

Effect of thermal metamorphic conditions on mineralogy and trace element retention in the Allende meteorite

HEATING carbonaceous chondrite from the Allende meteorite in a low pressure environment causes visible mineralogical alteration at 700–1,000° C but not at $T \leq 600^\circ$ C. Samples heated for 29 d at 500° C lose trace elements (Bi, In and Tl) more effectively than those similarly heated for 7 d. At 1,000° C with $\sim 10^{-5}$ atm initial pressure of O_2 , H_2 or He these elements, Ga and Se are comparatively more completely lost.

Chondritic meteorites provide valuable information about the condensation and early evolutionary histories of solid objects in the inner Solar System. Primitive chondrites probably reflect to some degree the condensation process(es) of solid material from the gaseous nebula and are particularly important in these respects. We take such chondrites¹ as comprising grades 1–4 of the accepted chemical-petrologic classification². These chondrites differ from their congeners of grades 5 and 6 in many respects including their higher contents of volatiles, such as the trace elements Bi, In and Tl (refs 3–10) postulated as cosmo-thermometers^{9–12}. These differences could be primary (chiefly arising from differences in condensation history^{9–14}) or secondary (chiefly arising from thermal alteration of appropriate primitive chondritic material^{15–19}). Both processes probably occurred and it is desirable to evaluate the relative importance of each in evolving primitive material.

Until recently there had been no empirical attempts to determine effects on trace elements of simulated metamorphism (artificial annealing) of any primitive chondritic material. In carrying out such a study by heating samples of Allende C3 chondrite at 100° increments over a reasonable metamorphic temperature range (400–1,000° C) in a low pressure environment (initially $\sim 10^{-5}$ atm H_2) we found substantial changes¹. After 1 week we observed minor loss of Ga and Se and major loss of the postulated cosmo-thermometric trace elements, but no loss of Co. This heating time is short compared with geological time; nevertheless two-element correlation patterns involving, Bi, In and Tl retained in heated Allende samples are similar to those for E3–6 chondrites¹, indicating possible metamorphic effects in enstatite chondrites.

As there is no consensus^{9–11,15–19} on ambient meteoritic metamorphic environments, quite probably our experiments do not duplicate effective conditions in meteoritic parent bodies or proto-planets. As a tentative step in the direction of establishing differences in trace element retention arising from variations in ambient conditions we have conducted similar experiments on Allende samples using O_2 or He rather than H_2 and also extended the heating period using H_2 . These gases were chosen be-

cause of their very different chemical properties and their high cosmic abundances. Here we report these results together with a mineralogical and petrographic description of the heated samples.

Each heating run included chips (from a large individual, USNM-3643) and aliquots of a single batch of <100-mesh homogenised powder. We placed samples (350 mg) of powder and 2–4 chips (for trace element analysis), a 300 mg chip (for mineralogy and petrology) and 100 mg of powder (a reserve sample) into separate quartz vials which we sealed on to the pre-cleaned heating apparatus¹. After evacuation, the system was purged with the appropriate gas (H_2 , He or O_2), re-evacuated to $\sim 10^{-5}$ atm and sealed. The end with the samples was then placed into a muffle furnace preheated to 500° or 1,000° C (Table 1). Condensable material liberated during heating was collected in a trap cooled with liquid nitrogen; the ambient gas pressure (as monitored with an ion gauge) jumped to ≥ 1 torr immediately on insertion of the apparatus into the muffle furnace but within 6–17 h the pressure reached a value which remained constant throughout the remainder of the run. After seven or 29 d we removed the sample assembly, quenched the vials in H_2O and sealed them off.

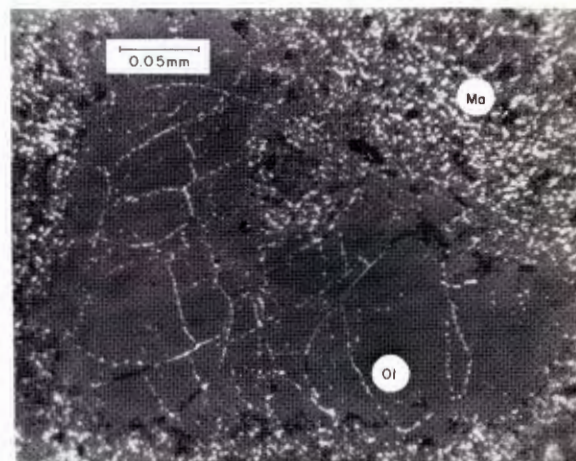


Fig. 1 Reflected light photomicrograph of Allende meteorite heated at 1,000° C, initially in H_2 atmosphere. Metallic iron particles rich in nickel are evident in matrix (Ma) and in fractures in the large olivine (Ol) crystal. Samples heated at 1,000° C, initially in He or O_2 atmosphere, seem essentially identical, implying insufficient O_2 to oxidise much of the metal formed by sulphide decomposition.

Table 1 Trace element contents of unheated and heated Allende samples

Heating temperature (° C)	Heating time (d)	Ambient atmosphere			Sample form*	Trace element contents					
		Initial gas	Initial pressure (mtorr)	Final pressure (mtorr)		Co (p.p.m.)	Ga (p.p.m.)	Se (p.p.m.)	Bi (10^{-3} p.p.m.)	Tl (10^{-3} p.p.m.)	In (10^{-3} p.p.m.)
unheated	—	—	—	—	powder	612 ± 10†	6.27 ± 0.30†	9.34 ± 0.16†	49.0 ± 0.7†	59.6 ± 2.2†	35.6 ± 1.0†
500	7	H_2	30	175	powder	642‡	—	9.2‡	30.2‡	23‡	37.3‡
					chips	650‡	—	9.2‡	35.7‡	34‡	37.9‡
500	29	H_2	1	36	powder	630	6.3	9.5	20.6	11	30.4
					chips	629	6.2	9.6	25.5	14	31.6
1,000	7	H_2	20	320	powder	624‡	5.7‡	7.9‡	6.13‡	4.3‡	3.67‡
					chips	602‡	5.9‡	8.1‡	7.66‡	6.1‡	4.15‡
1,000	7	O_2	5	240	powder	615	6.2	9.2	49.5	13.8	6.49
					chips	620	6.3	9.4	—	28.4	14.1
1,000	7	He	5	200	powder	630	4.8	5.1	10.3	2.3	≤ 4.7
					chips	651	6.1	9.6	26.7	2.4	6.10

* Powder samples were aliquots of a single homogenised batch; chips were taken from a large individual.

† Mean values of five determinations. Uncertainties listed are one estimated standard deviation from the mean calculated from the dispersion of the individual measurements¹.

‡ Data reported elsewhere¹.

Heated samples for mineralogy and petrology and an unheated sample were prepared as polished thin sections and examined under transmitted light and reflected light. In addition, compositions of the mineral phases in several of the sections were determined by electron microprobe. We irradiated samples for trace element analysis in the Argonne CP-5 reactor for 1 week and processed them to separate Bi, Co, Ga, In, Se and Tl which were counted as described elsewhere¹. R. N. Clayton determined the ¹⁸O/¹⁶O ratios in many of our reserve powder samples and concluded that these have not been altered measurably by our heat treatment.

The samples studied, their oxygen content (in weight per cent) and the $\delta^{18}\text{O}$ (SMOW) (per mille) are: unheated (35.1) 1.1; another Allende whole rock sample (36.0) 1.5; 500° C (H₂) 29 d (34.6) 1.4; 600° C (H₂) 7 d (34.5) 1.4; 900° C (H₂) 7 d (34.0) 1.2; 1,000° C (H₂) 7 d (34.6) 1.2; 1,000° C (O₂) 7 d (34.1) 1.5; 1,000° C (He) 7 d (34.6) 1.4.

Using transmitted light we observed no visible recrystallisation effects for the transparent minerals in any of the heated samples. In all cases we found sharp crystal boundaries and well preserved textures identical to those in unheated samples. We also tried to observe effects resulting from Fe²⁺ diffusion within and between olivine and pyroxene grains. Because of the small sizes of the heated samples (~ 3–4 mm) and the variability of the Allende samples in general, we could obtain no meaningful data for parameters such as mean iron content or percentage mean deviations (see refs 18, 19). Qualitatively, however, there was no indication of olivine or pyroxene compositions becoming more homogeneous—primary zoning was present and seemingly unaltered even for the 1,000° C run. In addition, we looked for and did not find evidence of Fe²⁺ diffusion into Fe-deficient olivine (Fa < 1–2) as a result of our heating experiments. In particular, where Fe-deficient interiors of broken, zoned olivine crystals were adjacent to Fe-rich matrix there was no evidence of a diffusion profile of Fe²⁺ into the olivine.

In reflected light the unheated sample and those heated to 400°–600° C were essentially identical; but samples heated at 700°–1,000° C were markedly different. In those samples we observed no sulphide, originally present mainly as pentlandite—(Fe,Ni)₉S₈—and as troilite—FeS (ref. 20). Instead we observed disseminated metal. This metal is particularly well developed in the samples heated at 900° C and 1,000° C (irrespective of original ambient atmosphere all three 1,000° C samples seem identical after heating), occurring both disseminated throughout the matrix and along fractures in larger silicate crystals (Fig. 1). Microprobe analyses of the olivine (Fa ~ 8) adjacent to metal-containing fractures in the grain shown in Fig. 1 showed no decrease in Fe²⁺ content toward the fracture, indicating that the metal did not form locally by reduction of Fe²⁺ from the adjacent silicate. Instead, the metal apparently migrated inwards either by surface diffusion or vapour transport. The metal itself, in both matrix or fractures, contains 25–30% Ni, appropriate for derivation by decomposition of the sulphides. (If the metal in the fractures had formed by reduction of Fe²⁺ in the silicate, it should be Ni-deficient since the Ni²⁺/Fe²⁺ ratio in meteoritic olivine and pyroxene is typically very low.)

Not surprisingly, the absence of discernable sulphides in samples heated at 700° C and above corresponds to the presence of off-white solid material (in the cold traps of these runs) which in one case at least was identified mass-spectrometrically (by M. Gay) as S₈. Thus, between 600° C and 700° C, for the conditions prevailing in our experiments, sulphides in Allende samples seem to decompose ultimately to metal and sulphur. These are not the products expected by heating pentlandite or troilite in equilibrium with vapour at these temperatures²¹, but our system is open to loss of sulphur or volatile compounds of sulphur. This raises some question as to the applicability of our results to possible metamorphic models for primitive bodies since even the most recrystallised chondrites (such as Type 6) contain abundant troilite or other sulphides. But

experiments in progress on enstatite chondrites show that some sulphides can be stable to higher temperatures (~ 900° C) and that trace element losses still occur at lower temperatures. This provides additional support for the idea that decomposition of sulphides is not prerequisite to the effects observed in samples from the Allende meteorite.

The absence of observable Fe²⁺ diffusion in any samples indicates that the diffusion rate for ferrous iron in olivine and pyroxene at the temperatures of our experiments is too slow to be observable over periods as short as a week. But this does not preclude Fe²⁺ diffusion being the principal mechanism by which uniform olivine and pyroxene compositions are produced in equilibrated ordinary chondrites^{18,19} since presumably much longer times were available.

Since the fractional loss of trace elements in Allende samples seems to depend on kinetics rather than thermodynamics¹ we were not surprised that Bi, In and Tl are lost to a greater extent from Allende samples heated for 29 d than from corresponding samples heated for 7 d at 500° C (Table 1). Relative to unheated material, In is not lost in 1 week but is lost to a minor extent by more extended heating at 500° C; Co Ga and Se seem unaffected even in 29 d (Table 1).

The nature of the gas initially present in the heating apparatus markedly influences trace element retentivity at 1,000° C (Table 1). Relative to corresponding samples heated initially in H₂, samples heated initially in O₂ retain the five mobile elements to a greater extent while those heated initially in He lose most of them more readily—Bi is exceptional in that it is somewhat better retained in He than in H₂. Selenium and, more surprisingly, Bi are quantitatively retained in the O₂ case; in the He case we could establish only a conservative upper limit for In. In each case the ambient atmosphere was present at nanomolar levels, negligible compared with the amount of sample present. So it seems unlikely that differences in retentivity of the trace elements can be due to their forming or failing to form volatile chemical compounds with the gas. (Indeed, as noted, irrespective of the original atmosphere the mineralogy of the three 1,000° C samples seem identical. In particular, disseminated metal formed in all three cases indicating that the internal atmosphere could not have been extensively oxidising.) It seems more likely that both O₂ and H₂ were adsorbed on to the samples, retarding loss of the mobile elements to a greater or lesser extent. Helium would not be troublesome in this regard and indeed loss of trace elements is generally greater using this gas.

To the extent that Allende meteorite can be used as a model for other primitive materials our results have several implications relative to retention of mobile trace elements during metamorphism in primitive parent bodies. As suspected^{1,18-19} such elements can be lost by diffusion even before their host mineral(s) undergo(es) chemical or phase change. Since the duration of our experiments is short compared with geological time, our results can provide only a lower limit to the loss of mobile elements in an open system in the 'real world.' But the results clearly indicate that kinetics rather than equilibrium could play a major role in determining trace element distribution in equilibrated or partially equilibrated chondrites¹. Further, primitive meteorites differ in the amount and kind of gases or readily volatile major components they contain. Trace element retentivity also is clearly influenced by ambient atmosphere and specific regions in primitive parent bodies could conceivably be gas tight. Future experiments should allow for this possibility as well as systems completely open to gas loss. Furthermore, it seems necessary to conduct additional experiments (which are planned) for studying retentivity as a function of gas fugacity. Finally, in the event that material from other solar system objects is thermally sterilised before return to earth²² it will be necessary to choose ambient temperature and atmospheric conditions carefully so as not to degrade the sample unnecessarily. By that time we will have considerably more information on the response of other sorts of primitive material to thermal alteration.

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- ¹ Ikramuddin, M., and Lipschutz, M., *Geochim. cosmochim. Acta*, **39**, (in the press).
- ² Van Schmus, W. R., and Wood, J. A., *Geochim. cosmochim. Acta*, **31**, 747 (1967).
- ³ Tandon, S. N., and Wasson, J. T., *Geochim. cosmochim. Acta*, **32**, 1087 (1968).
- ⁴ Laul, J. C., Case, D. R., Schmidt-Bleek, F., and Lipschutz, M. E., *Geochim. cosmochim. Acta*, **34**, 89 (1970).
- ⁵ Laul, J. C., Pelly, I. Z., and Lipschutz, M. E., *Geochim. cosmochim. Acta*, **34**, 909 (1970).
- ⁶ Case, D. R., Laul, J. C., Pelly, I. Z., Wechter, M. A., Schmidt-Bleek, F., and Lipschutz, M. E., *Geochim. cosmochim. Acta*, **37**, 19 (1973).
- ⁷ Krähenbühl, U., Morgan, J. W., Ganapathy, R., and Anders, E., *Geochim. cosmochim. Acta*, **37**, 1353 (1973).
- ⁸ Binz, C. M., Kurimoto, R. K., and Lipschutz, M. E., *Geochim. cosmochim. Acta*, **38**, 1579 (1974).
- ⁹ Keays, R. R., Ganapathy, R., and Anders, E., *Geochim. cosmochim. Acta*, **35**, 337 (1971).
- ¹⁰ Laul, J. C., Ganapathy, R., Anders, E., and Morgan, J. W., *Geochim. cosmochim. Acta*, **37**, 329 (1973).
- ¹¹ Larimer, J. W., and Anders, E., *Geochim. cosmochim. Acta*, **31**, 1239 (1967).
- ¹² Larimer, J. W., *Geochim. cosmochim. Acta*, **37**, 1603 (1973).
- ¹³ Blander, M., and Abdel-Gawad, M., *Geochim. cosmochim. Acta*, **33**, 701 (1969).
- ¹⁴ Blander, M., *Geochim. cosmochim. Acta*, **35**, 61 (1971).
- ¹⁵ Mason, B., *Geochim. cosmochim. Acta*, **30**, 23 (1966).
- ¹⁶ Keil, K., *J. geophys. Res.*, **73**, 6945 (1968).
- ¹⁷ Wasson, J. T., *Rev. Geophys. Space Phys.*, **10**, 711 (1972).
- ¹⁸ Dodd, R. T., Van Schmus, W. R., and Koffman, D. M., *Geochim. cosmochim. Acta*, **31**, 921 (1967).
- ¹⁹ Dodd, R. T., *Geochim. cosmochim. Acta*, **33**, 161 (1969).
- ²⁰ Clarke, R. S., Jarosewich, E., Mason, B., Nelen, J., Gomez, M., and Hyde, J. R., *Smithsonian Contrib. Earth Sci.*, No. 5 (1970).
- ²¹ Kullerud, G., Yund, R. A., and Moh, G. H., *Econ. Geol. Monogr.*, No. 4, 323 (1969).
- ²² Young, R. S., and De Vincenzi, D. L., *Science*, **186**, 495 (1974).

