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Trace Elements in Primitive Meteorites-VI
Interelement Relationships in Enstatite Chondrites

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Abstract - A search for statistically-significant (>95% confidence level) interelement relationships among 13 elements determined in the same samples of 9 different enstatite chondrites (grades E4-6) reveal that 40 element-pairs are linearly and/or exponentially correlated. Similar consideration of data for 34 elements in 12 chondrites (grades E3-6) reveals that 171 element-pairs exhibit such relationships, 152 involving linear and/or exponential correlations, the remainder involving anti-correlations. The patterns depicting these relationships - i.e. the correlation profiles - and other information - i.e. 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. 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.

Introduction

The trace element contents of primitive meteorites are generally thought to provide important clues to the evolutionary history of the early solar system. These meteorites include chondrites of the first four petrologic grades defined by the classification scheme of Van Schmus and Wood (1967). Chondrites of the remaining two petrologic grades and certain achondrites may be, according to some authors, equally primitive yet more highly evolved.

In earlier studies in this series (papers I-IV) we determined the abundance patterns of 13 trace elements (Laul _et_ _al_., 1970a, b; Case _et_ _al_., 1973) and interelement relationships among these and other trace elements (Kurimoto _et_ _al_., 1973) in some primitive meteorites - the carbonaceous and unequilibrated ordinary chondrites (UOC). Paper V (Binz _et_ _al_., 1973), which accompanies this one, describes the abundance pattern of 13 such elements in the remaining group of primitive meteorites, the enstatite chondrites. In papers I-III and V all elements were determined in the same sample of each chondrite so as to minimize the effects of sample inhomogeneity in interpreting the results. The elements were chosen so as to represent a broad range of volatilities, i.e. depletion in ordinary chondrites relative to Cl chondrites (Anders, 1964), as well as those thought to provide significant information on geochemical fractionation processes. Other authors (Keays _et_ _al_., 1971; Laul _et_ _al_., 1973) have taken a similar approach in determining 6-13 elements in ordinary and enstatite chondrites, concentrating upon the more volatile elements. In the specific case of the enstatite chondrites, they and Larimer (1973) compared theoretical predictions of a two-component mixing model (Larimer and Anders, 1967) with correlations between only a few pairs of elements.

In this paper we extend the more empirical approach of Paper IV by comparing the interelement relationships among all elements for which there exist considerable data in enstatite chondrites. As before, here we will use "relationships" to imply both correlations and anti-correlations and where only one of these is discussed we will specify the sort of relationship. We will place particular emphasis upon the information provided by this approach regarding the various models proposed for the origin of these chondrites.

Computations and Results

As emphasized in Paper IV comparison of interelement relationships is optimized if all elements were determined in the same sample of a given meteorite by the same group so as to minimize the obscuring effects of sample inhomogeneity and systematic differences. For enstatite chondrites the largest single body of trace element data is that of Paper V for As, Au, Bi, Cd, Co, Cu, Ga, In, Sb, Se, Te, Tl and Zn. We therefore gave preference to these data and ran them first separately (Case 1).

To make our study as complete as possible in the second run (Case 2) we used additional data determined by other groups. Laul et al. (1973) determined six of the above elements (Bi, Cd, In, Se, Tl and Zn) in 10 enstatite chondrites including 7 studied in Paper V. Although the data for these 7 chondrites are in reasonable accord with those of Paper V we chose to ignore them since they were necessarily obtained from other specimens and chemical inhomogeneity effects and systematic differences could mask real interelement relationships. We did however include the data of Laul et al. (1973) for these six elements in the three enstatite chondrites not studied in Paper V.

The major criterion for including data for additional elements was that the element had been determined in a substantial number of enstatite chondrites by a single group. Usually, several elements had been determined in a given study and there was little overlap in the elements determined by various investigators. Where overlap occurred we included only the set of data determined by the technique most sensitive or suitable for the particular element, i.e. X-ray fluorescence, neutron activation or wet chemical. Two sets of Mn data were available (Von Michaelis et al., 1969; Schmitt et al., 1972), the former employing X-ray fluorescence, the latter instrumental neutron activation analsis. We chose to treat these sets separately, designating the data of Schmitt et al., (1972) as Mn'. We treated both metallic Fe (designated as Fe°) and total iron (designated Fe) separately, these data (and those for other elements determined by wet chemistry) being obtained from references cited by Mason (1966) for all chondrites but Atlanta and St. Marks (Wiik, 1969) and Pillistfer (Jarosewich and Mason, 1969). No major-element data exist for Kota-Kota and we assumed an average E4 Si content for this chondrite. Apart from the 13 elements studied in Paper V the elements included are: C, Fe, Fe°, Mg, Ni, S, Si (Mason, 1966; Jarosewich and Mason, 1969; Wiik, 1969); primordial ^{36}Ar, ^{84}Kr, ^{132}Xe (Zähringer, 1968); Al, Ca, K, Mn, P, Ti (Von Michaelis et al., 1969); N (Gibson, 1969); Cr, Mn', Na, Sc (Schmitt et al., 1972); Ag, Cs, Rb (Laul et al., 1973). For reasons discussed above, we ignored other scattered data.

From the variance of the data, our computations, like those in Paper IV, tested the assumption that the abundance (atoms/10^6 Si atoms) of each element is independent of the abundance of each of all other elements considered. We continued to accept only those relationships significant at a statistically reasonable (>95%) confidence and determined the confidence levels of each using Fisher's z-transformation. For each pair of elements, x and y, we continued to test both linear relationships and exponential relationships, (i.e. $y = mx + b$ and $y = (kx)^m$, respectively) and to ignore linear-logarithmic relationships (Paper IV).

The correlation coefficients and levels of significance for statistically significant linear relationships in enstatite chondrites are listed in Tables 1 and 2 (Cases 1 and 2, respectively). As usual a negative correlation coefficient denotes an anti-correlation.

Most of the data of Paper V (i.e. Case 1) were studied by factor analysis in an accompanying note (Shaw, 1973) and these results will be discussed here. It would be improper to study Case 2 data by this technique since they were derived from different specimens.

Discussion

Case 1.

In limiting consideration to only those 13 elements determined in Paper V for 9 different E4-6 chondrites we minimize the obscuring effects of sample inhomogeneity and systematic analytical differences but also the extent of coverage. These elements could involve 78 different possible relationships and a surprisingly high percentage of these are statistically-significant (>95% confidence level) correlations, 38 (49%) linear and 22 (28%) exponential (Table 1).

The data of Table 1 are represented in Fig. 1 to clarify the interelement relationship pattern. As in Paper IV this figure is a correlation profile in which the elements are listed from left to right and top to bottom in order of increasing depletion, relative to Cl chondrites, in ordinary chondrites (Anders, 1964; cf. Paper V). Anders and co-workers suggested that such depletion provides a qualitative measure of volatility in chondrites, a now commonly-accepted idea that will be followed here. Relationships significant at >95% confidence level are indicated to the right of the diagonal line in Fig. 1; those passing a stricter test (>99% confidence level) are indicated to the left.

The two halves of Fig. 1 are not strikingly different suggesting that the commonly-accepted >95% confidence level is a reasonable one upon which to base further discussion. Although adoption of this facilitates discussion the minor drawback noted in Paper IV can be seen in Fig. 1, i.e. that 2 elements (e.g. Sb and Ga) are correlated with a third (Co), yet are not accepted as correlated with each other. These would appear were the acceptance level reduced; however additional fortuitous relationships would also be accepted.

As in carbonaceous chondrites (Paper IV) each of the 8 elements more depleted than Sb, i.e. Ga to In, is correlated with all others (Fig. 1). The variations of these 8 elements reflect the effects of a single factor (Shaw, 1973) which may well be a thermal fractionation process. However we note that most if not all of these 8 elements exhibit chalcophile geochemical behavior (cf. Paper V). Other fractionation processes must be responsible for the other correlations evident in Fig. 1 and this conclusion is re-enforced by the factor analytic approach, Co and Sb reflecting a second factor (Co partly reflects the first factor as well) and As a third (Shaw, 1973). From theoretical grounds the lack of a few Au and Cu data precludes application of factor analysis for these elements. We will defer further discussion of these points until later.

The extremes in the nature of accepted Case 1 relationships (Table 1) can be judged from Fig. 2 illustrating the As-Sb and Bi-Tl correlations which are significant at >95% and >99.99% confidence levels, respectively. (In this figure, as in Fig. 3, the individual Abee results are plotted separately whereas in our computations all Abee data for each element were averaged. We treated Abee as a single specimen so as to minimize the number of meteorites and conservatively maximize the requirements for a given relationship to be accepted.) Figure 2 serves an additional purpose. The As-Sb correlation in enstatite chondrites (Fig. 2a) may be compared with their correlation in carbonaceous chondrites and anti-correlation in unequilibrated ordinary chondrites (cf. Fig. 3a, Paper IV), each of which is significant at >99% confidence level. The Bi-Tl correlation in enstatite chondrites (Fig. 2b) similarly may be compared with the highly-significant correlations in carbonaceous and unequilibrated ordinary chondrites (cf. Fig. 3, Paper II). It is important to note that the empirical data illustrated in Fig. 2b are entirely consistent with a simple dependence between these elements (Paper II) and give no hint of a more complex relationship. We will return to this point in considering Case 2.

Pelly and Lipschutz (1971) observed that the mean Se/Te abundance ratios were virtually identical in all chondritic groups but C3 and E6. These elements are highly-correlated in enstatite chondrites (Table 1) and the exponential relationship is illustrated in Fig. 3a. Figure 3b illustrates that the Se/Te abundance ratio in E4-6 chondrites increases monotonically with increasing Te depletion. The E4 and E6 chondrites are distinctly separated while only one of the two E5 results is intermediate (Paper V). This monotonic direct relationship between two congeners is surprizing but not unanticipated and, in view of the differences in their volatilities as deduced from depletion factors, may be ascribed to thermal fractionation.

Case 2.

The more extended computations involved 34 elements but 36 entities (counting Mn', Mn, Fe and Fe°) in 12 different E3-6 chondrites and this array could involve 630 different possible relationships. Again, a surprising number of these are statistically significant (>95% confidence level), there being 152 (24%) linear and 136 (22%) exponential relationships (Table 2). Of these, there are 138 linear and 119 exponential correlations and 14 linear and 17 exponential anti-correlations. Possibly because of the inclusion of data from various sources the percentage of relationships significant at the same confidence level is lower in Case 2 than in Case 1.

The data of Table 2 are represented in Fig. 4 and, again, the correlation profiles of relationships significant at >95% and >99% confidence levels are not strikingly different. Indeed, the salient features of Fig. 4 are evident in similar correlation profiles of relationships significant at >99.9% and >99.99% confidence levels. The possibility for some chance relationships should always be borne in mind. We note that Mn and Mn' exhibit entirely different correlations and that the two are not correlated suggesting that one or the other set of correlations arise from chance.

One major feature of Fig. 1, the high concentration of entries in the lower right portion, is not altered by the addition of further data (Fig. 4). Indeed, the levels of significance of many correlations involving Se, Zn, Cd, Bi, Tl and In are increased with the addition of data for 3 more chondrites (Tables 1, 2) and some relationships not deemed significant in Case 1 - for example exponential correlations of In with Cd, Bi and Tl - are significant in Case 2 (Figs. 1, 4). We noted earlier that each element more depleted than Sb is correlated with every other such element and this is re-enforced by the addition of data for Ag, Cs and

S, the only such element-pair not significantly related being Ga-Cs. While these correlations at least partly reflect thermal fractionation the five most depleted elements - C, N, primordial Ar, Kr and Xe - exhibit few significant relationships in enstatite chondrites unlike the situation in unequilibrated ordinary chondrites (Paper IV). A variety of explanations spring to mind to account for the absence of relationships involving these five elements and we will not speculate upon these here.

The addition of data for a substantial number of elements less depleted than Sb yields numerous relationships reflecting geochemical fractionation processes (Table 2, Fig. 4), the effects of which are not easy to disentangle. From the correlations involving such elements as Au, Co, Ni and Fe° one of these processes apparently involved fractionation of siderophile elements. Some normally lithophile elements - primarily Mg, Sc, Al and Ca - exhibit anti-correlations with chalcophile elements and this, coupled with abundance trends discussed in Paper V, suggests that formation of enstatite chondrites involved a silicate:sulfide-plus-metal fractionation. The fact that, of all elements considered, only these last four elements exhibit both chalcophile and lithophile behavior in enstatite chondrites (cf. references in Paper V) may be significant and this dual behavior could complicate matters.

Perhaps the most striking feature of Fig. 4 is the numerous correlations between the less-depleted alkali metals (K, Na and Rb) and the depleted elements Ag to In. Most of these depleted (i.e. volatile) elements exhibit chalcophile geochemical behavior and this may provide an important clue to the origin of enstatite chondrites. Unless the ambient conditions of ordinary and enstatite chondrites were so different as to render inoperative the idea that an element's depletion in ordinary chondrites provides a measure of its volatility, these correlations point to chalcophile geochemical behavior of alkali metals in enstatite chondrites.

To investigate this possibility we calculated $\Delta G°$ values from all available $\Delta H°$ and $\Delta S°$ data (cf. references in Hall and Murthy, 1971) for the species in the reactions:

$$MeO + FeS \rightarrow MeS + FeO$$

$$MeO + Fe \rightarrow Me + FeO$$

$$Me + FeS \rightarrow MeS + Fe$$

where Me represents a metal. We recognize that this is a zeroth order approximation since the various species are not in their standard states in meteorites and equilibration, if it occurred, took place at temperatures other than 298°. We constructed correlation profiles analogous to Fig. 4 except that the elements were listed in order of more negative $\Delta G°$/mol Fe rather than increasing depletion. Figure 5 illustrates the results for the first reaction; similar but less coherent patterns are obtained for the other two reactions. The large number of correlations to the lower right of Fig. 5 and the anti-correlations of Al, Mg and Ca with chalcophile elements suggest that a silicate:sulfide separation was important in forming the enstatite chondrites. We cannot determine whether this geochemical fractionation or thermal fractionation were predominant in establishing the abundances of the more depleted elements. In fact we believe that both occurred simultaneously during condensation of solid material from the solar nebula, perhaps by the mechanism of Blander (1971).

We suggest that the combined geochemical and thermal fractionation process can be identified with factor 1 which is responsible for the variance of Ga, Se, Te, Zn, Cd, Bi, Tl and In (Shaw, 1973). We are puzzled as to the physical processes to be identified with the factors for the other three elements considered by Shaw (1973) - Co being loaded about equally by factors 1 and 2 and

Sb and As being loaded by factors 2 and 3, respectively. It seems difficult to ascribe factors 2 and 3 to separate geochemical processes since all three elements are partly or entirely siderophilic in ordinary chondrites (cf. references in Paper V). This behavior seems characteristic of these elements in enstatite chondrites as well since Co, As and Sb are each linearly and exponentially correlated with both Fe and Fe° (Table 2, Fig. 4). The other relationships exhibited by these three elements, both among themselves and with other elements, follow no other coherent trends suggesting that factors 2 and 3 are separate manifestations of the siderophilic fractionation indicated by other Case 1 and Case 2 data (Tables 1, 2, Figs. 1, 4). This suggestion is consistent with the fact that other Case 1 elements considered by Shaw (1973) generally do not exhibit siderophile geochemical behavior in chondrites and are not correlated with Fe° (Table 2, Fig. 4).

Genetic Models

Various models have been advanced to account for the origin of enstatite chondrites. Each can successfully account for the mineralogic and petrographic features, gross chemical composition and differences between Types I (E3, 4) and II (E5, 6) enstatite chondrites, i.e. higher Fe and volatile and chalcophile trace element contents in the former Type. At times these models invoke specific ad hoc assumptions to account for one or more of these features. We will mention these only incidentally in comparing the results of this study and Paper V with predictions of these models.

Conceptually, the most attractive of these models is that enstatite chondrites originated by metamorphism within a chemically-imhomogeneous parent body, the inhomogeneities having arisen from variations within the solar nebula or differences in the condensation histories of nebular material. Variants of this model are that all enstatite chondrites constitute a single suite, the progenitor being similar in composition to the E3 chondrite Adhi-Kot (Mason, 1966) or that Types I and II enstatite chondrites are collateral descendents of a common source material (Keil, 1968). The strength of this model lies in accounting for the mineralogic and petrographic character of enstatite chondrites and neither variant makes specific chemical predictions that can be tested. Several general trends however argue against these proposals, the relationship between highly-depleted elements and petrologic grade, i.e. E4 $\geq$ E3 > E6 $\geq$ E5 (Paper V), being the most cogent particularly with reference to Mason's (1966) variant. This trend is a serious stumbling-block to all other genetic models as well although it can be bypassed by one or more ad hoc assumptions that can be accommodated by all of these. Two-element correlation diagrams (e.g. Figs. 2, 3, 6 and others) suggest that all enstatite chondrites constitute a single evolutionary sequence. This would argue against Keil's (1968) proposal especially since the elements considered in some of these diagrams are affected by different factors (Shaw, 1973), hence different geochemical processes. It would appear therefore that metamorphism is not the sole nor even the major process responsible for formation of the enstatite chondrites although this process could conceivably have altered the distribution of highly-volatile elements somewhat.

We must therefore conclude that the primary chemical differentiation processes occurred prior to agglomeration of the enstatite chondrites, i.e. during condensation of solid material from the solar nebula and several such models have been proposed. Arrhenius and Alfvén (1971) propose that all primitive material condensed from a low-density, high-temperature, partly-excited gas. Their data predict observed correlations of Ni/Fe and among:

Bi, Tl and In; and Fe, As and Sb. However the predicted correlations of As/C, Sb/Ni, Cd/As, Cd/C and Bi/Ni are not observed and observed correlations of Cd with Bi, Tl and In are not consonant with their data. In balance, at present our data would not support this model strongly for the origin of enstatite chondrites. It remains conceivable (Paper IV) that the unequilibrated ordinary chondrites originated in this manner.

The two-component condensation model of Anders and co-workers (Anders, 1964; Larimer and Anders, 1967; Laul et al., 1973; Larimer, 1973 and others) rests mainly on chemical evidence and is most specific with regard to predictions. According to this model the trace element distributions in all primitive meteorites were established during accretion by the mixing of two components differing in thermal history, hence in composition. For carbonaceous chondrites, the empirical results are in very good agreement with the model; however the agreement is less good for unequilibrated ordinary chondrites (Paper IV). In subsequent papers we will present results of an extended study of these primitive ordinary chondrites. In enstatite chondrites the nearly ubiquitous correlations of the elements Ag to In (Fig. 4) together with covariance (Shaw, 1973) of the Ga, Se, Te, Zn, Cd, Bi, Tl and In data of Paper V are predicted by this model. Most remaining relationships are not predicted by this thermal fractionation model although clearly they are not excluded by it. The general lack of correlations of C, N and the noble gases both among themselves and with other volatile elements does seem an inconsistency but this can be removed by an ad hoc assumption (cf. Laul et al., 1973).

Larimer (1973) recently revised earlier calculations (Larimer and Anders, 1967) of the fractional condensation patterns of Bi, Cd, In, Pb and Tl according to the two-component model and compared the In and Cd data for enstatite chondrites (Laul et al., 1973) on a two-element correlation diagram with his calculations. He concluded that 7 of 10 chondrites agreed well (i.e. within a factor of 2) with the behavior predicted by this model for ambient pressures of 5×10^{-5} atm to 5×10^{-4} atm. Laul et al. (1973) slightly modified Larimer's (1973) calculations and concluded that on Tl/Bi and In/Tl two-element correlation diagrams their data generally agreed quite well with theoretical predictions of the two-component model for ambient pressures of 10^{-4} atm and 5×10^{-4} atm.

Our consideration of two-element correlation diagrams (Fig. 6) of Case 2 data for Bi, Cd, In and Tl compared with theoretical predictions of the two-component model (Larimer, 1973) does not lead to such an unambiguous conclusion. In two instances, i.e. Tl/Bi and In/Tl (Figs. 6a and 6c, respectively), most points lie within a factor of two of the theoretical curves but in four other cases, i.e. In/Bi, In/Cd, Tl/Cd and Bi/Cd (Figs. 6b, 6d, 6e and 6f, respectively), the general agreements are much poorer. One might rationalize the disagreements by adopting ad hoc assumptions but it is important to note that all six two-element diagrams involve correlations significant at confidence levels (Table 2) ranging from >96% (In/Cd) to >99.9999% (Tl/Bi). The data (Fig. 6; cf. Fig. 2b) indicate that these two-element relationships are more adequately described by straight-line relationships on linear or logarithmic diagrams rather than by the "sickle-shaped" theoretical curves of the two-component model (cf. Larimer, 1973; Laul et al., 1973).

We are forced to conclude that with respect to these specific predictions the two-component model as it now stands fails to explain adequately the condensation and accretion conditions of enstatite chondritic material. We do not feel justified therefore in calculating apparent accretion temperatures based upon Bi, Tl and In abundances for this sort of chondrite although conceivably these elements might act as suitable thermometers for other sorts of primitive chondrites. In this regard Clayton et al. (1973) and Onuma et al. (1973) report that while their previously-proposed oxygen isotope cosmothermometer (Onuma et al., 1972a) still appears valid in principle, the reported temperatures based upon it (Onuma et al., 1972a, b) are not correct.

The "Constrained Equilibrium Theory" of Blander (1971) postulates the importance of liquid troilite (FeS) in establishing the mineralogic and chemical composition of enstatite chondrites. In this respect the correlation profiles we observe (Figs. 1, 4, 5) tend to support this model. It is not clear whether the thermodynamic calculations of Larimer (1973) are qualitatively applicable to this multi-component model (Blander, 1971). If so it may be significant that most data points on two-element correlation diagrams involving volatile elements in enstatite chondrites (Fig. 6) lie well away from the theoretical condensation curves in the direction of the higher ambient pressures predicted by Blander's (1971) model. However this model predicts specific abundance pattern trends for only a very few elements and these predictions are not unique to this model. Beyond this, little can be said at this stage since the lack of appropriate thermodynamic data (Blander, personal communication) precludes prediction of additional abundance pattern trends or specific patterns of interelement relationships that can be tested by our data.

Conclusions

The patterns of interelement relationships, i.e. correlation profiles, determined in this study together with the abundance patterns discussed in Paper V indicate that the formation conditions of enstatite chondrites were substantially different from those of the carbonaceous and unequilibrated ordinary chondrites. These data suggest that enstatite chondrites constitute a single evolutionary sequence and indicate the predominant influence of thermal fractionation accompanied by geochemical fractionation of chalcophile-plus-siderophile elements from lithophile ones. The primary chemical fractionation probably occurred during condensation and accretion of solid material from the solar nebula although it is conceivable that subsequent metamorphic processes somewhat modified the distribution of the more volatile elements. The genetic models proposed thus far fail to account in detail for the chemical trends in enstatite chondrites although qualitatively the most satisfactory seem to be the theories of Blander (1971) and Anders and coworkers. It would appear that the thermodynamic bases of these models require re-evaluation and that in any event a model accounting satisfactorily for the enstatite chondrites need not be necessarily satisfactory for other primitive chondrites.

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Table 1. Correlation coeficients and levels of significance for statistically-significant (>95% confidence level) interelement relationships in enstatite chondrites studied by Binz <u>et</u> <u>al</u>. (1973).

Pair		No. of Meteorites	Linear		Exponential	
			Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
Co	Au	6	0.95	99	0.93	99
Sb	Co	9	0.76	98	0.81	99
Sb	As	9			0.67	95
Ga	Co	9	0.73	97	0.71	96
Ga	Cu	8	0.90	99.9	0.89	99
Se	Cu	8	0.88	99	0.87	99
Se	Ga	9	0.88	99.9	0.79	99
Te	Cu	8	0.81	98	0.77	97
Te	Ga	9	0.90	99.9	0.82	99
Te	Se	9	0.93	99.99	0.87	99
Zn	Au	6			0.81	95
Zn	Ga	9	0.79	99	0.70	96
Zn	Se	9	0.80	99		
Zn	Te	9	0.92	99.99	0.89	99.9
Cd	Co	8	0.79	98		
Cd	Ga	8	0.87	99		
Cd	Se	8	0.74	96		
Cd	Te	8	0.84	99		
Cd	Zn	8	0.83	99		
Bi	Co	9	0.74	97		
Bi	Ga	9	0.88	99.9		

Table 1 - Continued

Pair		No. of Meteorites	Linear Correl. Coeff.	Linear Signif. Level	Exponential Correl. Coeff.	Exponential Signif. Level
Bi	Se	9	0.78	99		
Bi	Te	9	0.82	99		
Bi	Zn	9	0.79	99		
Bi	Cd	8	0.98	99.9999	0.84	99
Tl	Co	9	0.76	98		
Tl	Cu	8	0.71	95	0.72	95
Tl	Ga	9	0.89	99.9	0.80	99
Tl	Se	9	0.80	99		
Tl	Te	9	0.82	99		
Tl	Zn	9	0.79	99		
Tl	Cd	8	0.98	99.9999	0.77	97
Tl	Bi	9	0.996	>>99.9999	0.95	99.99
In	Ga	9	0.79	99	0.68	95
In	Se	9	0.87	99.9	0.88	99.9
In	Te	9	0.93	99.99	0.89	99.9
In	Zn	9	0.97	99.99	0.77	98
In	Cd	8	0.83	99		
In	Bi	9	0.83	99		
In	Tl	9	0.84	99		

Table 2. Correlation coefficients and levels of significance for statistically-significant (>95% confidence level) interelement relationships in enstatite chondrites.

Pair		No. of Meteorites	Linear		Exponential	
			Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
Mg	K	7	-0.85	98	-0.86	98
Co	Au	6	0.95	99	0.93	99
Mn	K	7	0.83	98	0.83	97
Mn	Co	6	0.83	95	0.83	95
Fe	Mg	11	-0.72	98	-0.71	98
Fe	Co	8	0.77	97	0.78	98
Fe	Mn	7	0.86	99	0.81	97
Fe	Ni	11	0.81	99	0.84	99.9
Fe^0	Sc	6	-0.83	96	-0.85	96
Fe^0	Co	8	0.72	95	0.74	96
Fe^0	Ni	11	0.84	99.9	0.88	99.9
Fe^0	Fe	11	0.94	99.99	0.94	99.99
Na	K	5	0.91	96	0.91	96
Na	Mg	6	-0.94	99	-0.96	99.9
Na	Mn	6	0.84	96	0.82	95
Rb	Fe	10	0.64	95		
Ca	Ti	7	-0.85	98	-0.82	97
Ca	Mg	7	-0.78	96		
P	K	7	0.95	99.9	0.95	99.9
P	Mg	7	-0.87	99	-0.88	99
P	Mn	7	0.84	98	0.82	97

Table 2 - Continued

Pair		No. of	Linear		Exponential	
		Meteorites	Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
P	Fe	7	0.85	98	0.80	97
As	Fe	8	0.75	96	0.75	96
As	Fe^0	8	0.86	99	0.88	99
Cu	K	5	0.90	96	0.91	96
Cu	Fe	7	0.81	97		
Cu	Al	5	-0.90	96	-0.92	97
Cu	P	5	0.99	99.9	0.99	99.9
Sb	Ti	6	0.87	97	0.83	96
Sb	Co	9	0.76	98	0.81	99
Sb	Mn	6			0.86	97
Sb	Fe	8	0.72	95	0.84	99
Sb	Fe^0	8	0.83	99	0.88	99
Sb	As	9			0.67	95
Ag	K	7	0.91	99		
Ag	Mg	10	-0.75	98	-0.74	98
Ag	Au	5	0.95	99	0.98	99.9
Ag	Ni	10	0.64	95		
Ag	Fe	10	0.76	99		
Ag	Al	7			-0.79	96
Ag	Na	6	0.92	99	0.85	96
Ag	Rb	10	0.78	99		
Ag	Ca	7			0.93	99.9
Ag	P	7	0.88	99		
Ag	Cu	6	0.89	98	0.83	96

Table 2 - Continued

		No. of	Linear		Exponential	
Pair		Meteorites	Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
Ga	K	6	0.98	99.99	0.99	99.99
Ga	Mg	8	-0.81	98	-0.81	98
Ga	Co	9	0.73	97	0.71	96
Ga	Mn	6	0.87	97	0.86	97
Ga	Fe	8	0.88	99	0.89	99
Ga	Na	6	0.82	95	0.82	95
Ga	P	6	0.95	99	0.96	99
Ga	Cu	8	0.90	99.9	0.89	99
Ga	Ag	7	0.91	99		
Se	K	7	0.88	99		
Se	Mn	7	0.80	97		
Se	Ni	11			0.67	97
Se	Fe	11	0.68	97	0.72	98
Se	Fe^0	11			0.71	98
Se	Na	6	0.88	98	0.91	99
Se	P	7	0.92	99	0.80	97
Se	Cu	8	0.88	99	0.87	99
Se	Ag	10	0.85	99	0.64	95
Se	Ga	9	0.88	99.9	0.79	99
Cs	Na	6	0.86	97		
Cs	Rb	10	0.90	99.9	0.75	98
Cs	Ag	10	0.88	99.9	0.76	99
Cs	Se	10	0.71	97		
S	K	7	0.94	99.9	0.92	99

Table 2 - Continued

Pair		No. of Meteorites	Linear Correl. Coeff.	Linear Signif. Level	Exponential Correl. Coeff.	Exponential Signif. Level
S	Mg	11	-0.77	99	-0.75	99
S	Au	5	0.92	97	0.91	96
S	Fe	11	0.80	99	0.73	99
S	Na	6	0.85	97	0.85	96
S	P	7	0.96	99.9	0.94	99.9
S	Cu	7	0.94	99.9	0.91	99
S	Ag	10	0.88	99.9	0.81	99
S	Ga	8	0.92	99.9	0.93	99.9
S	Se	11	0.65	97		
S	Cs	10	0.88	99.9		
Te	K	6	0.98	99.99	0.98	99.9
Te	Mg	8	-0.88	99	-0.93	99.9
Te	Na	6	0.96	99.9	0.95	99
Te	P	6	0.91	99	0.97	99.9
Te	Cu	8	0.81	98	0.77	97
Te	Ag	7	0.95	99.9	0.81	97
Te	Ga	9	0.90	99.9	0.82	99
Te	Se	9	0.93	99.99	0.87	99
Te	Cs	7	0.82	97		
Te	S	8	0.91	99.9	0.92	99.9
Zn	K	7	0.92	99	0.86	99
Zn	Mg	11			-0.79	99
Zn	Au	6			0.81	95

Table 2 - Continued

Pair		No. of Meteorites	Linear		Exponential	
			Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
Zn	Fe	11	0.71	98	0.69	98
Zn	Na	6	0.92	99	0.95	99
Zn	Rb	10	0.91	99.99	0.77	99
Zn	Ca	7			0.76	95
Zn	P	7	0.80	97	0.84	98
Zn	Ag	10	0.88	99.9	0.84	99
Zn	Ga	9	0.79	99	0.70	96
Zn	Se	12	0.73	99	0.59	95
Zn	Cs	10	0.93	99.99	0.75	98
Zn	S	11	0.77	99	0.85	99.9
Zn	Te	9	0.92	99.9	0.89	99.9
Cd	K	6	0.85	96		
Cd	Cr	5	0.96	99		
Cd	Co	8	0.79	98		
Cd	Fe	10	0.66	96		
Cd	Rb	9	0.91	99.9	0.92	99.99
Cd	Ag	9	0.86	99	0.67	95
Cd	Ga	8	0.87	99		
Cd	Se	11	0.66	97		
Cd	Cs	9	0.94	99.99	0.95	99.99
Cd	S	10	0.68	97		
Cd	Te	8	0.84	99		
Cd	Zn	11	0.91	99.99	0.75	99

Table 2 - Continued

Pair		No. of Meteorites	Linear		Exponential	
			Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
Bi	K	7	0.87	99		
Bi	Mg	11			-0.65	97
Bi	Co	9	0.74	97		
Bi	Fe	11	0.66	97		
Bi	Na	6			0.86	97
Bi	Rb	10	0.84	99	0.74	98
Bi	Ag	10	0.90	99.99	0.78	99
Bi	Ga	9	0.88	99.9		
Bi	Se	12	0.72	99		
Bi	Cs	10	0.92	99.99	0.96	99.9999
Bi	S	11	0.72	98	0.62	95
Bi	Te	9	0.82	99		
Bi	Zn	12	0.83	99.9	0.59	95
Bi	Cd	11	0.95	99.9999	0.86	99.9
Tl	K	7	0.86	99	0.88	99
Tl	Mg	11	-0.69	98	-0.79	99
Tl	Co	9	0.76	98		
Tl	Fe	11	0.72	98	0.70	98
Tl	Na	6			0.95	99
Tl	Rb	10	0.78	99	0.72	98
Tl	P	7			0.78	96
Tl	Cu	8	0.71	95	0.72	95
Tl	Ag	10	0.89	99.9	0.84	99

Table 2 - Continued

		No. of	Linear		Exponential	
Pair		Meteorites	Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
Tl	Ga	9	0.89	99.9	0.80	99
Tl	Se	12	0.68	98		
Tl	Cs	10	0.86	99.9	0.86	99.9
Tl	S	11	0.76	99	0.79	99
Tl	Te	9	0.82	99		
Tl	Zn	12	0.78	99	0.65	98
Tl	Cd	11	0.89	99.99	0.78	99
Tl	Bi	12	0.98	99.9999	0.96	99.9999
In	K	7	0.91	99	0.80	96
In	Mg	11			-0.66	97
In	Ni	11			0.61	95
In	Fe	11	0.65	96	0.75	99
In	Fe^0	11			0.65	96
In	Na	6	0.89	98	0.97	99.9
In	Rb	10	0.86	99.9	0.68	96
In	P	7	0.79	96	0.78	96
In	Ag	10	0.90	99.9	0.75	98
In	Ga	9	0.79	99	0.68	95
In	Se	12	0.84	99.9	0.91	99.99
In	Cs	10	0.93	99.99	0.79	99
In	S	11	0.73	99	0.64	96
In	Te	9	0.93	99.99	0.89	99.9
In	Zn	12	0.95	99.9999	0.79	99

Table 2 - Continued

Pair		No. of Meteorites	Linear		Exponential	
			Correl. Coeff.	Signif. Level	Correl. Coeff.	Signif. Level
In	Cd	11	0.86	99.9	0.63	96
In	Bi	12	0.85	99.9	0.64	97
In	Tl	12	0.80	99.9	0.66	98
C	Cr	5	0.99	99.9	0.99	99.9
C	Mn	6	0.81	95	0.85	97
Ar	Co	4			-0.98	96
Ar	Ga	4	-0.99	99		
Kr	Ar	6			0.85	97
Xe	Ca	5			0.91	96
Xe	Se	6	0.83	96		

Figure Captions

Figure 1. Correlation profile indicating statistically-significant relationships among 13 elements in enstatite chondrites (Case 1 data). Elements are listed from left to right and top to bottom in order of increasing depletion in ordinary chondrites relative to Cl chondrites (i.e. increased volatility). Circles indicate linear:linear correlations and crosses indicate logarithmic:logarithmic correlations. Relationships significant at >95% confidence level are indicated to the right of the diagonal line; those significant at >99% confidence level are indicated to the left.

Figure 2. Correlations of a) As - Sb and b) Bi - Tl in enstatite chondrites. These correlations cover the extremes in significance of Case 1 data; the former is significant at >95% confidence level, the latter at >99.99% confidence level. Note that the Bi - Tl correlation appears to define a single straight-line relationship with E4 > E6 > E5.

Figure 3. Correlation of Se with Te (>99% confidence level) in upper part and variation of Se/Te ratio with Te depletion factor (lower part).

Figure 4. Correlation profile indicating statistically-significant relationships among 34 elements (36 entities) in enstatite chondrites (Case 2 data). As in Fig. 1, entities are listed in order of increasing depletion and relationships significant at >95% and >99% confidence levels are indicated separately. Circles and crosses have the same meaning as in Fig. 1; diamonds and plus signs indicate significant linear:linear and logarithmic: logarithmic anti-correlations, respectively. Note the correlations invol-

Figure Captions - continued

ving less-depleted alkali metals and more-depleted chalcophile elements.

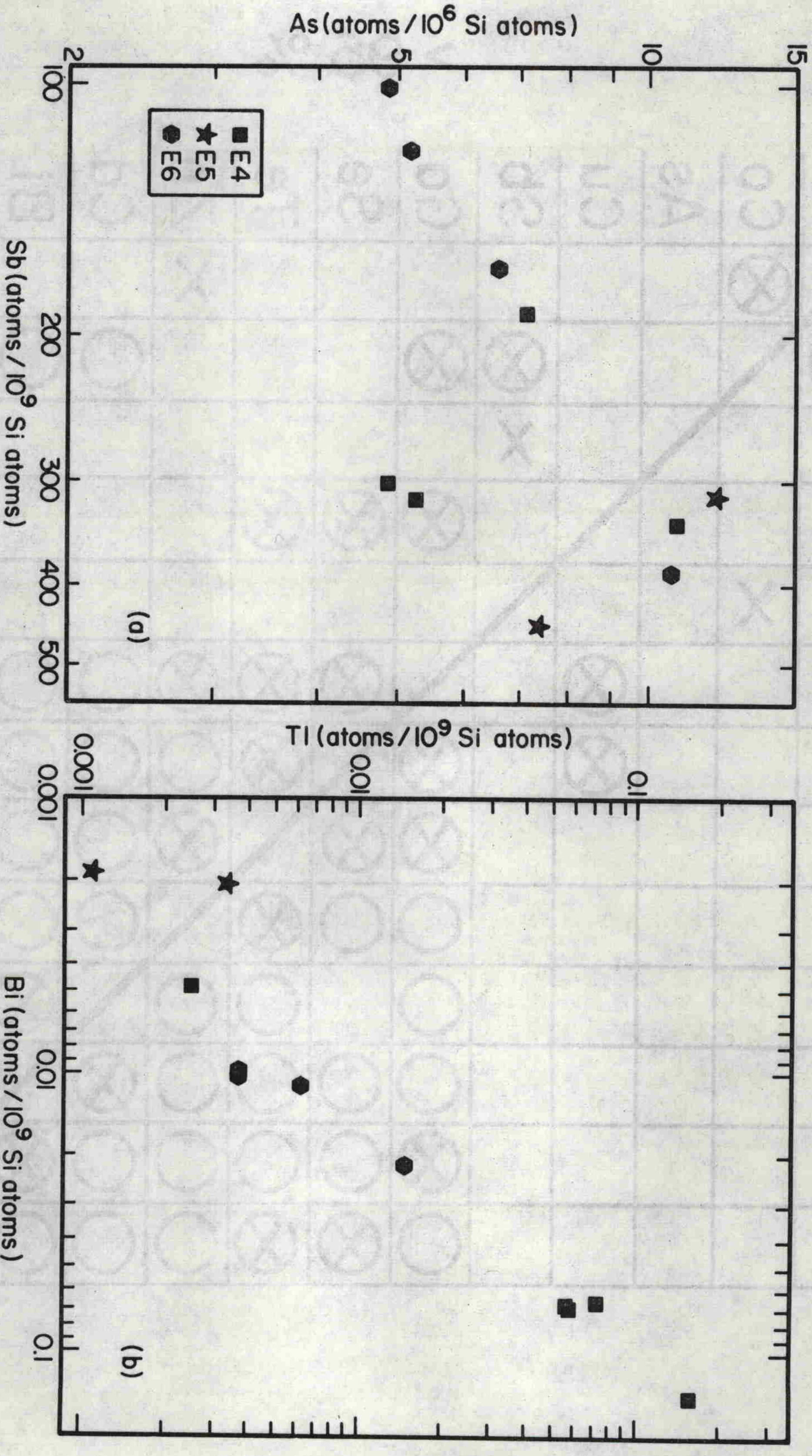
Figure 5. Correlation profile indicating significant relationships among 21 elements (22 entities) in enstatite chondrites. Relationships significant at >95% and >99% confidence levels are shown separately; symbols have the same meaning as in Figs. 1 and 4. Elements are listed in order of increasing chalcophile (compared with lithophile) character, i.e. more negative ΔG°. Apparently alkali metals have substantial chalcophile character in these chondrites.

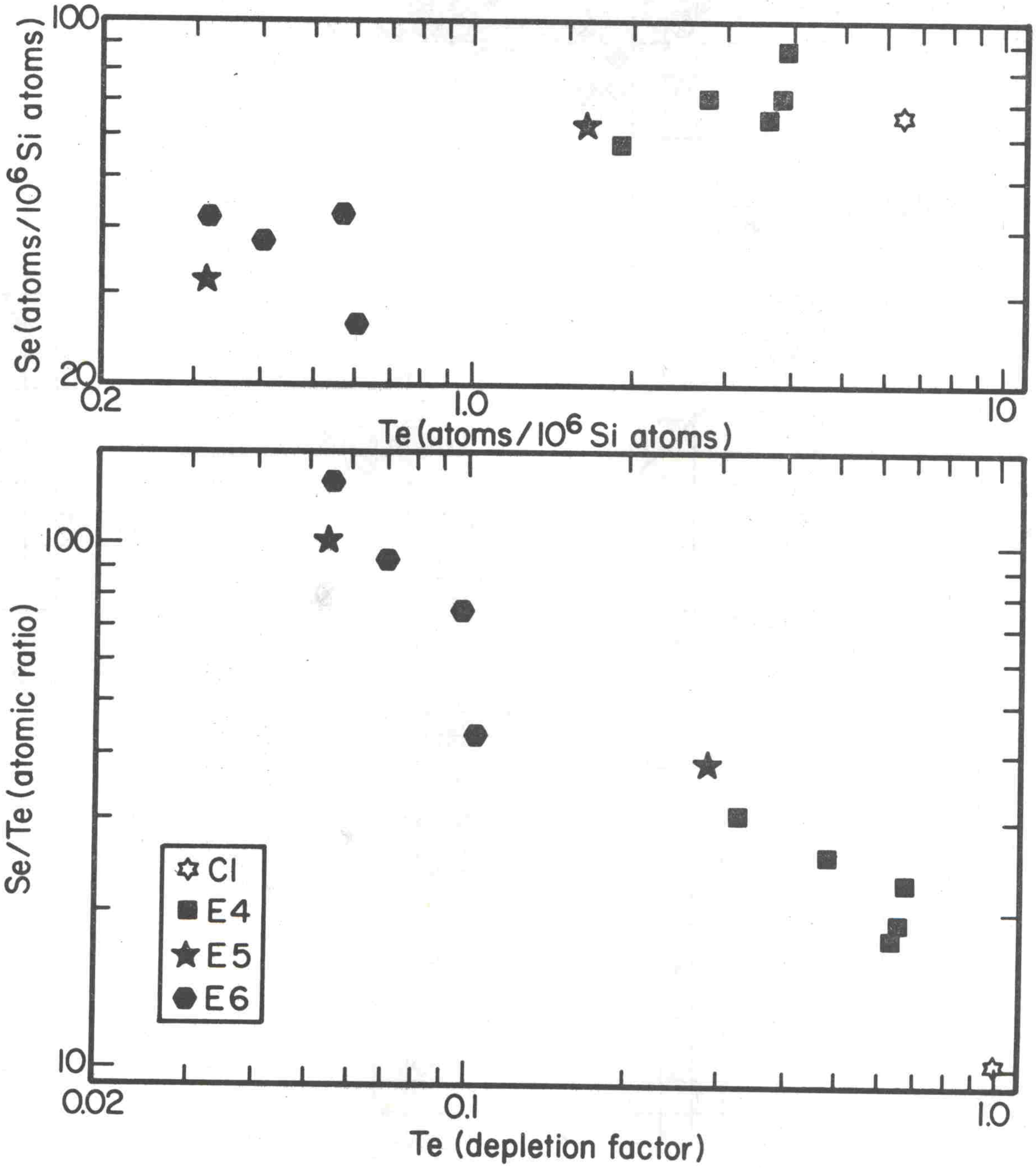
Figure 6. Empirical two-element correlation diagrams compared with theoretical condensation sequences predicted by the two-component model in enstatite chondrites. The correlations (and levels of significance) involve: a) Bi - Tl (>99.9999%); b) In - Bi (>97%); c) In - Tl (>98%); d) In - Cd (>96%); e) Tl - Cd (>99%); f) Bi - Cd (>99.9%). Filled symbols indicate data of Binz et al. (1973) and open symbols indicate data of Laul et al. (1973); tie-lines indicate data for the same meteorite. In no case do the empirical data follow unambiguously the "sickle-shaped" theoretical condensation curves for ambient pressures of 5×10^{-5}, 10^{-4} or 5×10^{-4} atm.

> 95 %

> 99 %

	Au	Co	As	Cu	Sb	Ga	Se	Te	Zn	Cd	Bi	Tl	In
Au		⊗							X				
Co	⊗				⊗	⊗				○	○	○	
As					X								
Cu						⊗	⊗	⊗				⊗	
Sb		X											
Ga				⊗			⊗	⊗	⊗	○	○	⊗	⊗
Se				⊗		⊗		⊗	○	○	○	○	⊗
Te						⊗	⊗		⊗	○	○	○	⊗
Zn						○	○	⊗		○	○	○	⊗
Cd						○		○	○		⊗	⊗	○
Bi						○	○	○	○	⊗		⊗	○
Tl						⊗	○	○	○	○	⊗		○
In						○	⊗	⊗	○	○	○	○	


As (atoms / 10^6 Si atoms)
2
5
10
15
Sb (atoms / 10^9 Si atoms)
100
200
300
400
500
■ E4
★ E5
⬢ E6
(a)
Tl (atoms / 10^9 Si atoms)
0.001
0.01
0.1
Bi (atoms / 10^9 Si atoms)
0.001
0.01
0.1
(b)


100
20
0.2
1.0
10
Se (atoms/10⁶ Si atoms)
Te (atoms/10⁶ Si atoms)
100
10
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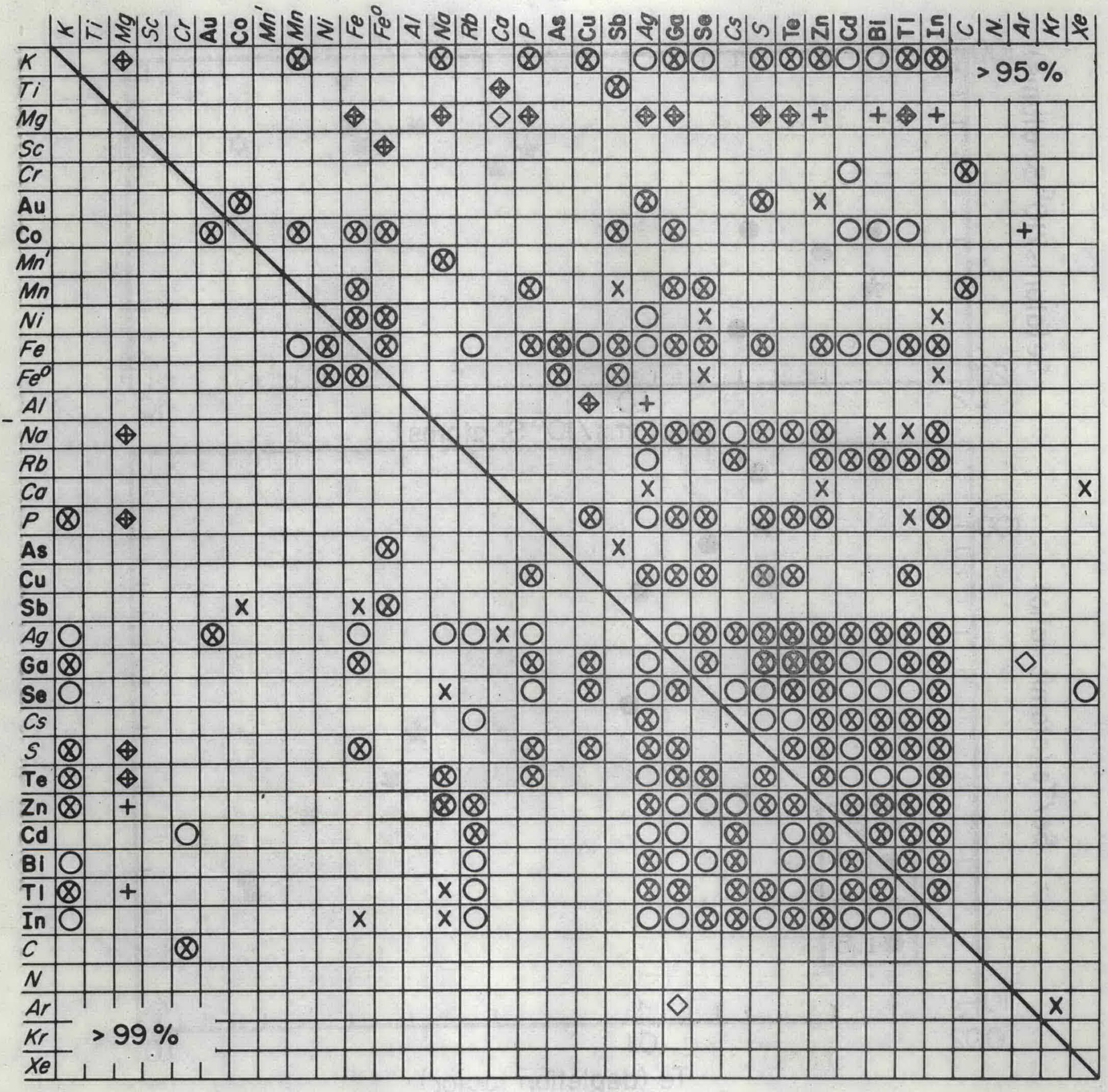
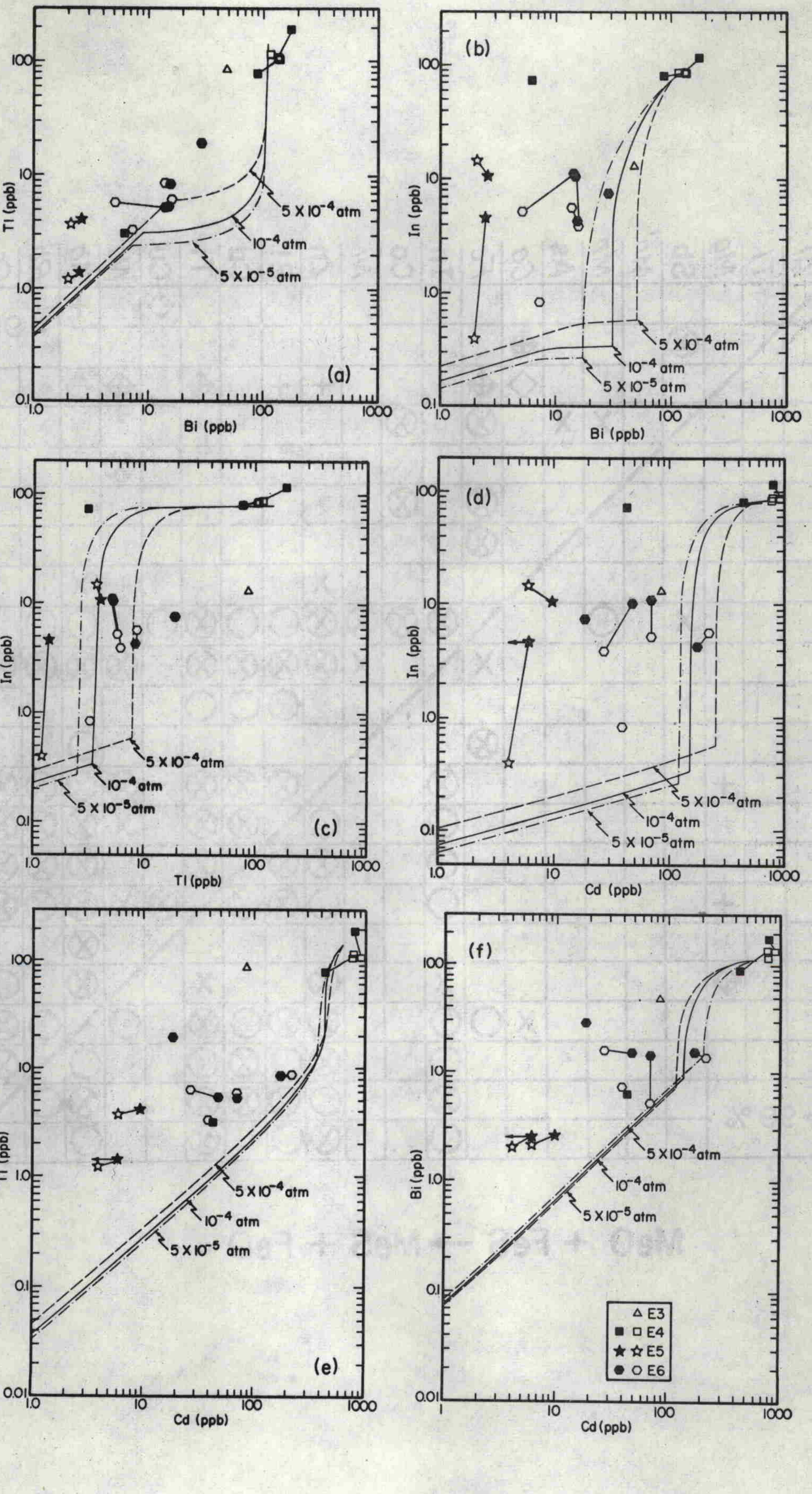
0.1
1.0
Se/Te (atomic ratio)
Te (depletion factor)
✡ CI
■ E4
★ E5
● E6


K
Ti
Mg
Sc
Cr
Au
Co
Mn'
Mn
Ni
Fe
Fe⁰
Al
Na
Rb
Ca
P
As
Cu
Sb
Ag
Ga
Se
Cs
S
Te
Zn
Cd
Bi
Tl
In
C
N
Ar
Kr
Xe
> 95 %
> 99 %

	Al	Ti	Mg	Sb	Mn'	Mn	As	Ca	Fe	In	Co	Ni	Zn	Bi	Cd	Tl	Cu	Na	Ag	Rb	Cs	K
Al																	◈		+	> 95 %		
Ti				⊗				◈														
Mg								◇	◈	+			+	+		◈		◈	◈			◈
Sb						X	X		⊗		⊗											
Mn'																		⊗				
Mn									⊗		⊗											⊗
As									⊗													
Ca													X						X			
Fe				X		○				⊗	⊗	⊗	⊗	○	○	⊗	○		○	○		
In									X			X	⊗	⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗
Co				X										○	○	○						
Ni									⊗										○			
Zn			+							⊗				⊗	⊗	⊗		⊗	⊗	⊗	⊗	⊗
Bi										○			○		⊗	⊗		X	⊗	⊗	⊗	○
Cd										○			⊗	⊗		⊗			⊗	⊗	⊗	○
Tl			+							○			○	⊗	⊗		⊗	X	⊗	⊗	⊗	⊗
Cu																			⊗			⊗
Na			◈							X			⊗			X			⊗		○	⊗
Ag								X	○	○			⊗	⊗	○	⊗		○		○	⊗	○
Rb										○			⊗	○	⊗	○			○		⊗	
Cs	> 99 %									⊗			○	⊗	⊗	⊗			⊗	○		
K										○			⊗	○		⊗			○			

$$MeO + FeS \rightarrow MeS + FeO$$


(a)
Tl (ppb)
Bi (ppb)
100
10
1.0
0.1
1.0
10
100
1000
5 X 10^{-4}atm
10^{-4}atm
5 X 10^{-5}atm
(b)
In (ppb)
Bi (ppb)
100
10
1.0
0.1
1.0
10
100
1000
5 X 10^{-4}atm
10^{-4}atm
5 X 10^{-5}atm
(c)
In (ppb)
Tl (ppb)
100
10
1.0
0.1
1.0
10
100
1000
5 X 10^{-4}atm
10^{-4}atm
5 X 10^{-5}atm
(d)
In (ppb)
Cd (ppb)
100
10
1.0
0.1
1.0
10
100
1000
5 X 10^{-4}atm
10^{-4}atm
5 X 10^{-5}atm
(e)
Tl (ppb)
Cd (ppb)
100
10
1.0
0.1
0.01
1.0
10
100
1000
5 X 10^{-4}atm
10^{-4}atm
5 X 10^{-5} atm
(f)
Bi (ppb)
Cd (ppb)
100
10
1.0
0.1
0.01
1
10
100
1000
5 X 10^{-4}atm
10^{-4}atm
5 X 10^{-5}atm
△ E3
■ □ E4
★ ☆ E5
● ○ E6