ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 8 NUMBER 7 JULY, 1975

The Allende Meteorite—Cosmochemistry's Rosetta Stone?

Brian Mason

Smithsonian Institution, Washington, D.C. 20560

Received November 20, 1974

1969 was a banner year for cosmochemistry, sparked by two unrelated events. In February, the Allende meteorite fell in northern Mexico; in July, the Apollo 11 astronauts brought back the first lunar samples. These two materials have enormously expanded our knowledge of the chemistry of the Solar System—one, the meteorite, probably represents matter in a primitive preplanetary condition; the lunar samples, the same material after an extensive period of preplanetary and planetary evolution. This fortuitous coincidence has resulted in a quantum jump in cosmochemical research.

The meteorite fell in the early morning of Feb 8, 1969. A brilliant fireball was observed over much of northern Mexico and adjacent areas of Texas and New Mexico. The most spectacular phenomena were centered around the city of Parral in the south-central part of the state of Chihuahua. The fireball approached from the south-southwest, and as it neared its terminal point, the brilliant light was accompanied by tremendous detonations and a strong air blast—many people feared that it was the explosion of an atomic bomb! Thousands of individual meteorites rained down over a large area of rural Mexico. No injuries or damage was caused, although one 15-kg stone fell within 4 m of a house in the town of Pueblito de Allende, 35 km east of Parral, awakening and thoroughly alarming the residents.

Our initial field investigation was undertaken after conferring by telephone with the Mexican authorities. Mr. R. S. Clarke and I arrived in Parral on Feb 12. As we drove into the city I saw, in the window of the newspaper office, what was undoubtedly a piece of the meteorite. One look was sufficient to convince us that we had here a remarkable meteorite—how remarkable was to be revealed by later research. The specimen had the black fusion crust produced by atmospheric ablation. A broken surface showed a dark gray interior densely spotted with chondrules (spherical aggregates of silicate minerals averaging 1 mm in diameter) and with larger white and pink aggregates (Figure 1). The dark gray matrix indicated that we had here a carbonaceous chondrite, a rare class of meteorite (some 30 in all, out of about 2000 known meteorites), but one of special significance for cosmochemistry, as this article will show.

We spent the next 5 days investigating the fall and collecting material for research and preservation. From this and subsequent visits to the area we showed that Allende is the largest recorded stony meteorite fall, both in its areal extent and in total weight of recovered meteorites. Thousands of stones were collected over an area exceeding 300 km^2 and extending some 50 km along the line of fall. At least 2 tons of material have been recovered, with individual stones ranging in weight from 1 g to one individual of 110 kg. This certainly represents only a modest fraction of the amount that fell—most of the meteorite probably still lies scattered through the dense scrub that covers much of this part of Mexico.

Information related to the fall and recovery was disseminated rapidly to interested scientists throughout the world by the Smithsonian Institution's Center for Short-Lived Phenomena. Distribution of samples began immediately on our return to Washington, and within a few weeks we had sent material to scientists in 37 laboratories in 13 countries. Several other scientific groups from institutions in Mexico, the United States, and Canada visited the area and obtained material for research. In view of the imminent prospect of lunar samples, many laboratories were tooled up for research on extraterrestrial material and welcomed the opportunity to work on this "manna from Heaven".

Chemical and Mineralogical Composition

It has been increasingly realized in recent years that carbonaceous chondrites probably approximate samples of the condensable fraction of primordial solar-system matter. This has led to intensive research on elemental and isotopic abundances in these meteorites. Unfortunately, they are few in number and the amounts recovered are small (prior to Allende). Our Allende collections enabled us to carry out a project we had long contemplated—the preparation of a large homogeneous meteorite sample, splits of which could be widely distributed for ana-

Brian Mason is Curator in the Division of Meteorites at the National Museum of Natural History, Smithsonian Institution, Washington, D.C. He is a native of New Zealand. He received the M.S. degree from the University of New Zealand, and returned there as Lecturer in Geology following receipt of the Ph.D. degree from the University of Stockholm in 1943. In 1947 he joined the faculty of Indiana University and in 1953 moved to New York, where he was Chairman of the Department of Mineralogy at the American Museum of Natural History and Professor of Mineralogy at Columbia University. He has been at the Smithsonian Institution since 1965, and has served as Chairman of the Department of Mineral Sciences.

Figure 1. Broken surface of the Allende meteorite showing large spherical Ca,Al-rich chondrules (white) and smaller irregular Ca,Al-rich aggregates in a dark gray fine-grained matrix; most of the small white spots in the matrix are olivine chondrules.

Table I
Elemental Abundances in the Allende Meteorite[a]

Li	2	Mo	2	Tl	0.06
Be	0.1	Ru	0.9	Pb	1.3
B	1	Rh		Bi	0.05
C	0.26%	Pd	1.6	Th	0.06
N	62	Ag		U	0.016
O	37.0%	Cd	0.6		
F	59	In	0.03		
Na	0.34%	Sn	1		
Mg	14.9%	Sb	0.08		
Al	1.74%	Te	1.1		
Si	16.0%	I			
P	0.11%	Cs	0.09		
S	2.10%	Ba	4		
Cl	220	La	0.51		
K	250	Ce	1.3		
Ca	1.85%	Pr	0.21		
Sc	11	Nd	0.97		
Ti	900	Sm	0.34		
V	90	Eu	0.11		
Cr	0.36%	Gd	0.42		
Mn	0.15%	Tb	0.08		
Fe	23.6%	Dy	0.42		
Co	610	Ho	0.11		
Ni	1.42%	Er	0.29		
Cu	130	Tm	0.06		
Zn	120	Yb	0.31		
Ga	6	Lu	0.05		
Ge	17	Hf	0.2		
As	3	Ta			
Se	9	W	0.2		
Br	1.5	Re	0.06		
Rb	1.3	Os	0.8		
Sr	14	Ir	0.8		
Y	3.1	Pt	1.5		
Zr	10	Au	0.15		
Nb	0.7	Hg	0.06		

[a] In ppm unless otherwise indicated; adequate data are lacking on Rh, Ag, I, and Ta.

lytical and other purposes. We ground up a 4-kg mass and divided it into 2-g and 5-g splits which have been provided to over 30 analytical laboratories. The results are still being received, but a preliminary compilation is given in Table I.

As can be seen, the bulk composition is dominated by O, Fe, Si, and Mg, which make up over 90% of the whole; these elements are present largely as olivine, $(Mg,Fe)_2SiO_4$. The validity of the concept of Allende as approximating the condensable fraction of primordial solar-system material is illustrated in Figure 2. This compares the solar and meteorite abundances for 19 elements, covering a wide range of abundance and of chemical properties. Most of these abundances are identical within a factor of 2, which, in view of the inherent uncertainty in the solar abundances derived from spectrographic analysis, must be considered highly significant.

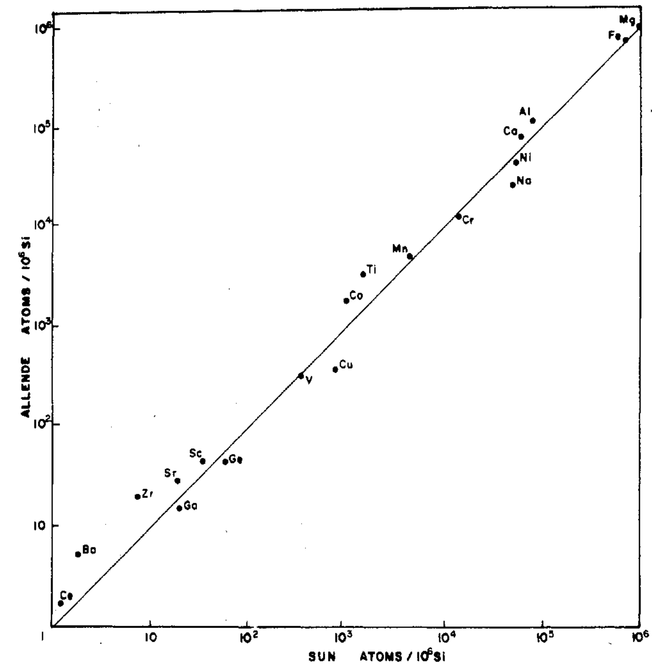

Figure 2. Plot (logarithmic scale) of elemental abundances in the Allende meteorite vs. solar abundances. The diagonal line represents equal abundances in the two materials.

Some comment should perhaps be made here on the carbon content. Allende has a relatively low carbon content (0.26%) for a carbonaceous chondrite, some of which contain 1% or more. Essentially all of the carbon in Allende is associated with the matrix material, being responsible for its dark gray color. Electron microscope examination of the matrix shows that it consists of micron-sized crystals of olivine which are evidently coated with a thin film of carbonaceous material; this material is not graphite, but probably consists of high-molecular-weight organic polymers. Work in other laboratories has yielded some indirect information on these carbon-containing compounds. Allende contains negligible quantities of solvent-extractable organic substances. Oró and Gelpi[1] have reported that direct volatilization or pyrolysis, or both, produces 10 to 20 ppm of a complex mixture of predominantly aromatic hydrocarbons, with smaller amounts of aliphatics and other compounds. Breger et al.[2] extracted formaldehyde from the meteorite by acid decomposition; they presume the formaldehyde is formed by the breakdown of paraformaldehyde. The carbonaceous material in Allende is evidence for the abiogenic synthesis of organic compounds in the primordial solar nebula.

(1) J. Oró and E. Gelpi, *Meteoritics*, 4, 287 (1969).
(2) I. A. Breger, P. Zubovic, J. C. Chandler, and R. S. Clarke, *Nature (London)*, 236, 155 (1972).

Table II
Minerals in the Allende Meteorite

Name	Formula	Matrix	Mg-rich chondrules	Ca, Al-rich chondrules	Ca, Al-rich aggregates
Kamacite	(Fe, Ni)		x		
Awaruite	$FeNi_3$	x	x		
Copper	Cu	x			
Troilite	FeS	x	x		
Pentlandite	$(Fe, Ni)_9S_8$	x	x		
Chromite	$FeCr_2O_4$	x			
Spinel	$MgAl_2O_4$			x	x
Hercynite[a]	$FeAl_2O_4$				x
Perovskite[a]	$CaTiO_3$			x	x
Hibonite[a]	$CaAl_{12}O_{19}$			x	
Olivine	$(Mg, Fe)_2SiO_4$	x	x	x	x
Enstatite	$MgSiO_3$				x
Clinoenstatite	$MgSiO_3$		x		
Clinohypersthene	$(Mg, Fe)SiO_3$	x			
Diopside	$CaMgSi_2O_6$			x	x
Fassaite[a]	$Ca(Mg, Al, Ti)(Al, Si)_2O_6$			x	x
Wollastonite[a]	$CaSiO_3$			x	
Anorthite	$CaAl_2Si_2O_8$			x	
Melilite	$Ca_2(Mg, Al)(Si, Al)_2O_7$			x	x
Grossular[a]	$Ca_3Al_2Si_3O_{12}$			x	x
Andradite[a]	$Ca_3Fe_2Si_3O_{12}$			x	
Rhønite[a]	$Ca_2Mg_3Ti_3Al_4Si_2O_{20}$			x	
Nepheline	$NaAlSiO_4$				x
Sodalite[a]	$Na_4Al_3Si_3O_{12}Cl$				x
Cordierite[a]	$Mg_2Al_4Si_5O_{18}$				x

[a] Mineral not previously found in meteorites.

While the bulk composition of Allende is similar to that of many other chondritic meteorites, its phase composition is remarkably diverse, including several minerals not previously found in meteorites (Table II). In our original description,[3] we commented on the unusually heterogeneous nature of Allende, and distinguished the following principal components: matrix, largely of Fe-rich olivine (~60%), Mg-rich chondrules (~30%), Ca,Al-rich chondrules (~5%), and Ca,Al-rich aggregates (~5%). Each of these has a rather distinctive mineralogy (Table II), although the Ca,Al-rich chondrules and aggregates have much in common. The investigation of these components has revealed a remarkable variety of chemical fractionations.

The Ca,Al-rich chondrules have attracted special attention, in part because of their giant size (up to 25 mm in diameter, compared to the average of about 1 mm in most chondrites) and unusual mineralogy. They consist mainly of melilite, pyroxene, and spinel, usually with some anorthite; the pyroxene, here referred to as fassaite, has a peculiar composition, being extremely rich in Ti and Al, and may be a new mineral.[4] The composition of this type of chondrule is similar to compositions studied by Prince[5] in the $CaO-MgO-Al_2O_3-SiO_2$ system. Using his diagram for the 10% MgO plane in this system, a melt of chondrule composition would begin to crystallize spinel at about 1550°C, followed by melilite at about 1400°C, anorthite at 1250°C, pyroxene at 1235°C.

The textural relations of these minerals in the chondrules are consistent with this sequence of crystallization. Small crystals of spinel are included within all the other minerals. Melilite is present as large prismatic crystals, suggesting crystallization over a considerable temperature interval, whereas the anorthite and pyroxene occur as small grains in the interstices of the melilite crystals and are evidently a late crystallization product. These chondrules must have been molten droplets at high temperature, and crystallized relatively slowly before being aggregated with the matrix.

Chemical fractionations within and between the different components of the Allende meteorite are most clearly demonstrated by the rare earth elements (REE), whose close correspondence in chemical properties and ionic size cause them to form a very coherent geochemical group. Gast et al.[6] analyzed one of these Ca,Al-rich chondrules and showed that it was enriched in the REE at about 14 times mean chondritic abundances, and had a slight positive Eu anomaly (20 times chondritic Eu abundance). We have confirmed this pattern in a total of ten of these chondrules.[7]

In order to explore this further, we separated the constituent melilite and pyroxene from one of these chondrules and analyzed them separately;[8] the results are shown in Figure 3. This shows that the relatively unfractionated pattern for the bulk composition comprises strongly fractionated patterns for the

(3) R. S. Clarke, E. Jarosewich, B. Mason, J. Nelen, M. Gómez, and J. R. Hyde, *Smithsonian Contr. Earth Sci.*, **5**, 1 (1970).
(4) B. Mason, *Am. Mineral.*, **59**, 1198 (1974).
(5) A. T. Prince, *J. Am. Ceram. Soc.*, **37**, 402 (1954).
(6) P. W. Gast, N. J. Hubbard, and H. Weismann, *Proc. Apollo 11 Lunar Sci. Conf.*, **2**, 1143 (1970).
(7) P. M. Martin and B. Mason, *Nature (London)*, **249**, 333 (1974).
(8) B. Mason and P. M. Martin, *Earth Planet. Sci. Lett.*, **22**, 1415 (1974).

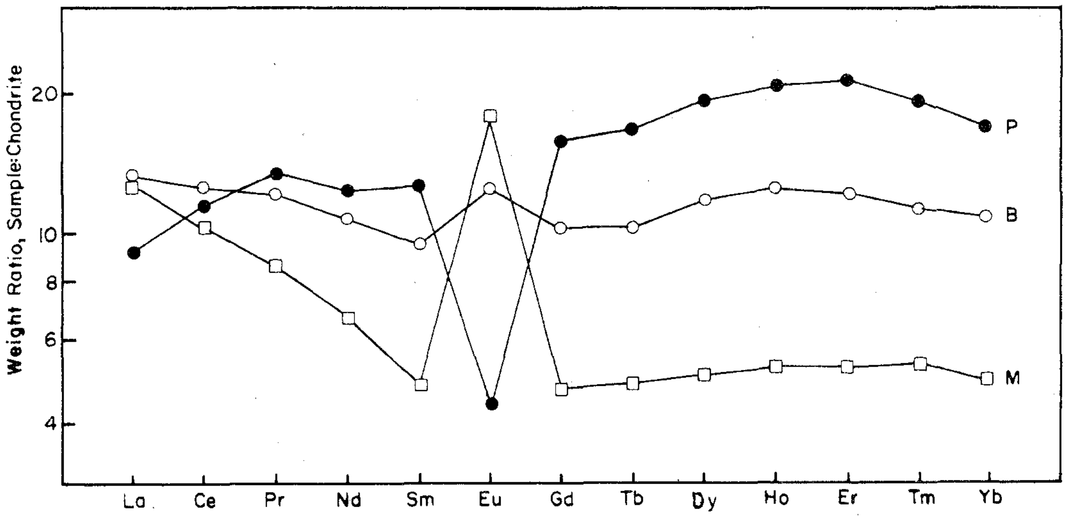

Figure 3. REE abundances, normalized to average chondritic abundances, in a Ca,Al-rich chondrule (B) and its constituent melilite (M) and pyroxene (P) (see ref 8).

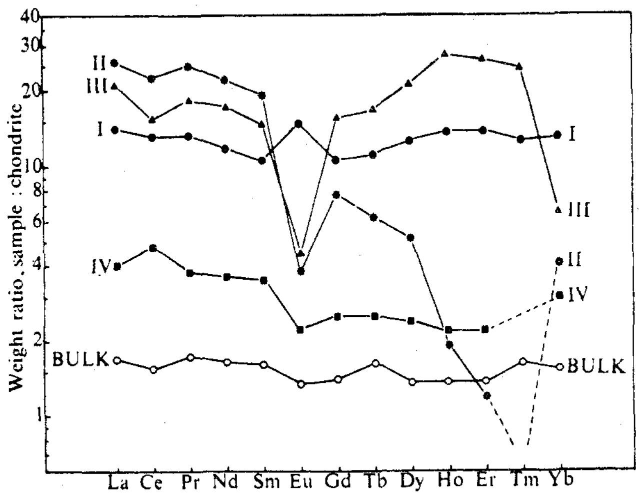

Figure 4. REE abundances, normalized to average chondritic abundances, for components of the Allende meteorite; I = Ca,Al-rich chondrules, II and III = Ca,Al-rich aggregates, IV = olivine chondrules (see ref 7).

constituent minerals. Of particular significance is the Eu distribution—pyroxene shows a strong depletion whereas melilite has a marked enrichment, relative to the other REE. Europium is almost certainly present as the Eu^{2+} ion, reflecting crystallization of the chondrule under highly reducing conditions. The Eu^{2+} ion has a radius close to that of Sr^{2+}; the geochemical coherence of Eu and Sr in this chondrule is illustrated by the relative uniformity of the Sr/Eu ratio: 120 in the melilite, 89 in the pyroxene, and 120 in the bulk chondrule.

The distribution of the remaining REE, which are in the trivalent state, shows a close correlation with relative ionic size. Pyroxene shows a higher concentration than melilite for the individual REE, except La, which has the largest ionic radius. The relative enrichment in pyroxene increases with increasing atomic number and decreasing ionic radius. Evidently under the conditions of crystallization the trivalent REE (except La) were more readily accommodated in the smaller Ca sites of pyroxene than in the larger Ca sites of melilite.

When we extended this research on the REE distribution in the Ca,Al-rich chondrules to the Ca,Al-rich aggregates, the results were surprising.[7] Despite an overall similarity in mineralogy and major-element chemistry, the REE distribution in the aggregates was quite distinct; two different groups have been recognized, each with a characteristic fractionation pattern. These have been designated group II and group III; group I comprises the Ca,Al-rich chondrules and group IV the olivine chondrules (Figure 4).

Group II aggregates exhibit remarkable REE abundance patterns. Although the light REE (La–Sm) show similar abundances in groups I, II, and III, group II aggregates have rapidly diminishing abundances of the heavier REE, superimposed on which are a marked negative Eu anomaly and a large positive Yb anomaly. Tanaka and Masuda[9] have described an Allende aggregate with a group II REE pattern. Group III have relatively unfractionated REE distribution patterns with concentrations at about 25 times average chondritic abundances, but with marked negative anomalies for both Eu and Yb. Group IV olivine chondrules have a relatively unfractionated REE distribution averaging three times chondritic abundances.

Europium anomalies have been observed not only in meteorites but also in lunar and terrestrial rocks, and have a ready explanation in terms of the formation and stability of the Eu^{2+} ion. However, to my knowledge, a Yb anomaly has not previously been found in geological materials. At first glance the behavior of Yb in the Allende aggregates is erratic, with a positive anomaly in Group II and a negative anomaly in Group III. However, the Eu/Yb ratios are essentially identical in these two groups, as can be seen in Figure 4.

The Yb anomalies are in different senses in the two groups simply because they are superimposed on very different REE distribution patterns. Thus in these two groups, Eu and Yb show a geochemical coherence unrelated to the other REE. After Eu, Yb is the REE most readily reduced to the divalent state, and this provides a possible explanation for this coherence. However, this explanation requires highly reducing conditions at some stage in the origin of group II and III materials, more reducing, for exam-

(9) T. Tanaka and A. Masuda, *Icarus*, 19, 523 (1973).

ple, than for lunar rocks, which show Eu anomalies but do not have Yb anomalies. In this connection, too, it is puzzling to find no Yb anomalies either in group I materials or in their constituent minerals (Figure 3).

Boynton[10] comments that it seems unlikely that divalent Yb can explain the Yb anomalies, since Sm is nearly as easily reduced as Yb and there is no evidence of an Sm anomaly. He points out that the condensation of REE from the solar nebula may be controlled by thermodynamic equilibrium between gas and condensed solids, and that highly fractionated REE patterns may result if condensates are removed from the gas before condensation is complete. Both Yb and Eu are predicted to be extremely depleted in the early condensate without the requirement of condensation in the divalent state. According to Boynton's model, the group II inclusions may be a condensate from a previously fractionated gas rather than from a gas of solar composition. Thus the cosmochemical properties of Eu and Yb (determined by gas–solid equilibria) may be quite different from crystallochemical properties (determined by liquid–solid and solid–solid equilibria), and may allow an unambiguous determination of which process is yielding a specific REE pattern.

The significance of the Ca,Al-rich chondrules and aggregates in the Allende meteorite has been the subject of extensive discussion. Marvin et al.,[11] who published the first description of these materials, pointed out the general similarity between their chemistry and mineralogy and the sequence of compounds calculated to be among the highest temperature condensates to form in a cooling solar nebula. They comment: "It is difficult to conceive of any origin other than high-temperature condensation for the Ca,Al-rich bodies, and equally difficult to conceive of mineral assemblages reproducing much more faithfully this predicted composition. If these bodies are condensates, they probably represent some of the most primitive matter preserved in the solar system."

Isotopic studies, discussed in the following section, support this hypothesis, at least for group I chondrules. However, other investigators, for example Wasson,[12] have argued that these chondrules are residues rather than condensates, being the refractory material remaining after selective volatilization of a prior condensate. A comprehensive review has recently been published by Grossman and Larimer.[13]

It is certainly true that if the Ca,Al-rich chondrules are derived from primordial high-temperature condensates, then the process must have been a complex one, involving separation of solid particles from a gaseous medium, aggregation, melting, and recrystallization. The fact that we can distinguish three groups of Ca,Al-rich materials with dissimilar REE distributions suggests that they may have formed by different processes or have been subjected to varying geochemical environments before final incorporation in the parent meteorite body. In this connection, Arrhenius and Alfvén[14] have pointed out that if primary condensation occurred in an ionized plasma, the formation of Ca,Al-rich refractory compounds might be expected to occur relatively late, nearer the end of the condensation sequence. The group II aggregates have textural and mineralogical features (fine grain size, presence of grossular and sodalite) suggestive of relatively low formation temperatures (<800°C); their highly fractionated REE distribution may also be the result of condensation at a late stage, after extensive geochemical differentiation.

(10) W. V. Boynton, *Geochim. Cosmochim. Acta*, **39**, in press.
(11) U. B. Marvin, J. A. Wood, and J. S. Dickey, *Earth Planet. Sci. Lett.*, **7**, 346 (1970).
(12) J. T. Wasson, *Eos*, **54**, 1125 (1973).
(13) L. Grossman and J. W. Larimer, *Rev. Geophys. Space Phys.*, **12**, 71 (1974).

Isotopic Studies

Isotopic studies on meteorites have been extensively employed to date specific events in their history. A specific event is defined by the particular age equation of the method and by the chemical and physical properties of the parent and daughter elements on which the method is based. Thus events such as nucleosynthesis, general chemical separation processes, mineral formation, subsequent heating and/or chemical alteration, and the breakup of a possible parent body may each be recorded by specific nuclear reactions and radioactive disintegrations. Allende, with its diverse components, has proved a particularly rewarding object for these studies.

Strontium is an element of special interest in this regard. Natural strontium consists of four isotopes, of which one, ^{87}Sr, can be radiogenic, produced by the β decay of ^{87}Rb. Hence the ratio of ^{87}Sr to one of the nonradiogenic isotopes (usually ^{86}Sr) varies in rocks and minerals, depending upon their source. In seawater (used as a standard) the ^{87}Sr/^{86}Sr ratio is 0.70909; in basalts from different regions this ratio ranges from 0.702 to 0.712, while in rocks richer in alkalies, such as granites, the ratio can be considerably higher. Much research has been done in recent years to establish the primordial ^{87}Sr/^{86}Sr ratio, i.e., the ratio established by nucleosynthesis, prior to the addition of any radiogenic ^{87}Sr.

Allende, with its variety of components, has provided information of fundamental importance. Melilite from the Ca,Al-rich chondrules is unique in having high Sr (100–500 ppm) and very low Rb (as little as 0.01 ppm, which thus can have contributed negligible ^{87}Sr); this Sr has the lowest ^{87}Sr/^{86}Sr ratio ever found, 0.69877, and is interpreted as a primitive condensate from the solar nebula.[15] The time of condensation was 4.6×10^9 years ago. Other components of the meteorite show higher ^{87}Sr/^{6}Sr ratios, due to the addition of radiogenic ^{87}Sr; thus for samples of the total meteorite, this ratio is about 0.713, and in some of the Ca,Al-rich aggregates (which contain up to 12 ppm Rb) this ratio may reach 0.784. Gray et al.[15] comment, "while total rock samples and several chondrules give a model age of ~4.6 ae (1 ae = 10^9 years), the data from a wide variety of phases do not define an isochron and show that this meteorite was subject to metamorphism or alteration in the past 3.6 ae, possibly recently. The major enrichment of alkalies and other volatiles in the "re-

(14) G. Arrhenius and H. Alfvén, *Earth Planet. Sci. Lett.*, **10**, 253 (1971).
(15) C. M. Gray, D. A. Papanastassiou, and G. J. Wasserburg, *Icarus*, **20**, 213 (1973).

fractory" aggregates must have taken place at ~4.5 ae ago. The late alteration could have taken place recently within a cometary nucleus." The strontium isotopic composition thus provides a significant amount of information concerning the geochemical processes operating during the early history of the solar system.

Intriguing anomalies have been found in the oxygen isotopic composition of Allende components. Clayton et al.[16] have found that the Ca,Al-rich chondrules and aggregates are strongly depleted in ^{17}O and ^{18}O; other carbonaceous chondrites also show this feature. These meteorites have lower $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios than all other meteorites studied. The depletion pattern is one in which ^{17}O and ^{18}O are equally depleted, whereas chemical processes that produce a 1% increase or decrease in the $^{17}O/^{16}O$ ratio produce a 2% increase or decrease in the $^{18}O/^{16}O$ ratio (since chemical isotope effects are almost linearly proportional to the relative mass difference of the isotopes). This indicates that the depletion pattern is the result of nuclear rather than chemical processes; Clayton et al. interpret it as resulting from the admixture of a component of almost pure ^{16}O. They suggest that this component may predate the solar system and may represent interstellar dust with a separate history of nucleosynthesis.

Allende has also proved to be a rewarding object for the investigation of short-lived radioisotopes, such as ^{129}I (half-life 1.6×10^7 years) and ^{244}Pu (half-life 8.2×10^7 years). These radioisotopes were presumably formed during nucleosynthesis but have long since disappeared; however, if condensation occurred soon after nucleosynthesis, then their original presence may be deduced from observation of their daughter products. For ^{129}I the daughter product is ^{129}Xe; the spontaneous fission of ^{244}Pu produces a variety of daughter products, the most easily recognized being ^{132}Xe. Fireman et al.[17] found the ^{129}Xe excess in Allende chondrules exceptionally high; two troilite-bearing chondrules had a $^{129}Xe/^{132}Xe$ ratio of 92, which is the highest ever recorded. The short half-life of ^{129}I is critical in identifying early solar system condensates and the formation of "cold" or gas-retentive objects such as the parent body of the Allende meteorite. The interval between the cessation of nucleosynthesis and the onset of xenon retention in the meteorite parent body is of the order of 60 million years.

Podosek and Lewis[18] infer an original $^{244}Pu/^{238}U$ ratio of 0.087 from the isotopic composition of fissiogenic Xe (a mixture of spontaneous fission of ^{244}Pu and neutron-induced fission of ^{235}U) in the Allende Ca,Al-rich inclusions. This ratio is by far the highest yet observed in any meteorite and could be interpreted as implying extremely early formation of these inclusions, roughly about the time that the solar nebula is believed to have been isolated from galactic nucleosynthesis. However, this would require no chemical fractionation between Pu and U, and this requirement may not have been satisfied, especially in view of the observed REE fractionations. Podosek and Lewis conclude that the various constituents of the Allende meteorite contain records of a complex early history which have not been destroyed by subsequent metamorphism.

The evidence for the original presence of ^{244}Pu in unusually large amounts naturally creates interest in the possibility of detecting other transuranium elements, and specifically the supereavy elements with $Z = 110$–114. Flerov[19] has searched for superheavy elements in several meteorites, including Allende, by looking for fission-produced neutrons in samples carefully shielded from extraneous sources (the shielding being provided by doing the experiments at a depth of 1100 m in a salt mine). In all cases the counting rate was very low, but it definitely exceeded the known sources of background. Dr. Flerov recently obtained a considerable amount of the Allende meteorite from us, with a view to chemical processing and separation of enriched fractions of the elements sought.

Allende and the Moon

Analyses of lunar samples have provided many geochemical surprises. Not the least of these was the high titanium content (averaging 12% TiO_2) of the basalts returned by the Apollo 11 mission (and by the Apollo 17 mission). Terrestrial basalts average 2% TiO_2, and very few contain as much as 5%. Meteorites contain comparatively little titanium; the commonest class, the chondrites, average 0.11% TiO_2, and the highest figure is 2.2% TiO_2 in the unique achondrite, Angra dos Reis. Chemical studies of the Apollo 11 and Apollo 17 basalts show that Ti is positively correlated not with any of the major elements but with refractory trace elements such as Ba, Zr, Hf, Nb, and the REE.

The Allende meteorite has a TiO_2 content (0.14%) only slightly higher than the average chondrite. However, titanium is notably enriched in the Ca,Al-rich chondrules; we have analyzed ten of them, and their TiO_2 content ranges from 1.0 to 1.5% TiO_2. Microprobe analyses show that the principal host mineral for the Ti is the pyroxene, spinel containing only minor amounts of this element and melilite being essentially Ti-free. The pyroxene in the Allende chondrules has a unique composition, quite different from any terrestrial pyroxene.[4] Microprobe analyses show a considerable composition range, from chondrule to chondrule, in individual chondrules, and within single grains. The ranges measured (weight percent) are: SiO_2 31–43, Al_2O_3 14–23, TiO_2 3–18, MgO 5–12, CaO 24–26; FeO and Na_2O are uniformly low, <0.1. The most variable component is TiO_2, which shows an approximately inverse relation with SiO_2.

Figure 3 gave a plot of REE distribution in a separated pyroxene. This plot is repeated in Figure 5 with the addition of data on Ti, Ba, Sr, Y, Zr, Hf, and Nb. These data were obtained by spark source mass spectrography, with the exception of Ti (microprobe analysis). Figure 5 compares the pyroxene data with those for basalt 10003 from the Apollo 11 mission; other basalts from that and the Apollo 17

(16) R. N. Clayton, L. Grossman, and T. K. Mayeda, *Science*, 182, 485 (1973).
(17) E. L. Fireman, J. DeFelice, and E. Norton, *Geochim. Cosmochim. Acta*, 34, 873 (1970).
(18) F. A. Podosek and R. S. Lewis, *Earth Planet. Sci. Lett.*, 15, 101 (1972).
(19) G. N. Flerov, in press (1974).

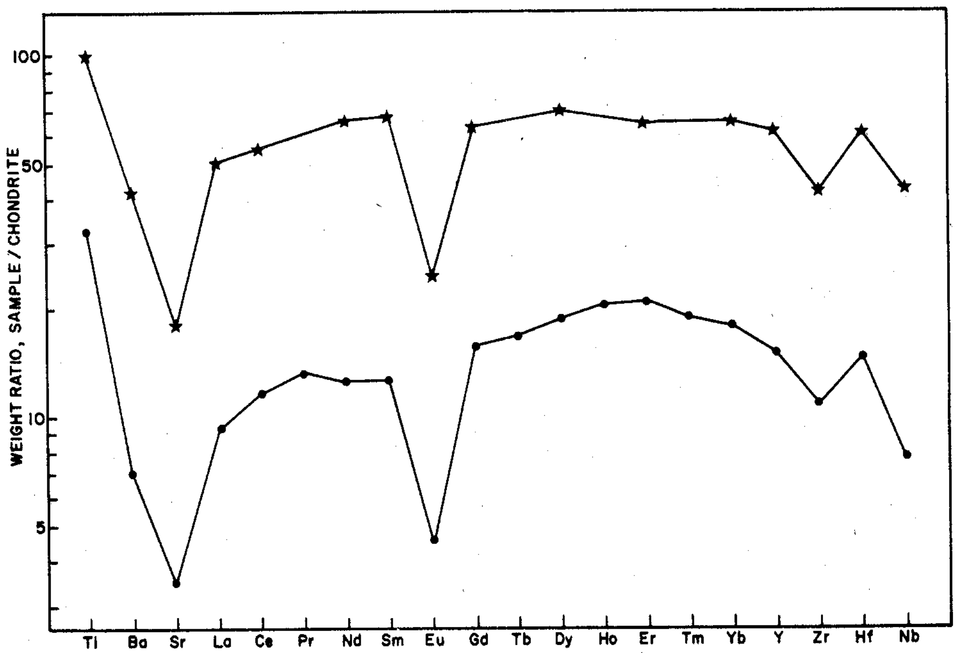

Figure 5. Chondrite-normalized elemental abundances for Apollo 11 basalt 10003 (upper curve) and Allende pyroxene (lower curve).

Table III
Age and Average TiO_2 Content of Lunar Basalts

Mission	Age ($\times 10^9$ years)	TiO_2 (wt %)
Apollo 11	3.7	12.2
Apollo 17	3.7	12.1
Luna 16	3.4	4.9
Apollo 12	3.2	3.2
Apollo 15	3.2	2.2

mission show closely similar element distribution patterns. The two distribution patterns have a truly remarkable parallelism for a total of 20 elements. Of particular significance is the marked negative Eu anomaly in both materials. The Allende pyroxene analyzed had a relatively low Ti content (3.9% TiO_2); other Allende pyroxenes, with higher TiO_2, would probably give parallel trace element distribution patterns even closer to that of 10003 (which contains 11.5% TiO_2).

The possible connection between the Allende pyroxenes and the high-Ti lunar basalts is fortified by evidence from phase relations at liquidus temperatures in the system CaO-MgO-Al_2O_3-TiO_2-SiO_2[20]. At compositions comparable to those for the Allende Ca,Al-rich chondrules, pyroxene is the only phase containing appreciable Ti, and is the final phase to begin crystallizing on cooling a melt, at about 1250°C. The textural relations of the Allende chondrules, with the pyroxene occupying the interstices between the earlier crystallized melilite and spinel, are consistent with the laboratory evidence. Therefore, if the Moon aggregated from solid material similar to that making up the Allende meteorite, and if this material were subsequently heated, the initial melt would incorporate much of this pyroxene, thereby partitioning most of the Ti and refractory trace elements into the liquid phase. Further melting, with the incorporation of melilite, olivine, and spinel, would result in dilution of the Ti and trace elements and the diminution of the negative Eu anomaly (since melilite has a strong positive Eu anomaly). This would give Ti and trace element concentrations characteristic of the younger basalts collected on the Apollo 12 and 15 and Luna 16 missions.

The age-sequence of the lunar basalts and their Ti content appear to be interrelated (Table III), although the number of sample locations is inadequate for categorical statements. Titanium contents are relatively uniform for all basalts from each lunar site, and possibly for all lunar basalts of similar age. Thus Apollo 11 and 17 basalts are similar in age and composition, although separated by over 600 km on the lunar surface; and Apollo 12 and 15 basalts have a comparable relation, although separated by about 1000 km. It thus appears that the Ti content of the lunar basalts is age-controlled rather than spatially controlled.

Further evidence favoring the origin of lunar basalts by the partial melting of material with composition similar to that of the Allende pyroxene comes from a consideration of the Rb–Sr isotopic data. An $^{87}Sr/^{86}Sr$ vs. $^{87}Rb/^{86}Sr$ plot of lunar basalts can be extrapolated to give the initial $^{87}Sr/^{86}Sr$ ratios, i.e., those of the source materials. These initial ratios all lie in a narrow range close to 0.6988, the primordial value for this ratio as found in Allende. Hurley and Pinson[21] deduce that the source material of the Apollo 11 basalts had a Rb/Sr ratio not greater than 0.006 ± 0.004, about one-fifth that of average Earth and one-fortieth that of average chondrites. In the analyzed Allende pyroxene, Rb is 0.07 ppm and Sr 30 ppm, giving a Rb/Sr ratio of 0.002. Material from the Allende Ca,Al-rich chondrules has the lowest $^{87}Sr/^{86}Sr$ ratios yet found, indicating that it is a primitive condensate from the solar nebula unmodified by the addition of radiogenic strontium. A magma derived in large part from such material

(20) A. Muan and E. F. Osborn, "Phase Equilibria among Oxides in Steelmaking", Addison-Wesley, Reading, Mass., 1965.

(21) P. M. Hurley and W. H. Pinson, *Proc. Apollo 11 Lunar Sci. Conf.*, 2, 1311 (1970).

would provide the characteristic Rb/Sr isochrons of the lunar basalts.

The origin of the lunar basalts was certainly more complex than the melting of material similar to the Allende pyroxene. In order to produce the Fe/Mg ratios of the lunar basalts the pyroxene would have to contain considerable iron, or iron would have to be introduced from another phase. The iron-rich olivine of the Allende matrix would satisfy this requirement. Several groups of investigators have proposed model Moons based on varying proportions of primitive condensates similar to the materials of the Allende meteorite. Ganapathy and Anders[22] have a compositional model incorporating six components, of which early condensate (similar to the Allende Ca,Al-rich chondrules) comprises 23.5% and remelted silicate (largely olivine) comprises 63.4% and thus provide the major part. Wänke et al.[23] propose a model with 60% HTC (high-temperature component, equated with Allende chondrules) and 40% ChC (chondritic component, largely olivine and pyroxene).

These ideas have a considerable bearing on a major controversy regarding lunar basalts, as to whether they originated by partial melting of an initial solid or represent residual liquids from an extensive sequence of fractional crystallization. Ringwood and Green[24] have strongly supported the partial melting hypothesis, and interpret the available data to indicate that Apollo 11 and 17 basalts represent 2–5% partial melts, Apollo 12 basalts 10–15%, and Apollo 15 basalts 10–20%. O'Hara et al.[25] have argued that the Ti-rich basalts represent residual liquids remaining after the fractional crystallization of anorthite-bearing cumulates. The hypothesis of partial melting, to an increasing degree in going from Apollo 11 and 17 to the Apollo 12 and 15 basalts, is consistent with the proposition that material similar to that of the Allende pyroxene provided the initial melt. The progressive decrease in Ti and other refractory elements, and in the Eu anomaly, is understandable in terms of progressive dilution of an initial liquid enriched in these elements and with a marked negative Eu anomaly. The relationship between age and composition of the lunar basalts agrees with this sequence, whereas progressive fractional crystallization should result in enhanced content of Ti and trace elements in the later, i.e. younger, lunar basalts.

Conclusions

It is worth more than a casual remark to point out the influence of chance events on scientific advances, as exemplified by the fall of the Allende meteorite. This unpredictable event provided a large supply of a unique research material, at a propitious time—when a large number of laboratories and scientists were geared up to investigate the first planned acquisition of extraterrestrial matter. A fruitful cooperation was immediately established, and concurrent investigations of the Allende meteorite and lunar material have provided comparative studies which yielded significant correlations of wide-ranging importance for the science of cosmochemistry.

Some years ago, Edward Anders of the University of Chicago aptly described meteorites as the poor man's space probe—extraterrestrial material, arriving cost-free from outer space, and carrying within it a history, albeit imperfectly preserved and difficult to decipher, of events in the universe over the past five billion years. Allende is the epitome of this description. Its bulk composition corresponds very well with elemental abundances in the sun, and it thus approximates a good average sample of the nonvolatile material of the solar system.

Nevertheless, it is a very heterogeneous object, containing components of markedly differing chemical composition—certainly a nonequilibrium mixture of materials formed under a wide range of physicochemical conditions. Some components, specifically the Ca,Al-rich chondrules, appear to be high-temperature condensates, and their $^{87}Sr/^{86}Sr$ ratio shows that they crystallized at least 4.6 billion years ago and are thus among the oldest materials of the solar system. The Mg-rich chondrules, the Ca,Al-rich aggregates, and the matrix must each record significantly different condensation events, separated in space and possibly in time.

The carbonaceous material, coating the minute crystals of the matrix, is another piece in this jigsaw puzzle. How did these contrasting materials, providing such a rich mine of information regarding conditions in the primitive solar nebula, aggregate into a single body, an asteroid or possibly a cometary core? In spite of the large amount of research already carried out on this meteorite, we have only begun to answer some of the fundamental questions it poses. Like the Rosetta Stone for Egyptology, it is probably the key to deciphering many of the fundamental questions concerning the physicochemical evolution of the solar system, and just as the analysis and decipherment of the Rosetta Stone took many years, so too will the full elucidation of the Allende meteorite.[26]

I wish to thank all of my collaborators in the work described here, especially Mr. R. S. Clarke, Jr., Mr. E. Jarosewich, and Mr. J. Nelen of the Smithsonian Institution. The work on the trace element distributions was carried out at the Australian National University with the analytical facilities of the Research School of Earth Sciences, by the courtesy of Dr. S. R. Taylor. These researches have been supported by grants from the National Aeronautics and Space Administration (NGR 09-015-170) and the Smithsonian Research Foundation.

(22) R. Ganapathy and E. Anders, *Lunar Sci.*, 5, 254 (1974).
(23) H. Wänke, H. Palme, H. Baddenhousen, G. Dreibus, E. Jagoutz, H. Cruse, B. Spettel, and F. Teschke, *Lunar Sci.*, 5, 820 (1974).
(24) A. E. Ringwood and D. H. Green, *Lunar Sci.*, 5, 636 (1974).
(25) M. J. O'Hara, G. M. Biggar, D. J. Humphries, and P. Saha, *Lunar Sci.*, 5, 571 (1974).

(26) For a more extended account of the research fields touched on in this Account reference may be made to "Meteorites and the Origin of Planets", by J. A. Wood (McGraw-Hill, New York, N.Y., 1968), and "Lunar Science: a Post-Apollo view", by S. R. Taylor (Pergamon Press, New York, N.Y., 1975).