

AN ABSTRACT OF THE THESIS OF

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Title: THE CHEMICAL COMPOSITION OF 61 INDIVIDUAL

ALLENDE CHONDRULES

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The abundances of 12 elements, Fe, Al, Na, Ni, Cr, Mn, Co, Ca, Sc, Ir, Sm and Eu have been determined by INAA in 61 individual chondrules (0.1-100 mg) separated from five Allende (C3) meteoritic fragments (25g). Ti and V have been determined in 18 of these chondrules, and Au in several others.

Average abundances of Al, Na, Sc, Sm and Eu are decidedly higher in chondrules compared to the matrix. The enrichments are (average % in chondrules/average % in bulk): Al, 2.6-3.4/1.6; Na, 0.61-0.74/0.33; Sc, 20.2-21.5/11.0; and Sm, 0.50-0.61/0.29. Determinations of Eu abundances are incomplete at this time. Abundances for Sc and Sm are in ppm. Cr and Ir abundances appear to be about the same in both chondrules and matrix; the corresponding abundances are: Cr, 0.43-0.44/0.38; and Ir, 0.59-0.60 ppm/0.71 ppm. Mn, 0.11-0.14/0.17 is slightly depleted and

Fe, (9.9-10.3/26.6); Ni, (0.64-0.82)/1.53 and Co, (260-330) ppm/640 ppm are markedly depleted. The low Fe content of chondrules is consistent with a much lower  $\text{Fe}^{2+}$  content of the olivine in chondrules relative to the matrix. The range of averages for chondrules given above represents average abundances by the normal average value and by mass weighted average value; in each case the mass weighted average was the largest. Since there is a definite mass-abundance correlation in the selected chondrules and larger chondrules were preferred in the selection process, the averages calculated by both methods represent reasonable upper and lower limits on the abundances found in chondrules.

The above averages conceal the tremendous variation in abundances among the individual chondrules. Ranges observed are: % Al, 0.44-17.3; % Fe, 0.37-17.7; % Na, 0.11-2.04; % Cr, 0.02-1.15; % Ni, 0.065-2.24; % Ca, 0.45-19.7; % Ti, 0.07-1.25; ppm V, 81-974; ppm Co, 7.6-877; ppm Ir, 0.035-5.8; ppm Mn, 240-3820; ppm Sc, 5.6-133; ppm Sm, .04-3.4. Abundances of Ni, Ir and Sm in some chondrules were depleted beyond detection and below the lower values indicated above. The ranges for Ti and V are for only 18 samples.

Despite a bewildering array of compositions and a large variation in abundances, the elements Ni and Co exhibit a remarkable correlation of abundances, yielding a correlation coefficient of about

unity. The resulting Ni/Co abundance ratio is 22.6, fairly close to the ratio of 21 found in fine octahedrites.

In 7 of the 8 chondrules for which Eu has been determined at this time, the Sm/Eu ratios are closely scattered, within statistical error, about a mean of 2.6 (one exhibits a ratio of  $5.0 \pm 1.8$ ). The average ratio of 2.7 agrees with the ratio found for the bulk Allende, as well as that for ordinary chondrites, both 2.7. Two explanations of the constancy of the Sm/Eu ratio in the face of such drastic elemental fractionations among the chondrules are possible. Either a magmatic differentiation process could have occurred under oxidizing conditions, and all Eu was present as trivalent Eu or the accretion of the chondrules was very rapid, volatile constituents were lost, and no magmatic differentiation occurred.

Only slight correlations among Na and Al, as well as Na and Ca are found, indicating a much more complex relationship among these elements than would be encountered with a simple plagioclase mineral system. Much of the sodium in chondrules is known to occur in the mineral nephilite, as well as sodalite. The albite content of the plagioclase in these chondrules is generally very small (Ab<sub>5</sub> being typical). Calcium is present largely in gehlenite, anorthite, and fassaite (augite with high Ti).

The Chemical Composition of 61 Individual  
Allende Chondrules

by

Richard Gregory Warren

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This work is dedicated to the cause of international peace and

friendship in hopes that as our knowledge of the world around us increases, we will learn that material things, like knowledge, are best shared with others.

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# THE CHEMICAL COMPOSITION OF 61 INDIVIDUAL ALLENDE CHONDRULES

## I. INTRODUCTION

### Meteorites: Characteristics and Classification

Three general types of meteorites have been recovered on earth after a fall; irons (siderites), stones (aerolites), and stony irons (siderolites). As the names imply, these classes represent meteorites chemically composed mainly of metal, silicate, and a mixture of both, respectively.

By far the most abundant type of meteorite, judging from the relative number of falls recovered (92% according to Mason (1962)), is the stone meteorite. The stone meteorites are classified into two chemically different groups, the chondrites and achondrites. Furthermore, chondrites are generally easily recognizable by the presence of spherical inclusions, typically 1 mm in diameter, known as chondrules. The presence of chondrules is a function of petrologic type. Type 1 chondrites contain no chondrules, while those in type 6 chondrites are very poorly defined, seemingly originally being present, later to be destroyed by metamorphism. The chondrules of type 2 and 3 chondrites are the most strikingly defined. Chondrules are a petrological feature unknown in terrestrial material, but spherules resembling chondrules have been found in lunar soil and breccia by

Fredriksson et al. (1970). These lunar "chondrules" are most likely produced from lunar material during meteoritic impact.

The real importance of accurate and thorough determination of the chemical and mineralogical composition of chondrites is due to close similarities of relative chemical abundances found in these meteorites and the relative abundances of the nonvolatile elements determined in the sun. Age dating of meteorites also provides evidence that chondrites represent matter "left over" from the condensation of the protosun (Mason, 1962). Thus knowledge of the processes of formation of chondritic matter may shed some light on processes such as the formation of our own planet.

The carbonaceous chondrites contain the solar abundances of the more volatile elements Ag, Pb, Bi, In, and Tl. Quite possibly the CI chondrites, containing the largest abundances of these elements, are the most primitive and undifferentiated matter available in the solar system (Anders, 1971).

Chondrites are classified by Van Schmus and Wood (1967) according to chemical and petrological differences into a 5 x 6 grid. The principal chemical differences that distinguish the classes of enstatite (E), carbonaceous (C), bronzite (H), hypersthene 'L), and amphoteric (LL) chondrites are:

1. The total Fe/SiO<sub>2</sub> weight ratio
2. The SiO<sub>2</sub>/MgO weight ratio

Petrologic type

	1	2	3	4	5	6
E	*	*			Enstatite Chondrites	
C	Carbonaceous Chondrites			C4	*	*
H	*	*	H3	#	Bronzite Chondrites	
L	*	*	L3	#	Hyperstene Chondrites	
LL	*	*	LL3	#	Amphoteric Chondrites	

+

+

\* unpopulated

+ ordinary chondrites

# unequilibrated ordinary chondrites

Figure 1. Proper names for chondrites.

3. The  $\text{FeO}/(\text{FeO} + \text{MgO})$  molecular ratio in the olivine  
and pyroxene

4. The metallic Fe/total Fe ratio

The petrologic grades 1-6 are established on the basis of mineral sizes and composition. For example, the Bjurböle chondrite, by chemical analysis a hypersthene chondrite and by petrographic analysis a grade 4 is designated a L4 chondrite.

For a more comprehensive discussion of meteorites, Mason (1962) or Osborn (1968) should be consulted.

The Allende Meteorite

About a ton of this meteorite has been recovered since its spectacular fall in the state of Chihuahua, Mexico, on February 8, 1969. The chemical analyses of the bulk meteorite by Clark *et al.* (1970) and others are shown in Tables 1 and 2. From these chemical and petrological studies, Allende has been classified as a type 3 carbonaceous chondrite (C3). According to Van Schmus and Wood (1967) the major criteria for inclusion in petrologic grade 3 are large variability of olivine and pyroxene composition, presence of igneous glass in chondrules, well defined chondrules and chondritic texture, absence ( $< 0.5\%$ ) of Ni from sulfide phases, more clinopyroxene relative to orthopyroxene, and significant carbon content (0.2-1.0%). All the above conditions are found in the Allende meteorite, with the single

Table 1. Analytical data on the Allende meteorite (wt %) by Clarke *et al.* (1970).

	Bulk	Dark Inclusion	Matrix	Chondrules	Chondrule (Type a)	Chondrule (Type c)	Single Aggregate
$\text{SiO}_2$	34.23	33.42	33.11	41.87	29.79	40.2	33.7
$\text{TiO}_2$	0.15	0.13	0.13	0.26	0.99	0.12	1.3
$\text{Al}_2\text{O}_3$	3.27	2.56	3.07	5.57	31.61	17.8	26.6
$\text{Cr}_2\text{O}_3$	0.52	0.56	0.55	0.47	0.06	0.2	0.1
FeO	27.15	31.48	29.68	9.44	0.37	8.8	2.3
MnO	0.18	0.26	0.22	0.14	0.02	0.1	0.0
MgO	24.62	23.91	21.42	34.34	10.82	15.2	13.1
CaO	2.61	3.00	2.67	4.06	26.76	5.3	21.6
$\text{Na}_2\text{O}$	0.45	0.34	0.44	0.82	0.11	10.6	1.1
$\text{K}_2\text{O}$	0.03	< 0.01	0.03	0.06	0.00	0.6	0.05
$\text{P}_2\text{O}_5$	0.23	0.31	0.25	0.11	0.00	n. d.	0.0
$\text{H}_2\text{O}(+)$	< 0.1	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
$\text{H}_2\text{O}(-)$	0.00	0.00	0.00	0.00	0.00	n. d.	n. d.
C	0.29	0.37	0.36	0.00	0.06	0.02	n. d.
Cl	0.022	n. d.	n. d.	n. d.	n. d.	1.5	n. d.
FeS	4.03	1.95	5.49	1.78	0.00	n. d.	n. d.
NiS	1.60	2.26	1.05	0.87	0.00	n. d.	n. d.
CoS	0.08	0.06	0.09	0.03	n. d.	n. d.	n. d.
Fe	0.17	n. d.	0.40	n. d.	n. d.	n. d.	n. d.
Ni	0.36	n. d.	0.85	n. d.	0.03	0.05	0.06
Co	0.01	n. d.	0.02	n. d.	n. d.	n. d.	n. d.
Total	99.98	100.61	99.83	99.82	100.62	100.6	99.9
Total Fe	23.85	25.71	26.56	8.47	0.29	6.82	1.76
$\frac{100 \text{ FeO}}{\text{FeO} + \text{MgO}}$	38	42	44	13	2	25	9

n. d. = not determined.

Table 2. Trace elements data for the Allende meteorite, ppm.

Element	King (1969)	Emery <i>et al</i> (1969)	Morgan <i>et al</i> (1969)	Wakita and Schmitt (1970)	Clark <i>et al</i> (1970)
B	108				1
Sc		10	12.2 ± 0.2	11.0 ± 0.5	11
V	170			130 ± 10	70
Rb				1.3 ± 0.1	0.9
Zr	60		12.0 ± 0.7		9
Cd				0.19 ± 0.01	
In				0.027 ± 0.001	
Cs				0.06 ± 0.01	
Ba	10				5
Hf		≤ 0.7	0.16 ± 0.02		
W			0.15 ± 0.02		
Ir			0.71 ± 0.03		
Pt			1.8 ± 0.2		
Au			0.26 ± 0.01		
U	.019				
La				0.44 ± 0.02	0.7
Ce				1.25 ± 0.06	1
Pr				0.20 ± 0.01	0.2
Nd				0.91 ± 0.05	0.9
Sm				0.29 ± 0.01	0.5
Eu				0.107 ± 0.005	0.1
Gd				0.43 ± 0.02	0.6
Tb				0.074 ± 0.005	0.09
Dy				0.42 ± 0.02	0.6
Ho				0.12 ± 0.01	0.1
Er				0.31 ± 0.02	0.3
Tm				0.049 ± 0.001	
Yb				0.32 ± 0.02	0.4
Lu				0.058 ± 0.002	
Y				3.0 ± 0.1	2

exception of large amounts of pentlandite  $(Fe, Ni)_9S_8$ , containing 16-21% Ni by microprobe analysis (Clarke et al., 1970). However, the troilite appears to be pure FeS, without detectable Ni.

Point counting by Clarke et al. (1970) on one prepared section of the meteorite indicates the following volume percent content: chondrules, 34%; white aggregates, 9%; and matrix, 57%. In addition small numbers of dark inclusions are found. These are essentially fine-grained matrix material containing extremely small chondrules. Marvin et al. (1970) showed that the white aggregates contain very fine-grained, high temperature minerals such as spinel ( $MgAl_2O_4$ ), hercynite ( $FeAl_2O_4$ ), gehlenite ( $Ca_2Al_2SiO_7$ ) and others. The minerals are rarely observed in meteoritic material. The matrix is largely iron-rich olivine (~ 50 mole percent  $Fe_2SiO_4$ ), while the chondrules present a tremendous variety of mineralogical types. According to Clarke et al. (1970), there are two general chemical classes of chondrules.

I. Magnesium-rich chondrules. These consist of magnesium-rich olivine, sometimes with clinoenstatite and interstitial glass (which may be partly devitrified). Individual olivine crystals are frequently zoned, with cores of almost pure  $Mg_2SiO_4$  and increasing iron content towards the surface. In this study, zoning has been observed in a few chondrules.

II. Calcium and aluminum-rich chondrules. These comprise only about 5% of the total chondrule population. The mineralogy of three types recognized are:

- a. Gehlenite - fassaite - anorthite - spinel
- b. Anorthite - forsterite - spinel
- c. Nepheline - sodalite - fassaite - olivine

Table 3 lists all known minerals of the Allende meteorite. The composition of one large type - a chondrule (see Table 1), 24 mm in diameter, was found to be 30% fassaite, 40% gehlenite, 20% spinel and 10% anorthite.

The boundaries between chondrules and matrix often exhibit features such as reaction rims or "rinds" and the presence of large amounts of sulfide, sometimes overlaying small crystals of metal in the chondrule.

#### Purpose

A very large amount of evidence points to the similarity of the nonvolatile elemental abundances of carbonaceous chondritic meteorites, especially those of petrological grade 1, to the corresponding abundances found in the sun. It is therefore hypothesized by a very large number of investigators that the carbonaceous chondrites closely approximate the condensable fraction of primordial solar system

matter. Evidence supporting this hypothesis has been recently reviewed by Anders (1970):

1. All elements fractionated in chondrites (some 50 at last count) are more abundant in Cl chondrites than any other class. No feasible enrichment process has been found to derive Cl chondrites from lower grade petrological chondrites.

2. The elemental abundances of non-volatile elements as determined in the sun agree very well with the elemental content of Cl chondrites. Due to the low accuracy of the solar abundances, C2, E3 and E4 chondrites also show reasonable agreement.

3. Elemental abundances determined from cosmic rays also agree with elemental abundances found in Cl meteorites.

4. The strongest argument for the primitive nature of Cl meteoritic material is the smoothness of the isotopic abundance curve. Any significant chemical fractionation could lead only to breaks in the curve.

The usual chondritic meteorite is composed of small (~ 1 mm diameter) spherical inclusions called chondrules and a fine grained matrix. Although these two components generally differ vastly in composition, very few chemical studies have been made on the individual constituents. Generally analyses are performed on the bulk meteorite.

The pioneering work in the analysis of individual chondrules was by Schmitt, Smith and Goles (1965) who reported the abundances of Na,

Table 3. Minerals in the Allende meteorite by Clarke *et al.* (1970).

Name	Formula	Matrix	Chondrules	Aggregates	Mineral Location
Kamacite	(Fe, Ni)		X		
Awaruite	Ni <sub>3</sub> Fe	X	X		
Copper	Cu	X			
Troilite	FeS	X	X		
Pentlandite	(Fe, Ni) <sub>9</sub> S <sub>8</sub>	X	X		
Chromite	FeCr <sub>2</sub> O <sub>4</sub>	X			
Spinel	MgAl <sub>2</sub> O <sub>4</sub>		X	X	
Hercynite	FeAl <sub>2</sub> O <sub>4</sub>			X	
Perovskite	CaTiO <sub>3</sub>			X	
Olivine	(Mg, Fe) <sub>2</sub> SiO <sub>4</sub>	X	X		
Enstatite	MgSiO <sub>3</sub>			X	
Clinoenstatite	MgSiO <sub>3</sub>		X		
Clinohyperstene	(Mg, Fe)SiO <sub>3</sub>	X			
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>			X	
Augite (fassaite)	Ca(Mg, Al, Ti)(Al, Si) <sub>2</sub> O <sub>6</sub>		X	X	
Ferroaugite	Ca(Fe, Mg, Al)(Al, Si) <sub>2</sub> O <sub>6</sub>			X	
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>		X	X	
Gehlenite	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>		X	X	
Grossular	Ca <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>			X	
Nepheline	NaAlSiO <sub>4</sub>		X	X	
Sodalite	Na <sub>4</sub> Al <sub>3</sub> Si <sub>3</sub> O <sub>12</sub> Cl		X	X	
Cordierite	Mg <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>18</sub>			X	

Sc, Cr, Mn, Fe, Co and Cu in 218 individual chondrules from 11 different chondrites. Two years later an extensive amount of information on abundances in individual chondrules had been gathered by Schmitt and Smith (1966). An extensive study of meaningful statistical value on individual chondrules from a single meteorite has been carried out only recently for the L4 chondrite Bjurböle, by Walter (1969). Based on this chemical analytical data for chondrules and petrological studies, a series of papers (Larimer (1967), Larimer and Anders (1967), Larimer and Anders (1970) and Keays, Ganapathy and Anders (1971)) has appeared postulating the strong depletion of volatile elements in the chondrules to account for observed trends in elemental abundances among the chondrites.

With the fall of the Allende meteorite in early 1969, large quantities (~ 1 ton) of carbonaceous meteoritic material were available for the first time. It is clear that the availability of large amounts of this material presents an excellent opportunity to investigate the validity of Larimer and Anders' very important hypothesis and to present more analytical data available for use in helping discover the historical origin of meteorites.

## II. EXPERIMENTAL

Separation of Chondrules for Analyses

About 120 chondrules were removed from 5 fragments of Allende which were obtained from the Smithsonian Institution. Chondrules were identified by numbers preceded by fragment number 1 through 5 (e.g., chondrule number 9 from fragment 2 = 209). After lightly crushing a fragment in a steel mortar, the chondrules were removed with stainless steel scalpels and fine tipped forceps under 5X magnification of a stereomicroscope. Each chondrule isolated was placed in a clean 1/2 dram polyvial, and descriptions were noted of its physical appearance and any peculiarities. About 65 of the largest and most positively identifiable specimens were then selected for analysis. Many chondrules were verified as true chondrules by the late Richard H. Smith. These chondrules were carefully cleaned under the stereomicroscope with a scalpel, care being taken to remove the last traces of matrix, which was generally considerably darker than the chondrule. In many cases the chondrule was surrounded by a jacket of sulfide crystals, under which could be seen often shiny plates of metal. Metal in the meteorite was rarely encountered; metal was not confined only to the chondrules. In addition, three large chondrules (600 series) were received from Dr. Brian Mason of the Smithsonian Institution. Each chondrule weight was a reproducible to .001 mg with a microbalance.

### Analysis of the Chondrules

Analysis of the chondrules was performed by INAA (instrumental neutron activation analysis). For a tabular description of the activation parameters, Table 2 of Nicholson (1970) should be consulted, keeping in mind the much smaller chondrule sample sizes of this work. The technique of INAA with Ge(Li) detectors as an analytical tool has been described by Gordon *et al.* (1968) and others.

Use of the Oregon State University 1 megawatt TRIGA reactor was made in the determination of Al, Na and Mn. The elements Ca, Ti and V were determined in 18 of the chondrules. Finally, Ca, Sc, Cr, Fe, Ni, Co, Sm, Eu and Ir were determined after an activation at a high flux reactor. About 50 chondrules with mass < 6 mg were activated in the flux trap at the high neutron flux research reactor in Columbia, Missouri. The remaining 9 chondrules of mass > 12 mg obtained the necessary integrated flux in the central core or thimble of the OSU TRIGA reactor as a "soaker", i. e., the chondrules were left in the reactor for about a month and allowed to receive whatever neutron flux was available during that time. A one week activation (88.3 hr) at a flux of  $1.7 \times 10^{14}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  was required at Columbia. Full power operation of the TRIGA (500 kw) corresponds to a thermal neutron flux of  $\sim 1.3 \times 10^{13} \text{cm}^{-2} \text{sec}^{-1}$  in the thimble.

The above list of analyzed elements includes many of the major and minor elements in the Allende chondrules, with the exception of Si, O, Mg, K, Ba, S, C and H<sub>2</sub>O. The procedure for determination of Si and O using INAA is outlined by Vogt and Ehmann (1965), but due to difficulties with obtaining precision at our laboratory, the analyses were not attempted. Magnesium can be measured from an activation with 23-28 MeV bremstrahlung, utilizing the  $^{25}\text{Mg}(\gamma, p)^{24}\text{Na}$  photonuclear reaction, as discussed by Schmitt et al. (1970).

The following is a description of the analyses and the resulting errors.

#### Aluminum

Aluminum is determined instrumentally by a short activation at low thermal neutron flux due to the short lived activity of 2.3 min  $^{28}\text{Al}$ . After a rapid return from the activation position by the pneumatic transfer system, the activated sample was transferred into a clean polyvial and counted about 1 min after EOB (end of bombardment). Particularly "hot" samples were allowed to decay longer until analyzer dead times of < 20% in the NaI well were obtained. All determinations were duplicated and with very few exceptions, the individual values agreed within counting statistical error ( $\pm 1\text{-}2\%$ ). These included samples determined with chondrule-sized aluminum foil standards of different weights.

Under the conditions of the activation, two main sources of error arise.

1. Contribution of the 1.81 MeV  $\gamma$ -ray activity of 2.58-h  $^{56}\text{Mn}$  to the 1.78 MeV  $\gamma$ -ray activity of  $^{28}\text{Al}$ . This was found to be negligible (< 0.5% error) for the chondrule samples.

2. Production of  $^{28}\text{Al}$  by  $^{28}\text{Si}(\text{n}, \text{p})^{28}\text{Al}$ , a reaction occurring only with fast neutrons. Experimentally, the interference was measured by activation of ultra-pure Si metal, and is given by:

$$f = 1 - 3.15 \times 10^{-3} \frac{\% \text{SiO}_2}{\% \text{Al}}$$

where  $\% \text{ true Al} = f' \% \text{Al}''$  and

$\% \text{Al}''$  = calculated Al abundances as if there were no Si present at all.

The interference is non-trivial in almost all cases and cannot be accurately determined since the Si content of each individual chondrule is unknown. In Table 4,  $f_{\min}$ , the smallest possible value of  $f$  is evaluated by assuming the maximum possible  $\% \text{SiO}_2$ . It can be seen that as much as a 53% interference (in the case of chondrule 50) is possible. Schmitt et al. (1967) determined Si in 56 chondrules from four C3 chondrites and found the mean  $\text{SiO}_2$  content to range from 35% to 44%. Thus, with an expected abundance of  $\text{SiO}_2$  of  $1/2 - 1/3$  that of  $\% \text{SiO}_2(\text{max})$ , the most probable value of  $f$  is  $1/2 - 1/3$

Table 4. Error in Al abundances from  $^{28}\text{Si}(n, p)^{28}\text{Al}$ .

Chondrule	"%Al"	%SiO <sub>2</sub> (max)	fmin	f(most prob)	Al(most prob)
50	0.56	93.9	0.47	0.72-0.86	0.40-0.48
210	0.61	94.2	0.51	0.74-0.87	0.45-0.53
313	0.73	95.1	0.59	0.78-0.89	0.57-0.65
109	0.76	94.3	0.61	0.79-0.90	0.60-0.68
510	0.82	88.9	0.66	0.81-0.90	0.66-0.74
214	0.82	85.4	0.67	0.81-0.90	0.66-0.74
219	0.98	90.6	0.71	0.84-0.92	0.82-0.90
340	1.05	83.3	0.75	0.85-0.93	0.89-0.98
303	1.11	88.7	0.75	0.86-0.93	0.95-1.03
305	1.23	88.1	0.78	0.87-0.94	1.07-1.16
413	1.27	84.3	0.79	0.88-0.94	1.12-1.19
407B	1.30	83.4	0.80	0.88-0.94	1.14-1.22
421	1.40	79.7	0.82	0.89-0.95	1.25-1.33
bulk	1.84	*34.2		0.94	1.73
601	13.6	45	0.990	0.993	13.5
335	17.4	39	0.993	0.995	17.3

\* Known SiO<sub>2</sub> abundance

between the value listed in Table 4 and 1.00. For a chondrule with Al and  $\text{SiO}_2$  composition of the bulk meteorite, the interference amounts to a 6% error in the Al abundances. Only in the case of 335 (17.4% Al) and 601 (13.6% Al) is the error trivial (~ 0.5%).

### Sodium and Manganese

An activation of up to one hour at moderate neutron flux suffices for the production of sufficient amounts of activity from 2.58-h<sup>56</sup>Mn and 14.96-h<sup>24</sup>Na in order to determine both of these elements in one activation. After a few hours of decay Mn is determined from the 0.845-MeV photopeak, and after a day or so, Na, by the 2.75-MeV photopeak in the  $\gamma$ -ray spectrum.

Due to the <sup>24</sup>Na activity arising from Na impurity in the polyvial, it was necessary to transfer 0.1 ml of the aqueous standard into a clean polyvial after activation. To minimize errors resulting from differences in activation geometry and the neutron flux gradient of about 3%  $\text{cm}^{-1}$  in the TRIGA rotating rack activation position, a volume of 0.25 ml (a 4 mm column in a 1/2 dram polyvial) was activated. Thus only ~0.5% error results from differences in the activation geometry of the standard and chondrule.

Half life determinations were carried out on about 20 chondrules, and for both <sup>24</sup>Na and <sup>56</sup>Mn, half lives were found to lie within the counting statistical error. Two U. S. G. S. (U. S. Geological Survey)

standard rocks were similarly analyzed for Na and Mn. The abundances found for these elements (see Table 7, p. 38) agreed favorably with the values listed by Flanagan (1969), with the exception of Mn in W-1. The poor agreement is thought to be due to the small sample size of W-1 (63 mg) and the large grain sizes of this rock standard, leading to minor and trace element inhomogeneity. From replicate analyses, the precision for Na and Mn is estimated to be  $\pm 5\%$ , quite larger than the  $\pm 1.5\text{--}2\%$  overall error obtained by Osborn and Schmitt (1970).

Errors arising from  $(n, p)$  reactions on  $^{56}\text{Fe}$  and  $^{24}\text{Mg}$  could interfere with the determination of Mn and Na. However, calculation of the ratio of specific activities of  $^{56}\text{Mn}$  from  $^{55}\text{Mn}$  and  $^{56}\text{Fe}$  yields a ratio of  $A_{\text{Fe}}/A_{\text{Mn}} \sim 5.4 \times 10^{-6}$ . These activities are based on computer calculated fluxes by Lukens (1963) in the TRIGA rotating rack and  $\phi(\text{thermal neutrons})/\phi(\text{fission neutrons})$  ratios of 10. Thus even for the largest Fe to Mn weight ratio (240) the interference is trivial.

From Hughes (1953),  $E_{\text{eff}}$  for the  $^{24}\text{Mg}(n, p)^{24}\text{Na}$  reaction is 7.2 MeV, with  $\overline{\sigma} = 1.0$  mb. For calculational purposes, fission spectrum neutrons with  $E < E_{\text{eff}}$  do not interact. The flux measurements of Upham (1968) for the OSU TRIGA reactor rotating rack give  $\phi(E > 5 \text{ MeV})/\phi_{\text{th}} = 0.075$ . Using the thermal neutron cross section of  $^{23}\text{Na}$ , a ratio of  $A_{\text{Mg}}/A_{\text{Na}} < 1.0 \times 10^{-4}$  is obtained for the production of  $^{24}\text{Na}$  from  $^{24}\text{Mg}(n, p)$  and  $^{23}\text{Na}(n, \gamma)$  reactions. For a high

olivine chondrule, containing about 20% Mg and about 0.2% Na, we calculate that less than 1% ( $n, p$ ) contribution is the maximum interference level. This error could be accurately evaluated by simultaneously activating Mg and Na standards.

#### Calcium, Titanium and Vanadium

It is necessary to use a Ge(Li) detector for the analysis of these elements, which are determined by counting the radionuclides: 8.8-m  $^{49}\text{Ca}$  (3.10 MeV  $\gamma$ ), 5.79-m  $^{51}\text{Ti}$  (0.32 MeV  $\gamma$ ) and 3.75-m  $^{52}\text{V}$  (1.434 MeV  $\gamma$ ). A pneumatic transfer system was used for activation of the samples.

The limiting factor in the analyses of these elements is generally the high relative activity of  $^{56}\text{Mn}$  induced in the sample during activation. Thus, the high Compton continuum, resulting from  $^{56}\text{Mn}$   $\gamma$ -ray interactions, precludes the attainment of statistically good ( $\pm 2\%$ ) counts for these elements. The standards and chondrules were very closely matched in geometry and thus the major error for these three elements is simply due to counting statistics.

The analysis of Ca is also possible, with much improved statistical certainty, by utilization of the 159 keV line of 3.4d  $^{47}\text{Sc}$  (see Table 5).

### High Flux Activations

Two aqueous standards, one containing Fe, Co, Cr and Sc, and the other containing Ir, Eu, Sm, La, and Yb were prepared such that the radioactivity of each primary radionuclide was about the same one week after EOB. An aliquot of each standard was pipetted into a separate clean quartz vial; the liquid was weighed and then evaporated. The vial was then sealed. Standard rock samples were also sealed in quartz vials, and each chondrule was individually wrapped in pure Al foil, the weight of each chondrule and the weight of chondrule plus foil serving as an identification. The entire assembly was sealed in an aluminum irradiation can. Compactness of chondrules and standards in the can is essential in order to activate as many chondrules as possible and to minimize the rather large flux gradient of  $7\% \text{ cm}^{-1}$  in the Missouri reactor flux trap. In retrospect, a small piece of iron wire packed with the chondrules would have served as a relative neutron flux monitor for the chondrules relative to the iron standard in the quartz vial. The irradiation assembly is illustrated below.

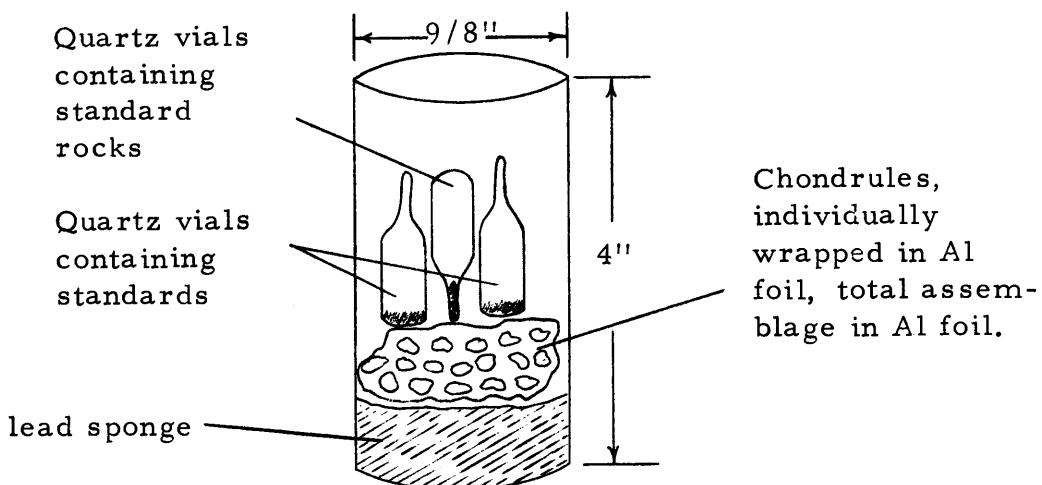


Figure 2. Irradiation assembly for high flux activations.

After activation and cooling, the chondrules were all removed from the Al foil, identified by weight, placed in a clean 1/2 dram polyvial, and counted. The standards were removed from the vial by dissolution in concentrated HCl and transferred with a capillary tube to a 1/2 dram polyvial. The solutions were evaporated under a heat lamp to chondrule sized droplets and the polyvial heat sealed. The quartz vials were counted before and after the dissolution to ensure complete removal of the standard.

The La and Yb levels in the chondrules were too low to determine by INAA; however, in addition to the above elements, Ni was detectable in most chondrules, while Au was detectable in a large number.

Table 5 lists all lines found in the  $\gamma$ -ray spectrum taken by the high-resolution 3.6-cc Ge(Li) detector employed in analysis (not all lines were present in any given chondrule), the lines used for analysis, and any possible interferences. The interfering  $\gamma$ -ray lines were obtained from Filby *et al.* (1970). Chondrules (mass > 12 mg) activated in the OSU TRIGA were counted about 5 days after EOB in hopes of determining La. Because a significant amount of residual  $^{24}\text{Na}$  activity was still present, this was not possible. However, statistically far more counts for the Sm and Au radionuclides, as well as for the Ni ( $n, p$ ) induced reaction product (due to the four fold increase in  $\phi_{\text{fast}}/\phi_{\text{th}}$  in the TRIGA central thimble compared to the flux trap at

Table 5. Photopeaks observed with 3.6 and 30 cc Ge(Li) detectors after high neutron flux activations.

$E_{\gamma}$ (keV)	Nuclide Used for Analysis	Interference or Assignment	$E_{\gamma}$ (keV)	Nuclide Used for Analysis	Interference or Assignment
2012		$^{46}\text{Sc}$ sum	<u>412</u>	$^{198}\text{Au}$	
<u>1596</u>	$^{140}\text{La}$		334		$^{59}\text{Fe}$
<u>1408</u>	$^{152}\text{Eu}$				
<u>1332</u>	$^{60}\text{Co}$	$^{60}\text{Ni}(\text{n}, \text{p})^{60}\text{Co}$ (a)	<u>320</u>	$^{51}\text{Cr}$	$^{317} \text{Ir}, ^{192}\text{Ir}, ^{54}\text{Fe}(\text{n}, \alpha)^{51}\text{Cr}$ (d)
<u>1291</u>	$^{59}\text{Fe}$		<u>317</u>		$^{192}\text{Ir}$
<u>1173</u>	$^{60}\text{Co}$	$^{60}\text{Ni}(\text{n}, \text{p})^{60}\text{Co}$ (a)	<u>308</u>	$^{192}\text{Ir}$	$^{169}\text{Yb}$ (e)
<u>1120</u>	$^{46}\text{Sc}$	$^{46}\text{Ti}(\text{n}, \text{p})^{46}\text{Sc}$ (b)	<u>296</u>	$^{192}\text{Ir}$	$^{160}\text{Tb}$ (e)
<u>1098</u>	$^{59}\text{Fe}$		269		
<u>889</u>	$^{46}\text{Sc}$	$^{46}\text{Ti}(\text{n}, \text{p})^{46}\text{Sc}$ (b)	206		$^{192}\text{Ir}$
<u>835</u>		$^{54}\text{Mn}$ from $^{54}\text{Fe}(\text{n}, \text{p})$	<u>191</u>		$^{59}\text{Fe}$
<u>811</u>	$^{58}\text{Ni}(\text{n}, \text{p})^{58}\text{Co}$	$^{59}\text{Co}(\text{n}, 2\text{n})^{58}\text{Co}$ (c)	<u>159</u>	$^{46}\text{Ca}(\text{n}, \gamma)^{47}\text{Ca}$ $^{47}\text{Ca} \xrightarrow{\beta} ^{47}\text{Sc}$	$^{47}\text{Ti}(\text{n}, \text{p})^{47}\text{Sc}$ (f) $^{197}\text{Au}(\text{n}, \gamma)^{198}\text{Au}(\text{n}, \gamma)^{199}\text{Au}$
612		$^{192}\text{Ir}$			
604		$^{192}\text{Ir}$	<u>142</u>		$^{59}\text{Fe}$
588		$^{192}\text{Ir}$	136		$^{192}\text{Ir}$
511		$\beta \pm$	130		$^{191}\text{Os}, ^{169}\text{Yb}$ (g)
484		$^{192}\text{Ir}$	122		$^{57}\text{Co}$ from $^{58}\text{Ni}(\text{n}, 2\text{n})^{57}\text{Ni} \xrightarrow{\beta}$
<u>468</u>	$^{192}\text{Ir}$		112		$^{177}\text{Lu}, ^{169}\text{Yb}, ^{177m}\text{Lu}, ^{175}\text{Yb}$ (h)
			<u>104</u>	$^{153}\text{Sm}$	$^{153}\text{Gd}$ (i)

Prominent lines underlined

- (a) Interferences determined from Ni std. are 0.66–1.07% of the Co abundances for eight of samples activated at OSU, with an average interference of 0.92%. For the remaining samples activated at Missouri, the average interference amounts to < 0.25%. Thus, these small corrections were neglected.
- (b) Ti/Sc ratios from 50–360 are found in Allende chondrules. For BCR-1 and G-2 (ratios of 390 and 610), Sc abundances agreeing exactly with literature values were obtained from the OSU activations. Therefore any correction for Sc abundances in chondrules is negligible.
- (c) Using a Co standard, the 811 KeV photopeak of  $^{58}\text{Co}$  was undetectable. The interference is certainly < 0.5% of the Ni abundance.
- (d) The  $^{54}\text{Fe}(n,\alpha)^{51}\text{Cr}$  reaction is severe for low (< 100 ppm) Cr abundances and high Fe content (~ 10%), as in BCR-1, especially for activations in the central thimble of TRIGA. The Cr abundance calculated for BCR-1 from the TRIGA activation indicates a constant contribution of about 20 ppm for 10% Fe from this source, and thus is negligible in all determinations. The interference from the 317 KeV  $^{192}\text{Ir}$  photopeak is discussed in the text.
- (e) Assuming that  $(\text{SM}) \sim (\text{Yb})$ , calculations with the activation conditions and detection parameters of  $^{192}\text{Ir}$  and  $^{169}\text{Yb}$  indicate that  $A_{\text{Ir}}/A_{\text{Yb}} \sim 32 \frac{\text{ppm}(\text{Ir})}{\text{ppm}(\text{sm})}$  (10 days after EOB). The  $^{160}\text{Tb}$  interference at 299 KeV is about the same, but remains fairly constant with time due to the 72.1 d half life of  $^{160}\text{Tb}$ . A calculation assuming the same Sm/Tb as in the Allende bulk gives  $A_{\text{Ir}}/A_{\text{Tb}} = 26 \frac{\text{ppm}(\text{Ir})}{\text{ppm}(\text{Sm})}$ . Thus for an Ir/Sm ratio of < 2, these two lines were not used for determination of the Ir abundances.
- (f) The interference from  $^{199}\text{Au}$  is trivial. The determination of Ca from this line is, however, fraught with difficulties. A very low  $E_{\text{eff}}$  of 3.7 MeV and  $\bar{O} = 16$  mb obtained from Upham (1968) combine to create a serious interference from the  $^{47}\text{Ti}(n, p)^{47}\text{Sc}$  reaction due to high fission neutron fluxes in both the Missouri and especially the TRIGA reactor activations (see discussion in text).
- (g) The constant Sm/Eu ratio in the chondrules is strong evidence for a constant Sm/Yb ratio, which Wakita and Schmitt (1970) determined to be about unity in the bulk meteorite. Crockett et al. (1967) determined Os and Ir in 7 carbonaceous chondrites and found abundances (relative to  $^{106}\text{Si}$ ) of  $0.79 \pm 0.12$  and  $0.76 \pm 0.28$ , respectively. A calculation assuming  $(\text{Yb}) \approx (\text{Sm})$  and  $(\text{Os}) \approx (\text{Ir})$ , employing the activation and detection parameters for Yb and Ir indicates that 12 days after EOB, when measurements of this line were made,  $A_{\text{Os}} = A_{\text{Yb}}$ . Thus neither element can be determined. Half life determinations on the 130 KeV line were inconclusive because of very poor counting statistics.
- (h) The relative activities are given by  $A_i \approx e_i \text{ ppm}_i f_i \sigma_i (1 - e^{-\lambda_i T}) e^{-\lambda_i T}$
- | nuclide            | $E(\text{KeV})$ | $t_{1/2}(\text{d})$ | $e_i$ | $f_i$ | $\sigma_i$ | $\text{ppm}_i(\text{bulk})$ | $A_{\text{EOB}}$ | $A_{10\text{d}}$ | $A_{30\text{d}}$ | $A_{60\text{d}}$ |
|--------------------|-----------------|---------------------|-------|-------|------------|-----------------------------|------------------|------------------|------------------|------------------|
| $^{169}\text{Yb}$  | 110.0           | 31.8                | 18.0  | .140  | 11,000     | 0.32                        | 680              | 550              | 350              | 180              |
| $^{175}\text{Yb}$  | 113.0           | 4.21                | 1.9   | 31.84 | 55         | 0.32                        | 484              | 93               | 4                |                  |
| $^{177}\text{Lu}$  | 113.0           | 6.74                | 2.8   | 2.60  | 2,100      | 0.058                       | 280              | 100              | 22               | 0.6              |
| $^{177m}\text{Lu}$ | 113.5           | 155                 | 23    | 2.60  | 1          | 0.058                       | .057             |                  |                  |                  |
- About 1 1/2 months delay is necessary before determining  $^{169}\text{Yb}$  by counting  $^{169}\text{Yb}$ . By this time the  $^{169}\text{Yb}$  activity has fallen to 1/3 of the activity at EOB, and the element is undeterminable. The  $^{169}\text{Yb}$  lines at 177 and 198 KeV are undeterminable due to the high  $^{192}\text{Ir} + ^{51}\text{Cr}$  Compton continuum and the 191-KeV Fe photopeak, respectively.
- (i) Using the activation and detection parameters for  $^{153}\text{Sm}$  and  $^{153}\text{Gd}$ , and assuming Gd and Sm abundances in the bulk meteorite, one obtains for the Missouri activation:  $A_{\text{Sm}}/A_{\text{Gd}} = 0.8 \times 10^4 e^{-352t(\text{d})}$
- Thus, for a 1% interference from  $^{153}\text{Gd}$ ,  $t = 12.5\text{d}$  after EOB. Since all measurements were determined from 10–14d after EOB, one expects < 5% error from this source, generally well within the counting statistical error. For the TRIGA activations, in which the saturation factor greatly favors  $^{153}\text{Gd}$  over  $^{153}\text{Sm}$  activity, all counts were taken five days after EOB.

the Missouri reactor) were obtained for this counting time after the TRIGA activation compared to the counting period of 10-14 days after EOB for the samples activated the Missouri reactor. The statistical accuracy for the remaining elements was about the same for both counting periods. Nickel was accurately determined by activating standards containing both Ni and Fe under similar conditions at both the TRIGA and Missouri reactor and then normalizing the Fe and Ni induced activities to that obtained in the activation of the chondrules as discussed below.

The determination of the correction factor for the ratios of specific activities for Ni and Fe during activation at the Missouri reactor for the chondrules and the standards is given by:

$$\frac{(A_{Ni}/A_{Fe})_{Chon}/(A_{Ni}/A_{Fe})_{std}}{(1-e^{-\lambda_{Co}T_{Chon}})(1-e^{-\lambda_{Fe}T_{std}})e^{-\lambda_{Co}(t_{std}-t_{Chon})}} = \frac{(1-e^{-\lambda_{Co}T_{Chon}})(1-e^{-\lambda_{Fe}T_{std}})e^{-\lambda_{Co}(t_{std}-t_{Chon})}}{(1-e^{-\lambda_{Co}T_{std}})(1-e^{-\lambda_{Fe}T_{Chon}})e^{-\lambda_{Fe}(t_{std}-t_{Chon})}}$$

where: T is the activation time, t is the decay time, and  $\lambda_{Co}$  and  $\lambda_{Fe}$  are the decay constants of  $^{58}Co$  and  $^{59}Fe$ .

The activation at the OSU TRIGA, however, took place over the period of about 1 month; the chondrules and accompanying Fe standard were exposed to different known flux levels for various known time periods. The Fe-Ni standard was simply activated once for a

short period. Since the activation periods were very short compared to the half lives, the saturation factor of  $1 - e^{-\lambda T} \approx \lambda T$ . Thus, for the TRIGA activations, the above ratio is given by:

$$\frac{(A_{Ni}/A_{Fe})_{Chon}/(A_{Ni}/A_{Fe})^{std}}{= \frac{\left( \sum \phi_i T_{Chon} e^{-\lambda_{Co} t_i, Chon} \right) e^{-(\lambda_{Co} - \lambda_{Fe})(t_{std} - t_{Chon})}}{\sum \phi_i T_{i, Chon} e^{-\lambda_{Fe} t_{i, Chon}}}}$$

where:  $\phi_i T_{i, Chon}$  is the individual power level and activation time product (arbitrary units) and  $t_{i, Chon}$  is the time from each individual EOB to the final EOB.

The above calculation carried out for an Fe and Ni standard activated at the Missouri high flux reactor gave poor agreement with the calculation resulting from activation of a similar standard at the OSU reactor. The two activations at the Missouri reactor were carried out in different positions in the flux trap, while the chondrules and standard were irradiated in the same position at the OSU TRIGA reactor, and thus the ratio of Fe and Ni activities resulting from the activation at OSU is felt to be superior. The specific activity of Ni from the activation of chondrules at the Missouri reactor was obtained by normalizing the Ni/Co ratio to that calculated for the 9 samples activated at OSU.

Europium can be determined instrumentally only by long counts with a 30 cc Ge(Li) detector on an elevated geometry position no earlier than one month after EOB. The elevated geometry is necessitated by the Compton continuum up to 2.5 MeV that results from the sum of Compton events from the  $\gamma$ -ray cascades of the radionuclides  $^{46}\text{Sc}$  and  $^{60}\text{Co}$ . The count rates of the coincidence continuum and the single line (1408 keV) are proportional to  $\Omega^2$  and  $\Omega$ , respectively, where  $\Omega$  is the solid angle subtended by the detector. The elevated geometry necessitates the use of a larger detector. A 3.6 cc Ge(Li) was used in the analysis of the other long-lived activation products because of its acceptable resolution of 4 keV (FWHM) at 1332 keV  $\gamma$ -ray energy. This detector was capable of resolving partially the 317 keV  $^{192}\text{Ir}$  and 320 keV  $^{51}\text{Cr}$  lines, even though relative activities differed by a factor of 10. Europium via  $12.5-\text{y}^{152}\text{Eu}$  was determined in a separate count from the other elemental abundances.

Since no gold standard was activated, the abundances of Au were calculated from activation and detection parameters, with an error of about  $\pm 30\%$  expected in addition to the rather large counting statistical errors.

$$\frac{A_{\text{Au}}}{A_i} = \frac{k e_{\text{Au}}^E W_{\text{Au}}^t f_{\text{Au}}^f GFW_i \sigma_{\text{Au}}^S e^{-\lambda_{\text{Au}} \Delta t}}{e_i^E W_i^t f_i^f GFW_{\text{Au}} \sigma_i^S e^{-\lambda_i \Delta t}}$$

$A$  = measured photopeak activity at counting time, counts  $\text{sec}^{-1}$

e = branching ratio fraction of  $\gamma$ -ray

E = Ge(Li) detector efficiency, %

f = isotopic abundance, %

Wt = mass in micrograms

GFW = gram formula weight

$\sigma$  = thermal neutron cross section, barns

S = saturation factor =  $1 - e^{-\lambda T}$  (Missouri) =  $\lambda \sum \phi_i T_i e^{-t_i}$  (TRIGA)

$e^{-\lambda \Delta t}$  = decay factor from EOB to time of count

$$k = \frac{A_{Au}(\text{double } n, \gamma)}{A_{Au}(\text{single } n, \gamma)}$$

Substituting the known values for Au, we have

$$\begin{aligned} Wt_{Au(\mu g)} &= \frac{Pe^{-\lambda_i \Delta t}}{A_i(\mu g^{-1} \text{ sec}^{-1})} \cdot \frac{A_{Au}(\text{sec}^{-1}) e^{\lambda_{Au} \Delta t}}{k} \\ &= \frac{c}{k} A_{Au}(\text{sec}^{-1}) e^{\lambda_{Au} \Delta t} \end{aligned}$$

$$\text{where: } P = \frac{e_i E_i f_i \sigma_i}{121.2 GFW_i}$$

The range of c about the average, calculated from activities of Sc, Fe, Co, and Cr, was about  $\pm 20\%$ .

The quantity k is the ratio of the true activity of  $^{198}\text{Au}$  and that calculated from simple neutron capture. Due to its abnormally huge thermal neutron capture cross section (26,000 barn),  $^{198}\text{Au}$  is

destroyed by the reaction  $^{198}\text{Au} (\text{n}, \gamma) ^{199}\text{Au}$ . The activity of  $^{198}\text{Au}$  can be calculated from the expression found in Friedlander, Kennedy and Miller (1955).

$$A_{198}(\text{EOB}) = \lambda_{198} \Lambda_{198}^* N_{197}^o \left( \frac{e^{-\Lambda_{197} T} - e^{-\Lambda_{198} T}}{\Lambda_{198} - \Lambda_{197}} \right)$$

where:  $\Lambda_{198}^* = \phi \sigma_{198}$

$$\Lambda_{197} = \phi \sigma_{197}$$

$$\Lambda_{198} = \lambda_{198} + \phi \sigma_{198}$$

Therefore,

$$k = \frac{A_{198}(\text{double n, } \gamma)}{A_{198}(\text{single n, } \gamma)} = \frac{N_{197}^o \phi \sigma_{197} \lambda_{198} (e^{-\Lambda_{197} T} - e^{-\Lambda_{198} T})}{N_{197}^o \phi \sigma_{197} (\Lambda_{198} - \Lambda_{197})(1 - e^{-\lambda_{197} T})}$$

$$k = \frac{\lambda_{198} (e^{-\Lambda_{197} T} - e^{-\Lambda_{198} T})}{(\Lambda_{198} - \Lambda_{197})(1 - e^{-\lambda_{197} T})}$$

For the activation in the OSU TRIGA, where  $\phi = 1.3 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ , and  $T = 4 \text{ hr}$  (the last activation at the above power),  $k = 1.00$ , but for the activation in the Missouri reactor where  $\phi = 1.7 \times 10^{14} \text{ cm}^{-3} \text{ sec}^{-1}$ , and  $T = 88.3 \text{ hr}$ ,  $k = 0.60$ .

That the photopeak at 412 KeV was due to  $^{198}\text{Au}$  was verified by determinations of the half lives of this line in several chondrules.

Simultaneously the half life of the photopeak at 104 KeV ascribed to

$^{153}\text{Sm}$  was determined. Only two counts were possible in the half life determination due to the very poor counting statistics for the later count.

A spread of values about the true half lives of Sm and Au (1.95 and 2.70 days, respectively) is apparent on examination of the results from Table 6.

Plots of the specific activity of the 159 KeV line ascribed to  $^{47}\text{Sc}$ , normalized for differing counting geometries to the  $^{60}\text{Co}$  specific activity at that geometry versus previously determined Ca and Ti contents are shown in Figures 3 and 4 for the activations at the Missouri and OSU reactors, respectively. Correlation of the 159 KeV activity with the Ca content is within counting statistical error except for the mysterious case of BCR-1 (Figure 4). The  $^{47}\text{Sc}(\text{n}, \text{p})$  contribution to the  $^{47}\text{Sc}$  activity will be minimized by longer decay and irradiation times, since the activity derived from Ca must first "pass through" 4.535d  $^{47}\text{Ca}$ , while the activity arising from Ti decays directly with the 3.43d half life of  $^{47}\text{Sc}$ .

Now, photopeak activity = S. A.  $_{\text{Ca}}(\text{Ca}) + \text{S. A. }_{\text{Ti}}(\text{Ti})$ , where S. A. = specific activity at a fixed time.

A straight line should result with a zero intercept of S. A.  $_{\text{Ca}}$  if  $(\text{Ti})/(\text{Ca})$  is plotted against the decay corrected photopeak activity/ $(\text{Ca})$ , as long as the decay correction is not too large (since  $^{47}\text{Sc}$  decay is different from the two sources). Such a plot is shown in

Table 6. Half lives of photopeaks at 104 and 412 KeV

Chondrule	Count time, sec.	104 KeV			412 KeV			
		Area	t, days *	$t_{1/2}^{(d)}$	Area	t, days *	$t_{1/2}^{(d)}$	
OSU Activation	311	1000	6326±620	5.916	1.70	698±392	5.916	2.6
		1000	1199±522	9.999	±0.46	238±381	9.999	±4.2
	503	1000	25284±558	6.999	1.86			
		1000	5631±426	10.021	±0.10			
	603	1000	14710±752	6.027	1.29	1948±514	6.027	3.6
		1000	1701±717	10.041	±0.26	892±282	10.041	±1.7
	102	1804	6889±507	6.054	2.04	488±312	6.054	1.6
		1000	964±353	10.058	±0.56	86±180	10.058	±2.0
	602	1000	23027±833	6.084	1.72			
		1000	4625±770	10.076	±0.18			
Missouri Activation	506	1000	4902±439	6.134	2.04			
		1000	1277±411	10.093	±0.52			
	501	1000	5090±389	6.157	1.77	1323±266	6.157	3.1
		1000	1083±356	10.108	±0.39	538±197	10.108	±1.4
	301	1000	3814±379	6.186	1.98	469±215	6.186	3.5
		1000	965±350	10.125	±0.54	214±202	10.125	±4.7
	407B	8000	2566±602	11.300	1.88	10061±390	11.300	4.1
		13496	731±755	14.699	±1.59	9511±496	14.699	±0.5
	421	8000	5799±707	11.781	1.87	2200±483	11.781	2.0
		15135	3700±921	14.708	±0.48	1521±645	14.708	±1.0
Missouri Activation	214	1000				1397±294	13.183	4.3
		2000				1449±405	17.215	±2.3
	340	26608				4928±701	13.983	1.8
		37055				1762±815	17.453	±0.6
	502	1000				838±339	14.189	4.2
		2000				940±464	17.692	±4.7

\* days after EOB

$$\text{the error is given by } \epsilon (t_{1/2}) = t_{1/2} \sqrt{\frac{(\frac{\epsilon(A_0)}{A_0})^2 + (\frac{\epsilon(A)}{A})^2}{2.3 \log \frac{A_0}{A}}}$$

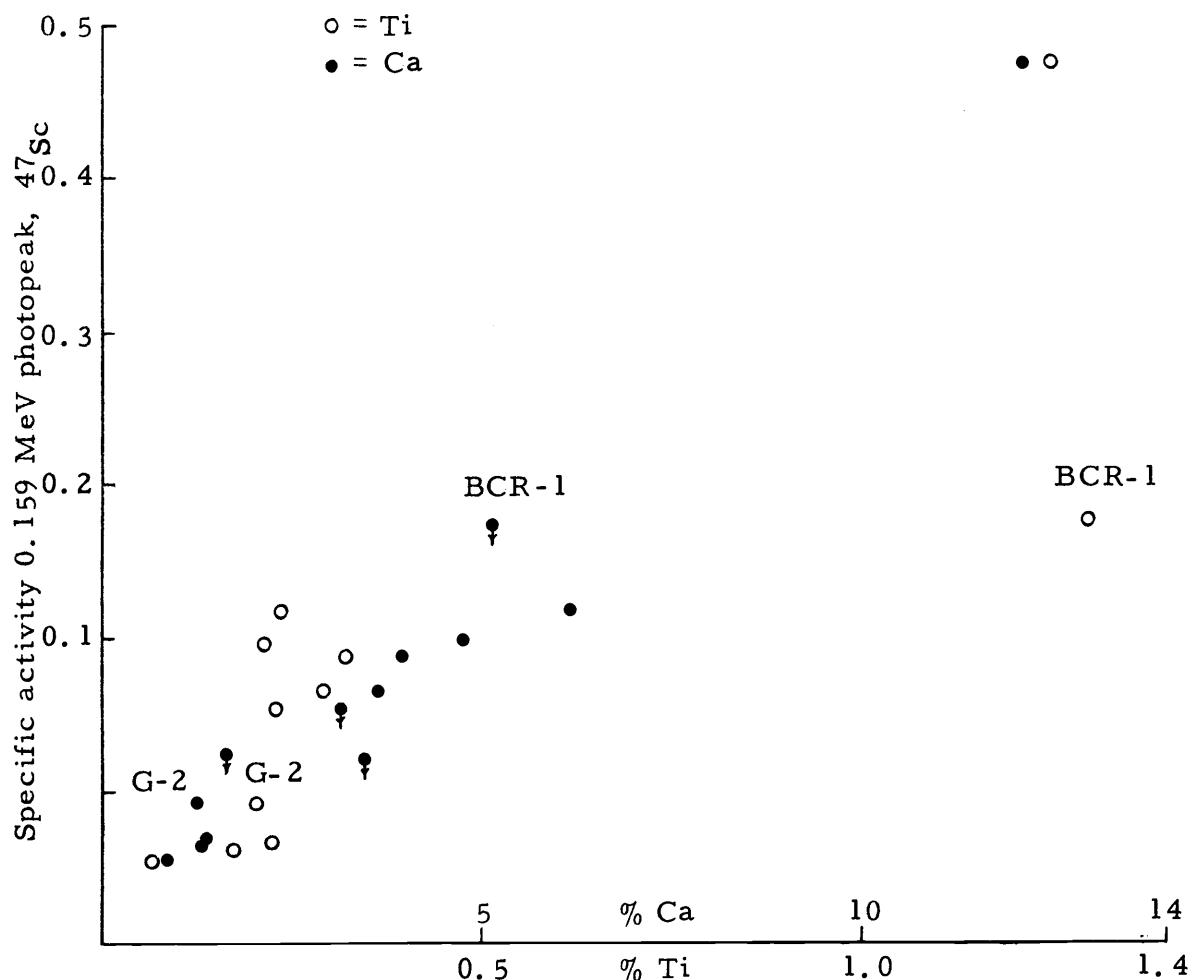


Figure 3. Missouri activation.. Determination of (Ca) via  $^{47}\text{Sc}$ .

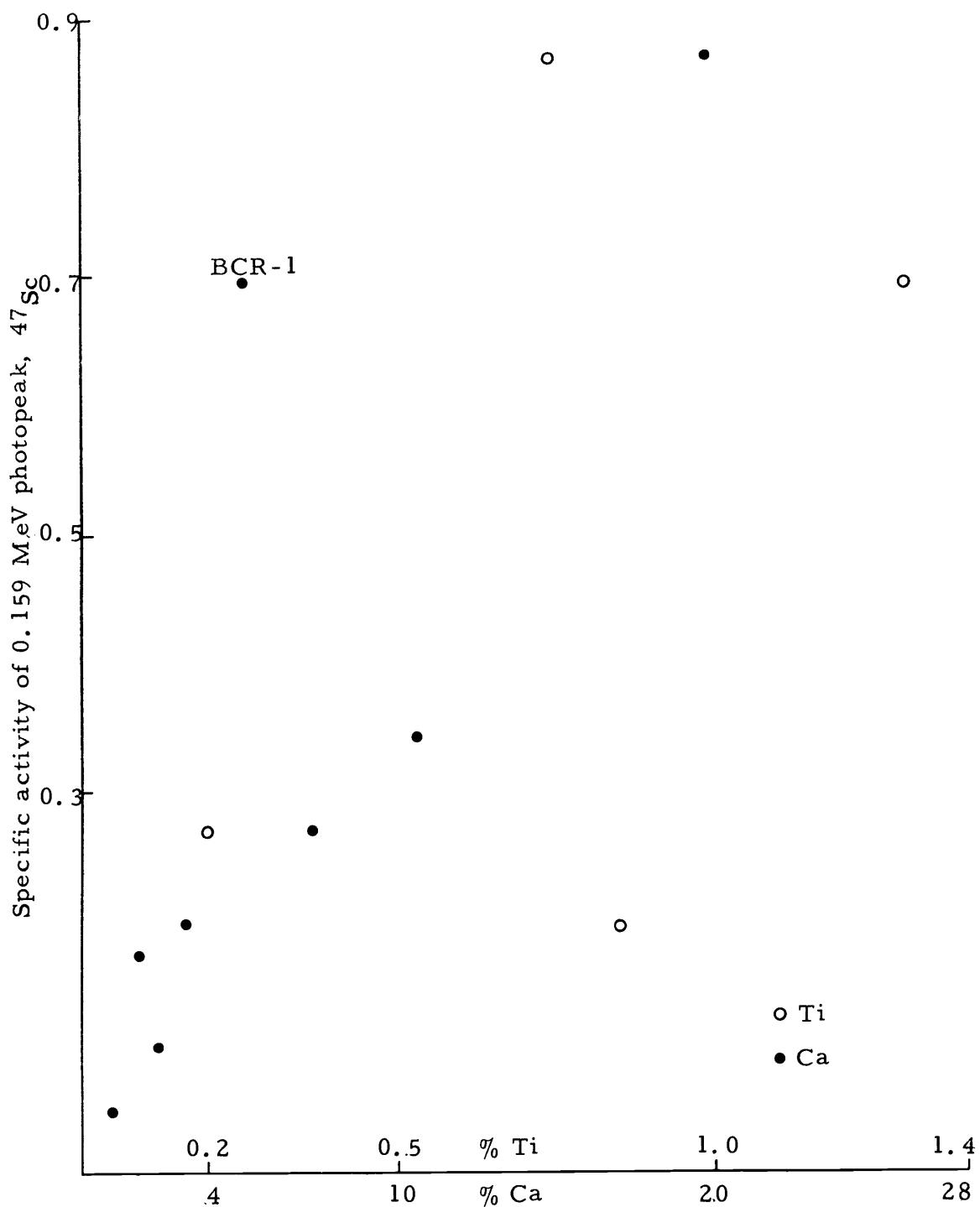


Figure 4. TRIGA activation. Determination of (Ca) via  $^{47}\text{Sc}$ .

Figure 5, which indicates negligible Ti contribution to the  $^{47}\text{Sc}$  activity. Error bars are given for the points with the most uncertainty.

The plot in Figure 5 was derived from the following equation:

$$\text{specific activity} = \frac{\text{(photopeak area, sec}^{-1})}{(\text{sample wt, mg})(\% \text{Ca})(^{60}\text{Co activity})(\text{decay correction})}$$

$$\text{decay correction} = \frac{\lambda_S}{\lambda_S - \lambda_C} (1 - e^{-\lambda_C T}) e^{-\lambda_C t} - \frac{\lambda_C}{\lambda_S - \lambda_C} (1 - e^{-\lambda_S T}) e^{-\lambda_S t}$$

where: S subscripts denote  $^{47}\text{Sc}$

C subscripts denote  $^{47}\text{Ca}$

T=irradiation time

t=decay time from EOB

The decay correction was normalized in the calculation to 1.00 for a convenient time.

From Figure 5, an average of all values plotted, excluding BCR-1 and G-2, gives  $S.A._{\text{Ca}} = 0.47$ , with a maximum error of  $\pm 15\%$  indicated by the close scatter of points about this value.

An examination of Figures 3 and 4 reveals no correlation of the  $^{47}\text{Sc}$  activity with the Ti content, even though equal activities from Ca and Ti are expected for a Ca/Ti ratio of 8 for the activation at the Missouri reactor ( $\phi_{\text{th}}/\phi_f \sim 4$ ). Large error limits ( $\pm 30\%$ ) are therefore ascribed to the Ca abundances calculated from the  $^{47}\text{Sc}$  activity.

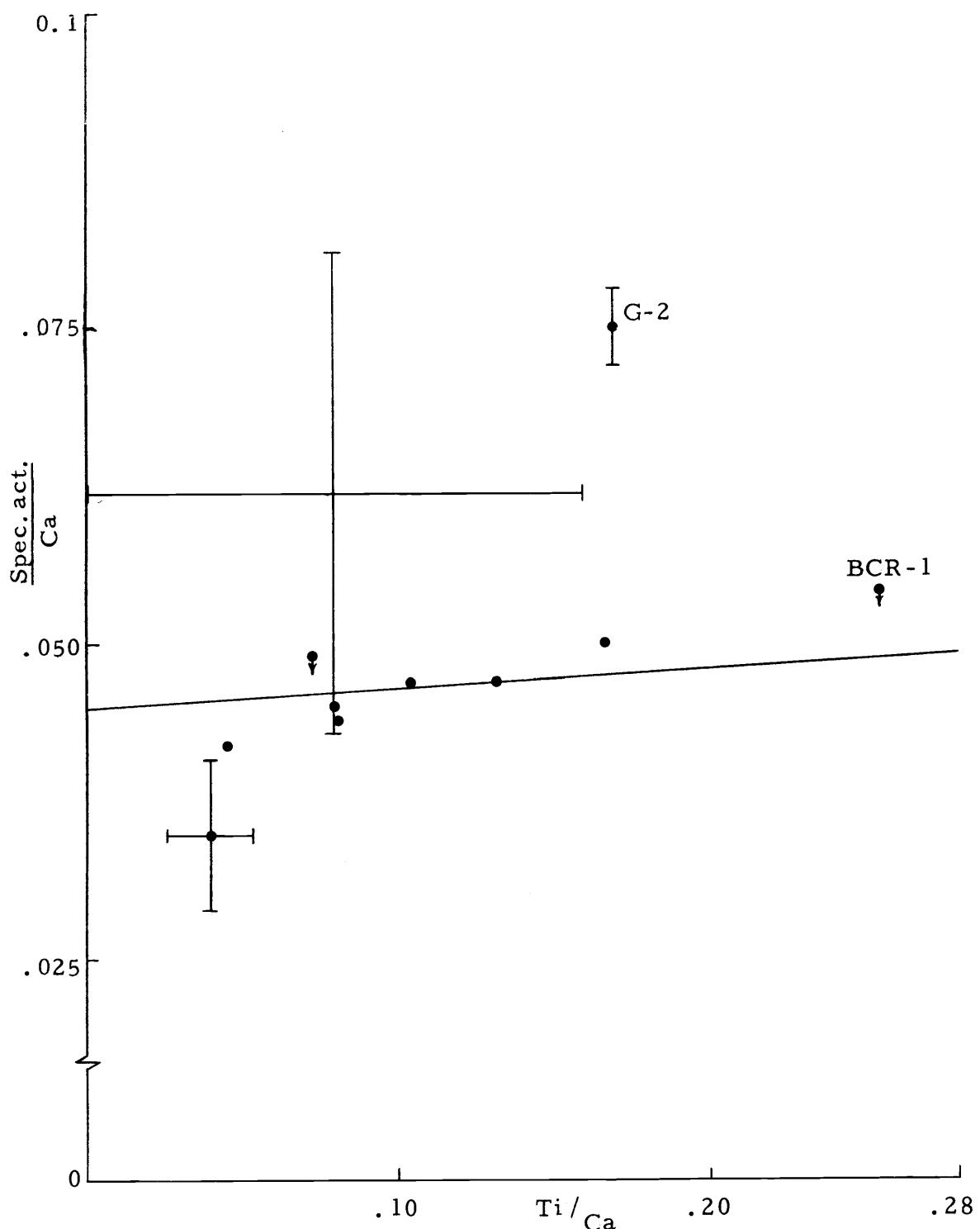


Figure 5. Determination of S.A.  $_{\text{Ca}}$  for  $^{47}\text{Sc}$  activity from Missouri activation.

Since the 317 MeV photopeak of  $^{192}\text{Ir}$  and the 320 KeV photopeak of  $^{51}\text{Cr}$  could not be completely resolved, the total area of both photopeaks was calculated by the baseline method. A correction for the  $^{192}\text{Ir}$  contribution was applied by adding the areas of the 295, 397, and 468 KeV peaks and multiplying by a factor calculated from these same areas and the 317 KeV peak area of the standard. Generally the  $^{192}\text{Ir}$  contribution to the total area was < 10%, but in one case, (601), it was over 95%, thus resulting in a large uncertainty in the Cr abundance. Contributions to the total photopeak area by  $^{192}\text{Ir}$  of 85% for chondrule 335, 34% for 307 and 111 and 31% for 506 were also noted. All other 317 KeV  $^{192}\text{Ir}$  contributions amounted to < 25% of the total area, giving very reliable Cr abundances.

The error limits other than counting statistical error for all elements in this work are: Al,  $\pm 2\%$ ; Na and Mn,  $\pm 5\%$ ; Ca, Ti and V,  $\pm 10\%$  (Ca  $\pm 30\%$  by  $^{47}\text{Sc}$ ); Ir, Ni, Sm  $\pm 20\%$ ; and Fe, Cr, Co, Sc, Eu  $\pm 10\%$ .

Table 7. Abundance in individual chondrules of the Allende meteorite.

Identification No.	Mass, mg	(g)														
		Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
116	.193	0.70 ±.01	1.86 ±.04	1.8 ±0.4	21.5 ±.3			0.375 ±.003	1020 ±20	12.0 ±0.2	266 ±3	0.64 ±.06	.34 ±.08		.97 ±.04	
111	.622	1.05 ±.01	4.65 ±.05	6.1 ±0.6	C	40.9 ±.6	0.24 ±.09	330 ±20	0.339 ±.004	690 ±20	12.2 ±0.3	399 ±6	1.05 ±.01	.79 ±.20	2.5 ±0.1	
112	.712	0.31 ±0.004	3.93 ±.05	4.8 ±0.4	C	32.5 ±.4	0.22 ±.08	210 ±20	0.467 ±.003	350 ±10	7.3 ±0.1	59 ±1	0.12 ±.05	.86 ±.13	.35 ±.08	.07 ±.02
109	.863	0.13 ±.003	0.76 ±.02	0.8 ±0.2	14.3 ±.2			0.181 ±.001	330 ±10	4.2 ±0.7	107 ±1	0.26 ±.02	.04 ±.06			
115	.951	0.50 ±.006	1.72 ±.03	1.7 ±0.5	12.5 ±.3			0.421 ±.003	820 ±20	10.8 ±0.2	408 ±5	0.88 ±.09	.30 ±.14		.71 ±.04	
105	1.09	1.18 ±.01	4.73 ±.07	1.6 ±0.8	C	17.1 ±.3		190 ±40	0.635 ±.004	1790 ±40	5.9 ±0.2	166 ±3	0.34 ±0.06	.90 ±.25	.18 ±.04	.17 ±.04
108	1.36	0.83 ±.01	2.20 ±.04	2.1 ±0.5	20.1 ±.3			0.426 ±.003	1130 ±20	8.1 ±0.2	141 ±2	0.29 ±.05	.33 ±.14		.33 ±.04	
117	1.60	0.55 ±.007	2.10 ±.03	1.7 ±0.4	14.2 ±.3			1.148 ±.007	860 ±20	14.2 ±0.3	812 ±8	2.01 ±.08	.49 ±.09		.71 ±.04	
107	2.10	0.98 ±.01	2.31 ±.04	1.9 ±0.4	18.1 ±.3			1.118 ±.006	1590 ±30	9.4 ±0.2	323 ±4	0.81 ±.05	.43 ±.08		.28 ±.02	0.15 ±.10
101	4.70	0.42 ±.005	3.11 ±.06	2.6 ±0.6	23.9 ±.3			0.485 ±.004	880 ±20	9.1 ±0.2	146 ±3	0.37 ±.06	.51 ±.34		.08 ±.04	

Table 7 continued.

Identification		(g)														
No.	Mass, mg	Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
102	12.19	0.33 ±.002	5.12 ±.07	7.2 ±.3	C	5.6 ±.3	0.20 ±.08	210 ±10	0.362 ±.003	1070 ±20	11.7 ±0.3	520 ±7	1.32 ±.03	.46 ±.03	.40 ±.04	0.11 ±.07
Avg <sub>1</sub> (100)	2.40	0.63	2.95	2.9	20.1	0.21	235	0.54	960	9.5	304	0.73	.50	.27	0.57	.13
Avg <sub>2</sub> (100)		0.49	4.00	4.6	13.8	0.20	210	0.50	1040	10.4	387	0.96	.48	.20	0.38	.12
Median (100)	1.09	0.55	2.31	1.9	18.1	0.21	210	0.43	880	9.4	266	0.64	.46	.27	0.33	.13
407B	.178	0.49 ±.006	1.30 ±.03	8.2 ±1.2	18.0 ±1.4			0.381 ±.003	940 ±20	12.6 ±.2	431 ±5	1.04 ±.06	.34 ±.08	.94 ±.04	3.2 ±0.1	
421	.333	0.54 ±.006	1.40 ±.03	1.6 ±0.3	18.8 ±.3			0.261 ±.002	870 ±20	16.8 ±.2	192 ±3	.40 ±.04	.48 ±.06	.26 ±.02	0.42 ±.09	
407A	.975	1.13 ±.01	2.36 ±0.04	2.2 ±0.6	33.0 ±.4			0.386 ±.003	1150 ±20	7.9 ±.2	101 ±2	.20 ±.07	.55 ±.15	1.25 ±.04		
410	1.10	0.38 ±.005	2.02 ±.03	1.8 ±0.5	15.8 ±.3			0.487 ±.003	960 ±20	11.2 ±.2	493 ±6	1.18 ±.07	.46 ±.15	.50 ±.04		
402	1.22	0.66 ±.01	2.49 ±.03	6.8 ±1.1	19.3 ±.3			0.328 ±.003	700 ±20	8.6 ±.2	318 ±4	.84 ±.06	.60 ±.09	1.1 ±.1	0.27 ±.15	
416	1.55	0.54 ±.01	1.53 ±.03	0.9 ±0.4	12.8 ±.2			0.639 ±.003	2300 ±30	8.0 ±.1	51 ±1		.14 ±.10			
413	2.22	0.27 ±.003	1.27 ±.03	0.95 ±0.3	12.9 ±.2			0.357 ±.002	710 ±10	12.0 ±.2	420 ±4	1.00 ±.05	.30 ±.11	.24 ±.02		

Table 7 continued.

Identification		No.	Mass, mg	Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
		405	2.36	0.24 ±.003	1.78 ±.03	1.6 ±0.3	14.2 ±.2		0.587 ±.003	2100 ±30	13.4 ±.1	52 ±1	.07 ±.02	.32 ±.03	.13 ±.03	.09 ±.02		
		403	5.37	0.81 ±.006	1.87 ±.06	1.8 ±0.5	12.6 ±.3		0.369 ±.003	600 ±20	13.0 ±.2	320 ±5	.86 ±.06			.10 ±.04		
		411	5.94	0.98 ±.01	2.70 ±.03	2.4 ±0.6	25.9 ±.4		0.449 ±.004	1510 ±30	9.5 ±.2	315 ±4	.85 ±.07	.59 ±.29		.44 ±.44		
	Avg <sub>1</sub>	(400)	2.12	0.60	1.87	2.8	18.3		0.42	1180	11.3	269	0.66	.40	.13	0.49	1.30	
	Avg <sub>2</sub>	(400)		0.69	2.05	2.1	18.2		0.44	1210	11.1	277	0.70	.36	.13	0.34	0.60	
	Median	(400)	1.48	0.54	1.83	1.8	16.9		0.38	950	11.6	317	0.84	.40	.13	0.35	0.42	
	(a)	BCR-1				4.8 ±0.8	30.9 ±.4		.0021 ±.0011		9.6 ±0.2	39 ±2		5.4 ±0.9	1.7 ±0.3			
	(b)			2.60 ±.03		5.5 ±0.5	C ±.5	34.7 ±.5	1.25 ±.14	410 ±20	.0033 ±.0016	1400 ±20	10.0 ±0.3	35 ±3	6.7 ±0.1	1.5 ±0.7		
	(lit)			2.57	7.62	5.09	33	1.30	384	.0016	1350	10.1	35	.0015	7.3	2.1	.0007	.0007
	(a)					2.2 ±0.4	3.3 ±.1			.0010 ±.0003		2.05 ±0.5	5.2 ±0.7		7.0 ±0.2	1.5 ±0.2		
	G-2 (b)			1.66 ±.02			3.6 ±1.2			1110 ±20	1.8 ±0.2				7.1 ±0.1	0.6 ±0.3		
	(lit)			1.64	8.02	1.23	3.5	.21	37	.0009	1290	1.96	4.9	.00064	8.3	1.5	.0007	.0011

Table 7 continued.

Identification		(g)														
No.	Mass, mg	Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
210	.139	0.19 ±.004	0.61 ±.03	0.9 ±0.2	8.9 ±.2			0.170 ±.001	330 ±10	4.3 ±0.1	38 ±1		.13 ±.04			
209	.476	0.87 ±.01	4.62 ±.06	3.9 ±0.5	C ±.4	29.6 ±.09	0.32 ±.09	130 ±20	0.325 ±.002	610 ±20	4.1 ±0.1	102 ±2	0.35 ±.04	.73 ±.10	0.32 ±.07	1.4 ±0.1
218	.830	0.59 ±.01	1.74 ±.03	2.5 ±0.6	15.0 ±.3			0.360 ±.003	830 ±20	8.6 ±0.2	314 ±4	0.78 ±.08	.54 ±.13		.35 ±.04	
212	.951	0.58 ±.01	1.88 ±.03	2.5 ±0.6	19.5 ±.4			0.486 ±.004	1010 ±20	13.2 ±0.3	626 ±7	1.50 ±.09	.46 ±.12		1.1 ±0.1	0.38 ±.18
214	1.20	0.20 ±.003	0.82 ±.02	1.8 ±0.5	9.1 ±.2			0.562 ±.003	1060 ±20	12.0 ±0.2	338 ±4	0.82 ±.06			.31 ±.04	0.84 ±.18
219	1.47	0.31 ±.004	0.98 ±.03	0.9 ±0.2	C ±.2	9.8 ±.06	0.07 ±.06	81 ±9	0.279 ±.002	540 ±10	6.0 ±0.1	242 ±3	0.54 ±.05	.13 ±.08		.07 ±.02
203	1.73	0.36 ±.004	1.95 ±.03	1.8 ±0.4	15.4 ±.2			0.298 ±.002	660 ±10	9.4 ±0.2	230 ±3	0.53 ±.05	.34 ±.08		.05 ±.02	
Avg <sub>1</sub>	(200) .971	0.44	1.80	2.0	15.3	0.20	105	0.35	720	8.2	270	0.66	.35	.32	0.47	0.61
Avg <sub>2</sub>	(200)	0.41	1.67	1.9	14.5	0.13	90	0.37	760	9.1	304	0.73	.32	.32	0.38	0.64
Median	(200) .951	0.36	1.74	1.8	15.0	0.20	105	0.325	660	8.6	242	0.54	.34	.32	0.31	0.61
510	.705	0.30 ±.003	0.82 ±.02	1.0 ±0.2	13.3 ±.2			0.305 ±.002	740 ±10	9.3 ±0.1	119 ±2	0.23 ±.03	.13 ±.08		.12 ±.02	0.15 ±.08

Table 7 continued.

Identification		(g)														
No.	mass, mg	Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
509	1.97	0.92 ±.01	1.98 ±.04	1.9 ±0.4	15.4 ±.2			0.678 ±.003	3790 ±40	8.9 ±0.1	73 ±2	0.16 ±.04	.45 ±.13			
504	3.70	0.69 ±.007	3.10 ±.04	2.3 ±0.7	14.1 ±.3			0.455 ±.004	1240 ±30	10.8 ±0.3	397 ±5	0.96 ±.08	.99 ±.42		.47 ±.04	
502	4.26	0.93 ±.03	7.40 ±.20	3.2 <sup>C</sup> ±0.4	18.3 ±.3	0.23 ±.13	450 ±20	0.501 ±.004	870 ±50	8.6 ±0.2	371 ±5	0.95 ±.08	1.0 ±0.4		.88 ±.04	0.81 ±.33
505	4.39	0.60 ±.01	3.50 ±.08	3.4 <sup>C</sup> ±0.3	27.1 ±.4		180 ±20	0.342 ±.004	710 ±10	6.6 ±0.2	327 ±4	0.84 ±.08	.60 ±.33		.87 ±.04	
507	4.43	0.80 ±.007	2.33 ±.05	2.0 ±0.7	18.7 ±.3			0.693 ±.005	1530 ±30	7.7 ±0.2	51 ±2	0.19 ±0.6	.48 ±.38		.98 ±.04	
506	12.58	0.29 ±.003	3.70 ±.08	3.4 <sup>C</sup> ±0.2	26.5 ±.5	0.85 ±.07	220 ±10	0.316 ±.005	620 ±10	8.9 ±0.3	481 ±8	1.28 ±.04	.59 ±.05		2.2 ±0.1	
501	16.78	1.05 ±.007	2.40 ±.04	1.8 <sup>C</sup> ±.10	16.3 ±.6		100 ±70	0.528 ±.003	3670 ±30	5.8 ±0.2	100 ±3	0.22 ±.02	.47 ±.04		.07 ±.05	0.39 ±.07
503	18.22	2.04 ±.02	9.38 ±.14	10.6 <sup>C</sup> ±1.6	57.1 ±.8		150 ±80	0.318 ±.004	850 ±20	6.0 ±0.3	227 ±5	0.56 ±.03	2.0 ±0.1		.87 ±.04	
Avg <sub>1</sub>	(500) 7.45	0.85	3.85	3.3	23.0	0.37	220	0.46	1560	8.1	238	0.60	.75		0.72	0.45
Avg <sub>2</sub>	(500)	1.09	4.94	4.7	30.1	0.35	180	0.43	1660	7.2	251	0.64	.98		0.87	0.46
Median	(500) 4.39	0.80	3.10	2.3	18.3	0.23	180	0.445	870	8.6	227	0.56	.59		0.87	0.39

Table 7 continued.

Identification		(g)														
No.	mass, mg	Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
603(d)	52.0	0.66 ± .006	1.79 ± .02	0.9 ± 0.5	10.8 C ± .2		90 ± 40	0.580 ± .00	2750 ± 10	10.0 ± 0.2	208 ± 3	0.44 ± .02	.30 ± .02	.19 ± .02	0.18 ± .04	
602	83.0	0.36 ± .003	2.50 ± .05	2.4 C ± 0.5	15.4 ± .2		90 ± 40	0.524 ± .001	1610 ± 10	10.5 ± 0.2	40 ± 1	0.065 ± .008	.42 ± .02			
601	107.0	0.16 ± .002	13.6 ± .1	19.7 C ± 0.3	133 ± 4	0.74 ± .04	710 ± 10	0.021 ± .005	26 ± 1	0.37 ± 0.13	7.6 ± 1.8		3.4 ± 0.1	1.15 ± .10	5.8 ± .1	
50(e)	1.13	0.11 ± .002	0.56 ± .02	0.45 ± .13	10.8 ± .1			0.225 ± .001	380 ± 10	4.7 ± 0.1	88 ± 1	0.18 ± .02			.035 ± .02	
335	.230	1.53 ± .04	17.4 ± .2	12.1 C ± 1.4	117 ± 2	1.25 ± .17	974 ± 50	0.070 ± .009	360 ± 10	5.8 ± 0.3	76 ± 5		3.0 ± 0.4		5.6 ± 0.2	
340	.255	0.26 ± .004	1.05 ± .03	1.6 ± 0.3	11.7 ± .2			0.459 ± .002	1020 ± 20	13.8 ± 0.2	292 ± 3	0.61 ± .03	.16 ± .08		.47 ± .02	0.65 ± .09
313	.258	0.20 ± .003	0.73 ± .02	0.7 ± 0.2	10.8 ± .1			0.172 ± .001	240 ± 10	3.6 ± 0.1	43 ± 1	0.10 ± .02	.13 ± .04			
303	.367	0.36 ± .005	1.11 ± .02	0.94 ± 0.2	8.8 ± .1			0.206 ± .001	750 ± 10	8.6 ± 0.1	173 ± 2	0.39 ± .03	.29 ± .03		.09 ± .02	
342	.505	1.05 ± .02	4.41 ± .06	3.6 C ± .6	17.8 ± .2	0.29 ± .11	320 ± 20	0.482 ± .003	1260 ± 30	15.6 ± 0.2	606 ± 6	1.48 ± .05	.47 ± .12		.45 ± .02	
315	.533	1.15 ± .01	3.58 ± .04	3.2 ± 0.6	33.7 ± .4			0.355 ± .003	660 ± 20	8.2 ± 0.2	198 ± 2	0.46 ± .06	.82 ± .16	.36 ± .08	1.06 ± .04	

Table 7 continued.

Identification		(g)														
No.	mass, mg	Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
306	.696	0.63 ±.01	2.03 ±.03	1.4 ±0.3	C 15.7 ±.2	0.23 ±.08	130 ±10	0.563 ±.003	1530 ±20	10.9 ±0.1	44 ±1		.38 ±.07		.66 ±.02	
319	1.05	0.57 .007	1.77 ±.04	1.3 ±0.3	16.2 ±.2			0.713 ±.003	2190 ±20	15.0 ±0.2	55 ±1		.29 ±.11		.10 ±.02	
312	1.07	0.41 ±.006	1.79 ±.04	2.2 ±0.5	17.0 ±.3			0.955 ±.004	3820 ±30	13.7 ±0.2	64 ±2		.44 ±.11			
305	1.09	0.55 ±.006	1.23 ±.02	1.2 ±0.2	11.7 ±.2			0.248 ±.002	560 ±10	8.7 ±0.1	184 ±2	0.44 ±.02	.30 ±.06	.11 ±.03	.05 ±.02	
318	1.42	0.70 ±.01	2.45 ±.03	1.9 ±0.5	16.5 ±.3			0.432 ±.003	970 ±20	11.8 ±0.7	442 ±5	1.15 ±.06	.35 ±.13		.56 ±.04	
320	2.12	0.40 ±.006	2.29 ±.03	1.8 ±0.3	17.8 ±.2			0.389 ±.002	920 ±10	9.5 ±0.1	537 ±5	1.40 ±.03	.37 ±.08		.72 ±.02	
339	2.34	0.77 ±.01	1.96 ±.04	1.4 ±.4	C 21.3 ±.3	0.18 ±.15	90 ±20	0.309 ±.002	760 ±20	5.9 ±0.1	93 ±2	0.19 ±.04	.33 ±.07		.05 ±.02	0.38 ±.10
321	2.40	0.63 ±.007	1.60 ±.03	1.6 ±0.3	17.4 ±.2			0.282 ±.002	780 ±10	7.3 ±0.1	164 ±2	0.38 ±.04	.40 ±.08	.13 ±.03	.47 ±.02	
328	2.87	0.58 ±.006	1.74 ±.02	1.7 ±0.3	13.7 ±.2			0.328 ±.002	720 ±20	7.5 ±0.1	84 ±1	0.14 ±.03	.33 ±.06		.05 ±.02	0.19 ±.18
334	3.86	0.24 ±.05	2.54 ±.03	1.6 ±0.6	18.2 ±.3			0.611 ±.004	2000 ±40	13.2 ±0.2	50 ±2		.61 ±.39			

Table 7 continued.

Identification No.		(g)														
	mass, mg	Na, %	Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
307	3.96	0.33 ± .004	3.64 ± .07	2.4 ± 0.7	26.2 ± .4			0.260 ± .004	570 ± 70	10.6 ± 0.2	408 ± 5	1.06 ± .09	.66 ± .41		1.7 ± 0.1	
333	5.78	0.74 ± .006	1.79 ± .03	1.4 ± 0.5	13.4 ± .3			0.405 ± .004	1620 ± 30	17.7 ± 0.3	533 ± 6	1.27 ± .08			.17 ± .04	
301	15.60	0.55 ± .005	2.06 ± .05	1.9 ± 0.6	15.6 ± .4			0.546 ± .003	2040 ± 20	13.3 ± 0.3	72 ± 3	0.15 ± .02	.38 ± .04		.10 ± .03	0.15 ± .07
311	19.13	0.48 ± .004	2.54 ± .10	2.9 ± 0.9	18.6 ± .4			0.397 ± .004	690 ± 10	16.3 ± 0.4	877 ± 10	2.24 ± .04	.47 ± .05		.94 ± .06	0.17 ± .10
Avg <sub>1</sub>	(300) 3.28	0.61	2.88	2.3	22.0	0.49	378	0.41	1170	10.8	250	0.60	.52	.20	.67	0.31
Avg <sub>2</sub>	(300)	0.53	2.32	2.1	17.8	0.27	180	0.44	1270	13.0	402	1.00	.43	.16	0.52	0.18
Median	(300) 1.25	0.56	2.00	1.6	16.7	0.26	225	0.393	850	10.7	178	0.38	.37	.13	.31	0.19
<hr/>																
Total <u>Chondrules (h)</u>																
Avg <sub>1</sub>	3.24	0.62	2.70	2.6	20.1	0.31	250	0.43	1120	9.8	261	0.64	.50	.22	.59	0.55
Avg <sub>2</sub>		0.74	3.40	3.4	21.5	0.31	180	0.44	1350	10.3	326	0.82	.61	.18	.60	0.27
Median	1.47	0.57	2.03	1.8	16.5	0.21	190	0.389	870	9.4	198	0.44	.43	.25	0.33	0.32

Table 7 continued.

Identification No.	mass, mg	Na, %	(g) Al, %	Ca, %	Sc, ppm	Ti, %	V, ppm	Cr, %	Mn, ppm	Fe, %	Co, ppm	Ni, %	Sm, ppm	Eu, ppm	Ir, ppm	Au, ppm
<u>Chondrules (I)</u>																
.1-.5 mg	.255(f)	0.61	3.51	3.3	27	.62	410	0.27	680	8.9	170	0.40	.63	.32	1.05	1.14
.5-1 mg	.712(f)	0.66	2.35	2.6	22	.24	240	0.39	840	9.6	270	0.63	.46	.35	.74	0.28
1-2 mg	1.22(f)	0.55	1.86	1.9	15	.10	130	0.54	1440	9.7	251	0.60	.36	.14	.27	0.55
2-6 mg	3.86(f)	0.65	2.78	2.1	19	.19	270	0.46	1160	10.4	280	0.70	.50	.13	.47	0.45
12-20 mg	16.19(f)	0.85	4.25	4.6	24	.34	160	0.41	1520	10.4	382	0.97	.76	.73	0.21	

avg<sub>1</sub> =  $\Sigma$  abundances/number of chondrules

avg<sub>2</sub> =  $\Sigma$  mass of element/total mass of chondrules

(a) Missouri Irradiation

(b) TRIGA irradiation, Na and Mn abundances listed under G-2 are for W-1

(c) Ca determined via <sup>49</sup>Ca. All others via <sup>47</sup>Sc

(d) La: 5.5  $\pm$  1.0 ppm

(e) Chondrule, fragment origin unknown

(f) median value

(g) see Table 4

(h) All averages do not include chondrules 601, 602, and 603. For the population standard deviation of these averages, see Table 8, which includes these chondrules.

(i) All abundances are mass weighted, i.e. avg<sub>2</sub> values.

### III. RESULTS AND DISCUSSION

#### Chondrule Average Abundances and Range

Computation of the number weighted and mass weighted averages ( $\text{avg}_1$  and  $\text{avg}_2$ , see Table 7 footnotes for definition) for the analytical results of all 61 chondrules are given in Table 8. The population standard deviation is also given, verifying the large variation in elemental abundances among the chondrules.

Table 8. Average abundances in the Allende meteorite.

Element	Clarke et al (1970)		Chondrules This Work		Abundance Variation
	Avg Bulk	Avg <sub>2</sub> Chondrule	Avg <sub>1</sub>	Avg <sub>2</sub>	
Na(%)	0.33	0.61	0.61 $\pm$ 0.36	0.52 $\pm$ 0.37	0.11- 2.0
Al(%)	1.7	2.94	2.9 $\pm$ 2.8	5.3 $\pm$ 3.7	0.44-17.3
Ca(%)	1.9	2.9	2.9 $\pm$ 2.8	7.1 $\pm$ 4.0	0.45-20
Sc(ppm)	11		22 $\pm$ 21	44 $\pm$ 30	5.6 -133
Cr(%)	0.37	0.32	0.43 $\pm$ 0.21	0.38 $\pm$ 0.21	0.02-1.15
Mn(ppm)	1450	1100	1140 $\pm$ 810	1280 $\pm$ 820	240 -3820
Fe(%)	22	8.5	9.7 $\pm$ 3.6	8.1 $\pm$ 3.9	0.37-17.7
Co(ppm)	640	200	250 $\pm$ 200	180 $\pm$ 210	8 -880
Ni(%)	1.4	0.56	0.61 $\pm$ 0.51	0.44 $\pm$ 0.54	<0.07-2.2
Sm(ppm)	0.29	0.61*	0.54 $\pm$ 0.58	1.15 $\pm$ 0.84	<0.04-3.4
Ir(ppm)	0.71		0.66 $\pm$ 1.08	1.6 $\pm$ 1.4	<0.04=5.8

\* Zellmer et al. (1970)

The averages for all chondrules in Table 7 do not include those chondrules obtained from Dr. Mason, since these chondrules were unusual in size and not randomly selected. The large effect of these chondrules (601, 602, and 603) on the number and mass averages, especially the latter, are noted by comparison of the total averages in Table 7 and 8. The mass of chondrule 601 is 25% of the total mass of all chondrules, and the three together amount to 57% of the mass of all 61 chondrules. It is therefore felt that the best representation of the average abundances in the Allende chondrules are the values listed in Table 7. The differences of the averages in Table 7 with those in Table 8 point out that with 61 (mostly small) chondrules the sample size is still too limited to establish average chondrule abundances accurate to  $\pm 20\%$ . Furthermore, according to Zellmer (1971), a large fraction of the chondrules may be of the highly friable variety, which are by nature difficult to remove from the matrix. Only 2 of the 61 chondrules analyzed (509 and 510) are definitely chondrules of this type. Only petrographic studies can establish the true relative numbers of the textural varieties of chondrules.

A comparison of the number average ( $\text{avg}_1$ ) and the mass weighted average ( $\text{avg}_2$ ) of the elemental abundances listed in both Tables 7 and 8 indicates a significant positive mass-abundance correlation for the elements Al, Ca, Sc, and Sm. The median abundance (Table 7) indicates that the abundances are Maxwellian distributed,

which is certainly to be expected from abundances showing mass-abundance correlations.

From Table 7, the average chondrule abundances within each fragment of the Allende meteorite are highly variable as well. It is not known whether there is a true variation of abundances among the individual fragments or what effect the contribution of a large chondrule with an extreme abundance may have on these rather limited sample sizes. Note that for fragment 3, from which 20 chondrules were selected for analysis, the agreement with the total average chondrule abundances (excluding the 600 series) is excellent. On the other hand, the exclusion of the abundances from fragment 5 would have changed the total average abundances considerably. If the Allende meteorite is to be used as a rock standard, care must be taken to insure the procurement of representative samples.

Schmitt et al. (1965) and Schmitt and Smith (1966) determined average abundances for Na, Sc, Co, Mn, Cr and Fe in chondrules from six C3 chondrites. Although classified as C2 chondrites by Van Schmus and Wood (1967), Kaba and Mokoia have been included as C3 chondrites on chemical grounds. The range of average abundances in chondrules from these six C3 chondrites is given in Table 9 and compared with the Allende avg<sub>1</sub> from Table 7.

Table 9. Average elemental abundances (ppm) in chondrules from ordinary, C3, and Allende chondrules.

Elements	Nine Ordinary Chondrites, Pet. Groups 3 & 4	Seven Ordinary Chondrites, Pet. Groups 5 & 6	Six C3 Chondrites	Allende This Work (avg <sub>1</sub> )
Na	5900-8400	7100-8200	2300-6600	6200
Sc	8.5-16.5	10.6-18.4	10-14	20
Cr	2400-4000	2000-3900	3300-4000	4300
Mn	1900-3200	2600-3000	800-1400	1120
Co	40-260	30-125	300-470	260
Fe(%)	5.9-11.4	8.2-15.6	6.2-9.6	9.8

#### Rare Earth Element (REE) Abundances

A mean Sm/Eu ratio of 2.7 with a range of  $2.3 \pm 0.5$  to  $5.0 \pm 1.8$  is found (the ratio of 5.0 is anomalously high) for the eight chondrules analyzed for Eu at this time. This ratio of 2.7 matches the ratio of 2.7 found in the Allende bulk (see Table 2). The type-a chondrule analyzed by Zellmer *et al.* (1970) and 601, both obtained from the same source, are undoubtedly fragments of the same 1.5g chondrule found by Clarke *et al.* (1970). The Sm and Eu abundances (ppm) in these fragments found by Zellmer *et al.* (1970) and from this work (601, Table 7) are  $2.82 \pm 0.14$  and  $1.19 \pm 0.06$  vs.  $3.4 \pm 0.1$  and  $1.15 \pm 0.10$ , respectively, yielding Sm/Eu ratios of

$2.4 \pm 0.2$  and  $2.9 \pm 0.2$ . Zellmer et al. (1970) also reports a mean Sm/Eu ratio of 2.7 for a 29-chondrite sample and  $2.9 \pm 0.2$  for "ordinary" Allende chondrules. The constancy of the Sm/Eu ratio in the Allende chondrules despite significant fractionation of other elements indicates lack of significant fractionation of Eu from the remaining REE and thus a probable oxidation number of +3 for Eu during the formation of chondrules.

The Relationship Between the Chondrules and  
Matrix of the Allende Meteorite

By comparing the average chondrule abundances in either Table 7 or 8 with the bulk chondritic abundances, the following chondrule/bulk abundance relations are found:

enriched	chondrules/matrix	Al, Ca, Sc, Ti, V, Sm, Eu, Na
similar	chondrules/matrix	Ir, Mn, Cr
depleted	chondrules/matrix	Fe, Co, Ni

The observed pattern of enrichment or depletion of abundance in chondrules/matrix is very similar in the 22 chondrites for which the data in Table 9 was taken. Only Na exhibits a variable character, being slightly depleted in chondrules from Kaba, Mokoia and Vigarano (all listed as C3 chondrites). Schmitt and Smith (1966) found Na slightly enriched in chondrules from all other C3 and ordinary chondrites, and strongly depleted in all C2 chondrules. Note that

Kaba and Mokoia are classified as C2 chondrites by Van Schmus and Wood (1967).

A recent petrographic study by Green et al. (1971) has provided strong evidence that the Allende chondrules have not chemically interacted with the matrix, and that the chondrules are now in the same condition in which they existed at the time of the formation. Radiation damage, apparently from the protosun, is apparent in the chondrules but is completely lacking in the matrix. Accretion of chondrules and matrix must have occurred at low enough temperatures ( $<500^{\circ}\text{K}$ ) so that the radiation damage was not annealed out. Furthermore, Fireman et al. (1971) report greater ages for Allende chondrules ( $4.4 \times 10^9 \text{ y}$ ) compared to whole rock ( $3.4 \times 10^9 \text{ y}$ ).

#### Correlations Among Chondrule Abundances

A list of correlation coefficients in Table 10 for ten of the analyzed elements reveals some striking relationships among the abundances found in the individual chondrules. For a sample size of 61, correlation coefficients (positive or negative) are significant at the following confidence levels: .25, 95%; .33, 99%; .41, 99.9%.

Table 10. Correlation coefficients of abundances in individual chondrules.

From Table 10, the following associations of elements is implied.

Table 11. Elemental associations inferred from correlation coefficients of abundances.

Group	Degree of Correlation	C. C.	Elemental Abundances Correlated
Ia	Excellent	$\geq 0.84$	Al, Ca, Sc, Ti, V, Sm, Eu
b			Include Ir in Ia
c			Co, Ni
IIa	Good	$\geq 0.5$	Cr, Mn
b			Include Fe in Ic
IIIa		$\geq 0.33$	Include Na in Ia
b			Include Fe in IIa
c			Include Ir in Ic
IVa	Anticorrelations		Ia with IIa
b			Ib with Fe
c			Ia with Ic

Condensation from solar gas and production from existing solid material by melting process (for example, the impact ignimbrite theory of Fredriksson *et al.*, 1970 and the lightning discharge theory of Whipple, 1966) are two of many possible models describing the origin of chondrules.

This study indicates that a magmatic process could not have been

operative in the formation of the Allende chondrules. It would be most difficult to explain the high degree of association of the strongly lithophilic elements Al, Sc and Sm with the strongly siderophilic element Ir, indicated by the high correlation coefficients of their abundances, by a magmatic process. Furthermore, magmatic processes predict the late appearance of the REE and the early appearance of Ca, in contradiction with the high degree of correlation of Ca and Sm abundances observed. These associations are, however, not inconsistent with a condensation model.

A condensation model predicts a positive mass-abundance correlation for all elements appearing early in the condensation history. Consider two chondrules formed early in a condensation sequence, one having accumulated a large mass of high temperature condensate, and the other a small amount. The condensation process continues as the temperature decreases, and the chondrules begin to incorporate elements appearing later in the condensation process. The fractional, or ppm incorporation of this later appearing condensate will be  $dm/m$ . The added amount of later condensate,  $dm$ , will be dependent on the surface area of the chondrule, or on  $r^2$  ( $r =$  chondrule radius), while the chondrule mass depends on  $r^3$ . Thus the fractional, or ppm incorporation of later appearing condensate will be larger for the smaller chondrule, being dependent on  $1/r$ . If there is a significant accumulation of lower temperature

condensate (i.e., silicate), then larger chondrules will be enriched in high temperature condensate (Ca-Al minerals) relative to smaller chondrules. Such a correlation of mass and fraction of high temperature condensate is not expected to be strong, due to the varying conditions of temperature and pressure undoubtedly present during such a condensation process. Since the minerals spinel, gehlenite, anorthite and fassaite are early condensates from a nebula of solar composition, Ca, Ti and Al will be enriched in the high temperature condensate. That  $\text{avg}_2$ , the mass weighted average abundance is significantly larger than  $\text{avg}_1$ , the number average abundance for these elements is evidence that a mass-abundance correlation exists among these elements. Thus the positive correlation of the abundances of these elements with chondrule mass is supportive evidence for a condensation process.

The Condensation of Chondrules from a Cooling  
Gas of Solar Composition

One of the current hypothesis for the origin of chondrites and chondrules was proposed by Wood (1958, 1963) and was developed further by Larimer and Anders and published as a four fold series of papers entitled "Chemical Fractionations in the Meteorites" (Larimer, 1967; Larimer and Anders, 1967; Larimer and Anders, 1970; and Keays et al., 1971). The most recent suggestions

concerning the origin of chondrites and chondrules are presented by Blander and co-workers (Blander and Katz, 1967; Blander and Abdel-Gawad, 1969; and Blanders, 1971). These authors propose the constrained equilibrium theory for the origin of chondrules.

Both theories predict the condensation order of the elements from a cooling gas of solar composition. Calculations by Lord (1965) taking into account molecular equilibria present in a cooling gas cloud of cosmic elemental abundances resulted in a condensation order of minerals and metals and descriptions of the relative importances of these condensates in determining the amount of a given condensed element. These calculations have been expanded upon in the "Chemical fractionations in meteorites" series of papers. Larimer (1967) considers two condensation paths - fast and slow cooling of the gas. In the first case, condensation of the various species are independent of one another, i. e., each species condenses as a pure material. All compounds of significance containing the element of interest must be considered. Calculations of equilibrium pressures of each compound are made from free energies, the molecular equilibria obtained from the JANAF (joint army, navy, air force) Tables, and with the simplifying assumption that the mole fraction of  $H_2$  in the nebular gas is unity. The temperature at which the equilibrium vapor pressure of the species of interest becomes equal to the partial pressure in the gas of solar composition is the

incipient condensation temperature of the element. In the latter case, the cooling of the gas is slow enough to allow formation of solutions. Early condensation for the case of slow cooling will be governed by a Henry's Law type of expression for the equilibrium vapor pressure. The effect of slow cooling is to broaden the temperature range of condensation, as well as to raise the temperature of initial condensation. Late condensation will be controlled by the rate of cooling of the condensate, as well as by grain size and diffusion coefficients, since the interior of the grain may not be participating in the solution equilibrium. The results of such calculations is shown in Figure 6 taken directly from Larimer (1967). Both models of condensation predict a set of refractory minerals as the first condensate from the solar nebula, containing most of the Al, Ca, and Ti as well as part of the Si and Mg. The iron group metals are predicted to condense next, followed by olivines and pyroxenes (which also contain some of the Fe). Finally a group of volatile elements, Pb, Bi, Ti and In are expected to condense at very low temperatures.

Any theory which attempts to explain the production of chondrules must resolve the dilemma of how chondrules formed from liquid drops, as evidenced by the presence of glass in chondrules, while the total gas pressures and temperatures predict direct condensation of solar gas to a solid. Wood (1963) adopts the explanation that chondrules were formed when shock waves from T-Tauri eruptions

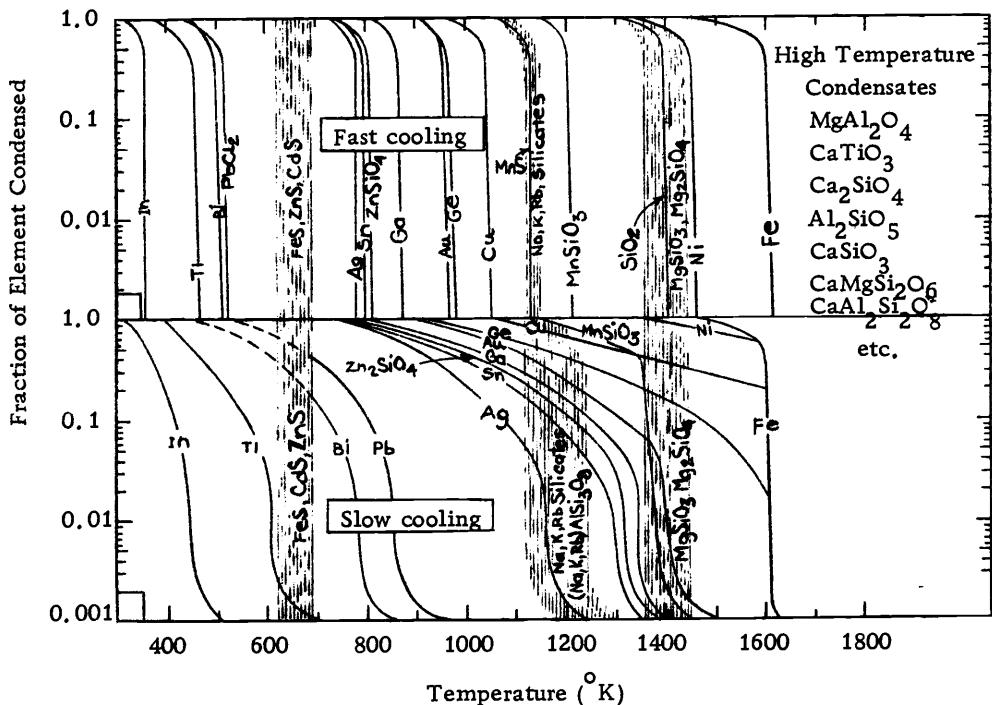


Figure 6. Condensation sequence of a gas of solar composition, at a total pressure of  $6.6 \times 10^{-3}$  atm. First major constituent to condense is nickel-iron, followed by magnesium and alkali silicates. By the time the temperature has fallen to 1100°K, more than 90% of all condensable matter has condensed, the principal straggler being sulfur. (a) "Fast cooling" sequence assumes deposition of thin surface coatings on preexisting grains, with no diffusion to the grain interior. (b) "Slow cooling" sequence assumes diffusion of condensate to grain interior, with solid-solution formation and consequent lowering of vapor pressure.

In a massive solar nebula with cooling times of  $10^2 - 10^4$  yr the slow-cooling sequence would apply for all elements down to Ag, the remaining ones (Pb, Bi, In, Tl) condensing more or less according to the fast-cooling sequence.

from the protosun produced transient pressures ( $10^2 - 10^3$  atm) sufficient to cause condensation of the gas into the liquid state. Since the field of iron liquid stability extends to lower pressures than that of silicates, metal-silicate fractional condensation is possible for shock waves which produce pressures sufficient to liquify iron but not silicate.

According to Blander and Katz (1967), the solar nebular gas became supersaturated due to lack of nucleation sites. Condensation directly to a liquid at much lower temperatures than equilibrium allows is favored rather than condensation to a solid due to much larger nucleation barriers for the latter.

Whipple (1966) postulates formation of chondrules by melting of a primordial dust by lightning flashes. The dust eventually accreted with the chondrules to form the whole meteorite.

#### Elemental Correlations and the Condensation Model

All important minerals known in the Allende chondrules are listed in Table 3. Of these minerals, spinel, fassaite, anorthite and gehlenite are expected to condense from a gas of solar composition at very high temperatures. These minerals contain almost all of the Ca, Ti and Al. According to the results of Table 11, Sc, V, Sm, Eu and Ir are highly correlated with Ca, Ti, and Al and therefore in some way associated with the above minerals. The inclusion of

Eu, V and Ti in the above group is made on the basis of correlation plots. Since Ir is strongly siderophilic, it certainly condenses as the metal in the same temperature range as the high temperature minerals. Crocket et al. (1967) calculate condensation temperatures of 1925°K and 1850°K for Ir and Fe, respectively, in a gas of solar composition at 1 atm total pressure. Consistent with these condensation temperatures, the close association of Ir with Ca, Al and Ti, and anticorrelation of Ca, Al, Ti and Ir with Fe indicates condensation of Ir before Fe metal. The condensation of Ir after Fe is predicted by Blander and Katz (1967), due to the extreme tendency of the noble metals to supersaturate in the vapor.

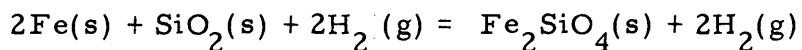
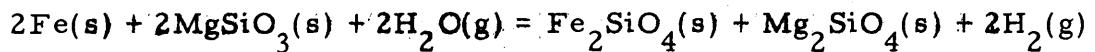
Sc, V, and the REE do not associate with high temperature minerals in magmatic differentiation processes. These elements could be present in accessory minerals such as zircon or apatite which are REE carriers in magmatic processes. Despite late appearance of these minerals in magmatic processes, early appearance of these minerals might be expected for a condensation process due to their refractory nature. It appears unlikely that apatite,  $\text{Ca}_5(\text{PO}_4)_3^-$  ( $\text{F}, \text{Cl}, \text{OH}$ ) is responsible for REE enrichment in the high temperature condensate, since the phosphorous content of chondrules is depleted relative to the matrix (see Table 1). Since Nagasawa (1970) has shown that the heavy REE are tremendously enriched relative to light REE in zircons compared to the chondritic abundance pattern,

and Zellmer et al. (1970) have shown that the REE in the Allende chondrules follow a normal abundance distribution, it appears unlikely that zircon is the REE carrier. Most likely the REE, as well as Sc and V, reside in a major high temperature mineral phase substituted for Ca(II).

The remarkable correlations of Co and Ni, and the good correlation of Fe with Co and Ni is taken as evidence that the condensation periods of these elements overlapped. The anticorrelation of the abundances of Ir and Fe, and the good positive correlations of Co and Ni with Ir indicates a complicated interrelationship of the abundances of these four siderophilic elements. The elements Al, Ca, Sc, Ti, V, Sm and Eu are all enriched in chondrules relative to matrix, consistent with the suggestion of Larimer and Anders (1967) that chondrules are formed at higher temperatures than the matrix. Fe, Co and Ni are depleted by almost identical factors of 0.44, 0.39 and 0.44, respectively. Ir exhibits little or no fractionation in chondrules/matrix, which is consistent with an association of Ir with both the enriched high temperature and depleted metallic fractions. These correlations are consistent with the condensation of Ir with Al, Ca, Sc, Ti, V, Sm, Eu, followed by condensation of metal and silicate phases in an unknown order, but not simultaneously due to anticorrelations of Co and Ni with Cr and

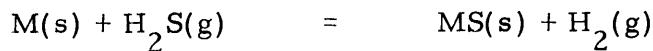
Mn. Incorporation of Fe into the silicate phases (Larimer, 1967)

by reactions such as



is responsible for the observed Fe, Mn and Cr correlation (see below), the anticorrelation of Fe and Ir, and the weak correlation of Fe with Co and Ni. Fractionation of the metal phase, containing Fe, Co, Ni and Ir, accounting for the depletion of these elements in chondrules/matrix, occurred before sulfide formation according to evidence cited by Larimer and Anders (1970). The mechanism of the metal/silicate fractionation is not clarified by the data at hand. The anticorrelation of Ir and Fe abundances, as well as the weak correlation of Fe with Co and Ni indicates fractionation after incorporation of Fe into the silicate phase by the above reactions. The majority of Fe in Allende chondrules is present in the silicate phase (see Table 1). The constant depletion of Fe, Co and Ni in chondrules/matrix, however, is evidence for fractionation of metal/silicate before incorporation of Fe into the silicate phase. It is possible that Fe, Co and Ni condensed as the sulfides, which, according to Blander (1971), is possible due to the lower supersaturation ratios for the sulfides relative to the metals. Direct condensation of these sulfides is not possible according to Larimer's model. Most of the iron group elements are present as sulfides

(see Table 1), and the sulfides can be formed by the reaction



occurring in the gas of solar composition and pressure for Fe, Ni and Co below 680°K (Larimer, 1967).

Ehmann et al. (1970) report Au and Ir abundances in carbonaceous chondrites and find strong correlations of both of these elements with both Fe and Ni in the individual chondrites. Furthermore, abundances of Fe, Ni, Ir and Au all exhibit a similar decrease from Type I to Type III carbonaceous chondrites (see last three columns of Table 12), suggesting simultaneous fractionation of these elements as metal.

A decrease in abundances of Fe, Co, Ni and Ir is observed in Table 12 below for chondrules relative to matrix in both the Allende and Chainpur (LL3) meteorites. The depletion is constant for the elements Fe, Co and Ni in Allende, and nearly constant for Fe, Co and Ir in Chainpur. The depletion factor for Ir in Allende chondrules, however, differs by a factor of 2 from those of Fe, Co and Ni. Enrichment of Ir by a factor of about 2 in a high temperature condensation process, followed by incorporation of Ir into the metallic phase after metal condensation, and then depletion of the metallic phase by a factor of 0.4 would account for the observed chondrule/bulk abundance ratio of Ir in Allende. Note that Sc abundances, which exhibit a high degree of correlation with Ir

abundances in Allende chondrules, are enriched by a factor of about 2 in the chondrules. Sc is not significantly enriched in Chainpur chondrules. Alternatively, median abundances in Allende chondrules may be compared with the bulk abundances. The resulting fractionation factors are 0.43, 0.31, 0.32, and 0.46 for Fe, Co, Ni and Ir. On the other hand, the most probable abundances of the above elements in the same order give fractionation factors of 0.39, 0.15, 0.16 and 0.07. Ir is very strongly depleted in the majority of chondrules compared to bulk. Thus the manner of depletion of these elements in chondrules is not clear, but most certainly is due to a metal/silicate fractionation.

The abundances of Mn and Cr are highly correlated. Cr is found largely as chromite ( $\text{FeCr}_2\text{O}_4$ ) in the matrix and may occur in the same mineral form in chondrules. Mn, which is highly enriched in two known olivine chondrules (602 and 603) most likely occurs in olivines and pyroxenes as  $\text{Mn}^{2+}$ (0.80A) substituted for  $\text{Fe}^{2+}$ (0.74A) and  $\text{Mg}^{2+}$ (0.66A).

The condensation of Na is a bit more difficult to account for in terms of the condensation model with the correlation coefficients observed. Of the elements studied, it apparently has the most complex condensation history. The fair correlation of Na with the high temperature group is not due to condensation of the Na with the plagioclase minerals, since the albite content of the plagioclase

Table 12. Siderophilic elemental abundances in carbonaceous chondrites.

Elements	Chainpur LL3			Allende C3			Carbonaceous Chondrites		
	Fractionation			Fractionation			I	II	III
	Chondrules	Bulk	Factor	Chondrules	Bulk	Factor			
Fe	10.3	19.8	0.52	9.7	22.0	0.44	0.90	0.84	0.82
Co	260	410	0.63	250	640	0.39	220	190	190
Ni				0.61	1.4	0.44	0.051	0.045	0.042
Au	0.047	0.15	0.31				0.19	0.19	0.17
Ir	0.175	0.375	0.47	0.66	0.71	0.93	0.68	0.66	0.60

Chainpur and Allende: Fe and Ni (%), Co, Au and Ir (ppm)

Carbonaceous chondrites: Fe and Ni (atoms/Si atom), Ir, Au and Co (atoms/ $10^6$  Si atoms)

Au and Ir abundances (except Allende) from Ehmann *et al.* (1970)

Fe and Co abundances for Chainpur from Schmitt and Smith (1966)

Fe and Ni abundances in carbonaceous chondrites from Anders (1964)

corresponds to Ab<sub>5</sub>. Clarke et al. (1970) have determined the mineralogy of a type-c chondrule with very high Na (7.9%) and Al (9.3%) contents. The minerals identified in this chondrule, sodalite, nepheline, clinopyroxene (fassaite) and olivine are extremely fine-grained, suggesting devitrification from a glass. Most likely Na can condense at the same stage as the high temperature condensate as a high alumina glass. Judging from the lack of any significant correlation or anticorrelation with any other elements, the remainder of the Na condensed continuously at decreasing temperature.

The diagram below, Figure 7, illustrates the condensation history of the chondrules which would account for the observed elemental correlations and relative proportions of abundances in the chondrules and the matrix.

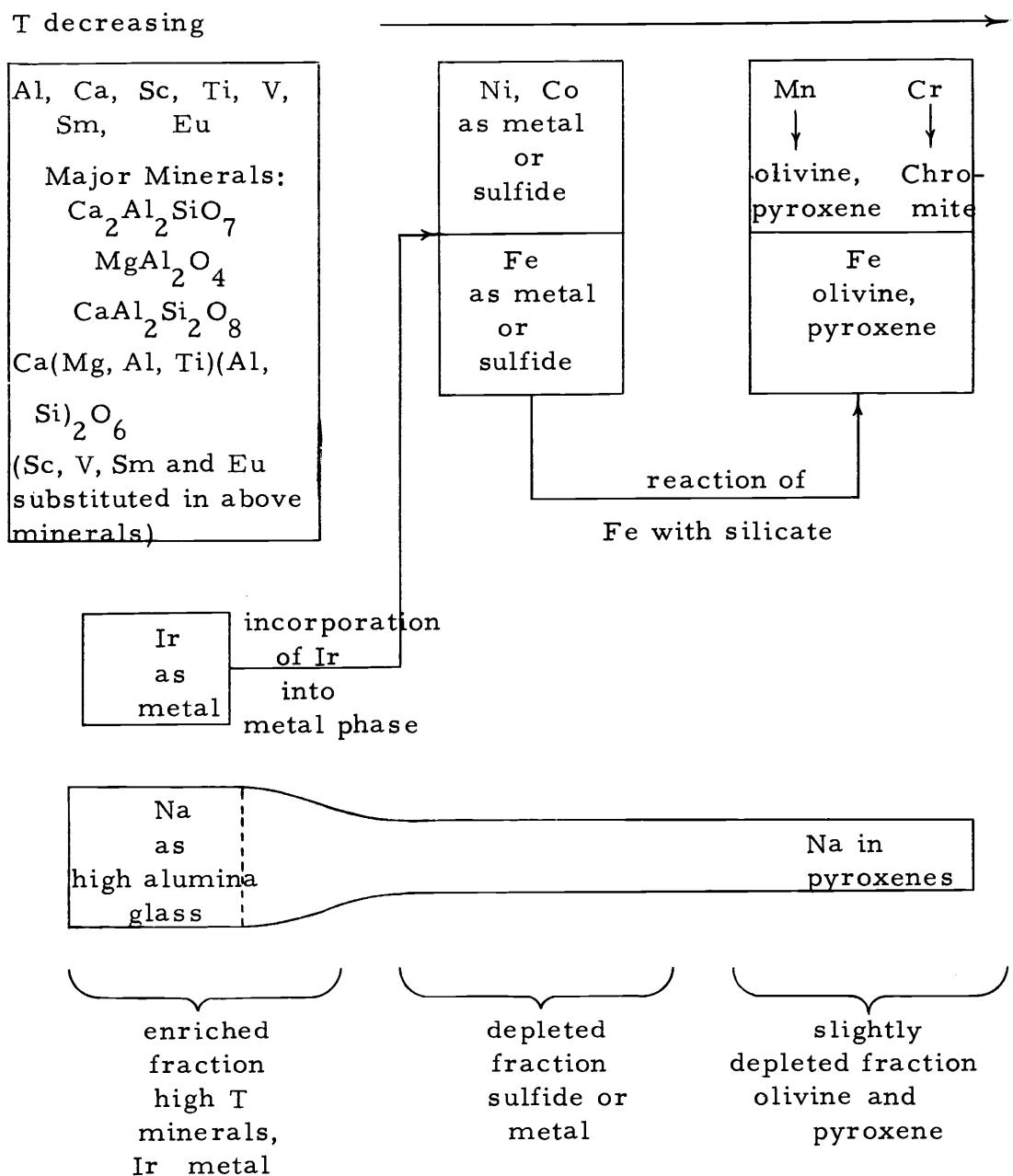


Figure 7. Implied condensation history of chondrules.

#### IV. SUMMARY AND CONCLUSION

Evidence from previous work by Green et al. (1971) indicates that the chondrules from Allende are now in the same state that they existed in when first formed. Thus relationships among the various elements are due to original chemical fractionations during chondrule formation and not reflections of metamorphism processes occurring after accretion with the fine-grained matrix material to form the chondrite.

That the physical processes responsible for the formation of chondrules took place via a condensation mechanism is supported by the positive mass-abundance correlations among elements (Al, Ca, Ti) known to occur in high temperature minerals in these chondrules, correlations among elements having widely different magmatic affinities (i. e., lithophilic Al and siderophilic Ir), and further supported by petrological evidence cited by Green et al. (1971).

The multi-elemental abundance correlations are consistent with the condensation processes as postulated by Wood, Larimer and Anders, and by Blander and co-workers. A condensation sequence can be ascribed to the analyzed elements based on their correlation coefficients and abundances relative to matrix abundances. The strong depletion of Fe, Co and Ni in chondrules relative to the

matrix is evidence for fractionation of these elements as metals during chondrule formation. The correlation of Ir abundances with those elements occurring in high temperature minerals rather than those of Fe, Co and Ni is consistent with the condensation model of Wood (1963) and Larimer (1967) and inconsistent with some aspects of the constrained equilibrium theory of Blander and Katz (1967).

It is apparent that, despite the excellent fit of the data obtained in this work to the current condensation models of chondrule formation, there is still much unknown about many subtle complexities, such as trace element condensation and metal/silicate fractionation. Much work in the future will be required to completely unravel the mechanism of the evolution of our early solar system. Many secrets are still locked up in the fragments of primitive matter floating around in space that we call meteorites.

## V. SUGGESTIONS FOR FURTHER RESEARCH

Several improvements are possible for the analyses. Two high flux activations would give far superior analyses for the short lived nuclides. An activation for a short period in a position with a low relative fast neutron flux would serve for more accurate determination of La, Sm, Au and Ca (via  $^{47}\text{Sc}$ ) via INAA. Activation of a Ti standard would allow the magnitude of the  $^{47}\text{Ti}(\text{n}, \text{p})^{47}\text{Sc}$  interference of the Ca determination to be calculated. Following this activation, a second, longer activation at a higher relative fast neutron flux would result in determination of Fe, Sc, Co, Ni, Cr and Eu abundances in the chondrules.

A knowledge of the abundances of the alkali series K, Rb, and Cs, and elements such as Ag, Zn, Pb, Cd, Bi, Tl, In and Hg in the individual chondrules is extremely important in determining the fraction of low temperature condensate in each chondrule. This would be achieved by radiochemical neutron activation analysis. In view of the importance of the platinum metals in differentiating between the condensation models of Wood (1963) and Blander and Katz (1967), Os and Ru (condensation temperatures of 2250°K and 1875°K at 1 atm total pressure, respectively, according to Crocket *et al.* (1967), abundances are of extreme importance and could be determined by RNAA.

Since all of the important minerals occurring in the chondrules are known, it would not be difficult to carry out a normative mineral analysis from the abundance data alone, once the Mg and Si abundance were determined. Determination of the Si abundances would also enable a correction of the (n, p) interference and a calculation of the true Al abundances.

An analysis of mineral separates from the chondrules would yield extremely valuable information on the residence of the various minor and trace elements. Considering the association of the REE with high temperature minerals, the results of such a study could be quite interesting and informative.

## BIBLIOGRAPHY

Anders, E. A. (1964). Origin, age and composition of meteorites. *Space Science Reviews* 3:583-714.

Anders, E. A. (1971). How well do we know 'cosmic' abundances? *Geochimica et Cosmochimica Acta* 35:516-22.

Blander, M. (1971). The constrained equilibrium theory: Sulphide phases in meteorites. *Geochimica et Cosmochimica Acta* 35:61-76.

Blander, M. and J. L. Katz (1967). Condensation of primordial dust. *Geochimica et Cosmochimica Acta* 31:1025-34.

Blander, M. and Abdel-Gawad (1969). Chondrules in unequilibrated meteorites and the constrained equilibrium condensation theory. *Geochimica et Cosmochimica Acta* 33:701-16.

Clarke, R. S., Jr., E. Jarosewich, B. Mason, J. Nelen, M. Gomez and J. R. Hyde (1970). The Allende, Mexico meteorite shower. Washington D. C., Smithsonian Institution Press. 53 pp.

Crocket, J. H., R. R. Keays and S. Hsieh (1967). Precious metal abundances in some carbonaceous and enstatite chondrites. *Geochimica et Cosmochimica Acta* 31:1615-23.

Ehmann, W. D., P. A. Baedecker and D. M. McKown (1970). Gold and iridium in meteorites and some selected rocks. *Geochimica et Cosmochimica Acta* 34:493-507.

Emery, J. F., J. E. Strain, G. D. O'Kelley and W. S. Lyon (1969). Nondestructive neutron activation analysis of the Allende meteorite. *Radiochemical Radioanalytical Letters* 1:137-41.

Filby, R. H., A. Davis, K. Shah, G. Wainscott, W. Haller and W. Casatt (1970). Gamma ray energy tables for neutron activation analysis. Pullman, Washington State University Press.

Fireman, E. L., J. DeFelice and E. Norton (1970). Ages of the Allende meteorite. *Geochimica et Cosmochimica Acta* 34: 873-81.

Flanagan, F. J. (1969). U. S. Geological Survey standards - II. First compilation of data for new U. S. G. S. rocks. *Geochimica et Cosmochimica Acta* 33:81-120.

Fredriksson, K., J. Nelen and W. Melson (1970). Petrography and origin of lunar breccias and glasses. In *Proceedings of the Apollo 11 lunar science conference*. Ed. A. A. Levinson. New York, Permagon. Vol. 1, 419-32.

Friedlander, G., J. Kennedy and J. Miller (1955). Nuclear and radiochemistry. 2d ed. New York, Wiley. pp. 79-81.

Gordon, G., K. Randle, G. Goles, J. Corliss, M. Beeson and S. Oxley (1968). Instrumental activation analysis of standard rocks with high-resolution  $\gamma$ -ray detectors. *Geochimica et Cosmochimica Acta* 32:369-96.

Green, H. W., II, S. Radcliffe and A. Heuer (1971). Allende meteorite: a high-voltage electron petrographic study. *Science* 172:936-9.

Hughes, D. J. (1953). Pile neutron research. Cambridge, Mass., Addison-Wesley. pp. 93-102.

Keays, R. R., R. Ganapathy and E. Anders (1971). Chemical fractionations in meteorites - IV. Abundances of fourteen trace elements in L-chondrites; implications for cosmo-thermometry. *Geochimica et Cosmochimica Acta* 35:337-63.

King, E. A., Jr. (1969). Petrography and chemistry of the Pueblito de Allende meteorite. *EOS Transactions, American Geophysical Union* 50:459.

Larimer, J. W. (1967). Chemical fractionations in meteorites - I. Condensation of the elements. *Geochimica et Cosmochimica Acta* 31:1215-38.

Larimer, J. W. and E. Anders (1967). Chemical fractionations in meteorites - II. Abundance patterns and their interpretations. *Geochimica et Cosmochimica Acta* 31:1239-70.

- Larimer, J. W. and E. Anders (1970). Chemical fractionations in meteorites - III. Major element fractionations in chondrites. *Geochimica et Cosmochimica Acta* 34:367-87.
- Lord, H. C., III (1965). Molecular equilibria and condensation in a solar nebula and cool stellar atmospheres. *Icarus* 4:279-88.
- Lukens, H. R. (1963). Estimated photopeak activities in reactor irradiations. Excerpt from GA-5073, Utilization of reactor fast neutrons for activation analysis.
- Marvin, U. B., J. A. Wood and J. S. Dickey, Jr. (1970). Ca-Al rich phases in the Allende meteorite. *Earth and Planetary Science Letters* 7:346-50.
- Mason, B. (1962). *Meteorites*. New York, Wiley. pp. 9-26.
- Morgan, J. W., T. Rebagay, D. Showalter, R. Nadakarni, D. Gillum, D. McKown and W. Ehmann (1969). Allende meteorite: Some major and trace element abundances by neutron activation analysis. *Nature* 224:789-91.
- Nagasawa, H. (1970). Rare earth concentrations in zircons and apatites and their host dacites and granites. *Earth and Planetary Science Letters* 9:359-64.
- Nicholson, B. H. (1970). Elemental abundances in selected Oregon basalts. Master's thesis, Corvallis, Oregon State University. pp. 10-15.
- Osborn, T. W. (1968). Sodium and manganese homogeneity in chondritic meteorites. Master's thesis, Corvallis, Oregon State University. 116 pp.
- Osborn, T. W. and R. A. Schmitt (1970). Sodium and manganese homogeneity in chondritic meteorites. *Icarus* 13:207-14.
- Schmitt, R. A. and R. H. Smith (1966). Research on elemental abundances in meteoritic and terrestrial matter. General Atomic report GA-7424. pp. 21-9.
- Schmitt, R. A., R. H. Smith and G. G. Goles (1965). Abundances of Na, Sc, Cr, Mn, Fe, Co and Cu in 218 individual meteoritic chondrules via activation analysis - I. *J. Geophys. Res.* 70:2419-44.

- Schmitt, R. A., R. H. Smith, W. D. Ehmann and D. McKown (1967). Silicon abundances in meteoritic chondrules. *Geochimica et Cosmochimica Acta* 31:1975-85.
- Schmitt, R. A., T. A. Linn and H. Wakita (1970). The determination of fourteen common elements in rocks via sequential instrumental activation analysis. *Radiochimica Acta* 13:200-12.
- Upham, G. L. (1968). Flux measurements in the Oregon State TRIGA reactor. Master's thesis, Corvallis, Oregon State University.
- Van Schmus, W. R. and J. A. Wood (1967). A chemical-petrologic classification of the chondritic meteorites. *Geochimica et Cosmochimica Acta* 31:747-65.
- Vogt, J. R. and W. D. Ehmann (1965). The nondestructive determination of silicon and oxygen in meteorites by fast neutron activation analysis. In Proceedings of the 1965 international conference on modern trends in activation analysis. College Station, Texas A & M Press. pp. 82-5.
- Wakita, H. and R. A. Schmitt (1970). Rare-earth and other elemental abundances in the Allende meteorite. *Nature* 227:478-9.
- Walter, L. (1969). The major-element composition of individual chondrules of the Bjurbole meteorite. In meteorite research. Ed. P. M. Millman. Dordrecht, Holland, D. Reidel.
- Whipple, F. L. (1966). A suggestion as to the origin of chondrules. *Science* 153:54-6.
- Wood, J. A. (1958). Silicate meteorite structure and the origin of meteorites. Technical report no. 10, Smithsonian Inst. Astrophys. Obs. (ASTIA Doc. No. AD158364)
- Wood, J. A. (1963). On the origin of chondrules and chondrites. *Icarus* 2:152-80.
- Zellmer, D. (1971). Assistant Professor, Fresno State College. Personal communication. Corvallis, Ore.
- Zellmer, D., H. Wakita and R. A. Schmitt (1970). Elemental abundances in meteoritic and terrestrial matter. Annual Progress Report to the National Aeronautics and Space Administration. Radiation Center, Corvallis, Oregon State University.