

A STUDY OF LARGE SCALE CHEMICAL VARIATIONS
IN THE ALLENDE METEORITE

A Thesis
Presented to
the Faculty of the Graduate School
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Pratt H. Johnson

May, 1978

ACKNOWLEDGMENTS

I am very grateful to Dr. Elbert A. King for his encouragement, technical support, and for making possible the opportunity of performing this research. I want to thank Dr. John C. Butler for his encouragement, statistical support and constructive criticism. I would further like to thank Dr. Everett K. Gibson for his criticism of this manuscript, technical support and the many references he both suggested and supplied. Thanks to other members of the Geology Department faculty, each of my colleagues at the University of Houston and in the Lunar Curatorial Laboratory for their various types of support and encouragement. Most of all I would like to thank Betty for her encouragement, patience, extra work at home, laboratory assistance and moral support during this period of study, research and thesis preparation. I want to recognize that her extra effort has been at least as much as mine in completing the work for this degree.

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ABSTRACT

The Allende, Mexico C3(V) is the largest stony meteorite fall recorded. Nine samples of six pieces of the meteorite were analyzed spectrochemically for large scale chemical variations. Nine elements from four geochemical divisions were used in the analyses.

Three slabs oriented to obtain the most representative portions were wire sawed from each sample. The slabs were crushed and screened through a 60 μ sieve. The homogenized slab material was then split into four splits for each slab. The 108 splits were numbered randomly and analyzed in random order.

An optical emission spectrographic analysis method using a demountable hollow cathode source was developed. The method has reduced matrix effects and uses less sample than previous optical emission spectrographic methods. A method for making background correction on a single spectrum when measuring the spectrographic plates on a densitometer was developed. The method requires a minimum of half the transmission readings of previous methods and allows many more samples to be exposed on a single spectrographic plate.

The data were evaluated statistically by several methods and the analysis indicates that the Allende meteorite is a well-indurated polymict breccia. The samples show less chemical variation than the slabs. The accuracy and precision of the results compare well with the data reported for the reference Allende bulk samples prepared by the Smithsonian Institution.

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A STUDY OF LARGE SCALE CHEMICAL VARIATIONS IN THE ALLENDE METEORITE

SECTION 1

INTRODUCTION

I. PURPOSE AND SCOPE

Stony meteorites generally are assumed to be chemically homogeneous in fragments as small as a few cubic centimeters. The Pueblito de Allende meteorite is the largest stony meteorite fall ever reported. Homogeneity of elemental abundances in this largest observed piece of stony extraterrestrial material may provide information to identify the formational conditions and possible later metamorphic changes it encountered during its history.

Nine elements were selected as representing the gross chemistry of this meteorite. These elements represent four of the six major geochemical divisions of elements described by S. R. Taylor (1966). They therefore, respond differently to conditions that cause geochemical differentiation. Nine samples from six different fragments of the meteorite were analyzed. Three aliquots were taken from each sample and four splits made from each aliquot. The data obtained were statistically analyzed to determine if these portions of Allende were homogeneous.

The previous paragraphs are a statement describing the purpose of the research performed in this project. A better understanding of the reason for this investigation can be obtained if two questions are considered prior to a presentation of the detailed study. First, what is a meteorite? The answer to this question involves a brief review of historical reports and a physical description of the phenomenon of their discovery. The other question is what are the different meteorite types and where does Allende fit into this classification.

Moore (1969) describes the variety of materials floating around in our solar systems. Most people are familiar with planets, satellites and other larger bodies that follow very predictable orbits. He tells of a significant number of small bodies whose motions are not always predictable. The size of these bodies range

from microscopic dust particles to asteroids 760 km in diameter. He estimates that as much as 10,000 tons of this cosmic material bombard the earth each day. These smaller particles, as they are floating in space, are called meteoroids. The material that enters the atmosphere and becomes incandescent because of friction between them and atmospheric gas particles are called meteors or "shooting stars." Most of these bodies never reach the earth as solid objects because they are too small, too friable or do not approach the earth on a course that will allow them to land. The fragments that are seen to land (falls) or later found (finds) are called meteorites. The word is derived from Greek that has the approximate meaning of "present in the airs."

II. FALL PHENOMENA

Heide (1963) divides the description of the fall phenomena into three parts. These parts are light, sound and impact.

1. Light

The light, depending on the size of the meteor and proximity of the observer to the path of the meteor, can vary in intensity. The display, depending on the size of the meteor, is visible in the sky for only two to three seconds. Until photographic equipment was set up to scan the night sky, the essentially non-scientific descriptions of casual observers was the only information available. The descriptions, however, are very similar, telling of a dazzling bright fireball leaving a cloud of smoke behind it. The intensity of the light, if the fall occurs during the day, rivals that of the Sun. When the fall occurs at night, the light path can be seen for great distances. The Bath Furnace, Kentucky, meteorite fall (1902) occurred in the evening and was seen by many people in the states of Louisiana, Mississippi, Alabama, Georgia, Tennessee and Kentucky. Its visible path covered a distance of nearly 1,000 kilometers. The light from Allende was seen over a large area of north central Mexico, south-eastern New Mexico and west Texas. At the end of the visible path, a brightening may occur accompanied by an explosion and break up of the meteorite. The point where the light terminates is called the retardation point.

The color of the light varies, but is usually white or blue white. Occasionally greenish, reddish or yellowish tints have been observed. The light changes for different stages of the flight path. A limited number of meteorite spectra have been recorded. These spectra are made up predominantly of lines from ionized oxygen and nitrogen atoms from the atmosphere. Lines of iron, nickel, calcium, magnesium, chromium, silicon, sodium and possibly aluminum that would come from the meteorite have been identified.

Another light phenomenon associated with the path of a meteorite is a luminosity or after glow. The persistence of this luminosity is usually only a few seconds. In the case of the Pasamonte, New Mexico meteorite (1933) it is reported to have lasted 45 minutes.

2. Sound

The second phenomenon involved in the falling of a meteorite is sound. The sound is even more impressive than the light. The sound depending upon the distance of the observer from the meteor usually comes two to three minutes after the light and has been described by many more people than the light. This probably is because an observer can be facing in any direction and still detect sound. Sound descriptions probably are even more subjective than light. Most people who have heard a meteorite fall associate it with the loudest sound they have heard or can imagine. The scale of sounds reported range from a thunder-like stroke to the boom of a cannon, from rifle fire to the clatter of wagon wheels. Roaring and hissing noises frequently are reported, probably because the sound of meteorite particles moving through the air would be similar to large artillery projectiles or aerial bombs and occur after the detonation associated with the retardation point. Prior to the retardation point the thunderous roar is caused by the particles moving through the atmosphere faster than the speed of sound causing a "sonic boom." One account of the sound phenomenon of the Allende fall quotes residents of the area as stating they thought an atomic bomb exploded. It is not hard to realize that many observers reactions have ranged from being frightened to terrorized. As a result many reports are subjective and not very accurate. This situation makes the location of falls more difficult since people in a frightened condition usually think the phenomenon was much closer to them than it really was.

3. Impact

Impact effect of most meteorites are suprisingly small when compared to the light and sound phenomena. There are spectacular craters on the earth such as Meteor Crater in Arizona, Ries Crater in Germany, Wabar Craters in Saudi Arabia, the Canadian craters and the Australian craters. Many more and much larger craters have been observed on the moon. However, the impact site of the average meteorite that lands on the earth is comparatively small and insignificant looking. The crater size is related to the mass, relative velocity and angle of contact with the earth that the meteorite has when it falls, but even relatively large meteorites commonly produce only a small indentation in the surface of the earth. An example is the 60 ton Hoba iron meteorite (found in 1920) in southwest Africa which is only imbedded 1.5 meters in friable limestone. The author became aware of this situation on observing a picture of the recovery site of the first stone found of the Lost City meteorite. The 9.8 kg meteorite was laying on top of a snow packed rut of a rural road. Elston and Scott (1971) studied the craters made by five fragments of the Allende meteorite. The deepest crater 32 cm deep was made by an 8 kg projectile in compact, loamy, clayey soil. Their study of the shapes of craters compared to experimental craters of rocks dropped from an airplane showed that some of these projectiles had horizontal direction vectors different than the path of the fire ball.

As stated previously, little really interesting scientific information is derived from the fall phenomena associated with most meteorites. There are, however, three instances where meteorite falls have been photographed by two or more cameras allowing pre-terrestrial orbits to be calculated. The trajectory of Pribram, Czechoslovakia in 1959 was calculated from the photographs of two cameras. Lost City, Oklahoma meteorite was photographed by the Smithsonian Institution Prairie Network in 1970, and its orbit in the solar system calculated. The third meteorite was Innisfree, Alberta. This meteorite fell February 5, 1977, and the information was recorded by Canada's Meteorite and Recovery Project. Besides calculating the pre-terrestrial orbit, they predicted Innisfree's impact point to within 0.5 km of

where it was actually recovered, Halliday et al. (1977). All three of these calculated orbits are rather similar. They are heliocentric, elliptical, with aphelion somewhere between just inside the earth's orbit and outside the asteroid belt.

III. CLASSIFICATION

The second question proposed earlier involves the classification of meteorites. Meteorites are composed of a variety of minerals and metallic components. When it was demonstrated by the German physicist E. F. F. Chladni in 1794 that meteorites were extraterrestrial material, many scientifically oriented people became interested in their composition (Sears, 1975). The names of early European investigators reads like a Who's Who of 19th century chemists in Europe. Lange (1975) describes the same background for the founders of American meteoritics. As more and more information was reported these meteoriticists became interested in comparing the different results, and classifications then began to be developed to allow similar types to be grouped together. Mason (1962) attributes the first simple classification identifying iron and stone meteorite groups to Klaproth in 1807. Merrill (1910) in an earlier work states that Blumenback as early as 1804 made the distinction between stones and irons. Both authors credit Professor H. Story Maskelyne in 1863 with identifying a third group, the stony-irons. He further proposed the names aerolites, aerosiderolites and aerosiderites for stony, stony-iron and iron meteorites respectively. Gustav Rose in 1862 suggested a finer subdivision of stony meteorites based on mineral composition and structure and divided them into chondrites and achondrites depending on whether or not they contained spherical inclusions called chondrules. This classification was enlarged and modified by Tschermak in 1883 and presented in its final form by Brezina in 1904. It is generally known as the Rose-Tschermak-Brezina system. These classifications generally were accepted and commonly used in the literature. The system had 75 different subgroups but some mineral identifications were imprecise or erroneous. In 1920 Prior pointed out these defects and proposed a revised and simplified classification scheme. This system was later modified by Mason (1962),

who based classification on the chemistry and mineralogy of meteorites. In 1967 Van Schmus and Wood presented a modification of the classification of chondrites based on chemistry, mineralogy and texture. This system is now widely used although the inferred progressive metamorphism in chondrites may be considered as erroneous or at least debatable conclusion by some investigators (King 1975).

The various characteristics used to classify meteorites are summarized in Table 1. The objective of this chart is to list not only the characteristics, but the various symbols that are in use as a result of the different classification schemes that have been developed. The chart simply provides a common reference source where the symbols and relationships are easier to compare. The chart form used was chosen as a more efficient method to remember these relationships. A chart with the summarized data listed can be understood and remembered better than a list of names, several paragraphs of prose, or a chart that only shows symbols. Schemes based on trace elements or other methods requiring special sophisticated instruments were not included.

To answer the question of where Allende is in this classification, King et al. (1969) and Clark et al. (1970) list it as a type 3 carbonaceous chondrite or a C3 chondrite. The chart shows that petrologically it has olivine and pyroxene with a range of compositions, large chondrules in a matrix less opaque than a type 1 or 2, the major pyroxene is clinopyroxene, and nickel in any metal present is <20%. NiS is <0.5%, water is <2.0%, carbon is 0.2-1.0% and the chondrules commonly contain some undevitrified glass. Chemically the Fa concentration is <15%, the Fe/SiO₂ ratios is between 0.70 to 0.84, the metallic iron to total iron ratio is near zero, the SiO₂/MgO ratio is between 1.37 to 1.47, there is little or no free metal present and the meteorite contains a relatively large amount of volatiles. A subdivision of the higher petrographic type carbonaceous chondrites was suggested by Van Schmus (1969), Van Schmus and Hayes (1974) and recently described in more detail by McSween (1977). The sub-types have been labeled O for Ornans and V for Vigarano. They primarily are distinguished by texture and chemistry. Allende belongs to the Vigarano sub-type having chondrules 1-2 mm and larger in diameter embedded in an abundant, fine grained, opaque

Table 1

CLASSIFICATION OF METEORITES
Iron Meteorites (Siderites)

Type Characteristic	Nickel-Rich Ataxites D	Octahedrites O	Hexahedrites H	Nickel-Poor Ataxites D	Metabolites	Brecciated Octahedrites
Nickel %	>14	6-14	<6	4-7	7-11	
Texture (Widmanstätten)	None	>2.5mm Coarsest Ogg 1.5-2.5mm Coarse Og 0.5-1.5mm Medium Om 0.2-1.5mm Fine Of <0.2mm Finest Off	None	None	Lost or not developed	Only 1-3 cm areas of pattern
Neumann Lines Cubic Structure	in Kamacite	Kamacite lamellae	Parallel bands	Parallel bands		
Minerals	Kamacite Plessite >27% Ni Taenite	Kamacite Taenite	Kamacite	Kamacite		Kamacite Taenite
Quantity	42	466	55	28	3	7

Table 1 (continued)

Stony-Iron Meteorites (Siderolites)

Type Characteristic	Pallasites P	Sidcrophyles	Lodranites	Mesosiderites M
Iron %	45% - 20%	40%	24%	23% - 48%
Nickel %	10% - 15%	10%	9%	7%
Total	55% - 35% Metal is continuous	50%	33%	30% - 55% Metal is discontinuous
Olivine	99% of non opaque		33 mole % (13% Fa)	2% (10 mole % Fa)
Orthopyroxene		50% O-py (20% Bz)	33 mole % (17% Bz)	40% - 80%
Plagioclase			Trace	~20% up to An 97
Trace Minerals	Troilite Schreibersite Farringtonite	Schreibersite Chromite	Chromite Troilite	Troilite Chromite Schreibersite Apatite Whitlockite
Quantity	45	1	1	25

Table 1 (con't)

ACHONDRITES

TYPE	ENSTATITE ACHONDRITES (Aubrites) Ae	HYPERSTHENE ACHONDRITES (Diogenites) Ah	OLIVINE ACHONDRITES (Chassignites)	OLIVINE- PIGEONITE ACHONDRITES (Ureilites)	AUGITE ACHONDRITES (Angrites)	DIOPSIDE- OLIVINE ACHONDRITES (Nakhlites) Ad	PYROXENE-PLAGIOCLASE ACHONDRITES (Eucrites) and (Howardites) THE BASALTIC ACHONDRITES Ap	
CHARACTERISTIC								
	Calcium-Poor 0-3 Wt % CaO				Calcium-Rich 5-25 Wt % CaO			
Major Minerals	MgSiO ₃ Fe free	Mg _{0.5-0.7} Fe _{0.5-0.3} SiO ₃	(Mg,Fe) ₂ SiO ₄ 33 mole % Fe ₂ SiO ₄	(Mg,Fe) ₂ SiO ₄ Ca _x (Mg,Fe) _{1-x} SiO ₃ (x=0.1)	(Ca,Mg,Fe ⁺² ,Al) ₂ (Si,Al) ₂ O ₆	Ca _{0.5} Mg _{0.5} SiO ₃ (Mg,Fe) ₂ SiO ₄	Py=Pigeonite Ca _x (Mg,Fe) _{1-x} SiO ₃ (x=0.1), NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈	Py=Hypersthene Mg _{0.5-0.7} Fe _{0.5-0.3} SiO ₃ , NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈
Minor Minerals	Fosterite Diopside Diopside Kamacite Troilite	Plagioclase Olivine Troilite Fe/Ni Chromite	Chromite Plagioclase hi-Ni Fe/Ni	Fe/Ni, troilite Diamond Graphite	Olivine Troilite Apatite CaO, TiO ₂ -hi	Plagioclase Magnetite	Olivine, quartz Troilite, Apatite, Ilmenite, Chromite	Similar to Eucrites
Ground Mass	Fine Enstatite	Fine Hypersthene	None	Carbonaceous			dark gray Plagioclase & Pyroxene	light gray Plagioclase & Pyroxene
Structure	Brecciated Coarse angular Enstatite	Brecciated coarse angular Hypersthene	Allotriomorphic granular recrystallized	Olivine Clinopyroxene grains	only meteorite with Augite	75% Diopside 15% Olivine Ol 66%, Fa, HiCa	Unbrecciated & monomict Breccia	Polymict Breccia
Quantity	8	8	1	3	1	2	30	14

Table 1 (con't)

CHONDRITES

PETROLOGIC TYPE	1 No chondrules All fine grained opaque matrix volatiles present ~2.8% C, ~20% H ₂ O least reheating	2 Variable Ol & Py Large matrix chondrules major Py-clino NiS >0.5%, 0.5-2.8%C 4-18% H ₂ O <20% Ni in metal Taenite absent or minor	3 Minerals like 2 >20% Ni in metal less opaque matrix NiS <0.5%, <2% H ₂ O 0.2-1.0 % C Ign. glass in chondrules	4 <5% Ol & Py Var. ~20% of Py clino Ing. glass turbid Transp. micxtal matrix, <0.2% C transition type	5 Uniform mineral comp. Ortho. Py., No Ign glass Rextal matrix, chondrules delineated, micro-xtal plag.	6 Flag. Clear grains coarse rextal matrix, poorly defined chondrules most reheating
CHEMICAL GROUP						
E Fa=0 Fe/SiO ₂ =0.47-1.07 Fe°/Fe=0.70-0.00 SiO ₂ /MgO=1.75-2.05 No FeO in silicates Highly reduced free SiO ₂			1	Enstatite Chondrites Ce MgSiO ₃ 4	2	6
C Fa<15% Fe/SiO ₂ =0.70-0.84 Fe°/Fe=0 metal SiO ₂ /MgO=1.37-1.47 Little free metal Large amount of volatiles	4	16	Carbonaceous Chondrites Cc Allende 9	2	Ordinary Chondrite Boundary	
H (high Fe & Fe°/Fe) Fa=16-20 M% Fe/SiO ₂ =0.70-0.84 Fe°/Fe=0.56-0.70 SiO ₂ /MgO=1.50-1.60 Less oxidation			7	Olivine 35	Bronzite Chondrites Cb (Mg,Fe)SiO ₃ (FeO 5-13%) 74	44
L (lower Fe & Fe°/Fe) Fa=22-26 M% Fe/SiO ₂ =0.50-0.60 Fe°/Fe=0.26-0.40 SiO ₂ /MgO=1.54-1.64 Higher oxidation			9	Chondrite 18	Hypersthene Chondrites Ch (Mg,Fe)SiO ₃ (FeO 13-20%) 43	152
LL (low, low Fe & Fe°/Fe) Fa=27-31 M% Fe/SiO ₂ =0.46-0.52 Fe°/Fe=0.01-0.15 SiO ₂ /MgO=1.53-1.63 Still higher oxidation			4	Border 3	Olivine-Pigeonite Amphoterite Chondrites Cp (Mg,Fe)SiO ₃ (FeO 19-25%) 7	21

(O)  Ormans - <0.5mm chondrule, matrix only between packed chondrules(V)  Vigrano - >0.5mm chondrules, abundant fine opaque matrix

Fe/Si <.77	Ca/Si >.076	Al/Si >.108	Ti/Si >3.5x10	Cu/Si <3.2x10
>.79	<.070	<.095	<3.1x10	>3.4x10

matrix. Chemically the Ca, Al and Ti to Si ratios are higher and the Fe and Cu to Si ratios are lower in the Vigarano sub-type than in the Ornans sub-type. The complete classification of Allende is a C3(V) chondrite. It is a median type of chondrite according to the chemical and petrologic characteristics, but it is just outside the boundary of the area that contains the major number of chondrite individuals.

Allende then is average enough to give information that can be generally extrapolated to other types of chondrites. At the same time with only nine meteorites of this type listed in 1970 it is unique enough to provide new information about this unusual group of meteorite. The large amount of material collected is the third factor that makes it significant in that possible variations of characteristics in a large amount of material can be measured. Allende is a much more representative sample of its parent body than any other stony meteorite because it is the largest stony meteorite fall. This study of the variability of major elements in nine large pieces of the meteorite will provide valuable data that can be used to develop a hypothesis as to the homogeneity and possible origin of its parent body.

Section 2 describes how these pieces were sampled to provide the most representative sample while using a relatively small amount of material. The sampled material is to be used for analyses other than those performed in this thesis project. Care was taken to keep the possibility of sample contamination to a minimum.

SAMPLING AND COMPONENTS ANALYZED

SECTION 2

I. INTRODUCTION

An ever present problem in geochemical analysis is how large a sample of the material being analyzed is necessary to properly represent the bulk composition of the geological sample of interest. There are two ways to approach the problem. One method is to use a microprobe or similar electron beam instrument and analyze a large number of each of the various mineral components present in the material. By this method one can count the relative amounts of each component present and then statistically calculate a weighted average for the desired elements or oxides. This method has the advantage of revealing the heterogeneity at that scale, but requires a relatively large number of determinations to obtain accurate representative values. Material with fine or irregular crystal structure can severely reduce precision.

The other method can be applied to almost any other analytical chemical measurement. This method involves obtaining a sample of the material large enough and oriented in a manner that it contains a representative amount of all the mineral components present in the sample. The sample is then ground, homogenized, and an aliquot of the size required for the geochemical analyses is split from the sample. The latter method was used to obtain samples used in the analysis of the Allende material supplied for this project.

II. LITHOLOGY

The lithology of a geological specimen must be considered before an adequate sampling plan can be devised. It is beyond the scope of this work to present a detailed petrographic study of the Allende meteorite. The meteorite is extremely heterogeneous at fine scale, on the order of a few millimeters. Much more of the sawn surfaces of the total sample was photographed than the portion reserved for analysis. An even larger volume of the bulk sample was observed during breaking and wire sawing allowing for a detailed visual examination of the structure and inclusions of the entire sample. A description of

meteorite components is necessary to understand the sampling problem and bulk chemistry of the Allende meteorite. Clarke et al. (1970) established the basic classification of the components of the meteorite. The Allende meteorite is composed of a wide variety of inclusions in a gray to black, fine-grained matrix. The inclusions are of three broad types: chondrules, irregularly-shaped mineral aggregates, and dark to light gray lithic inclusions. The chondrules were divided into the following groups:

A. Magnesium-rich

1. Granular olivine - euhedral crystals
2. Granular olivine plus clinoenstatite
3. Barred olivine chondrules
4. Monosomatic olivine chondrules, single crystals
0.5 mm dia.
5. Pyroxene-rich chondrules

B. Calcium and aluminum-rich chondrules

Three types with the following mineralogies:

1. Gehlenite-fassaite-anorthite-spinel to 24 mm dia.
2. Anorthite-fosterite-spinel 2 mm dia.
3. Nepheline-sodalite-fassaite-olivine to 8 mm dia.

Clarke et al. (1970) only briefly mention some of the variety of irregularly-shaped inclusions found in Allende. However, the most carefully studied inclusions, to date, are irregular, white, pale gray, or pale pink in color. Many are lensoid in shape and one as large as approximately 5 by 12 mm can be seen in 16-S-1-N. Another type of white inclusion is very fine grained and commonly elongated, only 0.5 to 1.5 mm wide and 4 to 8 mm long. To date, these inclusions have not been studied extensively in the literature. They are wispy white material that in many cases seems to be a coating on fine grains of dark matrix material. Many irregular yellow, opaque, relatively coarse crystalline inclusions of troilite are observed. Most show some reaction rims with the matrix, but others do not. Some troilite forms a partial crust-like coating on the chondrules.

A number of dark gray to light gray lithic clasts/inclusions are distributed throughout the samples. They range in size from a few to approximately 15 mm wide and to as much or more than 30 mm long. These lithic clasts/inclusions are composed of a very black, very fine-grained

matrix that contains chondrules and irregularly-shaped light-colored inclusions. This material is similar to the bulk Allende material, except that the grain size of the chondrules in the lithic clasts rarely was observed to be greater than 1 mm. In general, the dark lithic clast/inclusions appear finer-grained and better sorted than the bulk Allende meteorite. The lithic clasts show variation in the following characteristics: (1) the ratio of black fine-grained matrix to chondrules and other inclusions, and (2) the morphology of the inclusions within the lithic clasts. Some of these lithic clast/inclusions are predominantly matrix material. One lithic clast/inclusion was found to be composed predominantly of chondrules, mineral aggregates and clasts, with very little predominantly discontinuous matrix material. In addition, in many of the lithic clasts, the chondrules and mineral aggregates appear broken. In other, rarer lithic clasts/inclusions, the chondrules and irregular aggregates are rounded in appearance.

A general study of the structure of the sawn surfaces of the original samples reveals lineation and possible layering or compaction patterns. All types of inclusions, but especially the wispy white ones, are commonly aligned in these lineated patterns. The dark inclusions are mostly elongated. The alignment of grains, crystallites and clasts in the dark inclusions suggests definite "flow" or compaction patterns. The patterns seem to indicate that the original shape was more spherical and was then pressed into the elongated shape. The lack of strong cohesion in the matrix and the presence of friable and heat sensitive materials suggests that the final formation of the meteorite parent body was more by gentle deposition than any but the lowest energy metamorphic phenomena. This hypothesis was developed as a result of observation obtained during the fracturing of wire sawn slabs.

Photographs of the large flat sawn sides of the samples are found in Appendix A. The approximate 2 to 1 enlargements allows for easier observation of the components.

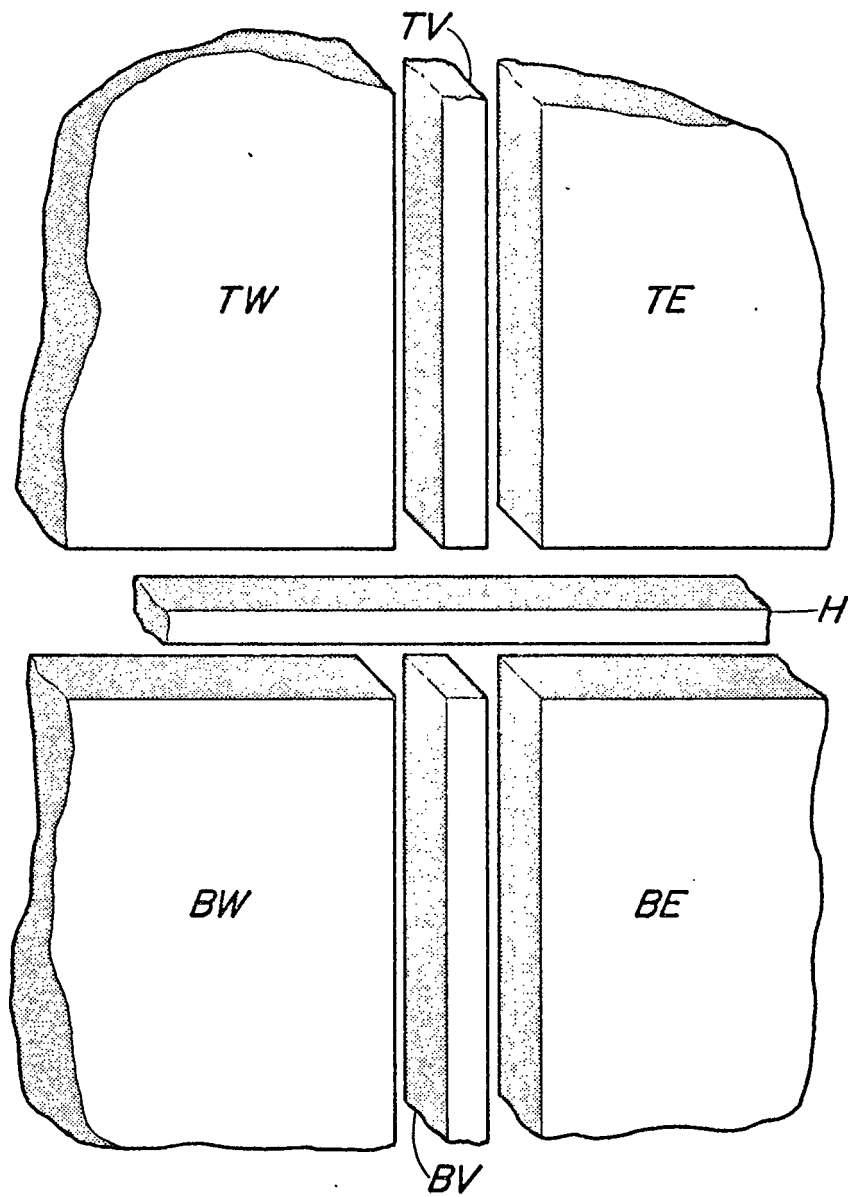
III. SAMPLE PROCESSING

The samples used for the work were nine pieces that had been cut from the original stones with a circular saw. Their dimensions averaged approximately 8 x 10 x 3 cm and the mean weight was approximately 90C grams.

A system based on area rather than weight or volume was used to obtain representative material from these heterogeneous samples. This system covers a relatively large area of the sample, but used only small volumes of meteorite. Figure 1 shows a drawing of a typical cutting plan for the samples. The slabs were 5 ± 0.5 mm thick and, based on the approximate sample dimension above, were about 11% of each sample by volume. The slabs were cut in the JSC Curatorial Laboratory with a wire saw used to slice small chips of lunar samples. The Allende material was soft enough that these relatively large pieces of material were easily cut. No lubricant was required. The 0.008 mm inch diameter wire used for the cutting was composed of stainless steel with a coating of cooper impregnated with diamonds. Following the wire sawing the saw fines were removed from the cut surfaces with a stainless steel wire brush and dusted with air from a freon propelled aerosol can. The saved pieces were stored in sealed polyethylene bags. The slabs were pulverized in three steps:

1. They were broken in approximate 1.5 cm^2 pieces by hand (the slab was held in aluminum foil).
2. The 1.5 cm^2 pieces were crushed in a steel percussion mortar (Diamond mortar).
3. The crushed material was screened through a $60 \text{ }\mu\text{m}$ stainless steel screen. Any material that did not pass through the screen was recycled into the mortar. The breaking of the slabs allowed close observation of the consistency of the components and matrix of Allende. Some chondrules were merely trapped in the matrix and essentially not bonded to it at all. Other "spongy" chondrules and most of the inclusions were either intimately bonded to the matrix or had reacted with it. Fracturing would typically go around the non-bonded chondrules, but would go through the bonded or "spongy" chondrules and inclusions. Following the screening, the $<60 \text{ }\mu\text{m}$ material was split into four aliquots with a stainless steel microsplitter.

Figure 1.



SAMPLE CUTTING PLAN

Each of the nine samples had 3 slabs cut from it for a total of 27 slabs. Each of the 27 slabs were pulverized and divided into four splits for a total of 108 splits. The typical sampling plan is shown in Figure 2. The weights of each of the samples and slabs are listed in Table 2. The total weight of the material in the slabs is 10% of the weight of the total weight of the samples. Portions of the splits have been reserved for several other types of analyses. The data at the bottom of Table 2 states the amount of material used in these analyses. The sample actually consumed in the analysis is only 0.0065% of the total sample material. The remainder is available for future work.

IV. GEOCHEMICAL SCHEME

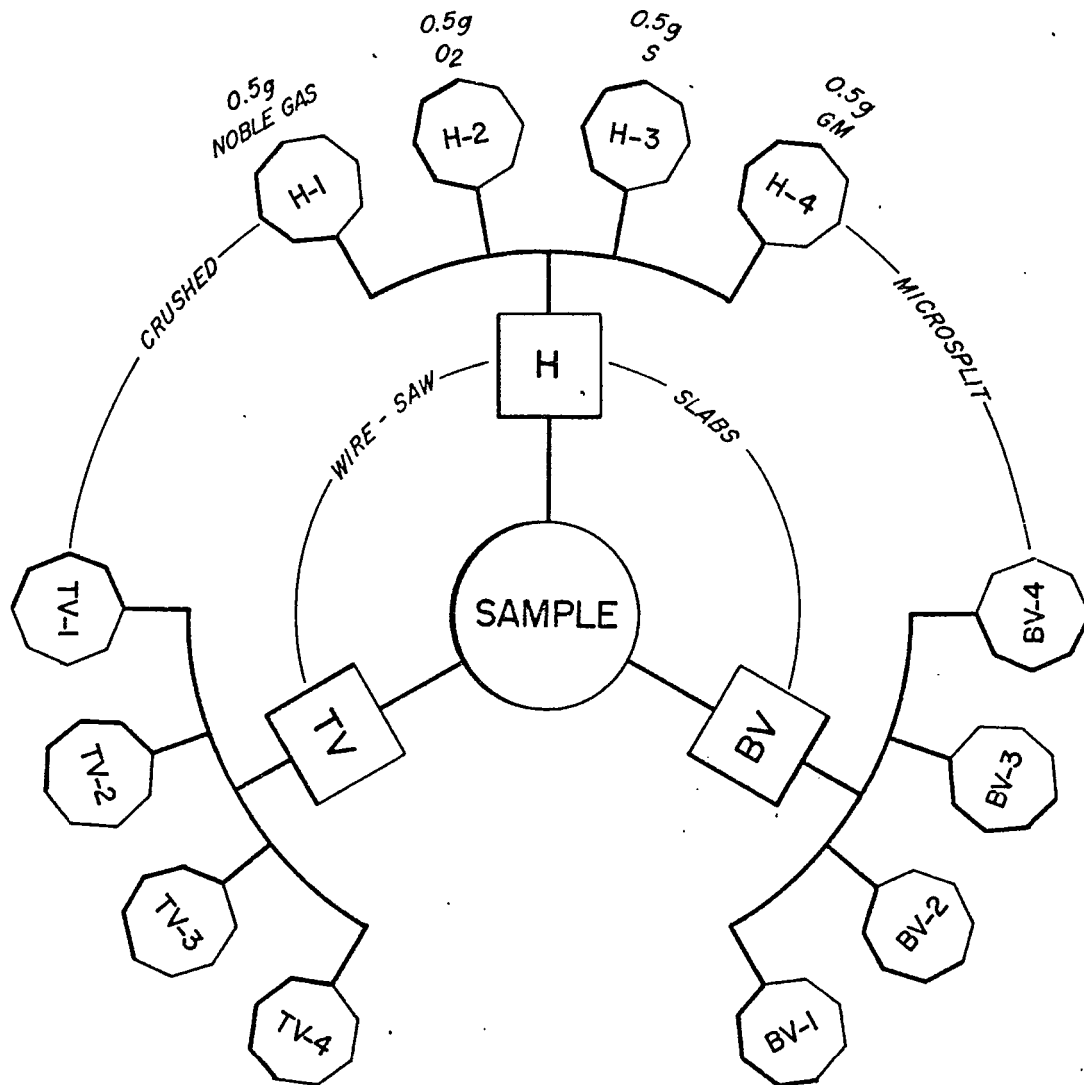
A study of the minerals of the meteorite and the chemical composition of these minerals identifies the major elements present. Table 3 lists most of the minerals and their chemical formulas found in Allende. All of the major minerals present are listed. The bulk chemistry of the meteorite consists of the elements in these minerals. The seven cation elements most common in these minerals are: silicon, iron, magnesium, aluminum, calcium, nickel, and chromium.

The geochemistry of the sample can be evaluated if the chemical elements are considered according to their geochemical association. S. R. Taylor (1966) used a combination of important geochemical factors for classification. The factors are size (ionic radius), valency (charge) and bond type (ionic-covalent). The divisions based on these factors are:

1. The large cation (potassium type)
2. The rare earth elements
3. The large highly charged cations (Zirconium type)
4. The ferromagnesian elements
5. The small cations (silicon type)
6. The chalcophile elements

If titanium is added to the list, only the rare earth and chalcophile elements are not represented in the elements to be analyzed. Manganese was added, to the list even though the ferromagnesian division is well represented, because it is a minor element with good sensitivity in the analytical system used. Silicon, iron, magnesium, aluminum, calcium,

Figure 2.



TYPICAL
SAMPLING PLAN

Table 2

SAMPLE WEIGHTS

<u>Sample No.</u>	<u>Weight</u>	<u>Sample No.</u>	<u>Weight</u>
9-S-1	1028.22 g	8-S-1	1424.85 g
9-S-1 H	48.88 g	8-S-1 H	52.39 g
9-S-1 TV	39.89 g	8-S-1 TV	40.02 g
9-S-1 BV	31.12 g	8-S-1 BV	33.22 g
9-S-2	964.81 g	8-S-2	1299.00 g
9-S-2 H	41.35 g	8-S-2 H	56.72 g
9-S-2 TV	29.38 g	8-S-2 TV	31.32 g
9-S-2 BV	30.20 g	8-S-2 BV	33.78 g
16-S-1	954.00 g	23A-S-1	987.10 g
16-S-1 H	47.18 g	23A-S-1 H	42.39 g
16-S-1 TV	20.49 g	23A-S-1 TV	25.30 g
16-S-1 BV	27.25 g	23A-S-1 BV	27.13 g
25-S-1	864.70 g	7-S-1	715.28 g
25-S-1 H	43.59 g	7-S-1 H	39.87 g
25-S-1 TV	23.87 g	7-S-1 TV	19.27 g
25-S-1 BV	25.22 g	7-S-1 BV	24.90 g
25-S-2	1015.49 g		
25-S-2 H	50.98 g		
25-S-2 TV	26.61 g		
25-S-2 BV	30.18 g		
Total meteorite material weight			9253.45 g
Total sample weight			942.50 g
Percent of meteorite material in samples			10.0 %
Total material mixed from 108 splits			6.91 g
Total material loaded into electrodes			0.61 g
Percent of total meteorite material used in these analyses			0.0065 %

Table 3

SOME MINERALS IN ALLENDE METEORITE¹

<u>Name</u>	<u>Formula</u>
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
Augite (fassaite)	$\text{Ca}(\text{Mg}, \text{Al}, \text{Ti})(\text{Al}, \text{Si})_2\text{O}_6$
Chromite	FeCr_2O_4
Clinoenstatite	MgSiO_3
Clinohypersthene	$(\text{Mg}, \text{Fe})\text{SiO}_3$
Cordierite	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$
Diopside	$\text{CaMgSi}_2\text{O}_6$
Enstatite	MgSiO_3
Ferroaugite	$\text{Ca}(\text{Fe}, \text{Mg}, \text{Al})(\text{Al}, \text{Si})_2\text{O}_6$
Gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$
Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Hercynite	FeAl_2O_4
Kamacite	(Fe, Ni)
Nepheline	$(\text{Na}, \text{K})\text{AlSiO}_4$
Olivine	$(\text{Mg}, \text{Fe})_2\text{SiO}_4$
Pentlandite	$(\text{FeNi})_9\text{S}_8$
Perovskite	CaTiO_3
Sodalite	$\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$
Spinel	MgAl_2O_4
Troilite	FeS

¹ Clark et al. (1970)

Manganese and Titanium are calculated as the following oxides:

SiO ₂	CaO	MgO	TiO ₂
FeO	MnO	Al ₂ O ₃	

When oxygen is added to the determination, greater than 97% of the bulk chemistry of the meteorite is included in the bulk analysis,

E. Jarosewich (1975). Sulfur is the only other element present with a concentration of greater than one percent. Most of it is combined with the iron and trace amounts with the nickel. Reporting the nickel as the element leaves its part of the sulfur out of the total. Calculating the total iron as the ferrous oxide compensates for most of the error caused by some small amount of it being present as the metal and another portion combined with sulfur. Chromium listed as the element further corrects for the iron sulfide.

Section 3 describes the analytical method used to determine the concentrations of these oxides and elements in the 108 splits taken from the samples.

ANALYTICAL METHOD

SECTION 3

I. INTRODUCTION

The optical emission spectrograph has been recognized as one of the most powerful tools available for investigating the natural universe Harrison et al. (1948). Analytical chemistry has continued to grow and expand. Analysts now have at their disposal a variety of tools and procedures such as colorimetric, polarographic, x-ray fluorescence, neutron activation, isotope dilution, spectrochemical, gamma ray spectrometry and classical method available for the detection and measuring the amounts of chemical elements Ahrens & Taylor (1961). The advent of solid state electronics has provided a major advancement in stability, sensitivity and precision possible with these methods. The electronic revolution has introduced new instruments such as the transmission electron microscope, electron microprobe and scanning electron microscope that provide both physical and elemental analyses. However, the single general method that detects the most elements and can quantitatively analyze minerals, soils, rocks and meteorites is spectrochemical analysis. This method has the advantage of relatively simple and rapid sample preparation. It provides a permanent record of analysis of both elements sought and others which may be of interest at some time in the future. The precision and accuracy of analyses performed with the optical emission spectrograph have, in the past, commonly not been as high as other techniques listed above. A major contributor to the lack of stability was the use of the DC arc for the sample excitation source. The introduction of atomic absorption spectrometry has had associated with it the development of hollow cathode lamps as stable precise sources of elemental emission lines. The use of a demountable hollow cathode lamp as a small excitation system provides a means to improve the precision and accuracy of optical emission spectroscopy as an analytical tool.

The principle of the hollow cathode source was introduced by Pachen in 1905. McNally et al. (1947) reported that there was a quantitative relationship between the amount of material placed in the hollow cathode and the resulting emission intensity. Stukenbroeker et al. (1952) later applied this to spectro-isotopic analysis. Mandelstam and Nedler (1961) calculated that the theoretical ultimate sensitivity obtainable from hollow cathode excitation was greater than for conventional spectrographic analysis. The expected advantages of this source over arc and spark emission spectrography include (a) less selective volatilization thus making matrix effects almost insignificant; (b) excellent discharge stability that increases the precision of the method; (c) the use of the inert gas plasma eliminates interferences from refractory oxide formation, atmospheric contamination and bands such as cyanogen; (d) production of extremely sharp spectral lines because of small temperature and pressure broadening effects; and (e) a simple inexpensive means of exciting elements with very high excitation potentials.

Several secondary objectives were pursued in the development of the method. The first was a sample preparation procedure that was as direct as possible. The number of steps must be as few as possible. Second, possible contamination be kept to a minimum. Reagents and utensils used must be the minimum number possible and the purest economically available. Finally, complicated steps that require a relatively high level of analyst skills, such as fusion, acid digestions or extration should not be used.

II. METHOD DEVELOPMENT

Method development includes evaluating the following variables:

1. Sample preparation methods
2. The best internal standard
3. Possible use of a buffer
4. What buffer to use, if one was needed
5. Method of electrode loading
6. The best carrier gas
7. Gas pressure

8. Gas flow rate
9. Current limiting resistance (open circuit voltage)
10. Plasma current
11. Exposure time
12. Comparison standards
13. Method of calculation of results
14. Type of spectrographic plates
15. Wavelength region to be photographed
16. External optical arrangement

Some of these variables are interrelated. Examples of the variable interactions are, method of electrode loading partially determined by sample preparation; wave length region photographed is fixed by the type of spectrographic plates and exposure time depends on both gas pressure and plasma current. This dependance of one parameter on another meant that if one were changed some or all of the others had to be retested.

Other variables were fixed by sample and equipment configurations. Instrument and source specification fixed the external optics and the type of spectrographic plates. The wavelength region to be photographed was regulated by the type of sample and the type of spectrographic plates. The external optical system which was selected for its simplicity, used a spherical collimating lens as the front window of the demountable hollow cathode unit and a cylindrical lens to focus the light on the slit of the spectrograph. Eastman Kodak type SA III spectrum analysis plates were selected for good sensitivity and satisfactory contrast in the spectral region of the maximum number of lines of elements found in the sample. The wavelength region photographed was from 2450 Å to 4950 Å.

Six electrode loading methods are suggested by the developer of the dismountable hollow cathode unit, J. D. Johnson (1974). They are evaporation, filtration, micro-ashing, electrolysis, impaction and fusion. Filtration, micro-ashing and electrolysis were eliminated for being either not applicable or too complicated to use for geological samples. The fusion method even though sample preparation involves several steps was tested first because it can produce more precise results than the other

more direct methods. The initial tests were unsuccessful because the electrode was severely oxidized in the muffle furnace at fusion temperatures with an air atmosphere. A furnace with an inert atmosphere was not available and the method was discarded.

Evaporation was the next loading method tested. Geological samples were first put into solution by an alkali fusion and subsequently the solidified melt was dissolved in dilute acid. A weighed amount of internal standard was added to the solution. A measured amount of solution was placed in electrodes. The initial test electrodes were heated on a hot plate and later others were heated in a vacuum oven. Evaporation of the water from the samples in a reasonable amount of time was not practical. If only a slight excess of heat were applied to the electrodes the solution at the bottom would boil first and much of the remaining liquid would spatter out of the electrodes. Finally impaction was tested. It is the most direct method and the most rapid. A test with a standard indicated that the precision would be satisfactory using strontium carbonate as an internal standard. Strontium carbonate was chosen because of several possible internal standard lines available and stable excitation Kvalheim (1947) and Dennen (1949). The sample aliquots and internal standard were weighed and combined in a 9:1 ratio and the powders were mixed by grinding with a mortar and pestle. The only strontium line with a useable intensity ($2931.83 \text{ \AA}$) was found to have interference from a weak iron line. The interference was not significant for the U.S.G.S. standards because their iron (as FeO) concentrations are less than 15%. The interference effect was significant for Allende, which has reported bulk analysis values for total iron (as FeO) near 30%.

Palladium was chosen as the replacement internal standard element for strontium. Palladium has more lines available and higher energy excitation conditions. The pure form of palladium sold commercially is tetraamminepalladusdinitrate. Because this salt is soluble in H_2O , a method of adding the internal standard to the electrode as a solution and drying the solution in the electrode was tested. The result met with the same difficulty as the sample solutions and was abandoned. This salt when used directly released gases when excited by the plasma causing

unstable excitation, sputtering and high background. The salt was then converted to the oxide by heating to 120°C in a muffle furnace, weighed and combined with sample material in a 1:9 ratio and mixed by grinding in a mortar and pestle. The precision of this method for quantitative analysis was unsatisfactory. The strontium carbonate is known to have stable burn characteristics making it a good buffer. A mixture of one part strontium carbonate as a buffer, one part palladium oxide as an internal standard and eight parts of sample provided satisfactory results.

The demountable hollow cathode (DMHC) produces a considerably different excitation than the DC arc. The resulting spectrum is very different from a DC arc spectrum. Cyanogen and other bands formed from atmospheric gases are greatly reduced in the DMHC, but the lines of plasma gases are enhanced. Some lines such as the 3100 Å iron triplet have very weak intensities and other lines such as nickel 3619.399 Å and titanium 3234.52 Å have significantly stronger intensities. The differences in the spectra of the two methods were great enough to require the detailed study of a master plate. The master plate was prepared using three electrodes, one loaded with 5 mg of 9:1 ratio Spex standard mix and strontium carbonate, one loaded with 5 mg of 9:1 graphite powder and strontium carbonate and one loaded with 5 mg of pure Fe₂O₃ powder. The range of the spectrum photographed was from 2440 to 5000 Å and 133 possible analytical lines and 30 argon lines were verified and marked on the plate.

Plasma gases consisting of argon, argon with 0.09% hydrogen and helium were tested. The excitation of heavier elements with helium is weak. The argon-hydrogen produced the best average excitation and provided a reducing atmosphere to break down refractory oxides. Plasma gas pressure of 1-4 mm of mercury absolute were tested and 2 mm of mercury absolute pressure produced the best line to background intensity ratio. A vacuum pump with a rated capacity of 160 l/hr was more satisfactory than the original one used that had a capacity of 25 l/hr. The larger pump provided a higher gas flow rate that allowed the system to be cleared of atmospheric gases faster and lowered pump down pressures which reduced the concentration of adsorbed atmospheric gases in the system to a lower level.

The current in the excitation system was set by an adjustment in the power supply. The voltage output of the power supply was varied to maintain the set current constant. The current limiting resistance was adjusted for the minimum value that allowed the power supply to control the current except for momentary flashes. A warm up time was required and during this period of time the current gradually was increased to the desired stable value. The exposure was begun after the current was stable at the set value. A current value of 150 ma was used in the beginning, but reduced as the maximizing of other parameters increased sensitivity. The value used for the analysis of the Allende samples was 75 ma.

Exposure times tested ranged from 1 to 30 minutes. It was decreased as other parameter changes increased sensitivity. The lack of line broadening that is a characteristic of the hollow cathode excitation allows long exposure times with a minimum of increase in background. The time of exposure used to measure the standards and samples was 4.6 minutes.

The materials used for comparison standards were: Spex Mix; synthetic lunar material; United States Geological Survey standards G-2, BCR-1, G-1, W-1, PCC-1 and DTS-1; the Smithsonian Allende sample and Johnson Mathey spectroscopically pure ferric oxide. The U.S.G.S. standards and the Allende standard were used only for final calibration curve development in order to conserve these materials as much as possible. The synthetic lunar material (SLM) was prepared for an abandoned botanical research project. The material is a mixture of Hawaiian basalt and a Montana ilmenite concentrate. It was analyzed spectrographically in the Lunar Receiving Laboratory at the Johnson Space Center and in the spectrochemical analysis laboratory of the U.S.G.S. located at that time in Washington D.C. Several pounds of this material became surplus when the project was terminated and was used as a control with each batch of sample prepared as well as a standard. The preferred concentration values of the standards used were from S. R. Taylor (1975); the U.S.G.S. report on the 1972 compilation of standard data by Flanagan (1973), and the Allende data from E. Jarosewich (1975). The Allende iron value (reported as ferrous oxide)

was from E. A. King et al. (1969). The concentrations of the nine elements in the standards analyzed vary over a wide range. In several standards the concentrations of the elements are below the detection limit for that element on the spectrum line used for the analysis. At least three standard reference samples were used in calculating each calibration curve. The data used to obtain the calibration curves are listed in Table 4.

An emulsion calibration was calculated to obtain γ (gamma), the slope of the emulsion characteristic curve, for each different batch of plate emulsion used. An electrode loaded with seven mgs of 1:1:8 SrCO_3 to PdO to sample was exposed for evenly stepped logarithmic time intervals of 2.15, 4.60 and 10.00 minutes. Eleven lines from random locations across the entire spectrum photographed and with %T values ranging from 19% to 85% were measured with the clear plate background set to 100%T for each line. The data were converted to γ by the relationship in equation 1.

$$\gamma = \frac{[\text{Log} (\frac{100}{T_2} - 1) - \text{Log} (\frac{100}{T_1} - 1/SC)] + [\text{Log} (\frac{100}{T_3} - 1) - \text{Log} (\frac{100}{T_2} - 1/SC)]}{2} \quad (1)$$

2

T_i is the %T values for each step and SC is the stepped logarithmic time interval. The Seidel transform $\text{Log} (T_i/T-1)$ calculation of intensity is used in this relationship to extend the linear portion of the emulsion characteristic curve. An average gamma of all the lines was calculated and this value used for the correction factor for emulsion in calculating elemental concentrations. The Hewlett Packard HP-25 program used for this calculation is listed in Appendix B.

The concentrations of the elements in the samples were calculated from peak height percent transmissions of designated element lines of each spectrum. Calibration curves were calculated by first using the Seidel transform to convert %T to intensity for the internal standard line and all the element lines. Then each element line was ratioed to the internal standard. Element calibration curves were calculated using intensity ratios vs. concentrations in a curve fitting-linear regression by the method of least squares. The calibration curve

Table 4
STANDARDS CALIBRATION DATA
Concentrations and Intensity Ratios

Oxide		MgO	SiO ₂	FeO	Al ₂ O ₃	Ni	TiO ₂	MnO	Cr	CaO
STD										
SLM	Conc	5.99	45.75	16.51	11.11		8.81	0.60	0.029	10.82
	Ratio	0.001	3.767	0.701	1.419		0.809	2.094	0.316	1.896
ALL	Conc	24.63	34.28	30.70		1.40	0.15	0.19	0.360	2.29
	Ratio	0.016	1.648	2.132		0.080	0.004	0.401	1.808	0.147
BCR-1	Conc			12.06			2.20	0.18		6.92
	Ratio			0.384			0.106	0.408		0.846
PCC-1	Conc	43.18	41.96	7.51	0.74	0.250		0.12	0.280	
	Ratio	0.086	2.039	0.184	0.084	0.001		0.242	1.832	
W-1	Conc			9.98	15.00		1.07			
	Ratio			0.254	1.636		0.062			
G-2	Conc		69.11		15.40		0.52			1.94
	Ratio		8.546		2.218		0.023			0.133
DTS	Conc		40.50	7.77		0.245			0.400	
	Ratio		2.295	0.166		0.001			2.081	
Points		3	5	6	4	3	5	4	4	4
Calibration curve coefficients										
Slope m		383.755	4.646	11.482	7.347	14.589	10.414	0.266	0.193	5.303
Intercep b ₂		11.425	29.310	6.776	0.728	0.233	0.459	0.085	-0.020	1.664
r		0.877	0.974	0.983	0.942	1.00	0.989	0.986	0.965	0.972

coefficients were determined from equations 2 and 3.

$$\text{Slope } m = \frac{\sum IR \cdot C - \frac{\sum IR \cdot \sum C}{n}}{\sum IR^2 - \frac{(\sum IR)^2}{n}} \quad (2)$$

$$\text{Intercept } b = \bar{c} - m\overline{IR} \quad (3)$$

Where IR is the intensity ratio, c is the concentration, n is the number of data points, $\bar{c} = \sum c/n$ and $\overline{IR} = \sum IR/n$. The data reduction program used for these calculations is listed in Appendix B and includes the calculation of the coefficient of determination r^2 , the goodness of fit value for each curve.

The elemental concentration in each sample was determined by calculating the intensity ratios in the same manner they were obtained for the standards and substituting them in equation 4.

$$\text{Concentration } c = m \cdot IR_s + b \quad (4)$$

The Fortran IV program for the calculations of sample intensity ratios and concentrations is listed in Appendix C.

A unique densitometer technique for making background corrections for each line including the internal standard line will be discussed in Section 4. This precision densitometry required only a peak scan and a background scan for each line. The common densitometer method that corrects for background requires a peak and a background scan for a minimum of two and preferably three intensity steps for each line.

III. APPARATUS AND PROCEDURES

The spectrograph used for this work is a Jarrell-Ash 3.4 meter mark IV Ebert mount with 1200 lines per millimeter grating. The excitation source unit is a Spectrogram Corporation Miniglow, model MG-10S, demountable hollow cathode shown in Figure 3. The plasma gas control unit was constructed in this laboratory. A schematic diagram of this unit is shown in Figure 4. This gas control unit has a by-pass

1. NYLON NUT
2. QUARTZ WINDOW
3. WINDOW "O" RING
4. THRUST WASHER
5. ANODE "O" RING
6. ANODE SUPPORT
7. ANODE
8. MAIN BODY ASSEMBLY
 - 8A. MINIATURE PLUG
 - 8B. CATHODE LEAD AND CLIP
 - 8C. GAS INLET
 - 8D. VACUUM OUTLET
 - 8E. BASE WATER COOLING
9. SHIELD
10. INSULATING ADAPTER ASSEMBLY
11. CATHODE
12. CATHODE HOLDER
 - 12A. CATHODE COOLING
13. PHENOLIC HOUSING
14. HOUSING SUPPORT
15. COVER WITH MINIATURE JACKS

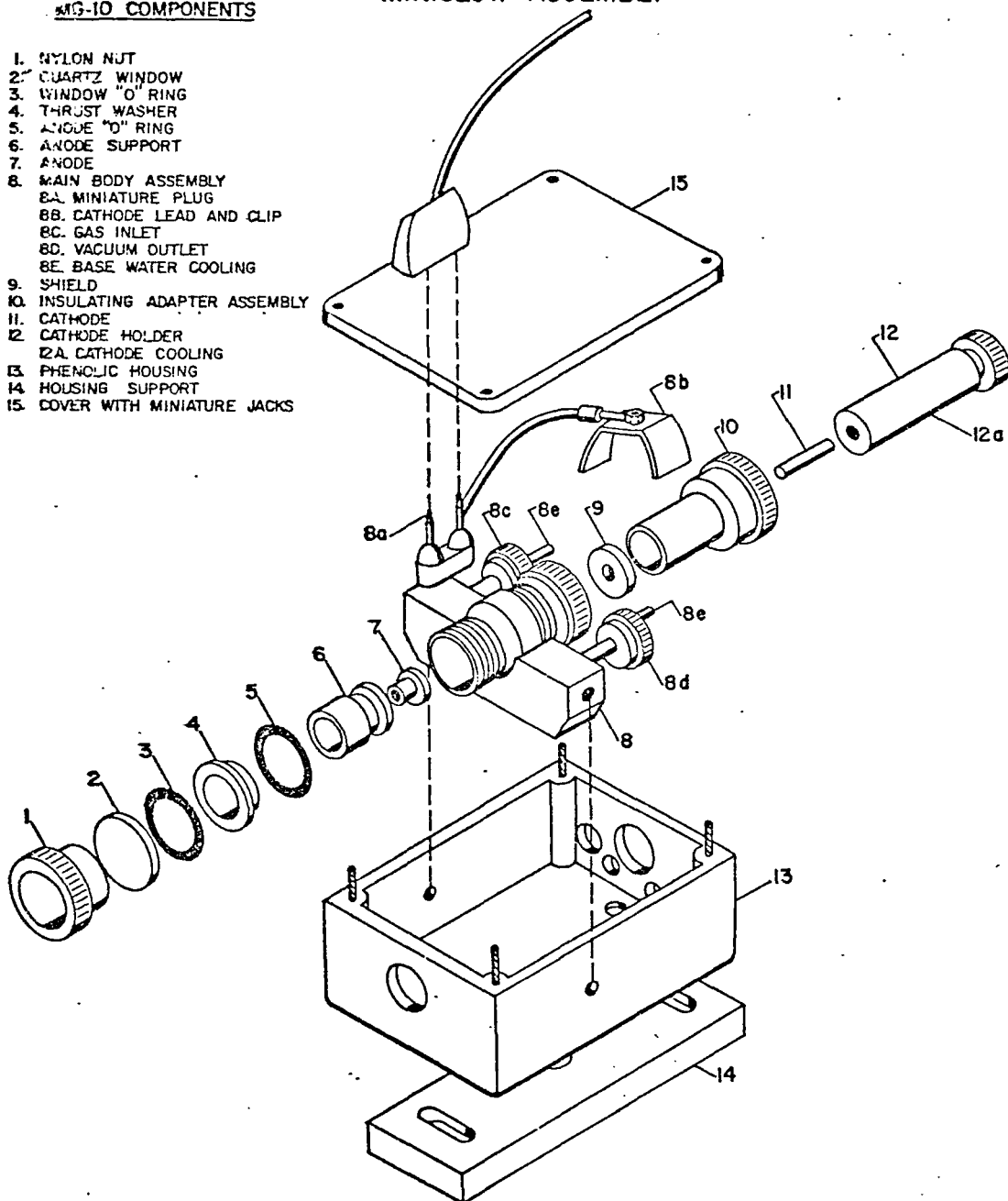
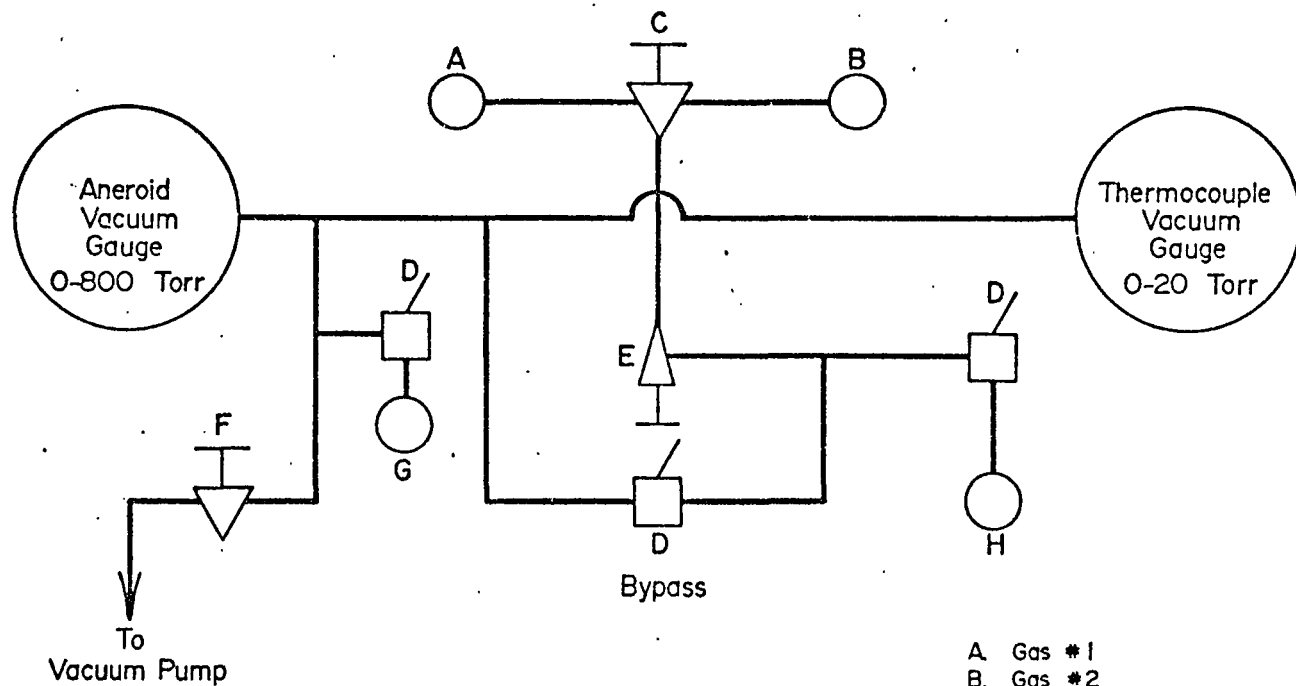


Figure 4.

HOLLOW CATHODE GAS CONTROL SYSTEM SCHEMATIC



- A. Gas #1
- B. Gas #2
- C. Three-way valve
- D. Toggle valve
- E. Flow control needle valve
- F. Vacuum valve
- G. Hollow cathode outlet
- H. Hollow cathode inlet

system that allows the unit to be pumped down and functionally checked internally while the lines to the hollow cathode unit are closed. The power supply is a stabilized current controlled radio plate type power supply with a maximum output of 500 volts and 200 ma. An external manually switched bank of current limiting resistors is placed in series between the source and the power supply. The system is evacuated and the plasma gas circulated by a Welch Duo-seal model 1402 mechanical vacuum pump. The spectrographic plates were processed in a temperature controlled Jarrell-Ash model 34-100 photoprocessing machine. The lines and background percent transmissions were determined on a Jarrell-Ash model 23-100 recording microrphotometer. Experimental conditions are listed in Table 5.

The 108 splits from the sample processing were numbered serially and then according to random numbers generated in a table by the University of Houston Univac 1108 computer. All sample processing and data reduction was done according to this random number sequence. Not until the statistical evaluation of the results by slab and sample were those data reassembled in serial form.

The strontium carbonate buffer and the internal standard palladium oxide mixture were prepared by weighing 1.000 g of each into a boron carbide mortar and ground 2 hours with a boron carbide pestle. This same mixture was used for all of the samples and standards analyzed. Samples were prepared for analysis by weighing 16 mg of the 1:1 buffer-internal standard mix and 64 mg of sample (or standard) into a boron carbide mortar and ground at least 20 minutes with a boron carbide pestle. The ground material was then transferred to 0.1 N nitric acid and demineralized water rinsed vials for storage. Seven milligrams of the ground material was weighed into a electrode and mixed on a Spex Inc. "wiggie bug" mixer for 1.5 minutes using a steel ball in the electrode and a teflon disc for a cover on the electrode. The cover and ball were removed and the electrodes were evacuated for 48 hours in a vacuum oven at 120° C and minus 30" of mercury.

Table 5
EXPERIMENTAL CONDITIONS

1. Spectrograph	- Jarrell-Ash 3.4 meter mark IV Ebert mount model 70-334
Grating	- 1200 lines per mm
Reciprocal linear dispersion	- $5.4 \frac{\text{\AA}}{\text{mm}}$
Slit width	- 50 μ
Wedge	- 1.5 mm
Wavelength	- 3700 $\text{\AA}$ at center of plate holder
Spectrographic plates	- 4"x10"x0.040" Kodak spectrum analysis #3
Rack	- 2 mm
2. Source	- Spectrogram Corp. miniglow model H-10
Current	- 75 ma
Limiting resistance	- 800 ohms
Plasma gas	- 0.090% hydrogen in Argon
Gas pressure	- 2 torr
Electrode	- Ultra carbon type 623203,U-7 (ASTM-PC-2)
Sample size	- 7 mg of 1:1:8, buffer to interval standard to sample
3. Densitometer	- Jarrell-Ash model 23-100 recording microphotometer
Slit height	- 1.2 mm
Slit width	- 0.45 mm
Scan rate	- 1 inch per minute
4. Photoprocessing	
Developer	- Kodak D-19
Time	- 4 minutes at 68° F
Stop bath	- Kodak stop bath solution
Time	- 0.5 minutes
Fixer	- Kodak rapid fixer
Time	- 4 minutes
Washed	- 20 minutes
Dried	- maximum drier temperature, 5 minutes

The electrodes were loaded into the holder in the demountable hollow cathode in random order. A clean dried anode and ceramic insulator disc were inserted into the unit during each electrode charge. The valve connecting the gas control system to the vacuum pump was opened and the entire system was pumped down to less than 0.05 torr gauge reading. The Ar/H supply valve and control needle valves were opened all the way and the system was flushed with Ar/H. After about 30 seconds the latter valves were closed and the system was pumped down again to less than 0.05 torr gauge reading or lower if possible. When a minimum value was reached or after about a minute the Ar/H supply valve was opened and the control needle valve adjusted until the system pressure was 2 torr argon pressure.

With the cooling water flowing, the current limiting resistance set at step nine or ten and the current adjustment control set at the minimum value, the high voltage power was turned on by plugging the cover onto the miniglow unit. The current limiting resistance was reduced to step 3 (800 ohms). When the glow in the cathode ignited a ten minute warm up period started. During this time the current was gradually increased until it reached 75 ma. The voltage was kept below 420 volts during this period. If the current and voltage were stable at the end of the 10 minute interval the shutter was opened for 4.6 minutes. Following the exposure the plate holder was racked, the current reduced to the minimum setting, the vacuum valve closed, and the control valve opened. When the pressure on the aneroid vacuum gauge reached 800 torr the Ar/H inlet valve was closed and the unit was ready to be opened for the electrode to be replaced. Approximately 25 exposures filled a set of plates, the plate holder then was removed and the plates developed by normal procedures.

IV. DENSITOMETRY

Densitometers are usually constructed as a combination comparitor and densitometer. The comparitor is used for the qualitative determination of the various elements present in a sample. The data is obtained by comparing the sample spectrum with a standard material spectrum that has the lines of 50 or 60 elements identified along a wavelength scale. The plate with the standard spectrum is called a master plate. The wavelengths of the elements selected for these analyses are listed in Table 6.

The 3242.70 Å palladium internal standard line was investigated thoroughly by S. R. Taylor et al. (1970) and found to be free of any interference by any of the more abundant elements. No evidence of interference is detectable on this line either from the hollow cathode excitation or the Allende matrix. Two criteria were used to select the analytical lines of the elements. One is that they have no interferences from lines of other elements. The second is that the line is located in a low background area of the spectrum. The quantitative determinations of the concentrations of the elements analyzed are made by measuring the relative darkness of the lines recorded on the photographic plate compared to the darkness of the interval standard line. The raw data obtained from the photographic plate are percent transmission (%T) values. The measurement is converted to electrical energy by passing the plate through a light beam focused on a slit mounted in front of a photomultiplier tube. The electrical energy is measured on a 0-100 scale strip chart recorder. The minimum values of the peaks are read as %T values.

Previously the concentrations of the elements in a sample were calculated from the %T data by one of two basic methods. They both involve using the Seidel transform to determine line intensities. The method used to measure the spectrum directly without attenuation requires the setting of the clear plate above the line at 100% scale and the output when an opaque card placed in the light beam at 0% scale. The intensity of each analytical line is calculated and then the ratio of the intensity of each line with the interval standard intensity is found. The concentration of each element is determined from a calibration curve for each element. The calibration curve is a plot of the intensity

Table 6

WAVELENGTHS OF ELEMENT LINES MEASURED

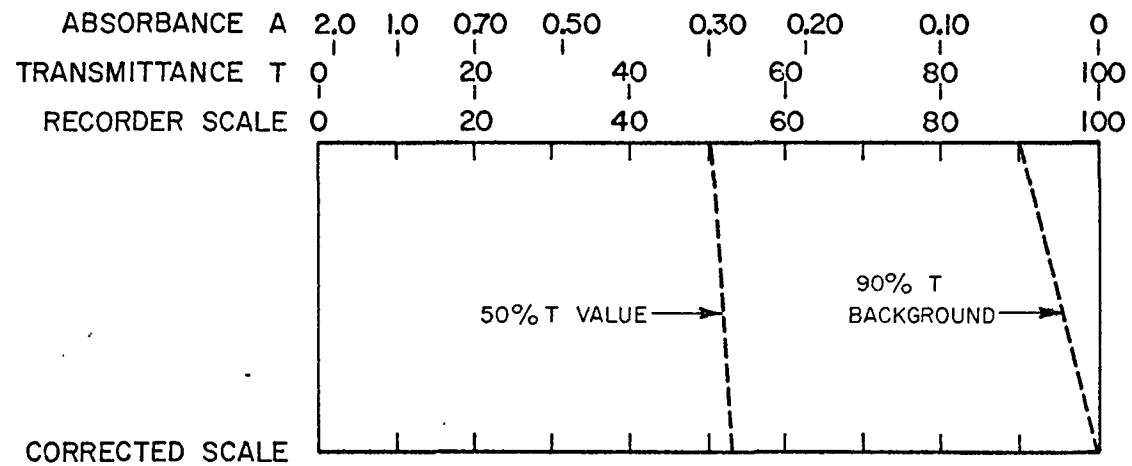
<u>Element</u>	<u>Å</u>	<u>Element</u>	<u>Å</u>
Pd	3242.70	Ti	3254.52
Mg	2779.83	Ni	3619.39
Si	2881.58	Mn	4033.07
Fe	3020.64	Cr	4289.72
Al	3082.16	Ca	4454.76

ratio values from standards vs. the concentrations of the element in the standards. There is no compensation for background variations. The alternate method described by Ahrens and Taylor (1961) requires each spectrum to have several steps of attenuation. The attenuation is achieved either optically or mechanical with a stepped neutral density filter or a rotating step sector in front of the entrance slit of the spectrograph. This method is called the self calibrating method because the calculation compensates for variations in emulsion characteristics along with the determination of elemental concentrations. The %T values for element lines and backgrounds must be determined on at least two steps and preferably three or more attenuation steps. The intensities are referenced to an arbitrary scale and concentrations determined by comparing samples intensity ratios with a calibration curve plot of standard intensity ratios, calculated in the same manner, vs. the concentrations of the elements in each standard.

This research has developed a third method that has the advantage of background correction and requires only two %T readings, one for the line and one for background. The %T values cannot be subtracted directly as they vary logarithmically and the function would be division of the real values and the output meaningless. The quantities used by C. F. Hiskey (1949) in proving his principles of precision colorimetry are absorbance (A) rather than %T. This method is later discussed by Willard, Merritt and Dean (1965) as relative absorbance spectrophotometry. Absorbance values have a linear relationship and corrections can be calculated using simple arithmetic. If the densitometer is considered a broad band spectrophotometer the same principles can be applied. A graphic representation of the calculation is shown in Figure 5. The full scale A value of 2 may introduce some error, but the ends of the emulsion characteristic Hurter and Driffield curve are not linear and %T values greater than 96 and less than 10 are questionable. The %T background reading is obtained by setting clear plate value at 100 and reading the minimum background next to each element line. A background correction factor is determined by calculating the transmittance T from

Figure 5

REAL AND EFFECTIVE OPTICAL SCALES



the %T background reading,

$$T = \%T/100\%$$

converting transmittance to absorbance,

$$A = \log_{10}(1/T)$$

determining the A length of the compressed scale for the element line,

$$Sc = 2-A$$

then finding the scale correction factor F,

$$F = 2/SC.$$

Each element line %T is measured by setting the minimum background next to the line at 100% scale and then scanning and reading the peak value as %T. Each %T value is multiplied by the scale correction factor prior to calculating the elemental intensity to the internal standard intensity ratio and concentration by the direct method described above.

The results obtained using this method are presented in the next section. Relative standard deviations are consistantly lower than those of the direct method and at least 25 electrode exposures can be recorded on each set of plates.

RESULTS AND STATISTICAL EVALUATION

SECTION 4

I. INTRODUCTION

Analytical information was obtained from the spectrographic plates in the same random order as the analyses were performed. Electrodes were burned in eleven exposure groups and exposure groups were distributed on five sets of spectrographic plates. Internal standard intensities and raw concentration values for the synthetic lunar material had different levels for different exposure groups which required development of an exposure group correction calculation to normalize these differences. The correction was made by calculating a new intercept coefficient for each burn in an exposure group. These new coefficients were averaged and divided by the intercept coefficient of the original calibration curve. The original intercept coefficient was then multiplied by this correction factor to obtain a corrected intercept value and this correction was made for each oxide/element in each exposure group. Corrected concentrations were then calculated for each exposure group using the original slope coefficient for each oxide/element and the corrected intercept coefficient for each oxide/element in each exposure group.

Reading the spectra on the densitometer revealed that the background was high across 16 of the 108 spectra. The excess background darkness was most obvious around nickel, chromium and manganese lines, but had an effect across most of the length of the spectra photographed. These high backgrounds were caused either by water or air still absorbed in the electrode, a leak in the plasma gas system or an incomplete pump down prior to starting the burn. Results for these spectra were among some of the most extreme values of the oxide/element concentrations and the total concentrations for each split. The results for these bad burns were not included in the data reported except for the summary of all analyses in random order.

Table 7 is a compilation of summary statistics for concentrations of the oxide/elements in all 108 splits. Variations include both the actual difference between the aliquots analyzed and differences caused by less than perfect analytical precision.

Table 7

SUMMARY STATISTICS OF ALL ANALYSES IN RANDOM ORDER

	MgO	SiO ₂	FeO	Al ₂ O ₃	TiO ₂	Ni	MnO	Cr	CaO	Total
Means	24.64	34.26	30.59	3.32	0.157	1.42	0.190	0.357	2.29	97.23
Std Dev	1.60	1.56	3.54	0.51	0.027	0.25	0.035	0.094	0.39	5.66
Variance	2.55	2.42	12.50	0.26	0.001	0.06	0.001	0.009	0.16	31.99
Coef of Var	0.06	0.05	0.12	0.15	0.170	0.18	0.183	0.265	0.17	0.06

II. RESULTS

The data were rearranged in serial sample number order, grouped according to sample and slab and summary statistics were calculated. Table 8 contains the results obtained for each sample. Table 9 has the concentrations of the oxide/elements found in each slab.

The standard deviations (listed under each average value) show the precision of the analysis for each oxide/element in each sample and slab. The precision for silica is in the range desired for all the greater than 5% oxide/elements. Magnesia standard deviations are typically larger than those for silica. The approximately 10% lower concentration of magnesia results in a larger coefficient of variation than desired. Ferrous oxide standard deviations are approximately two or three times larger than silica. These variations and those for nickel and probably chromium can be explained by the fact that the meteorite contains fine particles of metal. The metal particles are primarily iron, but they do contain some nickel (kamecite) and possibly some chromium. The variability is caused by the fact that when the aliquots taken from the splits are ground with the internal standard/buffer the metal particles do not break into finer grains as the minerals do and the larger or possibly smeared metal particles are not homogeneous in the mixture. When the 7 mg electrode charge is removed from the mixture the metal will not be representative of the average amount of metal in that sample or slab.

The aluminum and calcium oxide standard deviations are larger than desired for the analytical method but there is no obvious reason why these oxides should have a higher variability. They are relatively refractory oxides, but titania is even more refractory and considering the small amount present has relatively good precision. The spectral lines have relatively clear areas on both sides of these lines. Titanium and manganese oxides have similar concentration values and their analyses have approximately the same precision. The precision of the analyses of the oxide/elements with less intense spectral lines such as titania and nickel was increased at least ten fold by the use of the background corrected densitometry. For many of the uncorrected data the standard

Table 8

ANALYSES OF SAMPLES

Sample	9-S-1	9-S-2	16-S-1	25-S-1	25-S-2	8-S-1	8-S-2	23A-S-1	7-S-1
Oxide or Element									
MgO	24.78 ±1.52	24.37 ±2.19	24.00 ±1.41	24.93 ±1.68	24.52 ±1.37	24.18 ±1.49	24.65 ±1.60	25.17 ±1.13	25.10 ±1.90
SiO ₂	34.18 ±1.18	34.08 ±1.56	33.76 ±1.08	33.99 ±0.95	33.27 ±1.56	34.52 ±1.36	35.23 ±2.58	34.57 ±1.08	35.15 ±1.59
FeO	31.82 ±3.02	29.41 ±3.13	29.51 ±3.73	31.14 ±3.51	28.42 ±4.32	30.17 ±2.28	30.52 ±3.44	32.91 ±3.24	31.59 ±3.69
Al ₂ O ₃	3.62 ±0.51	3.03 ±0.49	2.91 ±0.25	3.33 ±0.58	3.19 ±0.48	3.44 ±0.63	3.46 ±0.53	3.41 ±0.32	3.45 ±0.44
TiO ₂	0.157 ±0.019	0.145 ±0.022	0.147 ±0.036	0.166 ±0.026	0.151 ±0.026	0.166 ±0.037	0.156 ±0.027	0.168 ±0.021	0.155 ±0.188
Ni	1.393 ±0.152	1.364 ±0.148	1.481 ±0.159	1.394 ±0.155	1.398 ±0.178	1.411 ±0.206	1.326 ±0.170	1.606 ±0.633	1.460 ±0.074
MnO	0.188 ±0.021	0.170 ±0.019	0.204 ±0.056	0.191 ±0.039	0.202 ±0.049	0.196 ±0.030	0.180 ±0.024	0.195 ±0.033	0.186 ±0.018
Cr	0.367 ±0.048	0.402 ±0.165	0.353 ±0.056	0.355 ±0.126	0.337 ±0.051	0.372 ±0.082	0.323 ±0.076	0.358 ±0.091	0.325 ±0.089
CaO	2.49 ±0.45	2.21 ±0.46	1.99 ±0.21	2.42 ±0.43	2.23 ±0.39	2.27 ±0.18	2.36 ±0.24	2.31 ±0.25	2.27 ±0.63
Total	99.00 ±5.55	95.17 ±6.10	94.33 ±5.31	97.91 ±6.05	93.72 ±4.40	96.76 ±4.48	98.20 ±5.45	100.71 ±3.64	99.69 ±6.61

TABLE 9
ANALYSES OF SLABS

SLAB NUMBER	9-8-1 N	9-8-1 TV	9-8-1 NV	9-8-2 N	9-8-2 TV	9-8-2 NV	16-8-1 N	16-8-1 TV	16-8-1 NV	25-8-1 N	25-8-1 TV	25-8-1 NV	25-8-2 N	25-8-2 TV	25-8-2 NV
OXIDE OR ELEMENT															
MgO	24.02 ±2.07	25.45 ±1.12	24.86 ±1.25	23.89 ±3.49	23.80 ±1.18	25.29 ±2.16	22.84 ±1.50	24.53 ±1.34	24.47 ±1.14	25.34 ±1.70	25.56 ±1.87	23.87 ±1.30	24.31 ±1.65	23.72 ±1.27	25.14 ±1.15
SiO ₂	34.78 ±1.00	33.96 ±1.08	33.81 ±1.28	34.33 ±0.79	33.98 ±2.43	33.99 ±1.29	34.10 ±0.19	33.18 ±0.90	33.93 ±1.57	34.12 ±1.66	33.67 ±0.19	34.18 ±0.56	34.16 ±0.65	33.93 ±0.39	32.10 ±1.94
FeO	30.88 ±4.05	32.47 ±2.70	32.12 ±3.03	29.99 ±1.71	29.32 ±1.09	29.06 ±3.68	29.23 ±4.32	29.87 ±4.81	29.45 ±3.71	30.30 ±4.45	32.93 ±2.82	30.19 ±3.33	25.75 ±4.92	28.45 ±1.25	31.07 ±3.54
Al ₂ O ₃	3.66 ±0.56	3.36 ±0.43	3.86 ±0.55	3.42 ±0.23	2.82 ±0.49	2.96 ±0.57	2.94 ±0.14	2.79 ±0.19	2.98 ±0.35	3.06 ±0.69	3.47 ±0.75	3.45 ±0.21	3.60 ±0.43	3.21 ±0.15	2.78 ±0.21
TiO ₂	0.153 ±0.021	0.163 ±0.021	0.156 ±0.019	0.145 ±0.019	0.139 ±0.010	0.150 ±0.034	0.115 ±0.038	0.174 ±0.034	0.150 ±0.021	0.183 ±0.023	0.164 ±0.015	0.152 ±0.033	0.162 ±0.022	0.139 ±0.013	0.148 ±0.034
Mn	1.41 ±0.12	1.38 ±0.24	1.38 ±0.11	1.24 ±0.10	1.41 ±0.15	1.42 ±0.15	1.61 ±0.06	1.35 ±0.21	1.48 ±0.11	1.40 ±0.14	1.33 ±0.23	1.46 ±0.05	1.31 ±0.10	1.37 ±0.08	1.50 ±0.24
NaO	0.190 ±0.007	0.193 ±0.028	0.182 ±0.028	0.179 ±0.017	0.161 ±0.010	0.172 ±0.026	0.190 ±0.058	0.229 ±0.078	0.196 ±0.048	0.224 ±0.037	0.186 ±0.013	0.164 ±0.041	0.227 ±0.070	0.183 ±0.008	0.166 ±0.029
Cr	0.358 ±0.013	0.348 ±0.050	0.394 ±0.064	0.448 ±0.113	0.388 ±0.127	0.381 ±0.252	0.342 ±0.040	0.366 ±0.070	0.352 ±0.069	0.407 ±0.147	0.394 ±0.107	0.355 ±0.133	0.311 ±0.068	0.359 ±0.018	0.351 ±0.040
CaO	2.19 ±0.18	2.32 ±0.58	2.67 ±0.53	2.01 ±0.24	2.23 ±0.65	2.34 ±0.43	1.85 ±0.16	1.99 ±0.22	2.09 ±0.22	2.42 ±0.57	2.45 ±0.48	2.38 ±0.35	2.75 ±0.29	2.22 ±0.18	2.21 ±0.68

SLAB NUMBER	8-8-1 N	8-8-1 TV	8-8-1 NV	8-8-2 N	8-8-2 TV	8-8-2 NV	23A-8-1 N	23A-8-1 TV	23A-8-1 NV	7-8-1 N	7-8-1 TV	7-8-1 NV
OXIDE OR ELEMENT												
MgO	23.72 ±0.68	25.18 ±1.18	24.03 ±2.06	23.59 ±0.89	24.81 ±1.67	25.85 ±1.70	25.55 ±1.12	24.90 ±1.49	25.15 ±0.50	23.08 ±1.03	26.17 ±1.17	26.52 ±0.89
SiO ₂	35.13 ±1.56	34.91 ±1.88	33.87 ±1.05	33.68 ±0.98	36.87 ±3.75	35.10 ±0.87	35.07 ±0.35	34.25 ±1.61	34.48 ±0.06	34.68 ±0.37	35.93 ±2.68	34.69 ±0.35
FeO	30.20 ±0.97	33.24 ±0.60	28.62 ±1.90	29.52 ±2.46	29.74 ±4.76	32.90 ±2.10	32.99 ±0.76	34.44 ±3.25	29.72 ±4.61	30.01 ±4.28	32.78 ±1.44	32.17 ±6.49
Al ₂ O ₃	3.89 ±0.85	3.31 ±0.24	3.17 ±0.50	3.03 ±0.38	3.56 ±0.33	3.90 ±0.58	3.44 ±0.25	3.45 ±0.47	3.30 ±0.03	3.44 ±0.78	3.52 ±0.22	3.35 ±0.18
TiO ₂	0.174 ±0.053	0.176 ±0.049	0.155 ±0.028	0.143 ±0.075	0.156 ±0.021	0.174 ±0.036	0.188 ±0.021	0.151 ±0.007	0.171 ±0.009	0.139 ±0.006	0.166 ±0.012	0.164 ±0.027
Mn	1.46 ±0.03	1.34 ±0.15	1.42 ±0.32	1.39 ±0.20	1.30 ±0.20	1.28 ±0.11	1.30 ±0.28	1.89 ±0.873	1.51 ±0.38	1.44 ±0.05	1.48 ±0.06	1.48 ±0.15
NaO	0.194 ±0.035	0.215 ±0.063	0.188 ±0.007	0.167 ±0.022	0.187 ±0.030	0.188 ±0.016	0.221 ±0.040	0.173 ±0.023	0.201 ±0.016	0.172 ±0.017	0.193 ±0.015	0.198 ±0.013
Cr	0.304 ±0.086	0.308 ±0.032	0.420 ±0.070	0.303 ±0.063	0.327 ±0.105	0.345 ±0.069	0.402 ±0.055	0.318 ±0.125	0.374 ±0.034	0.289 ±0.042	0.405 ±0.065	0.257 ±0.105
CaO	2.34 ±0.09	2.28 ±0.11	2.21 ±0.26	2.21 ±0.17	2.46 ±0.25	2.41 ±0.27	2.22 ±0.35	2.37 ±0.18	2.33 ±0.33	1.83 ±0.43	2.34 ±0.25	2.84 ±1.03

deviations were larger than the mean values. Titania, although the intensity of the spectral line for the concentrations in the samples are near the detection limit the average percent relative deviation is only approximately 10%.

III. STATISTICAL ANALYSIS

The variances for the determination of each oxide/element in each sample are compiled in Table 10. Noted under each variance is the result of an F-Test for the significance of that variance compared with the variance of the mean value for 108 splits of that oxide/element.

The null hypothesis in each test is:

$$H_0: \sigma_1^2 = \sigma_2^2$$

and the alternative is:

$$H_1: \sigma_1^2 \neq \sigma_2^2$$

The null hypothesis states that the parent population variances of the two are the same and the alternative states that they are not the same. NS means not significant or that the value of the F-Test at the 1% level is less than the critical value for the degrees of freedom used in calculating each variance. Five values are significant. The alternative is true and the parent population are not the same. These significant values are for chromium in 9-S-1 and 9-S-2, manganese oxide in 16-S-1 and nickel in 23A-S-1 and 7-S-1.

The variances for the determination of each oxide/element in each slab are compiled in Table 11. The results of the same F-Test as for the samples is listed under each value. Nine values for the slabs are significant at the 1% level for the degrees of freedom used in calculating each variance. The significant values are: chromium in 9-S-2B; manganese oxide in 16-S-1T and 25-S-2H; nickel in 25-S-1B and 23A-S-1T; silica in 25-S-1H, 8-S-2T and 23A-S-1B; and alumina in 23A-S-1B.

A method to compare the variations in groups of observations is described by Davis (1973). The method is analysis of variance and was used to determine the equivalency of the nine samples. The same calculation was repeated for each of the nine oxide/elements. The hypothesis and alternative are:

$$H_0 : u_1 = u_2 = u_3 = u_4 = u_5 = u_6 = u_7 = u_8 = u_9$$

$$H_1 : \text{at least one mean is different.}$$

Table 10 .

SAMPLES
Variance and F Test

Sample	9-S-1	9-S-2	16-S-1	25-S-1	25-S-2	8-S-1	8-S-2	23A-S-1	7-S-1
Oxide or Element									
MgO	2.32 NS	4.78 NS	1.98 NS	2.82 NS	1.87 NS	2.22 NS	2.54 NS	1.28 NS	3.63 NS
SiO ₂	1.23 NS	2.43 NS	1.17 NS	0.90 NS	2.44 NS	1.86 NS	6.65 NS	1.16 NS	2.53 NS
FeO	9.47 NS	9.82 NS	13.93 NS	12.34 NS	18.69 NS	5.19 NS	11.84 NS	10.48 NS	13.60 NS
Al ₂ O ₃	0.26 NS	0.24 NS	0.06 NS	0.33 NS	0.23 NS	0.40 NS	0.28 NS	0.10 NS	0.20 NS
TiO ₂	0.000 NS	0.000 NS	0.001 NS	0.001 NS	0.001 NS	0.001 NS	0.001 NS	0.000 NS	0.000 NS
Ni	0.023 NS	0.022 NS	0.025 NS	0.024 NS	0.032 NS	0.042 NS	0.029 NS	0.401 S	0.005 S
MnO	0.000 NS	0.000 NS	0.003 S	0.002 NS	0.002 NS	0.001 NS	0.001 NS	0.001 NS	0.000 NS
Cr	0.002 S	0.027 S	0.003 NS	0.016 NS	0.003 NS	0.007 NS	0.006 NS	0.008 NS	0.008 NS
CaO	0.20 NS	0.21 NS	0.04 NS	0.19 NS	0.15 NS	0.03 NS	0.06 NS	0.06 NS	0.40 NS
Total	30.84 NS	37.24 NS	28.21 NS	36.62 NS	19.32 NS	20.03 NS	29.75 NS	13.25 NS	43.75 NS

TABLE 11

SLAB
VARIANCE AND F TEST

SLAB NUMBER	9-8-1 N	9-8-1 TV	9-8-1 NV	9-8-2 N	9-8-2 TV	9-8-2 NV	16-8-1 N	16-8-1 TV	16-8-1 NV	25-8-1 N	25-8-1 TV	25-8-1 NV	25-8-2 N	25-8-2 TV	25-8-2 NV
OXIDE OR ELEMENT															
MgO	1.29 NS	1.26 NS	1.57 NS	12.16 NS	1.39 NS	1.66 NS	2.26 NS	1.79 NS	1.31 NS	2.88 NS	3.50 NS	1.70 NS	2.73 NS	1.60 NS	1.32 NS
SiO ₂	1.00 NS	1.17 NS	1.63 NS	0.62 NS	5.91 NS	1.67 NS	0.04 NS	0.80 NS	2.18 NS	2.76 NS	0.03 NS	0.31 NS	0.12 NS	0.15 NS	3.75 NS
FeO	16.42 NS	7.27 NS	9.17 NS	2.93 NS	16.73 NS	13.54 NS	18.62 NS	23.09 NS	13.77 NS	19.78 NS	7.94 NS	11.12 NS	24.17 NS	1.57 NS	12.53 NS
Al ₂ O ₃	0.31 NS	0.19 NS	0.30 NS	0.05 NS	0.14 NS	0.32 NS	0.02 NS	0.03 NS	0.12 NS	0.17 NS	0.57 NS	0.05 NS	0.19 NS	0.02 NS	0.04 NS
TiO ₂	0.000 NS	0.000 NS	0.000 NS	0.000 NS	0.001 NS	0.001 NS	0.001 NS	0.001 NS	0.000 NS	0.001 NS	0.000 NS	0.001 NS	0.000 NS	0.000 NS	0.001 NS
Mn	0.013 NS	0.059 NS	0.011 NS	0.011 NS	0.023 NS	0.021 NS	0.003 NS	0.043 NS	0.012 NS	0.020 NS	0.054 NS	0.002 NS	0.009 NS	0.007 NS	0.057 NS
MnO	0.000 NS	0.001 NS	0.001 NS	0.000 NS	0.000 NS	0.001 NS	0.003 NS	0.006 NS	0.002 NS	0.001 NS	0.000 NS	0.002 NS	0.005 NS	0.000 NS	0.001 NS
Cr	0.000 NS	0.002 NS	0.004 NS	0.013 NS	0.016 NS	0.004 NS	0.002 NS	0.005 NS	0.005 NS	0.022 NS	0.011 NS	0.018 NS	0.005 NS	0.000 NS	0.002 NS
CaO	0.03 NS	0.34 NS	0.28 NS	0.06 NS	0.13 NS	0.18 NS	0.03 NS	0.05 NS	0.05 NS	0.33 NS	0.23 NS	0.13 NS	0.08 NS	0.01 NS	0.36 NS
Total	50.97 NS	20.70 NS	39.09 NS	17.18 NS	66.34 NS	44.32 NS	36.92 NS	48.77 NS	25.33 NS	62.98 NS	27.13 NS	33.54 NS	33.85 NS	3.66 NS	15.02 NS

SLAB NUMBER	8-8-1 N	8-8-1 TV	8-8-1 NV	8-8-2 N	8-8-2 TV	8-8-2 NV	23A-8-1 N	23A-8-1 TV	23A-8-1 NV	7-8-1 N	7-8-1 TV	7-8-1 NV	Total
OXIDE OR ELEMENT													
MgO	0.46 NS	1.39 NS	1.26 NS	0.79 NS	2.79 NS	2.90 NS	1.26 NS	2.23 NS	0.35 NS	1.06 NS	1.37 NS	0.79 NS	2.55 NS
SiO ₂	2.13 NS	3.54 NS	1.10 NS	0.80 NS	14.07 NS	0.75 NS	0.12 NS	2.60 NS	0.00 NS	0.14 NS	7.18 NS	0.12 NS	2.42 NS
FeO	0.93 NS	0.36 NS	3.62 NS	6.04 NS	22.69 NS	4.39 NS	0.58 NS	10.56 NS	21.26 NS	18.22 NS	2.07 NS	42.14 NS	12.50 NS
Al ₂ O ₃	0.73 NS	0.06 NS	0.25 NS	0.14 NS	0.11 NS	0.34 NS	0.06 NS	0.22 NS	0.00 NS	0.60 NS	0.05 NS	0.03 NS	0.26 NS
TiO ₂	0.003 NS	0.002 NS	0.001 NS	0.001 NS	0.000 NS	0.001 NS	0.000 NS	0.000 NS	0.000 NS	0.000 NS	0.000 NS	0.001 NS	0.001 NS
Mn	0.001 NS	0.023 NS	0.100 NS	0.039 NS	0.040 NS	0.012 NS	0.077 NS	0.761 NS	0.147 NS	0.003 NS	0.004 NS	0.023 NS	0.062 NS
MnO	0.001 NS	0.004 NS	0.000 NS	0.000 NS	0.001 NS	0.000 NS	0.002 NS	0.001 NS	0.000 NS	0.000 NS	0.000 NS	0.000 NS	0.001 NS
Cr	0.007 NS	0.001 NS	0.005 NS	0.004 NS	0.011 NS	0.005 NS	0.003 NS	0.016 NS	0.001 NS	0.002 NS	0.004 NS	0.011 NS	0.009 NS
CaO	0.01 NS	0.01 NS	0.07 NS	0.03 NS	0.06 NS	0.07 NS	0.12 NS	0.03 NS	0.11 NS	0.18 NS	0.06 NS	1.05 NS	0.16 NS
Total	7.61 NS	0.96 NS	26.00 NS	11.11 NS	33.05 NS	21.05 NS	0.21 NS	15.92 NS	26.35 NS	42.61 NS	17.99 NS	81.54 NS	31.99 NS

TABLE 12

ANALYSIS OF VARIANCE BY SAMPLES

MgO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	10.05	8	1.26	
WITHIN REPLICATIONS	220.17	99	2.22	0.5649
TOTAL VARIATION	230.22	107		

SiO ₂				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	26.32	8	3.29	
WITHIN REPLICATIONS	193.96	99	1.96	1.6793
TOTAL VARIATION	220.28	107		

FeO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	127.86	8	15.98	
WITHIN REPLICATIONS	997.06	99	10.07	1.5869
TOTAL VARIATION	1124.92	107		

Al ₂ O ₃				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	3.90	8	0.49	
WITHIN REPLICATIONS	20.29	99	0.20	2.3776
TOTAL VARIATION	24.19	107		

TiO ₂				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	0.01	8	0.00	
WITHIN REPLICATIONS	0.06	99	0.00	1.0572
TOTAL VARIATION	0.06	107		

TABLE 12

ANALYSIS OF VARIANCE BY SAMPLES

Continued

Ni				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	0.42	8	0.05	
WITHIN REPLICATIONS	5.22	99	0.05	0.9833
TOTAL VARIATION	5.64	107		

MnO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	0.01	8	0.00	
WITHIN REPLICATIONS	0.10	99	0.00	1.0562
TOTAL VARIATION	0.11	107		

Cr				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	0.04	8	0.01	
WITHIN REPLICATIONS	0.76	99	0.01	0.7037
TOTAL VARIATION	0.81	107		

CaO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	1.61	8	0.20	
WITHIN REPLICATIONS	12.40	99	0.13	1.6014
TOTAL VARIATION	14.01	107		

TABLE 13

ANALYSIS OF VARIANCE BY SLABS

MgO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	55.80	26	2.15	
WITHIN REPLICATIONS	174.39	81	2.15	0.9968
TOTAL VARIATION	230.19	107		

SiO ₂				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	67.65	26	2.60	
WITHIN REPLICATIONS	152.65	81	1.88	1.3806
TOTAL VARIATION	220.30	107		

FeO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	302.67	26	11.64	
WITHIN REPLICATIONS	822.23	81	10.15	1.1468
TOTAL VARIATION	1124.90	107		

Al ₂ O ₃				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	8.86	26	0.34	
WITHIN REPLICATIONS	15.33	81	0.19	1.8206
TOTAL VARIATION	24.19	107		

TiO ₂				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	0.02	26	0.00	
WITHIN REPLICATIONS	0.05	81	0.00	1.0857
TOTAL VARIATION	0.06	107		

TABLE 13
ANALYSIS OF VARIANCE BY SLABS

Continued

Ni				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	1.36	26	0.05	
WITHIN REPLICATIONS	4.28	81	0.05	0.9893
TOTAL VARIATION	5.64	107		

MnO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	0.03	26	0.00	
WITHIN REPLICATIONS	0.08	81	0.00	1.1196
TOTAL VARIATION	0.11	107		

Cr				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	0.14	26	0.01	
WITHIN REPLICATIONS	0.67	81	0.01	0.6298
TOTAL VARIATION	0.81	107		

CaO				
SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN, SQUARES	F-TEST,
AMONG SAMPLES	3.00	26	0.12	
WITHIN REPLICATIONS	11.01	81	0.14	0.8492
TOTAL VARIATION	14.01	107		

Three assumptions are required to preform a test to choose between the two hypotheses. The assumptions are (1) each set of replicates represents random samples, (2) each population is normally distributed, and (3) each population has the same variance. For these calculations the oxide/element mean values are substituted for the bad burn values. The results are listed in Table 12. The total variation is separated into two parts; the variance among samples and the variance within each set of replicates. The corresponding degrees of freedom are in the second column. The sample based variances are in the next column. The calculated F-Test value is listed last.

The variances for the samples are all less than the variation for the replicates. Statistically this statement means that with the precision found for the analysis of the replicates it is not possible to observe any differences among the samples. The F-Test values are all less than the critical value at the degrees of freedom listed and 1% ($\alpha=0.01$) level of significance confirming the hypothesis that all of the means for the samples are the same. The program was adapted from Davis (1973).

The values in the program for the number of samples and number of replicates were changed to calculate the equivalency of the 27 slabs. The same hypothesis, alternative and assumptions were used and data are given in Table 13. The results are essentially the same except that the difference between the variances in the slabs and the replicates is less than the differences between the variances of the samples and the replicates. The sample based estimates of variances (mean squares) are in most cases nearly equal for the slabs. The null hypothesis that there is no difference between samples based on these calculations holds for the slabs as well as it did for the samples.

A more sophisticated way to classify objects into groups is called cluster analysis. Numerically derived groupings from a mathematical calculation are a more exact classification. A test of the significance of the results is not available, but the tabular and graphical results make objective speculation about grouping possible. Measures of similarity used in the calculations are the correlation coefficient and a standardized m-space Euclidian distance. The advantage of the distance measurement is that the best similarity is zero and the dissimilar distances are carried

out to values greater than one. The distance coefficient is computed from the following relationship:

$$d_{ij} = [\sum_{k=1}^m (x_{ik} - x_{jk})^2 / m]^{1/2}$$

The features of this method of correlation are:

1. The highest similarities are clustered first.
2. Two objects can be connected only if they have the highest mutual correlation with each other.
3. After two objects are clustered their similarity distances with all other objects are averaged.

Table 14 is a list of sample combinations, distance differences and a key matching sample numbers to matrix row and column numbers. Table 15 is a similarity matrix for samples. Figure 6 shows a dendrogram depicting the sample similarity relationships. The distance values are normalized to a maximum value of one in order to simplify the scale. Table 16 is a list of slab combinations, distance differences and a key matching slab numbers to matrix row and column numbers. Table 17 is a similarity matrix for slabs. Figure 7 shows a dendrogram depicting the slab similarity relationships. The distance values are normalized to one as they were for the samples. The 0.3 level line is drawn as a logical level for separating groups. Five groups are at similar distance levels below this value. Several slabs, however, do not show a similarity until the distance is much greater. These are outliers and should not be considered in evaluating the significance of cluster groups. A method to determine a significant grouping level mathematically was sought. A multivariate discriminate analysis was considered. This approach was rejected because discrimination depends on a prior knowledge of a relationship between samples. The results of the previous statistical analyses did not show a function that could be used to define samples or slabs as belonging to specific groups.

Rather than select any further arbitrary limits the dotted lines were drawn through the similarity matrixes. These follow the groups suggested by the dendograms. Inspection of the similarity values on opposite sides of the lines are a further suggestion to the significance of the grouping.

Table 14

SAMPLE	CLUSTER	SIMILARITY LEVELS	SAMPLE KEY
2	8	0.25615	1, 9-S-1
7	9	0.43262	2, 9-S-2
1	7	0.63138	3, 16-S-1
2	3	0.29944	4, 25-S-1
2	6	0.41024	5, 25-S-2
2	4	0.50370	6, 8-S-1
2	5	0.93219	7, 8-S-2
1	2	1.03599	8, 23A-S-1
			9, 7-S-1

Table 15

SIMILARITY MATRIX FOR SAMPLES
 ---- Boundries of Dendogram Groupings

	1	7	9	2	8	3	6	4	5
1	0.0000	0.6087	0.6541	1.0802	0.8410	0.9641	1.2307	0.7530	0.7818
7	0.6087	0.0000	0.4326	1.3824	1.1579	1.3374	1.6242	1.1713	1.2550
9	0.6541	0.4326	0.0000	1.1594	0.9735	1.1941	1.4883	1.1272	1.0829
2	1.0802	1.3824	1.1594	0.0000	0.2562	0.3171	0.4544	0.6302	0.9246
8	0.8410	1.1579	0.9735	0.2562	0.0000	0.2817	0.5325	0.4594	0.8185
3	0.9641	1.3374	1.1941	0.3171	0.2817	0.0000	0.3270	0.3745	0.8462
6	1.2307	1.6242	1.4883	0.4544	0.5325	0.3270	0.0000	0.5478	1.0818
4	0.7530	1.1713	1.1272	0.6302	0.4594	0.3745	0.5478	0.0000	0.8941
5	0.7818	1.2550	1.0829	0.9246	0.8185	0.8462	1.0818	0.8941	0.0000

Figure 6.
CLUSTERING BY SAMPLES

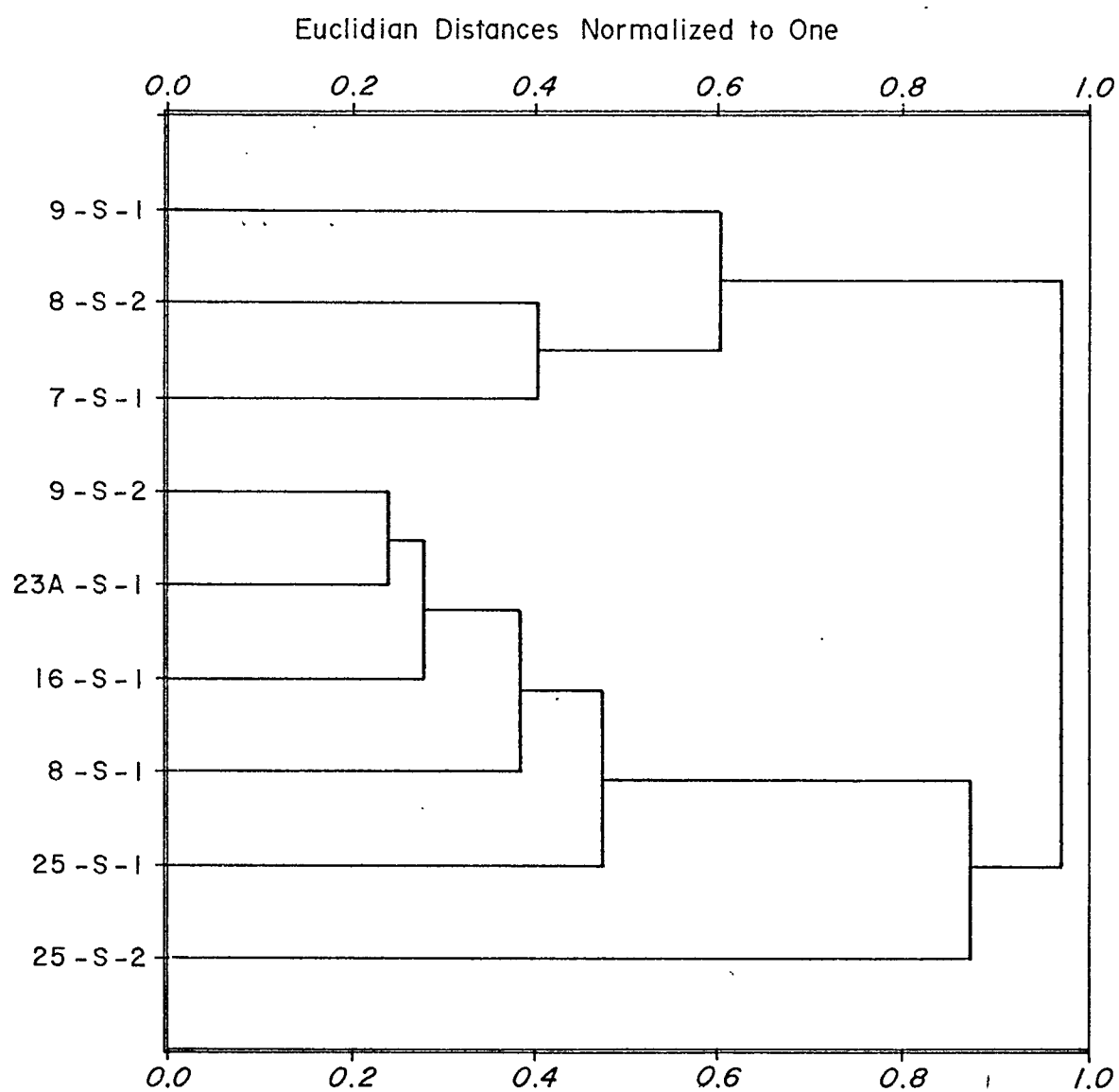


Table 16

SLABS	CLUSTERED	SIMILARITY LEVELS	SLAB KEY
1	16	0.28963	1, 9-S-1 H
2	11	0.19488	2, 9-S-1 TV
4	12	0.16946	3, 9-S-1 BV
5	19	0.15854	4, 9-S-2 H
10	24	0.22497	5, 9-S-2 TV
14	18	0.12798	6, 9-S-2 BV
17	22	0.16597	7, 16-S-1 H
2	3	0.35084	8, 16-S-1 TV
4	25	0.33965	9, 16-S-1 BV
5	9	0.27603	10, 25-S-1 H
17	21	0.26307	11, 25-S-1 TV
1	4	0.38608	12, 25-S-1 BV
5	8	0.35017	13, 25-S-2 H
6	10	0.33745	14, 25-S-2 TV
17	26	0.38496	15, 25-S-2 BV
5	6	0.45686	16, 8-S-1 H
7	14	0.45630	17, 8-S-1 TV
17	27	0.50073	18, 8-S-1 BV
2	17	0.62757	19, 8-S-2 H
5	7	0.62145	20, 8-S-2 TV
1	5	0.65055	21, 8-S-2 BV
2	23	0.80535	22, 23A-S-1 H
1	20	0.99196	23, 23A-S-1 TV
2	15	1.18587	24, 23A-S-1 BV
1	2	1.41852	25, 7-S-1 H
1	13	1.89143	26, 7-S-1 TV
			27, 7-S-1 BV

Figure 7.
CLUSTERING BY SLABS

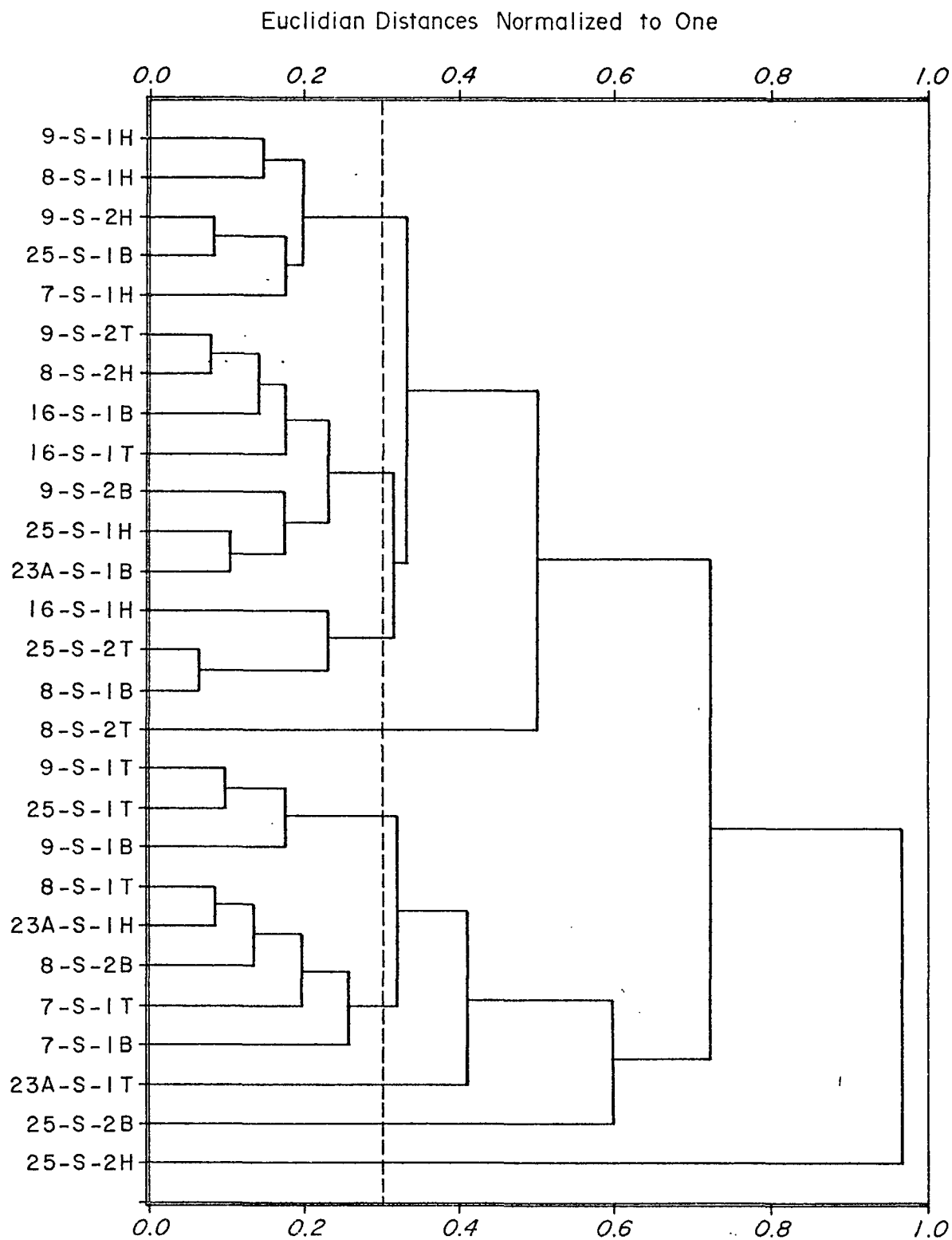


TABLE 17
SIMILARITY MATRIX FOR SLABS

	1	16	4	12	25	5	19	9	8	6	10	24	7	14	18	20	2	11	3	17	22	21	26	27	23	15	13
1 1	0.0000	0.2896	0.3259	0.3192	0.4876	0.6580	0.6433	0.6296	0.7344	0.8208	0.5661	0.6035	0.7848	0.8937	0.8339	0.8379	0.7721	0.9343	0.6018	0.8886	0.6830	0.9199	1.0329	0.9519	1.2475	1.0183	1.7276
2 16	0.2896	0.0000	0.3515	0.3534	0.3517	0.6029	0.6096	0.6186	0.8107	0.8123	0.6964	0.6442	0.6622	0.7632	0.7250	0.7131	1.0437	1.2099	0.8726	1.1441	1.1249	1.1402	1.2223	1.1766	1.5102	1.2114	1.5350
3 4	0.3859	0.3515	0.0000	0.1695	0.3120	0.3369	0.3284	0.3411	0.4907	0.6052	0.5344	0.4622	0.4874	0.5549	0.4992	0.9190	0.9917	1.1592	0.8433	1.1863	1.1717	1.2159	1.3216	1.1826	1.5419	0.9563	1.4259
4 12	0.3192	0.3534	0.1695	0.0000	0.3673	0.3687	0.3316	0.3745	0.4079	0.6302	0.5101	0.4594	0.5327	0.6029	0.5470	0.9643	0.9287	1.0070	0.7530	1.1353	1.1311	1.1713	1.2940	1.1272	1.4649	0.8941	1.4098
5 25	0.4876	0.3517	0.3120	0.3673	0.0000	0.4760	0.4490	0.5053	0.7331	0.8460	0.8177	0.7464	0.3701	0.6459	0.6434	0.9600	1.1757	1.1173	1.0151	1.2460	1.3040	1.3654	1.4555	1.3957	1.6700	1.1030	1.4944
6 5	0.6580	0.6029	0.3369	0.3687	0.4760	0.0000	0.1585	0.7413	0.4141	0.5077	0.6193	0.4996	0.3560	0.3740	0.2749	1.0620	1.1995	1.3527	1.0602	1.4294	1.4190	1.4717	1.5599	1.3622	1.7684	0.9664	1.2323
7 19	0.6433	0.6096	0.3284	0.3316	0.4490	0.1585	0.0000	0.3107	0.3905	0.5987	0.6604	0.5520	0.3350	0.3676	0.3455	1.1579	1.1721	1.3235	1.0165	1.4132	1.4145	1.4667	1.5854	1.3799	1.7222	0.9055	1.3038
8 9	0.6296	0.6186	0.3411	0.3745	0.5853	0.2413	0.3107	0.0000	0.2980	0.3171	0.4251	0.2817	0.5593	0.4354	0.3270	1.0191	1.0661	1.2335	0.9641	1.3300	1.2994	1.3374	1.4248	1.1941	1.6849	0.8462	1.2599
9 8	0.7344	0.8107	0.4907	0.4879	0.7331	0.4141	0.3905	0.2980	0.0000	0.4771	0.4698	0.4242	0.6852	0.6111	0.5260	1.2707	0.9804	1.1227	0.8932	1.2965	1.2835	1.3344	1.4679	1.1830	1.5999	0.5824	1.4419
10 6	0.8208	0.8123	0.6052	0.6302	0.8668	0.5077	0.5987	0.3171	0.4771	0.0000	0.4187	0.2562	0.8383	0.5779	0.4544	1.0208	1.1459	1.3097	1.0802	1.4324	1.3720	1.3824	1.4413	1.1594	1.8145	0.9246	1.1730
11 10	0.5661	0.6954	0.5344	0.5101	0.8177	0.6193	0.6604	0.4251	0.4698	0.4187	0.0000	0.2250	0.9303	0.8344	0.7196	0.9676	0.7342	0.9039	0.6948	1.0209	0.9648	0.9835	1.0719	0.7821	1.4046	0.7343	1.5671
12 24	0.6235	0.6442	0.4622	0.4594	0.7464	0.4996	0.5520	0.2817	0.4242	0.2562	0.2250	0.0000	0.8131	0.6516	0.5325	0.9448	0.9243	1.0916	0.8410	1.2071	1.1505	1.1579	1.2418	0.9735	1.5824	0.8185	1.3588
13 7	0.7131	0.6622	0.4874	0.5327	0.3781	0.3568	0.3350	0.5593	0.6852	0.8383	0.9303	0.8131	0.0000	0.4332	0.4794	1.1365	1.4055	1.5634	1.2513	1.5851	1.5957	1.6625	1.7525	1.6231	1.8062	1.1946	1.2895
14 14	0.8937	0.7632	0.5549	0.6029	0.6459	0.3240	0.3676	0.4354	0.6111	0.5779	0.8344	0.6516	0.4332	0.0000	0.1280	1.1702	1.4634	1.6221	1.3099	1.7100	1.6877	1.7179	1.8069	1.5971	2.0507	1.1611	0.9368
15 18	0.8339	0.7250	0.4992	0.5478	0.6434	0.2749	0.3455	0.3270	0.5260	0.4544	0.7196	0.5325	0.4794	0.1280	0.0000	1.1106	1.3704	1.5321	1.2307	1.6256	1.5954	1.6242	1.7085	1.4883	1.9751	1.0818	0.9782
16 20	0.8379	0.7131	0.9190	0.9643	0.9600	1.0628	1.1579	1.0191	1.2707	1.0208	0.9676	0.9448	1.1665	1.1702	1.1106	0.0000	1.3498	1.5271	1.2985	1.3470	1.2662	1.2614	1.1561	1.2386	1.8052	1.6781	1.6180
17 2	0.7721	1.0437	0.9917	0.9287	1.1757	1.1995	1.1721	1.0661	0.9804	1.1459	0.7342	0.9243	1.4055	1.4634	1.3704	1.3498	0.0000	0.1949	0.3105	0.4185	0.4137	0.4661	0.7097	0.4779	0.7097	0.8082	2.2747
18 11	0.9343	1.2099	1.1592	1.0878	1.3373	1.3627	1.3235	1.2335	1.1227	1.3097	0.9039	1.0916	1.5634	1.6221	1.5321	1.5271	0.1949	0.0000	0.3911	0.4521	0.4749	0.5678	0.7852	0.5508	0.6121	0.8608	2.4362
19 3	0.6528	0.8726	0.8433	0.7530	1.0151	1.0682	1.0165	0.9641	0.8932	1.0802	0.6948	0.8410	1.2513	1.3099	1.2307	1.2905	0.3105	0.3911	0.0000	0.5797	0.5971	0.6087	0.8743	0.6541	0.8232	0.7818	2.1411
20 17	0.8356	1.1441	1.1863	1.1353	1.2908	1.4294	1.4132	1.3350	1.2965	1.4324	1.0209	1.2071	1.5851	1.7100	1.6256	1.3470	0.4185	0.4521	0.5797	0.0000	0.1660	0.3285	0.5055	0.6091	0.5042	1.1982	2.5279
21 22	0.6830	1.1249	1.1717	1.1311	1.3048	1.4190	1.4145	1.2994	1.2835	1.3720	0.9648	1.1505	1.5957	1.6877	1.5964	1.2662	0.4137	0.4749	0.5971	0.1660	0.0000	0.1976	0.3685	0.4949	0.6306	1.2092	2.4680
22 21	0.9199	1.1482	1.2159	1.1713	1.3654	1.4717	1.4667	1.3374	1.3344	1.3824	0.9835	1.1579	1.6625	1.7179	1.6242	1.2614	0.4661	0.5078	0.6087	0.3285	0.1976	0.0000	0.3329	0.4326	0.7127	1.2560	2.4607
23 26	1.2475	1.2223	1.3216	1.2940	1.4555	1.5599	1.5854	1.4248	1.4679	1.4413	1.0719	1.2418	1.7525	1.8069	1.7085	1.1561	0.7097	0.7852	0.8743	0.5055	0.3685	0.3329	0.0000	0.5091	0.9052	1.4614	2.4959
24 27	0.9519	1.1766	1.1826	1.1272	1.3957	1.3622	1.3799	1.1941	1.1030	1.1594	0.7821	0.9735	1.6231	1.5971	1.4883	1.2386	0.4779	0.5508	0.6541	0.6091	0.4949	0.4326	0.5091	0.0000	0.9646	1.0329	2.2809
25 23	1.2475	1.5102	1.5419	1.4649	1.6200	1.7684	1.7222	1.6849	1.5999	1.8145	1.4046	1.5824	1.8062	2.0507	1.9751	1.8052	0.7097	0.6121	0.8232	0.5042	0.6306	0.7127	0.9052	0.9646	0.0000	1.3605	2.9107
26 15	1.0183	1.2114	0.9563	0.8941	1.1838	0.9664	0.9055	0.8462	0.5824	0.9246	0.7343	0.8185	1.1946	1.1611	1.0818	1.6781	0.8082	0.8608	0.7818	1.1982	1.2092	1.2560	1.4614	1.0829	1.3605	0.0000	1.9422
27 13	1.7276	1.5350	1.4259	1.4898	1.4964	1.2323	1.3038	1.2599	1.4419	1.1730	1.5671	1.3588	1.2895	0.9368	0.9782	1.6180	2.2747	2.4362	2.1411	2.5279	2.4680	2.4607	2.4959	2.2809	2.9107	1.9422	0.0000

The conclusions that are suggested by these results and the significant information derived from this project are discussed in Section 5.

CONCLUSIONS

SECTION 5

I. INTRODUCTION

The conclusions are divided into two parts. The first part discusses the results of the development of the spectrochemical analysis method using the demountable hollow cathode source and relative absorbance densitometry. The second part is geochemical conclusions relating to potential large scale chemical variation in the Allende meteorite. The results considered from these almost unrelated fields of scientific investigation provide significant information that must be evaluated when studying processes in both fields.

II. SPECTROCHEMICAL ANALYSES CONCLUSIONS

The data included in Table 7 and Table 18 show the precision and accuracy of this method of spectrochemical analysis. The fact that the standard deviation decreases and approaches values reported by Jarosewich for bulk chemical analysis as the size of the aliquot of the meteorite increases shows that the precision of the method is in the range of that of a well accepted wet chemical laboratory.

The method has several advantages over the classical methods. The analysis requires only 64 mg of sample and can be performed on as little as 8 mg of sample. The minimum amount of sample will correspondingly be accompanied by some loss of precision. Sample preparation is direct and requires less than 30 minutes of analyst time. Sample analysis can be completed in another hour and a half for the analysis of 9 elements.

The desired advantages of the demountable hollow cathode source over the standard D.C. arc spectrochemical method for geological samples were achieved. Matrix effects are reduced. Excitation conditions for the silica rich U.S.G.S. standard G-2 and the FeO-rich Allende meteorite are essentially the same. The goodness of fit values r^2 for the calibration curves in Table 4 further substantiate this statement. Electrodes can be reused for total burn times of up to 4 or 5 hours without changing the elemental ratios in the electrode charge. The plasma burns with the steadily glow of a lamp and does not exhibit any

Table 18

COMPARISON OF BULK CHEMICAL ANALYSES

<u>OXIDE/ELEMENT</u>	<u>SLABS</u>	<u>SAMPLES</u>	<u>JAROSEWICH</u>	
	% Conc. S. D.	% Conc. S. D.	% Conc. S. D.	
MgO	24.65 ± 0.94	24.63 ± 0.40	24.63 ± 0.16	
SiO ₂	34.33 ± 0.88	34.31 ± 0.63	34.28 ± 0.21	
FeO	31.39 ± 2.83	30.61 ± 1.40	30.77 ± 0.11	2
Al ₂ O ₃	3.32 ± 0.32	3.32 ± 0.23	3.29 ± 0.09	
TiO ₂	0.16 ± 0.016	0.16 ± 0.01	0.15 ± 0.01	
Ni	1.42 ± 0.13	1.43 ± 0.08	1.39 ± 0.02	2
MnO	0.19 ± 0.02	0.19 ± 0.01	0.19 ± 0.01	
Cr	0.36 ± 0.04	0.36 ± 0.03	0.36 ± 0.01	
CaO	2.29 ± 0.22	2.28 ± 0.14	2.29 ± 0.03	

1 Jarosewich (1975)

2 Clarke et al. (1970)

of the sputtering or flashing that commonly is encountered with D.C. arc. The method for densitometry of the spectrographic plates requires fewer measurements, allows more samples per spectrographic plate and the calculations are simpler than other background correction methods.

Several characteristics of the method need improvement. The most important disadvantage of the demountable hollow cathode spectrochemical analysis method is its lack of sensitivity. Satisfactory results were obtained for the major and minor elements reported in this project, but the method should be useful for more minor and for trace element analysis. An exposure was made with the by-pass valve of the plasma gas control unit open. In this configuration the plasma gas in the hollow cathode unit retains the set pressure, but the flow through the unit was either very small or stopped. The same atoms recycle between an excited state and the ground state allowing better sensitivity. Further development and testing will be required to prove this possibility. The precision of the method probably can be improved as experience with the method increases. Sample loading and pump down procedures were improved during the processing of these samples. The modifications made during this study reduced the background more consistently and allows even better precision and sensitivity. Increased sensitivity allows the width of the entrance slit of the spectrograph to be reduced. The narrower slit produces narrower lines on the spectrographic plate and results in better resolution when the lines are measured on the densitometer.

Minor modifications to the external optics of the spectrograph may improve sensitivity and reduce backgrounds. Any or all of these improvements will reduce exposure time and the time to measure the lines on the densitometer.

III. GEOCHEMICAL CONCLUSIONS

The results from the quantitative statistical analyses of the data show Allende's chemical composition to be homogeneous for the volume of the material sampled and the precision of the analyses. The typical area of the surfaces of the slabs are 2,400 mm² for the horizontal slabs and 1,500 mm² for the top and bottom vertical slabs.

Their respective volumes are 12,000 mm³ and 7,500 mm³. The various types of clasts distributed in the polymict texture surfaces of Allende range in size from a few mm² to several hundred mm². Adequate sampling of average clasts with areas of 15-20 mm² were well represented within the areas sampled for each slab. Figure 8 is a photomicrograph of a thin section of Allende material. The varied composition of clasts and matrix can be seen even at this small scale. Areas much larger than the area of this thin section are required to produce major element homogeneity. Table 18 contains a comparison of chemical data from this project and a compilation by E. Jarosewich (1975). Each value is followed by its standard deviation. The standard deviation is at least partially an indication of the variations between the units analyzed. The table shows that in all cases the standard deviation for the nine samples are smaller than they are for the 27 slabs, a further indication that as the sampled area increases the unit is more homogeneous.

All of the standard deviation, except FeO, are in the same order of magnitude as the precision reported by Jarosewich. Thus, these data have a level of precision that is sufficient to evaluate some aspects of the major element geochemistry of the Allende meteorite.

Most of the previous studies of Allende have been focused on analysis of the many clasts, chondrules, and inclusions. The conclusions of these reports discussed the hypotheses of the original formation of these components. Some of these various components have physical and chemical characteristics that are very different. The white, pink and light gray inclusions are mostly melilite with some minor perovskite, other minor minerals and glass. They are very refractory materials. The dark to light gray chondrules are olivine and orthopyroxenes. These minerals are medium temperature to refractory. Other chondrules and inclusions are primarily triolite and low temperature materials. The matrix consists of fine grains and small lithic fragments of most of the minerals found in the larger components, but coating most of these grains is a thin layer of carbonaceous material. The composition of the carbonaceous material ranges from graphite to fairly complex hydrocarbons. The approximately

Figure 8

Photomicrograph of Allende

Thin Section



—
250u

0.2% water found in the meteorite is probably associated with the matrix. How do these high temperature and temperature sensitive materials, reduced and mildly oxidized components, glass and devitrifying water exist in the same rock? How did they become compacted at a low temperature to form a well-indurated polymict breccia? The data from this research study provides some information as to processes that may have happened on the parent body. More geochemical information is needed including the large scale variations of volatile, minor and trace elements; the large scale variation of both stable and radioactive isotopes; and a quantitative petrographic study of the large scale variations of the lithology of the meteorite. These data could then be used for very comprehensive studies that might lead to the development of hypotheses about some of the geological processes on the Allende parent body.

IV. SUMMARY

A satisfactory method for analyzing small aliquots of geological samples using the demountable hollow cathode as a source for the optical emission spectrograph was developed. The method provided better precision than the D.C. arc method normally used for the spectrochemical analysis of geological sample.

The analytical results and subsequent statistical tests used to examine the data show that, for the size of the sample homogenized and the precision of the analyses of the nine oxide/elements, the Allende meteorite is virtually homogeneous. The results was not what was expected. Further study is needed on other components in these samples. Than all of the data, if it is consistant with these results, should be used to develop a hypothesis of a process or processes that could produce a large clastic rock with the uniformity of the Allende meteorite.

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Appendix A

Photographs of the sawn surfaces of the samples

Magnification is 1.5 to 2x and can be determined by the portions of cm scales and the one inch orientation cube.

Figure 9

N view of sample 9-S-1

Large gray holocrystalline anhedral inclusion is in the lower part of NW quadrant. Various homogeneous and zoned chondrules can be seen throughout the view. Various irregular shaped white inclusions are present throughout the specimen. Some dark inclusions are in the upper center. The texture of the center third suggests a separate clast with less matrix and perhaps a swirl pattern. A SE to NW lineation is evident especially as outlined by the white clasts.

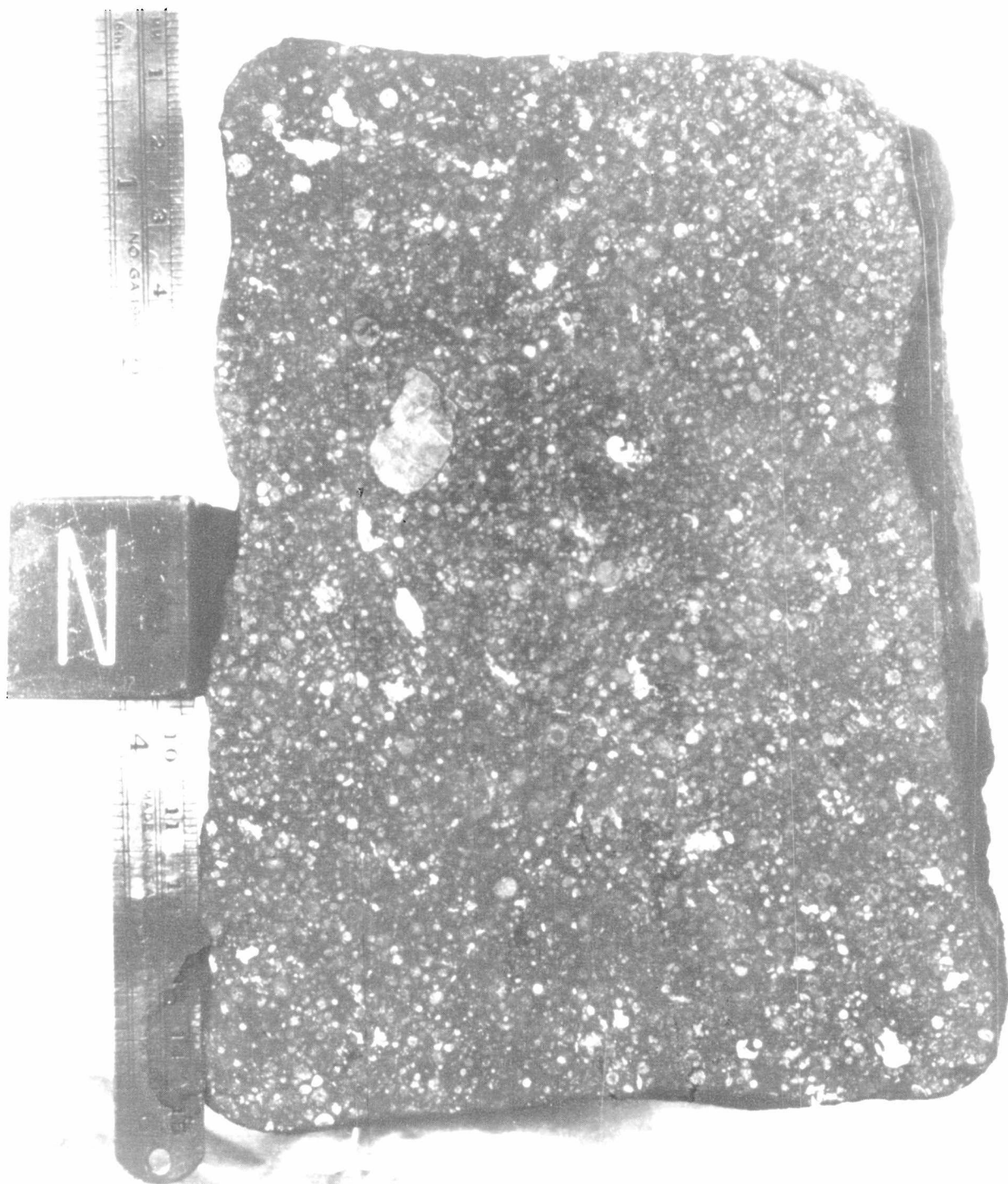


Figure 10

S View of sample 9-S-1

A large dark inclusion is seen near the left edge of the sample. The texture of this inclusion is fine grained phaneritic with less than the average amount of matrix. In the bottom left is a zoned chondrule with a thin black matrix ring around it and a portion of a white inclusion curved over the top of it. The usual Allende clasts and chondrules are distributed over this surface. The center clast with its suggested swirl pattern and the lineation is not as evident in this view as it is in the N view.



Figure 11

N view of sample 9-S-2

Two large aphanitic dark inclusions are in the center of this view. Three large white inclusions are seen at the bottom. A zoned white inclusion is in the lower center part of the SW quadrant. Slightly above and to the right is a chondrule with a vug in it, a black border and a white inclusion curved over the top of it. The dark inclusions, the chondrules and the white inclusions show definite lineation from SE to NW.



Figure 12

S view of sample 9-S-2

This side of the sample is the opposite side of the saw cut that separated it from 9-S-1-N. The other part of the large holocrystalline anhedral inclusion is visible in NE quadrant. At the top of the NE quadrant is a white inclusion that seems to have zoned edges. Some inclusions seem to be aligned vertically. The clast at the center with the suggested swirl texture is evident in this portion.



Figure 13

N view of sample 16-S-1

The outstanding features of this view are the large light colored inclusions. The largest one in the center is zoned and has a pink center. Two large white chondrules, NW and lower center, are visible. Two chondrules in the lower center have white inclusions curved around them. Just above and to the left of the large inclusion is a triply zoned predominantly light gray clast. The horizontal lineation is easily discerned.



Figure 14

S view of sample 16-S-1

This view shows a small dark inclusion with a streak of white material throughout it. The texture of the remainder is fine except for one white chondrule near the east edge. There are several zoned clasts at the bottom to the right center. Many small to medium sized white lithic fragments are evenly distributed over the surface. The lineation in the left quarter is almost verticle. The right three quarters is slightly less than horizontal sloping to the right.



Figure 15

N view of sample 25-S-1

The features of this view are dominated by the crescent shaped holocrystalline inclusion. A large dark grey crystalline chondrule is in the center near the top. Some medium to small sized aphanitic dark inclusions are in the center near the bottom. There are several medium sized light gray inclusions that have what seem to be reacted perimeters. Two lithic inclusions with essentially the same textures as the main body of the meteorite are at the upper right. The piece was sawn from 25-S-2-S.

PC-033-002 4011Z 7 4
12 16 20 24 28 4 8 12 16 20 24 28 4 8 12 16 20 24
25-S-I-N
10 20 30 40 50 60 70 80 90 100 110 120

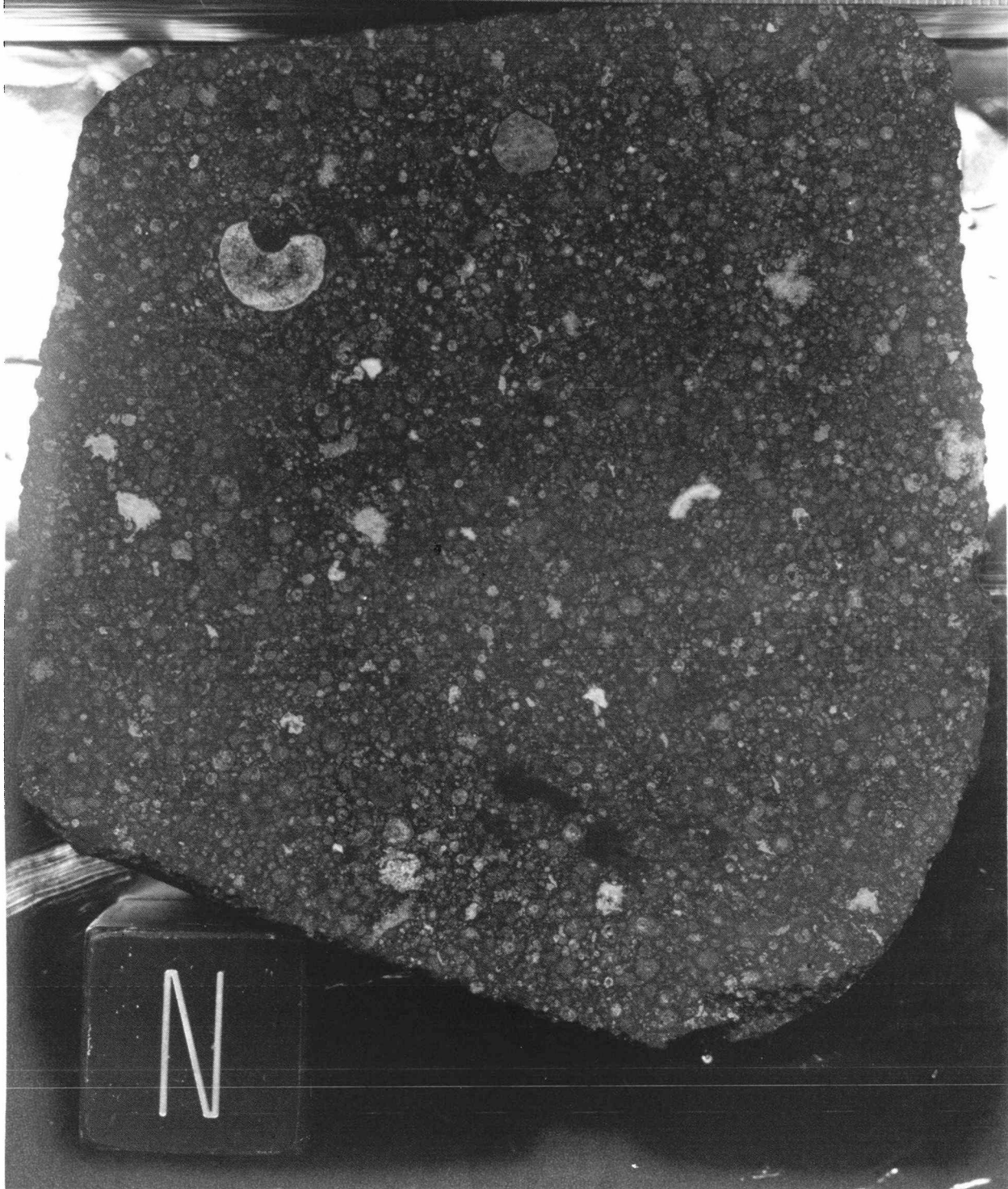


Figure 16

S view of sample 25-S-1

This view contains a medium grained dark inclusion and a irregular shaped inclusion. A large number of one to several mm diameter dark gray chondrules are seen in most of this surface. Some larger than average elongated wispy inclusions are near the top. They are aligned in a near vertical lineation.

25-S-I-S



Figure 17

N view of sample 25-S-2

Two types of dark inclusions are seen in this surface. One in the lower left corner is medium grained and one of the largest ones in this group of samples. The other is a very fine grained black inclusion near the bottom to the right of center. Several larger than average white inclusions can be seen. Several 3-4 mm both light and dark chondrules are in the lower half of the sample.

25-S-2-N

N

Figure 18

S view of sample 25-S-2

The surface matches 25-S-1-N. A small part of the light gray crescent shaped inclusion is in the upper left quadrant. In the middle near the left side is a larger part of the holocrystalline chondrule. To the right of this chondrule and toward the top is a light gray chondrule with a white zone around the rim. Near the bottom and slightly to the left of center is a light gray clast with a white zone on the three sides of it. Several wispy inclusions are distributed in a linear pattern from the center top toward the lower right corner.

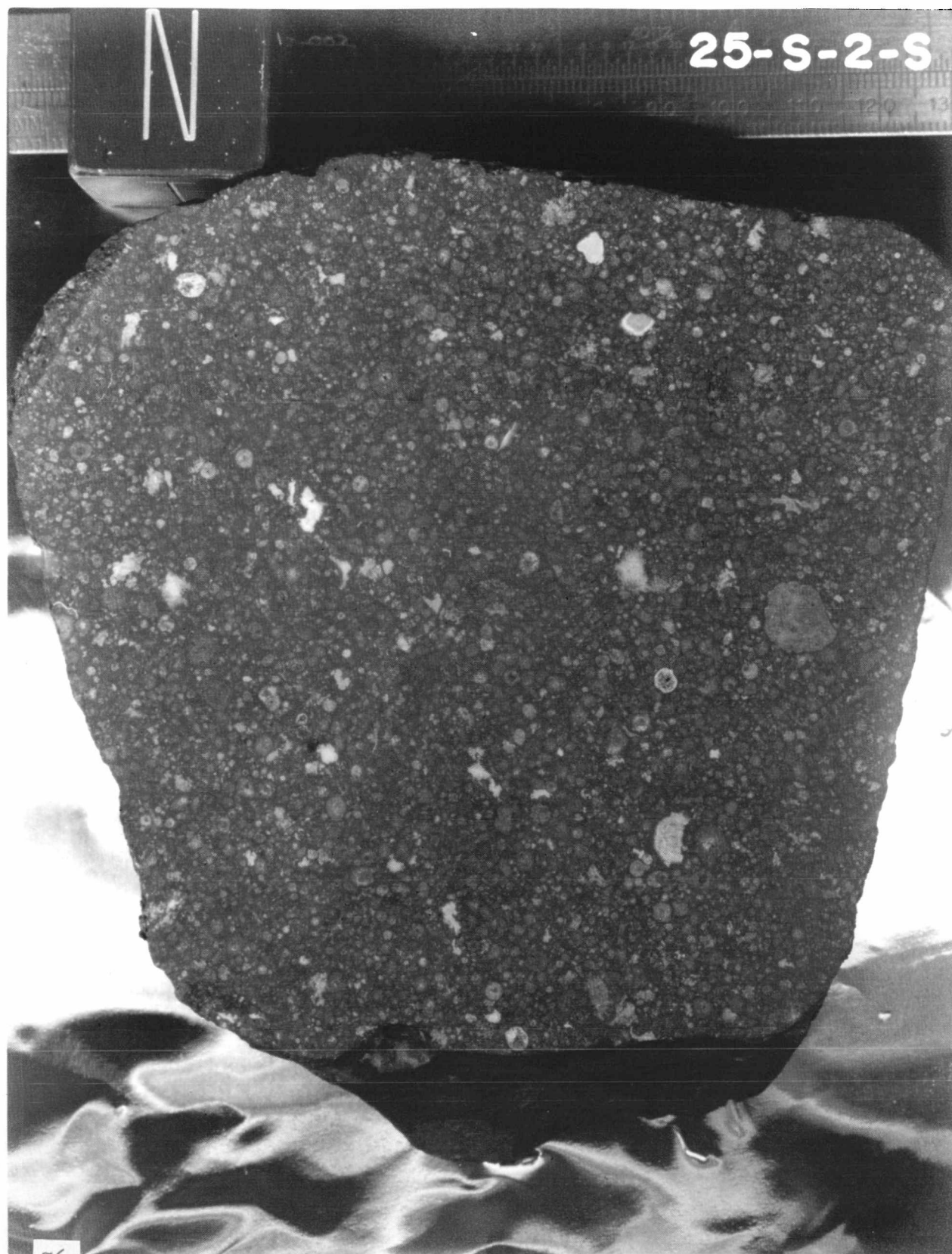


Figure 19

N view of sample 8-S-1

A very large medium grained dark inclusion is in the lower right corner. There are a few several mm sized chondrules. The wispy white inclusions show a lineation alignment from the upper right to the lower left.

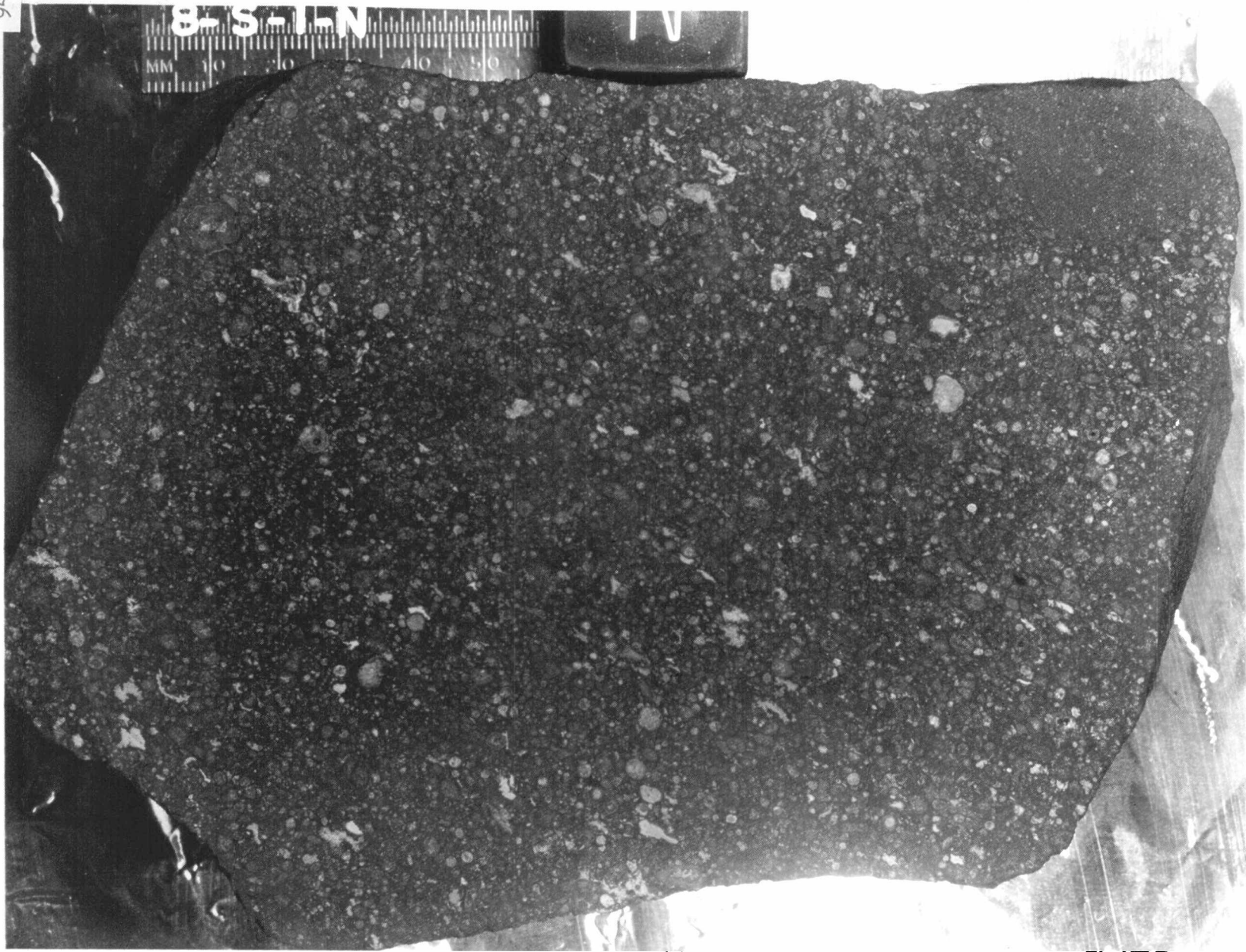


Figure 20

S view of sample 8-S-1

The inclusions in the upper right quadrant have a circular pattern. They may be a separate clast. The elongated aphanitic dark inclusions suggest this pattern as well as the wispy white inclusions and chondrules. The remainder of the surface shows a lineation from upper left to lower right. Two light inclusions are in the lower left quadrant and several irregular white inclusions are in the upper right quadrant. This surface and 8-S-2-N are on opposite sides of the saw cut that separated the 8-S samples.

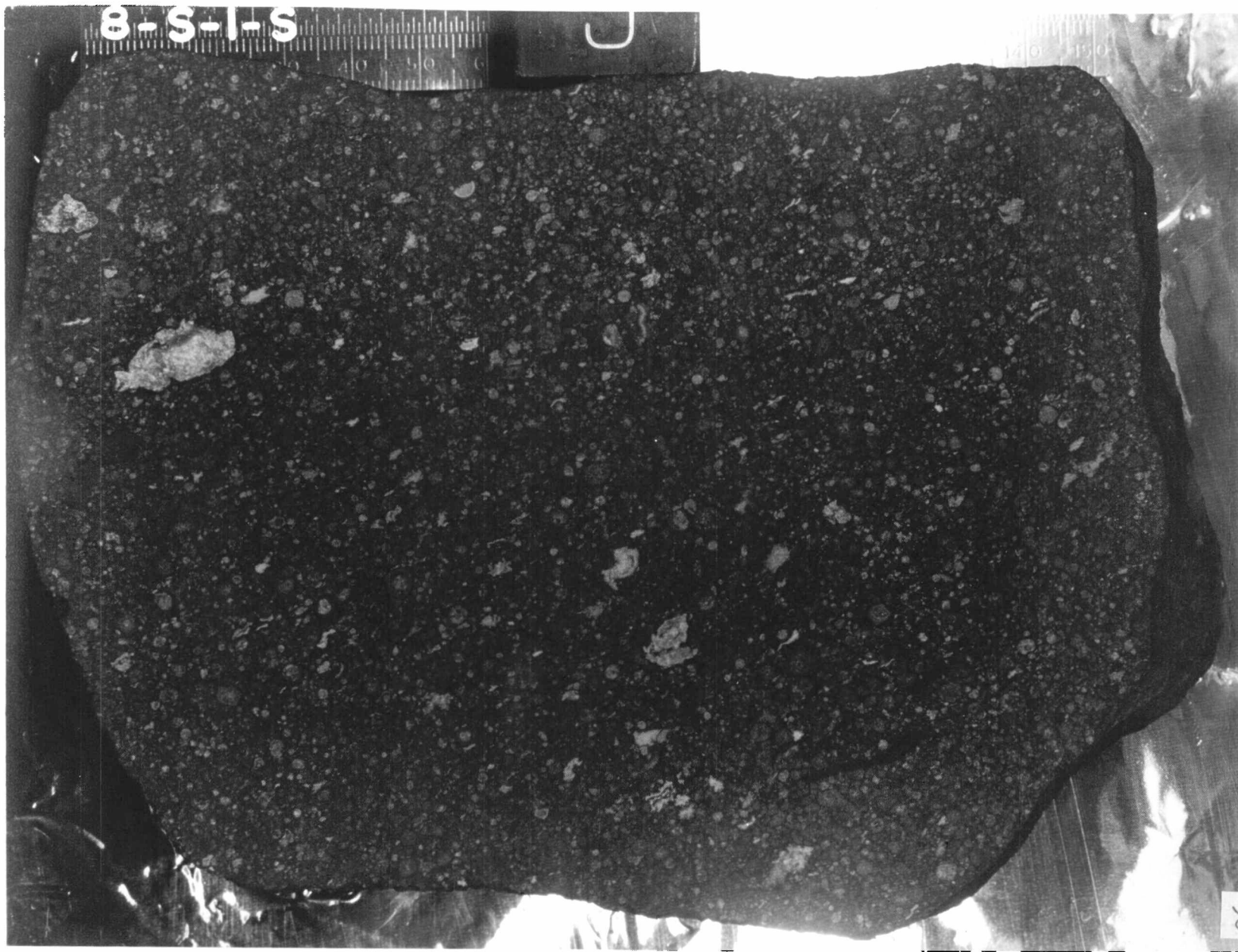


Figure 21

N view of sample 8-S-2

The same suggestion of the circular pattern of 8-S-1-S exists in the upper half of this surface. The aphanitic elongated dark inclusions continue in the upper left quadrant of this surface. Continuations of the white inclusions show at lower left. A small medium to small grained dark inclusion is in the middle near the bottom edge. The lineation runs from upper right to lower left.

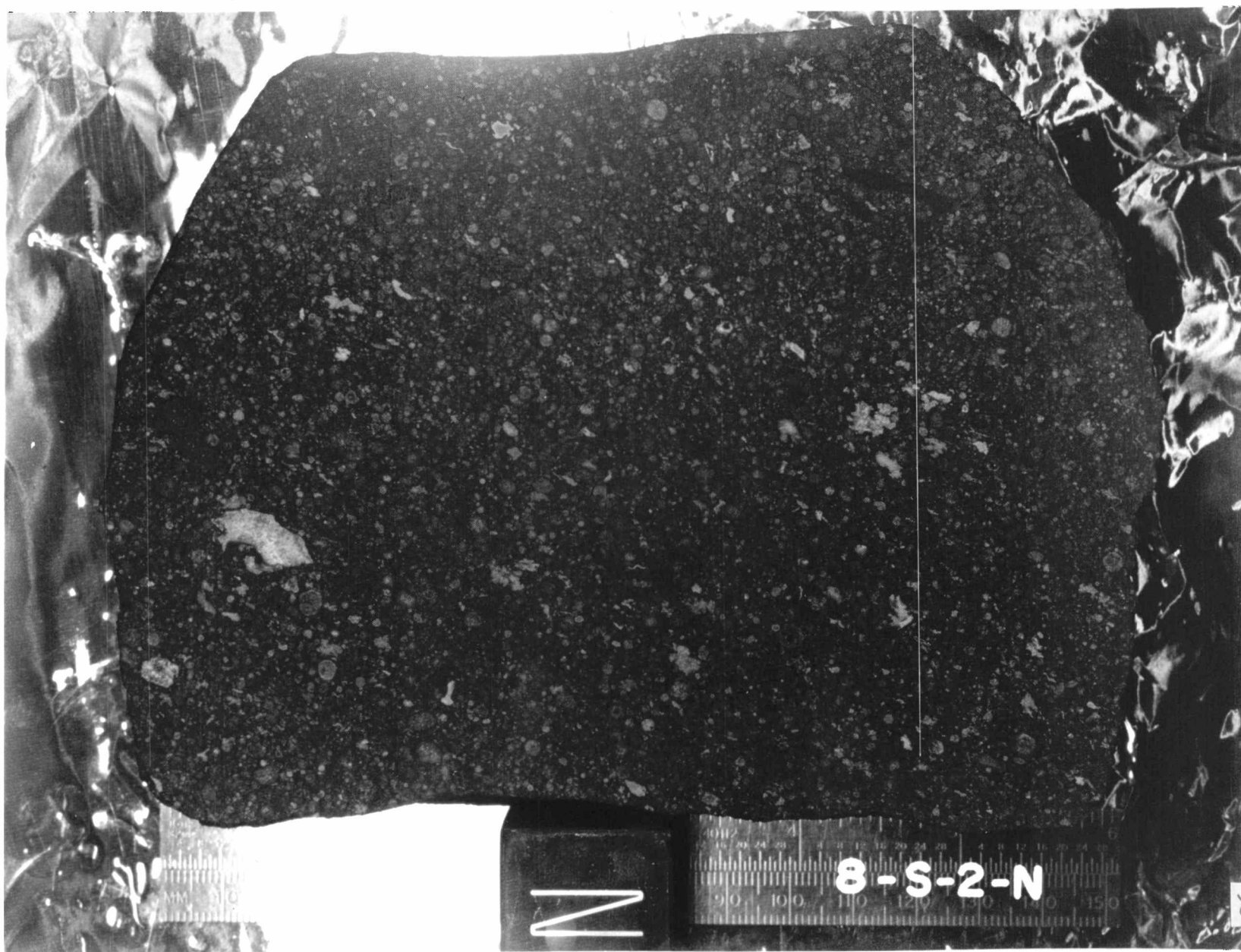


Figure 22

S view of sample 8-S-2

The lineation continues through from the N side from the upper left to lower right. The light inclusions are almost all elongated in this direction. An aphanitic dark inclusion is in the lower right corner.

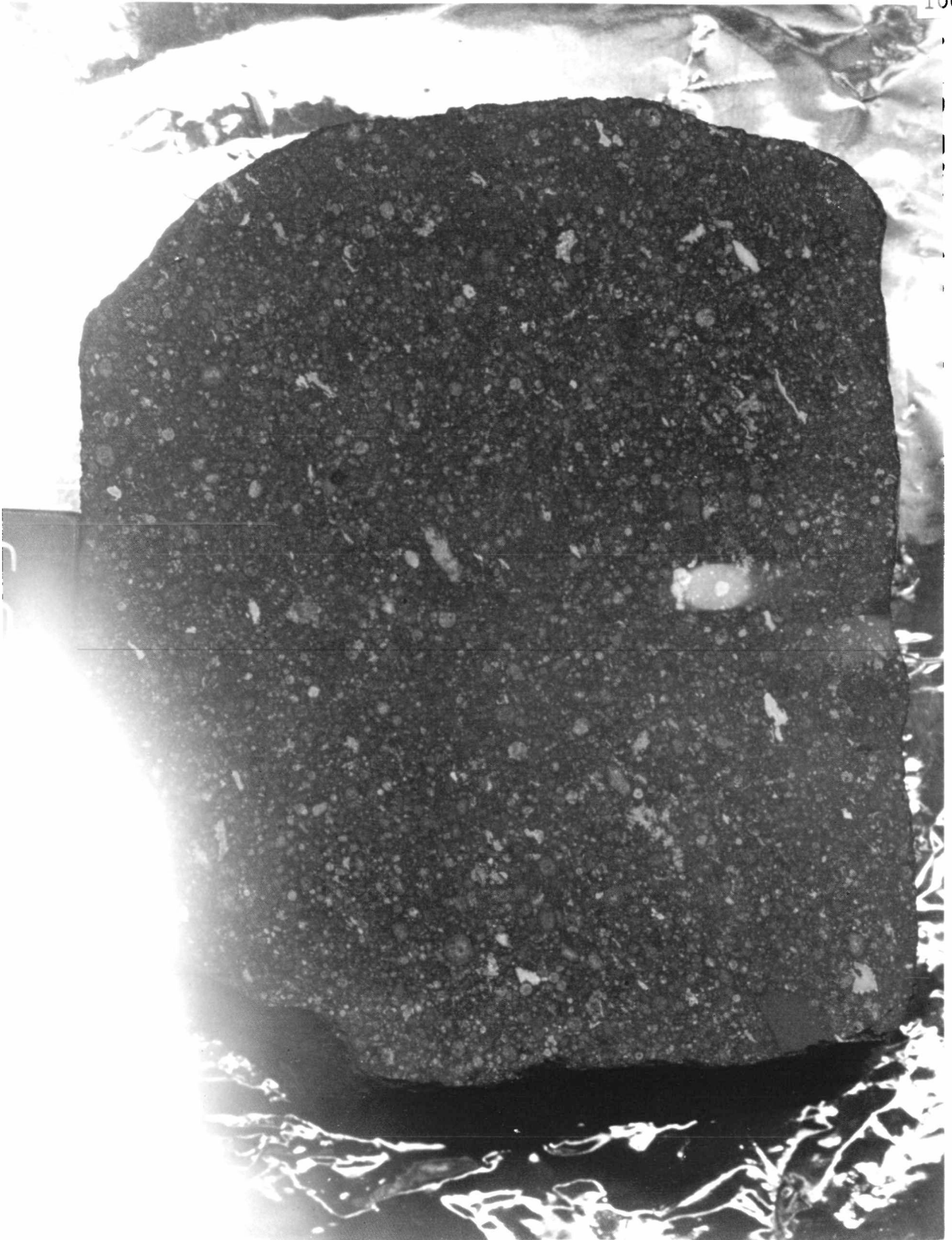


Figure 23

N view of sample 23A-S-1

This surface is generally average in almost all characteristics. There is, however, a more than average number of chondrules with dark areas in them. These dark areas appear to be vugs and they are especially in light gray and white chondrules.

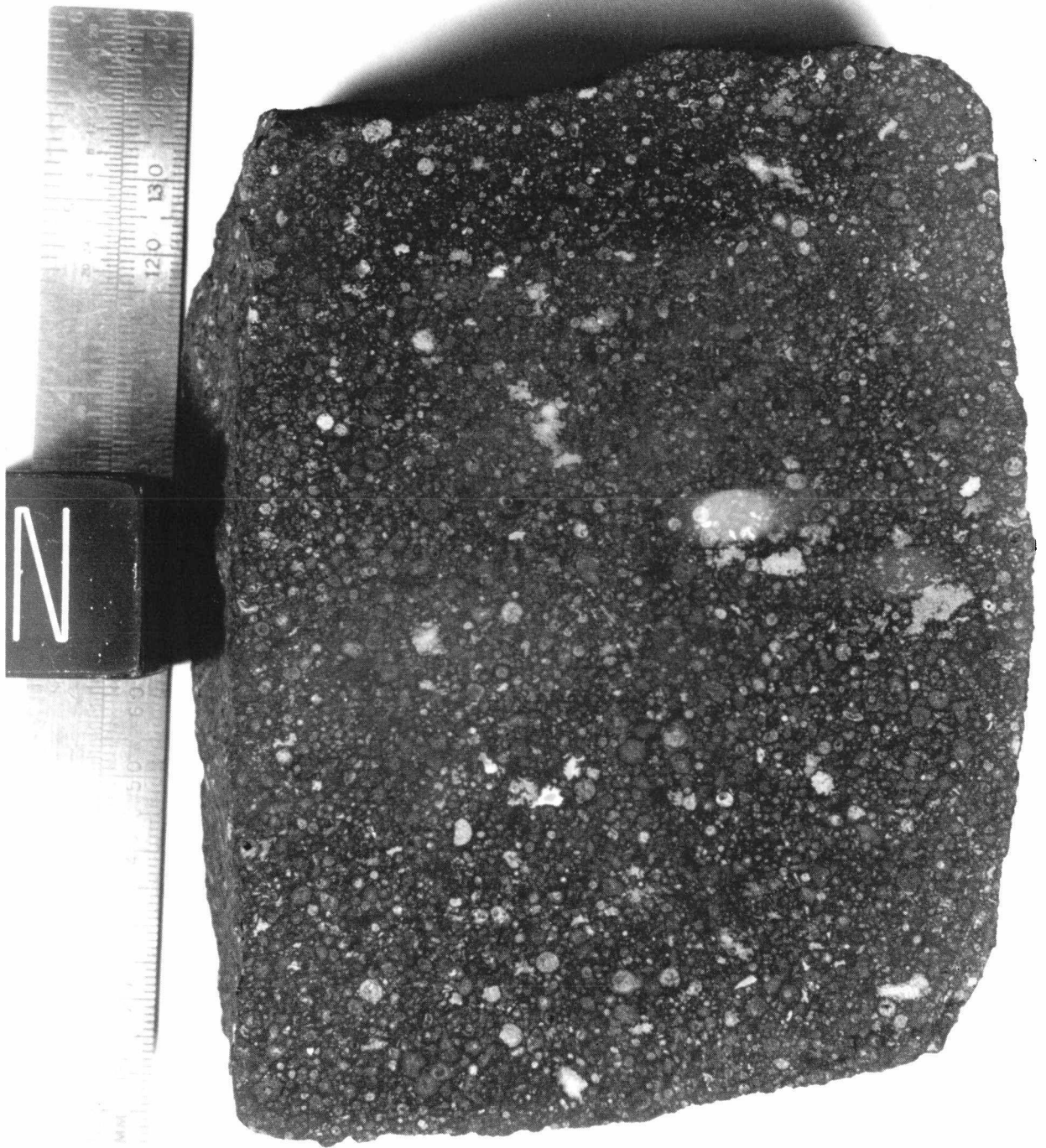


Figure 24

S view of sample 23A-S-1

The two irregular white clasts are in the left edge and several medium sized white irregular and chondrule shaped inclusions are distributed over the total area. Two dark inclusions are near opposite sides in the middle of the surface. The one on the left is very dark aphanitic. The one on the right is medium grained with some dark aphanitic inclusions.

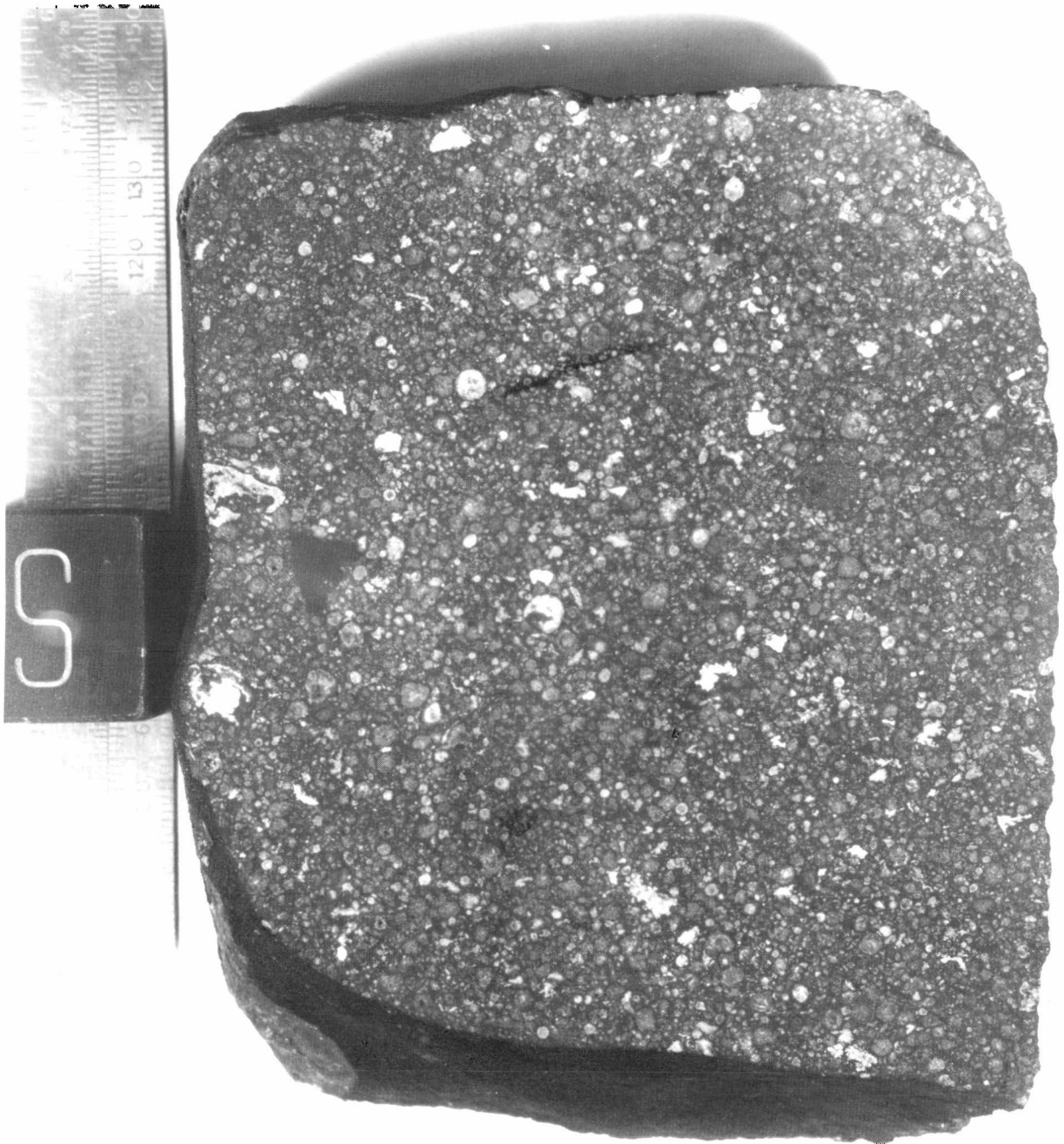


Figure 25

In the lower middle of this specimen is an example of how loosely some of the chondrules are bonded to the matrix. There is a hemispherical void where half of a chondrule fell out during the sawing operation. In the broken area in the upper left quadrant is a hemispherical void as the result of the impression of a chondrule. It can be seen that the break went through the white inclusion in the same area.

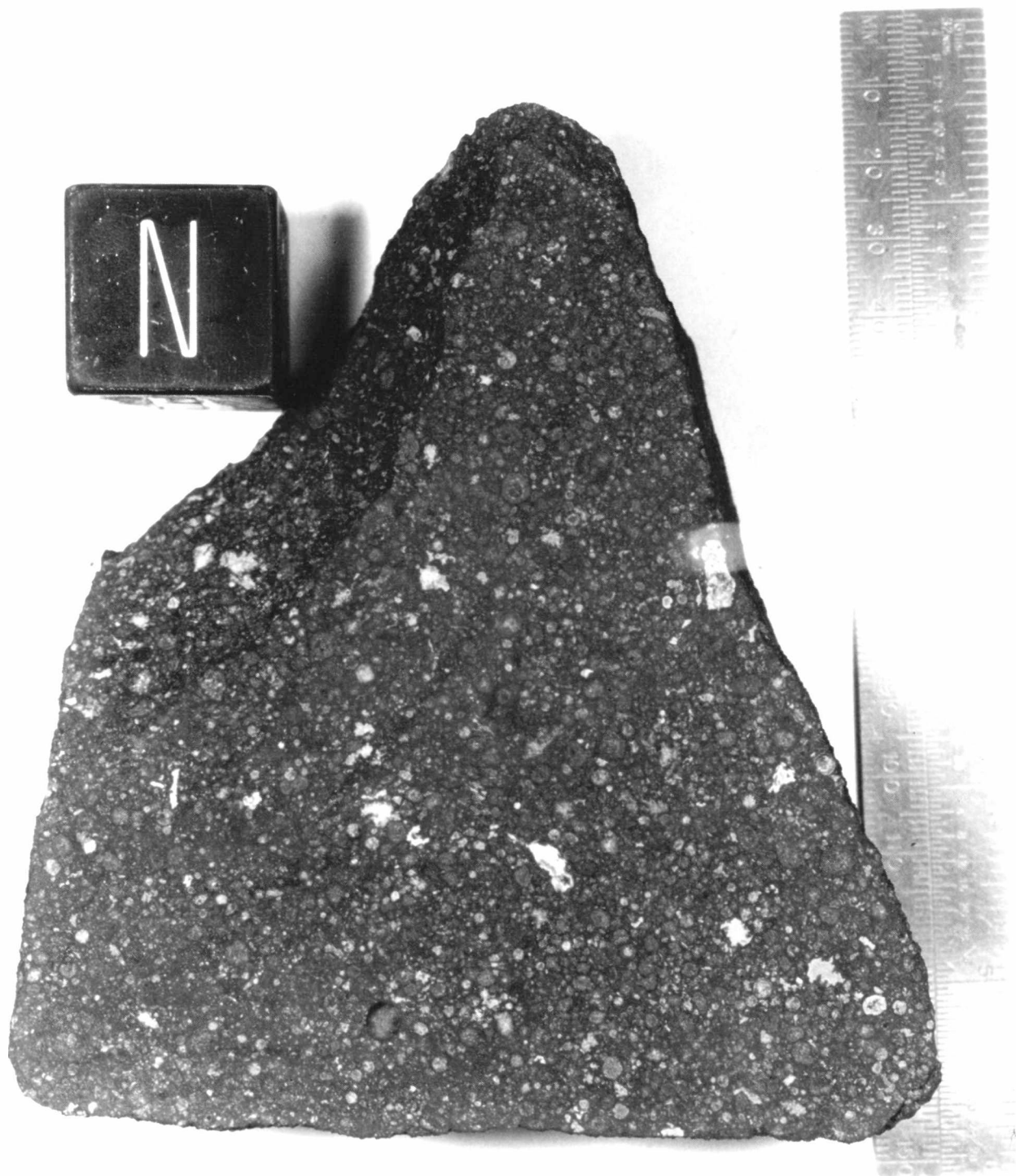


Figure 26

S view of sample 7-S-1

This surface has a relatively large white inclusion with edges that appear to be reaction zones. The outer part is a white zone around a light gray area. A small chondrule with a vug almost half the volume of the chondrule is below and slightly to the right of the large inclusion. At the bottom center is a several mm gray chondrule with a vug in the center. It has some small particles and a large dark chondrule in the upper left corner.



APPENDIX B
Calculator Programs

Display		Key	Display		Key	Register	
Line	Code	Entry	Line	Code	Entry	R0	a
1	31		23	2407	RCL 7	R1	a
2	1502	gx^2	24	61	x	R2	Σy^2
3	235102	STO+2	25	32	CHS	R3	n
4	22	R↓	26	2404	RCL 4	R4	Σy
5	21	$x \Rightarrow y$	27	51	+	R5	Σxy
6	25	$\Sigma +$	28	2403	RCL 3	R6	Σx^2
7	1300	GTO 00	29	71	-	R7	Σx
8	2405	RCL 5	30	2300	STO 0		
9	2407	RCL 7	31	74	R/S		
10	2404	RCL 4	32	2401	RCL 1		
11	61	x	33	74	R/S		
12	2403	RCL 3	34	21	$x \Rightarrow y$		
13	71	÷	35	22	R↓		
14	41	-	36	61	x		
15	2406	RCL 6	37	2402	RCL 2		
16	2407	RCL 7	38	2404	RCL 4		
17	1502	gx^2	39	1502	gx^2		
18	2403	RCL 3	40	2403	RCL 3		
19	71	÷	41	71	÷		
20	41	-	42	41	-		
21	71	÷	43	71	÷		
22	2301	STO 1	44	1300	GTO 00		

1 From HP-25 Applications Programs Rev. 7/75, pp 87-91

Step	Instructions	Input	Keys	Output
1	Key in program			
2	Initialize		f REG f PRGM	
3	Perform for $i=1 \dots n$			
	Input x value and y value	x_i y_i	R/S	i
4	Compute regression constants		GTO 08 R/S	a_0^*
			R/S	a_1^*
5	compute coefficient of determination		R/S	
6	To calculate projected y value, input x value	x	RCL 1 x RCL 0 +	y
7	Perform step 6 as many times as desired.			
8	For new case go to step 2. *The contents of the stack should not be disturbed at these points.			

HP-25 Program Gamma Calibration

111

Display	Key	Display	Key	Register
Line Code	Entry	Line Code	Entry	R ₀ 100.00
1 2401	RCL 1	21 71	$\div$	R ₁
2 74	R/S	22 31	ENTER↑	R ₂ Σy^2
3 71	$\div$	23 2401	RCL 1	R ₃ n
4 01	1	24 74	R/S	R ₄ Σy
5 41	-	25 71	$\div$	R ₅ Σxy
6 1408	f Log	26 01	1	R ₆ Σx^2
7 31	ENTER↑	27 41	-	R ₇ Σx
8 2401	RCL 1	28 1408	f Log	
9 74	R/S	29 2400	RCL 0	
10 71	$\div$	30 41	-	
11 01	1	31 73	.	
12 41	-	32 03	3	
13 1408	f Log	33 03	3	
14 2300	STO 0	34 07	7	
15 21	$x \Rightarrow y$	35 71	$\div$	
16 41	-	36 51	+	
17 73	.	37 02	2	
18 03	3	38 73	.	
19 03	3	39 71	$\div$	
20 00	0	40 25	$\Sigma+$	

Step	Instructions	Input	Keys	Output
1	Key in Program			
2	Initialize		f REG f PRGM	
3	Store 100	100.	STO 1	
4	Calculate gamma for each line. Input 3 exp. values largest % T first	% T ₁ % T ₂ % T ₃		S ₁ S ₂ S ₃
5	Enter S value after each calculation.		ENTER↑	
6	Store gamma for each line in $\Sigma+$.			Gn
7	Calculate average gamma		f $\bar{x}$	f $\bar{x}$

APPENDIX C

Fortran IV Computer Programs

Calculations of Intensity Ratios and Sample Concentration

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This program calculates the intensity ratio and the concentration of each variable in each sample. The input cards are; 1. N - the number of samples in I3 format, 2. M - the number of variables and then the data cards with each minimum % T of the variable values card followed by a card with % T peak background data for each variable. The data cards are arranged in an A3, 10F 4.1 format.

C	CALCULATE INTENSITY RATIOS
C	CALCULATE SAMPLE CONCENTRATIONS
	DIMENSION T(50,15),SMPL(50),PDT(50,15)
	DIMENSION PDS(50,15),R(50,15),BGRD(50),B(50,15)
	DIMENSION CN(50,15),A0(15),A1(15),SUM(50)
	DATA IN/1/,IC/2/,KB/6/,LP/5/
	G=0.558
	READ(IN,1)N
	READ(IN,1)M
1	FORMAT(I3)
	DO 5 K=1,N
	READ(IN,4)SMPL(K),(T(K,I),I=1,M)
	READ(IN,4)BGRD(K),(B(K,I),I=1,M)
4	FORMAT(A3,10F4.1)
	IF (SMPL(K).NE.BGRD(K)) STOP
	DO 10 J=1,M
	PDB=B(K,J)/100.
	PD1=ALOG10(1./PDB)
	PD2=(2.-PD1)
	PD3=(2./PD2)
	PDT(K,J)=T(K,J)*PD3
	PDS(K,J)=ALOG10(100./PDT(K,J)-1.)
	IF (J.EQ.1) GO TO 10
	R(K,J)=10.**((PDS(K,J)-PDS(K,1))/G)
10	CONTINUE
5	CONTINUE
	WRITE(LP,25)
25	FORMAT(/25X,'INTENSITY RATIO')
	WRITE(LP,26)
26	FORMAT(' SMPL PDI MGO SI02 FEO AL2O3 TI02',
	1' NI MNO CR CAO')
	DO 8 L=1,N
	WRITE(LP,7)SMPL(L),PDS(L,1),(R(L,IR),IR=2,M)
7	FORMAT(3X,A3,10(1X,F5.3))
8	CONTINUE

Calculations of Intensity Ratios and
Sample Concentration
Continued

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```

MC=M-1
READ(IC,13)(A0(IE),IE=1,MC)
READ(IC,13)(A1(IE),IE=1,MC)
13  FORMAT(9F7.3)
DO 12 IC=1,N
    SUM(IC)=0.0
DO 14 MA=1,M
    MR=MA+1
    CN(IC,MA)=A1(MA)*R(IC,MR)+A0(MA)
    SUM(IC)=SUM(IC)+CN(IC,MA)
14  CONTINUE
12  CONTINUE
    WRITE(LP,20)
20  FORMAT(//25X,'SAMPLE CONCENTRATIONS')
    WRITE(LP,28)
28  FORMAT(' SMPL  MGC  SI02  FEO  AL2O3  TI02',
1    '  NI  MNO  CR  CAO  TOTAL')
    DO 15 LC=1,N
    WRITE(LP,16)SMPL(LC),(CN(LC,MW),MW=1,MC),SUM(LC)
16  FORMAT(X,A3,4(X,F6.2),4(X,F6.3),2(X,F6.2))
15  CONTINUE
    WRITE(LP,27)
27  FORMAT(//)
    STOP
    END

```

FORTRAN PROGRAM
for Elementary Statistics

115

This program calculates the means, the standard deviations, the variances and the coefficients of variation for each variable. The data are then arranged into a variance-covariance matrix and a correlation coefficient matrix. The following input cards are used. A card with M, the number of variables in I3 format and then the data cards. The first entry of each data card is the sample number in A3 format. Some of the variables used are:

N = No. of samples
M = No. of variables
AN = No. of samples N
ANI = No. of samples (N-1)
Sx1 = Sum of samples
Sx2 = Sum of the variables
Sx1x2 = Sum of X squared
F = Mean of the variables Sx1/AN
SD = Standard deviation
VAR = Variance A
CV = Coefficient of variation SD/F
X = Value of variable

```

      DIMENSION X(100,12),A(12,12),R(12,12),F(12),SD(12)
      DIMENSION CV(12),VAR(12),SMPL(100)
      DATA IO/1/,KB/6/,LP/5/
      READ(IO,1)M
1      FORMAT(I3)
      DO 3 I=1,1000
      READ(IO,2,END=4)SMPL(I),(X(I,J),J=1,M)
2      FORMAT(A3,4(F6,2),4(F6,3),F5,2,F7,2)
      N=I
3      CONTINUE
4      AN=N
      ANI=N-1
      DO 100 I=1,M
      DO 102 J=1,M
      SX1=0.0
      SX2=0.0
      SX1X2=0.0
      DO 101 K=1,N
      SX1=SX1+X(K,I)
      SX2=SX2+X(K,J)
101    SX1X2=SX1X2+X(K,I)*X(K,J)
      A(I,J)=(SX1X2-SX1*SX2/ANI)/ANI
102    A(J,I)=A(I,J)
      F(I)=SX1/AN
      VAR(I)=A(I,I)
      SD(I)=SQRT(VAR(I))
100    CV(I)=SD(I)/F(I)

```

```

      DO 105 I=1,M
      R(I,I)=1.000
      DO 105 J=1,M
105    R(I,J)=A(I,J)/(SD(I)*SD(J))
      R(J,I)=R(I,J)
      WRITE(LP,200)
200    FORMAT(25X,'INPUT DATA')
      DO 205 I=1,N
      WRITE(LP,203) SMPL(I), (X(I,J), J=1,M)
203    FORMAT(6X,A3,4(X,F6.2),4(X,F6.3),2(X,F6.2))
205    CONTINUE
      WRITE(LP,27)
27    FORMAT(1H1)
      WRITE(LP,28)
28    FORMAT('          MGO      SIQ2      FEO      AL203      TIQ2',
1      '      NI      MNO      CR      CAO      TOTAL')
      WRITE(LP,12)
12    FORMAT(' MEANS=')
204    FORMAT(6X,4(X,F6.2),4(X,F6.3),2(X,F6.2))
      WRITE(LP,204) (F(I), I=1,M)
      WRITE(LP,13)
13    FORMAT(' SD      =')
      WRITE(LP,204) (SD(I), I=1,M)
      WRITE(LP,14)
14    FORMAT(' VAR      =')
      WRITE(LP,204) (VAR(I), I=1,M)
      WRITE(LP,17)
17    FORMAT(' C OF V')
      WRITE(LP,206) (CV(I), I=1,M)
206    FORMAT(6X,10(X,F6.3))
      WRITE(LP,15)
15    FORMAT(1H1,10X,'VARIANCE-COVARIANCE MATRIX')
      WRITE(LP,22) ((A(I,J), J=1,M), I=1,M)
22    FORMAT(10(F8.3))
      WRITE(LP,16)
16    FORMAT(1H1,10X,'CORRELATION COEFFICIENT MATRIX')
      WRITE(LP,22) ((R(I,J), J=1,M), I=1,M)
      STOP
      END

```