Seventh Semiannual Progress Report

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Origin of Chondrites from Relationships Between and Thermal Retentivity of Key Trace Elements

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I. General Remarks

Since submission of our Sixth Semiannual Progress Report (March - August, 1974) the following papers have been published, are in press or have been submitted for publication:

(1) "Trace Elements in Primitive Meteorites-V. Abundance Patterns of Thirteen Trace Elements and Interelement Relationships in Enstatite Chondrites," C. M. Binz, R. K. Kurimoto and M. E. Lipschutz, Geochimica et Cosmochimica Acta, 38, 1579-1606 (1974).

(2) "R-Mode Factor Analysis on Enstatite Chondrite Analyses," D. M. Shaw, Geochimica et Cosmochimica Acta, 38, 1607-1613 (1974).

(3) "Thermal Metamorphism of Primitive Meteorites-I. Variation of Six Trace Elements in Allende Carbonaceous Chondrite Heated at 400-1000°C," M. Ikramuddin and M. E. Lipschutz, Geochimica et Cosmochimica Acta, 39, 363-375 (1975).

(4) "Allende Meteorite : Effect of Thermal Metamorphic Conditions on Mineralogy and Trace Element Retention," M. Ikramuddin, M. E. Lipschutz and W. R. Van Schmus, Nature (London), in press (1975).

(5) "Trace Elements in Primitive Meteorites-VI. Abundance Patterns of Thirteen Trace Elements and Interelement Relationships in Unequilibrated Ordinary Chondrites," C. M. Binz, M. Ikramuddin, P. Rey and M. E. Lipschutz, Geochimica et Cosmochimica Acta, submitted (1975).

(6) "Contents of Eleven Trace Elements in Ureilite Achondrites," C. M. Binz, M. Ikramuddin and M. E. Lipschutz, Geochimica et Cosmochimica Acta, submitted (1975).

As noted in the Sixth Semiannual Progress Report paper (2) above does not acknowledge NASA support but it is based upon research (i.e. paper (1)) supp-

orted by this grant.

II. Trace Element Studies

As discussed in the Fourth (March-August, 1973) Fifth (September, 1973-February, 1974) and Sixth Semiannual Progress Reports, our investigations are proceeding along two major avenues: studying effects of extended heating (i.e. simulated metamorphism) of primitive meteorites; establishing key trace element contents in primitive chondrites and meteorites suspected of being derived directly from them.

A. Laboratory Simulation of Thermal Metamorphic Effects

Since this avenue represents a new approach to trace element studies we continue to emphasize this strongly. In the first paper reporting such experiments, paper (3) cited in part I, we report that determination by neutron activation of 6 trace elements retained in Allende (C3) samples heated at 400-1000°C for 1 week in a low-pressure (initially $\sim 10^{-5}$ atm) H_2 atmosphere reveals loss of small proportions of Ga and Se and large proportions of Bi, In and Tl - Co being unaffected. The retentivity patterns for the 5 mobile elements differ and in no way duplicate the step-function assumed previously. In contrast to these trace elements sulfur is initially present in discrete mineral(s) and visually it appears to be released over a narrow temperature range. Elements are lost more easily from powder than from chips but the difference is $\leq$ 35%. Above 600°C, the process of loss appears due to process(es) with apparent activation energies of 2 kcal/mole (Bi, Tl), 4 kcal/mole (Se) and 22 kcal/mole (In). Loss of Bi and Tl below 600°C involves higher apparent activation energies. Two-element correlation diagrams involving Bi, In and Tl are consistent with the idea that trends among highly-volatile elements in enstatite chondrites arise from metamorphism.

In the second of our studies, paper (4) cited in part I, we report that heating Allende carbonaceous chondrite in a low-pressure environment causes mineralogic alteration at 700-1000°C but not at $T \leq 600°C$. Samples heated for 29 days at 500°C lose Bi, In and Tl more effectively than those similarly heated for 7 days. At 1000°C with $\sim 10^{-5}$ atm. initial pressure of O_2, H_2 or He these elements, Ga and Se are comparatively more completely lost. These results indicate the necessity for additional experiments in order to study elemental loss patterns in primitive objects.

Such studies are now in progress. We have completed determination of 10 trace elements (Ag, Bi, Co, Cs, Ga, In, Se, Te, Tl and Zn) in samples at 100° increments over the 400-1000°C range, including duplicates at 800° and 900°C with a molecular sieve in the cold trap to study internal atmospheric effects. We have also analyzed these data statistically (by factor analysis and to establish the pattern of significant interelement relationships); all results are consistent with the idea that enstatite chondrites reflect metamorphic effects. We are currently preparing a manuscript describing these results.

We have completed trace-element measurements of BCR-1 powder heated at 100°C increments over the 500-1000°C temperature span. This study is aimed at comparing trace element retentivity in a sample formed at high temperatures with retentivities in low-temperature accumulates like primitive meteorites. The elements studied include Ag, Bi, Cd, Co, Cs, Ga, In, Se, Tl and Zn (Te was below our detection limit). While most elements yielded coherent trends, Ag, Cd and Se were erratic; we now suspect the cause for this and plan a series of experiments using BCR-1 chips similarly heated.

We have completed heating samples (at 100°C increments over the 400-1000°C range) of an unequilibrated ordinary chondrite (UOC) and will shortly begin

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analyzing these to extend our studies to this third major sort of primitive chondrite.

As in our Allende study, in addition to trace elements, we are continuing to determine the mineralogic and petrologic characteristics of heated samples (Abee, BCR-1, etc.) in cooperation with Professor W. R. Van Schmus of the University of Kansas. We are continuing to study the nature of the organic compounds generated during the heating of meteoritic and geologic samples in cooperation with Professor C. Ponnamperuma of the University of Maryland.

We have assembled a system that will enable us to extend the studies above to temperatures in the 1000-1400°C range but, because of the pressure of other studies, we have not yet conducted a systematic study of any sample type. We plan to attend to this in the near future.

B. Key Trace Elements in Primitive Meteorites

We have also made substantial progress in this area during the period covered by this report. In paper (1), cited in part I, we describe our determinations of As, Au, Bi, Cd, Co, Cu, Ga, In, Sb, Se, Te, Tl and Zn in 11 samples representing 9 chondrites of grades E4-6. These chondrites exhibit systematic intra- and inter-grade differences particularly for highly-variable elements, the differences being E4 $\geq$ E3 > E6 $\geq$ E5. The abundance pattern for these 13 and an additional 16 elements in E3-6 chondrites differs from those of other primitive meteorites - the carbonaceous and unequilibrated ordinary chondrites. A search for statistically-significant interelement relationships among the 13 elements (for grades E4-6) reveal that 40 element-pairs are linearly and/or exponentially correlated. Similar consideration of data for 37 elements in 12 chondrites (grades E3-6) reveals that 191 element-pairs exhibit such relationships, 170 involving linear and/or exponential correlations,

the remainder involving anti-correlations. The patterns depicting these relationships - i.e. the correlation profiles - and elemental abundance patterns, factor analysis and two-element correlation diagrams are consistent with all enstatite chondrites representing a single evolutionary sequence. The primary process responsible for the chemical trends of these chondrites involved thermal fractionation accompanied by geochemical fractionation of sulfide-plus-metal from silicate, probably during condensation and accretion of solid material from the solar nebula. Chalcophile elements may have been fractionated during condensation or, after accretion, during thermal metamorphism in the parent body. Indeed as described in paper (3) of Part I, the trends of Bi, In and Tl in "as-received" enstatite chondrites are consistent with those in heated Allende samples. No genetic model proposed thus far accounts for the detailed chemical trends although the constrained equilibrium theory and two-component condensation theories qualitatively seem most satisfactory. The correlation profiles of enstatite, carbonaceous and unequilibrated ordinary chondrites are distinctly different pointing to major differences in the formation conditions of these different sorts of primitive meteorites.

As mentioned, our data were supplied to D. M. Shaw and were used by him for factor analysis. These results were published by him (cf. paper (2) in part I) and appeared simultaneously with our study of the enstatite chondrites.

Paper (5) cited in Part I describes our determinations of As, Au, Bi, Cd, Co, Cu, Ga, In, Sb, Se, Te, Tl and Zn in 13 different unequilibrated ordinary chondrites (UOC), i.e. those having chemically-inhomogeneous silicates. This study, together with prior data for key trace elements, completes coverage of this important group of 23 primitive chondrites. Five elements are quite variable in UOC (As and Cd - 10x, In - 15x, Bi - 300x and Tl - 1000x), the

others varying only by 2-4x. Three highly-depleted elements - Bi, In and Tl - are richer by 5-35x in unequilibrated chondrites than in their equilibrated congeners. All 3 elements vary directly in characteristic fashion with disequilibrium parameters for olivine and pyroxene in UOC and generally with petrologic type 3 > 4 > 5 ≥ 6. When normalized to Ni, less-depleted elements vary with chondritic groups in UOC. Examination of statistically-significant interelement relationships among various ordinary chondrite populations involving 34 elements reveals patterns distinct from those of other chondritic groups. These patterns reflect nebular metal-silicate fractionation which preceded or accompanied thermal fractionation. Metamorphic effects are not pronounced among volatile/mobile elements in UOC and, although condensation models seem generally more satisfactory, none successfully accounts for all observations.

Thus it appears that primitive chondrites originated in several ways: carbonaceous chondrites by the mixing of two components differing in thermal history; enstatite chondrites by a nebular thermal fractionation accompanied by a sulfide-plus-metal separation from silicate and followed by metamorphism in a parent body; and UOC by a nebular thermal fractionation accompanied by metal separation from silicate. It seems that there is no unique process by which primitive solar material condensed to form early objects.

In paper (6) cited in Part I we report our determinations of Ag, Bi, Cd, Co, Cs, Ga, In, Se, Te, Tl and Zn in the 6 known ureilites. All 11 elements are depleted below cosmic, i.e. Cl, levels and their characteristic abundance pattern differs substantially from those of the chondritic groups. These and other data can be treated under a variety of assumptions and all treatments lead to the same conclusion: ureilites do not derive from a simple mixture

of volatile-rich chondrites with achondritic material. We suggest, rather, that they derive from a mixture of cosmochemically-fractionated achondritic material (similar but not identical to Chassigny) and a "distillate" of thermally mobile elements which was then shocked during breakup of the parent object.

III. Other Studies

We are continuing our studies of shock effects in meteorites at a low-priority level. We are now preparing a manuscript describing our shock- and cosmogenic gas-study (with Professor G. Herzog of Rutgers University) of samples from known geographic locations around the Odessa crater.

IV. Administrative Information:

The following individuals are co-workers at Purdue currently doing research on this grant:

A. Dr. C. M. Binz, Postdoctoral Research Associate

B. Dr. M. Ikramuddin, Postdoctoral Research Associate

C. Mr. S. Matza, Graduate Assistant in Research

D. Mr. J. Carvalho, Graduate Research Assistant

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