

MELTING EXPERIMENTS ON ALLENDE COARSE-GRAINED INCLUSION COMPOSITIONS.

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Controversy has arisen in recent years about the processes responsible for the textures and mineralogy of coarse-grained, Ca-Al-rich inclusions (CAI) in carbonaceous chondrites. Much of this concerns whether or not a given inclusion was ever melted and, if so, what the mechanism was for melting. Certain textures have been proposed as evidence in favor of diametrically opposed modes of origin, with no experimental basis for the different points of view. Unfortunately, many mineralogical data critical to understanding CAI origin also do not exist. Essentially no data exist on the thermodynamics or kinetics of the Ti^{3+} -containing pyroxenes (Px) found in some inclusions. The system CMAS (CaO-MgO-Al₂O₃-SiO₂) (2,11) is insufficient for modelling phase relations in CAI with significant Ti contents. Because of the lack of data, little progress has been made in evaluating physical processes involved in CAI formation. The objective of this work is to define features of CAI which are readily explicable by a simple melting process and to point out those which can not be explained in this way.

Synthetic analogues of CAI were melted into droplets using a Pt-wire loop technique in a 1-atm, H₂-CO₂ gas mixing furnace at the University of Massachusetts so that both T and f_{O_2} could be controlled. Compositions were selected to correspond to the petrographic classes of CAI's (6) and include those of a fluffy type A, AF-1 (36.8 wt % CaO, 3.0 MgO, 34.7 Al₂O₃, 20.1 SiO₂, 5.4 TiO₂); two compact type A's, AC-1 (33.8, 10.4, 29.0, 26.1, .7) and AC-2 (37.0, 6.1, 31.9, 24.5, .5); and a type B1, B1-1 (28.1, 8.5, 31.8, 27.6, 4.0). These bulk compositions were determined (1,2) by combining modes with microprobe analyses of primary phases for Allende CAI and assuming that alteration affected all primary phases equally. A few runs, B1-2, were also performed on Stolper's (11) average type B composition. Equilibration experiments used starting materials of either glass or glass + spinel (Sp) and were step cooled in 20-40° intervals from at least 1500°C to the run T of interest. All runs were performed in a gas mix of roughly 73 vol % CO₂, about half-way between the FMQ and IW buffers. Higher vol % H₂ was avoided because significant Ti diffused into the Pt wire at f_{O_2} 's near IW.

Crystallization sequences inferred from this work and those of (10,11) are summarized in Table 1. Reversals were denoted by r, but most data represent synthesis results. Except where perovskite (Pv) occurs, the phase relations are similar to previous efforts in CMAS. The crystallization sequence for AF-1 is melilite (Mel), Sp, Pv and anorthite (An). In AC-1, Sp is the liquidus phase, followed by Pv and Mel. No other phases appeared above 1375°C. B1-1 has a similar crystallization sequence with Px and An appearing ≈200° after Mel. B1-2 differs from B1-1 in that B1-2 lacks Pv in the crystallization sequence, has a higher liquidus T and a lower T of appearance for Mel. AC-2 is essentially on the Mel-Sp cotectic.

The early occurrence of Sp and Mel in the crystallization sequence and the late appearance of Px is characteristic of Type B1 compositions (see also 11). One proposal (7) for producing isotopic heterogeneities within CAI involves crystallization of ¹⁶O-enriched droplets in the presence of a gas which is less ¹⁶O-rich and which exchanges isotopically with the liquid during crystallization. This requires Sp and Px to crystallize well before Mel which is not consistent with the sequence observed experimentally in B1 compositions. Since Px does not tend to crystallize metastably before Mel, this model is probably not viable.

The two principle solid solution phases in CAI are Mel and Ti-Al-rich Px. Mel produced experimentally and as found in most CAI is zoned from gehlenitic cores to progressively more akermanitic (Ak) rims. A notable exception is CG-11 (1) in which Mel often has cores of Ak₂₀ and gehlenite rims. A Ti-Al-rich Px roughly comparable to those found in CAI has been produced by melting in air (9). The Px appears, however, to have a stoichiometric formula when Ti is calculated as TiO₂. In CAI, the same calculation usually results in low cation sums (6). This, together with the green pleochroism, low residual structure refinement based on a stoichiometric cell and Ti^{3+} absorption peaks (5), is evidence for significant Ti^{3+} in CAI Px. In the present experiments, Px appears to be essentially stoichiometric based on Ti as TiO₂ ($Ti^{3+}/(Ti^{3+} + Ti^{4+}) < \approx .1$ molar) suggesting that there is little Ti^{3+} in these runs. However, the similarity between experimental and natural Px can be seen by comparing analyses: (25.54 wt % CaO, 7.19 MgO, 21.85 Al₂O₃, 35.15 SiO₂, 10.80 TiO₂) for TS-33, a natural B1 (8) and (23.93, 9.98, 20.45, 33.11, 10.56) from B1-1, its synthetic analogue. This is an intriguing similarity as it implies that Px with compositions like those in CAI can be formed by melting the inclusions. The relative lack of Ti^{3+} in the experimental Px implies that the f_{O_2} of CAI droplets would have been below 10^{-10} at 1500°K. This is consistent with the presence of Fe₃₃Ni₆₇ alloy and absence of wüstite in CAI (6) which also places the droplet f_{O_2} at $< \approx 10^{-10.6}$ at 1500°K (4). Unfortunately, these are only upper limits on the f_{O_2} . The importance of finding a lower limit can not be overemphasized as it provides a direct indicator of the gas composition at the time of pyroxene formation. The ideas that CAI were liquid droplets in metastable equilibrium (3) with a solar gas ($f_{O_2} \approx 10^{-18}$ at 1500°K, 10^{-3} atm P_{tot}) or that they are remelted low-T, relatively oxidized, assemblages which did not reequilibrate with a solar gas ($f_{O_2} < 10^{-18}$ at 1500°K, 10^{-3} atm P_{tot}) would become testable hypotheses.

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There is, in general, good agreement between observed mineral chemistries and inferred crystallization sequences for natural inclusions and those in the experiments. There are also some interesting discrepancies. Fluffy type A inclusions do not contain primary An, which is found in the experiments, but do contain hibonite (Hib), which is not. If the bulk composition used is correct, then either fluffy type A's did not crystallize from melts or, if they did, Hib crystallized metastably and An was completely suppressed for kinetic reasons. An alternative is that the bulk composition used for fluffy type A's was incorrect, being based on a point-count (1) of a heavily altered and heterogenous inclusion. Had ≥ 1 vol % more hibonite been found, that phase would have crystallized from a melt of the resulting composition, although the complete absence of An must still be due to kinetics, as suggested for type B's (11). Another apparent discrepancy is that TS-33, the natural analogue of B1-1, does not contain Pv, although it appears in the experiments. This may be due to failure of Pv to nucleate because of rapid cooling, which is also suggested by its axiolytic melilite mantle (8).

Some experiments were done to reproduce CAI textures. Near-liquidus Sp frequently forms clumps and sheets, a common feature of many CAI. On quenching, Sp rims sometimes form on the surfaces of liquid droplets in the B1-1 and AC-1 runs, suggesting that rapid cooling through the Sp field could result in the ubiquitous Sp rims found in types AC and B (12) inclusions. Sp formed in runs moderately supercooled ($>30^\circ\text{C}$) below the liquidus tends to contain glass inclusions. These are not seen in natural CAI Sp, suggesting that they did not form in this way. Since bubbles disappeared in $<2-3$ hours from droplets heated more than $\approx 30^\circ\text{C}$ above the liquidus, the presence of vesicles in some natural samples suggests that these CAI liquids were not superheated for long periods of time. Sp grown by melting of powdered starting material tend to be small, homogeneously distributed, isolated crystals and small clumps, a texture sometimes observed in type B2 inclusions. Sp framboids (13) were formed experimentally by surface nucleation and growth on bubbles and preexisting Sp. They are most readily formed when copious Sp is present prior to crystallization of other phases. Sp framboids occur in natural B2 inclusions, but not in B1's (13). This may be due to the larger Sp field of the former and does not necessarily require different cooling histories (13). Capture and preservation of small CAI droplets by larger ones (13) is not needed to explain Sp framboids. Devitrification of glasses and large supercoolings of liquids into the melilite field resulted in dendritic melilite crystals, which are not observed in natural inclusions. If such processes occurred in CAI, they must have been followed by subsolidus recrystallization or remelting.

In conclusion, except for fluffy type A inclusions, the mineralogical compositions and textures of CAI are consistent with a model involving simple melting of some precursor material. In the last melting event, the inclusions were probably not completely molten for very long and their melts had an f_{O_2} below the $\text{Fe}_{33}\text{Ni}_{67}$ -wüstite buffer.

Bulk Comp	Natural Analog	Crystallization Sequence, T($^\circ\text{C}$); (r) = reversal
AF-1	CG-11 (1)	Mel,1542-53(r); Sp,1479-1514; Pv,1453-79; An,1373-99
AC-1	TS-2	Sp, >1520 ; Mel,1441-74; Pv,1441-74
AC-2	TS-19	Sp, ≥ 1510 ; Mel,1480-1503
B1-1	TS-33 (8)	Sp,1518-1521(r); Pv,1477-86; Mel,1432-60; Px,1228-50; An, 1206-28
B1-2	(11)	Sp, >1540 ; Mel, 1376-1407; An, <1222 ; Px, <1222
SK	B2 (10)	Sp, ≈ 1460 ; Px, ≈ 1220 ; An, ≈ 1200 ; Mel, ≈ 1170
St	B1 (11)	Sp,1540-60(r); Mel, 1390-1410(r); An,1260; Px,1230

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