

Volatile elements in Allende inclusions

LAWRENCE GROSSMAN

Department of the Geophysical Sciences and Enrico Fermi Institute

R. GANAPATHY

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637

Abstract—There are two types of Ca–Al-rich inclusions in the Allende meteorite. Coarse-grained inclusions are composed of phases thought to be high-temperature condensates from the solar nebula: melilite, spinel, perovskite, Ti-pyroxene, and anorthite. Fine-grained inclusions contain nepheline, sodalite, grossular, spinel, and pyroxene. The mean Na and Mn contents of ten coarse-grained inclusions are 2122 ppm and 98 ppm and the average concentrations in ten fine-grained inclusions are 2.74% and 511 ppm, respectively. Cl contents of fine-grained inclusions reach 1.32%. Both types of inclusions contain volatiles which were emplaced during metamorphism of the parent body but, in addition, the fine-grained inclusions contain a primary volatile element component that was incorporated during condensation from the solar nebula, accounting for their higher contents of these elements.

INTRODUCTION

A RELATIVELY RECENT TREND in cosmochemistry is the use of the different chemical components found inside the chondritic meteorites as end-members in mixing models of planetary compositions. Several investigators (Gast *et al.*, 1970; Anderson, 1973; Ganapathy and Anders, 1974; Wänke *et al.*, 1974b) have proposed that the moon is composed of super-chondritic abundances of high-temperature condensates similar in composition to the Ca-rich inclusions in the Allende meteorite.

In reality, however, there are two distinctly different types of Ca-rich inclusions in this meteorite which are distinguishable from one another on the basis of their textures and mineralogy. One type, which we define as coarse-grained inclusions, occurs as white, rounded, centimeter-sized objects containing millimeter-sized crystals of melilite with smaller grains of spinel and perovskite (Grossman, 1975) or containing large grains of a Ti–Al-rich pyroxene with smaller crystals of spinel, melilite, anorthite, and perovskite (Clarke *et al.*, 1970). The second type, the fine-grained inclusions, are several millimeters in size and irregularly shaped. They vary in color from purple to pink to white and contain submicron-sized crystals of pyroxene, grossular, spinel, nepheline, and sodalite (Clarke *et al.*, 1970; Grossman *et al.*, 1975). Because of their exceedingly fine grain size and high porosity (Grossman *et al.*, 1975), it is very difficult to prepare polished thin sections of the fine-grained inclusions. In our collection of 30 Allende sections, we have never observed crystals large enough in them to permit textural descriptions by means of the polarizing microscope. Although relatively little bulk chemical information is available on these objects, particularly for

major elements, there is sufficient information in the literature to suggest that there are chemical differences, as well, between the two types of inclusions. The purpose of this paper is to present some new data on the relatively volatile elements, Mn, Na, and Cl, in both types of inclusions, to review the existing data on the inclusions in the light of these measurements and to investigate their implications for models of condensation and accretion.

ANALYTICAL TECHNIQUE

All samples used in this study were excavated from slab surfaces of the Allende meteorite using stainless steel dental tools and a binocular microscope in a clean laboratory. Great care was taken to avoid contamination of the inclusions by adjacent matrix material. Visual inspection of the final sample powders revealed a maximum of 1–2% matrix contamination. Ten fine-grained inclusions were selected and identified on the basis of their color, shape and soft, sugary consistency. Ten coarse-grained inclusions were also selected. These were identified on the basis of their color, shape, and resistance to digging and scraping. In addition, polished thin sections were made from 6 of them and studied by electron microprobe techniques among the samples in Grossman (1975).

All samples, 3–23 mg, were weighed into clean supersilica quartz tubes which were sealed, washed in hot HNO_3 , and weighed. They were then irradiated in the isotope tray at the Argonne National Laboratory CP-5 reactor for 30 min at a thermal neutron flux of $5 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$. Measurements of the spatial variation of the flux indicate that all samples received neutron doses within 1.9% of those received by the standards. No corrections were made for these small differences. Within 3 hr after the end of the irradiation, the silica tubes had again been washed in hot HNO_3 and counting had begun on a 50 cm^3 Ge(Li) detector. Gamma-ray peak assignments were made on the basis of both energy and half-life.

A blank silica tube, 2 samples of Orgueil, 1 of Alais, 1 of bulk Allende, (USNM Split 17, Position 25) and 1 of BCR-1 were irradiated and counted at the same time as the inclusions and the standards. A sample of the “standard pot” containing 2610 ppm Na and 40.9 ppm Mn (Perlman and Asaro, 1969) was used as a standard for these elements. A powdered sample of CaCl_2 containing 13 mg Cl was used as a Cl standard.

RESULTS

The analytical data for Mn, Na, and Cl are shown in Table 1. Errors quoted are based on the 1σ counting statistics for both samples and standards. Our data for Mn and Na in BCR-1 are in excellent agreement with the average value of 1406 ppm and the recommended value of 2.43%, respectively (Flanagan, 1973). In addition, our Mn and Na data for bulk Allende are well within the ranges of literature values, as summarized in Grossman (1973). Similarly, our data for Orgueil are in good agreement with those of Schmitt *et al.* (1972) and Wiik (1969), although our values for Alais are unusually low, perhaps due to the heterogeneity of this meteorite.

Because of the very short half-life of ^{38}Cl , 37.3 min, our counting errors are much greater for this element. The coarse-grained inclusions were counted last, resulting in very few net counts and very large decay corrections for Cl. So few counts were recorded that it was not possible to determine the half-life in the coarse-grained inclusions and we were unable to ascribe these counts conclusively to ^{38}Cl . As a result, this element was not determined in these inclusions

Table 1. Volatile elements* in Ca-rich Allende inclusions.

Sample	Mn	Na	Cl
Coarse-grained			
1	46.4 ± 0.9	1287 ± 10	n.d.
2	182 ± 4	620 ± 15	n.d.
3	22.5 ± 0.5	1374 ± 11	n.d.
4	98 ± 2	1523 ± 19	n.d.
5	79 ± 2	1639 ± 15	n.d.
6	19 ± 1	271 ± 7	n.d.
7	427 ± 7	8329 ± 55	n.d.
8	20.4 ± 0.6	903 ± 7	n.d.
9	72 ± 2	4710 ± 32	n.d.
10	9.4 ± 0.3	568 ± 5	n.d.
Fine-grained			
11	383 ± 6	1.40 ± 0.01%	0.44 ± .13%
12	403 ± 6	3.10 ± 0.02%	0.69 ± .16%
13	374 ± 7	5.14 ± 0.03%	0.49 ± .30%
14	696 ± 10	4.23 ± 0.03%	1.32 ± .24%
15	898 ± 13	1.08 ± 0.01%	n.d.
16	509 ± 8	2.59 ± 0.02%	0.15 ± .28%
17	161 ± 3	1.89 ± 0.01%	0.49 ± .11%
18	348 ± 6	3.40 ± 0.02%	0.10 ± .19%
19	865 ± 13	3.09 ± 0.02%	< 0.27%
20	475 ± 7	1.44 ± 0.01%	< 0.17%
Allende bulk	1528 ± 21	3417 ± 22	n.d.
Orgueil	1813 ± 25	5167 ± 34	n.d.
Orgueil	2030 ± 51	5474 ± 35	n.d.
Alais	658 ± 17	2201 ± 18	n.d.
BCR-1	1414 ± 36	2.42 ± 0.01%	n.d.

*Values in ppm unless otherwise indicated. n.d.—not determined.

although, taken literally, the count rates would imply that some of the coarse-grained inclusions contain up to several tenths of a percent Cl, a highly uncertain inference.

DISCUSSION

Differences between coarse- and fine-grained inclusions

From the data in Table 1, the fine-grained inclusions are consistently and substantially higher in Mn and Na than the coarse-grained inclusions. The mean Mn and Na contents in the fine-grained inclusions are 511 ppm and 2.74%, respectively, compared to 98 ppm and 2122 ppm for the coarse-grained ones. The Cl contents of the fine-grained inclusions are probably also higher than the coarse-grained ones. Both Na and Cl are enriched in the fine-grained inclusions relative to their abundances in the bulk meteorite and in Cl chondrites. There are thus marked chemical differences between the fine- and coarse-grained inclusions, in addition to the aforementioned textural and mineralogical contrasts.

Table 2. Bulk chemical data for Allende inclusions (wt.%).

	Coarse-grained			Fine-grained			
	1 Type a Chondrule	2 Chondrule	3 Low-Rb Aggregate	4 Aggregate	5 High-Rb Aggregate	6 Group III Aggregates	7
SiO ₂	29.79	31.1	36.6	33.7	37.3	20.5	24.5
TiO ₂	0.99	1.1	0.4	1.3	0.6	0.74	0.96
Al ₂ O ₃	31.61	27.3	39.3	26.6	24.9	43.3	40.3
FeO	0.37	1.4	0.6	2.3	10.1	3.7	3.9
MgO	10.82	12.6	5.2	13.1	11.6	15.4	13.6
CaO	26.76	23.2	16.7	21.6	10.9	11.4	11.4
Na ₂ O	0.11	0.56	0.7	1.1	4.1	1.3	1.8
Total	100.45	97.26	99.5	99.7	99.5	96.34	96.46

References: (1, 4) Clarke *et al.* (1970). (3, 5) Gray *et al.* (1973). (2) Mason and Martin (1974). (6, 7) Martin and Mason (1974).

The key similarity between these two types of inclusions, major-element chemistry, is illustrated in Table 2. In spite of the great significance attached to these objects, very few complete major-element bulk chemical analyses are available for individual inclusions whose descriptions are detailed enough to allow their classification as fine- or coarse-grained. In fact, those in Table 2 are the only such analyses which sum to more than 95% which we can locate in the literature, although concentration *ranges* for additional fine- and coarse-grained inclusions are given in Martin and Mason (1974). Both types of inclusions are substantially enriched in CaO, Al₂O₃, and TiO₂ relative to MgO and SiO₂ compared to the bulk meteorite or to CI chondrites. It is probably this fact, more than any other, which has caused these two distinctly different types of objects to be classified under a single label, "Ca-rich inclusions." Even in these analyses, however, it is apparent that the fine-grained inclusions are richer in the more volatile oxides Na₂O and FeO than the coarse-grained ones.

The coarse-grained inclusions, particularly those composed of melilite + spinel + perovskite, are believed to be high-temperature condensates from the solar nebula because they contain precisely the same mineral assemblage as that predicted from thermodynamic models to condense first in a cooling gas of solar composition at temperatures between 1625°K and 1400°K (Grossman, 1972). Mn, Na, and Cl, however, are relatively volatile elements compared to Ca, Al, and Ti. Na and Cl probably condense below 1100°K at 10⁻³–10⁻⁴ atm total nebular pressure (Grossman, 1972; Grossman and Steele, 1975). Mn was calculated to condense as MnS at 1139°K by Grossman (1972) but it is conceivable that it could have begun to condense at a higher temperature in solid solution in olivine and pyroxene. Even these phases, however, condense at lower temperatures than Ca, Al, and Ti. Thus, the abundances of Mn reported in the coarse-grained inclusions in Table 1 and of Na in Tables 1 and 2 are difficult to explain by the condensation

model, particularly in the absence of huge amounts of Fe, Mg, and Si which condense totally between 1400°K and 1200°K. In addition, Wänke *et al.* (1974a) reported 1000 ppm Cl in a coarse-grained inclusion which is also anomalous in this regard.

In contrast to the coarse-grained inclusions, the fine-grained ones contain little mineralogical evidence of being high-temperature condensates in spite of their Ca–Al-rich compositions. In fact, spinel is the only phase so far reported in these inclusions which appears at high temperatures in the equilibrium condensation sequence (Grossman, 1972). This, together with their high volatile element contents reported here and elsewhere, suggests that the fine-grained inclusions are not high-temperature condensates. The terms “refractory condensate inclusions in Allende” and “Ca-rich inclusions in Allende” are thus not synonymous with one another, as has been assumed in the past. Only the coarse-grained inclusions are refractory condensates. The fine-grained inclusions have a more complex origin.

Origin of the volatiles

Before the differences between these two types of inclusions were recognized, they were both thought of as high-temperature condensates and the presence of volatile Na and Cl in the form of the feldspathoid minerals nepheline and sodalite was considered an outstanding discrepancy (Grossman and Larimer, 1974). Early descriptions of these phases (Fuchs, 1969; Kurat, 1970) reported them to be found interstitially or on the rims of the inclusions, suggesting that they are secondary in origin, having formed after the more abundant Ca–Al-rich phases. More recently, Wänke *et al.* (1974a) showed Na, Mn, Cl, and several other volatile elements to be enriched by factors of 1.5–29 in the outer part of a coarse-grained inclusion compared to the inner part. In a microprobe study, Grossman (1975) reported Na and Cl enrichments in fine-grained, opaque areas found interstitially and in the outer zones of coarse-grained inclusions. Gray *et al.* (1973) noted that the Na contents of fine-grained inclusions increase toward their rims. These studies thus demonstrate rather conclusively the secondary origin of the volatiles.

Grossman (1972) proposed that Na and Cl were introduced into the inclusions during metamorphism of the parent body, long after condensation was over. He suggested that the volatile elements were leached from the matrix and reacted with the high-temperature phases in the inclusions to form the feldspathoids. An alternative suggestion was made by Grossman and Larimer (1974) who speculated that the secondary process could have taken place in the nebula by the reaction of the gaseous volatiles with the surfaces of the inclusions during a lower-temperature stage of condensation. The problem with this explanation is the absence of nickel-iron and forsterite which condense at temperatures intermediate between the Ca-rich phases and the feldspathoids. Arrhenius and Alfvén (1971) and Arrhenius (1972) favored a primary origin for the volatiles, hypothesizing that they condensed simultaneously with the refractories due to ionization-controlled sublimation from a low-pressure, high-temperature plasma in which

solid particles were not in thermal equilibrium with gaseous molecules. This model cannot explain the apparent secondary origin of the volatiles nor can it account for the absence of metal and forsterite (Grossman, 1973).

None of these suggestions alone seems to be able to explain the observation that the fine-grained inclusions are much richer in volatile elements than the coarse-grained ones. An important clue to the resolution of this problem comes from the scanning electron microscope work of Grossman *et al.* (1975). They observed a fine-grained, pink inclusion to be a delicate, cavernous aggregate of euhedral crystals, honeycombed with interstitial void space. They interpreted these textural features as very compelling evidence for direct condensation of the inclusion from the vapor of the solar nebula. Intimately intergrown with the Ca-Al-rich phases are discrete, euhedral crystals and crystal fragments of alkali- and Cl-rich phases, interpreted as nepheline and sodalite. The mode of occurrence of the feldspathoids strongly suggests that they condensed simultaneously with the Ca-Al-rich phases to form these inclusions, indicating a primary origin for at least some of the volatiles (Arrhenius and Alfvén, 1971) in the fine-grained inclusions. No such textures have been reported from the coarse-grained inclusions. Perhaps the volatiles in the coarse-grained inclusions are secondary but those in the fine-grained ones are primary.

This interpretation receives considerable support from the Rb-Sr study of Gray *et al.* (1973). They found that the fine-grained inclusions contain 5–1000 times more Rb than the coarse-grained inclusions, thus adding one more volatile element to the list of those displaying this trend. They also found that a variety of inclusions, chondrules, and aggregates from Allende fail to define an isochron. One interpretation proposed by Gray *et al.* (1973) for their data is the addition of Rb to both types of inclusions within the past 3.6 b.y. during a mild metamorphism of the Allende parent body. If other volatiles accompanied Rb in this process, this would account for those observations of their spatial distribution which indicate that they are secondary in origin. The relatively recent element migration suggested by these data rules out the possibility that the secondary process took place in the nebula. From the age systematics, Gray *et al.* (1973) pointed out, however, that the bulk of the Rb must have been incorporated in the fine-grained inclusions at an early time which is consistent with our suggestion that some of the volatiles entered these inclusions during condensation, 4.6 b.y. ago.

We conclude that the coarse-grained inclusions condensed from the solar nebula at high temperature and contained vanishingly small quantities of volatile elements at that time. Later, volatiles were added to these during the metamorphism of the Allende parent body. The fine-grained inclusions were also affected by the addition of volatiles during this metamorphism but, in contrast to the coarse-grained ones, they also incorporated large amounts of volatiles when they condensed from the nebula, accounting for their higher volatile element contents.

Implications for condensation and accretion

The problem of the origin of the fine-grained inclusions remains. Because of their high porosity and exceedingly fine grain size, making useful polished thin

sections of these objects is nearly impossible. Our only textural and mineralogical information about them comes from X-ray powder patterns (Clarke *et al.*, 1970) and scanning electron microscopy (Grossman *et al.*, 1975). Although the textures strongly indicate that they are condensates and their high CaO and Al₂O₃ contents suggest high condensation temperatures, the mineral assemblage spinel, pyroxene, grossular, nepheline, and sodalite is not a high-temperature equilibrium condensate assemblage.

Could these inclusions simply be mixtures of high-temperature spinel and pyroxene with lower-condensing nepheline and sodalite? Aside from the fact that one would again predict large amounts of forsterite and nickel-iron to be present because they would condense at temperatures intermediate between these others (Grossman, 1972), a serious objection arises from the textural information. According to equilibrium thermodynamic calculations (Grossman, 1972), Ca and Al should have been virtually completely condensed before the nebular temperature fell to 1500°K. It is not known which alkali silicates are stable condensates from a gas of solar composition but it is certain that Na and K cannot condense in significant amounts above 1100°K at equilibrium (Grossman, 1972; Grossman and Steele, 1975). This means that, if nepheline and sodalite do become stable in the nebula, they must form at the expense of preexisting solid grains of high-temperature condensates which contain all the Al. They could condense by the reaction of gaseous Na and Cl with the surfaces of Al-bearing grains in which case they would tend to form thin crusts or fine-grained overgrowths, rather than discrete, euhedral crystals. Such crystals could result, however, if the reaction took place via the complete resorption of the Al-rich, high-temperature phases by the vapor followed by the direct condensation of the feldspathoids. Perhaps a more likely alternative is that the fine-grained inclusions formed under nonequilibrium conditions, with residual, uncondensed Ca and Al condensing together with the volatiles at temperatures < 1000°K, as indicated by the FeO contents.

The coarse-grained inclusions demonstrate that it was possible for the refractories to separate themselves completely from the volatiles during condensation. Regardless of the exact process which formed the fine-grained inclusions, they clearly imply that this separation was not always complete. The fact that both types of inclusions are present in the Allende meteorite means that they coexisted in at least one part of the solar nebula. So far, models of lunar composition have not taken this into account and have assumed the volatiles to be present in different components from the refractories. This is largely because, until now, the fine-grained inclusions were not recognized in those models as a distinct petrographic component.

We believe that modeling the compositions of the planets from the different chemical components found within the carbonaceous chondrites is a sound and reasonable approach. We also believe, however, that there will be considerable uncertainty associated with such models until the whole range of these components is studied carefully by mineralogical, chemical, and isotopic techniques.

Acknowledgments—We are indebted to E. Anders, R. N. Clayton, G. W. Reed, and A. Turkevich for the loan of various items of laboratory equipment and supplies. We thank E. Olsen of the Field

Museum of Natural History for providing generous samples of carbonaceous chondrites. This work was supported by funds from the Louis Block Fund of the University of Chicago and from the National Aeronautics and Space Administration through grant NGR-14-001-249.

REFERENCES

- Anderson D. L. (1973) The composition and origin of the moon. *Earth Planet. Sci. Lett.* **18**, 301–316.
- Arrhenius G. (1972) Chemical effects in plasma condensation. In *From Plasma to Planet* (editor A. Elvius), p. 117–129. Almqvist and Wiksell, Stockholm.
- Arrhenius G. and Alfvén H. (1971) Fractionation and condensation in space. *Earth Planet Sci. Lett.* **10**, 253–267.
- Clarke R. S., Jr., Jarosewich E., Mason B., Nelen J., Gómez M., and Hyde J. R. (1970) The Allende, Mexico, meteorite shower. *Smithson. Contrib. Earth Sci.*, No. 5.
- Flanagan F. J. (1973) 1972 values for international geochemical reference samples. *Geochim. Cosmochim. Acta* **37**, 1189–1200.
- Fuchs L. H. (1969) Occurrence of cordierite and aluminous orthoenstatite in the Allende meteorite. *Amer. Mineral.* **54**, 1645–1653.
- Ganapathy R. and Anders E. (1974) Bulk compositions of the moon and earth, estimated from meteorites. *Proc. Lunar Sci. Conf. 5th*, p. 1181–1206.
- Gast P. W., Hubbard N. J., and Wiesmann H. (1970) Chemical composition and petrogenesis of basalts from Tranquillity Base. *Proc. Apollo 11 Lunar Sci. Conf.*, p. 1143–1163.
- Gray C. M., Papanastassiou D. A., and Wasserburg G. J. (1973) The identification of early condensates from the solar nebula. *Icarus* **20**, 213–239.
- Grossman L. (1972) Condensation in the primitive solar nebula. *Geochim. Cosmochim. Acta* **36**, 597–619.
- Grossman L. (1973) Refractory trace elements in Ca–Al-rich inclusions in the Allende meteorite. *Geochim. Cosmochim. Acta* **37**, 1119–1140.
- Grossman L. (1975) Petrography and mineral chemistry of Ca-rich inclusions in the Allende meteorite. *Geochim. Cosmochim. Acta* **39**, 433–454.
- Grossman L. and Larimer J. W. (1974) Early chemical history of the solar system. *Rev. Geophys. Space Phys.* **12**, 71–101.
- Grossman L. and Steele I. M. (1975) Amoeboid olivine aggregates in the Allende meteorite. *Geochim. Cosmochim. Acta*. In press.
- Grossman L., Fruland R. M., and McKay D. S. (1975) Scanning electron microscopy of a pink inclusion from the Allende meteorite. *Geophys. Res. Lett.* **2**, 37–40.
- Kurat G. (1970) Zur Genese der Ca–Al-reichen Einschlüsse im Chondriten von Lancé. *Earth Planet. Sci. Lett.* **9**, 225–231.
- Martin P. M. and Mason B. (1974) Major and trace elements in the Allende meteorite. *Nature* **249**, 333–334.
- Mason B. and Martin P. M. (1974) Minor and trace element distribution in melilite and pyroxene from the Allende meteorite. *Earth Planet. Sci. Lett.* **22**, 141–144.
- Perlman I. and Asaro F. (1969) Pottery analysis by neutron activation. *Archaeometry* **11**, 21–52.
- Schmitt R. A., Goles G. G., Smith R. H., and Osborn T. W. (1972) Elemental abundances in stone meteorites. *Meteoritics* **7**, 131–214.
- Wänke H., Baddenhausen H., Palme H., and Spettel B. (1974a) On the chemistry of the Allende inclusions and their origin as high temperature condensates. *Earth Planet. Sci. Lett.* **23**, 1–7.
- Wänke H., Palme H., Baddenhausen H., Dreibus G., Jagoutz E., Kruse H., Spettel B., Teschke F., and Thacker R. (1974b) Chemistry of Apollo 16 and 17 samples: Bulk composition, late stage accumulation and early differentiation of the moon. *Proc. Lunar Sci. Conf. 5th*, p. 1307–1335.
- Wiik H. B. (1969) On regular discontinuities in the composition of meteorites. *Commentat. Phys.-Math.* **34**, 135–145.