

Thermal metamorphism of primitive meteorites—IX. On the mechanism of trace element loss from Allende heated up to 1400°C

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Abstract—We report data for Ag, Bi, Cd, Co, Cs, Ga, In, Se, Te, Tl and Zn determined by neutron activation in Allende samples heated for one week at 100° increments in the 1000–1400°C range in a low pressure (initially 10^{-5} atm H_2) environment using an apparatus of novel design. In the extremes, concentrations of these trace elements—initially present at ppm–ppb levels—in unheated material are lowered even farther by factors of 10^{-4} – 10^{-5} over a broad temperature span. Loss of some elements above 1000°C extends trends evident below 1000°C; loss of others is even more extreme. On Arrhenius diagrams some elements exhibit but one apparent activation energy over the entire temperature span of loss while others exhibit 2 or 3, each operative in a particular temperature region. These discontinuities seem related to mineralogic/petrologic alteration and probably reflect differences in diffusion mechanism rather than siting differences. The extension of previous experiments into the temperature regime postulated for chondritic differentiation should lead to a better understanding of the evolution of meteoritic parent bodies.

INTRODUCTION

IN PAPER I of this series, IKRAMUDDIN and LIPSCHUTZ (1975) demonstrated volatilization and loss, i.e. mobilization, of Bi, Ga, In, Se and Tl from the Allende (C3V) chondrite during week-long heating in a low pressure environment (initially $\sim 10^{-5}$ atm H_2) at temperatures reasonable for metamorphism of ordinary and enstatite chondrites, 400–1000°C. In Allende (and other similarly-treated chondrites and a terrestrial basalt) these and additional elements (Ag, Cd, Cs, Te, Zn) exhibit remarkably similar trends—despite great differences in the samples' origin and oxidation state—although minor differences are apparent (IKRAMUDDIN *et al.*, 1976a, b, 1977a, b, MATZA and LIPSCHUTZ, 1977a—hereafter referred to as Papers II–VI, respectively). For example, though each chondrite tends to show characteristic retention for all elements relative to other chondrites, each element generally is progressively lost over a broad temperature span, exhibits a similar mobility in all samples studied relative to other elements and behaves similarly on Arrhenius diagrams (Papers I–VI).

Sequences of mineralogic and petrologic modifications of postulated thermal origin (e.g. metamorphic and shock-associated alterations) in ordinary and C30 chondrites (DODD *et al.*, 1967; VAN SCHMUS and WOOD, 1967; MCSWEEN, 1977; SMITH and GOLDSTEIN, 1977) are paralleled by changes in heated Murchison

(MATZA and LIPSCHUTZ, 1978—hereafter, Paper VII) but not, for several reasons, in heated Krymka (MCSWEEN *et al.*, 1978). Comparison of mobile element trends in heated chondrites of low petrologic type with those in more evolved congeners yields additional clues to thermal events in chondritic evolution. Data for heated Abee and E4-6 chondrites are consistent with the interpretation that enstatite chondrites reflect a substantial open-system, thermal metamorphic episode (Paper II). The H3-6 and L3-6 chondrites apparently escaped such an event (Papers II, III) and may well have been metamorphosed under closed conditions such that their contents of most mobile elements would reflect primary condensation and accretion of nebular material into primitive parent objects [cf. BINZ *et al.* (1976), WAI and WASSON (1977), ANDERS (1977), WASSON (1977), HEYSE (1978) and HUTCHISON *et al.* (1979) for discussion and earlier references]. However, prior data hint that contents of the most mobile elements may have decreased during extended cooling of some L3-6 parent material (HERZOG *et al.*, 1978—hereafter denoted Paper VIII) shock-heated in a late, massive collision (ANDERS, 1964; cf. SMITH and GOLDSTEIN (1977) for other references). Mobile element trends in C3-4 chondrites present a less clear picture (MATZA and LIPSCHUTZ, 1977b, 1978; TAKAHASHI *et al.*, 1978a). Mobile trace element changes doubtless accompanied major element fractionations during formation of more evolved meteorites, such as achondrites, from chondritic material.

To the extent that such experiments simulate meteorite evolution, extension of trace element studies to temperatures above 1000°C could yield information on the alteration of shock-heated chondrites and,

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in this region of partial melting, on the formation of differentiated meteorites. Furthermore, such an extension should yield additional information on elemental loss processes and establish whether activation energy trends reflect siting differences or variation of trace element loss mechanisms in different temperature intervals. We anticipated numerous experimental problems in any such extension, one being a severe decrease in trace element contents (approaching detection limits) at higher temperature. Accordingly, we chose to measure the 10 mobile elements listed above (and Co) first in Allende—generally, the most retentive meteorite studied (Papers I-III, V, VI). Data for additional elements are reported in another study (NGO and LIPSCHUTZ, 1980—Paper X).

EXPERIMENTAL

Design of an apparatus capable of sample containment under contamination-free and chemically-unreactive conditions in a low-pressure environment (initially $\sim 10^{-5}$ atm H_2) during week-long heating at temperatures of 1000–1400°C, proved fairly difficult; numerous trials ultimately yielded a suitable design (Fig. 1). Pre-weighed homogenized powder samples or chips from the specimen used in Paper I were placed in small ZrO_2 crucibles held upright by holes in an AD-998 Coors tube dee. [R. T. Dodd has questioned whether the response of homogenized chondritic powder is similar to that of whole chondrites. At temperatures of 400–1000°C, trace element losses from Allende chips parallel those from powder aliquots and lag behind them by only 0–35% (Paper I) so that Dodd's fears may be allayed.] This ensemble was placed into a mullite or AD-998 combustion tube (3.81 cm dia) and connected to a pyrex assembly (Fig. 1) designed to trap volatiles and monitor the ambient pressure (cf. Papers I, II). After purging and re-filling with H_2 , the system was pumped to $\sim 10^{-5}$ atm (Paper I) and the assembly was sealed.

The high temperatures of this study required changes in heating equipment and procedures of Paper I. We used a Lindberg model 51333 box furnace and 59545 temperature controller for all heating runs, additionally monitoring temperatures with an external Pt/Pt(13%Rh) thermocouple. At 1000–1200°C, temperatures could be set accurately on the controller but above 1200°C, the controller setting differed by $\sim 10^\circ C$ from the actual temperature (hence, ir-

regular temperature values in some runs). The overall temperature variation over the course of any run was $< 2^\circ C$. The poor response to thermal shock of heating elements and sample assembly necessitated insertion of the sample-containing end of the assembly in the furnace at room temperature. We raised the furnace temperature to 500°C within 1/2 hr and increased it to the desired value in 50–100°C steps every 20 min; during cooling, we reversed this process. Each heating run was nominally 1 week; the actual time at temperature was somewhat less (Table 2). The temperature increase resulted in a pressure increase inside the assembly; once at temperature, the pressure decreased within 1–2 hr to a value—usually not very different from the initial one—which remained constant to termination of the run (Table 2).

We observed no evidence indicating reaction between ZrO_2 cylinders and meteorites during heating. Heated samples—which exhibited weight losses of $< 4\%$ at 1000–1200°C and 33.8, 51.9 and 82.9% at 1268, 1316 and 1393°C, respectively—were transferred to Suprasil quartz irradiation vials. Because of extensive vaporization above 1200°C, we increased initial sample weights to 400–900 mg rather than 300 mg (Paper I); thus, samples actually irradiated always exceeded 150 mg.

Sample irradiations in the Argonne CP-5 reactor, general chemical processing, counting and data reduction techniques were as described in Paper II. However, we precipitated all elements but Co and Ga to count them in improved geometry and lower our detection limits. Thus, we counted Ag as $AgCl$, Bi as $BiOCl$, Cd as $CdNH_4PO_4$, Cs as Cs_2PtCl_6 , In as $In(C_9H_6NO)_3$, Se and Te as metals, Tl as TlI and Zn as $ZnHg(SCN)_4$ in both samples and monitors. Overall chemical yields for samples averaged 25–30% for Cs and Ga, 75% for Co and 45–65% for other elements; monitor yields were considerably higher because of abbreviated purification procedures.

RESULTS AND DISCUSSION

Replicate analyses of unheated Allende homogenized powder are listed in Table 1 together with data from Papers I and X and TAKAHASHI *et al.* (1978b). The precision of our measurements and the agreement with prior results is excellent for the most elements. Selenium is rather imprecise due to one datum; if this is ignored, the mean becomes 8.38 ± 0.10 ppm. This 1.2% relative uncertainty seems somewhat low: prior samples yield relative uncertain-

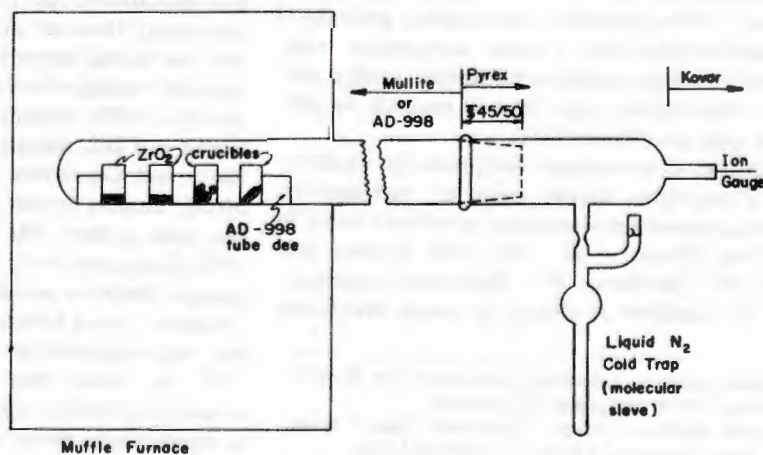


Fig. 1. Schematic diagram for apparatus used in heating experiments from 1000–1400°C.

Table 1. Trace element contents in unheated Allende powder compared with recent literature data

Sample	Ag (ppb)	Bi (ppb)	Cd (ppb)	Co (ppm)	Cs (ppb)	Ga (ppm)	In (ppb)	Se (ppm)	Te (ppb)	Tl (ppb)	Zn (ppm)
(1)	87.1	—	498	638	90.4	7.57	30.6	11.15	1040	56.1	127
(2)	91.0	—	455	615	84.5	7.13	36.2	8.42	1030	56.2	120
(3)	98.2	50.6	431	616	94.5	6.31	37.0	8.26	1020	63.5	118
(4)	103	—	532	607	—	5.90	31.7	8.45	986	62.2	114
Mean§	94.9±	50.6	479±	619±	89.8±	6.73±	33.9±	9.07±	1020±	59.5±	120±
	7.2		45	13	5.0	0.76	3.2	1.39	23	3.9	6
Prior data§	101±	49.0±	519±	612±	89.3±	6.27±	35.6±	9.34±	1090±	59.6±	115±
	4†	0.7*	51†	10*	3.3†	0.30*	1.0	0.16	130†	2.2*	3†
	91±	44±	474±	645±	92±		30±	8.1±	960±	61.8±	113±
	2¶	2¶	10¶	23†	14¶		15¶	0.6¶	50¶	3.4†	1¶
										59±	
										1¶	

References: *—Paper I; ¶—Takahashi *et al.* (1978b); †—Paper IX.

§ Each uncertainty is one standard deviation estimated from the dispersion of the individual measurements.

ties of 1.7–5.3% (mean, 3.7%) from replicate analyses of five chondrites and BCR-1 (Papers I–VI). We chose to use the value in Table 1 as the Se mean because of its similarity to the mean of Paper I. Due to a processing error we have but one Bi datum; it agrees well with other data (Table 1).

Among data for heated samples listed in Table 2 are two sets for samples heated at 1000°C. This duplication is intended to tie together the two series of runs at high and low temperature which involved different sorts of heating apparatus. In either run at 1000°C, Co is unaffected; the other elements for which comparison is possible—Bi, Ga, In, Se and Tl—are depleted to some extent. Indium is virtually identical in the two runs; other elements differ significantly, assuming that relative standard deviations determined for unheated samples hold in cases where concentrations are lowered by heating (cf. IKRAMUDDIN *et al.*, 1979). We attribute these small absolute variations to minor differences in the f_{O_2} in the two runs.

The erratic data for Ag and Cd in all heated samples (Table 2) suggest contamination introduced either during heating or from shards of the irradiation vial (cf. Papers IV, V). Other data support this suggestion; Ag concentrations in Allende decrease monotonically $\geq 700^\circ\text{C}$ to 79 ppt at 1315°C while Cd decreases monotonically from 500–900°C and is erratic at or above 1000°C (Paper IX). A few other results (Bi

at 1316°C and Ga $\geq 1268^\circ\text{C}$) may also reflect such contamination.

Relative retentivities

The data of Tables 1 and 2 depicted in Fig. 2 graphically illustrate the extent of losses. At 1393°C many elements are undetectable. Those elements which could be detected include Te, Cs, Se and Zn, depleted by factors of 3×10^{-4} – 10^{-5} relative to unheated Allende: even Co is highly-volatile, 99% being lost. At 1268°C, where most elements are still measurable, depletion factors are 0.78 for Co, 8×10^{-3} for Bi and Cs, 2×10^{-3} for Se and Te, 10^{-4} for Zn, $<3 \times 10^{-2}$ for Ag, Cd and Ga, $<3 \times 10^{-3}$ for In and $<10^{-4}$ for Tl.

The majority of elemental contents decrease progressively and sharply over the 1000–1393°C temperature interval to low ppb to ppt concentrations, i.e. achondritic or lower levels (Table 2, Fig. 2). While the concentration decrease of Ga, In, Te and Zn above 1000°C apparently extend trends evident at lower temperatures, Cs, Ga, Se and Tl (and other elements) decline much more precipitously than trends below 1000°C would indicate (Papers I and X). While Bi, like Cs or Se, is lost extensively above 1000°C, the extent of retention at these temperatures is surprisingly high. Below 1000°C, only Tl and In equal or exceed Bi in mobility (Paper I); above 1000°C, Se and

Table 2. Trace element contents of heated Allende

Heating temperature (°C)	Heating time (d)	Pressure (mtorr)		Ag§ (ppb)	Bi (ppb)	Cd§ (ppb)	Co (ppm)	Cs (ppb)	Ga (ppm)	In (ppb)	Se (ppm)	Te (ppb)	Tl (ppb)	Zn (ppm)
		Initial	Final											
1000*	7.00	20	320	—	6.13	—	624	—	5.7	3.67	7.9	—	4.3	—
1000	6.78	38	100	(2.5)	4.97	(18)	619	9.1	4.1	3.5	4.3	56.0	7.3	3.91
1100	6.69	70	165	(3.9)	2.66	(18)	574	—	0.32	0.54	0.23	17.3	0.60	0.484
1200	6.69	95	130	(5.7)	2.55	(300)	546	—	0.20	1.0	0.084	2.94	0.24	0.104
1268¶	6.82	50	2200	(2.0)	0.35	6.9	300	4.5	(1.0)	0.19	0.026	2.07	<0.07	0.0339
				(2.4)	0.38	(17)	483	0.79	(0.82)	<0.09	0.021	1.62	≤ 0.06	0.0148
1316	6.66	45	50	(2.1)	(0.60)	(15)	76.5	0.18	(0.76)	≤ 3	0.0081	0.56	—	0.0056
1393	6.64	50	640	—	—	—	6.05	0.048	—	—	0.0042	0.30	—	0.0016

* Data from Paper I for homogenized powder aliquots heated in SiO_2 . We obtained all other data from samples heated in ZrO_2 .

¶ Data in italics are from analysis of a single chip; all other data are from aliquots of homogenized powder.

§ Data in parentheses probably reflect contamination during heating and/or processing.

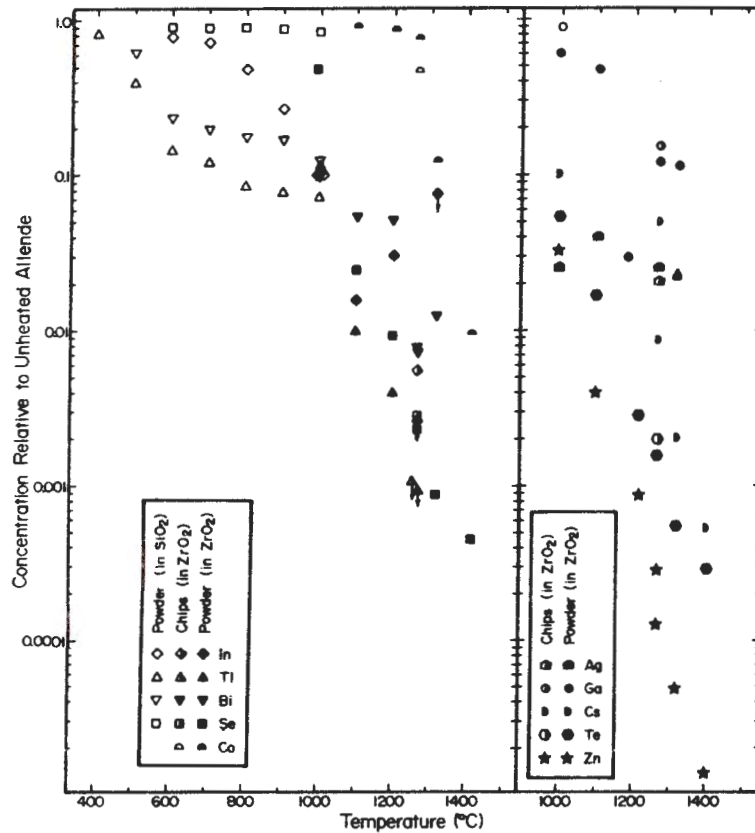


Fig. 2. Trace element concentrations in heated Allende samples relative to values for unheated material. Open symbols represent data published in Paper I for runs $\leq 1000^\circ\text{C}$ in quartz (we omit results for Allende chips); other symbols represent data from this study. The discontinuous and sharp decline of Bi, Se and Tl indicates an accelerated loss process $\geq 1000^\circ\text{C}$ compared with those at lower temperatures; In exhibits no such discontinuity. Other elements also exhibit such differences (see text).

Te join them (Fig. 2). Cobalt is lost only above 1000°C (Table 2).

Apparent activation energies

The data of Tables 1 and 2 and Paper I can be used to calculate apparent activation energies for trace element loss between 400 and 1400°C . To do this, we adopt the assumptions of Papers I–VI, VIII and X: (1) elemental loss proceeds from homogeneous spherical grains of size a , such that a diffusion parameter, D/a^2 (where D is the temperature-dependent diffusion coefficient), can be calculated from the relative trace element retention, C/C_0 , after a heating episode of time t (CRANK, 1956), e.g.

$$(1 - C/C_0) = 6\sqrt{Dt/a^2} \left[1/\sqrt{\pi} + 2 \sum_{n=1}^{\infty} \text{ierfc } n\sqrt{(a^2/Dt)} \right] - 3Dt/a^2; \quad (1)$$

(2) the diffusion parameter-dependence upon temperature is that described by the Arrhenius equation:

$$D/a^2 = D_0/a^2 e^{-Q/RT} \quad (2)$$

so that the slope of a line on a plot of $\ln D/a^2$ vs $1/T$

corresponds to the apparent activation energy, Q . ALAERTS and ANDERS (1979) have questioned this approach; we discuss our assumptions and their treatment of our data below.

We depict Arrhenius diagrams for 9 elements in Fig. 3. (Contamination prompts omission of Ag and Cd.) Extension to higher temperatures reveals that, as in Papers I–VI, VIII and X, trends for specific elements differ. For example, In data for samples heated above 1000°C extend the line defined by data at 500 – 1000°C . On the other hand, the bifurcate (two-pronged) character of Bi or Tl data below 1000°C is complicated by the definition of yet a steeper line above 1000°C (Fig. 3). The Se data of Paper I defined a line of relatively shallow slope at 600 – 900°C and hinted at another steeper one at 1000°C ; the additional data support this and delineate a third line between 1100 and 1400°C . Data for other elements—Co, Ga, Cs, Te and Zn—each seem to define a single line (Fig. 3). Other information (Paper X) reveals that trends for Cs, Te and Zn continue to 900°C with steeper lines being evident at lower temperatures. Cobalt and Ga are not lost below 1100 and 1000°C , respectively. We list numerical values for Q in Table 3: the values listed for Cs, Te and Zn are not altered significantly by inclusion of numerous ad-

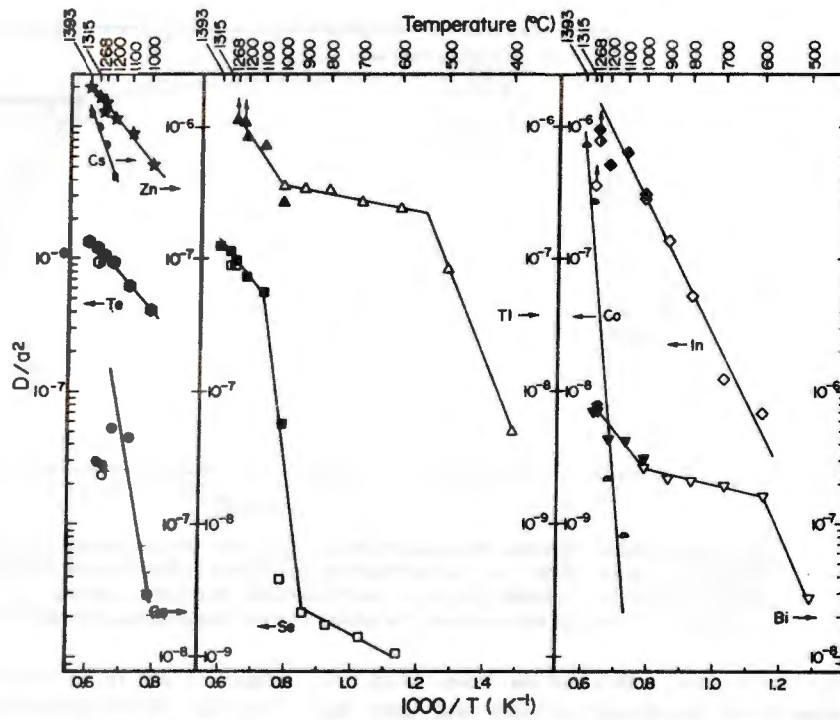


Fig. 3. Arrhenius diagrams for loss of 9 trace elements from heated Allende samples. Different scales have been used to compress these diagrams into minimum space; the arrow associated with each element designates the operative ordinate (e.g. 10^{-9} – 10^{-6} for Co). Half-filled symbols denote data from Allende chips; open and filled symbols represent results for powder aliquots from Paper I and this study, respectively. Trends for specific elements differ markedly; from 400–1400°C, In apparently is lost by a single process while Bi reflects different processes in 3 temperature intervals (see text).

ditional data (Paper X). Prior to discussing these results, we digress to consider other matters.

Models for loss

Although chondritic grains are neither spherical nor uniformly-sized (and, indeed, are altered in form, dimension and composition as a function of temperature [BART, PELLY and LIPSCHUTZ, unpublished data; Paper VII]), our choice of these conditions as a model system does not markedly affect relationships evident in Fig. 3. Treatment of elemental retentivity as reflecting diffusion from uniform hollow spheres of radius b

and thickness $(b - a)$ according to the relationship (CRANK, 1956):

$$C/C_0 = 6/\pi^2(a^2 + ab + b^2) \sum_{n=1}^{\infty} \times [(b \cos n\pi - a)/n]^2 e^{-[Dn^2t/(b-a)^2]} \quad (3)$$

leads to a dependence of relative retentivity with diffusion parameter similar to that for the solid sphere (Fig. 4). [As a check, we calculated the relationship of $a = 0$ for eqn 3, i.e.

$$C/C_0 = 6/\pi^2 \sum_{n=1}^{\infty} [(\cos n\pi)/n]^2 e^{-[(Dt/b^2)/(n^2\pi^2)]} \quad (4)$$

The resultant curve is completely coincident with the solid sphere curve calculated according to eqn (1) despite the difference in form of eqns (1) and (4)]. We depict two hollow sphere cases in Fig. 4; a relatively thick shell where $b/a = 10$ and an infinitely thin one, i.e. $a \rightarrow b$. (The latter case mathematically reduces to that of diffusion from an infinite sheet.) As can be seen, the thick-shell case is virtually superimposable upon the relationship of a solid sphere over most of the C/C_0 range; the thin-shell trend is displaced from that of the solid sphere but tends to approach it as C/C_0 values decrease. Where the solid sphere $Dt/(b - a)^2$ value is 2×10^{-2} (which corresponds to a diffusion parameter value of 3×10^{-8} in 1 week and a C/C_0 value of 0.58; cf. Fig. 3), the value for the infinitely

Table 3. Apparent activation energies for trace element loss from heated Allende

Element	Temp. Range (°C)	Q(kcal/mol)
Bi	500–600	24
	600–1000	3.0
	1000–1268	12
Co	1100–1393	110
Cs	1000–1393	15
Ga	1000–1200	55
In	600–1200	21
	600–900	5.5
Se	900–1100	86
	1100–1393	14
Te	1000–1393	13
Tl	400–500	29
	600–1000	2.3
Zn	1000–1200	22
	1000–1398	14

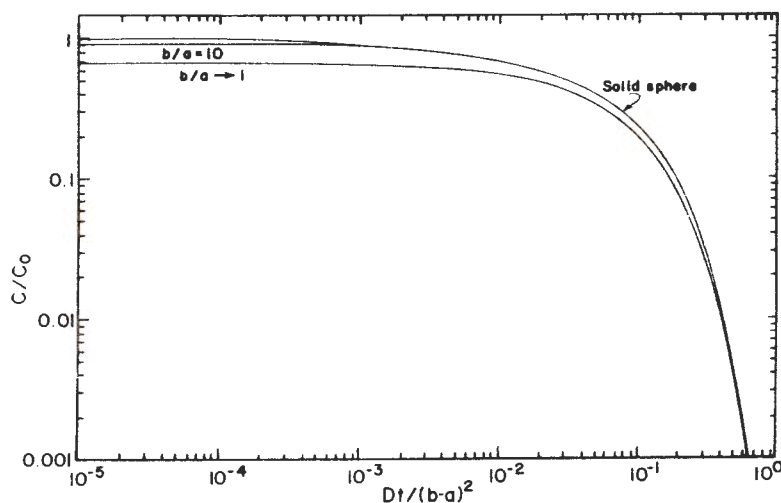


Fig. 4. Relationship between elemental retentivity in heated sample relative to initial value, C/C_0 , vs diffusion parameter, $Dt/(b-a)^2$, for solid sphere ($a=0$) and hollow spheres with thick ($b/a=10$) and infinitely thin ($b/a \rightarrow 1$) shells. The last is mathematically identical to diffusion from an infinite sheet. Since all relationships are so similar, the choice of a particular diffusion model is not a critical one.

thin shell is about a factor of two lower. Most C/C_0 values in our experiments are very much lower (e.g. Fig. 2) and the difference in $Dt/(b-a)^2$ values would be much smaller. Thus, when the solid sphere $Dt/(b-a)^2$ value is 0.1 (corresponding to a diffusion parameter value of 2×10^{-7} and C/C_0 of 0.23), the value for the infinitely thin hollow sphere is only 16% lower, e.g. 0.084 (Fig. 4). At C/C_0 values ≤ 0.1 , differences in diffusion parameter values would be 10% or less, i.e. of minor importance (Fig. 4).

The discussion above points up one more characteristic of Fig. 3 and similar diagrams, i.e. that a given experimental uncertainty affects diffusion parameters (hence, apparent activation energies) more at high retentivities than where losses are very substantial. For example, let us assume that the relative uncertainty for determination of a given element derived from replicate analyses of unheated samples is the same as that for the element in heated samples; this is probably an underestimate in cases where substantial loss occurred. The mean uncertainty for all elements listed in Table 1 is 7.4%, a value close to that of Tl, 6.6%, an element we may therefore consider as representative. At 400°C, Tl is lost significantly and it is still measurable at 1200°C. At these temperatures, C/C_0 values (assuming 6.6% relative uncertainty) are 0.822 ± 0.061 and 0.00403 ± 0.00030 , respectively. At 400°C, the C/C_0 values correspond to a D/a^2 range of $(2.1-9.5) \times 10^{-9}$, i.e. a variation of 452%, while at 1200°C, the corresponding D/a^2 range, $(8.3-8.5) \times 10^{-7}$, varies by but 3% (cf. Fig. 3). Thus, apparent activation energies for processes occurring at low temperatures (hence high retentivities) are more uncertain than those occurring at high temperatures where retentivities are very much lower.

Trace element siting

ALAERTS and ANDERS (1979) re-interpreted our data

(Papers I and II) to arrive at conclusions different from ours. Before commenting on their treatment of our data, we summarize their arguments.

1. Apparent activation energies from Paper I indicate that Tl loss from Allende at 400–600°C is controlled by a process with a more positive entropy change than that occurring from 600–1000°C.

2. Since trace elements are undergoing a solid-to-vapor transition, the smaller entropy increase at higher temperatures seems paradoxical to ALAERTS and ANDERS (1979) who eliminate the possibility of a high-temperature, low activation energy process following a lower-temperature, high activation one during heating.

3. Thus, ALAERTS and ANDERS (1979) postulate that either bifurcate lines, e.g. those of Bi or Tl $\leq 1000^\circ\text{C}$ (cf. Fig. 3), or substantial trace element loss at low temperatures reflect the emptying of two reservoirs rather than the existence of two different loss processes, each rate-determining in a separate temperature interval. They consider apparent activation energies of 2–5 kcal/mol as unreasonably low and, hence, artifacts. LARIMER and ANDERS (1967) and LARIMER (1973) previously postulated that Bi, Tl and In each were present in two different host sites.

4. ALAERTS and ANDERS (1979) postulate the need to determine the proportion of each element in each site. They attempt to do this by recasting integral release data (such as those reported here and in Papers I–VI and X) as differential release histograms.

5. ALAERTS and ANDERS (1979) resolve each histogram into two or three 'peaks' (each covering a few hundred degrees), which they treat separately to compute apparent activation energies according to eqn (2). The resulting lines, each of 2 or 3 points, have slopes corresponding to 18–35 kcal/mole. These, they argue, correspond to activation energies for volatile element release from the various host sites.

We disagree with this interpretation on both substantive and circumstantial grounds and present our arguments in response to questions implied by the points above.

Paradoxical data treatment? We agree that the loss process at 400–600°C apparently involves a more positive entropy change than that at 600–1000°C but this is not paradoxical. In solids, diffusive processes often exhibit several activation energies over different temperature spans (e.g. SATO and KIKUCHI, 1971) and, more often than not, the higher temperature process has a lower activation energy than that occurring at lower temperature (Sato, personal communication). For example, ionic conductivities (which can be readily identified with the diffusion of specific ions) in AgI, RbAg₄I₅ and various solid state fluorides exhibit such behavior (cf. review by SATO (1977) and personal communication). Argon loss from KCl and KBr single crystals heated in the solid state also proceeds in this manner (RICHTER and ZIMEN, 1965). This is particularly relevant since KCl and KBr are both simple and well-characterized and loss of Ar involves both diffusion and volatilization as does trace element mobilization from heated chondrites.

HAVEN and VAN SANTEN (1952) very early recognized the consequences of this behavior, i.e. a less positive entropy at higher temperatures (cf. JOST, 1960), and it has since been understood as reflecting changes in the diffusion mechanism and/or structural change (HAVEN, personal communication; cf. review by SATO, 1977). In the present case, i.e. the heating of primitive chondrites, structural changes abound in all major phases—and nearly all minor ones—in carbonaceous chondrites (Paper VII; BART *et al.*, unpublished data). Mobile trace elements may be sited in a particular host or be dispersed among several phases but for most elements there are virtually no experimental data available bearing on host phases or siting. Bismuth is exceptional. As hypothesized by Anders and co-workers, it may be sited in matrix and metal but this may well reflect secondary processes. A search for Bi enrichment in metal in Allende and other carbonaceous and enstatite chondrites was unsuccessful and WOOLUM *et al.* (1977) concluded that it is a dispersed element, i.e. relatively homogeneously distributed in a number of host sites in such chondrites during nebular condensation. WOOLUM *et al.* (1978a) did observe Bi enrichment in metal from L3 chondrites; however, this enrichment is much larger than that calculated by LARIMER (1973) and seems to reflect processes other than primary nebular ones (WOOLUM *et al.*, 1978a, b, 1979). In passing, we should correct a misapprehension of ALAERTS and ANDERS (1979). In Papers I–VI and X, we repeatedly referred to data such as those of Tl in the 600–1000°C temperature interval as denoting ‘a low-energy process, like *desorption*’. Actually, diffusive processes have equally low activation energies (SATO, 1977; FARRINGTON and BRIANT, 1979; cf. VAN GOOL, 1974). Volatile loss may involve desorption but, as will be discussed,

we observe no evidence that this process is rate-determining.

Release curve calculations? In computing differential release curves from our integral release data, ALAERTS and ANDERS (1979) and we disagree as to how to calculate experimental uncertainties for our measurements. In most cases this is critical since, in attempting to recast integral as differential data, one obtains a very small difference between two large numbers. Partly for this reason, we measured the amount *retained* in each heating run, not the amount *lost*. Each concentration we measure, C_i , has an associated uncertainty, σ_i , that reflects heterogeneity (sample-to-sample variability), experimental uncertainties arising from our analytical procedures and statistical uncertainties of counting. Thus, the initial concentration of an element in an unheated sample is $C_0 \pm \sigma_0$; the amount of that element retained after heating another aliquot of that sample at temperature T_1 is $C_1 \pm \sigma_1$ while that in a third aliquot heated at a higher temperature T_2 is $C_2 \pm \sigma_2$. We explicitly treat:

$$\frac{\sigma_0}{C_0} = \frac{\sigma_1}{C_1} = \frac{\sigma_2}{C_2} = \dots = \frac{\sigma_n}{C_n} \quad (5)$$

[Analysis of Abee samples heated in separate runs at 700°C demonstrates that this assumption holds for Bi and Tl but not In, when concentrations are reduced moderately, i.e. by factors of 3–15 (IKRAMUDDIN *et al.*, 1979). Clearly, where losses are greater, σ_n/C_n should exceed σ_0/C_0 ; thus the latter is a lower limit to the experimental relative uncertainty.] The amount of an element *lost* per gram in heating an aliquot at T_1 is, then, the difference between the initial concentration and the amount retained, or:

$$(C_0 - C_1) \pm \sqrt{\sigma_0^2 + \sigma_1^2} \quad (6)$$

The amount lost in heating another aliquot at T_2 is then:

$$(C_0 - C_2) \pm \sqrt{\sigma_0^2 + \sigma_2^2} \quad (7)$$

Thus, the uncertainty, $\sigma_{1,2}$, in the amount lost, $(C_1 - C_2)$, over the temperature interval $(T_2 - T_1)$ is:

$$\sigma_{1,2} = \pm \sqrt{2\sigma_0^2 + \sigma_1^2 + \sigma_2^2} \quad (8)$$

For the second and later steps, $\sigma_{1,2} \geq 1.4\sigma_0$ and is as small as $1.4\sigma_0$ only when $C_0 \gg C_n$.

ALAERTS and ANDERS (1979) contend that since ratios are involved, i.e. $(C_1 - C_2)/C_0$, $\sigma_{1,2}$ should be calculated by:

$$\sigma_{1,2} = (C_1 - C_2)/C_0 \sqrt{(\sigma_0/C_0)^2 + (\sigma_1^2 + \sigma_2^2)/(C_1 - C_2)^2} \quad (9)$$

where σ_0 contributes little to $\sigma_{1,2}$. They did not plot these uncertainties on the differential release histogram that they calculated from our data.

It is important to note that the only uncertainty estimated directly is σ_0 ; all others are calculated

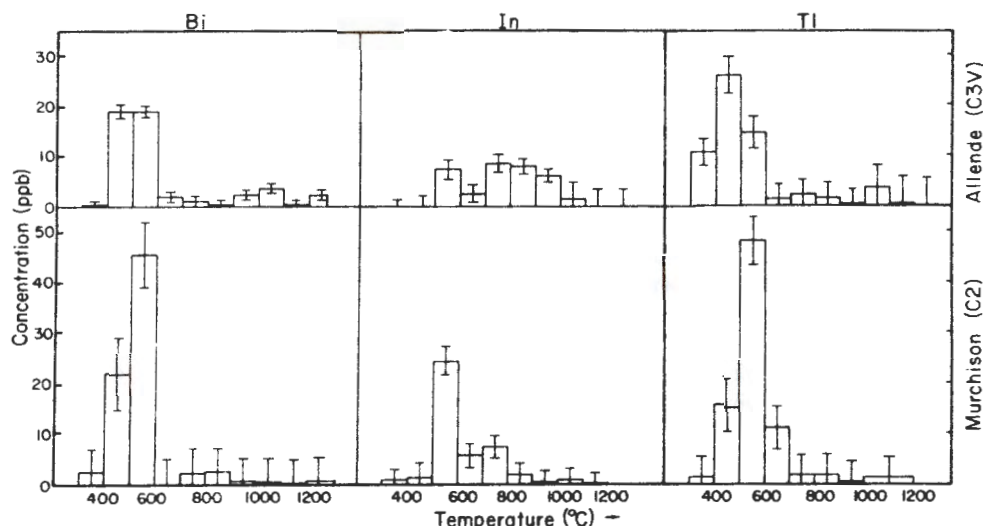


Fig. 5. Differential release histograms calculated from integral release experiments for Bi, In and Tl in Murchison (C2) and Allende (C3V). Error bars shown are 1σ . A large proportion of each element is lost at low temperatures (400–600°C) but experimental uncertainties are large enough to obscure the fine structure at higher temperatures.

according to eqn (5) where σ is assumed proportional to C . Thus, in calculating $\sigma_{1,2}$ from eqn (9), ALAERTS and ANDERS (1979) implicitly assume that *all* sources of error are proportional to the quantity of trace element remaining after heating. As corollaries, *real sample-to-sample trace element variations are either zero or proportional to the amount of that element present*. Neither corollary seems justified to us.

We maintain that $\sigma_{1,2}$ must be calculated from eqn (8) and the uncertainties shown in Fig. 5, were determined in this manner. We plot elemental concentration rather than percentage loss as the ordinate in the calculated differential release curves for Bi, In or Tl from Murchison (Paper VI; MATZA, 1978) and Allende (Table 1 and 2; Paper I) to emphasize the small quantities involved. For example, the putative Bi peak of ALAERTS and ANDERS (1979), 2.2 ± 1.0 ppb, in the 900–1000°C temperature interval of Allende corresponds to 0.66 ng Bi, i.e. the difference between the 2.49 and 1.83 ng Bi we actually *measured* in the 0.3 g aliquots heated at 900 and 1000°C, respectively. If one heated an aliquot of Allende *seriatim* and attempted to measure directly an evolved Bi 'essence' of 0.66 ng we would not expect the precision to be very high. It seems to us that the proper way to determine a differential release curve and establish its precision is to conduct differential heating experiments such as are used for most noble gas studies. Failing this, due account must be kept, as in eqn (8), of all sources of error.

Figure 5 illustrates that a large proportion of each mobile element is lost at quite low temperatures—but we knew this from our own data-treatment (cf. Fig. 2). We submit that the remaining trends are too imprecise—*because of the manner in which measurements were made*—to be definitive. It should be pointed out that eqns (1), (3) and (4) indeed depend

upon the proportion of each element *retained*. Since this is actually measured, the uncertainty at each temperature step is given by:

$$\sigma_i = (C_i/C_0) \sqrt{(\sigma_i/C_i)^2 + (\sigma_0/C_0)^2} \quad (10)$$

and, if eqn (5) holds, the relative uncertainty at each temperature is $1.4 \times$ that for unheated material.

Two reservoirs? ALAERTS and ANDERS (1979) suggest that either bifurcate lines on an Arrhenius diagram or a substantial low-temperature release constitute criteria for postulating location of a given trace element in two or more sites. We cannot verify their suggestions.

The solid-state diffusion of Na^+ in β or β'' -alumina and of Ag^+ in $(\text{C}_5\text{H}_5\text{NH})\text{Ag}_5\text{I}_6$ are among the few well-studied cases (cf. GELLER, 1977a; FARRINGTON and BRIANT, 1979) and both yield bifurcate lines on Arrhenius diagrams, with the high-temperature limb having a lower activation energy than the low-temperature portion. In β or β'' -alumina, Na^+ is known to occupy but one site at low temperature; during heating, Na^+ diffusion apparently involves additional sites (SATO and KIKUCHI, 1971; SATO, unpublished data; cf. FARRINGTON and BRIANT, 1979). In the case of $(\text{C}_5\text{H}_5\text{NH})\text{Ag}_5\text{I}_6$, several mechanisms have been proposed, most of which involve phase transitions (GELLER and OWENS, 1972; HIBMA, 1977; PARDEE and MAHAN, 1975; cf. GELLER, 1977b). Similarly, Ar-loss from heated KCl or KBr also seems to reflect changes in diffusion mechanism at low and high temperatures (RICHTER and ZIMEN, 1965).

The evidence above demonstrates that a species may be sited in one location, yet yield bifurcate lines on an Arrhenius plot: we now examine data showing that elements sited in 2 or more locations can yield one line on such a plot. In Allende, Ne is a mixture of trapped and cosmogenic components, presumably

sited differently (MANUEL *et al.*, 1972; SRINIVASAN *et al.*, 1977). The trapped component is released preferentially in integral release experiments, yet each Ne isotope exhibits but one apparent activation energy (Paper VIII). Bismuth is apparently a dispersed element in chondrites; it is, in addition, sited in kamacite in unequilibrated ordinary chondrites but not, apparently, in carbonaceous or enstatite chondrites (WOOLUM *et al.*, 1977, 1978a, b, 1979). Despite these siting differences, Arrhenius diagrams for Bi release from artificially heated carbonaceous, enstatite and unequilibrated ordinary chondrites (and terrestrial basalt BCR-1) are essentially similar, i.e. bifurcate with low apparent activation energies at high temperatures. Indeed, we noted earlier that considering the genetic, chemical and mineralogic diversity of the samples in Papers I–VI, the similarity in retentivity patterns for a given trace element is surprising, not the few subtle differences. These facts suggest that Arrhenius diagrams cannot be used to deduce the number of possible reservoirs (cf. HUTCHINSON *et al.*, 1979).

Substantial proportions of noble gases are released from Allende during heating at quite low temperature [Paper VIII; cf. MANUEL *et al.* (1972) and SRINIVASAN *et al.* (1977)]. The release patterns for ^{20}Ne and ^{40}Ar are quite similar despite the fact that several components (presumably sited differently) contribute to ^{20}Ne while ^{40}Ar is largely, if not entirely, radiogenic and therefore associated with K. Apparently, degree of low temperature release seemingly gives no clues to number of reservoirs.

ANDERS (personal communication) suggests that each noble gas nuclide exhibits but one apparent activation energy in Allende (Paper VIII) simply because, unlike trace elements like Bi or Tl, noble gases do not absorb well on surfaces. Hence, noble gases should not exhibit bifurcate character on Arrhenius diagrams since, in the view of ALAERTS and ANDERS (1979), the only elements capable of exhibiting such character are those whose loss, in part, reflects a rate-determining desorption step. This suggestion is contradicted by the Ar-release data of RICHTER and ZIMEN (1965). During the heating of KCl and KBr, Ar exhibits a high apparent activation energy below $\sim 400^\circ\text{C}$ (55 and 36 kcal/mol, respectively) and a lower one above 400°C (14 and 8 kcal/mol, respectively). Thus, a noble gas exhibits bifurcate lines on Arrhenius diagrams because of changes in diffusion mechanism and not from a rate-determining desorption step.

Thus, experimental data and theoretical considerations argue against the imaginative interpretation of our results by ALAERTS and ANDERS (1979). During the many years of development of solid state experiment and theory there appears to have been no necessity to invoke 'deconvolution' of diffusion data. Indeed, different apparent activation energies in specific temperature ranges are common, even where morphologic, mineralogic and compositional changes are much less extreme than are observed in heated

primitive chondrites. Such differences are ascribed to changes in diffusive mechanism from lower to higher temperature regions (cf. GELLER, 1977a). Hence, we see no advantage or reason to abandon conventional wisdom and we will follow established procedures in assuming that trace element mobilization reflects variation in loss mechanism rather than host site differences.

Trace element loss and meteoritic alteration

There appears ample justification for concluding that kinetics of trace element loss reflect processes occurring over different temperature spans rather than siting differences. These processes, in turn, seem related to mineralogic/petrologic alterations in heated samples which, unfortunately, are not yet as well-characterized in Allende as in Murchison (Paper VII). Where comparison is possible, the response of the two carbonaceous chondrites to heating is generally similar although, as summarized below, differences in detail appear. These minor differences are understandable since mineral assemblages and compositions differ in Allende and Murchison (CLARKE *et al.*, 1970; FUCHS *et al.*, 1973)—as indeed in all C2 and C3 chondrites. For example, Murchison's matrix contains much less Fe and is more extensively hydrated than is Allende, the relative pentlandite/troilite ratio is much higher and these sulfides are compositionally more uniform in Allende than Murchison and metal in Allende is taenite rather than kamacite as in Murchison.

Texturally, matrix-coarsening in both chondrites advances with temperature until matrix transforms to olivine between 1000 and 1100°C in Murchison (Paper VII) or between 1100 and 1200° in Allende (BART *et al.*, unpublished data). We observed no evidence for matrix-melting below the olivine transformation-temperature; above these temperatures, partial melting occurred (cf. Paper VII). In Allende, as in Murchison, Cr-rich magnetite apparently forms at $\geq 1315^\circ\text{C}$ from pre-existing metal and sulfides. In Murchison, metal and sulfides form and/or survive to $\leq 1200^\circ\text{C}$ (Paper VII); in Allende, metal also persists to 1200°C but we could not identify sulfides positively above 1000°C (BART *et al.*, unpublished data). Microscopically, sulfides in heated Allende are difficult to identify and IKRAMUDDIN *et al.* (1975) reported them absent $\geq 700^\circ\text{C}$; we identified Ni-containing sulfides in samples heated at 700 – 1000°C , however (BART *et al.*, unpublished data). Isolated olivine grains in Murchison become progressively Fe-rich and more equilibrated with increasing temperature to 1200°C , after which Fe-volatilization causes a decrease in $F\bar{a}$ (Paper VII). [At 1100 and 1200°C , massive transformation of Fe-rich matrix to olivine exaggerates the Fe-enrichment in Murchison olivines.] In Allende, olivine tends to equilibrate and $F\bar{a}$ contents increase with heating temperature to 1100°C . At 1200°C , the $F\bar{a}$ content is lowered as the olivine reservoir is diluted by transform-

ation of Fe-deficient matrix and at higher temperatures, Fe volatilization lowers F_{a} contents further (BART *et al.*, unpublished data). Thus, thermally-induced mineralogic alterations in Allende and Murchison are so similar that photomicrographs in Paper VII generally depict changes in heated Allende as well.

For the elements considered here, discontinuities occur in Arrhenius diagrams (Fig. 3; cf. Paper X) at 600°C (Bi, Tl), 900°C (Cs, Se, Te, Zn) and 1000–1100°C (Bi, Se, Tl); these are temperatures at which major mineralogic/petrologic alterations occur in matrix, sulfides and/or metal. These include: matrix coarsening from 500–600°C to 1000 or 1100°C above which it transforms to olivine; decomposition of Ni-rich sulfides $\geq 600^\circ\text{C}$, sulfide disappearance at 1000°C (presumably from formation of Fe–FeS eutectic at 98°C) and formation of a new S-bearing phase at 1000–1200°C; formation of secondary metal $\geq 600^\circ\text{C}$ from a variety of sources with substantial grain-growth to 1200°C; compositional changes at 400–1400°C in ferromagnesian silicates having stability fields extending over the entire experimental temperature range. We could speculate upon the specific phase(s) hosting some element at a given temperature but this would be unproductive since, for most elements, host site(s) or even host minerals (if there are specific ones) are unidentified in unheated chondrites. One might suggest that such elements are located in very minor and, as yet, undiscovered phase(s) but this is immaterial unless one adopts the additional *ad hoc* assumption that the host(s) will not alter during heating. In fact, as discussed earlier, Bi host(s) in ordinary chondrites apparently are affected by secondary processes (WOLLUM *et al.*, 1978a, b, 1979).

Several reviewers suggest that partial melting may alter trace element loss patterns in our experiments but all evidence contradicts this suggestion. Relative retentivities of In, Se and Tl (Fig. 2) and Cu (Paper X) in Allende decrease markedly at 1100°C (i.e. below the onset of detectable melting) and decline smoothly thereafter. Retentivities of other elements—Bi, Cs, Ga, Te and Zn (Fig. 2) and Ag, As, Cu, Rb and Sb (Paper X)—at temperatures $\geq 1000^\circ\text{C}$ extend trends evident at even lower temperatures. Cobalt is not lost significantly (Fig. 2) until 1315°C, i.e. where metal disappears, while Cd declines below detectable limits by 1000°C (Paper IX). [Discontinuities in relative retentivities for such elements as Ag, Bi, In, Te, Tl or Zn (Fig. 2; cf. Paper X) would not, of course, be discernible in differential release histograms calculated from integral release data (e.g. Fig. 5).] Arrhenius diagrams (e.g. Fig. 3; cf. Paper X) are consistent with these observations.

Thus, during heating, numerous opportunities arise for changes in the local environment of a trace element and hence, its diffusive properties: e.g. mineralogic phase transformations; generation or destruction of lattice imperfections or defects; changes in lattice dimension; oxidation or reduction of the trace ele-

ment itself. These and other explanations have been advanced to account for temperature-dependent ionic mobility changes similar in kind to those of Bi or Tl below 1000°C, which involve host structural changes much less severe than those observed in heated meteorites (GELLER, 1977b; KENNEDY, 1977; SATO, 1977). Indeed, even a macroscopically-homogeneous system may exhibit Bi- or Tl-like behavior on an Arrhenius diagram. Nearly three decades ago, HAVEN (1950) reported such behavior for the temperature-dependent ionic conductivity in LiF–MgF₂ mixed crystals with the high-energy, low-temperature line partly reflecting the energy of solution of the mixed crystal into the matrix, the low-energy, intermediate-temperature line reflecting impurity—determined conduction and the high-energy, high-temperature line reflecting the intrinsic conduction (HAVEN, personal communication). In the absence of additional information it is impossible to specify the exact mechanism controlling loss of a specific mobile trace element over a given temperature interval. It should be noted that activation energies for ions such as Ag⁺ or Tl⁺ in β -alumina (measured by tracer diffusion) can be as low as 4–8 kcal/mol (KENNEDY, 1977); even activation energies of 2–4 kcal/mol are not rare (SATO, 1977; FARRINGTON and BRIANT, 1979; cf. VAN GOOL, 1974). Thus, known diffusion processes have activation energies as low as those we determined.

While the trifurcate character of Bi, Tl or Se (or bifurcate character of other elements) in Fig. 3 may well indicate changes in specific diffusion mechanism with temperature, we need not even require this. For example, let us assume that Tl resides only in one site in the matrix and that the mechanism by which it diffuses to grain surfaces at 500°C is identical to that at 800°C. Over this temperature span, grain sizes increase very perceptibly as determined by electron microscopy (BART *et al.*, unpublished data) so that the denominator in the diffusion parameter (which is the square of the grain size) increases markedly, decreasing the slope of the line between 600 and 1000°C. At temperatures above 1000°C, incongruent melting or massive phase transformations would involve additional processes. This is, of course, merely a permissive argument. It is at least equally probable that diffusion mechanisms do change in different temperature regions and that the apparent activation energies listed in Table 3 reflect these processes.

HAVEN (personal communication) suggests yet another possibility: that trace element loss requires a cooperative series of steps, e.g. diffusion in part through a portion of a macroscopically homogeneous grain followed by diffusion along a grain boundary or dislocation. In this event the macroscopic diffusion coefficient, D , would reflect diffusion both through the grain (i.e. D_1) and along the boundary or dislocation (i.e. D_2) by the relationship:

$$\frac{2}{D} = \frac{1}{D_1} + \frac{1}{D_2} \quad (11)$$

so that:

$$D = \frac{2D_1 D_2}{D_1 + D_2} \quad (12)$$

HAVEN (personal communication) also suggests that this cooperative series might even involve a fraction of the atoms, X, diffusing through the grain while the remainder diffuse along the boundary or dislocation such that

$$\left[\frac{1}{D} = X \cdot \frac{1}{D_1} + (1 - X) \cdot \frac{1}{D_2} \right] \quad (13)$$

According to HAVEN (personal communication), one could reasonably postulate that diffusion through the grain is the rate-determining step at low temperature and boundary or dislocation diffusion is the limiting factor at high temperature. In this event, the latter sites—being relatively few in number—would be saturated at higher temperatures by material diffusing from the grains and would then determine the loss-rate of the diffusing species. Thus, the macroscopic diffusion coefficient D would, according to eqn (12), delineate a high activation energy at low temperature and a low activation energy at higher temperatures. Of course there is no need to limit such a cooperative series to two steps; a third separate diffusive process could be invoked or one could postulate by-passing the boundary/dislocation process at yet higher temperatures. In any event, the essential point is that here again, the macroscopic coefficient measures the total process.

One might envision other scenarios with which the activation energies in Table 3 could be consonant but only additional experiments can decide among the various possibilities.

CONCLUSIONS

Extension of the temperature range of heating experiments upon primitive chondrites into the thermal regime of chondritic differentiation markedly affects retentivity trends of many trace elements. Losses of some mobile elements at temperatures above 1000°C monotonically extend trends evident below 1000°C while other trends are markedly increased. Apparent activation energies apparently reflect diffusive processes that vary in specific temperature regions and do not yield siting information. Due to their temperature-dependence, these energies should be directly applicable to heating episodes in parent bodies unless subsequent loss steps, rapid in our experiments, become rate-determining in these bodies. The successful construction of an apparatus capable of withstanding extended heating at 1000–1400°C in a contamination-free, low-pressure environment now makes possible trace element vaporization studies in primitive materials subjected to simulated differentiation. These data, in concert with other results, should shed light

on possible relations between differentiated meteorites and less evolved ones.

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