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## CONDENSATION AND/OR METAMORPHISM: GENESIS OF E- AND L-GROUP CHONDRITES FROM STUDIES ON ARTIFICIALLY HEATED PRIMITIVE CONGENERES

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*Primitive chondrites heated for one week under conditions reasonable for early solar system objects readily lose volatile/mobile trace elements, e.g., Ag, Bi, Cs, Ga, In, Se, Te, Tl and Zn. Trace element contents decrease by 10-100x progressively with temperature up to 1000° C; apparent activation energies calculated from these data suggest bonding differences between chondrites. Comparison of data for E3-6 chondrites and heated Abee (E4) indicates that volatile/mobile trace elements in E-group chondrites reflect metamorphic loss from a parent object; prior nebular cosmochemical fractionation modified non-volatile element contents. Apparently L3-6 chondrites escaped such open-system metamorphism. Information on nebular condensation process(es) may be gained from L-group compositional data; only non-volatile elements in E-group chondrites should be used for this purpose, however.*

### INTRODUCTION

Highly variable chondritic contents of more or less volatile trace elements obviously reflect the condensation and/or evolutionary histories of their parent objects. Thus, their study should yield important genetic information for these objects and, by extension, for other primitive solid bodies in the early solar system. Elements present at the ppm-ppb level cannot form discrete minerals and must reside in host phases; thus trace element volatilities cannot be determined directly. Anders (1964) suggested that the depletion factor of an element, i.e., its abundance in ordinary (H, L, LL) chondrites - particularly equilibrated ones (cf. Binz *et al.* 1976) - relative to that in CI chondrites, provides a qualitative measure of its volatility in chondrites. We adopt this as a working hypothesis although in the strict sense an element's depletion factor may be only related to its volatility in the nebula and not necessarily to its volatility in chondritic parent objects.

The accepted chondritic classification (Van Schmus and Wood, 1967) based upon petrologic criteria demonstrates that all chondrites are not equally evolved; whether they are equally primitive is a matter of debate. Some authors believe

that all members of a given chemical group (e.g., E, H, L, LL, C) formed from material condensed contemporaneously but at differing temperatures from the chemically-inhomogeneous nebula. Others argue that each chondritic chemical group represents a metamorphic suite of samples derived from an evolved parent body or planetesimal whose primitive composition is most closely approximated by known congeners of lower petrologic grades. To some extent chondrites probably reflect both processes (indeed proponents of one scheme often invoke the other to account for otherwise exceptional trends); they obviously are composed of condensed nebular matter and less-altered material should have survived the chondritic differentiation which probably produced achondrites and most iron meteorites. Thus some workers propose that one or the other process predominated depending upon the specific group considered. Trends of trace elements - particularly volatile ones - provide important clues to these processes and recent studies have focussed on these; references to those studies, including more extensive descriptions of genetic models are to be found in Anders *et al.* (1976); Binz *et al.* (1974, 1976); Blander (1975); Dodd (1969); and Wasson (1972, 1974).

To establish criteria suitable as valid nebular condensation boundary conditions it seems essential to distinguish metamorphic effects from prior condensation-induced effects. Possibly thermodynamic data can be used to deduce chondritic compositional trends (cf. reviews in this book) but such data cannot predict effects of post-accretion metamorphic alteration. Recently we began a series of laboratory simulations intended to study such alterations in the envelope of genetically-reasonable conditions so as to identify possible metamorphic effects. Here we briefly summarize the present status of these studies with particular emphasis upon the principal genetic evidence for E- and L-group chondrites from comparison of trace element trends in these chondrites and in artificially heated primitive congeners.

#### SCOPE OF INVESTIGATIONS

Each study of trace element retention in heated geologic samples involves determination (by neutron activation analysis) of 6-10 of the following elements, nearly all having substantial depletion factors - i.e., volatilities - in ordinary chondrites, Ag, Bi, Cd, Co, Cs, Ga, In, Se, Te, Tl and Zn. Generally retentivity is a function of: specific starting material and its physical form, i.e., powder *vs.* chips; heating temperature and duration; ambient atmospheric composition and pressure. Most studies involve systematic investigation of trace elements retained in separate aliquots of homogenized powder heated at 100° C increments from 400-1000° C for 1 week in a low-pressure environment (initially  $10^{-5}$  atm H<sub>2</sub>). During each heating run the ambient pressure in the apparatus (Ikramuddin and Lipschutz, 1975) is monitored constantly and volatiles are condensed continuously in a cold-trap at -196° C, sometimes on a molecular sieve. Samples already investigated systematically include: Allende (C3) - Ikramuddin and Lipschutz (1975); Abee (E4) - Ikramuddin *et al.* (1976a); Krymka (I3) - Ikramuddin *et al.* (1976b); terrestrial basalt BCR-1 - Ikramuddin *et al.* (1976c). [Hereafter, these will be referred to as Papers I-IV, respectively]. Similar studies of other primitive meteorites are in progress; coverage is also being extended to 1400° C. Cooperative studies of temperature-induced alterations of other chemical and physical properties are also in progress but these have not generally advanced sufficiently far to be discussed; passing reference will be made to mineralogic/petrologic observations by Professor W. R. Van Schmus. A few preliminary excursions into effects of variations in these conditions have been made: Allende samples were heated at 500° C for a longer period, 29 days, and at 1000° C in an initial ambient atmosphere of  $10^{-5}$  atm O<sub>2</sub> or He (Ikramuddin *et al.* 1975); Abee samples were heated at 700° C under ambient Ne pressures ranging from  $10^{-5}$  -  $10^{-3}$  atm (unpublished data).

## TRENDS OF THE DATA

Trace Element Retentivity and the Loss Process

Samples studied thus far represent compositional extremes: primitive chondrites (which are low-temperature accumulates) vs. BCR-1 (which is of igneous origin); highly-oxidized Allende (C3) vs. highly-reduced Abee (E4). Despite this diversity general trace element retentivity trends seem remarkably similar although, of course, differences exist in detail. Accordingly unless a specific sample is identified in the discussion which follows, a general trend may be assumed.

With the exception of Co all elements studied are progressively lost to some extent - sometimes by astonishingly large amounts - with increasing temperature. The loss process(es) appears kinetic rather than thermodynamic in nature: we therefore refer to this as elemental mobilization rather than volatilization (Papers I-IV). Although Tl is among the most mobile elements, its retentivity patterns (Fig. 1) are generally typical of such elements: significant losses begin at remarkably low temperatures, e.g., 400-500° C, continue over a broad temperature range and for primitive chondrites, at a given temperature, are ordered as Krymka > Abee > Allende. Most elements are less mobile in BCR-1 than in primitive chondrites; Tl and Bi are exceptions (Paper IV).

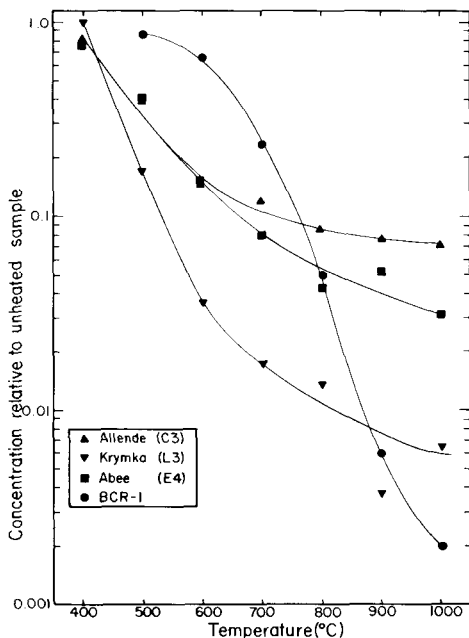


Figure 1. Thallium retentivity patterns for 3 primitive chondrites and terrestrial basalt BCR-1. All data are normalized to the respective unheated material and represent measurements for homogenized powder aliquots heated for 1 week in a low-pressure environment (initially  $10^{-5}$  atm  $H_2$ ) at the temperatures indicated. Losses clearly progress with temperature and in the extreme can be as high as 99.8%.

The rate-determining step for trace element loss may be treated as a process in which an element having a diffusion coefficient,  $D$ , diffuses from uniform spherical grains of radius,  $a$ . A diffusion parameter,  $D/a^2$ , may be calculated

from the retention of this element at a given temperature (Papers I, II) and the logarithm of this may be plotted *versus* the reciprocal of the absolute temperature according to the Arrhenius equation. Data obeying such an exponential relationship define a straight line whose slope corresponds to the apparent activation energy for loss; most mobile elements exhibit this property (Papers I-IV). In many instances results for mobile elements are consistent with two straight lines of differing slope over different temperature regions; in other cases a single straight line is indicated. For example apparent activation energies in kcal/mole (and temperature ranges) for Tl are 29(400-600° C) and 2.2(600-1000° C) for Allende; 22(400-600° C) and 4.1(600-1000° C) for Abee; 3.5(500-1000° C) for Krymka; and 24(500-800° C) and 11(800-1000° C) for BCR-1 (Papers I-IV, respectively).

These Tl data again are generally typical of those for other elements. Except for Se, when an element exhibits two apparent activation energies in a given sample the value in the higher temperature region is lower than in the lower temperature region. Selenium in Allende and Abee (Papers I, II), like Ar in geologic material (Fechtig *et al.*, 1963) - the only other element for which analogous data exist - shows the opposite and more expected trend. The proportion of elements exhibiting a single apparent activation energy differs in the samples studied: 1 of 4 elements in Allende, 2 of 7 in Abee, 6 of 6 in Krymka and 2 of 5 in BCR-1 (Papers I-IV, respectively). Using Tl - which falls with the majority in each case - as an example, data for Allende, Abee or BCR-1 may be interpreted as indicating residence in 2 different host sites, the different activation energies corresponding to loss from each site. An alternate view is that in each case Tl resides in a single site but that loss mechanisms differ over different temperature regions. Thallium data for Krymka may argue against this alternate view since only a single host site or loss-process is indicated. Naturally two or more elements could reside in a single host.

Apparent activation energy magnitudes may give clues to trace element bonding in chondrites and geologic materials. Values of tens of kcal/mole, e.g., Tl data from 400-600° C in Allende and Abee and in BCR-1, suggest a diffusion-controlled process whereas values of 2-4 kcal/mole, e.g., Tl data above 600° C in Allende and Abee and in Krymka, suggest a more facile rate-determining loss mechanism, like desorption (Papers I-IV). Clearly, as data for Tl (and other elements) indicate, a given mobile element may be bound differently in different primitive chondrites (Papers I-IV).

### Comparison of Trends

Here we compare trends for artificially heated Abee and Krymka - with each other and with their respective unheated groups of congeners, i.e., E3-6 and L3-6 chondrites - to examine the possible role of metamorphism in the formation of these chondritic groups. A 1:1 correspondence between results for "as-received" chondrites and artificially heated congeners should not be expected since we cannot hope to duplicate metamorphic conditions exactly; time, for example, presents an obvious difficulty. As a working hypothesis, however, we assume that our experiments effectively simulate metamorphic conditions in primitive parent bodies; as will be seen, results for enstatite chondrites provide support for this notion.

### Abundance Patterns

Overall trace element variations in heated Abee and Krymka homogenized powder and in E3-6 and L3-6 chondrites (Papers II, III; Binz *et al.* 1974, 1976) are illustrated in Figure 2. Elements are listed in order of greater depletion factor in all ordinary chondrites or in equilibrated ordinary chondrites, if there exist significant concentration differences between these and unequilibrated ordinary chondrites (Binz *et al.* 1976). As noted, mobile elements are more easily lost

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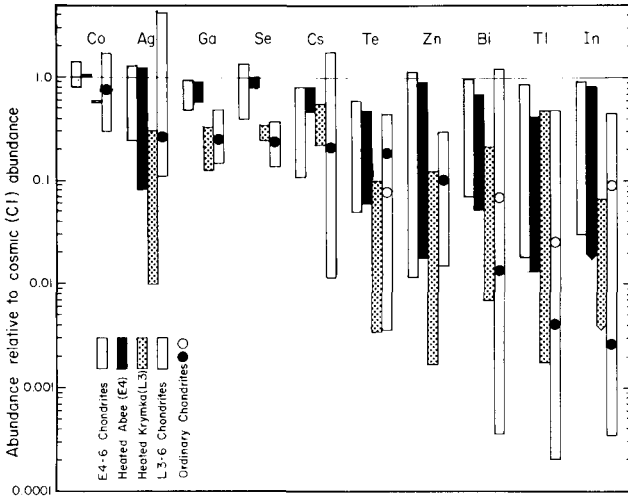


Figure 2. Overall variation of trace elements in heated homogenized powder samples of Abee and Krymka compared with variations in E4-6 and L3-6 chondrites. All data are normalized to cosmic (i.e., C1) abundances and elements are ordered by increasing mean depletion in ordinary chondrites (filled circles). Means of those 4 elements differing significantly in unequilibrated and equilibrated ordinary chondrites are indicated by open and filled circles, respectively. All are arithmetic means except for Bi, Tl and In which are geometric means. Ranges of data for Abee and E3-6 chondrites are substantially similar; those for Krymka and L3-6 chondrites differ.

from Krymka than from Abee by heating (Fig. 2). These data also indicate the importance of distinguishing between elemental mobility and volatility; overall Ag variations in heated Abee and Krymka exceed those of Te while its depletion factor for ordinary chondrites places Ag between Co and Ga (Fig. 2). Similarly Se should lie between Co and Ga from its mobility. Experiments on additional chondrites and at higher temperature will reveal whether these differences persist.

Overall ranges for mobile elements (e.g., Ga, Te, Zn, Bi, Tl, In) in heated Abee are similar to those in E4-6 chondrites but differences emerge in the cases of Co, Ag, Se and Cs which are also less volatile (Paper II). The data are consistent with the suggestion that volatile/mobile element abundances were initially established at near-cosmic levels during condensation and accretion of primitive enstatite chondrite material into a parent object and subsequently decreased by thermal metamorphism in this object (Binz *et al.* 1974). Except for Ga, overall ranges in L3-6 chondrites differ from those in heated Krymka and thus our experiments fail to support the idea that thermal metamorphism played a significant role in the formation of these chondrites (Paper III; Binz *et al.* 1976).

Factor Analysis

When applied to data for E4-6 chondrites, heated Abee or Krymka (Binz *et al.* 1974; Papers II, III) this statistical method (cf. Shaw and Harmon, 1975) indicates that the overall abundance variations are functions of three factors in each case. Elements affected by each of these factors in heated Abee and Krymka are virtually identical (Paper III); for example, elements reflecting the primary factors are, respectively, Ag + Te + Zn + Tl + In + (Se + Cs + Bi) and Ag + Te + Zn + Bi + In + (Se + Cs + Tl). These elements, Co and Ga also reflect the primary factor for E3-6 chondrites (Binz *et al.* 1974), suggesting qualitative consistency with the

idea that volatile/mobile element trends in enstatite chondrites reflect substantial metamorphic loss (Paper II). In contrast, data for ordinary chondrites yield 4-7 factors depending upon the population considered, none of which groups elements rationally (Binz *et al.* 1976). Once again a substantial difference in the formation conditions of E- and L-group chondrites is indicated.

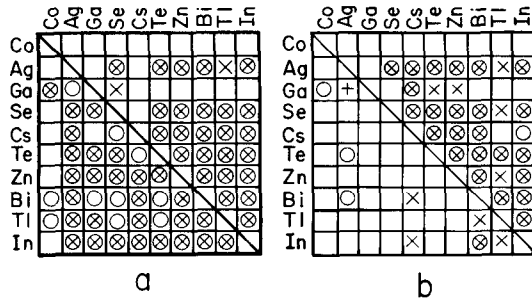


Figure 3. Patterns of statistically significant (>95% confidence level) inter-element relationships in: (a) E3-6 chondrites (left of diagonal) and heated Abee (right of diagonal); (b) 17 L3-6 chondrites (left of diagonal) and heated Krymka (right of diagonal). Elements are listed from left to right and top to bottom in presumed order of volatility; circles, crosses and plus sign indicate linear:linear and logarithmic:logarithmic correlations and a logarithmic:logarithmic anti-correlation, respectively. The pattern for L3-6 chondrites is distinctly different from those of the other 3 populations.

### Correlation Profiles

Patterns of statistically-significant interelement relationships (Fig. 3) indicate substantial differences between E3-6 chondrites, heated Abee and Krymka on the one hand and L3-6 chondrites on the other (Binz *et al.* 1974, 1976; Papers II, III). Each pattern represents results of testing pairs of elements,  $x$  and  $y$ , for significance at >95% confidence level when linear and exponential behavior (i.e.,  $y = mx + b$  and  $y = kx^m$ , respectively) is assumed. The first 3 populations demonstrate many such correlations involving volatile/mobile elements apparently reflecting thermal fractionation; E3-6 chondrites exhibit additional correlations involving Co, Cs and Ga which seem to reflect prior nebular, cosmochemical fractionation (Fig. 3). In contrast, the profile for L3-6 chondrites (Fig. 3b) shows relatively few relationships (one of which, Ga/Ag, is even an anti-correlation) and these exhibit no obvious coherence.

### Two-Element Correlation Diagrams

The most direct test of the extent to which compositional trends in E- and L-group chondrites can be duplicated by heating primitive congeners involves comparison of two-element correlation diagrams for highly-variable, volatile/mobile elements, i.e., Te, Zn, Bi, Tl, In (Papers II, III). Two examples, Tl/Bi and In/Bi, are illustrated by Fig. 4 which depicts trends for Abee and E3-6 chondrites (Figs. 4a,b) and Krymka and L3-6 chondrites (Figs. 4c,d). Figure 4 also includes, for reference, theoretical condensation curves proposed by Anders and co-workers (e.g., Anders *et al.* 1976 and earlier references cited therein) from the only model making such detailed predictions. As Fig. 4 shows, Tl/Bi (a) and In/Bi (b) trends for heated Abee seem more consistent with those for E-group chondrites than are theoretical predictions; indeed even the heretofore puzzling Se/Te trend in enstatite chondrites is generally reproduced in heated Abee (Paper II). On the other

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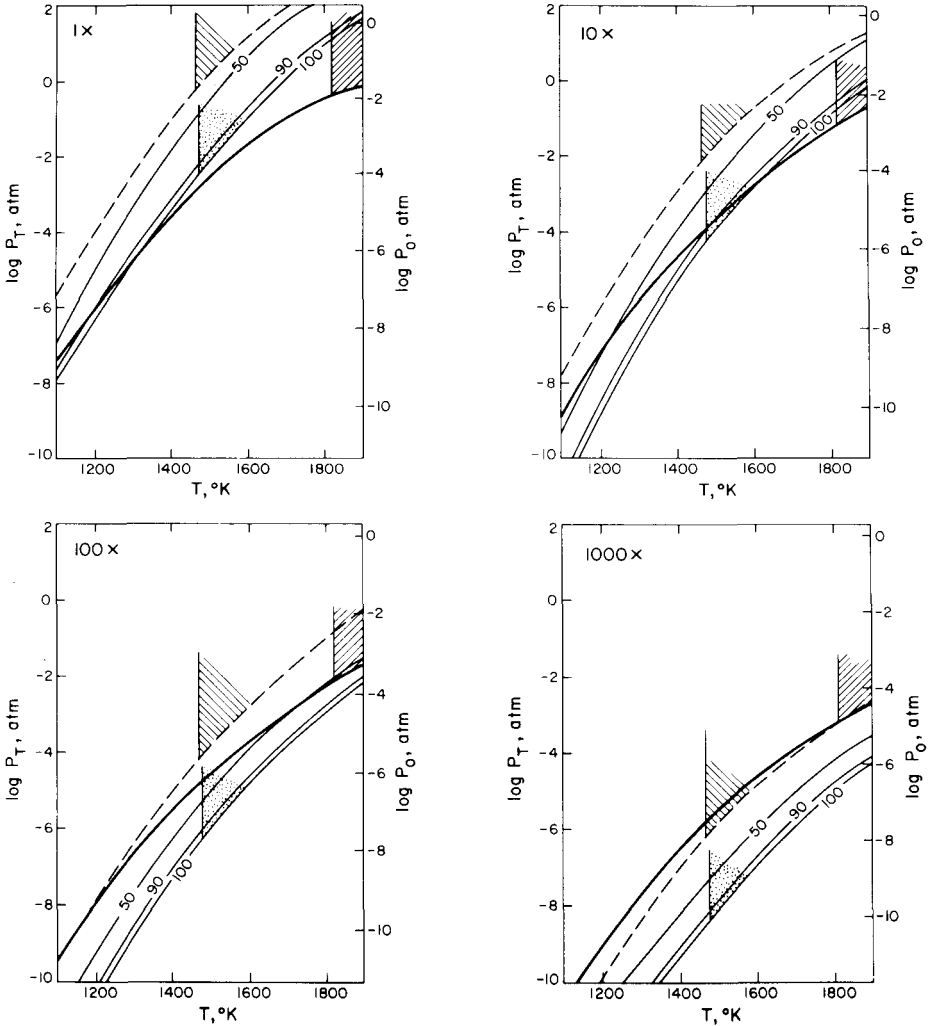


Figure 4. Comparison of empirical results for enstatite chondrites and heated Abee, (a) and (b), and L-group chondrites and heated Krymka, (c) and (d), with theoretical predictions of trends for condensation of volatile elements from a gaseous nebula of cosmic composition at ambient pressures of  $5 \times 10^{-5}$ ,  $10^{-4}$  and  $5 \times 10^{-4}$  atm (Larimer 1973). Sources for empirical data: heated samples - Papers II, III; E-group chondrites - Binz et al. (1974); L-group chondrites - Binz et al. (1976) and references cited therein.

hand, Tl/Bi (c) and, particularly, In/Bi (d) trends for heated Krymka differ from those of L-group chondrites; the theoretical predictions appear somewhat more consistent with the empirical data but the agreement still seems far from convincing.

Mineralogy/Petrology

At this point we have only preliminary data for Abee and Krymka and neither

sample is altered at temperatures of  $\leq 800^{\circ}\text{C}$  by week-long heating. The sample of Abee heated at  $1000^{\circ}\text{C}$  contains small amounts of an as-yet unidentified eutectoid-like growth, also present in lesser quantities in the sample heated at  $900^{\circ}\text{C}$ . Even in these samples, however, sulfides remain unaltered. Inclusions of FeS in Krymka apparently melt (but do not decompose) at temperatures of  $900\text{--}1000^{\circ}\text{C}$  and flow into fine, pre-existing cracks in the samples and the matrix minerals of these two samples apparently also undergo detectable change. The temperature range of these experiments is similar to that deduced from the mineralogy and petrology of enstatite and ordinary chondrites (cf. references in Dodd, 1969; Wasson, 1972; Paper II). Failure to reproduce the texture of grades 5 and 6 chondrites by laboratory experiments using less evolved congeners may be ascribed reasonably to heating times too short to allow diffusion of non-mobile elements

## SUMMARY

The chemical and mineralogic evidence in both E3-6 chondrites and heated Abee is consistent with the view that trends of major non-volatile elements were established by cosmochemical fractionation of chalcophile and siderophile elements from lithophile ones during condensation and accretion of solid material from the nebula into a parent object(s). Abundances of volatile/mobile elements were subsequently modified by open-system, thermal metamorphism within the parent object(s); trends exhibited by such elements should not therefore be used to deduce information on conditions within the nebula except, perhaps, in the cases of the most volatile-rich E4 chondrites, Indarch and Abee.

The genesis of L-group chondrites is more of an open question. Trends for volatile/mobile elements in Krymka generally differ from those in L3-6 chondrites. This suggests that these chondrites escaped substantial metamorphism and that their volatile/mobile element trends can provide information on condensation and/or accretion conditions of solid material from the nebula. However it could be argued that, in contrast to enstatite chondrites, heating experiments on Krymka do not effectively simulate metamorphic conditions within the L-group parent object(s) and closed-system metamorphism on the mm-scale is conceivable. In the latter event, volatile element trends established by nebular processes would be preserved as though metamorphism had never occurred.

## ACKNOWLEDGEMENT

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### (DISCUSSION)

EL GORESY: *I think it is important to know where the volatiles are located (silicates, sulfides, oxides, etc.) before drawing conclusions from these experiments.*

LIPSCHUTZ: *In our experiments we are interested in simulating open-system metamorphism in parent objects by comparing the results for heated samples with those for "as-received" chondrites. Thus, it is essential for this purpose to use whole-rock samples and knowledge of the specific siting of mobile elements seems not to be essential. Naturally we would like to know what the host sites are: we hope to identify these from comparison of apparent activation energies in various types of heated samples.*

DONN: *The use of a liquid nitrogen trap indicates you are using an open system. Would not the solar nebula more nearly resemble a closed system when volatiles are not lost?*

LIPSCHUTZ: *I believe that the cold-trap serves as the means by which the simulation is effective, i.e., as the trade-off for time. The experiments are intended to simulate parent body metamorphism (not nebular processes). We have not yet heated chondrites in a closed system.*

VAN FLANDERN: *The preceding talks have assumed a connection with the primordial solar nebula. Recent dynamical evidence has suggested a viable alternative: the origin of comets, and perhaps also asteroids and some meteors, was apparently from a relatively recent break-up event in the solar system. Hence there need not be any connection with the solar nebula.*

LIPSCHUTZ: *This statement is not relevant to our studies of simulated secondary alteration of primitive objects derived from the solar nebula.*