

SIDEROPHILE GEOCHEMISTRY OF UREILITES: READING THE RECORD OF EARLY STAGES OF PLANETESIMAL CORE FORMATION

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Ureilites, the second most abundant type of achondrite, formed as partial melt restites (olivine + pyroxene + minor, 0.2-6 wt%, carbon) in the mantles of carbonaceous asteroids. Degrees of melting were sufficient to virtually eliminate plagioclase from the entire ureilite milieu; at temperatures of ~1210-1300°C [1]. According to some recent interpretations [e.g., 2,3] core formation commences not long after an asteroidal interior reaches the Fe-FeS eutectic (~990°C). This scenario seems implausible for the interior of an asteroid, where extensive mobilization of solid components (without implausibly high S, only minor proportions of metal will melt near the eutectic) can only be expected as a concomitant of extensive matrix melting. At any rate, at about the same time the ureilites underwent partial melting, they acquired moderate to major depletions in siderophile elements. Natural siderophile variations are notoriously untidy, but collectively the many ureilite samples can potentially furnish important insight into the early stages of core formation.

For this work, we employed INAA to determine trace elements (including highly siderophile elements Ir, Os, Au, Ni and Ru) in 22 ureilites, including several with unusual traits, such as high-mg silicates. Samples studied were typically 300-500 mg in mass. Ureilites have Ni, Au and Ir concentrations that are very high in relation to NAA detection limits, so analytical precision should be excellent. Os is also easily detected, given a favorable counting schedule; Ru and some interesting moderately siderophile elements such as As and Se are doable but more challenging. Selected results are shown in Table 1. Except for the uncommonly fresh FRO90054, warm-desert ureilites (about 1/3 of the samples studied) have been excluded from Table 1. The results for such samples typically show weathering-contamination effects for moderately siderophile elements such as As and Sb (highly siderophile elements are seldom noticeably affected, however).

One of the more interesting samples studied is MET01085, classified as a ureilite [4] even though it is devoid of olivine (as sampled in one set of thin sections; the meteorite's total mass is only 30.6 g), consisting wholly of pigeonite + minor carbon. Our bulk-rock data reflect the dominance of pigeonite; the HREE/LREE ratio is exceptionally high, and the olivophile element Co is uncommonly low (23 µg/g) and pyroxophile Sc is high (15 µg/g). Our *e*-probe results (97 analyses; randomly selected spots) indicate remarkable uniformity for the pigeonite: $\text{Fs}_{10.77} \pm 0.17 \text{Wo}_{4.57} \pm 0.07$. The minor element

Table 1. Bulk-rock ureilite compositions determined by INAA.

	Na	Mg	Al	Ca	Sc	V	Cr	Mn
	mg/g	mg/g	mg/g	mg/g	µg/g	µg/g	mg/g	mg/g
Asuka 881931	0.73	192	4.1	12.7	10.3	111	4.4	2.8
EET87511	0.26	211	2.7	8.0	8.2	99	5.0	3.3
EET96328	0.24	242	4.0	6.5	7.0	113	4.5	3.2
EET90019	0.24	213	2.4	7.5	7.9	91	4.1	3.1
EET96001	0.23	189	2.9	7.7	6.6	93	3.2	2.6
FRO90054	0.76	175	6.6	47	24.3	151	5.4	3.2
GRA95205	0.28	213	2.6	5.1	6.3	101	4.4	2.8
GRO95575	0.16	213	2.0	9.7	8.1	119	4.9	3.0
LEW88006	0.17	213	3.2	12.3	11.5	136	5.4	3.1
QUE93341	0.44	207	3.2	9.9	9.7	101	4.3	2.9
Y791538	0.28	206	2.4	14.8	11.79	101	4.8	3.4

	Fe	Co	Ni	Zn	Ga	As	Se	Br
	mg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Asuka 881931	119	74	820	260	2.4	0.18	2.1	1.4
EET87511	93	21	200	260	1.15	<0.06	0.27	0.4
EET96328	83	21	230	250	1.36	0.03	0.36	1.4
EET90019	94	139	1690	330	2.2	0.43	—	0.41
EET96001	117	146	2090	200	2.9	0.52	4.0	0.39
FRO90054	110	80	1260	92	5.4	0.10	2.6	1.4
GRA95205	122	117	1350	180	1.83	0.21	1.0	2.1
GRO95575	116	55	490	170	1.91	0.08	0.64	2.2
LEW88006	120	43	540	360	3.0	<0.29	0.66	1.8
QUE93341	136	139	1550	175	3.2	0.33	1.2	2.2
Y791538	77	103	1220	290	2.8	0.34	0.62	0.76

	La	Sm	Eu	Yb	Lu	Os	Ir	Au
	µg/g	µg/g	µg/g	µg/g	µg/g	ng/g	ng/g	ng/g
Asuka 881931	0.04	0.019	0.02	0.078	0.014	108	105	15
EET87511	0.03	0.006	<0.005	0.038	0.007	<150	74	4.2
EET96328	0.02	0.004	0.005	0.028	0.009	119	109	6.4
EET90019	0.04	0.020	<0.03	0.082	0.011	290	260	42
EET96001	<0.02	0.015	<0.004	0.056	0.012	370	340	55
FRO90054	0.07	0.14	0.04	0.21	0.039	120	117	19
GRA95205	<0.05	0.006	0.009	0.024	0.007	450	390	26
GRO95575	0.014	<0.01	0.005	0.028	0.009	260	221	10.8
LEW88006	<0.2	<0.02	0.008	0.059	0.013	170	131	18
QUE93341	<0.2	0.010	0.01	0.054	0.014	460	420	35
Y791538	<0.06	0.015	<0.009	0.11	0.018	300	230	34

Preliminary data from Dec 2004 INAA

	Ni	As	La	Sm	Yb	Os	Ir	Au
GRA98032a	760	0.15	<0.02	<0.01	0.018	330	250	19
GRA98032b	910	0.19	<0.01	<0.003	0.021	330	250	23
MET01083	930	0.12	<0.02	0.010	0.036	110	100	19
MET01085	370	0.11	0.014	0.031	0.16	200	190	11.7

contents (0.94 wt% Cr₂O₃, 0.52 wt% MnO) are at least broadly consistent with trends among pigeonites of similar major-element composition [5] from "certifiable" ureilites. But this mineralogical test is not definitive. An almost equally close resemblance could be claimed for some pyroxenes from lodranites and acapulcoites [5]. However, our bulk-rock siderophile data (e.g., Au/Ir, Ni/Ir, As/Ir systematics) also conform with previous trends among ureilites. The extraordinarily ferroan (Fo75) ureilite GRA98032 appears rather nondescript, from a trace-element bulk chemistry perspective.

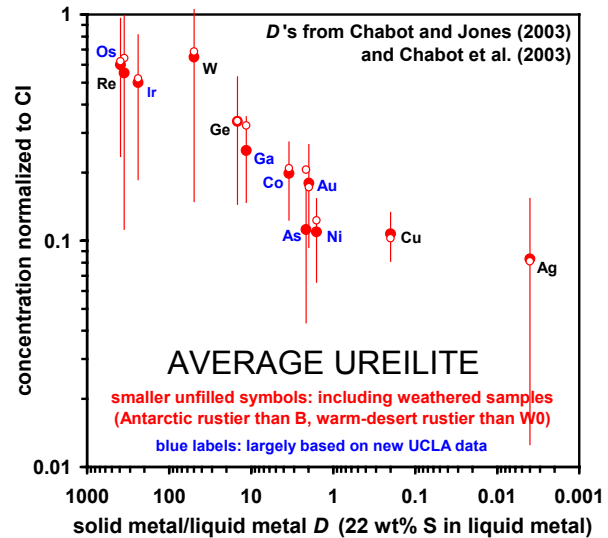
Combined with literature data (sources too numerous to list here; partly UCLA [e.g., 6], with [7-9] among the most noteworthy additional sources),

we now have constraints for Ir in 44 ureilites; with similar tallies for Ni (47) and Au (39). Unfortunately, about 1/3 of these data represent significantly weathered samples. In the remaining discussion, unless specifically noted, weathered samples are excluded from consideration. A plot of Au vs. Ni shows a good, approx. linear correlation ($r = 0.87$), which interestingly extrapolates to a much lower Au/Ni (by a factor of ~ 2) than the range for carbonaceous chondrites. Au vs. Ir and Ni vs. Ir show much more scatter. But a very strong correlation ($r = 0.95$) is manifested by Au/Ir vs. Ni/Ir, which parallels a trend among carbonaceous chondrites, but is offset (toward lower Ni/Au) by a large and clearly significant factor. Analogous distributions are found if As/Ir, Co/Ir, Se/Ir or Te/Ir are substituted for Ni/Ir, except with these parameters the carbonaceous chondrite and ureilite trends approximately overlap.

Evidently, the final levels of Au and Ni among ureilites were established by a different process than the process(es) that had earlier depleted both, but Au more than Ni. Also, the effect of metal removal should be to drive a restite composition toward higher Au/Ir and Ni/Ir (since Ir is the most highly siderophile of these elements), yet the main direction of ureilite differentiation, assuming the precursor materials were chondrite-like, was toward lower Au/Ir and Ni/Ir.

We now address the origin of the overall siderophile depletion pattern in the grand average composition of all ureilites. When this composition is normalized to CI and plotted as a function of the elements' solar nebula 50% condensation T [10], the depletions in elements like Au, Co, Ni and As appear to be in conformity with a loose overall correlation. However, two somewhat siderophile elements (Ge and Zn) are little-depleted even though moderately volatile; instead, Ge and especially Zn plot near C, which is highly volatile (in a solar-nebula setting) and yet only marginally depleted relative to CI.

The grand average ureilite composition yields a tidier trend when instead of a measure of volatility, we make the x-axis parameter a measure of affinity of the elements for S-rich metallic melt (Fig. 1). Even though we have no way of determining how much S became differentiated away from the protoureilitic matter, the first metal-rich melts (which were quite possibly the first traces of melt of any kind) presumably contained about 20-30 wt% S, as an inevitable consequence of the Fe-FeS eutectic relationship [11]. Chabot and her colleagues [12,13] have constrained the relevant partitioning relationships for many elements. It would be good to obtain solid metal/liquid metal D 's for some additional elements, most notably Zn, but the available data manifest an impressive match between



ureilite observed compositions and a model assuming that the major yet not exhaustive depletions of typical ureilites formed by down-seepage of small proportions of S-rich metallic melt.

Such a model seems plausible from the perspective of independent constraints on the nature of ureilite partial melting. Seepage of S-rich metallic melt was probably facilitated within the nascent restites by the lubrication effect of a considerable proportion (f) of temporarily stored $1250 \pm 50^\circ\text{C}$ [1] silicate melt. We know from the virtually complete removal of plagioclase that a total f of (at least) 20-25 wt% of silicate melt was ultimately extracted. Application of compaction theory [e.g., 14] to the scenario of asteroidal partial melting suggests that the melt could never escape in time (before the decay of ^{26}Al and/or other short-lived primordial heat sources) by steady, low- f percolation. Thus, paradoxically, melt build-up to high- f "batch" partial melting would be a more temporally efficient melt removal mechanism. Moreover [6], the incompatible element levels of typical ureilites militate for a melting style much closer to batch (a.k.a. "equilibrium") melting than to fractional fusion.

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