

OCCURRENCE OF WOLLASTONITE, RHÖNITE, AND ANDRADITE IN THE ALLENDE METEORITE¹

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ABSTRACT

The first meteoritic occurrence of wollastonite, rhönite and andradite is reported. All occur within white inclusions in the *Allende* meteorite. The composition of this rhönite differs markedly from those of terrestrial rhönites. X-ray diffraction data indicates that it is probably monoclinic in contrast to triclinic terrestrial rhönite. Associated with rhönite is a pyroxene with an unusually high TiO₂ content of 17%. Euhedral wollastonite and andradite are associated in the interior of open cavities and may have formed by a metasomatic reaction between the inclusion and black matrix. Mineral paragenesis is deduced from the texture of one of the inclusions.

INTRODUCTION

The *Allende* meteorite, a Type III carbonaceous chondrite, contains white inclusions (1–2 cm across) which are predominantly high in Ca–Al rich phases and which may contain high Ti-bearing minerals. These Ca–Al rich assemblages appear to be characteristic of several Type III carbonaceous chondrites (actually, the term carbonaceous is somewhat misleading as the carbon contents are less than 1 percent for most meteorites of this class). Several papers have now appeared describing some of these white inclusions in various Type III meteorites: for *Allende*, papers by Marvin, Wood, and Dickey (1970), Clarke *et al.* (1971), and Fuchs (1969); for *Lancé*, Kurat (1970); for *Leoville*, Keil *et al.* (1968); and for *Vigarano*, Reid *et al.* (1970). Undoubtedly these meteorites contain literally thousands of such inclusions and since only a few have been described in detail, it may be premature to draw general conclusions regarding their composition and modes of origin. A definite need exists for detailed descriptions of individual inclusions because the composition and distribution of the minerals are not the same, even within the same meteorite.

The present paper is believed to be the first report of the meteoritic occurrence of three minerals, andradite, wollastonite, and rhönite. All three are associated in one inclusion of *Allende* (designated hereafter as A) which was sampled during a brief visit to the U. S. National Museum. The primary attraction to this inclusion was the presence of conspicuous dark red specks (rhönite) distributed in the white matrix. A few milligrams of broken pieces and powder were later studied and component minerals identified. It was not possible, however, to gain quantitative

¹ Based on work performed under the auspices of the U. S. Atomic Energy Commission.

information of the mineral frequencies and relationships. Andradite and wollastonite were identified in samples of several other inclusions in *Allende* but this account is restricted to their occurrence in one of these (designated hereafter as B), a portion of which was mounted as a polished section and microprobed.

WOLLASTONITE

This mineral occurs as acicular crystals partially filling irregularly-shaped cavities about 0.5 mm in diameter. The needles are from 2–5 μm in cross-section and about 100 μm long. The degree of filling of the cavities varies; the wollastonite aggregates appear either as felted masses or as a delicate open framework of randomly-oriented needles as shown in Figure 1. The wall of each cavity is lined with a thin crust of diopside about 20 μm thick. Occasionally, euhedral crystals of andradite protrude into the cavities from the diopside wall. Diopside and wollastonite are not intergrown, suggesting that they did not form by eutectic crystallization from a residual melt. If, at one time, both phases were intergrown, then subsequent conditions favored the separation and growth of the needles from the poorly crystallized diopside. Separation by vapor fractionation, in the presence of an $\text{H}_2\text{-H}_2\text{O}$ buffer, however, would have been unlikely since the calculated condensation temperature is higher for

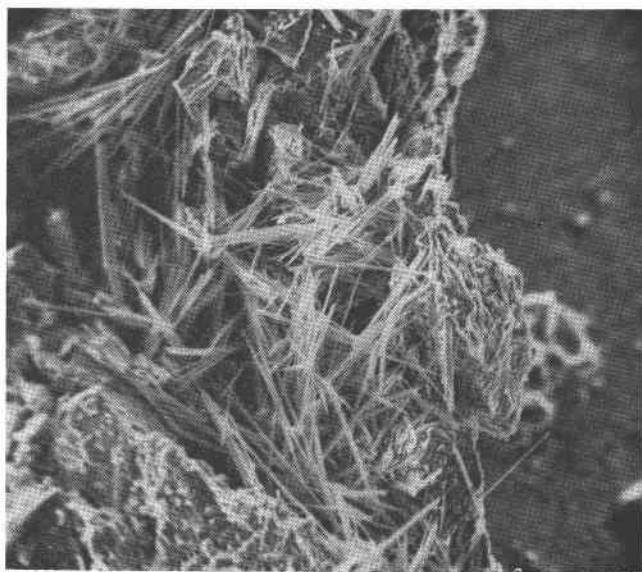


FIG. 1. Scanning electron microscope photograph of wollastonite needles in cavity. Width of field is 0.4 mm,

TABLE 1. ELECTRON MICROPROBE COMPOSITION OF SELECTED MINERALS FROM INCLUSIONS A AND B

	INCLUSION A			INCLUSION B			
	Gehlenite	Augite	Spinel	Spinel	Gehlenite	Diopside	Wollastonite
SiO ₂	28.8	33.5	bg	bg	23.0	53.5	50.3
CaO	40.4	24.1	0.1	bg	40.8	25.2	46.8
MgO	4.4	7.7	27.0	27.0	0.5	17.1	0.05
FeO	0.1	0.03	0.1	na	bg	0.1	0.4
Al ₂ O ₃	24.3	17.2	71.0	70.9	34.6	3.1	bg
TiO ₂	bg	16.9	1.5 ^a	0.2	bg	0.7	bg
Cr ₂ O ₃	bg	bg	0.2	na	na	na	bg
Sum	98.0	99.4	99.9	98.1	98.9	99.7	97.6

Analysts: K. Anderson and L. Fuchs.

Approximately 10 grains of each mineral were analyzed, corrections applied were the same as indicated in Table 2.

bg = background

na = not analyzed

^aTiO₂ 0.7 - 2.2

wollastonite than for diopside (Lord, 1965). Similar calculations for an inert atmosphere, or vacuo, lead to the same conclusion. Thus, diopside by virtue of its greater volatility would grow into the cavity openings instead of wollastonite. Further consideration on the formation of wollastonite will be given later in the paper.

The composition of wollastonite (Table 1) is close to pure CaSiO₃, the low summation (97.6 percent) being due to the small width of the needles relative to that of the microprobe beam. The X-ray powder pattern contains 24 wollastonite lines with *d*-spacings greater than 1.36 Å. The presence of a line at 4.05 Å serves to distinguish wollastonite from parawollastonite as noted by Heller and Taylor and quoted in Deer, Howie, and Zussman (1963).

RHÖNITE

This mineral, when first detected in the *Allende* meteorite, was thought to be a new mineral because of its unique composition and its X-ray properties. At that time, no powder patterns had been published for rhönite and the differences between the relative intensities of the

strongest lines for the "new mineral" and those listed for aenigmatite in the XPDF File (1968 Edition) prevented recognition of the fact that these two minerals were related. Dr. Fleischer, the Secretary of the IMA Commission on New Minerals and Mineral Names, recognized that the composition bore certain resemblances to that for terrestrial rhönite and informed me of some X-ray studies on terrestrial rhönite from Big Bend, Texas by K. L. Cameron *et al.* of Virginia Polytechnic Institute. These authors kindly sent me their powder data (then unpublished) together with a sample of their material. It was then apparent that the "new mineral" was rhönite, but its monoclinic symmetry did not correspond to the triclinic symmetry assigned by Kelsey and McKie (1964) for aenigmatite which many thought should be iso-structural with rhönite. A review of the single crystal photographs indicates that the symmetry of rhönite by usual tests, is probably monoclinic for this occurrence in *Allende*. An adequate review of the literature on rhönite is given by Cameron, Carman and Butler (1970) in their paper describing the occurrence of rhönite at Big Bend. Not included in their review, is a concurrent report by Walenta (1969) on the crystallography of rhönite from Rhön, Germany.

X-ray Data. The largest mineral grains pried from the inclusion measured from 100 to 200 microns across, but none of these was suitable for single crystal studies, since they were either multi-grains of rhönite or contained other crystalline impurities. It was necessary to select smaller grains (less than 40 μ) to find single crystals free of inclusions. These grains showed no crystal faces or cleavage which necessitated laborious procedures to locate the crystallographic axes. Results using Weissenberg methods and with rotation about three crystallographic axes yielded a monoclinic cell: a 9.78(2) Å, b 14.84(3) Å, c 5.18(2) Å, β 101.2°(1). A least squares refinement of 12 indexed lines from the powder pattern gave: $a = 9.83$ Å, $b = 14.92$ Å, $c = 5.18$ Å, $\beta = 101.04^\circ$, the probable errors being about the same as above. Systematic extinctions observed were: hkl , $h+k=2n$; $00l$, $l=2n$; $0k0$, $k=2n$; and $h0l$, $h=2n$, $l=2n$. Hence a monoclinic C -lattice cell was indicated, the dimensions of which correspond to those of a pseudo-monoclinic C -lattice derived by Kelsey and McKie from the triclinic lattice of aenigmatite, which is thought to be iso-structural with rhönite. Their pseudo-monoclinic constants are: a_m 9.888 Å, b_m 14.814 Å, c_m 5.203 Å, α_m 89°56', β_m 102°21', and γ_m 90°17'. They suggested that the polysynthetic twinning characteristic of aenigmatite from volcanic rocks, may be the result of inversion during cooling from a high-temperature monoclinic polymorph whereas the mineral from plutonic rocks is untwinned. The possibility that rhönite in *Allende*,

by virtue of its unique composition, is strictly monoclinic cannot be decided at this time due to a few provisos. Oscillation photographs of long exposures (10 hours) rotated about the c -axis show a few faint diffraction maxima located between the prominent layer-lines of 5.18 Å. There are some ambiguities as to their interpretation. They have shapes different from that of those spots which lie along the well-defined layer-lines. If these few maxima are not spurious then a doubling of the c -axis may be required which in turn modifies the extinctions so that $h+k+l$ becomes equal to $2n$. The cell is then body-centered indicating that the one chosen was only pseudo-monoclinic; rhönite in this meteorite could then be triclinic or require some other choice of monoclinic axes. An added complication involves the indexing of a weak line present on some, but not on all, powder patterns at a d -spacing of 2.78 Å. This line, indexed as (141), violates all other observations that $h+k$ is even. Its absence on about half of the powder patterns of different specimens suggests that *Allende* rhönite contains both triclinic and monoclinic forms as this line is prominent on the patterns published for both the Rhön and Big Bend rhönites.

After the single crystal results for the *Allende* rhönite were obtained, the X-ray work of Walenta (1969) on twinned crystals of rhönite from Rhön, Germany was brought to my attention. He concluded that rhönite is triclinic based in part on extinction angles and its structural similarity to aenigmatite. His pseudo-monoclinic cell (a_m 10.163 Å, b_m 14.9015 Å, c_m 5.2075 Å, $\alpha_m = \gamma_m = 90^\circ$, β_m 108°54'), however is not in agreement with the monoclinic cell found for the meteoritic rhönite. The most significant difference lies in β_m which is more than 7° higher than β_m for either aenigmatite or meteoritic rhönite. This discrepancy may be due to compositional differences as suggested by Walenta, although the powder patterns of the two rhönites are in essential agreement. Many of his assignments are such that $h+k$ is not even; it is therefore possible that rhönites from *Allende* and Rhön have different symmetries.

The powder data for the *Allende* rhönite is not duplicated here as it is in close agreement with that recently published for rhönite from Big Bend, Texas by Cameron *et al.*¹ These authors, apparently unaware of Walenta's paper, suggested that rhönite is probably triclinic based on certain similarities between the powder patterns of rhönite and aenigmatite. In order to obtain a preliminary cell, they had to assign unique indices to the powder data of aenigmatite although Kelsey and McKie

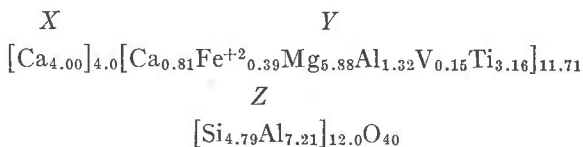
¹ My powder pattern (film) of Big Bend rhönite contains a line at 3.12 Å, intensity of 20, which the authors may have inadvertently omitted from their table. The spacings (Å) and relative intensities of the strongest lines for *Allende* rhönite are: (002) 2.542 (10), (221) 2.935 (9) (330 and 241) 2.686 (7), (351) 2.105 (6), (0.10.0 and 602) 1.489 (5), (551 and 622) 1.469 (5), (221) 3.440 (5), (310) 3.126 (4).

could not do this from their single crystal results (except for the first three lines). The agreement between calculated and observed d -spacings indicated to Cameron *et al.* that rhönite is triclinic; however, they correctly point out that the method is subject to limitations.

The X-ray density calculated for a monoclinic cell based on 40 oxygens, with $c = 5.18 \text{ \AA}$ and the other parameters the same as before for *Allende* rhönite, is 3.43 g/cc. The density measured on the small quantity (20 μg) of mineral available was 3.4(1) g/cc. The volume was determined by recording the displacement of a meniscus of oil in a thin-walled, uniform bore capillary, before and after inserting and centrifuging the mineral grains.

Composition. The composition (Table 2) was determined by electron microprobe analysis on eight epoxy-mounted grains. The large ranges observed for each component oxide may have resulted from rapid cooling. The average composition, however, is quite different from those of any analyzed terrestrial rhönites and should provide an insight into the substitutional relationships in this mineral. The similarity between aenigmatite and rhönite was first noted by Fleischer (1936). Cameron *et al.* pointed out that if these minerals were members of a solid solution series, the mechanism is more complex than the coupled Si+Na substitution by Ca+Al in rhönite suggested by Fleischer. They proposed that only limited solid solution between these minerals occurred at magmatic temperatures and that aenigmatite and rhönite were actually end members in a substitutional series. In view of the present analysis of the *Allende* rhönite, it is not clear what the rhönite end member might be.

The structural formula calculated from the composition and stated in terms of 8, 6 and 4-fold coordination (X , Y and Z atoms resp.) and based on 40 oxygens is:



An idealized formula, close to the above, can be derived from the aenigmatite formula $Na_4(Fe, Mg)_{10}Ti_2Si_{12}O_{40}$ by several coupled substitutions: CaAl-SiNa, TiMg-2Al, SiMg-2Al, and Ca-Mg-Fe to give $Ca_4(Ca_{1.1}Mg_{6.1}Fe_{0.5})_{7.7}Al_{1.3}Ti_{3.0}(Si_{4.7}Al_{7.3})_{12.0}O_{40}$. The calculated composition agrees within 0.6 wt. percentage points for the analyzed amounts of each oxide except for TiO_2 , where the analyzed amount is 1.1 weight percent too high. Further refinement requires the substitution of trivalent and quadrivalent for divalent ions, which is not possible without involving

TABLE 2. COMPOSITION OF RHÖNITE FROM THE ALLENDE METEORITE COMPARED WITH 2 TERRESTRIAL RHÖNITES

	Allende ^a	Big Bend Texas ^b	Rhön Germany ^c	Ranges for Allende
SiO ₂	19.1	24.82	24.42	18.6 - 20.1
TiO ₂	16.8	9.09	9.46	14.1 - 18.4
Al ₂ O ₃	28.9	17.24	17.25	27.6 - 29.6
Fe ₂ O ₃	-	9.48	11.69	-
FeO	1.9	15.98	11.39	0.3 - 4.2
MgO	15.7	10.67	12.62	13.9 - 17.8
CaO	17.9	11.97	12.43	17.0 - 19.6
Na ₂ O	bg	0.72	0.67	
K ₂ O	bg	0.02	0.63	
MnO	bg	0.26	Tr	
Rem.	0.7	0.44		
Sum	101.0	100.7	100.6	

^aElectron microprobe analysis, average of 8 grains, analyst: J. E. Sanecki, Argonne National Laboratory. Remainder is 0.7 V₂O₃ based on 0.2 V₂O₃ content of a standard chromite. Compositions were corrected for deadtime, background, absorption, fluorescence, and atomic number according to Smith (1965).

^bCameron, *et al.* (1970).

^cQuoted in Walenta (1969).

bg = background.

lattice vacancies to maintain charge balance. But considering the large variation in the grain to grain compositions, the agreement is not too bad and probably does not warrant the application of additional conditions to bring closer agreement. These substitutions however when similarly applied to derive the composition of Big Bend rhönite from the aenigmatite formula give excellent agreement with the analysis given by Cameron *et al.* provided that a Fe⁺³-Al substitution be added.

Optical properties. Thin edges of grains are reddish-brown in transmitted light, very much like chromite but differs in being distinctly anisotropic. Grains 30–40 microns thick are opaque. Refractive indices are somewhat variable and difficult to determine: $\alpha = 1.79$, $\gamma = 1.83$. The interference figure is indistinct due to the intense coloration and to the small size of those grains which transmit sufficient light. The optical axial angle is large but its size or optic sign could not be determined. Some grains exhibit pronounced pleochroism from reddish brown to reddish-green; however, the powder patterns are identical. Most grains have spinel inclusions. The deep color of this mineral is puzzling in view of its composition. A few grains when heated in air at 1000°C for two days became creamy white with no significant changes in the powder pattern. Other grains heated to 600°C in air for several days remained colored. The oxidation state of Ti may play a role if the coloration is caused by trivalent Ti, then oxidation to quadrivalent Ti, at 1000°C may account for the loss of color.

ANDRADITE

Euhedral equant andradite crystals up to 50 microns across were easily separated from both inclusions. In inclusion *B*, it occurs associated with wollastonite inside cavities (Fig. 2) and also in small areas of the black matrix where the matrix protrudes into the inclusion (Fig. 3). The crystals are clear greenish-yellow and isotropic with $N = 1.885(5)$. The X-ray powder pattern contained only andradite lines. The cell size, calculated from the α_1 and α_2 lines of the (12, 6, 0), (14, 4, 0) and (14, 4, 2) reflections, is 12.057(2) Å which is in good agreement with 12.059 Å for synthetic andradite given by Swanson *et al.* (1960). The average probe composition of several grains from each inclusion is, in weight percent: CaO 32.5, Fe₂O₃ 31.4, SiO₂ 36.1. The theoretical composition is CaO 33.1, Fe₂O₃ 31.4, SiO₂ 35.5. The standard used was a glass of andradite composition kindly prepared by Dr. H. G. Huckenholz of the University of Munich. A wave-length scan showed no other elements present above 0.1 weight percent. Noteworthy is the absence of Ti considering the high Ti contents of associated perovskite, rhönite and titano-augite. According to Deer, Howie, and Zussman (1962), high Ti contents in terrestrial garnets are restricted to andradite where the TiO₂ content may amount to 17 percent. The absence of Ti together with the presence of Fe⁺³ in this garnet suggests that it was formed after crystallization of the Ti-rich, Fe-poor phases and in a local environment which became oxidizing and enriched in Fe. The occurrence of andradite in *Allende* is of interest as the only other meteoritic mineral known to contain essential ferric iron is magnetite.

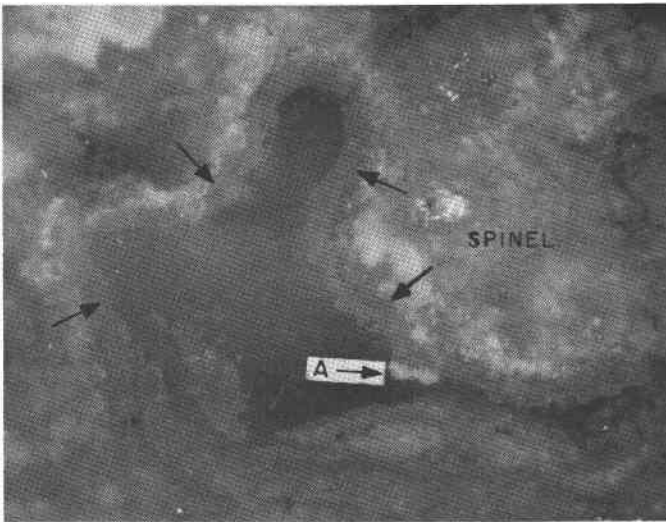


FIG. 2. Arrows outline diopside wall of epoxy-filled cavity which contains wollastonite (not shown) and two euhedral andradite crystals (A). White specks in spinel are perovskite. Polished section, reflected light, oil immersion; width of field is 0.45 mm.

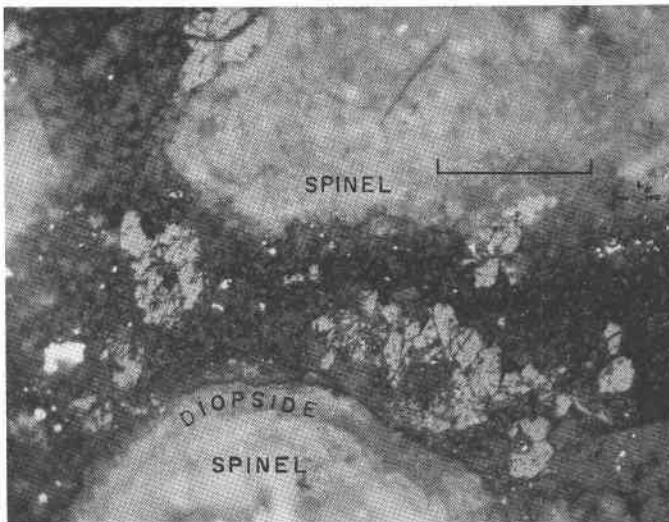


FIG. 3. Formation of subhedral andradite $20\mu\text{m}$ gray grains within black matrix of *Allende* where it protrudes into white inclusion B. Diopside rims spinel in the inclusion. Polished section, reflected light, oil immersion; scale bar is 0.1 mm.

MINERAL ASSEMBLAGE, INCLUSION A

Associated with wollastonite, rhönite, and andradite in this inclusion are grossular, perovskite, spinel, gehlenite ($\text{Ge}_{67}\text{Ak}_{33}$), and a mineral tentatively identified as a titano-augite, compositions of the last three are given in Table 1. A rough estimate shows that gehlenite is most abundant (70 percent), followed by spinel (25 percent) and the remaining constituting about 5 percent. The identification of grossular rests on its presence as an impurity in two powder patterns, but it could not be identified optically to permit a separation. Similarly, a small amount of anorthite may be present. Perovskite was identified from its powder pattern but its composition was not determined except for an uncorrected 55 percent TiO_2 content obtained on a few micron-sized spots.

As mentioned earlier in this paper, textural relationships between all phases could not be decided because only a part of the inclusion was sampled as powder, nevertheless a few relationships are evident from the individual grain-mounts in the probe section. Perovskite occurs as thin stringers ($2 \times 15 \mu$) within massive spinel and in a mesostasis adjacent to, but not within, rhönite. Micron-sized perovskite frequently rim small spinel inclusions in rhönite and gehlenite, indicating an exsolution of perovskite from spinel upon cooling. Euhedral spinel crystals ($20\text{--}80 \mu$) are included in augite (140μ) whereas smaller rounded to subhedral spinel grains occur within rhönite. The order of crystallization appears to be: spinel, rhönite or augite, and gehlenite last. The remaining relationships could not be determined.

The dark-green titano-augite is of interest because of its unusually high Ti and Al content for a pyroxene. Its occurrence was previously noted by Fuchs (1969) in another inclusion in *Allende*, and the analysis of this mineral has since been completed and corrected. The probe composition, in weight percent is: SiO_2 31.3, Al_2O_3 22.0, CaO 24.9, TiO_2 17.7, MgO 5.1, FeO none. A general similarity is indicated with the composition of the same mineral in inclusion A (Table 1). Optical properties are not easily determined but both compositions have refractive indices in the range 1.73 to 1.76, are optically positive, and have $2V$ about $65^\circ\text{--}75^\circ$. Although the X-ray powder patterns are practically identical to those for diopside or augite, it would be desirable to confirm the identification as a pyroxene from single crystal studies. So far, I have not found suitable crystals for this purpose. Another occurrence of a mineral related in composition to these two occurrences in *Allende*, has been reported in *Vigarano* (also a Type III carbonaceous meteorite) by Michel-Levy and Nelen (1970). Their reported probe composition is, in weight percent: SiO_2 27, Al_2O_3 26, CaO 25, TiO_2 17, MgO 4, FeO none. Common to all three compositions is the low number of cations (1.88–1.91) which remain after assigning

$\text{Si} + \text{Al} = 2$ as for an ideal pyroxene formula. Hence it is possible that these unusual compositions were formed under some extreme P - T conditions which may not have formed an ideal pyroxene composition. The problem may be resolved in the near future. Brian Mason (personal communication) has found an inclusion containing some large (1 mm) crystals of this phase which may prove suitable for single crystal studies.

MINERAL ASSEMBLAGE IN INCLUSION B

This inclusion was found in a specimen obtained from the Field Museum of Natural History. Possession of the specimen provided the opportunity to mount a piece of the inclusion as a polished section so that textures and mineral relationships are shown (Fig. 4) which could not be observed for inclusion A. The compositions of most of the minerals in this inclusion are given in Table 1. Andradite here has the same composition as before.

Spinel is most abundant, comprising about $\frac{2}{3}$ of the inclusion, most of the remaining $\frac{1}{3}$ is occupied by areas of gehlenite ($\text{Ge}_{95}\text{Ak}_5$) which may be a few mm across but smaller "pools" of gehlenite are typically enclosed in massive spinel. Minor amounts of aluminous diopside occur as veins or ribbons surrounding or within spinel and also as crustal linings surrounding wollastonite-occupied cavities, but diopside does not surround the gehlenite areas. Euhedral crystals of andradite appear within the inclusion on the inside walls of the diopside crust which lines the cavities whereas subhedral andradite grains are found embedded in the black matrix where it just penetrates the inclusion. The composition of andradite in either location is the same. No andradite was observed at those matrix-inclusion contacts where mixing was not evident. Not shown in the photographs accompanying this report are small micron-sized grains of hibonite of two compositions which are surrounded by spinel which in turn is immersed in large areas of gehlenite. Both compositions of hibonite can be expressed in terms of the formula for calcium hexaluminate, $\text{CaAl}_{12}\text{O}_{19}$.¹ Perovskite grains occur only within spinel and serve to outline the hibonite-spinel contacts. The composition of perovskite was only qualitatively assessed from its high Ca and Ti contents. Appreciable alkali-contents were found in one area about 20 microns in diameter, its approximate composition in weight percent is: SiO_2 41, CaO 4, Al_2O_3 33, Na_2O 16, K_2O 2. No further attempt was made to relate this analysis to mineral content as no X-ray patterns could be obtained. Neither rhönite nor augite are found in this inclusion.

¹ Further details on the composition and meteoritic occurrence of this mineral will be presented in a paper currently in preparation with Prof. Klaus Keil.

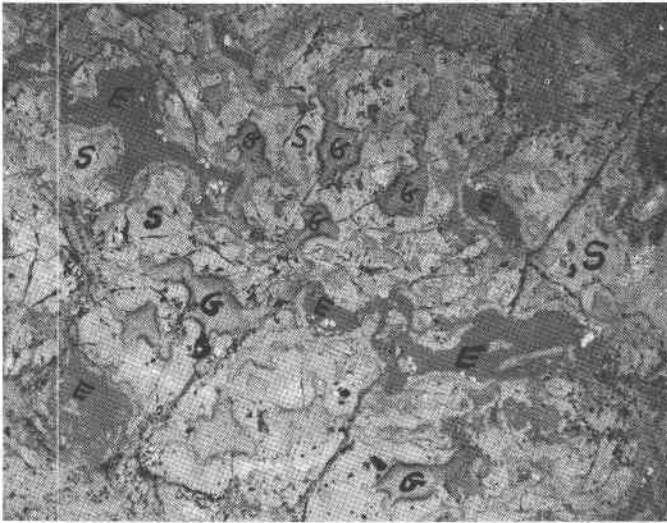


FIG. 4. Textural features of a portion of inclusion B. Diopside walls, about 15 microns thick, rim epoxy-resin-filled cavities (E) which contain wollastonite needles (not shown) and andradite (bright spots). Major minerals are gehlenite (G) and spinel (S). Most andradite crystals are attached to diopside walls, but some have been detached during epoxy-impregnation. Small white specks in spinel are perovskite. Reflected light photograph of polished section. Width of field is 1.0 mm.

Of special interest are the numerous cavities partially filled with wollastonite needles which form a delicate, open, barely self-supporting framework. The thin crust of diopside forming the cavity walls is easily punctured to reveal the intricate array of wollastonite needles. Unfortunately, we were unable to preserve one of these crust-capped "geodes" for a scanning electron microscope photograph, but several photographs were obtained of the wollastonite aggregates *in situ* without crust (Fig. 1). On the polished sections, these cavities appear as areas of epoxy-resin as a result of the vacuum impregnation. The needles are faintly visible when they appear at the surface of the section, but their presence in each filled-cavity is made evident by focusing the microscope through the epoxy, preferably using an oil-immersion objective.

PARAGENESIS OF THE MINERAL ASSEMBLAGE IN INCLUSION B

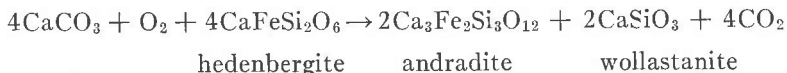
Although the purpose of this paper is to present mineralogical data in accord with the title, a few remarks can be made regarding some aspects of the origin of these inclusions. The comments are by nature highly speculative since the conditions of formation may be considerably dif-

ferent than those normally encountered within the confines of laboratory systems or terrestrial environments. One illustrative example concerns the comparison of the TiO_2 contents of terrestrial and synthetic pyroxenes with those of the titano-augites given under inclusion A. Yagi and Onuma (1967) have pointed out that the pyroxenes in alkalic basalts or related rocks have TiO_2 contents which may be as high as 5 percent. This agrees well with maximum values of from 4 to 6 percent obtained by these authors and others for various synthetic systems investigated. It was also found that the maximum amount is obtained at one atmosphere and that this decreases with increasing pressure. Thus, one is at a loss to extrapolate to conditions leading to concentrations as high as 17 percent. Similar considerations might apply to associated rhönite in the same inclusion because of its unique composition compared with those known from terrestrial rocks. On the other hand, the other minerals in inclusion B apparently have no unusual compositions and may be compared to equilibrium diagrams of the pertinent systems.

If it is assumed that the complex texture shown in Figure 4 can form by crystallization from a melt, and andradite neglected for the moment, then the observed assemblage of aluminous diopside-spinel-gehlenite is not an equilibrium assemblage according to the most recent investigations of the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. Portions of this system which are most pertinent are included in the work by O'Hara and Biggar (1969), Schairer and Yoder (1970), and Yang (1970). Their results verify the compatibility of an aluminous diopside-spinel-melilite assemblage at temperatures around 1200°C but the melilite should be richly akermanitic in contrast to the $\text{Ge}_{95}\text{AK}_5$ composition present in the inclusion. W. R. Foster (personal communication) suggests that, since akermanite is unstable below 700°C (being replaced by wollastonite and monticellite) a gehlenite-rich melilite may be stable at low temperatures with spinel and aluminous diopside, with either wollastonite or monticellite as a possible additional phase. If this is true, the aluminous diopside-spinel-gehlenite-wollastonite assemblage in this inclusion could be an equilibrium assemblage but would require crystallization temperatures below 700°C .

Aside from equilibrium considerations, the fabric suggests that the two main phases, spinel and gehlenite crystallized over a narrow temperature interval to form gehlenite within spinel and spinel within gehlenite. A small amount of residual liquid of diopside composition then filled narrow fissures and partially filled open cavities in spinel. The fairly uniform thickness of the diopside walls presents a problem but could be accounted for if this last liquid coated the cavity walls while the body was tumbling in a gravitational field. The mass which was later to become an inclusion

remained plastic while some kneading occurred to distort the shapes of the cavities but did not cause their collapse because of some internal gas pressure. The white crystalline mass, still hot, was somehow incorporated in the black matrix of Allende, where metasomatic reactions between matrix and inclusion led to the formation of euhedral crystals of andradite and wollastonite. The reasoning for this last step is based upon several considerations. (1) Ferric iron had to be introduced into the iron-poor inclusion following oxidation of ferrous iron in the iron-rich matrix. (2) Andradite of the same composition occurs as subhedral crystals within the matrix where it has invaded the inclusion but as euhedral crystals within the cavities in the inclusion. (3) Euhedral wollastonite and andradite are intimately associated and both protrude from the cavity walls. (4) Wollastonite formed only within the diopside-crusting cavities, it is not found with diopside in the fissures; therefore conditions for the formation of the wollastonite had changed following diopside formation. From these considerations it would appear that wollastonite and andradite formed by vapor transport in a metasomatic reaction between matrix and inclusion. A hypothetical overall reaction is:



The ferrous iron source is arbitrarily selected from the hedenbergite molecule in the matrix pyroxenes, the source of additional Ca ions is expressed as calcite with no concern given as to the actual state involved. If water vapor were present, the temperature of the reaction must have exceeded 400–450°C to inhibit formation of a hydrated calcium silicate from wollastonite (Harker, 1964). High temperatures would also be required to prevent serpentinization of the ferro-magnesian silicates in the black matrix.

COMMENTS

Throughout this paper it has been assumed that the starting compositions which gave rise to the mineral assemblages had already existed. Although the mineralogy of these inclusions bears a general resemblance to terrestrial skarn-type deposits, the chemical fractionation required in an extra-terrestrial environment may be exceedingly complex and quite different than those encountered in magmatic processes. Marvin *et al.* have noted that there is a general similarity between the chemistry and mineralogy of the Ca-Al rich inclusions in *Allende* and the sequence of compounds which might be expected as early condensates in a solar nebula. Alternatively, Kurat has proposed that these compositions were residual, being derived by the evaporation of ordinary chondritic ma-

terial at elevated temperature which were generated by impacts on a parent body. Kurat's stimulating proposal was largely based upon a general correlation between the observed concentration factors and the boiling points of the oxides of Ca, Al, Ti, Zr, and Y. While the impact model provides an easily acceptable explanation to account for the association of the marked compositional contrasts of matrix and inclusions, there are some objections that evaporation of chondritic material produced the fractionations. One question why Cr, for instance, is not concentrated to the same degree as Ti. The boiling points of both oxides are about the same and since Cr exceeds Ti in abundance in meteoritic matter, Cr should be more abundant in the inclusions than Ti. Abnormally high concentrations of Cr have not been observed. Furthermore, impacts such as those which have taken place on the lunar surface have not produced any appreciable fractionation in the composition of the impacted material even though melting had occurred (see Keil et al., 1970). Thus it seems clear that there is no straightforward mechanism that will account for the formation of these unique compositions.

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NOTE ADDED IN PROOF

Prof. K. Keil informs me that he has observed grains of wallastonite composition in white inclusions in the *Leoville* Type III carbonaceous chondrite. Dr. Brian Mason has recently found several grains of rhönite in a white inclusion in the *Allende* meteorite which have higher TiO₂ contents than that reported in Table 2. His tentative probe results are, in weight percent: SiO₂ 16.5, TiO₂ 23.3, Al₂O₃ 28.2, FeO 0.5, MgO 14.6, CaO 14.4.

REFERENCES

- CAMERON, K. L., M. F. CARMAN, AND J. C. BUTLER (1970) Rhönite from Big Bend National Park, Texas. *Amer. Mineral.* **55**, 864-874.
- CLARKE, R. S., JR., E. JAROSEWICH, B. MASON, J. NELEN, M. GOMEZ, AND J. R. HYDE (1971) The Allende, Mexico, Meteorite Shower. *Smithsonian Contrib. Earth Sci.* **5**.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock-forming minerals*, Vol. 1., *Ortho- and ring silicates*. John Wiley and Sons, Inc., New York, 90-92.
- , ———, AND ——— (1963) *Rock-forming minerals*, Vol. 2., *Chain silicates*. John Wiley and Sons, Inc., New York, 169.

- FLEISCHER, M. (1936) The formula of aenigmatite. *Am. J. Sci.* **32**, 323-348.
- FUCHS, L. H. (1969) Occurrence of cordierite and aluminous orthoenstatite in the Allende meteorite. *Amer. Mineral.* **54**, 1645-1653.
- HARKER, R. I. (1964) Dehydration series in the system $\text{CaSiO}_3\text{-SiO}_2\text{-H}_2\text{O}$. *J. Am. Ceram. Soc.* **47**, 527.
- KEIL, K., G. I. HUSS, AND H. B. WIJK (1969) The Leoville, Kansas, meteorite: a polymict breccia of carbonaceous chondrites and achondrite (Abstr.). *Meteorite Res.*, ed. P. Millman (Reidel, Dordrecht) 217.
- , T. E. BUNCH, AND M. PRINZ (1970) Mineralogy and composition of Apollo 11 lunar samples. *Geochim. Cosmochim. Acta, Suppl.* **1**, 596.
- KELSEY, C. H., AND D. MCKIE (1964) The unit-cell of aenigmatite. *Mineral. Mag.* **33**, 986-1001.
- KURAT, G. (1970) Zur genese der Ca-Al-reichen einschlüsse im chondriten von Lance. *Earth Planetary Sci. Lett.* **9**, 225-231.
- LORD, H. C. III (1965) Molecular equilibria and condensation in a solar nebula and cool stellar atmospheres. *Icarus* **4**, 279-288.
- MARVIN, U. B., J. A. WOOD, AND J. S. DICKEY, JR. (1970) Ca-Al rich phases in the Allende meteorite. *Earth Planetary Sci. Lett.* **7**, 346-350.
- MICHEL-LEVY, C., R. CAYE, AND J. NELEN (1970) A new mineral in the Vigarano meteorite. (Abstract) *Meteoritics* **5**, 211.
- O'HARA, M. J., AND G. M. BIGGAR (1969) Diopside-spinel equilibria, anorthite and forsterite reaction relationship in silica-poor liquids in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ at atmospheric pressure and their bearing on the genesis of melilitites and nephelinites. *Amer. J. Sci., Schairer Volume 267-A*, 364-390.
- REID, A. M., R. J. WILLIAMS, E. K. GIBSON, JR., AND K. FREDRIKSSON (1970) A refractory glass chondrule in the Vigarano chondrite. (Abstract) *Meteoritics* **5**, 218.
- SCHAIRER, J. F., AND H. S. YODER, JR., (1970) Critical planes and flow sheet for a portion of the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ having petrological applications. *Carnegie Inst. Washington Year Book* **68**, 202-214.
- SMITH, J. V. (1965) X-ray emission microanalysis of rock-forming minerals. I. Experimental techniques. *J. Geol.* **73**, 830-864.
- SWANSON, H. E., M. I. COOK, T. ISAACS, AND E. H. EVANS (1960) Standard X-ray diffraction powder patterns. *Nat. Bur. Stand. [U.S.] Circ.* **539**, 9, 22-23.
- WALENTA, VON KURT (1969) Zur kristallographie des Rhönites. *Z. Kristallogr.* **130**, 214-230.
- YAGI, K., AND K. ONUMA (1967) The join $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{O}_6$ and its bearing on the titanaugites. *J. Fac. Sci., Hokkaido Univ., Ser. IV, Geol. Mineral.* **13**, 463-83.
- YANG, H-Y. (1970) *Phase Equilibria of the Join Akermanite-Anorthite-Forsterite in the System $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ at Atmospheric Pressure*. Ph.D. Diss., Ohio State University.

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