

## Chemical characterization of a "mysterite"-bearing clast from the Supuhee chondrite

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**Abstract**—HIGUCHI *et al.* (1977) proposed the existence of Ti-rich and Ti-poor "mysterite" to explain Ti and Bi contents of dark clasts in the Supuhee H6 chondrite and of bulk Supuhee. They suggested that these two components formed by gas-dust fractionation during condensation. An aliquot of one of the clasts studied by Higuchi *et al.* and found to contain Ti-poor mysterite was analyzed by instrumental neutron activation in this paper. A complex assortment of element fractionations was found. Data for rare earth and other refractory lithophiles and refractory and moderately volatile siderophiles are consistent with random separation and reunification of gas and dust throughout the condensation sequence. Independent evidence thus exists that processes like those invoked by Higuchi *et al.* to explain mysterite did occur in the region of the nebula sampled by this clast.

### INTRODUCTION

DURING a study of volatile element abundances in ordinary chondrites, LAUL *et al.* (1973) found that four samples of the brecciated H6 chondrite Supuhee showed striking enrichments in the siderophile volatile elements Ag, Bi and Ti. They noted strong positive correlations between these elements and proposed that a late condensate, "mysterite", from a metal-depleted region was added to Supuhee in a brecciation event. HIGUCHI *et al.* (1977) have made a detailed study of trace element abundances in four dark clasts and a vein sample from Supuhee. They found that one clast was uniformly enriched in all volatile elements relative to C1 chondrites. The other four samples were enriched only in the siderophile volatiles Ag, Bi and Ti relative to H5 and H6 chondrites. The proportions of Ag, Bi and Ti in the clasts and in the meteorites analyzed by LAUL *et al.* (1973) suggest to HIGUCHI *et al.* (1977) the existence of two varieties of mysterite: Ti-rich ( $Ti/Bi = 7.2$ ), which dominates in the bulk samples of Supuhee and Krymka and Ti-poor ( $Ti/Bi < 0.1$ ), which dominates in the bulk sample of Mezö-Madaras and in the Supuhee clasts. We decided to analyze an aliquot of one of the dark clasts studied by HIGUCHI *et al.* (1977) in order to further characterize the material proposed to contain Ti-poor mysterite.

### EXPERIMENTAL METHODS AND RESULTS

E. Anders kindly provided us with a 1.17 mg piece of Clast 4J, separated from British Museum specimen 39714. No petrographic description of the clast is available. We have analyzed the clast for 24 elements by INAA, using techniques described in previous publications from this laboratory (GROSSMAN and GANAPATHY, 1975; 1976a; DAVIS *et al.*, 1977).

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The results are shown in Table 1, along with  $1\sigma$  errors based on counting statistics in sample and standard. The results of HIGUCHI *et al.* (1977) for Supuhee Clast 4J are also shown in Table 1 for comparison. Our value for Se has a large uncertainty, reflecting the poor counting statistics in our irradiation standard. Thus, the Se value of HIGUCHI *et al.* (1977) is to be preferred. Our result for Sb is a factor of four lower than that of HIGUCHI *et al.* (1977) who believe their sample to be contaminated with Sb. Since our sample is a split of the one analyzed by them, ours may also be contaminated with Sb. Our results for Os, Ir and Au are based on standards which had been run in previous irradiations. The specific activities of  $^{191}\text{Os}$ ,  $^{192}\text{Ir}$  and  $^{198}\text{Au}$  at the end of the Supuhee irradiation were calculated from their values in a previous irradiation by correcting for differences in neutron fluence using  $^{46}\text{Sc}$  in the irradiation standard SP. Both irradiations were made in the same reactor position for the same length of time. Our values for Ir and Au are lower than those of HIGUCHI *et al.* (1977) by a factor of  $\sim 2$ , but excellent agreement was obtained for Os. The discrepancies between our laboratories for Ir and Au cannot, therefore, be due to errors in the fluence correction, but may be due instead to sample heterogeneity.

### DISCUSSION

The enrichment factors relative to C1 chondrites are given in Table 1. Also listed in Table 1 are the C1 values used for normalization and the literature sources for these data. For Na, we averaged values for Ivuna and Orgueil of SCHMITT *et al.* (1972) and NICHIPORUK and MOORE (1974) with those for Orgueil of GROSSMAN and GANAPATHY (1975). For Mn, we averaged values for Ivuna and Orgueil of SCHMITT *et al.* (1972) with those for Orgueil of GROSSMAN and GANAPATHY (1975). For Cr, we averaged values for Ivuna and Orgueil of SCHMITT *et al.* (1972) with those for Orgueil of GROSSMAN and GANAPATHY (1976a). For Cu, we averaged values for Ivuna and Orgueil of SCHMITT *et al.* (1972).

The enrichment factors for Supuhee Clast 4J are plotted in Fig. 1, with the lithophile elements divided

Table 1. Elemental abundances and enrichment factors relative to C1 chondrites in Clast 4J of the Supuhee chondrite (concentrations in ppm unless otherwise indicated)

	This work	Higuchi <i>et al.</i> (1977)	C1 Chondrites	Clast 4J/C1
Na	7396 ± 9		5040(1)	1.47
Ca	1.22 ± 0.10%		0.975%(2)	1.25
Sc	10.76 ± 0.02		6.4(2)	1.68
Cr	4860 ± 10		2660(1)	1.83
Mn	2790 ± 50		1920(1)	1.45
Fe	22.9 ± 0.2%		18.40%(3)	1.24
Co	462 ± 2		478(10)	0.97
Cu	169 ± 1		119(1)	1.42
Ga	6.8 ± 0.7		9.6(4)	0.71
As	3.5 ± 0.3		1.8(5)	1.94
Se	22 ± 13	6.6	19.5(6)	0.34*
Sb	0.55 ± 0.07	2.12	0.138(6)	3.99
La	0.97 ± 0.03		0.253(7)	3.83
Ce	1.8 ± 0.3		0.645(7)	2.79
Sm	0.325 ± 0.010		0.154(7)	2.11
Eu	0.119 ± 0.014		0.0587(7)	2.03
Yb	0.22 ± 0.04		0.168(7)	1.31
Lu	0.047 ± 0.004		0.0253(7)	1.86
Hf	0.22 ± 0.06		0.11(8)	2.00
Os	1.05 ± 0.15	1.04	0.451(9)	2.33
Ir	0.472 ± 0.002	0.852	0.514(6)	0.92
Au	0.126 ± 0.002	0.245	0.152(6)	0.83

(1) See text. (2) Average computed by GROSSMAN and GANAPATHY (1976a). (3) MASON (1971). (4) FOUCHÉ and SMALES (1967). (5) LIPSCHUTZ (1971). (6) KRÄHENBÜHL *et al.* (1973). (7) NAKAMURA (1974). (8) GANAPATHY *et al.* (1976). (9) HIGUCHI *et al.* (1977). (10) GROSSMAN and GANAPATHY (1976a). \*Value of HIGUCHI *et al.* (1977) used for enrichment factor.

into refractory (condensation temperature above that of metallic iron) and less refractory (condensation temperature below that of metallic iron) groups and the siderophile elements in approximate order of volatility (WAI and WASSON, 1977).

The REE pattern for the clast (Fig. 1) is decidedly non-chondritic and is characterized by a sloping pattern with enrichment factors ranging from four for La to two for Lu. The apparent negative Yb anomaly may not be real since the enrichment factors for Yb and Lu agree within 2σ error limits. Although the steep negative slope of the REE pattern from La to

Sm is suggestive of igneous differentiation processes, the pattern also closely resembles those of Allende matrix and whole rock samples (TANAKA and MASUDA, 1973) which certainly escaped such processes. All Allende bulk samples are mixtures of several independently-formed components, some of which underwent fractionation of rare earth elements during the condensation process (GROSSMAN and GANAPATHY, 1976a; 1976b). The oxygen isotopic composition of this clast would be a good test of fractionation of REE during condensation, since all samples showing REE patterns fractionated in this

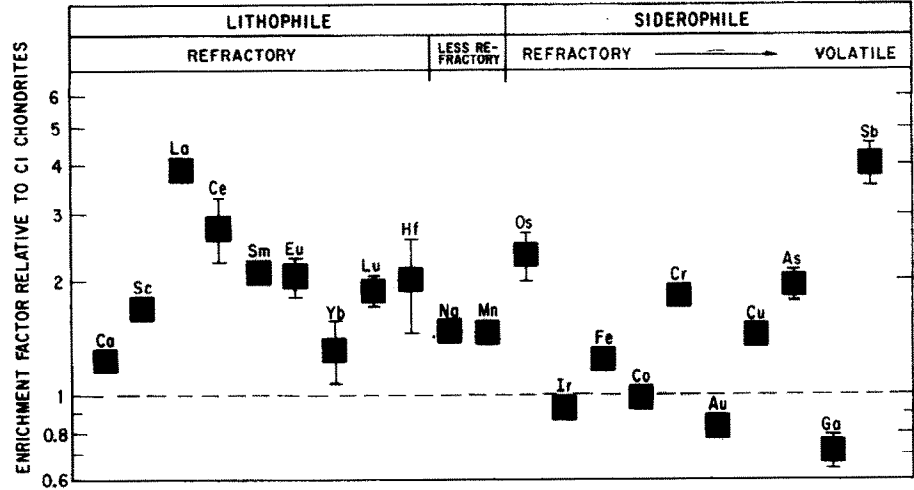


Fig. 1. Element enrichment factors relative to C1 chondrites in dark Clast 4J from the Supuhee H6 chondrite (1σ error bars are shown when the errors are larger than the symbols).

Table 2. Refractory siderophile element ratios in Clast 4J, H5 and H6 chondrites and C1 chondrites

	This work Clast 4J	Clast 4J	Higuchi <i>et al.</i> (1977) H5 and H6	C1
Re/Ir		0.091	0.101	0.068
Os/Ir	2.22	1.22	1.03	0.88

manner are accompanied by an enrichment in  $^{16}\text{O}$  (CLAYTON *et al.*, 1977). A more complete REE pattern would also be useful in identifying REE fractionation processes in Clast 4J.

Ca, Na and Mn are enriched in the clast by similar factors relative to C1 chondrites, 1.25–1.47, while Sc and Hf have higher enrichment factors, 1.68 and 2.00, respectively. Because Sc and Hf are  $\sim 90\%$  condensed before Ca begins to condense (GROSSMAN, 1972; 1973), the lithophile element abundance pattern suggests admixture of early condensate dust to material of approximately chondritic major element composition. It is conceivable that igneous processes also could have produced these chemical characteristics.

The enrichment factors of the siderophiles show substantial variations from element to element which are not correlated with volatility. The ratios Re/Ir and Os/Ir are higher than in C1 chondrites in the sample of Clast 4J analyzed by HIGUCHI *et al.* (1977) and in the mean of several H5 and H6 chondrites reported by them. We find that our sample of this clast has a substantially higher Os/Ir ratio than theirs. The variability of the Os/Ir ratio in the clast, Table 2, suggests the presence of at least two refractory siderophile element components. The only processes known to fractionate noble siderophile elements from one another in meteorites are condensation and solid–liquid differentiation of metal. Differentiation processes such as fractional crystallization or partial melting and liquid loss of the metal phase do not fractionate Re, Os and Ir from one another because these elements have virtually identical solid–liquid distribution coefficients (SCOTT, 1972; KELLY and LARIMER, 1977). Thus, even if the REE pattern is interpreted to have resulted from igneous differentiation processes, such processes cannot have fractionated Re, Os and Ir from one another. These elements can be fractionated from one another during condensation, however. The condensation temperatures of Os and Re are 280 and 200°K higher, respectively, than that of Ir (PALME and WLOTZKA, 1976). The component with high Re/Ir and Os/Ir ratios may represent metal grains removed from equilibrium with the vapor before complete condensation of Ir. The enhanced Re/Ir and Os/Ir ratios in H5 and H6 chondrites may indicate that this component is fairly widely distributed.

Figure 1 shows that with falling condensation temperature, the enrichment factors of the siderophile elements continue to vary even if Fe and Cr, which have some lithophile and chalcophile tendencies, and Sb,

which may be contaminated, are excluded. The enrichment factor for Co and Au is the same as for Ir, rises to Cu, rises further to As and drops to Ga.

The As/Au ratio in Clast 4J, 27.8, is significantly higher than the cosmic ratio, 11.8. Igneous differentiation of metal does not seem to fractionate As from Au by more than 50%, as observed in the group IIIAB irons (FOUCHÉ and SMALES, 1966; SMALES *et al.*, 1967). Because As is more chalcophile than Au, addition of sulfides to chondritic material could conceivably increase its As/Au ratio. This cannot be the cause of the high As/Au ratio in the clast, however, since its Se content is actually depleted relative to C1 chondrites, indicating no excess sulfide component. Fractionation of As from Au can occur during condensation, however. According to WAI and WASSON (1977), the 50% condensation temperatures of Au and As are 1284 and 1050°K, respectively, at  $10^{-4}$  atm. total pressure, assuming ideal solution in metal. If some dust were removed prior to complete condensation of As, the remaining gas would condense with a high As/Au ratio, as observed in the clast. Although differentiation of metal cannot be ruled out as the cause of the variations in enrichment factors of the remaining siderophile elements in the clast, all such variations may be due to gas–dust fractionation throughout the condensation sequence, with dust sometimes being removed and then returned at a lower temperature.

We have found that Supuhee Clast 4J has variable enrichments relative to C1 chondrites of many siderophile and lithophile elements, with the variations showing no correlation with condensation temperature. Some, and perhaps all, of these variations were caused by random separation and reunification of gas and dust throughout the condensation sequence in the region of the nebula sampled by Clast 4J. HIGUCHI *et al.* (1977) propose that the two varieties of mysterite observed in Supuhee formed by gas–dust fractionation during condensation. They suggest that Ti-poor mysterite formed by condensation of Ag and Bi and removal of dust before Ti could condense and that the Ti-rich variety formed during condensation of the remaining gas. Such processes are completely consistent with our findings.

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