (1988) and EBIHARA et al. (1990).

These samples represent a range of ureilite compositions with respect to Fa content in olivine, oxygen isotopic composition, and degree of shock (Table 1). The Fa content in olivine and degree of shock were determined from literature references (BERKLEY et al., 1980; GOODRICH and BERKLEY, 1986; GOODRICH, 1986). The oxygen isotopic composition is given in CLAYTON and MAYEDA (1988). ALHA81101 is the only one of our samples with a high degree of shock, and it also has a distinct oxygen isotopic composition (CLAYTON and MAYEDA, 1988). The three other Antarctic specimens have low-to-medium degrees of shock and sample each of the three oxygen isotope-iron content groups of CLAYTON and MAYEDA. ALH82130 is the ureilite with the highest MgO content, has one of the highest pyroxene-to-olivine modal ratios (1:1), and contains approximately 10% augite (DELANEY and PRINZ, 1987).

MATERIALS AND METHODS

Three neutron activation analysis (NAA) experiments were performed. The first experiment included only INAA, while the second and third included both INAA and RNAA.

TABLE 1. Analysed ureilites. These samples cover a range of ureilites' other characteristics such as Fe content and O isotopic composition. In addition to the forsterite content of olivine, the BERKLEY et al. (1980) Fe content groups are given in parentheses. Sources: O isotopes—CLAYTON and MAYEDA (1988); Fo in olivine—BERKLEY et al. (1980), GOODRICH et al. (1987a), AMN 6 (1983); Shock—BERKLEY et al. (1980), GOODRICH and BERKLEY (1986), AMN 6 (1983).

Sample	Fo in Olivine	Shock Degree	$\delta^{18}\text{O}\%$	$\delta^{17}\text{O}\%$
PCA82506	78.3 (1)	Low	7.02	2.72
Novo Urei	78.9 (1)	Medium	7.21	2.76
Kenna	79.2 (1)	Medium	7.54	2.90
ALHA81101	78-90 (2)	High	8.09	3.97
ALHA77257	84.9 (3)	Low	6.91	2.51
ALH82130	84.9 (3)	Low	4.85	-0.01

Experiment 1—University of Arizona INAA Run

Bulk samples of Kenna and Novo Urei (both acquired from USNM/Smithsonian) and ALHA77257, ALHA81101, ALH82130, and PCA82506 (from the Meteorite Working Group of NASA); three olivine-pyroxene separates from San Carlos nodules (supplied by Michael J. Drake), USGS Twin Sisters dunite, DTS-1 (split 61, position 8), and USGS Cazadero peridotite, PCC-1 (split 71, position 2) (supplied by Paul E. Damon) with masses of approximately 500 mg were selected and crushed to powder/granular form in an agate mortar. The samples were irradiated twice in the University of Arizona TRIGA reactor at a flux of 0.7×10^{12} n/cm² sec at 100 kilowatts, first for 10 min and later for 3 h. Chemically prepared mixed standard solutions and samples of the standard rocks, CRB-1 (Columbia River Basalt supplied by R. A. Schmitt), NBS SRM688 (Basalt Rock), NBS SRM1633a (Coal Fly Ash), and NMNH Allende, of similar sizes were also irradiated.

Experiment 2—University of Missouri INAA/RNAA Run

Three bulk samples of Kenna, PCA82506, USGS standard dunite, DTS-1 (split 61, position 8), and USGS standard peridotite, PCC-1 (split 71, position 2) were selected and crushed. The masses were approximately 100 mg each. They were irradiated in the University of Missouri reactor at a flux of 4.9×10^{13} n/cm² sec for 37 h. Chemical standards and samples of the standard rocks, CRB-1, NBS SRM688, NMNH Allende (each approximately 1–2 mg), and Tocapilla (supplied by Daniel Malvin; approximately 0.6 mg) were also irradiated. Upon return from the reactor, each ureilite was split in the manner depicted in Fig. 1. The irradiated sample was split into portions for bulk INAA analysis and leaching. The leachate was then split into portions for INAA and RNAA analyses. There was no bulk sample

in the RNAA portion and no residue sample in the INAA or RNAA segments of the experiment. Chemical standards were dissolved with the appropriate acids and aliquants taken for counting. The appropriate acids are those in which the chemical standards were originally prepared as solutions prior to drying for irradiation. These were HCl, HNO₃, and HF.

Experiment 3—University of Missouri INAA/RNAA

Three bulk samples of ALHA77257, ALHA81101, and ALH82130 with masses of approximately 150 mg each were selected and crushed. These were irradiated at the University of Missouri reactor at a flux of 4.9×10^{13} n/cm² sec for 47 h. Chemical standards and samples of the standard rocks, CRB-1, NBS SRM688 basalt, Allende (all about 2 mg), and Tocapilla (about 0.4 mg) were also irradiated. Upon return from the reactor, the samples were split in the manner depicted in Fig. 2. Bulk samples were analysed using both INAA and RNAA. Residues and leachates produced from the acid leaching procedure were analysed using both INAA and RNAA. Chemical standards were dissolved and aliquanted as in experiment 2.

Leaching Procedure

Because of indications in earlier work (BOYNTON et al., 1976) that leaching with HNO₃ removed the carrier of the light rare earth elements (LREEs) in ureilites, leaving a residue thought to more closely represent an original partial melt residue or cumulate, we decided to duplicate the BOYNTON et al. (1976) procedure. These leached samples would then provide compositions more representative of the residue or cumulate material—the ureilite's ultramafic (olivine + pyroxene) silicate component—on which REE petrogenetic modelling should be based.

Prior to the irradiations, a 0.5 cm² slab of Kenna was subjected to various strengths of HNO₃ for a sequence of time intervals (1 min to 15 min) and examined with both the optical microscope and the electron microprobe to determine the effect of different time exposures on the different textural components of the meteorite. From these experiments, we determined that a 15-min leach with concentrated nitric acid would be appropriate.

A crushed sample (grain sizes from powder to 0.8 mm diameter) was placed in a beaker and concentrated nitric acid added. The beaker was agitated at 1-min intervals for 15 min then poured through filter paper which was then rinsed with concentrated HNO₃ once, with distilled water three times, and with acetone one time. The water and acetone were discarded. The leachate was then divided for INAA (placed in a counting vial) and RNAA (sent through the RNAA procedure). After the filter paper and the residue on it were dry, the residue was split to INAA (into counting vial) and RNAA (sent through procedure). Because of the difficulty in completely removing the sample from the filter paper, the filter papers were also counted. The samples were weighed at all stages in the procedure, i.e., at each split into parts and upon final encapsulation. The masses of the

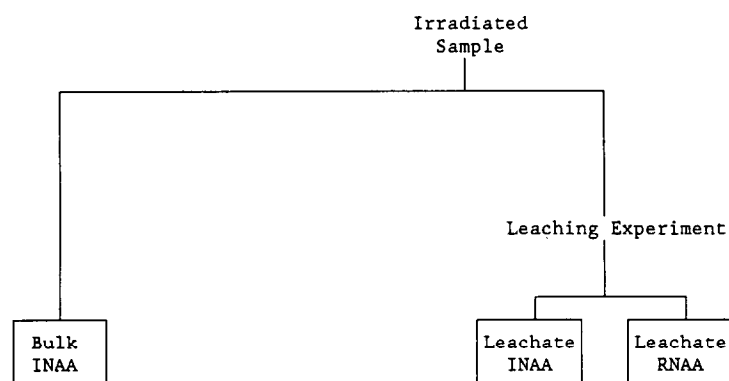


FIG. 1. Experiment 2 schematic.

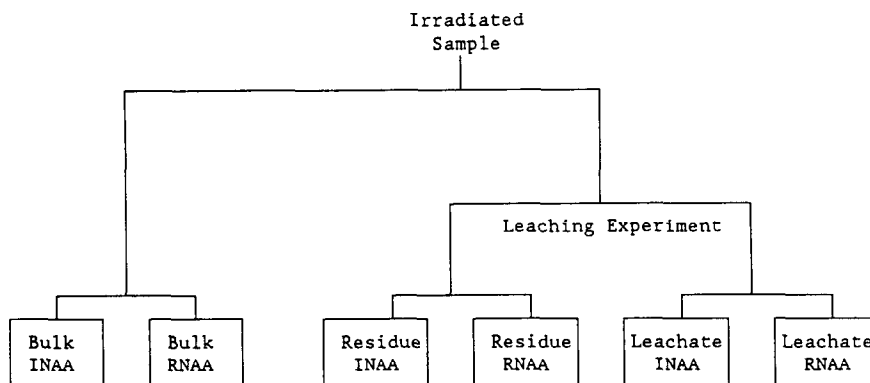


FIG. 2. Experiment 3 schematic.

leachates were determined by subtraction of the residue masses from the bulk masses. They range from 0.56 mg to 1.72 mg. Because the mass loss was small and the weighings were made on the filter paper, the masses of the leachates, and hence the concentration, are somewhat uncertain.

Radiochemistry Procedure

Weighed samples were added to Ni crucibles containing mixed REE carriers and fused with Na_2O_2 . The fusion cake was dislodged with H_2O and HCl and the REEs were then isolated by centrifuging as hydroxides, first with NH_4OH , then with NaOH . After centrifuging, the hydroxides were dissolved and precipitated with HF , centrifuged and dissolved with HBO_3 and HNO_3 . After another hydroxide isolation, the sample was passed through an anion exchange column with 6N HCl to remove Fe. It was then passed through a second anion exchange column with NH_4SCN to remove Sc; the solution was converted to SCN^- in the Cl^- column. Both anion exchange columns are Dowex $\text{AGI} \times 8 (\text{Cl}^-)$, 100–200 mesh. The final sample was gamma counted as a 1.0 mL solution in HNO_3 .

At the end of the gamma counting period (approximately two months), the samples were re-irradiated for chemical yield determinations. A solution prepared from the standard solution of REEs at the time of the initial irradiation was sent with the samples for a second irradiation. This monitor was used to determine the yield of the sample through the RNAA procedure. The yields varied for individual elements and samples but ranged from a low of approximately 24% to a high of 73%. Most yields were in the range of 40 to 46%.

Gamma Counting and Data Processing

INAA and RNAA samples and standards were counted on one of two gamma-ray detectors: Detector B is a Ge(Li) detector with an efficiency of 17% and resolution of 1.75 keV at 1332 keV; detector C is a high-purity Ge detector with an efficiency of 23% and resolution of 1.80 keV at 1332 keV. Detector C is surrounded by a large (33 cm \times 36 cm diameter) NaI(Tl) scintillation detector. Pulses from the Ge detector are analyzed and stored in one of two memories depending on whether the event is in coincidence with an event in the NaI(Tl) detector. This Compton suppression mode provides an increase in signal-to-noise ratio of about a factor of fifty in samples such as those that are dominated by ^{46}Sc and ^{192}Ir , two nuclides that emit coincident gamma rays. The samples and standards were counted several times over a period of about two months. Every element reported in Tables 1 and 2 has been determined a minimum of two times—with either multiple gamma-ray energies or multiple count intervals. Discrepancies (1–20%) between multiple counts on detector C and between detector C and detector B counts of the same sample became evident during the data processing. This problem was due to the malfunction of our sample changer which normally maintains reproducible geometry to within $\pm 1\%$. The detector C data were corrected by normalizing to Fe values determined on detector B. Prob-

lems with chemical standards due to incomplete dissolution or other unknown causes were corrected by using the standard rocks as our primary standards for elements.

RESULTS

Rare Earth Elements

We obtained trace element results for bulk, residue, and leachate samples of ALHA77257, ALHA81101, and ALH82130 and for residue and leachate samples only of Kenna and PCA82506 (Table 2; Fig. 3). As with previously studied ureilites (BOYNTON et al., 1976; WÄNKE et al., 1972; GOODRICH et al., 1987c), the absolute abundances of the rare earth elements (REEs) are low (heavy rare earth elements (HREEs) $< 0.8 \times \text{CI}$, light rare earth elements (LREEs) $< 0.3 \times \text{CI}$). The v-shape REE pattern is much less pronounced than in previously studied non-Antarctic ureilites. The LREEs in bulk ALHA77257 and ALHA81101 are less enriched than in many previously studied samples, and ALHA82130 displays no LREE enrichment at all. The LREE concentrations for those three samples are less than for any other bulk non-Antarctic ureilite except for one of two splits of Roosevelt County (RC) 027 (GOODRICH et al., 1987c). The HREE absolute abundances for ALHA77257 and ALHA81101 are within the range of previously analyzed ureilites. The REE pattern of the bulk ALHA77257 sample we analysed displays LREE enrichment but that analysed by EBIHARA et al. (1990) does not. This is reminiscent of the difference found between two bulk samples of RC027 by GOODRICH et al. (1987c). The HREE abundances of ALH82130 are the highest of any ureilite yet analyzed. This result is expected since this meteorite has a high pyroxene content and contains augite.

As stated earlier, in addition to crushed bulk samples, we also leached a slab of Kenna. It was examined using both optical and electron imaging before and after treatments with nitric acid to document our acid leaching of powdered samples. The microprobe examination included major silicates, interstitial silicate (as defined by GOODRICH et al., 1987c), and carbon-rich areas. The acid leaching of the slab indicated that carbon-rich areas were attacked to a significant extent, major silicates to a small extent, and the interstitial silicate not at all. Because our analysis of acid-leached powders and leachates showed more LREEs in the leachate, the probable

TABLE 2. Trace element abundances in ureilites.* CC, CD, and CK are experiment codes: CC is Experiment 1—University of Arizona INAA Run; CD is Experiment 2—University of Missouri INAA/RNAA Run; and CK is Experiment 3—University of Missouri INAA/RNAA Run.

Sample	Type	Mass(mg)	Ca(%)	Sc	Cr	Mn	Fe(%)	Co
ALHA77257	CC	490.25	.7	7.5	5260	3519	11	97
	bulk	4.03	1.3	8.6	5650		11.5	103
	residue	4.48	1.3	9.2	5660		10	68
	leachate	0.57	.1	.62	2550		14	290
ALHA81101	CC	600.60	.6	7.3	5240	3500	16.0	75
	bulk	4.27	1.7	7.2	4997		16.6	98
	residue	4.28	1.4	8.8	5955		14.1	47
	leachate	1.72	.1	.77	860		9.3	90
ALH82130	CC	532.83	1.7	11.7	4130	4080	5.4	117
	bulk	2.9	1.4	11.3	4438		6.5	119
	residue	2.88	3.8	17.9	3897		3.5	38
	leachate	0.56		1.3	10010		29	100
PCA82506	CC	540.13	.69	7.5	5230	3440	14	92
	leachate		.77	.64	1340		3.9	623
Kenna	CC	552.52	.765	8.08	4890	3560	15	160
	leachate		.60	2.34	900		3.3	980
Novo Urel	CC	511.21	1.03	9.09	5100	3720	14.9	143
Average % error based on counting statistics			13	1	1	1	1	1

Sample	Type	Ni	Zn	Ga	W	Re	Os	Ir	Au
ALHA77257	CC	940	280	1.6	.04	.01	.19	.18	.02
	bulk	1160	314.1	1.9			.17	.17	.02
	residue	737	319				.11	.13	.02
	leachate	3330	44	5.9		.01	.50	.43	.08
ALHA81101	CC	750	168	1.3	.01			.04	.01
	bulk	1306	143					.05	.02
	residue	547	182					.03	.01
	leachate	1200	23				.06	.05	.01
ALH82130	CC	1440	231	1.8	.04	.01	.19	.16	.04
	bulk	1670	303	2.9			.16	.14	.03
	residue	490	200					.03	.01
	leachate	13300	280	29.8		.17	1.5	1.4	.24
PCA82506	CC	800	242	1.7	.04	.02	.24	.18	.02
	leachate	5200	18				1.4	1.8	.11
Kenna	CC	1430	220	2.2	.11	.05	.71	.6	.04
	leachate	9190	67				1.7	2.2	.55
Novo Urel	CC	1340	220	2.8	.09	.04	.53	.4	.04
Average % error based on counting statistics		2	2	13	15	10	6	1	2

* In ppm unless noted otherwise.

location of the LREEs is the carbon-rich areas. These conclusions are corroborated by preliminary ion probe work on ALHA78019, Kenna, and RC027 in which the LREEs were detected only in the carbon-rich areas and not in graphite (ALHA78019 only), sulfides, major silicate minerals, or interstitial pyroxene (SPITZ et al., 1988).

The results of the leaching experiments are given in Table 3 and Fig. 4. In each case the leach selectively removed the LREEs in preference to the HREEs. This is so, although to a lesser extent, even for ALH82130 which has no light REE component discernible in the whole rock analysis (Fig. 3). In no case, however, were the majority of the LREEs in the leach; the ALHA77257 leach contained about 35% of the LREEs, but the other two had around 15%. We must note that measurement of the leachate weights may be suspect due to the non-trivial analytical task of measuring such small quantities and dealing with problems of moisture evaporation and static discharge during weighing. This can explain why

the leachate and residue concentrations (as measured) do not bracket those of the bulk sample—for both the LREEs and HREEs. This issue is not trivial and not easily resolved. In order to lessen its impact on the study, we place emphasis on elemental patterns and ratios rather than absolute concentrations.

The residue samples of Kenna and PCA82506 showed LREE depletion as expected but when mass balance calculations for bulk samples were done (no bulk samples were counted), we were perplexed initially as they indicated no significant LREE enrichment (i.e., comparable to measured bulk samples of Kenna and other ureilites; BOYNTON et al., 1976). The results of the leaching experiment on the other three Antarctic samples appeared even more puzzling at first: the leachates generally show the LREE enrichment but the relative behavior of bulk and acid residues was not as simple as expected. For example, ALH82130 residue is similar to the bulk; ALHA77257 residue has more LREEs than the

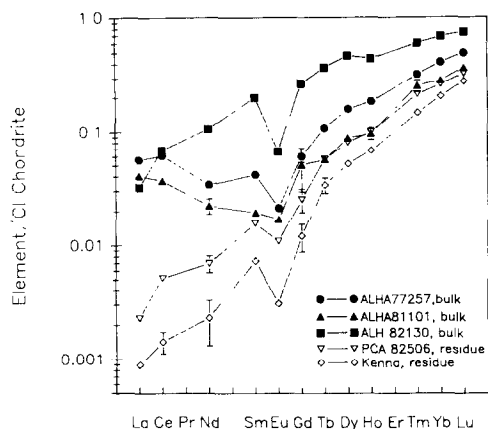


FIG. 3. Chondrite-normalized REE abundances. Bulk samples are shown with filled-in symbols; residue samples with open symbols. The bulk samples show little LREE-enrichment indicating that these samples contained little of this component. The acid-leached samples of PCA82506 and Kenna represent the ultramafic rock component. All REE chondrite values from EVENSEN et al. (1978).

bulk; we had expected a residue depleted in the LREEs and a leachate highly enriched in the LREEs.

We do not believe that this is an artifact of our technique nor an error in our procedures but an indication of the inherent difficulties of the leaching technique in separating the different components of the ureilites. The depletion of the LREEs is due more to sampling than to the nitric acid treatment because the LREE host phase is so heterogeneously distributed, and such a minor part of any given bulk ureilite, it is easily possible to obtain a bulk sample without a LREE carrier. This is seen most clearly in the comparison of the bulk and residue samples for ALH82130 which show very similar abundance results for the bulk sample and the acid-treated (residue) sample. Acid leaching also removes HREEs from bulk samples—perhaps the minor damage done to the olivine and pyroxene grains is evidence for the major silicates as the source of the HREEs in the leachates. Recent isotopic work by GOODRICH et al. (1991) has amplified these observations on the heterogeneity of the LREE component.

Our future work will address some of the uncertainties.

TABLE 3. REE abundances in ureilites.*

Sample	Type	Weight(mg)	La	Ce	Nd	Sm	Eu	Gd	
ALHA 77257	Bulk	53.96	13.8	39.2	16.2	6.4	1.24	12.4	
	Residue	70.9	21.0	59	23.9	6.1	1.44	10.4	
	Leachate	5.1	148.0	421.5	177.4	33.4	7.52	47.8	
ALHA 81101	Bulk	39.46	9.9	23.4	10.6	3.0	0.96	10.4	
	Residue	58.17	1.4	3.9	2.3	1.00	0.51	3.8	
	Leachate	0.58	23.5	62.5	23.6	4.5	1.74	7.0	
ALH 82130	Bulk	59.83	7.9	43.8	50.7	31.3	3.89	55.4	
	Residue	87.16	6.9	32.9	46.8	29.6	3.44	53.6	
	Leachate	5.06	23.5	71.1	50.9	19.3	8.94	70.3	
PCA 82506	Residue	106.79	.6	3.3	3.3	2.4	.63	5.2	
Kenna	Residue	81.17	0.2	.9	1.09	1.13	.18	2.5	
Average % error for element: based on counting statistics			3	7	10	1	3	15	
Sample	Type	Tb	Dy	Ho	Tm	Yb	Lu		
ALHA 77257	Bulk	4.1	40.6	10.6	8.3	68.8	12.7		
	Residue	2.3	22.1	5.8	4.7	36.4	6.7		
	Leachate	4.9	31.3	5.3	4.1	21.4	3.2		
ALHA 81101	Bulk	2.1	22.5	5.5	6.6	47.5	9.4		
	Residue	1.1	11.7	3.3	3.6	26.4	5.2		
	Leachate	0.9	4.6	1.1	1.9	7.3	1.5		
ALH 82130	Bulk	14.0	120.6	25.3	15.6	114.9	19.2		
	Residue	12.6	117.9	26.2	15.0	109.2	18.9		
	Leachate	9.3	40.2	16.5	12.2	45.7	6.3		
PCA 82506	Residue	2.1	20.5	5.7	5.6	43.9	8.5		
Kenna	Residue	1.3	13.2	3.9	3.8	34.4	7.2		
Average % error for element: based on counting statistics			3	5	5	7	2	2	

* In ppb.

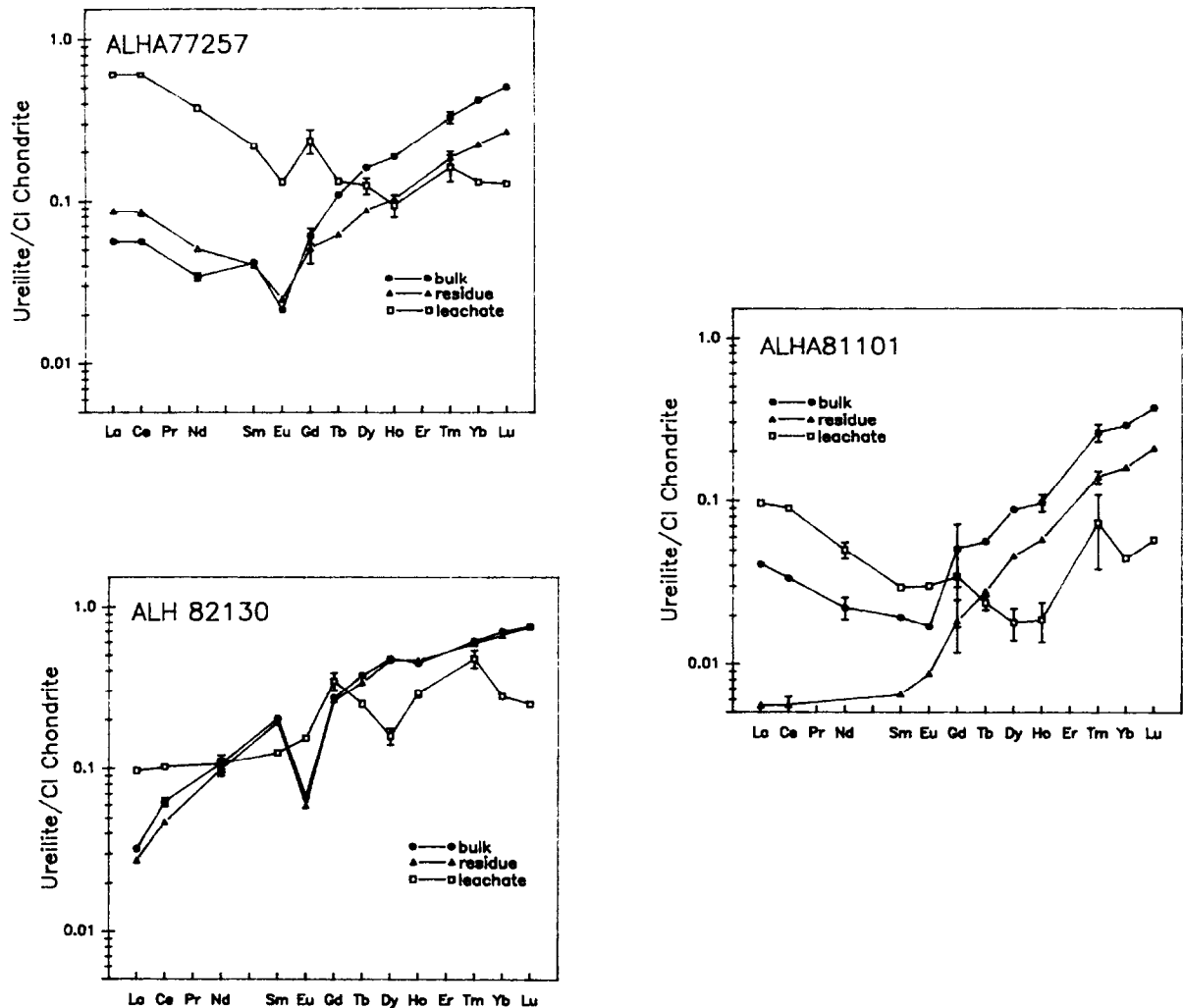


FIG. 4. Acid treatment of ureilites. Bulk and acid-treated samples of ureilites (procedure residue and leachate) indicate that separation of ureilite components with acid-leaching does not provide consistent results—element abundance levels are almost fully controlled by the content of the original sample. For example, ALH82130 had little LREE-enriched component to remove giving, therefore, bulk and residue abundances that are nearly identical.

We will attempt to leach components with HCl and other acids and to employ mechanical separation techniques to compare the acid effects and to eliminate the ambiguities inherent in the acid-leaching technique. Because different minerals are sensitive to different acids, the LREE host phase may be determined by comparing the leachates resulting from exposure to different acids. For example, if the LREE host phase is a phosphate, the leachate produced from treatment with HCl would show high LREE concentrations. Although this work indicates that any chemical treatment of ureilites prior to analysis may produce puzzling results, it has revealed that the amount of LREE-enriched component varies from sample to sample and that HNO₃ does remove the LREE-enriched component.

Siderophiles

Our siderophile data for bulk samples indicate results similar to those of other workers (HIGUCHI et al., 1976; JANSSENS

et al., 1987; WÄNKE et al., 1972), but with a wider range of variability (Table 3; Fig. 5). For the refractory siderophiles, Re, Os, W, and Ir, the absolute abundances range from $0.1 \times \text{CI}$ to just over $1.0 \times \text{CI}$. The volatile siderophiles, Ni, Co, Au, and Ga, range from $0.068 \times \text{CI}$ to $0.281 \times \text{CI}$ —a much narrower range of composition than that for the refractory siderophiles. Duplicate bulk samples of ALHA77257, ALHA81101, and ALH82130 analysed during our second University of Missouri experiment are in close agreement with those given here and therefore are not duplicated in the table. Ranking of samples on the basis of element concentration patterns (HIGUCHI et al., 1976; JANSSENS et al., 1987) has less significance than it was given in these earlier studies which used smaller sample populations.

Other Elements

We also determined lithophiles, Ca, Sc, Cr, and Zn, for bulk samples. None of these groups of elements shows the

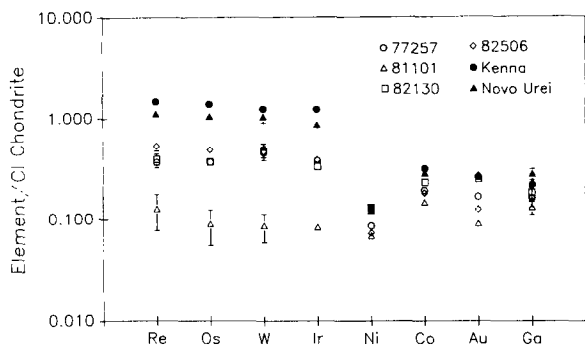


FIG. 5. Chondritic-normalized siderophile element abundances. Antarctic samples are shown with open symbols; non-Antarctic samples with filled-in symbols. Refractory siderophiles show more variation in abundances among the ureilites than do the volatile siderophiles. Apparently the host phase for the refractory siderophiles is more heterogeneously distributed among ureilites. All siderophile chondrite values are from ANDERS and EBIHARA (1982) except the Os concentration which is from JONES and ANDERS (pers. comm., 1986).

patterns evident in the siderophile abundance rankings. Calcium, Sc, Cr, and Zn have abundances around $1.0 \times$ CI chondrites.

DISCUSSION: IMPLICATIONS FOR THE PETROGENESIS OF UREILITES

Rare Earth Elements

Generally, ureilites display a v-shaped REE pattern showing enrichment in both the LREEs and HREEs and variable negative Eu anomalies when normalized to CI chondrites (Fig. 3). All the REEs reported or calculated here are normalized to CI chondrite values from EVENSEN et al. (1978). Because the mineral/melt distribution coefficients of the REE are a smooth function of atomic number (with the exception of Ce and Eu which have two valence states), no single phase could produce such a pattern. The major silicate phases (primary constituents of ureilites)—olivine and pyroxene—are the hosts for the HREEs, but the major host phase of the LREEs is unknown. Acid treatment of bulk samples produces LREE-enriched leachates and LREE-depleted residues. These acid-treated residues represent the olivine-pyroxene assemblage which is probably a product of igneous processes—partial melting or crystallization and accumulation. We then attempt to fit the REE patterns using constraints proposed in the models. Figure 6 presents the results of this modelling.

REE modelling is useful in distinguishing among the petrogenesis models now extant. The hypotheses that we have attempted to model are the Ostwald ripening model of TAKEDA (1987) and variations (TAKEDA, pers. comm., 1988); the partial melting residue model of BOYNTON et al. (1976); the three-stage model of GOODRICH and JONES (1987); and the four-stage model of GOODRICH et al. (1987b). These are most constrained, cover a wide range of possible petrogenic processes, and allow simple REE modelling.

In all models we consider, the source material is chondritic with respect to mineralogy and trace element abundances. Chondritic source material was chosen because as the ca-

nonical source material in cosmochemical modelling it was employed by each of the authors in their models. We have evaluated a range of modal mineralogies which can be considered "chondritic," and the representative mineralogy presented in these model calculations is 59% olivine, 24% clinopyroxene, 3% orthopyroxene, and 14% plagioclase. The clinopyroxene distribution coefficients used are for pigeonite. Other chondritic concentrations were employed and produce similar results. For example, we used 53% olivine, 32% clinopyroxene + orthopyroxene, and 15% plagioclase. Changes in the relative amounts of the pyroxenes and plagioclase, however, do affect the final result of the models in that the Eu anomaly is dependent on the amounts of clinopyroxene and plagioclase. For example, until plagioclase is exhausted in melting models, Eu is enriched in the residue. Other than this constraint, various "chondritic" source materials are appropriate (from carbonaceous chondrites to ordinary chondrites) for all models evaluated. We employed trace element data from both CI (EVENSEN et al., 1978) and CV chondrites (ALLENDE—JAROSEWICH et al., 1985) for completeness. CI chondrites are most often considered to have elemental abundances which approximate the source material for igneous meteorites, but CV chondrites (or CV-like) have been proposed for the ureilite precursor material (BOYNTON et al., 1976; JANSSENS et al., 1987). The difference between the two with respect to REEs is simply one of absolute amounts rather than relative differences among the REEs.

The distribution coefficients are for oxygen fugacity and temperature appropriate to conditions of ureilite formation: $\log f_{O_2}$ of between -11 and -14 and temperature of approximately 1200°C . These oxygen fugacity values are similar to those determined for eucrites (STOLPER, 1977). Calculations based on Fe content of silicates give $\log f_{O_2}$ between -12.8 and -13.9 (GOODRICH et al., 1987a). Temperatures for crystallization of ureilites have been estimated from pyroxene geothermometers (TAKEDA, 1987), oxygen geothermometers (CLAYTON and MAYEDA, 1988), and petrogenetic considerations (GOODRICH et al., 1987a). The petrogenetic considerations and the pyroxene geothermometers provide temperatures of approximately 1200°C , while comparisons using oxygen isotope equilibration temperatures yield much lower temperatures of 600 to 1100°C (CLAYTON and MAYEDA, 1988). Resolution of the discrepancy is necessary. There is some evidence that the oxygen isotopes are questionable measurements of the conditions at the time of ureilite petrogenesis. First, this is a consequence of the linear dependence on temperature making the O-isotope fractionation relatively much more susceptible to retrograde adjustments than is element fractionation (GANGULY and SAXENA, 1987). In addition, as pointed out by JOHN JONES (pers. comm.), the equilibrium temperatures derived from the O-isotope measurements are backwards with the Mg-rich assemblage of lower equilibration temperature—in opposition to magmatic equilibria and subsolidus kinetics. Clearly, the O-isotopes in ureilites are not completely understood and the results and conclusions drawn from their values must be tempered. The distribution coefficients are from MCKAY and WEILL (1977), MCKAY (1982), MCKAY (1986), and MCKAY et al. (1990).

Our modelling uses a program written by Spitz which allows calculations of partial melting and fractional

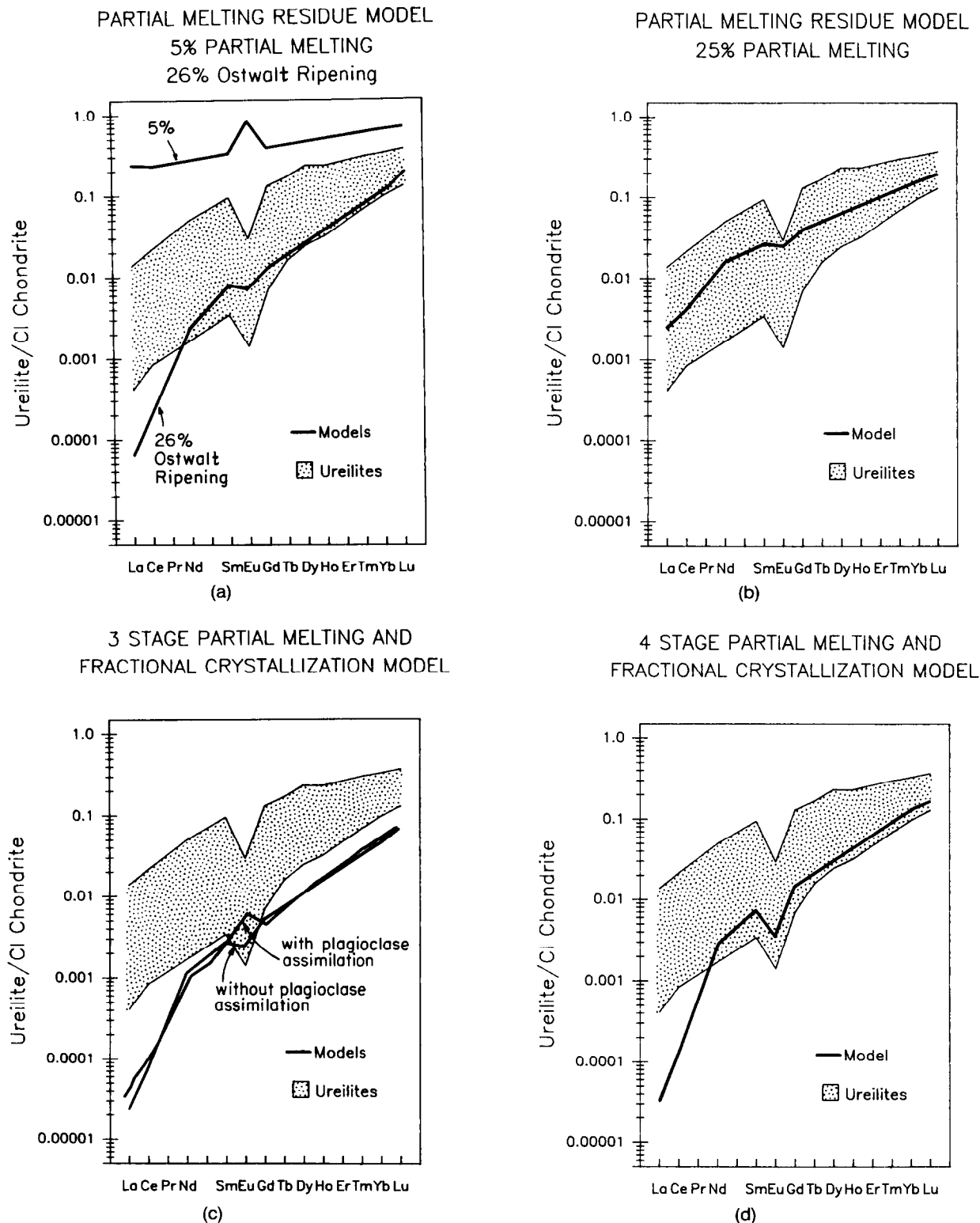


FIG. 6. REE Modelling. (a) TAKEDA models: 5% partial melting residue (1987) and 26% Ostwald Ripening (1987, 1989). (b) BOYNTON et al. (1976) partial melting residue. (c) GOODRICH and JONES (1987) three-stage model. (d) GOODRICH et al. (1987a) four-stage model. Model results are shown as solid black lines. Range of ureilite samples is indicated as stippled area on plots.

crystallization processes using the initial source material discussed earlier, distribution coefficients and variations in the model conditions such as source and product materials,

amounts and types of melting or crystallization, and melting proportions of minerals. The results of the modelling presented here employ equilibrium partial melting equations

because fractional partial melting calculations using this program produce patterns far too depleted in LREEs to model actual ureilites. The actual conditions of ureilite formation are, no doubt, intermediate to these two paradigms.

The program has flexibility in accounting for changes in modal mineralogy with melting and formation of cumulates from fractional crystallization. For example, we assume that melting of the chondritic material begins at the peritectic point in the system olivine-anorthite-silica at which the composition remains until the plagioclase is exhausted. After this, new melting proportions of the remaining minerals are supplied. For crystallization, percentages of crystallizing phases and, if applicable, proportions of minerals in the cumulate are supplied.

We originally modelled the TAKEDA (1987) hypothesis as a partial melting residue model (SPITZ and GOODRICH, 1987). This scenario called for 5.0% partial melting of chondrite source material which resulted in a mafic silicate residue and the extraction of the partial melt by gravitational "squeezing out." The ureilites then grow from the remaining residue of mafic silicates and the partial melt. With such a small degree of melting, however, all the plagioclase is not removed from a chondritic source region. The result is a REE pattern unlike those of any ureilite—it displays a positive Eu anomaly and abundances 10–100 times those of the observed ureilites (Fig. 6a).

Revised models (TAKEDA, 1989) incorporate multistage aspects. Chondritic source material undergoes a large degree of partial melting leaving a mafic silicate residue. This melt is extracted. Another rise in temperature produces additional melt: smaller crystals melt and from this melt the larger crystals grow in a process Takeda termed Ostwald Ripening. In his multistage model, the first stage requires between 20 and 25% partial melting of chondritic source material to produce a residue of mafic silicate that has a negative Eu anomaly. The mafic silicates then undergo a second stage of melting—the amount of which is determined by the model's requirement that total melting is 26%. This limitation to the partial melting amount is required in order to preserve the orientation of the grains (TAKEDA, pers. comm.). The growth of the larger crystals from the melt in this stage does not change the abundances of the elements—material is melted and then crystallizes, reaggregating to the grains in a closed system (Fig. 6a).

The BOYNTON et al. (1976) residue model proposed generation of the ureilites' HREE pattern as a result of high degrees of partial melting. As proposed initially, this model required fractional partial melting to achieve steep enough REE patterns. With revised distribution coefficients (MCKAY, 1982, 1986; MCKAY et al., 1990), however, fractional melting is not necessary and equilibrium partial melting is applicable. For these calculations, plagioclase is exhausted between 20 and 25% partial melting of a chondritic source. Consequently, using the 25% value as representative, calculated patterns display REE abundances with negative Eu anomalies; they also have HREE to LREE ratios and abundances comparable to analysed ureilites (Fig. 6b). Once plagioclase is exhausted in the source region, it is only the pigeonite distribution coefficient which controls the Eu distribution and which provides the changes in the negative Eu anomaly. The result is that the anomaly is small. Using recently determined coefficients

for Eu distribution in pigeonite (MCKAY et al., 1990) alleviates this somewhat; the negative anomaly is somewhat greater. Even if the initial oxidation conditions were more reducing ($\log fO_2$ were lower) causing the Eu distribution coefficient of plagioclase to increase, or after the exhaustion of plagioclase, causing the pigeonite distribution coefficient to decrease, the anomaly remains largely unaffected—we cannot produce the magnitude of observed anomalies found in some ureilites. This suggests that the source region must have had a negative Eu anomaly prior to formation of the ureilites.

The next simplest scenario—remelting of the residue to create a second residue—does not produce the REE abundances seen in ureilites either. Again, the fractionations among the REEs, i.e., Eu negative anomaly, is not of the degree seen in the actual samples.

Just as simple partial melting residue models do not reproduce the observed range of REE patterns of ureilites, neither can one-stage cumulate models. Clearly, some additional complexity is required to produce these meteorites.

GOODRICH and JONES (1987) proposed a model which combined partial melting and fractional crystallization steps based on Ca/Al ratios. The basic tenets of this model are (1) 25–30% partial melting of a chondritic source to produce a plagioclase-free residue (as in the BOYNTON et al., 1976, model); (2) this initial melting is followed by a second, 4–13%, partial melting of the residue to produce ureilite parent magmas; and (3) finally, followed with the assimilation of small amounts of plagioclase into these magmas—to account for the high Ca/Al ratios observed in ureilites—there is 1–5% crystallization of olivine and pigeonite to produce cumulate ureilites. Again, the large degree of partial melting produces HREE enrichment and negative Eu anomalies in the residues. Liquids derived from melting the residue in the second step retain the anomalies as can the final solids. With the assimilation of completely melted plagioclase, however, the Eu anomaly disappears and the calculated patterns no longer mimic those of ureilites—instead they show a positive Eu anomaly (Fig. 6c).

The more recent revision of this multistage model prompted by these Eu anomaly inconsistencies adds to the complexity of the ureilite evolution (GOODRICH et al., 1987b). This model proposes four steps:

- 1) 10–20% partial melting of a chondritic source to produce a liquid;
- 2) 1–5% fractional crystallization of this liquid with the formation of a cumulate olivine-pigeonite;
- 3) 2–10% partial melting of this cumulate to produce ureilite parent magmas;
- 4) 1–5% fractional crystallization of these magmas to form a cumulate with minerals in the proportions found in ureilites—80% olivine and 20% pigeonite.

Calculations based on this complex history provide the absolute abundances and the negative Eu anomalies displayed in ureilite analyses. It can, in fact, mimic even the RC027 or ALH82130 anomalies which are the largest seen [Fig. 6d].

The only apparent discrepancy is seen in the LREE pattern and can be explained simply if these analysed samples are not completely devoid of the LREE host phase—a very small amount of trapped liquid is all that is required to increase

the LREE abundances dramatically and this is not accounted for in the model calculations. A final point is that because this model calls for different magmas on the ureilite parent body, it can also provide the variety of abundances and range of Eu anomalies seen in samples. Significant problems with this model are not apparent in the REE modelling but will be discussed vis-à-vis other aspects of ureilites.

Modelling of the REE patterns shows that both the residue of a partial melting event and complex, multistage processing can produce LREE-depleted patterns which match those displayed by the ureilites (acid-leached and unleached specimens with low LREE abundances). To produce the extreme negative Eu anomaly and the variability of this anomaly, multistage processing was invoked. The lack of correlation between the degree of Eu anomaly and Fe content in olivine (a measure of the amount of reduction) of the various samples indicates that the anomaly cannot be controlled simply by changing oxygen fugacity. For example, Kenna with fosterite in olivine of 79.2 has Sm/Eu of 5.15 and ALHA77257 with fosterite in olivine of 84.9 has Sm/Eu of 5.19. LREE depletion also is not directly correlated with the anomaly degree.

REE modelling does suggest that large degrees of partial melting are required and that a combination of igneous processes is necessary in the petrogenesis of ureilites. Simple one-stage models do not suffice to produce the variety, but multistage models do not produce the REE absolute abundances as closely.

Consideration of the enriched LREE abundances in the ureilites presents more of a problem and allows less quantitative consideration. V-shaped REE patterns have been noted in some terrestrial rocks such as DTS-1 and PCC-1 (FREY et al., 1971). Even for these terrestrial rocks, for which we have potentially much better control because of placement information, such enrichments promote controversy. Metasomatism, alteration and metamorphism, and formation from a magma with high LREEs/HREEs have been suggested as possible causes of LREE enhancements (FREY, 1984). Because the ultramafic rocks have such low abundances of REEs, small amounts of "foreign" material such as metasomatic fluids can provide significant enrichments. A simple calculation for ureilites indicates that $\leq 1\%$ of an early formed partial melt added to calculated partial melt residue abundances is sufficient to produce the LREE abundances seen in samples. This implies that the LREE host phase is minute as implied by abundance variations in samples and in the difficulties in finding it (SPITZ and GOODRICH, 1987).

Siderophile Elements

Siderophile element behavior/relationships are also useful in providing constraints on ureilite formation conditions. Correlation diagrams are useful in discussing the results presented for these elements. Again, our values for previously studied ureilites, Kenna and Novo Urei, are compatible with those of prior studies and give us confidence in our results. The leaching procedure we employed appears to affect the volatile siderophiles to a far greater extent than the refractory siderophiles (note the difference between 7 and 7L on Fig. 7 for ALHA77257 bulk and ALHA77257 leachate). Correlations of the refractory siderophiles (for example Ir) with the

more volatile siderophiles (for example, Ni and Au) confirm the distinct host phases of these elements determined previously (BOYNTON et al., 1976; JANSSENS et al., 1987; Fig. 7). As with the REE results, however, the results of the leaching experiment have some ambiguity—concentrations of siderophiles in residues and leachates are not identical in the different samples.

As suggested by others (BOYNTON et al., 1976; HIGUCHI et al., 1976; JANSSENS et al., 1987), these correlations may represent mixing between a low-Ir component (ultramafic rock) and a high-Ir component (vein material). These two components can be represented by our value for ALHA81101 and data for the vein material (BOYNTON et al., 1976; HIGUCHI et al., 1976; WASSON et al., 1976; JANSSENS et al., 1987). ALHA81101, the ureilite with the highest $\delta^{17}\text{O}\%$ (CLAYTON and MAYEDA, 1988), extends the ureilite range closer to the low-Ir endmember.

The three-element plot of siderophiles normalized to CI chondrite values and to Ni further delineates the host components of the siderophile elements and mixing trends (Fig. 8). The low content of vein material for ALHA81101 is again evident for each of the elements. The refractory siderophiles' (Re, Os, W, and Ir) concentrations display tight correlation with one another; the volatile siderophiles (Co and Au) less so.

Addition of the Antarctic ureilites to the data base does not significantly affect the correlation coefficients for the elements considered yet provides some intriguing questions. For example, for the Ni vs. Ir, the correlation coefficient drops from .8946 to .8676 and for Au vs. Ir from .8722 to .8363. There is no effect, however, on the confidence limit which remains .9999; and so this may be a further reflection of the increased variability brought to the abundance data by the Antarctic samples, or simply statistical fluctuation. The patterns identified with non-Antarctic samples only in previous

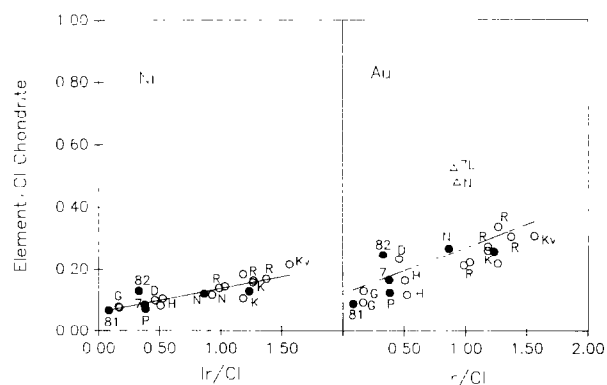


FIG. 7. Siderophile element correlations in ureilites. Volatile siderophile elements correlate with refractory siderophile elements in bulk and vein separates. We have plotted results from our experiments with filled-in symbols and literature data (BOYNTON et al., 1976; HIGUCHI et al., 1976; JANSSENS et al., 1987; and WANKE et al., 1972) with open symbols. Ureilites are given the following labels: D = Dyalpur, G = Goalpara, H = Haverö, Hv = Haverö vein, K = Kenna, Kv = Kenna vein, N = Novo Urei, R = Roosevelt County 027, 7 = ALHA77257, 7L = ALHA77257 leachate, 81 = ALHA81101, 82 = ALH82130, P = PCA82506. (The Kenna vein value is plotted for a reference of vein material. Other vein and metal samples plot along the same regression line but with much higher abundances.)

work (BOYNTON et al., 1976; JANSSENS et al., 1987) are confirmed. Although the sample population is as yet too small for meaningful statistical analysis, there is an intriguing suggestion that differences in trace element concentrations exist between non-Antarctic and Antarctic samples: Antarctic samples lie closer to the CI endmember on the correlation plots than do non-Antarctic samples with the exception of Goalpara, and absolute abundances between non-Antarctic and Antarctic samples have different means. If these are indications of true effects, it must be determined whether it is due to differential terrestrial weathering conditions or is indigenous to the meteorites. Such differences do not correlate with other ureilite characteristics but petrographic distinctions have been noted between Antarctic and non-Antarctic ureilites (BERKLEY, pers. comm.).

GOODRICH et al. (1987b) modelled the siderophile elements of bulk ureilites and concluded that complex processing was required. This model relied on 10–25% partial melting in the absence of metal, i.e., under oxidizing conditions, with siderophiles partitioned between solid silicates and liquid. In the second stage, early mafic cumulates were remelted to produce ureilite parent magmas with siderophile partitioning based on the same distribution coefficients as in stage one.

Finally, these magmas were reduced to make 20–30% metal with siderophile elements partitioning between solid and liquid silicates and metal. The partition coefficients used were for a S-rich system.

Our refractory siderophile data, however, present problems for this scenario. The similarity of the chondrite-normalized abundances of tungsten and the other refractory siderophiles, Re, Os, and Ir, requires that W is in the metallic phase—not the silicate phase—when fractionation occurs. The tight correlation of W with the other refractory siderophiles (Fig. 8) does not permit W to fractionate into the silicate phase, yet the first two stages of the GOODRICH et al. (1987b) model require this. The solid silicate/liquid silicate distribution coefficients for W and Ir are 0.01 and 1.7, respectively (GOODRICH et al., 1987b).

Because of the wide divergence of the distribution coefficients, the W/Ir ratio becomes highly fractionated following stage one. The only way for the ratio to return to an unfractionated state following the second stage is for the degree of melting in the second stage to be exactly that required to reverse the fractionation. Such a circumstance is highly unlikely to occur, especially when we consider that the abundance information applies to several different ureilite

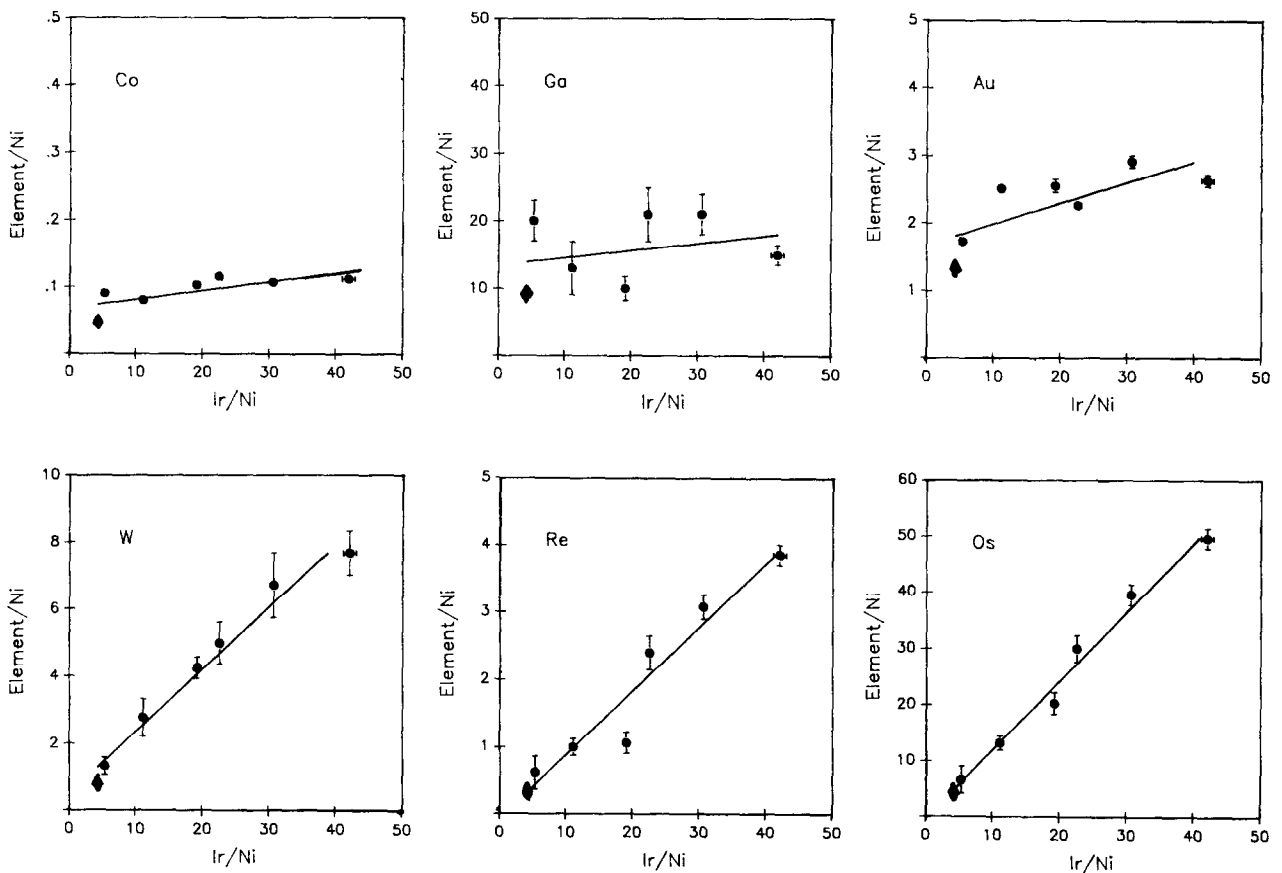


FIG. 8. Three-element plot of element abundances over Ni in ureilites analyzed in this experiment. The ratios are plotted as follows: Co/Ni as ppm/ppm; Ga/Ni as ppm/ppm $\times 10^4$; and W/Ni, Re/Ni, Os/Ni, Ir/Ni, and Au/Ni as ppm/ppm $\times 10^5$. The chondrite value is plotted with the \blacklozenge symbol; the ureilite results with \bullet symbols. The refractory siderophiles, including W, exhibit excellent correlation indicating that bulk samples are a mixture which can be represented by two endmember components, ultramafic rock, and vein material. The volatile siderophile correlations indicate that more than this simple two endmember model is required.

specimens which may represent similar processes in different places rather than co-magmatic samples. Instead, what the data show is that the refractory siderophile abundances are more simply determined by solid metal/liquid metal distribution coefficients (for a S-rich system)—the $D^{sm/lm}$ for a $\log f_{O_2} = -12.2$ at 1250°C are Re = 83, Os = 83, Ir = 83, and W = 36 (GOODRICH et al., 1987b). The volatile siderophile abundances indicate, however, that this model is too simplistic—the $D^{sm/lm}$ for the same conditions are Ni = 1.3, Pd = 0.9, Au = 1.3, and Ge = 10 (GOODRICH et al., 1987b). As more of these element concentrations are determined, they may or may not match the order of abundances as well as the refractory siderophiles.

In summary, the addition of the Antarctic ureilites to the siderophile data base provokes additional questions about ureilite groupings and does not aid in correlating the conclusions drawn from studies of other elements. The behavior of W with respect to the other refractory siderophiles precludes fractionation under oxidizing conditions and limits complexity but the volatile siderophiles (in addition to the REE abundances) call for some complexity. Other considerations must be used in addition to the trace element data to come closer to a petrogenic model for the ureilites.

Other Considerations

In addition to the difficulties presented by the trace element data, both the GOODRICH et al. (1987b) model and the JANSSENS et al. (1987) proposal have material-yield problems. Multistage scenarios not only require time and large parent bodies but allocate only a minute portion of the original material to the final product. For example, the GOODRICH et al. (1987b) scenario converts only 10^{-5} to 10^{-7} of the starting material into ureilites. The GOODRICH et al. (1987b) model further proposes that the magmas are emplaced at several different depths, i.e., not all at one spot on the parent body, which increases the difficulty in removing (increasing the unlikelihood) minute amounts of material. The JANSSENS et al. (1987) suggestion, at best, delivers only 10^{-3} as ureilitic material. Thus, a significant sampling problem exists if these complex models are accurate scenarios; not only do we sample a small fraction of the parent body but we see no complementary fractions, i.e., crustal material, in our collections.

Other models now extant do not constrain parameters well enough to employ our computer modelling for the REEs. They can, nevertheless, be considered in light of the general chemistry and physics that they require.

KURAT (1988) proposed that ureilites were products of 'primitive' processes rather than igneous processing on a parent body(ies). This is in opposition to the age data of GOODRICH et al. (1988) indicating activity at 3.74 Ga and other data which argue for petrogenic processing or metasomatism of the earlier-formed material, such as the REE results. The KURAT (1988) model can be discussed based on REE considerations. First, the KURAT (1988) argument that peridotite values for HREEs vary widely, yet ureilites do not, in themselves prove a primitive and simple origin for the meteorites. Many peridotites do have fairly uniform HREE contents and with additional HREE values presented here, it is obvious that ureilites do not. Second, the abundances of HREEs reside in both olivine and pyroxene and are not too high for olivines

having attained equilibrium with a coexisting melt. As seen in Fig. 4 the modelling for ureilites based on accepted coefficients (more recent ones than KURAT, 1988, cites) are bracketed by the analysed ureilites. Third, the model proposes that olivine condensed from the vapor phase. In this case, the distribution coefficients are based on volatility—the REE abundances in early condensates determined by volatility. REE volatilities are not a smooth function of size, so nebular fractionation based on REE volatility can be readily distinguished from later planetary fractionations (BOYNTON, 1989). In addition, because even the general fractionation between LREEs and HREEs is so great, it is hard to envision a mineral preference effect that would completely negate this nebular process. In the case of ureilites, the abundance pattern for olivine/pyroxene is strikingly similar to that produced during igneous processing, not that produced during nebular condensation. Finally, KURAT (1988) states that during heating the LREEs are remobilized and leave the olivines but that the HREEs are not and remain in the mineral. No temperature is given for this phase. Again, if this model is correct, the resulting concentration must overprint that derived from nebular processes. Not only is the diffusion of LREEs alone highly unlikely under plausible scenarios but the overprint is as well.

WARREN and KALLEMEYN (1989) presented an intriguing model for ureilite petrogenesis which they termed a "partially-disruptive impact model." As with the KURAT (1988) model, this is also problematic to the modeller of ureilite petrogenesis because the parameters are ill defined. Essentially, it is an *ad hoc* model; it presents specific elements that must occur in specific proportions in order to explain the concentrations which we observe in ureilites.

Problems arise in the physical assumptions of this model. First, it is not clear that in an asteroid-size body the density stratification is great enough to dislodge the crust or magma ocean more easily than the paracumulate. While it is true that material strength is important in collisional disruption and that the stronger, more centrally located basalt-poor portions of the target will be favored in reassembly, it is unclear as to whether one can expect any reassembly of such molten particles. If the material is partially molten, the melt will break up into smaller pieces than a solid material. It will, therefore, be less likely to reassemble. The WARREN and KALLEMEYN (1989) model requires that the partially molten material resist dissipation to great extent.

Second, the size and impact velocity must be just right for the C-rich material to disperse throughout the crystal mush. It is highly unlikely that such an impact can occur to melt the impactor (silicates as well as C-rich material) and not the partially molten crystals which are represented by the silicates in ureilites today and are said to preserve their original orientation.

Third, according to the authors' mass-balance calculations, the final mixture contains varying amounts of C (82.5%), O (9.0%), Fe (5.1%), Mg (2.8%), and Al (0.17%). These proportions require the authors to present additional constraints to resolve the problem of disposing of the different amounts of these elements. Again, a series of more complex and *ad hoc* events is called upon to occur—and perhaps on several different parent bodies.

The oxygen isotope dilemma

The O isotope values presented to date, and upon which the primitive origin argument is based, are only for bulk ureilites. When trying to reconcile the bulk data on O and the major, minor, and trace element data, one must consider that we may be confusing components from various sources and not examining the primary constituent. For example, if the WARREN and KALLEMEYN (1989) model were correct, what is the projectile's contribution to the resulting body and how would this effect the O isotopes or metasomatism on the parent body? The O isotope data and correlations which call for a primitive origin of ureilites (no igneous process imprint is observable) may in fact reflect the effects of mixing an exotic component into an igneous process-derived product. There are few data on element concentrations of separate minerals from the ureilites and data on oxygen isotopes from separates of ureilites. Distinct components or areas of minerals could conceivably have different isotopic signatures. If, for instance, the olivines are zoned with respect to O isotopes, it could be the result of reaction between original ureilitic material and exotic material. The trace element concentrations—the differences in leaching components and mineral separates—certainly makes one consider the implications for O isotopes and models based on the bulk data.

Summary

The data which point to complex origins for the ureilites are (1) Ca/Al ratios in major silicates (GOODRICH et al., 1987a), (2) the Eu anomaly variability and degree, (3) REEs showing two components (LREE and HREE enrichment) and age data which suggests activity at 3.74 Gy (GOODRICH et al., 1987a, 1988). Simple petrogenesis is implied by O isotope data for bulk meteorites (CLAYTON and MAYEDA, 1988), carbon isotope data (GRADY et al., 1985), siderophile

data, and an age of 4.55 Gy for acid-leached samples (GOODRICH et al., 1988).

The trace element data do not correlate with the groupings displayed by any other ureilite characteristics and do not provide a simple or conclusive answer to the dilemma of ureilite petrogenesis. Instead, they do point to ureilites as mixtures of materials analogous to terrestrial ultramafic rocks. Similar geochemical data (especially the REEs) on such rocks can, therefore, provide further insights on ureilite formation.

Our analyses of terrestrial samples (Table 4) reinforce the idea of small-scale heterogeneity in ultramafic petrogenesis as suggested by FREY and PRINZ (1978). While our data are broadly consistent with earlier analyses (FREY et al., 1971; FREY and PRINZ, 1978), they do promote the idea that heterogeneity of the mantle exists on a small scale in these localities: the three San Carlos separates that we analysed mimic the variety of trace-element abundances seen in spinel dunite, spinel lherzolite, spinel-olivine orthopyroxene + websterite, and spinel-olivine-clinopyroxene + websterite samples (FREY and PRINZ, 1978). Our analysis of Twin Sisters dunite is also comparable to the earlier analyses but shows less LREE enrichment (La/Yb at 1.1 vs. 5.2 and 4.4). The Cazadero peridotite analysis shows less difference from previous studies. These trace element abundances in the terrestrial ultramafic bulk rocks have been attributed to the trapping of migrating melts in residues which remained from previous melting episodes (FREY and PRINZ, 1978; FREY, 1984). The variation of the REE abundances in samples which lie in close proximity is then easily understandable as a reflection of the heterogeneous distribution of the melt within a fairly uniform residue. Extrapolating this to the ureilite parent body(ies), the heterogeneity of trace elements within and among samples is not unexpected—such mixtures of material are common in ultramafic rocks on Earth and apparently in our collections

TABLE 4. REE abundances (in ppb) in terrestrial ultramafic rock.

Sample	Type	Weight(mg)	La	Ce	Nd	Sm	Eu	Gd
DTS-1	bulk	537.71	25.1			3.9	2.9	
	residue	56.44	7.4		6.7	1.6	0.02	
PCC-1	bulk	445.44	43.9			5.1	2.7	
	residue	73.09	6.8		59.9	1.6	0.02	
PM-2-18	ol-rich sep.	457.55	623.4	1440	573.0	129.6	48.5	
PM-2-31A	ol.pyx sample	500.61	78.1	567.8		244.1	110.8	
PM-2-42E	pyx-rich sep.	494.10	769.6	3379	3725	1203	422.8	
Sample	Type	Tb	Dy	Ho	Tm	Yb	Lu	
DTS-1	bulk	23.7		6.9		22.3		
	residue	2.3	2.4	0.7	0.6	3.7		
PCC-1	bulk	22.9		7.1		18.6		
	residue	0.12	4.8	1.5	1.3	9.7		0.2
PM-2-18	ol-rich sep.	24.2		209.7		79.9	8.9	
PM-2-31A	ol.pyx sample	68.2		131.8		447.4	66.9	
PM-2-42E	pyx-rich sep.	207.9		236.8		621.6	79.9	

Bulk and separate samples determined by INAA. DTS-1 and PCC-1 errors \leq 30%, San Carlos samples' errors \leq 20%, except those of La and Ce for PM-2-31A which are $<$ 30%. Errors based on counting statistics.

of extraterrestrial ultramafic rocks. This heterogeneity and the mixing of materials may result from solely parent body activity or from the introduction of physical and chemical effects from an impact event. This viewpoint provides a revised leitmotif with which we can look at the ureilites; considering them as mixtures of materials and designing future research in line with this premise may be the only way to unravel the ureilites.

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