

## Thermal metamorphism of primitive meteorites—X. Additional trace elements in Allende (C3V) heated to 1400°C

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**Abstract**—We report data for Ag, As, Cd, Cs, Co, Cu, Rb, Sb, Te, Tl and Zn in Allende samples subjected to week-long heating at 400–1400°C in a low-pressure H<sub>2</sub> environment. Temperatures of incipient release for these 11 and 5 additional elements tend to be ordered in a manner similar to postulated condensation sequences during cooling of nebular material but there are differences. Losses progress with temperature but neither the extent of loss nor apparent activation energies for mobilization would have been predictable to even a zeroth order approximation. Elemental retentivity trends and interelement correlation patterns for Allende (C3V) and Murchison (C2) differ markedly indicating a substantially different trace element siting, hence loss trends for these two chondrites.

### INTRODUCTION

TRACE ELEMENT retentivities in primitive chondrites—i.e. those with compositions primarily reflecting nebular processes—artificially heated for 1 week at low pressures (initially  $\sim 10^{-5}$  atm H<sub>2</sub>) illuminate thermal episodes in meteoritic parent bodies. Initially, six elements (Bi, Co, Ga, In, Se, Tl) were surveyed in Allende (C3V) samples heated at 100°C increments from 400–1000°C; subsequently, these and 5 other elements (Ag, Cd, Cs, Te and Zn) were determined in similarly-heated Abee (E4), Krymka (L3), Tieschitz (H3) and Murchison (C2) (IKRAMUDDIN and LIPSCHUTZ, 1975; IKRAMUDDIN *et al.*, 1976, 1977a, b; MATZA and LIPSCHUTZ, 1977—hereafter denoted Papers I–V, respectively). In each case, all elements but Co are progressively mobilized, i.e. volatilized and lost, over a broad temperature range. Although differences between specific meteorites occur; e.g. in general retentivity or trends of particular elements—trace element mobilization patterns for these mineralogically and chemically diverse meteorites are surprisingly similar. These trends may yield siting information (ALAERTS and ANDERS, 1979) although it seems more likely they reflect specific loss mechanisms (BART *et al.*, 1980—hereafter Paper IV). Comparison of trace element trends in artificially heated primitive chondrites and more evolved congeners (e.g. cf. references in BINZ *et al.*, 1974, 1976; Papers I–V) suggests that enstatite chondrites and achondrites compositionally reflect open-system metamorphic loss and subsequent partial melting (cf. BISWAS *et al.*, in preparation). Ordinary and most carbonaceous chondrites seem to have escaped open-system metamorphism,

except that L-group chondrites contain hints of trace element loss during extended cooling of shock-heated material (Paper VII; NEAL *et al.*, in preparation).

While comparison of retentivity data for the same elements in heated primitive chondrites of various chemical groups is productive, particularly where more evolved chondrites of the same group exist, it is also useful to study a larger number of elements in a single chondrite. Allende seems a natural candidate for this since retentivities of C, S and noble gas nuclides have been established for samples heated at 400–1000°C (HERZOG *et al.*, 1979—hereafter Paper VII) as have major, minor and other trace elements (including rare earths) in samples heated at 1800–2000°C, albeit in a significantly-different manner (NOTSU *et al.*, 1978). Furthermore, elemental retentivity in Allende is generally so high that the probability of measuring additional trace elements of intermediate-to-high volatility is reasonable even at quite high temperatures (Papers I–V). To broaden the coverage, we decided to measure Ag, Cd, Cs, Te and Zn—i.e. those elements determined in Papers II–VI but not in I—in heated samples, thus completing coverage of these highly-mobile elements over the entire temperature range, 400–1400°C. We felt it worthwhile including Co and Tl to assess measurement reproducibility in different heating experiments for the least- and most-mobile elements, despite some overlap with data in Papers I and VI. Our major interest, however, was to determine the behavior of hitherto unstudied As, Cu, Rb and Sb—elements thought to be of intermediate nebular volatility (ANDERS *et al.*, 1976; WAI and WASSON, 1977)—under simulated metamorphic conditions known to cause substantial loss of more volatile elements. We report these results here together with a summary of all data for Allende.

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Table 1. Trace element contents of unheated Allende homogenized powder

| Sample No. | Ag (ppb) | As (ppm) | Cd (ppb) | Cs (ppb) | Co (ppm) | Cu (ppm) | Rb (ppm) | Sb (ppb) | Te (ppm) | Tl (ppb) | Zn (ppm) |
|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1          | 96.6     | 1.35     | 590      | 89.0     | 604      | 110      | 1.06     | 82       | 0.95     | 58.1     | 118      |
| 2          | 103      | 1.71     | 549      | 91.0     | 644      | 105      | 1.08     | 92       | 0.95     | 61.9     | 116      |
| 3          | 98.2     | 1.58     | 555      | 95.0     | 658      | 107      | 1.15     | 82       | 0.93     | 66.7     | 115      |
| 4          | 97.3     | 1.13     | 568      | 92.0     | 623      | 106      | 1.11     | 70       | 1.17     | 65.7     | 114      |
| 5          | 96.2     | 1.11     | 481      | 88.5     | 651      | 106      | 1.04     | 82       | 1.14     | 64.3     | 114      |
| 6          | 102      | 1.30     | 539      | 86.0     | 620      | 105      | 1.16     | 67       | 1.20     | 59.4     | 119      |
| 7          | 108      | 1.74     | 462      | 85.2     | 675      | 109      | 1.09     | 63       | 1.16     | 63.6     | 116      |
| 8          | 97.8     | 1.56     | 465      | 84.8     | 648      | 105      | 1.17     | 58       | 0.92     | 61.8     | 111      |
| 9          | 104      | 1.46     | 466      | 89.6     | 670      | 110      | 1.15     | 66       | 1.28     | 61.4     | 119      |
| 10         | 105      | 1.46     | ---      | 91.5     | 660      | 110      | ---      | 85       | 1.18     | 55.6     | 108      |
| mean*      | 101      | 1.44     | 519      | 89.3     | 645      | 107      | 1.11     | 75       | 1.09     | 61.8     | 115      |
|            | ±4       | ±0.22    | ±51      | ±3.3     | ±23      | ±2       | ±0.05    | ±11      | ±0.13    | ±3.4     | ±3       |
| 11†        | 96.1     | 1.59     | 526      | 96.8     | 637      | 110      | 1.12     | 69       | 1.05     | 58.8     | 108      |

\* Uncertainties listed are one estimated standard deviation from the mean calculated from the dispersion of the individual measurements.

† This sample irradiated in the University of Missouri Research Reactor. Other trace elements determined in this sample are: Au—142 ppb; Bi—50.0 ppb; Ga—6.09 ppm; In—31.8 ppb (Biswas, unpublished data).

### EXPERIMENTAL

All Allende samples were aliquots of homogenized powder from NMNH 3529, split 22, position 32. Samples heated >1000°C were separate aliquots included in runs listed in Paper VI while those heated ≤1000°C were from runs separate from those reported in Paper I: the heating apparatuses and techniques used are described in those Papers.

We prepared all samples and monitors for neutron activation analysis as described in Paper II except that we used four monitor vials: (A) Bi, Tl; (B) Co, Ga, In, Se, Zn; (C) As, Au, Cs, Cu; (D) Ag, Cd, Rb, Sb, Te. With but two exceptions, an unheated sample (Table 1) and one heated at 1000°C (Table 2), all irradiations were performed in the CP-5 Reactor of the Argonne National Laboratory at a thermal flux of  $2 \times 10^{13}$  neutrons/sec cm<sup>2</sup>. [To clarify a

point raised by a reviewer, samples were heated *prior* to neutron irradiation. Thus, radiation damage could not affect trace element loss trends.] To maximize sensitivity, unheated samples and those heated to ≤1000°C were initially 300–400 mg and were irradiated for five days; those heated >1000°C initially weighed 400–500 mg and experienced two 5-day irradiation cycles bracketing a 2-day reactor shut-down. After this study, the closing of the CP-5 forced a shift to the Univ. of Missouri Research Reactor (UMRR). While the latter has a significantly higher thermal neutron flux, the fast/thermal ratios are also substantially higher, possibly causing self-shadowing and resonance absorption. For future reference, it was necessary to assess any effects by analysis of bulk Allende for elements studied here and a few others—Au, Bi, Ga, In (Tables 1 and 2); these samples were irradiated for four days at a thermal flux of  $1.2 \times 10^{14}$  neutrons/sec cm<sup>2</sup>.

Table 2. Trace element contents of heated Allende homogenized powder

| Heating Temp (°C) | Pressure        |               | Ag (ppb) | As (ppm) | Cd (ppb) | Cs (ppb) | Co (ppm) | Cu (ppm) | Rb (ppm) | Sb (ppb) | Te (ppm) | Tl (ppb) | Zn (ppm) |
|-------------------|-----------------|---------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|                   | Initial (mtorr) | Final (mtorr) |          |          |          |          |          |          |          |          |          |          |          |
| 400               | 50              | 48            | 109      | 1.6      | 280      | 86.1     | 665      | 106      | 1.10     | 68       | 0.95     | 55.3     | 110      |
| 500               | 52              | 65            | 113      | 1.7      | 27       | 86.1     | 670      | 112      | 1.07     | 68       | 1.4      | 24.2     | 116      |
| 600 A             | 20              | 26            | 106      | 1.7      | 46       | 88.0     | 642      | 114      | 1.21     | 42       | 1.1      | 7.0      | 122      |
| 600 B             | 88              | 95            | 101      | 1.7      | 20       | 83.1     | 610      | 106      | 0.97     | 38       | 0.93     | 6.4      | 108      |
| 700               | 62              | 60            | 64.1     | 1.8      | 15       | 86.4     | 660      | 103      | 0.96     | 66       | 0.67     | 5.8      | 91.5     |
| 800               | 50              | 65            | 45.9     | 1.6      | 7.0      | 58.2     | 628      | 101      | 0.82     | 59       | 0.47     | 4.5      | 36.1     |
| 900               | 100             | 100           | 14.5     | 1.4      | 1.8      | 32.0     | 654      | 99.5     | 0.60     | 83       | 0.10     | 3.13     | 8.93     |
| 1000 A            | 145             | 110           | 2.62     | 1.2      | ---      | 9.67     | 649      | 102      | 0.095    | 19       | 0.069    | 1.0      | 2.43     |
| 1000 B*           | 145             | 110           | ---      | 0.92     | (5.4)†   | 9.54     | ---      | 86.8     | 0.13     | 22       | 0.051    | 0.90     | 2.27     |
| 1100              | 20              | 30            | 2.45     | 0.30     | ---      | 4.07     | 631      | 1.76     | 0.036    | 11       | 0.024    | (41)†    | 0.666    |
| 1200              | 40              | 28            | 2.10     | 0.16     | ---      | ---      | 554      | 1.23     | ---      | 17       | 0.0030   | (2.3)†   | 0.028    |
| 1268              | 50              | 2200          | 0.33     | 0.14     | ---      | 0.96     | 477      | 0.29     | 0.011    | 1.0      | 0.0012   | 0.24     | 0.0038   |
| 1315              | 45              | 50            | 0.079    | 0.06     | ---      | 0.20     | 60.3     | 0.027    | 0.0008   | 0.65     | 0.0015   | 0.06     | 0.0013   |
| 1393              | 50              | 640           | 0.19     | 0.03     | ---      | 0.14     | 10.6     | 0.0076   | 0.0007   | 0.20     | 0.0003   | ---      | 0.0035   |

\* Sample irradiated in the University of Missouri Research Reactor. Other data for this sample are: Au—122 ppb; Bi—5.1 ppb; Ga—3.3 ppm; In—3.1 ppb (Biswas, unpublished data).

† Data suspected of contamination and subsequently ignored.

Chemical processing techniques for irradiated samples and monitors included procedures described in BINZ *et al.* (1974, 1976), Papers I, II and VI and references cited in these papers plus some additions. Accordingly, we must summarize our overall procedure. [Details are listed in NGO (1979) and can be obtained on request from M.E.L.] After cracking open Suprasil quartz irradiation vials with a tube cutter, each sample was fused with NaOH–Na<sub>2</sub>O<sub>2</sub> in a Zr crucible containing 20–100 mg of inert carriers for each element; carrier-free <sup>137</sup>Cs was also present as tracer for chemical yield assessment. After solution of the fusion cake in H<sub>2</sub>O, we added Na<sub>2</sub>S.

The basic sulfide precipitate (containing Ag, Au, Bi, Cd, Co, Cu, In, Tl and Zn) was dissolved in aqua regia; HNO<sub>3</sub> was then boiled off by evaporation twice with HCl. We dissolved most of that residue with 0.55 N HCl; Ag<sup>+</sup> was separated from undissolved SiO<sub>2</sub> with NH<sub>3</sub> and, after purification, we precipitated AgCl for counting. On loading the 0.55 N chloride solution onto a AG 1 × 8 anion exchange column, Co, Cu and In were not adsorbed. The effluent was made 2 N in HCl, CuS was precipitated and, after dissolution and extensive purification, CuSCN was precipitated for counting. We separated In from Co by solvent extraction and, after purification, precipitated it for counting as In(C<sub>9</sub>H<sub>6</sub>NO)<sub>3</sub>. Cobalt was precipitated as CoS, redissolved and counted as a solution. The column was eluted sequentially with 0.1 N HCl, 0.002 N HCl, 2 N H<sub>2</sub>SO<sub>4</sub>, 2 N H<sub>2</sub>SO<sub>4</sub> saturated with SO<sub>2</sub> and, finally, 2 M KCN followed by 90/5/5 (by volume) acetone/HCl/H<sub>2</sub>O; respectively, these fractions yielded on further purification ZnHg(SCN)<sub>4</sub>, Cd(NH<sub>4</sub>)PO<sub>4</sub>, BiOCl, TlI and Au precipitates for counting.

The supernate remaining after precipitation of basic sulfide was acidified with HCl to precipitate sulfides of As, Sb, Se and Te; Cs<sup>+</sup>, Ga<sup>3+</sup> and Rb<sup>+</sup> remained in solution. Ga(OH)<sub>3</sub> was separated from the alkalis, dissolved, purified and precipitated as Ga(C<sub>9</sub>H<sub>6</sub>NO)<sub>3</sub> for counting. We precipitated Cs and Rb with (NH<sub>4</sub>)<sub>3</sub>P(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub> and converted these to the tetraphenylborate salts. After determining the chemical yield of Cs by counting <sup>137</sup>Cs, Rb was computed by difference. Acid sulfides were heated with HCl to dissolve Sb<sub>2</sub>S<sub>3</sub>; Sb<sup>3+</sup> was purified further and precipitated as metal for counting. The remaining sulfides were dissolved in HNO<sub>3</sub> and then taken up in 3 N HCl. We precipitated Se and Te; As<sup>3+</sup> in solution was purified further and precipitated as metal for counting. Metallic Se and Te were dissolved in HNO<sub>3</sub>, taken up in 3 N HCl and separated on an AG 1 × 8 anion exchange column. After purification, each was precipitated as metal for counting. Average chemical yields were: Ag (57%), As (50%), Au (35%), Bi (27%), Cd (68%), Co (58%), Cs (30%), Cu (34%), Ga (20%), In (35%), Rb (38%), Sb (22%), Se (34%), Te (38%), Tl (46%), Zn (55%). We established all chemical yields gravimetrically except for Co which we accomplished by atomic absorption spectroscopy and Cs which we determined radiometrically.

Monitors were dissolved in HCl and—except for Co which was counted directly in solution—individual ions were separated, purified by abbreviated cleanup procedures similar to those used for samples and prepared for counting in the same chemical form as sample fractions. Typical yields for monitors were: Ag (90%), As (85%), Au (96%), Bi (65%), Cd (64%), Co (100%), Cs (54%), Cu (80%), Ga (66%), In (85%), Rb (87%), Sb (76%), Se (94%), Te (60%), Tl (87%), Zn (90%). These were determined as were yields for samples.

We counted and reduced data for the beta emitters, <sup>210</sup>Bi and <sup>204</sup>Tl, as in LAUL *et al.* (1970a, b) except that we assured radiochemical purity of Tl by running an Al absorption curve for each sample (BINZ *et al.*, 1974). We counted all gamma emitters using coaxially mounted Ge(Li) detectors coupled to either 1024 or 4096-channel multi-channel analyzers; Co solutions were contained in

counting cylinders (LAUL *et al.*, 1970c) while all other elements were precipitates on glass-fiber discs. To determine Cu, we were forced to use 511 keV annihilation radiation; we assured radiochemical purity by counting 12.7 hr <sup>64</sup>Cu five times over a three-day period (thus following its decay over five half-lives) and reducing the data with the CLSQ program (CUMMING, 1963). We determined all other gamma emitters via photopeak energies.

## RESULTS

### Unheated samples

The large number of replicate analyses of unheated Allende (Table 1) reflect a vain attempt to improve experimental precision for some elements, primarily As and Sb. Relative estimated standard deviations for these two elements remained ±15%. The precision for Cd and Te is ±10% and ±12%, respectively, and 2–5% for the other seven elements. To assess the accuracy of our measurements, we compare our mean values with published data and find very few differences exceeding 10%. The analogous comparison in Paper VI includes most elements in Table 1 so we consider only As, Cu, Rb and Sb here. The single published As datum, 2 ppm, was obtained by spark-source mass spectrometry (CLARKE *et al.*, 1971) and is thus imprecise, while that for Cu, 100 ppm, obtained similarly by that group agrees well with our data. One Rb datum, 1.3 ppm (WAKITA and SCHMITT, 1970), is higher and one, 0.9 ppm (CLARKE *et al.*, 1971), is lower than ours; however, other data (KAUSHAL and WETHERILL, 1970; ANDERS *et al.*, 1976; TAKAHASHI *et al.*, 1978), 0.95–1.10 ppm, agree with our results. The Sb datum of CLARKE *et al.* (1971), 200 ppb, greatly exceeds our values but replicate analyses ranging from 72–80 ppb (ANDERS *et al.*, 1976; TAKAHASHI *et al.*, 1978) accord well with our results.

There is no evidence for self-shadowing or resonance effects in the sample irradiated at the UMRR. Every datum for that sample is statistically indistinguishable from results obtained using the CP-5 reactor, both for elements listed in Table 1 and Bi, Ga and In (Papers I, VI). Our Au datum is similarly indistinguishable from results for five Allende replicates, 137 ± 10 ppb (TAKAHASHI *et al.*, 1978).

### Heated samples

In contrast to unheated samples, where our results (Table 1) and previously published data agree so well, variations for heated samples (Table 2) are more severe. We quantify this by calculating the ratio of each value for Tl (400–1000°C), Co (>1200°C) and Cs, Te and Zn (>1000°C) to the corresponding datum in Paper I or VI. [We chose not to include additional data for Cs because of its quantitative retention at ≤1100°C; the remainder are the only other duplicated data.] For each element the mean and corresponding standard deviation of these ratios is: Co, 0.96 ± 0.29; Cs, 0.75 ± 0.28; Te, 0.87 ± 0.32; Tl, 1.8 ± 1.8; Zn, 2.4 ± 1.7. The more mobile elements, e.g. Tl and Zn, are more discrepant and, as expected, the discrepancies tend to increase at higher temperature as depletion becomes severe. The extent of variation can be judged from the standard deviations. These discrepancies must reflect two factors: reproducibility of loss from sample to sample during heating and the decrease in analytical precision as concentrations decrease by factors of 10<sup>1</sup>–10<sup>5</sup>. We suspect that the former effect is more serious but, whatever the cause, differences of the magnitude reported here do not affect our conclusions even marginally (cf. Paper VI).

From the foregoing it is not surprising that results for samples irradiated at the CP-5 and UMRR are more discrepant for the pair heated at 1000°C (Table 2) than for the unheated pair. In the former, differences 1–3% for 8 elements; in the latter they are 1–10% for 15 elements. Again, we do not ascribe these to irradiation effects.

In the following discussion, we omit data that we suspect reflect contamination: Ag, 1100–1315°C (Paper VI) and our datum at 1396°C; Cd, all data  $\geq 1000^\circ\text{C}$  (This work, Paper VI); Tl, 1000° (Papers I and VI), 1100 and 1200°C (This work) and 1268°C (Paper VI); Zn, our datum at 1396°C. We used all other data in this study and Papers I and VI, averaging any replicate results.

## DISCUSSION

### Elemental retention

The data of Tables 1 and 2 are depicted in Fig. 1 in terms of relative retention; as previously seen, all elements are lost progressively over a broad temperature span (cf. Papers I–VI). Temperatures of incipient loss vary markedly. Based on the data here and in Papers I and VII these are: 400°C—Cd, Tl; 500°C—Bi,  $^3\text{He}$ ,  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ; 600°C—In, Se; 700°C—Ag, C, Te, Zn,  $^{21}\text{Ne}$ ,  $^{22}\text{Ne}$ ; 800°C—Cs, Rb, S; 900°C—Ga,  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ,  $^{84}\text{Kr}$ ,  $^{132}\text{Xe}$ ; 1000°C—As, Cu, Sb; 1200°C—Co.

We note with interest those elements lost incipiently at 1000°C. In the context of the two-component model of Anders and co-workers which is so successful in accounting for the chemical properties of petrologic types 1–3 *carbonaceous* chondrites, CASE *et al.* (1973) proposed that As and Sb are elements 'partly-depleted' by incomplete volatilization during formation of chondrules and associated coarse metal. ANDERS *et al.* (1976) and TAKAHASHI *et al.* (1978) added Au, Cu, K, Mn and Na to this category. To the extent that Allende models the behavior of other chondrite parent material, it is intriguing that As, Au,

Cu and Sb are lost incipiently at a temperature above that needed for loss of 'normally' or 'strongly depleted' elements (cf. ANDERS, 1964), i.e. those vaporized completely during chondrule formation and below that required for loss of 'undepleted' (i.e. completely retained) Co. [We have no information on incipient release temperatures for K, Mn or Na but Au in Allende heated at 1000°C is 0.86 $\times$  that in unheated Allende (Tables 1 and 2). Our analytical precision for Au in Allende is  $\pm 2.6\%$  (BISWAS, unpublished data)].

The 'volatile-loss' model for origin of ordinary chondrites (WASSON and CHOU, 1974) has been suggested by WAI and WASSON (1977) as possibly applicable to C2 chondrites. This model interposes Ag and Ga between As, Au and Cu and Sb in condensation temperature. The low temperature of incipient loss and high mobility of Ag (Fig. 1) in particular, argue against applicability of this model to C2 chondrites; however, we cannot comment on whether ordinary chondrites provide evidence for it.

While elemental ordering by temperatures of incipient release resembles proposed sequences for elemental condensation during nebular cooling over the 1400–400 K interval—Co, Cu, Sb, Rb, Ag, Cs, Se, Zn, S, Te, In, Cd, Bi, Tl, C (TAKAHASHI *et al.*, 1978; cf. GROSSMAN and LARIMER, 1974) or Rb, As, Cu, Sb, Ga, Ag, Se, Te, Zn (WAI and WASSON, 1977)—there are some differences. The two processes—volatilization and elemental loss *from* solid parent material during heating (i.e. mobilization) and elemental introduction

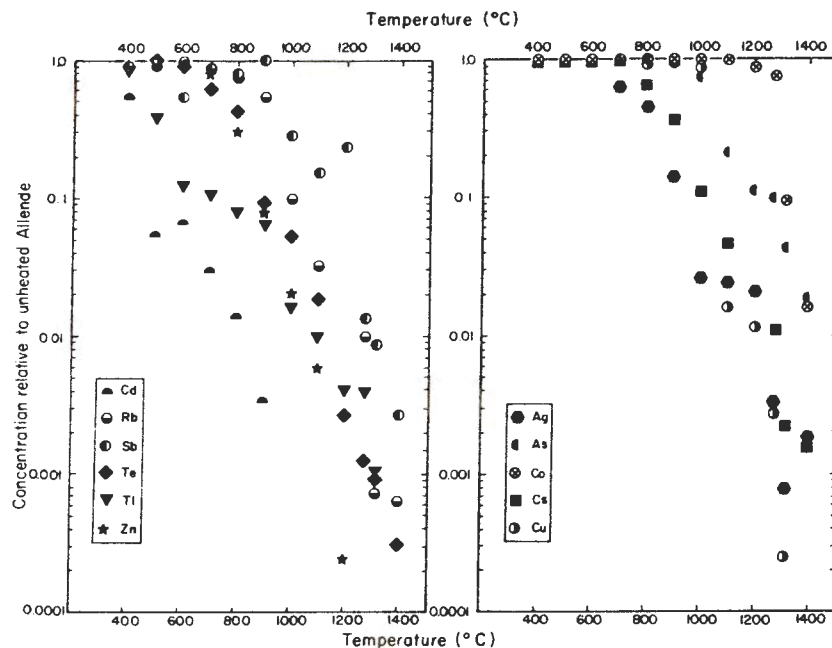


Fig. 1. Trace element contents as a function of temperature in heated Allende relative to those of unheated material. Relative retentivities shown are mean values of data reported here and, if appropriate, in Papers I or VI. (To conserve space, Zn data  $> 1200^\circ\text{C}$  are not shown. These extend to  $\sim 3 \times 10^{-5}$ .) Temperatures of incipient release vary widely but all elements are lost progressively over a broad temperature range to extremes of as much as five orders of magnitude lower than initial values (cf. Paper VI).

into solid parent material during nebular condensation and accretion—are phenomenologically opposite so that a 1:1 correlation would not be expected. The rough correspondence between elemental mobility (as determined from temperature of incipient release) and volatility does not extend to the noble gases. In Allende,  $^3\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$  are lost at temperatures  $\geq 500^\circ\text{C}$ ,  $^{21,22}\text{Ne}$  at  $\geq 700^\circ\text{C}$  and  $^{36,38}\text{Ar}$  and Kr and Xe isotopes only  $\geq 900^\circ\text{C}$  (Paper VII). It is well-known that these gases and C are highly-depleted even in primitive chondrites relative to cosmic abundances—probably due to inefficient accretion. Thus, we may be observing the behavior of that portion of these atmophile species sited in especially retentive sites.

The maximum extent of elemental loss in our experiments only roughly corresponds to temperature of incipient release or postulated nebular volatility. Of all species considered, Cd clearly is the most mobile by this definition. Its relative retention is 0.003 at only  $900^\circ\text{C}$  and it is undetectable (i.e.  $\leq 0.0003$ ) above this temperature (Fig. 1); only  $^3\text{He}$  is nearly this mercurial (Paper VII). At  $1316^\circ\text{C}$ , relative retentions for all other elements can be determined or estimated from lower-temperature data (Fig. 1; Paper VI); by degree of loss, these are ordered at  $\text{Zn} > \text{Cu} > \text{Ag}, \text{Rb} > \text{Sb}, \text{Se}, \text{Te} > \text{In}, \text{Tl} > \text{Bi}, \text{Cs}, \text{Ga} (?) > \text{As} > \text{Co}$ . [As discussed in Paper VI, the partial melting of Allende, which begins between  $1100$  and  $1200^\circ\text{C}$ , does not seem to alter loss trends for most trace elements; Co may be an exception.] At  $1000^\circ\text{C}$ , where additional data exist, the order is  $\text{Cd}, ^3\text{He} > ^4\text{He} > \text{Ag}, \text{Tl}, \text{Zn} > \text{Te} > \text{Bi}, \text{Cs}, \text{In}, ^{20}\text{Ne}, \text{Rb} > ^{40}\text{Ar}, ^{21,22}\text{Ne} > \text{Sb} > ^{84}\text{Kr}, ^{132}\text{Xe} > ^{36,38}\text{Ar}, \text{C} > \text{As}, \text{S}, \text{Se} > \text{Ga} > \text{Au} (?)$ ,  $\text{Cu} > \text{Co}$ ; in fact, only Co is

retained quantitatively. At both temperatures, but particularly at  $1000^\circ\text{C}$ , the relative positions of many of these species are surprising considering theoretical suggestions of the relative extent of loss of particular species from meteoritic parent-body material during post-accretion heating (ANDERS, 1964 and subsequent papers; DODD, 1969; WAI and WASSON, 1977). We suggest that experimental observations be given the greatest weight.

The addition of Ag, Cs, Te and Zn data for Allende modifies a conclusion of Paper V. When data for ten elements are compared (Fig. 2), Allende tends to be more retentive than other primitive chondrites subjected to simulated metamorphism, but not systematically so; for Cs, at least, Allende is less retentive than the others. We note that the initial Rb/Cs weight ratio of 12 never increases above 19 over the entire temperature span and, in fact, decreases to 4–5 at the highest temperatures (Table 1 and 2). If the behavior of Allende is at all similar to that of ordinary chondrites, the high Rb/Cs ratios of grades 5 and 6 ordinary chondrites compared with those grades 3 and 4 (GOLES, 1971) must be attributed to primary condensation effects and not to secondary thermal events as previously suggested.

#### Correlation profiles

Compared with Murchison, Allende exhibits an unusually high proportion of statistically significant ( $>95\%$  confidence level) interelement correlations for linear and, especially, exponential (or power curve) relationships between each pair of elements  $x$  and  $y$ , i.e.  $y = mx + b$  and  $y = kx^m$ , respectively. For samples heated at  $400$ – $1000^\circ\text{C}$ , the 27 elements or nuclides determined in this work and Papers I, VI

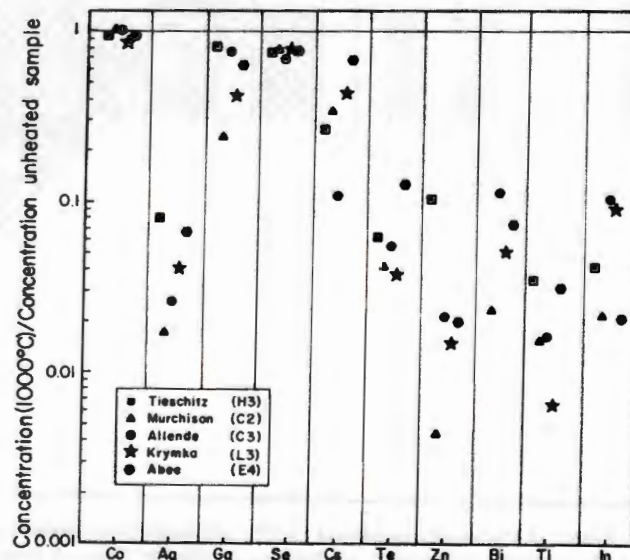


Fig. 2. Retentions of ten trace elements in samples of five primitive chondrites heated at  $1000^\circ\text{C}$  under simulated metamorphic conditions relative to the respective unheated material. While Allende (C3V) and Murchison (C2) tend to be the most and least retentive chondrites, respectively, exceptions occur.

and VII could yield up to 351 pairs of relationships. Of these, 195 (56%) linear and 263 (75%) exponential correlations are statistically significant (Fig. 3). In contrast, the 11 elements determined in similarly treated Murchison (Paper V) could yield 55 pairs of related elements; only 24 (44%) linear and 26 (47%) exponential correlations are statistically significant. Murchison is disproportionately affected by inclusion of uncorrelated Co because of the fewer elements determined in it, but the Allende-Murchison difference persists even on omission of Co. In Allende, the 195 linear and 263 exponential correlations correspond to 60 and 81%, respectively, of the 325 possible relationships. In Murchison, the 24 linear and 26 exponential correlations amount to 53 and 58%, respectively, of the possible 45 relationships.

The Allende-Murchison difference also persists if comparison is limited to the 11 elements determined

in both (Fig. 3). Allende exhibits 27 linear and 41 exponential correlations (49 and 75%, respectively, of the 55 possible relationships) compared with the 24 linear and 26 exponential correlations in Murchison. Specific differences among linear correlations involve Ag with Bi, Ga with Te, Zn and In and Cs with Ag, Te, Zn and In present in Allende but not in Murchison and of Bi with Se, Te and Zn and Tl with Te and Zn present in Murchison but not in Allende. Differences among exponential correlations involve Ga with Zn, Tl and In, Cs with Ag, Te, Zn, Tl and In and Cd with Ag, Se, Cs, Te, Zn, Bi and Tl present in Allende but not in Murchison while Bi and Zn correlate in Murchison but not in Allende.

Differences between the In/Bi and In/Tl two-element correlation diagrams for Allende and Murchison samples pointed to some genetic differences of these two carbonaceous chondrites (Paper V). Dis-

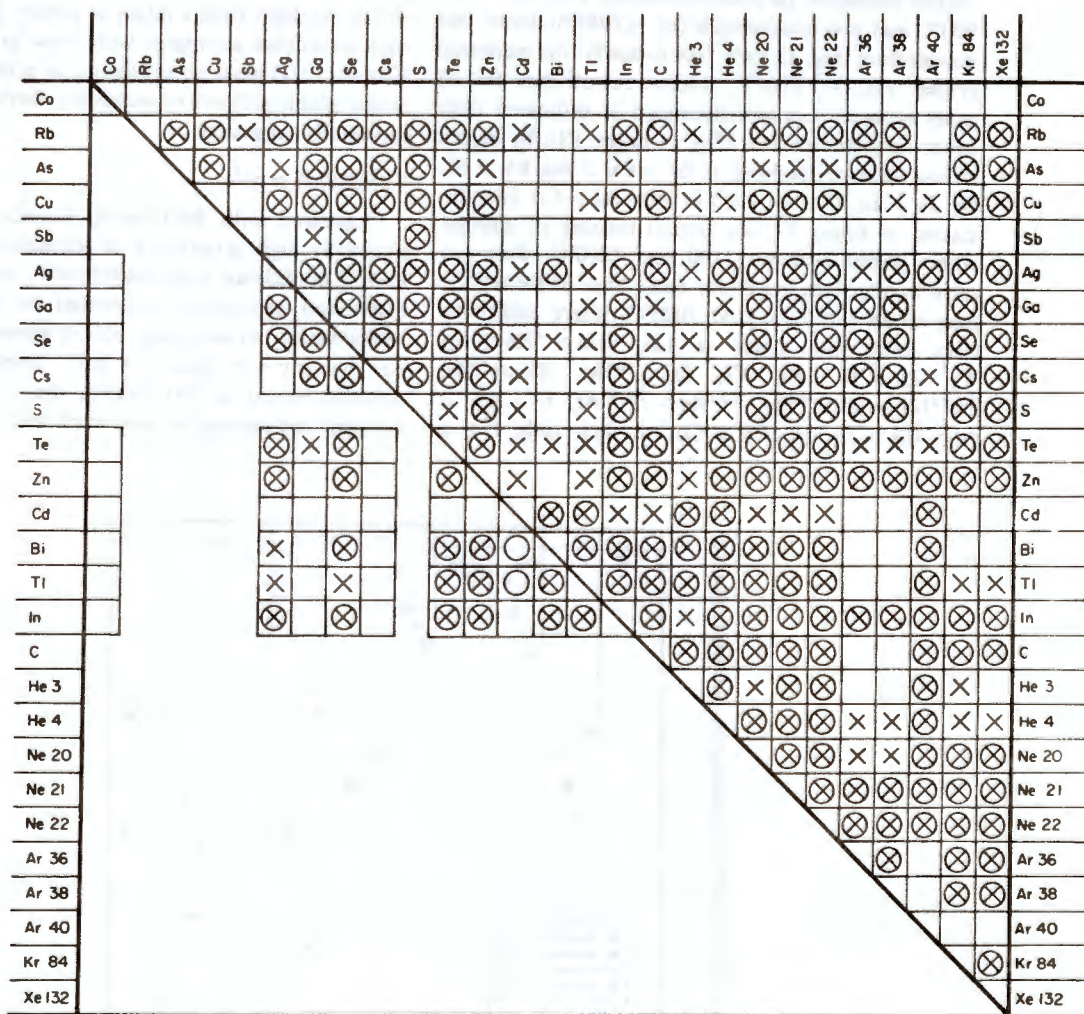


Fig. 3. Pattern of statistically significant (>95% confidence level) linear/linear (circles) and logarithmic/logarithmic (crosses) interelement correlations in Allende (right of diagonal) and Murchison (left of diagonal) samples heated similarly at 400-1000°C. Elements are listed from left to right and top to bottom by depletion factor (i.e. presumed order of volatility) in ordinary chondrites. No matter what the sampling of elements, Allende exhibits a higher proportion of correlations, particularly exponential ones, involving mobile/volatile elements than Murchison (see text).

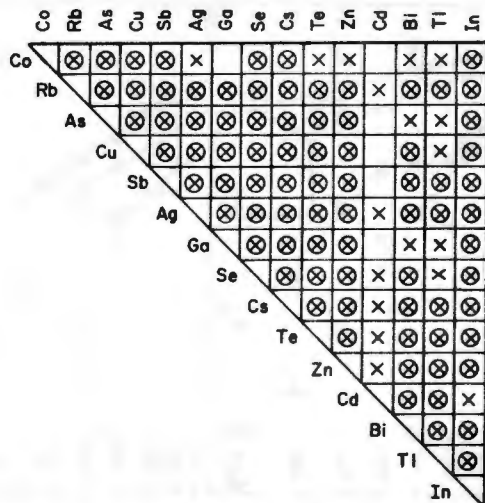


Fig. 4. Pattern of statistically significant (>95% confidence level) linear and exponential interelement correlations in Allende samples heated at 400–1400°C. Symbols have the same meaning as in Fig. 3.

similarities of correlation profiles (Fig. 3) in response to heating under similar conditions strongly support the conclusion that these chondrites are not merely mixtures in different proportions of the same materials (ANDERS, 1964; ANDERS *et al.*, 1976). The difference in both correlation profiles and diagrams may merely reflect an episode of low-temperature, closed-system sintering of Allende parent material (Paper V; MCSWEEN, 1977) and/or even lower-temperature closed-system alteration of Murchison (BUNCH and CHANG, 1978); a more fundamental difference in volatile element host sites in the two carbonaceous chondrites is also possible, however.

As expected, the more extreme elemental loss from Allende samples heated >1000°C yields even greater proportions of significant linear and exponential interelement correlations (Fig. 4) than are evident in the profile for samples heated at 400–1000°C (Fig. 3). Of 105 interelement relationships possibly generated by 15 elements, 81 linear and 99 exponential correlations are statistically-significant, i.e. 77% and 94%, respectively (Fig. 4). Indeed, the proportion of such correlations is so high that one could almost compute compositional trends for all other elements knowing the trend for one. Cadmium is, of course, unique in its failure to correlate significantly with moderately or non-mobile elements; this doubtless reflects its unusually facile loss.

#### Apparent activation energies

We may calculate diffusion parameters for trace element loss from relative retentivities (e.g. Fig. 1). [ALBERTS and ANDERS (1979) treat our data quite differently. We evaluate their suggestions extensively in the accompanying Paper VI and, for reasons considered there, conclude that our treatment is preferable.] At high retentivities, numerical values for these parameters are somewhat model-dependent but these

differences are insignificant for  $\leq 10\%$  retention; fortunately, apparent activation energies are not model-dependent (cf. Paper VI). For our calculations we adopt assumptions of Papers I–IV and VI that elemental loss proceeds from homogeneous spherical grains of radius  $a$ , such that the parameter,  $D/a^2$ , (where  $D$  is the temperature-dependent diffusion coefficient), can be calculated whose variation with temperature is described by the Arrhenius equation

$$D/a^2 = D_0/a^2 e^{-Q/RT} \quad (1)$$

Thus  $Q$ —the apparent activation energy—can be calculated from the slope of the line defined on a plot of  $\ln D/a^2$  vs  $1/T$ . [Dr Urs Frick (personal communication) suggests additional emphasis of the apparent nature of  $Q$  values we calculate; he notes further that, in the absence of dynamic experiments (which are dif-

Table 3. Apparent activation energies for loss of trace elements and noble gas nuclides from heated Allende

| Element or Nuclide | Temperature range (°C) | Q(kcal/mol) | Ref.* |
|--------------------|------------------------|-------------|-------|
| Ag                 | 700–1000               | 26          | d     |
|                    | 1000–1200              | 2.1         | d     |
|                    | 1200–1315              | 28          | d     |
| <sup>36</sup> Ar   | 900–1000               | 45          | b     |
| <sup>38</sup> Ar   | 900–1000               | 45          | b     |
| <sup>40</sup> Ar   | 500–1000               | 8.1         | b     |
| As                 | 1000–1100              | 98          | d     |
|                    | 1100–1393              | 18          | d     |
| Bi                 | 400–600                | 25          | a,c   |
|                    | 600–1000               | 3.0         | a,c   |
|                    | 1000–1315              | 12          | a,c   |
| C                  | 700–1000               | 19          | b     |
| Cd                 | 400–900                | 8.0         | d     |
| Co                 | 1200–1393              | 140         | a,c,d |
|                    | 700–900                | 38          | d     |
| Cu                 | 1000–1393              | 14          | d     |
|                    | 700–1000               | 18          | d     |
|                    | 1000–1100              | 200         | d     |
| Ga                 | 1100–1393              | 16          | d     |
|                    | 900–1200               | 63          | a,c   |
| <sup>3</sup> He    | 500–900                | 13          | b     |
| <sup>4</sup> He    | 500–1000               | 13          | b     |
| In                 | 600–1268               | 21          | a,c   |
| <sup>84</sup> Kr   | 900–1000               | 45          | b     |
| <sup>20</sup> Ne   | 500–1000               | 13          | b     |
| <sup>21</sup> Ne   | 700–1000               | 20          | b     |
| <sup>22</sup> Ne   | 700–1000               | 18          | b     |
| Rb                 | 700–1000               | 37          | d     |
|                    | 1000–1393              | 14          | d     |
|                    | 700–1393               | 29          | d     |
| Sb                 | 600–900                | 11          | a,c   |
|                    | 1000–1100              | 120         | a,c   |
|                    | 1100–1315              | 15          | a,c   |
| Te                 | 600–900                | 39          | d     |
|                    | 900–1393               | 12          | d     |
| Tl                 | 400–600                | 25          | a,c,d |
|                    | 600–900                | 2.4         | a,c,d |
|                    | 900–1315               | 8.6         | a,c,d |
|                    | 900–1000               | 44          | b     |
| <sup>132</sup> Xe  | 700–800                | 59          | d     |
|                    | 900–1393               | 16          | d     |

\* References: (a) IKRAMUDDIN and LIPSCHUTZ (1975); (b) HERZOG *et al.* (1979); (c) BART *et al.* (1980); (d) This work.

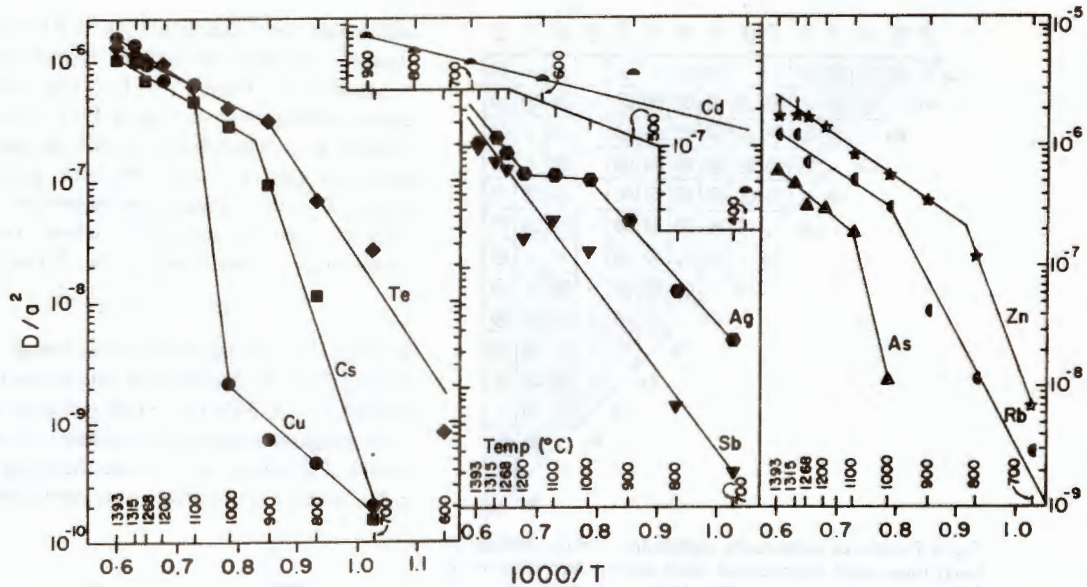


Fig. 5. Arrhenius diagrams for loss of 9 trace elements from Allende during heating. The diffusion parameter ( $D/a^2$ ) scales differ: the left one, i.e.  $2 \times 10^{-6}$ – $10^{-10}$ , is applicable to Cs, Cu and Te; that at right, i.e.  $10^{-3}$ – $10^{-9}$  is applicable to Ag, As, Rb, Sb and Zn; and that at top center, i.e.  $3 \times 10^{-6}$ – $10^{-5}$ , is for Cd. Most elements (i.e. all but Cd and Sb) exhibit two or three apparent activation energies applicable in different temperature regimes suggesting diffusion-controlled processes (see text).

difficult if not impossible to conduct for the elements we consider), "it is difficult to get better modeling of activation" than we have done. We concur that  $Q$  values are *apparent* activation energies and have repeatedly referred to them as such. In the accompanying Paper VI we discuss difficulties in assigning absolute values; for example, such values cannot be used to establish absolute time-temperature relationships in meteoritic parent bodies. It is safe to say, however, that the  $Q$  values systematize the temperature dependence of the diffusion and, in a relative sense at least, indicate the relative ease with which elements are lost. Thus, in cases where more retentive elements are lost by thermal processes, more poorly retained ones should also be lost (e.g. Paper VII). Furthermore, the magnitude of the  $Q$  values gives some clues to the diffusive process by which loss occurs (cf. Paper VI.)

We depict Arrhenius diagrams for nine elements (Table 2) in Fig. 5 omitting Co and Tl as these essentially duplicate similar diagrams in Paper VI. Table 3 lists  $Q$  values for all 11 elements as well as those for other elements and noble gas nuclides determined in heated Allende samples (Papers I, VI and VII). Trends for the 9 elements of Fig. 5 differ widely: Cd and Sb—like C, In and noble gas nuclides—exhibit but one apparent activation energy each while As, Cs, Rb, Te and Zn each show two. [But, data for C and noble gases are available only up to 1000°C.] While Ag and Cu exhibit three energies each, there are differences: the intermediate slope for Ag—like those of Bi and Tl—is shallower than at higher and lower temperatures while that for Cu—like Se—is much steeper. As

discussed in Paper VI, each line seems to reflect the elemental loss process in that temperature interval.

Magnitudes of apparent activation energies (Table 3) suggest specific loss processes. The relatively abrupt loss of As, Cu and Se in the 1000–1100°C interval and Co  $\geq$  1200°C, with attendant energies of 100–200 kcal/mole, imply decomposition of host phases, presumably sulfides for As, Cu and Se and taenite for Co (cf. Papers V and VI). Other apparent activation energies seem to reflect diffusive processes;  $Q$  values of tens of kcal/mole suggest volume diffusion, lower values of 2–8 kcal/mole (Table 3) imply more interesting phenomena like fast ion conduction (cf. Paper VI for a more complete discussion).

As we found in considering elemental retentivities, elemental ordering by apparent activation energy for mobilization (Table 3) bears little resemblance to that expected from macroscopic physical (i.e. melting or boiling points of elements or reasonable compounds) and/or chemical (e.g. reactivity) properties. *Over the same temperature range* most noble gas nuclides exhibit energies similar to or even greater than those for elements capable of forming chemical bonds (e.g. Bi, Cd, Cu, In, Se, Te, T and Zn). This latter group includes many elements that are strongly depleted in ordinary chondrites but it also includes some elements only moderately depleted in these meteorites (ANDERS, 1964). Some similar elements have higher apparent activation energies. Thus, elemental mobility during simulated (and, probably, actual) metamorphism cannot be predicted *a priori* but must be determined experimentally.



## CONCLUSIONS

Results reported here and previous information for Allende samples heated for 1 week at 400–1400°C under low-pressure conditions, provide retentivity data for 16 trace elements and 10 noble gas nuclides. They are the most complete body of data on the responses of such elements to heating of a primitive meteorite under simulated metamorphic/differentiation conditions. Temperatures of incipient release vary from 400°C (Ti) to 1200°C (Co) and ordering of elements according to these temperatures is qualitatively similar to but not identical with postulated sequences of elemental condensation during nebular cooling. Trace element loss progresses with temperature to extreme retentions as low as  $10^{-5}$  of the initial concentration. In most cases, neither relative retention factors nor apparent activation energies could have been predicted *a priori*; models invoking loss of specific elements during thermal outgassing events should be re-examined in the light of empirical results. Correlation profiles for Allende exhibit many more interelement correlations than those for Murchison, re-emphasizing extensive genetic differences between these carbonaceous chondrites.

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