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MULTIDISCIPLINARY RESEARCH LEADING TO UTILIZATION OF EXTRATERRESTRIAL RESOURCES

Annual Status Report
Fiscal Year 1969

TWIN CITIES MINING RESEARCH CENTER

Walter E. Lewis, Research Director

NASA Contract R-09-040-001

MULTIDISCIPLINARY RESEARCH LEADING TO UTILIZATION OF EXTRATERRESTRIAL RESOURCES

Annual Status Report
Fiscal Year 1969

U.S. Bureau of Mines NASA Program of Multidisciplinary Research
Leading to Utilization of Extraterrestrial Resources

ANNUAL STATUS REPORT — FISCAL YEAR 1969

Contents

	Page
Background analysis and coordination	1
Chemical reactivity of freshly formed surfaces	6
Surface properties of rock in lunar environment	8
Rock failure processes and strength and elastic properties in lunar environment	17
Feasibility of thermal fragmentation studies in vacuum	25
Thermophysical properties of rock over lunar temperature range	31
Basic problems of drilling in lunar environment	37
Use of explosives on the Moon	40
Effect of lunar environment on behavior of fine particles	43
Support for underground lunar shelter	47
Electrowinning of oxygen from silicate rocks	50
Reduction of silicates with carbon	52
Stability of hydrous silicates and oxides in lunar environment	63
Magnetic and electrostatic properties of minerals in a vacuum	66

ANNUAL STATUS REPORT FISCAL YEAR 1969

U.S. Bureau of Mines NASA Program of Multidisciplinary Research Leading to Utilization of Extraterrestrial Resources

July 1, 1969

Task title:	Background analysis and coordination
Investigator:	Thomas C. Atchison, Program Manager
Location:	Twin Cities Mining Research Center Minneapolis, Minnesota
Date begun:	April 1965 To be completed: Continuing
Personnel:	Thomas C. Atchison, Supervisory Research Physicist Other Bureau personnel, as assigned

PROGRESS REPORT

Objective

The objective of the program is to help provide basic scientific and engineering knowledge needed to use extraterrestrial mineral resources in support of future space missions. Under this component, background and supporting studies and coordinating and liaison activities for the program are carried out.

Summary

During the year the various research tasks at the seven research centers making up the Bureau's extraterrestrial resource utilization program were monitored. We continued to obtain, evaluate, and distribute information applicable to the program by literature search and direct contact with groups conducting related research. We also continued to extract and organize material from Bureau reports to provide periodic status reports for NASA and prepared special studies related to the program when requested by NASA.

This spring the third formal review of the Bureau's program was held for a panel of NASA scientists and engineers. Continuation of the program into the fifth and sixth contract years was approved by NASA and funding was continued at the rate of $300,000 per year.

Progress During the Year

Assistance to the experimental work of the program was continued by providing technical information and guidance to the task investigators. Many of the tasks were completed this year and, in accord with NASA recommendations, effort has been increased on the more basic studies of material properties and behavior in simulated lunar environment.

Efforts continued on obtaining, evaluating, and distributing background information of importance to the research program. Visits were made to the Jet Propulsion Laboratory in Pasadena, Calif., the Space Sciences Laboratory at the University of Pittsburgh, and the Civil Engineering Department of Carnegie-Mellon University, also in Pittsburgh, to discuss research on lunar surface problems. T. C. Atchison, D. E. Fogelson, and D. P. Lindroth participated in a Symposium on Lunar Transients held at the Douglas Advanced Research Laboratories in Huntington Beach, Calif. in February, and Atchison and Fogelson presented papers summarizing progress in the Bureau's program at a Symposium on the Chemistry and Physics of Lunar Surface Materials at the Metallurgical Society Spring Meeting in Pittsburgh in May. In June detailed results of several research tasks were presented at the Seventh Annual Meeting of the Working Group on Extraterrestrial Resources in Denver. D. E. Fogelson (substituting for T. C. Atchison) served as acting chairman of the Subgroup on Mining and Processing at the meeting.

D. E. Fogelson and B. L. Vickers made a trip through Oregon and northern California in October to replenish our supply of the 14 simulated lunar rocks being used in the Bureau's program. The supply now on hand should be adequate for the coming year. Samples were furnished to additional outside research groups engaged in lunar surface studies, including several of the investigators concerned with the returned lunar sample program. A summary of the property data being obtained by the Bureau on the simulated lunar rocks is given in table 1 for solid rock samples and in table 2 for powdered samples.

A meeting was held at the Twin Cities Mining Research Center in May to review and evaluate progress on the Bureau's program during the year. Several scientists and engineers from NASA headquarters and field laboratories served as a review panel. Members of the research task teams from each of the Bureau centers engaged in the program attended and discussed the results of their studies.

A proposal was prepared and submitted to NASA for continuing the Bureau's program into its fifth and sixth years. The proposal was accepted and funds have been made available for continuing the work at the $300,000 level during fiscal year 1970.

TABLE 1. - Properties of simulated lunar rocks in earth environment

Rock type	Bulk density (g/cc)	Apparent porosity (percent)	Permeability (millidarcys)	Hardness (Shore units)
Dunite	3.19	1	<<1	73
Gabbro	3.11	<1	<1	84
Tholeiitic basalt	2.84	2	<<1	84
Granodiorite	2.58	1	<1	87
Serpentinite	2.56	3	<<1	68
Obsidian	2.39	1	<<1	103
Altered rhyolite	2.36	8	<1	59
Rhyolite	2.35	8	<<1	79
Vesicular basalt #1	2.25	20	Varies	81
Vesicular baslat #2	2.22	24	Varies	67
Dacite	1.98	17	4	35
Vesicular basalt #3	1.52	46	Varies	80
Semiwelded tuff	1.15	50	58	10
Pumice	.76	62	840	5

Rock type	Pulse velocity (m/sec)	Young's modulus (10^6 psi)	Compressive strength (psi)	Tensile strength (psi)	Strength coefficient (ratio)
Dunite	7,500	18.7	27,000	2,000	1.32
Gabbro	7,100	16.6	30,000	2,000	.96
Tholeiitic basalt	6,000	10.3	53,000	3,400	1.91
Granodiorite	3,000	6.1	21,000	950	.51
Serpentinite	6,000	5.7	18,000	800	1.37
Obsidian	5,600	9.2	65,000	2,200	.53
Altered rhyolite	3,300	2.6	16,000	1,100	.74
Rhyolite	4,200	2.4	22,000	1,200	.89
Vesicular basalt #1	3,800	2.8	10,000	1,100	1.01
Vesicular basalt #2	4,500	2.5	5,500	590	.75
Dacite	4,500	2.0	6,000	620	.42
Vesicular basalt #3	4,800	2.7	5,600	810	.77
Semiwelded tuff	2,500	.3	850	100	.10
Pumice	2,500	.5	1,500	240	.08

Rock type	Thermal expansion (10^{-6}/°F)	Magnetic susceptibility (10^{-6} cgs units)	Dielectric constant (ratio)	Dissipation factor (ratio)
Dunite	6.2	400	5.0	0.008
Gabbro	3.9	6,000	15.4	.081
Tholeiitic basalt	4.5	2,000	11.1	.099
Granodiorite	5.6	Negligible	5.5	.004
Serpentinite	5.3	6,000	([1])	([1])
Obsidian	4.1	100	6.3	.010
Altered rhyolite	4.7	Negligible	4.8	.017
Rhyolite	4.5	400	5.1	.003
Vesicular basalt #1	3.2	400	6.0	.012
Vesicular basalt #2	3.6	500	6.7	.036
Dacite	3.1	600	5.0	.008
Vesicular basalt #3	3.8	200	4.2	.005
Semiwelded tuff	3.3	400	2.9	.015
Pumice	4.5	Negligible	2.3	.008

[1]Not yet measured.

TABLE 2. - Properties of powdered simulated lunar materials

Rock type	Solid rock bulk density (g/cc)	Powder bulk density (g/cc)	Intrinsic density (g/cc)	Magnetic susceptibility (10^{-6} cgs units)	Dielectric constant (ratio)	Specific surface area (m^2/g)
Dunite	3.19	1.69	3.17	60	3.19	4.8
Gabbro	3.11	1.70	3.22	3,500	3.30	.6
Tholeiitic basalt	2.84	1.45	2.95	1,400	3.02	.8
Granodiorite	2.58	1.45	2.69	30	2.53	.6
Serpentinite	2.56	1.43	2.73	3,500	4.94	3.8
Obsidian	2.39	1.16	2.40	50	2.46	.5
Altered rhyolite	2.36	1.19	2.63	30	2.72	3.3
Rhyolite	2.35	1.04	2.60	220	2.08	1.4
Vesicular basalt #1	2.25	1.37	2.86	340	2.63	.8
Vesicular basalt #2	2.22	1.52	3.02	350	2.83	1.3
Dacite	1.98	1.31	2.47	460	2.63	.5
Vesicular basalt #3	1.52	1.31	2.84	260	2.45	.7
Semiwelded tuff	1.15	1.02	2.46	270	2.20	1.2
Pumice	.76	1.20	2.40	10	2.56	1.4

Status of Manuscripts

Proposal for Continuing Bureau Extraterrestrial Resource Utilization Program, by T. C. Atchison, was submitted to NASA in July.

Bureau of Mines Research on Lunar Resource Utilization, by T. C. Atchison and C. W. Schultz, and Simulated Lunar Rocks, by D. E. Fogelson, were published in NASA SP-177, pp. 65-74 and 75-95, in December.

Utilization of Lunar Surface Materials, by T. C. Atchison, and Simulated Lunar Surface Materials, by D. E. Fogelson, were presented at a Symposium on the Chemistry and Physics of Lunar Surface Materials at the Metallurgical Society Spring Meeting in Pittsburgh in May.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Chemical reactivity of freshly formed surfaces		
Investigator:	Clifford W. Schultz, Project Leader		
Location:	Twin Cities Mining Research Center Minneapolis, Minnesota		
Date begun:	April 1966	To be completed:	September 1969
Personnel:	Clifford W. Schultz, Metallurgist William H. Engelmann, Research Chemist		

PROGRESS REPORT

Objective

The objective of this task is to define the equilibrium state of mineral surfaces with respect to adsorbed gases. Further, it is intended that existing adsorption isotherms be clarified in the low pressure end of the scale.

Summary

The level of effort on this project was reduced to 1/6 man-year for fiscal year 1969.

It was found that the measurement of the total adsorption isotherm of water vapor on quartz was impossible with the equipment available. The reversible portion of the adsorption isotherm will be measured in the first quarter of fiscal year 1970 and the project will then be terminated.

Progress During the Year

An attempt was made to determine the adsorption isotherm of water vapor on quartz in a dynamic system. In that system, new quartz surface was being created by grinding while a controlled helium - H_2O atmosphere was passed through the reaction vessel. The change in gas composition was indicative of the amount of water being adsorbed. By measuring the isotherms in such a system the amount of irreversibly adsorbed water could be measured. This assumes that an atom, such as oxygen or a hydroxyl ion, which adsorbed at a lattice termination (Tamm state) would be indistinguishable from that which was originally there and would form a bond as stable as the original and be irreversibly adsorbed. Subsequent layers or fraction thereof would still be reversible.

As was reported, this technique proved unsuitable because background noise obscured the sensor output. A new static system has been assembled and will be used to determine the reversible portion of the isotherm before termination of the project.

Status of Manuscripts

None scheduled until the experimental work is completed.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Surface properties of rock in lunar environment		
Investigator:	Wallace W. Roepke, Project Leader		
Location:	Twin Cities Mining Research Center Minneapolis, Minnesota		
Date begun:	April 1966	To be completed:	June 1969
Personnel:	William H. Engelmann, Research Chemist Wallace W. Roepke, Principal Vacuum Specialist Kenneth G. Pung, Physical Science Technician		

PROGRESS REPORT

Objective

The goal of this task is to measure the surface properties of rocks and rock forming minerals in a simulated lunar environment. Because friction is an important feature of many mining operations, the immediate objective is to measure the coefficients of friction of several mineral and mineral-metal (tungsten carbide) pairs in ultrahigh vacuum.

Summary

This past year's effort has emphasized friction testing and surface cleaning. Final development, checking and preliminary testing of the friction apparatus has been completed using quartz to establish baseline control. Work has begun on use of the CO_2 laser as a cleaning mechanism to approach an atomically clean surface of quartz. Results were reported at the annual meeting of the Working Group on Extraterrestrial Resources in June. The studies will be continued as part of a new expanded task in the coming fiscal year.

Progress During the Year

Figure 1 shows the laboratory arrangement for the equipment being used in this task. The long horizontal tube on the bench to the right is the 100-watt CO_2 laser aligned for cleaning the surface of a sample in the Ultek ultrahigh vacuum (UHV) chamber.

Figure 2 shows the window arrangement developed to transmit the 10.6 micrometer laser beam into the chamber. The germanium disk was epoxied to the Pyrex and the small fillet of epoxy was coated with silicone resin providing better UHV compatability than the exposed epoxy. Since the IR beam has a fairly small diameter (1.5 cm maximum) much of the Pyrex window area is available for visual or photographic observation in the chamber. A paper on the window design has been submitted for publication.

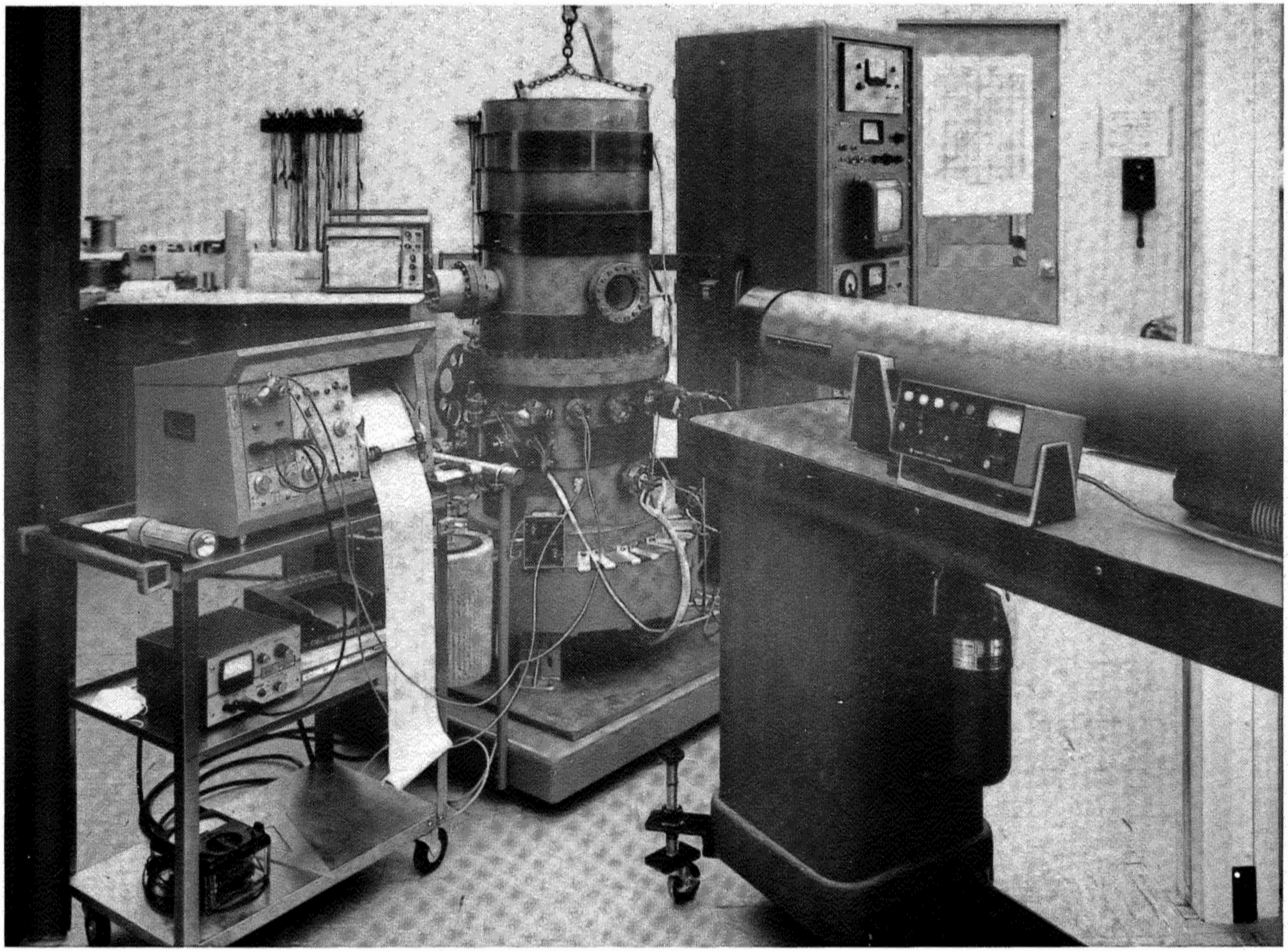

FIGURE 1. - Ultrahigh Vacuum Surface Properties Laboratory.

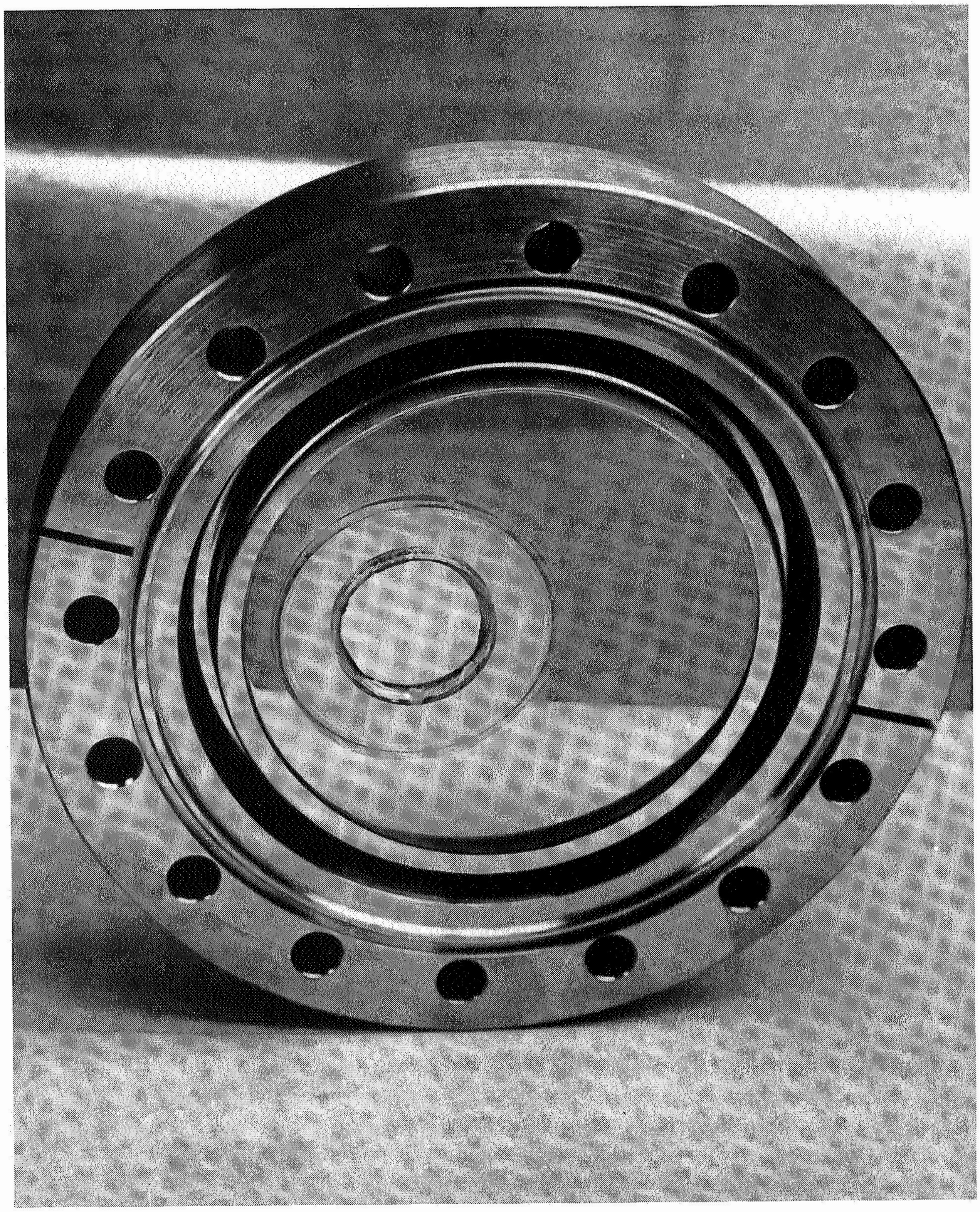

FIGURE 2. - IR-Pyrex Window.

The friction apparatus itself is shown mounted in the chamber in figure 3. The top portion of the driving mechanism for the sample wheel is at the 10 o'clock position on the back side of the chamber. This mechanism allows a variation in speed from 0.48 to 4.8 degrees per minute, producing linear velocities in the range of 0.72 to 6.9 mm per minute. A closer view of the sample wheel and friction probe is shown in figure 4. Both the sample wheel and friction probe can be moved from outside the UHV system by bellows-sealed, rotary motion feedthroughs. The friction probe moves linearly by translation of the rotary motion into a ball-screw. This movement allows a specified load to be applied to the sample. The changing of samples merely requires that the friction probe be backed away from the sample to clear the sample mounting screws.

A closeup of the friction probe is shown in figure 5. The probe consists of a 0.053-inch carbide drill steel with a hemispherically shaped tip. The beam material and end caps are beryllium copper with two full strain gage bridges mounted on the beams. The upper bridge (just below the probe) measures tangential force while the lower bridge measures normal load. The strain gages are epoxied to the beams using as little adhesive as possible so that it is contained only between the gage and the beam. This exposes a minimum amount of epoxy to the vacuum system and results in no degradation of performance.

Preliminary runs with the CO_2 laser were first conducted in the high vacuum system with a pressure range of 5×10^{-7} torr to 2×10^{-6} torr. These runs were designed to measure the type and amount of gas produced by a single pulsed laser irradiation of the surface of dacite, dunite, and basalt specimens using the quadrupole mass spectrometer. Also of interest was the effect of repeated pulsing on the same spot. From this work we found that the major specie released was water vapor. Successive pulsing did not release more than a trace of additional water from which we inferred that very little water remained on the surface after the initial pulse. Further work is anticipated in this area at a later date.

After preliminary testing of the laser surface cleaning technique in the high vacuum system, the laser was aligned with the mineral samples through the germanium window of the UHV system and used in the friction testing. Tests were conducted under four environmental conditions: UHV cleaned, UHV uncleaned, dry atmosphere, and normal (room) atmosphere. The room atmosphere must be considered relatively wet and contaminated. Preliminary results (figure 6) show an increasing coefficient of friction as the environment changes from normal atmosphere through dry atmosphere to UHV. Surface cleaning of the samples under light load (10 g) resulted in a marked increase in friction coefficient.

Several other tasks have received significant support by personnel from this group. These include: UHV lunar drill experiment, Spokane UHV particulate shear study, thermal spalling of rock in vacuum, compression studies in UHV of simulated lunar materials, and the scanning electron microscope. This work is reported by the principal investigators in each of their respective areas.

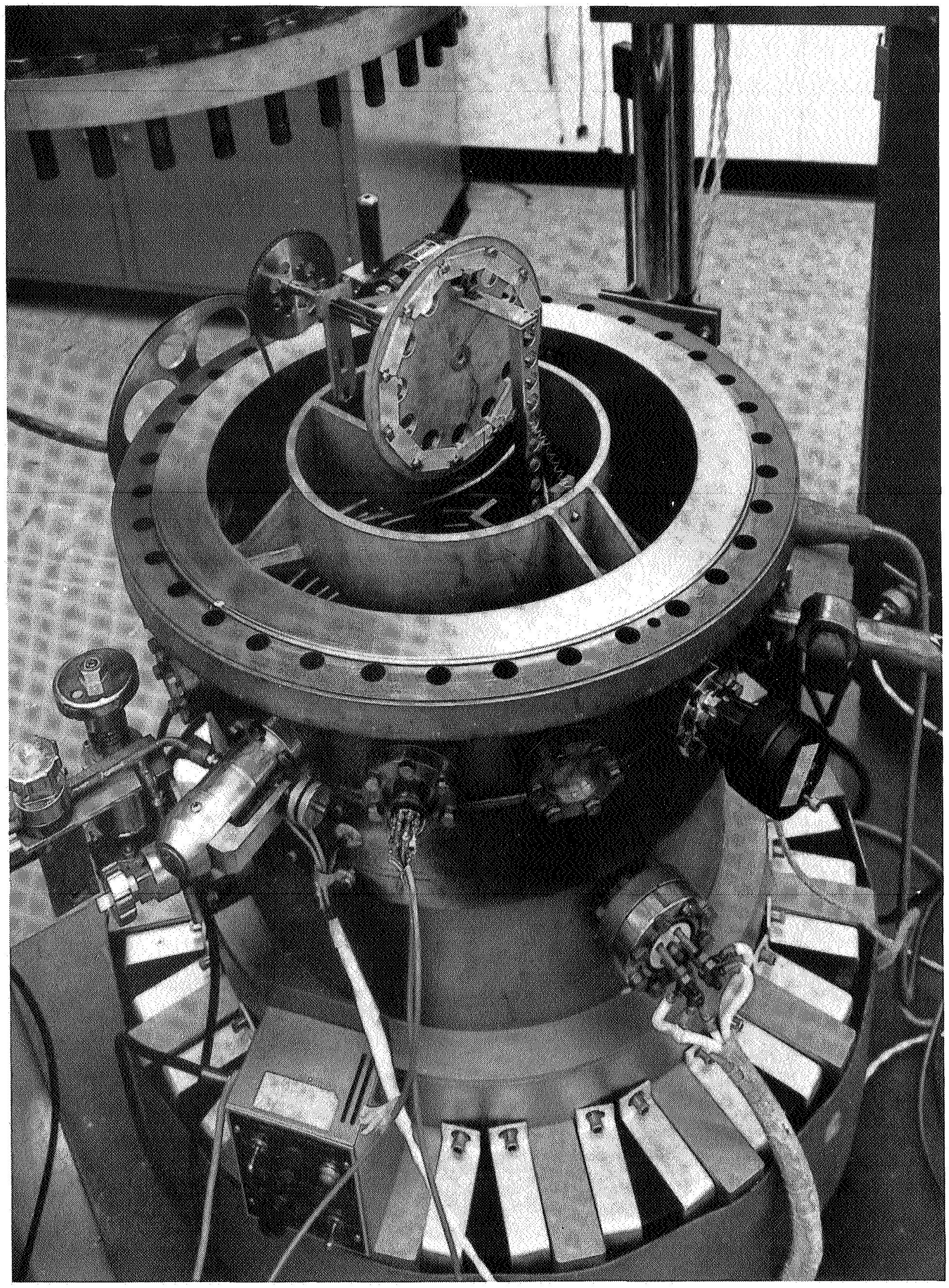

FIGURE 3. - Friction Test Apparatus Mounted in UHV System.

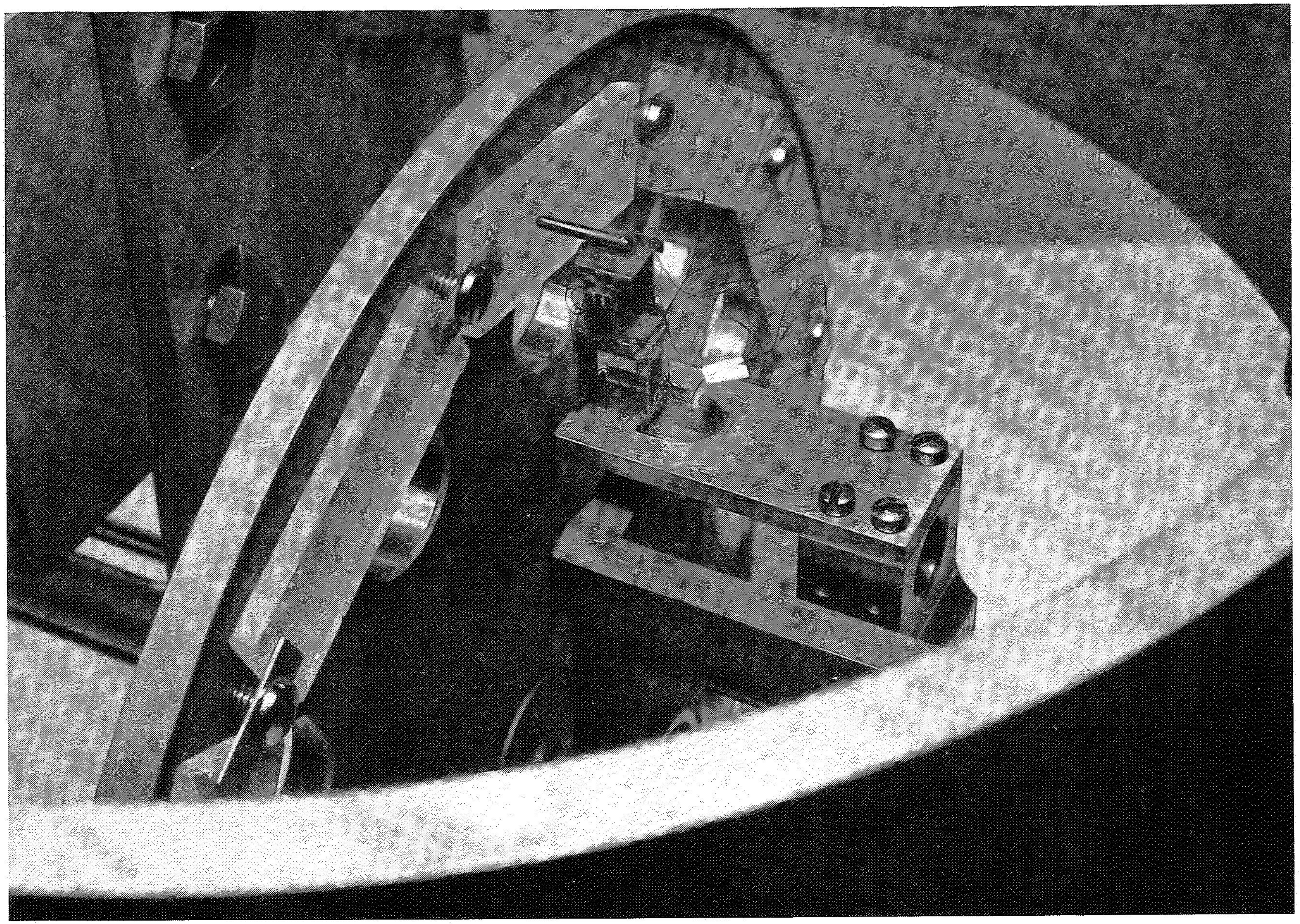

FIGURE 4. - Detailed View of Friction Probe and Sample Mounting Configuration.

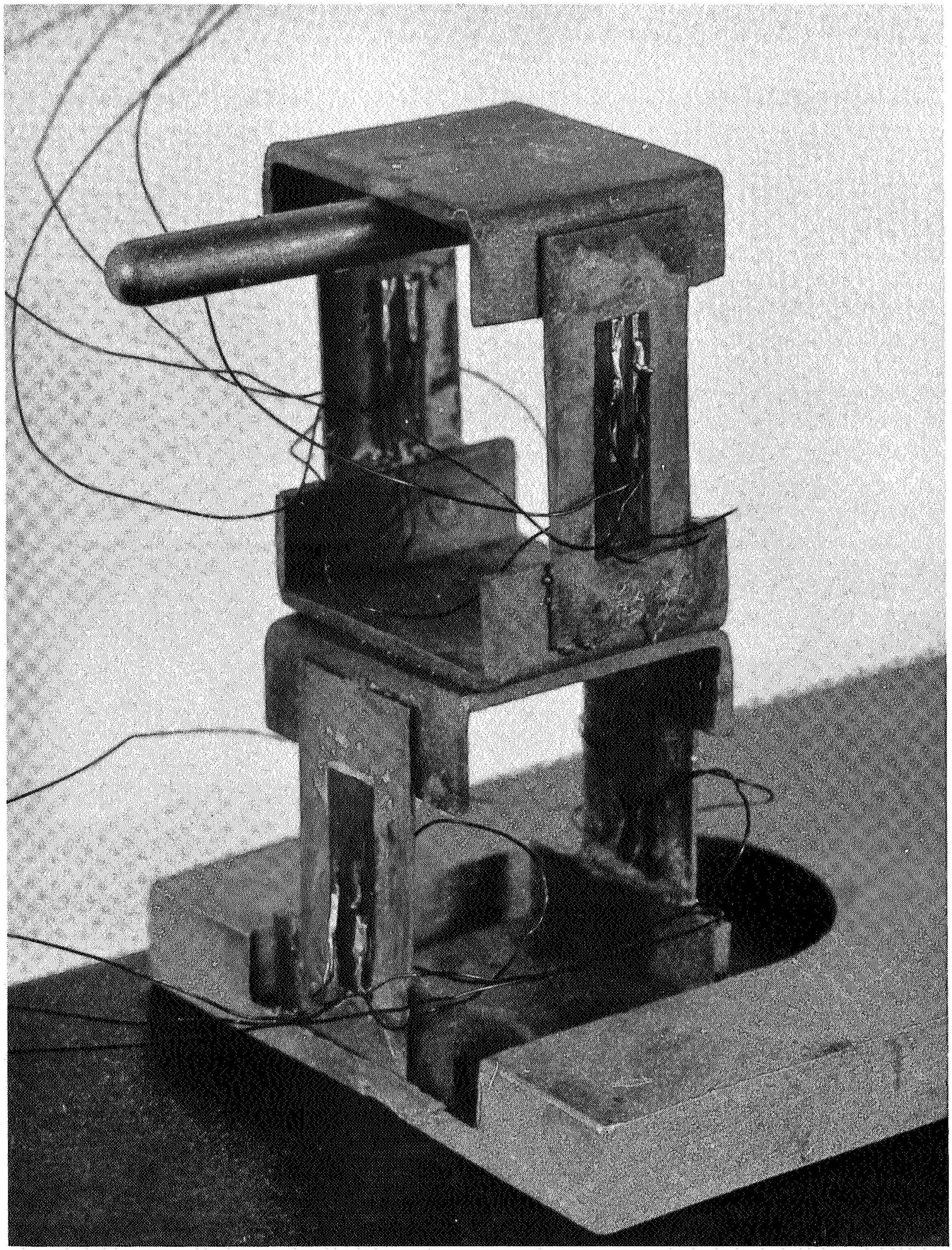

FIGURE 5. - Enlarged View of Friction Probe Showing Double Bridge Arrangement.

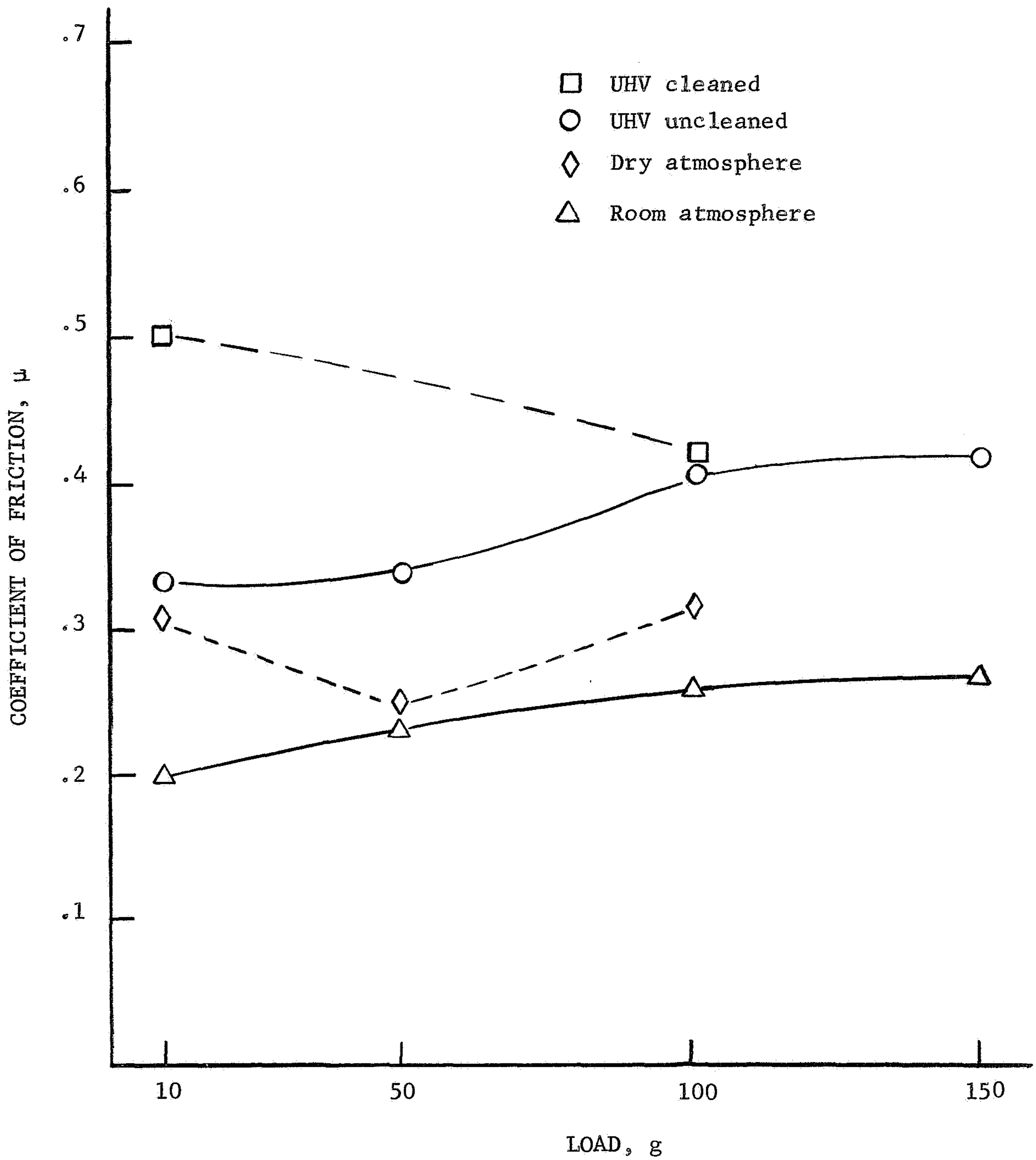

FIGURE 6. - Coefficient of Friction for Tungsten-Carbide or Unoriented Polycrystalline Quartz.

Status of Manuscripts

Inexpensive Oil Vapor Trap for Use with Rotary Vacuum Pumps, by W. W. Roepke and K. G. Pung, was published in the International Journal of Vacuum in August.

Mass Spectrometer Studies of Outgassing from Simulated Lunar Materials in Ultrahigh Vacuum, by W. W. Roepke and C. W. Schultz, was submitted to the Journal of the American Vacuum Society in April.

Friction Tests in Simulated Lunar Vacuum, by W. W. Roepke, was presented as a part of a panel discussion at the Seventh Annual Meeting of the Working Group on Extraterrestrial Resources in Denver in June.

IR-Visible Window Composite for UHV, by W. W. Roepke, is being prepared as a journal article.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Rock failure processes and strength and elastic properties in lunar environment
Investigator:	Egons R. Podnieks, Project Leader
Location:	Twin Cities Mining Research Center Minneapolis, Minnesota
Date begun:	June 1966 To be completed: June 1969
Personnel:	Egons R. Podnieks, Supervisory Mechanical Engineer Robert J. Willard, Geologist Richard E. Thill, Geophysicist Peter G. Chamberlain, Geophysicist Rollie C. Rosenquist, Engineering Technician

PROGRESS REPORT

Objective

The objective of this project is to study the effect of ultrahigh vacuum on rock deformation and failure processes at the macrostructural and the microstructural level and to measure rock strength and elastic properties in ultrahigh vacuum environment.

Summary

As a preliminary step in testing rock in ultrahigh vacuum, anisotropy tests were performed on all of the simulated lunar rocks in a terrestrial environment. Instrumentation of the ultrahigh vacuum chamber for compression tests was completed and preliminary tests were run on semi-welded tuff. Microstructural studies on fractured dacite disks were completed. A scanning electron microscope was purchased and installed, thus providing a new and powerful tool for microstructural studies. Work to accomplish the objectives of this task will be continued in the coming fiscal year under a new reorganized task.

Progress During the Year

Anisotropy Studies

When considereing the expected range of elastic and strength properties of rock on the Moon, the variation of these properties with direction must be taken into account. Furthermore, experimental study of the effect of ultrahigh vacuum on the properties requires a knowledge of the anisotropy symmetry pattern for orienting specimens in meaningful and easily reproducible directions, and for predicting behavior in directions other than those in which properties are actually measured.

Spheres of each of the simulated lunar rocks were pulsed with ultrasonic longitudinal waves in multiple directions to determine anisotropy. Pulse velocities and relative amplitudes were then plotted on equal area projections and contoured. As examples, the plots for dacite and granodiorite are given in figure 1.

The results showed that all of the simulated lunar rocks except obsidian and tholeiitic basalt were significantly anisotropic. Although the amplitude measurements were generally more sensitive to differences in rock fabric with direction than were the velocity measurements, both showed essentially the same symmetry pattern. This observation suggests that the same structural factors probably control both the amplitude of a transmitted signal and the elastic wave velocity in these rocks.

Anisotropy symmetry patterns may be classified according to crystallographic terminology. Figure 2 shows equal area projections of theoretical velocity surfaces calculated from elastic constants for several crystallographic symmetry systems. The patterns for both dacite and granodiorite in figure 1 are classified as orthorhombic. The high value (H), low value (L), and medium value (M) axes located on the plots are valuable for use in orienting rock source blocks for other experiments.

Further microstructural studies relating petrofabric to directionality of rock properties are expected to provide information on the factors controlling directional properties of the simulated lunar material. Similar studies in past Bureau work have proved quite successful.

Compression Tests in Ultrahigh Vacuum

Preparations were completed to extend compression testing into ultrahigh vacuum following preliminary tests performed last year in a medium vacuum. Although basic components for these tests were purchased and assembled in the vacuum chamber last year, the following additional fixtures were constructed this year (see figure 3):

1. Stiffening springs designed to eliminate the force on the platens due to atmospheric pressure.

2. Rigid guiding apparatus designed to prevent lateral popout of specimens under compressive loading.

3. Two load cells, suitable for use inside the chamber to monitor axial load applied to 1- or 2-inch diameter cores.

4. Cantilever beam extensometer, also suitable for use inside the chamber to measure axial deformation of cores.

5. Protective screening device to shelter delicate portions of the ultrahigh vacuum chamber from rock fragments.

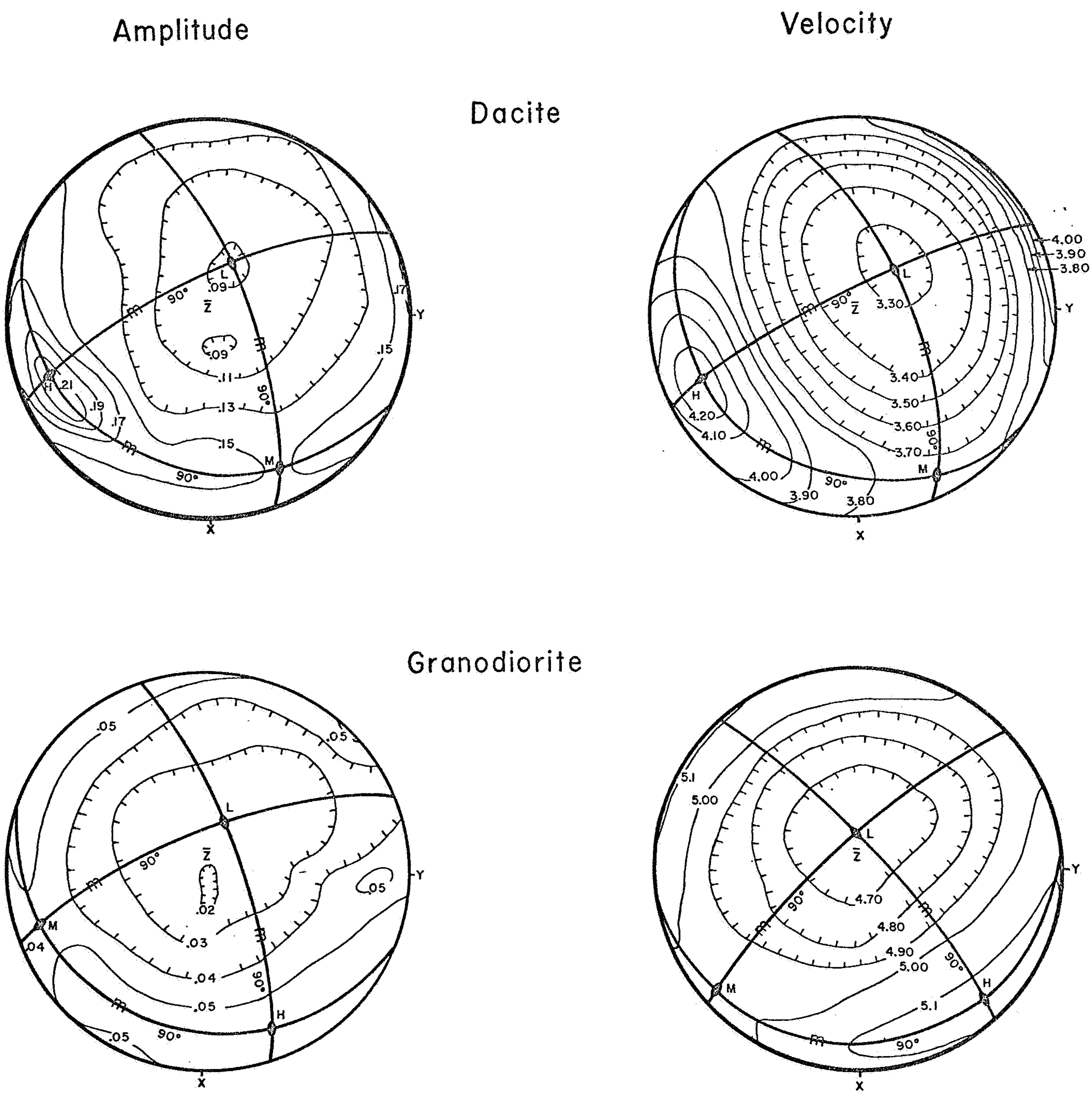

FIGURE 1. - Equal Area Polar Projections of Relative Amplitude and Velocity.

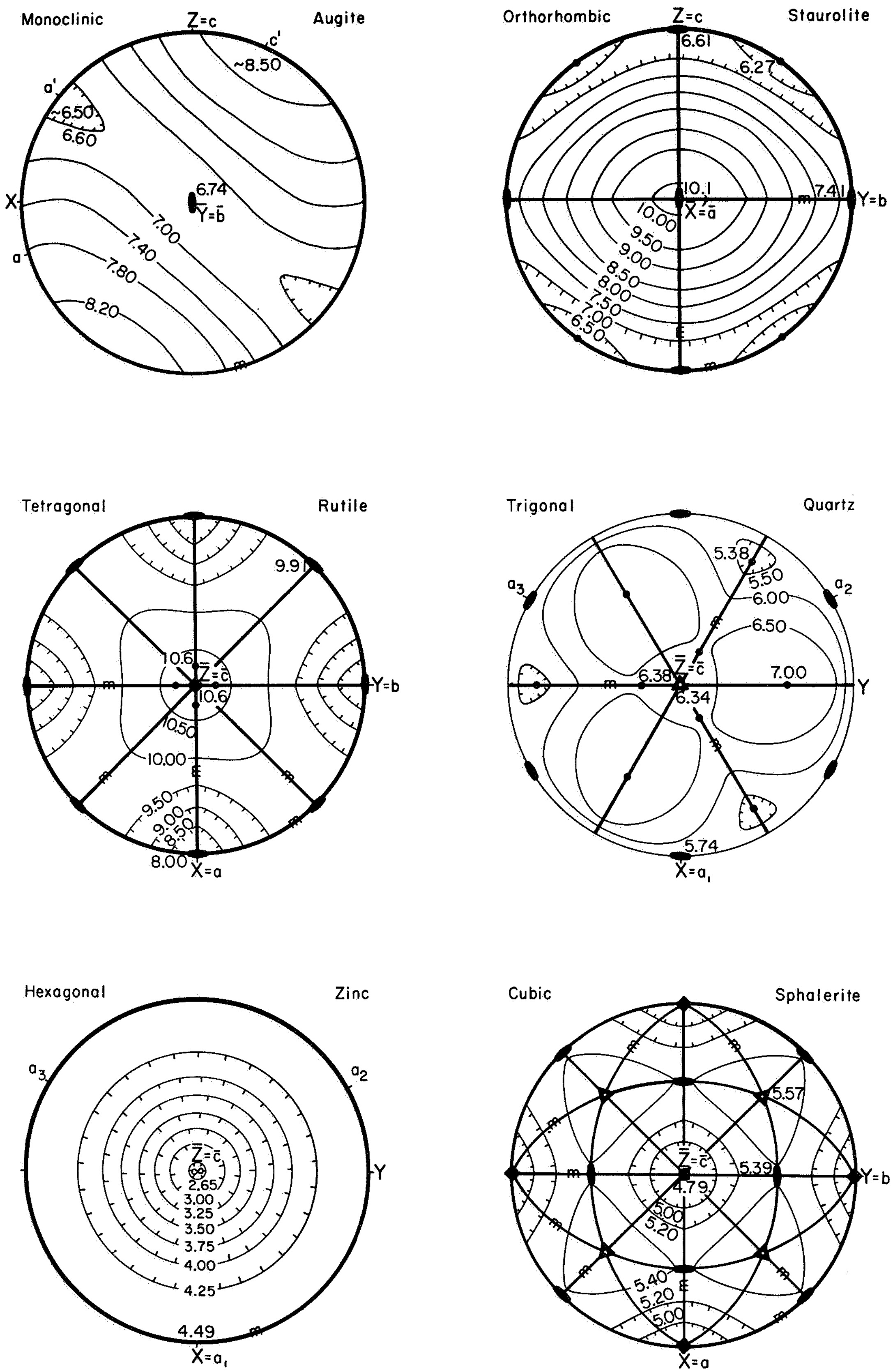

FIGURE 2. - Equal Area Polar Projections of the Velocity Surface for Single Crystals.

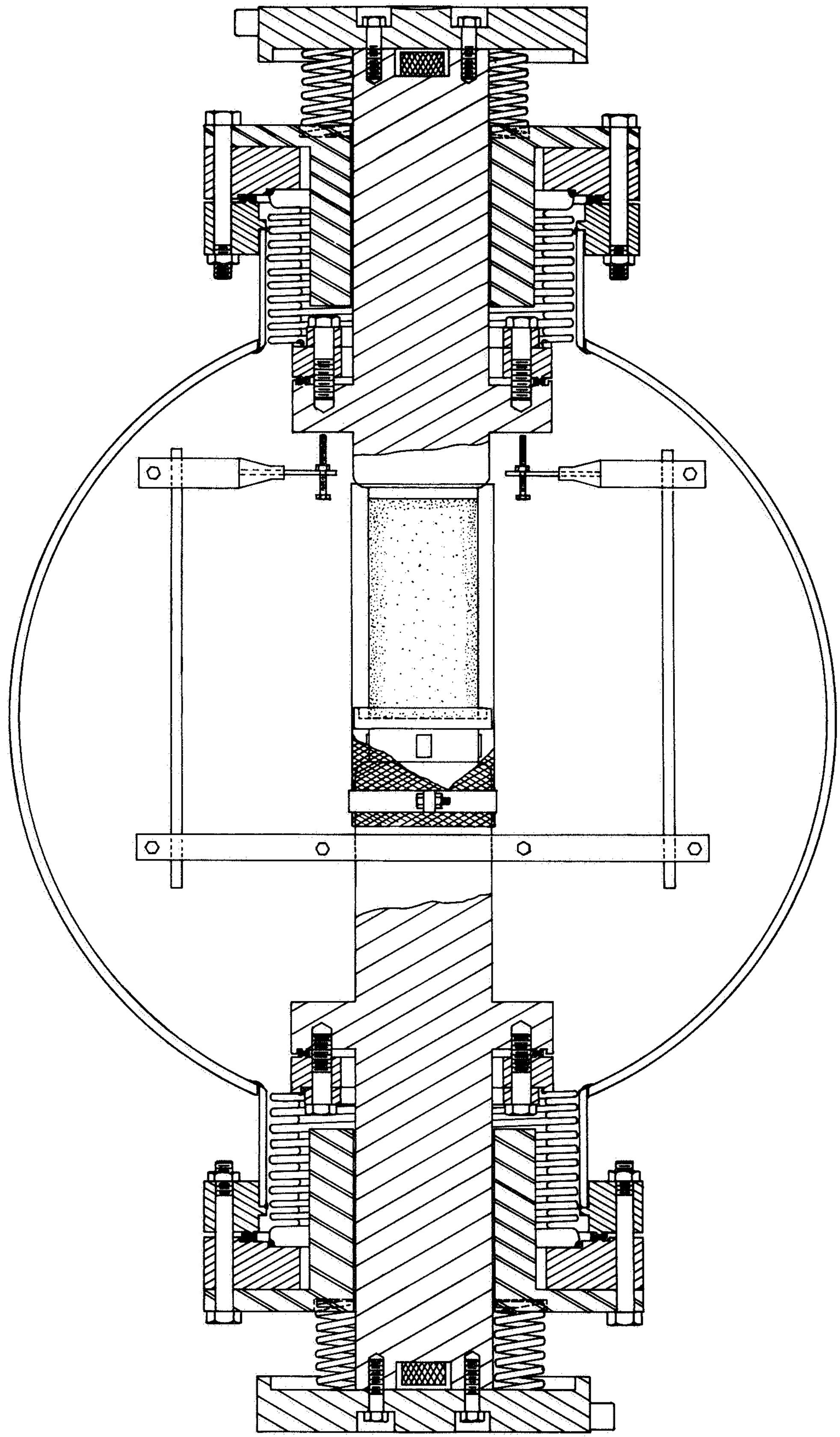

FIGURE 3. - Compression Test Fixture for Use in the Vacuum Chamber.

Following baseline pumpdown to determine degassing characteristics of each of the three rock types selected for initial testing, several preliminary compression tests were performed on semiwelded tuff specimens. The tests were performed in the ultrahigh vacuum chamber at atmospheric pressure, roughed out vacuum (10^{-3} torr), and ultrahigh vacuum (10^{-11} torr). Degassing of the specimen was detected by a mass spectrometer during loading of the rocks in the ultrahigh vacuum. Degassing occurred throughout the test, and increased rapidly as the rock was stressed beyond the linear elastic limit. Sporadic bursts of different gases were detected during loading along with the expected overall uniform increase in the amount of gas.

We had planned to conduct acoustic tests simultaneously with the compression tests. However, we postponed the acoustic tests after we found that the long column length and numerous interfaces traversed by the acoustic waves adversely affected the validity of measurements.

Fabric Analysis

A scanning electron microscope (SEM) has been purchased for studies of the relation between the macrostructural and microstructural behavior of rock under various environmental and loading regimes. The SEM permits examination of natural microcracks and pores and induced fracture surfaces on a scale unavailable with a standard light microscope. Detailed study of these features is expected to provide information on the factors governing the gross behavior of rock on the Moon and the relationship between these factors and factors governing rock behavior in earth environment.

The SEM, purchased and installed during the fourth quarter, has been successfully checked out while observing surfaces of several rock types used extensively in Bureau research (see figure 4). Techniques for applying the SEM to rock mechanics research were developed during demonstrations provided by various SEM manufacturers before our unit was purchased. Gold coatings for the specimens were applied in the vacuum facilities of the Chemically Assisted Fragmentation Laboratory.

Fabric analysis of point-loaded dacite disks reported last year was carried over into this year. The additional studies showed that the volume of rock between pores is filled with microcracks, presumably providing paths allowing moisture to corrode and weaken structural bonds when water is present within the specimen. Since vacuum effects on compressive properties of rock may be due to increased moisture removal, the results of these studies and the environmental studies are integrally related to the problem of predicting properties of rock as they occur on the Moon. Results of the microstructural study are scheduled for publication in FY 1970.

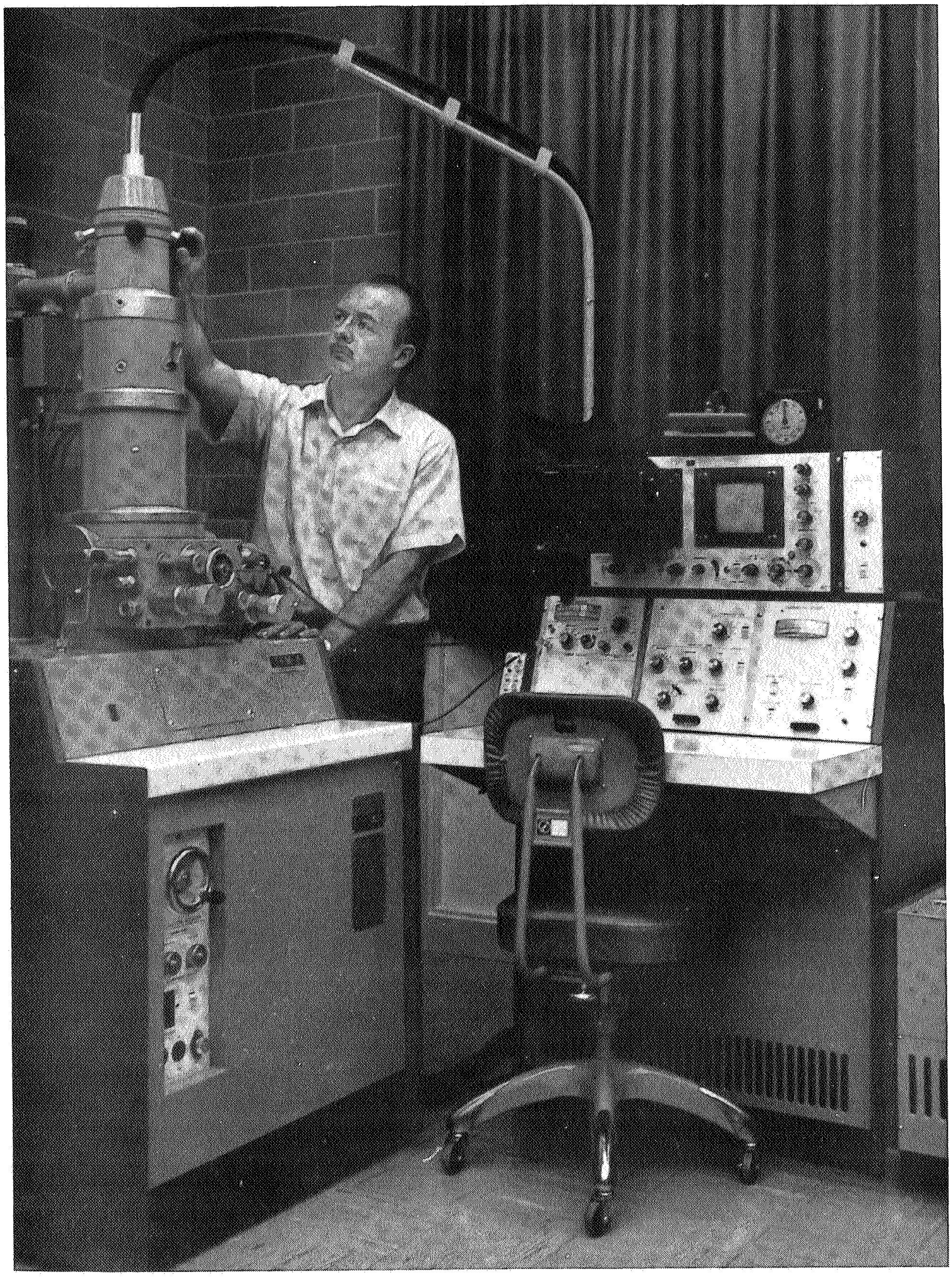

FIGURE 4. - Twin Cities Mining Research Center Scanning Electron Microscope Installation.

Status of Manuscripts

Environmental Effects on Rock Properties, by E. R. Podnieks, P. G. Chamberlain, and R. E. Thill, has been submitted for publication in the Proceedings of the Tenth Symposium on Rock Mechanics held at the University of Texas in May 1968.

Elastic Symmetry and Attenuation Variations for Fourteen Simulated Lunar Rocks, by T. R. Bur and K. E. Hjelmstad, is being prepared as a journal article.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Feasibility of thermal fragmentation studies in vacuum
Investigator:	Kuppusamy Thirumalai, Project Leader
Location:	Twin Cities Mining Research Center Minneapolis, Minnesota
Date begun:	October 1966 To be completed: June 1969
Personnel:	Joseph M. Pugliese, Supervisory Geophysicist Kuppusamy Thirumalai, Mining Engineer Russell E. Griffin, Electronic Research Engineer Sam G. Demou, Physicist

PROGRESS REPORT

Objective

The objective of this task is to investigate the feasibility of extending thermal fragmentation studies to lunar vacuum environment.

Summary

Investigations during this fiscal year evinced the feasibility of studying thermal fragmentation in vacuum environment. The experimental studies of thermal fragmentation in vacuum were carried out with the help of incident heat energy from the CO_2 laser source. Additional theoretical and experimental investigations to evaluate the susceptibility of simulated lunar rocks to the process of thermal fragmentation in vacuum were carried out.

Failure of rocks by thermal energy was broadly grouped into two main classes: (1) fragmentation by thermal stresses and (2) disintegration by melting. The main parameters governing the failure by thermal stresses and thermal melting were evaluated. Experimental determinations of the effect of vacuum on thermal softening and thermal expansion characteristics of simulated lunar rocks were carried out. New experimental techniques to measure the effect of vacuum on thermal expansion of rocks with strain gages were formulated.

The results of the study indicate that the vacuum environment does not have adverse effects on fragmentation of rocks by induced thermal stresses, and rock disintegration by melting appears particularly favorable in vacuum environment. Investigation of thermal fragmentation techniques in ultrahigh vacuum will be carried out under a new task beginning next fiscal year.

Progress During the Year

Effect of Vacuum on Fragmentation of Rocks by Thermal Stresses

Basic studies pertaining to the fragmentation of rocks by thermal stresses indicate the dependence of such failure on thermal softening and thermal expansion properties of rocks. Failure induced by thermal stresses for increments of surface temperature is limited by the temperature at which the rocks soften and relieve thermal stresses. For surface temperatures above this limit, the rock behaves as a fully inelastic material and is incapable of thermal stress formation. Experimental determinations of the effect of vacuum up to 10^{-7} torr on the thermal softening behavior in rocks were carried out on granodiorite, Dresser basalt, and obsidian in the vacuum shock furnace. The experimental details and the results have been reported in previous quarterly reports. The study showed that thermal softening limits in rocks are not significantly affected by vacuum environment.

Experimental measurements of the effect of vacuum on the thermal expansion behavior of rocks were necessary. A new technique of thermal expansion measurement with high temperature strain gages was developed. The tests were conducted on prismatic rock specimens 1/2- by 1/2- by 1-inch long. The compensating gages were bonded to an identical specimen of fused quartz. The active and compensating elements were connected in a half bridge circuit and placed in a vacuum furnace. The ceramic insulated leads were passed through holes drilled in the quartz window and sealed with vacuum proof epoxy. A comparative measurement of the linear expansion of the test rock as a function of temperature was achieved. The temperature was measured at the surface of the rock specimen and was increased at a programmed rate of 5° C/min. The strain versus temperature readout was continuously plotted on an X-Y recorder. Figure 1 shows an example of placement of test specimens in the vacuum furnace. Figure 2 shows an example of results obtained using a sample of obsidian in N_2 atmosphere and vacuum conditions up to 10^{-6} torr. The results show in general that the thermal expansion of rocks is not adversely affected by vacuum environment.

Thermal fragmentation effects in prismatic specimens 1- by 1- by 2-inch long were tested in a vacuum chamber for a continuous incident energy at 150×10^4 w/m^2. The unfocused laser beam was passed through a germanium window into the vacuum chamber and focused by concave mirrors placed within the chamber. Failure of the specimen by thermal stresses was observed both in atmosphere and in vacuum conditions up to 10^{-6} torr. A detailed report on the experiments and results is being prepared.

Effect of Vacuum in Rock Disintegration by Thermal Melting

Increasing surface temperature above the limit of thermal softening, i.e., the absence of rock failure by thermal stresses, results in melting. The melting of rock surface by incident heat flux prevents continuous exposure of free face and forms an insulating layer. Removal of melt soon after its formation poses technical problems.

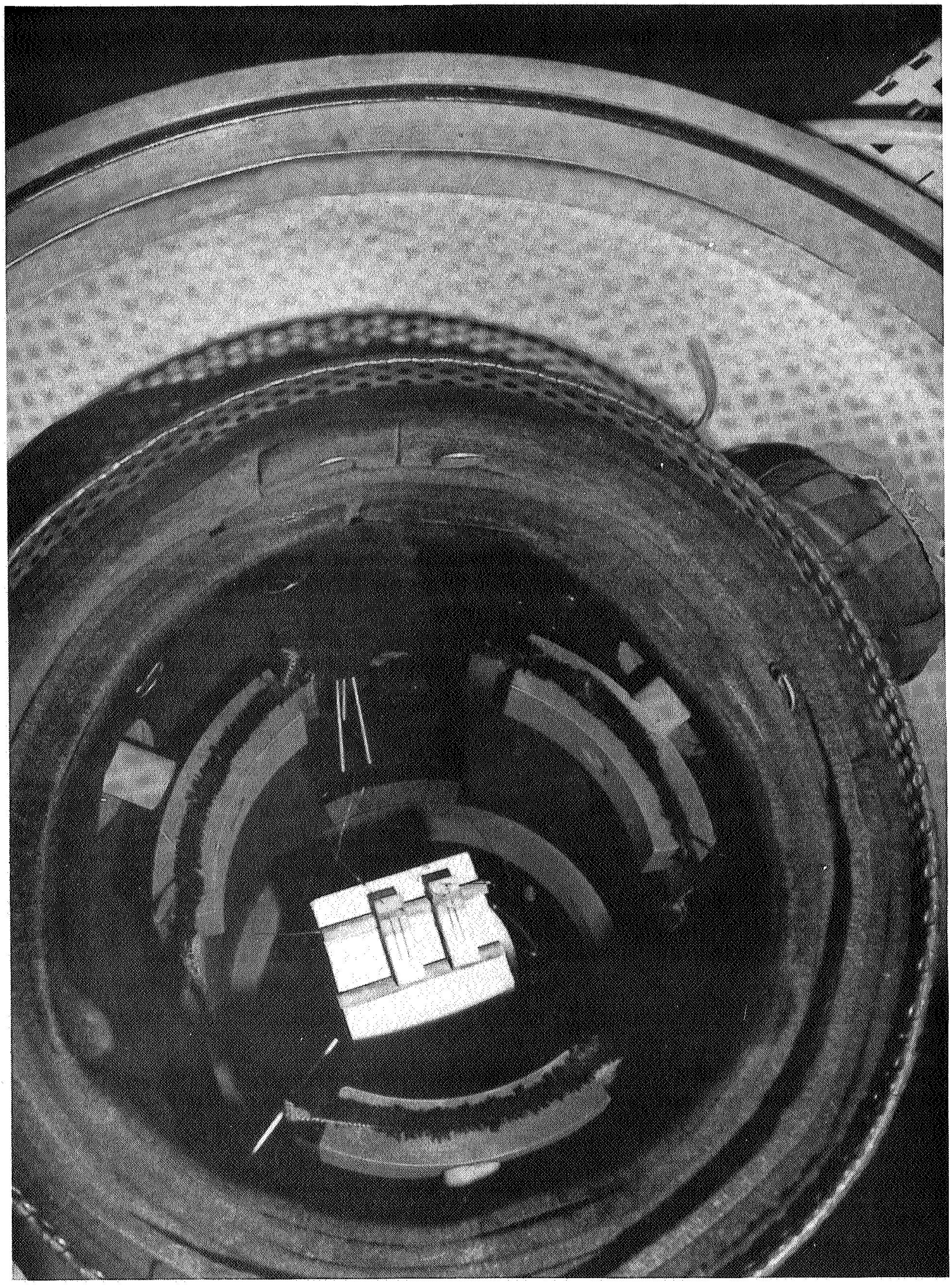

FIGURE 1. - Test Setup for Linear Expansion Measurements in Vacuum Shock Furnace.

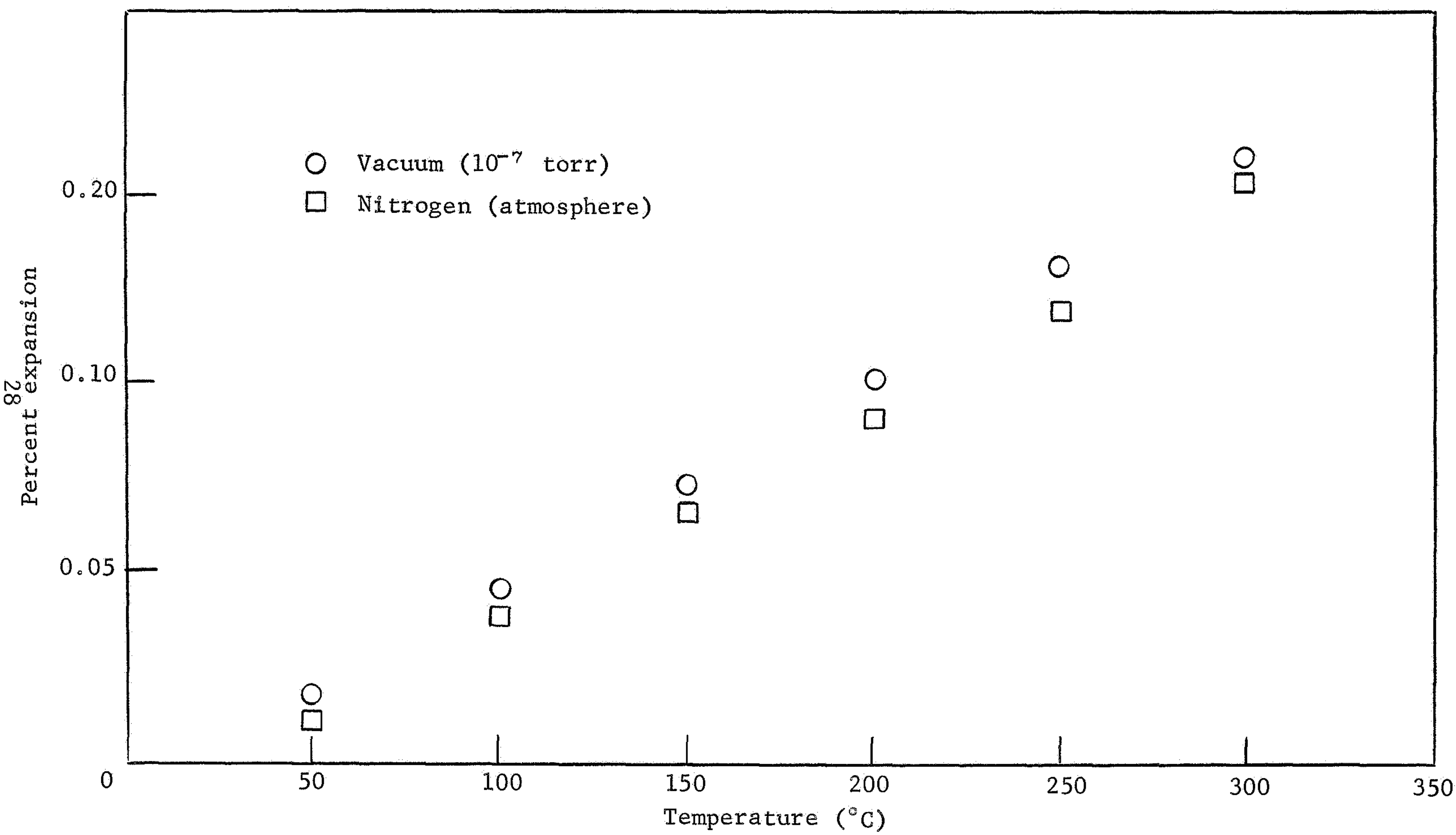

FIGURE 2. - Effect of Vacuum on Thermal Expansion of Obsidian.

In vacuum conditions up to 10^{-6} torr, a continuous self-ejection of the melt and exposure of free rock face to incident heat flux was noticed in basaltic type of rocks (tholeiitic basalt and Dresser basalt). Figure 3 shows an example of comparative results of rock disintegration by melting in Dresser basalt under atmospheric and vacuum conditions. The power density of the incident focused laser beam was 250 x 10^4 w/m^2. The specimen width shown in the figure is 1 inch. The ejection of the melt in vacuum as observed in figure 3 may be due to evaporation of contained gases or moisture or due to the vigorous agitation produced in the melt cavern by the vaporizing material ejecting the melted rock off the walls in the cavern. This expulsion of the melt and progression of crater continued as long as sufficient energy was available.

These results show that the study of thermal fragmentation in vacuum environment is feasible. Vacuum environment does not have adverse effects on fragmentation of lunar rocks by induced thermal stresses. Rock disintegration by melting appears particularly favorable in vacuum environment.

Status of Manuscripts

Effect of Vacuum on Thermal Fragmentation of Rocks, by K. Thirumalai and S. G. Demou, is under preparation as a journal article.

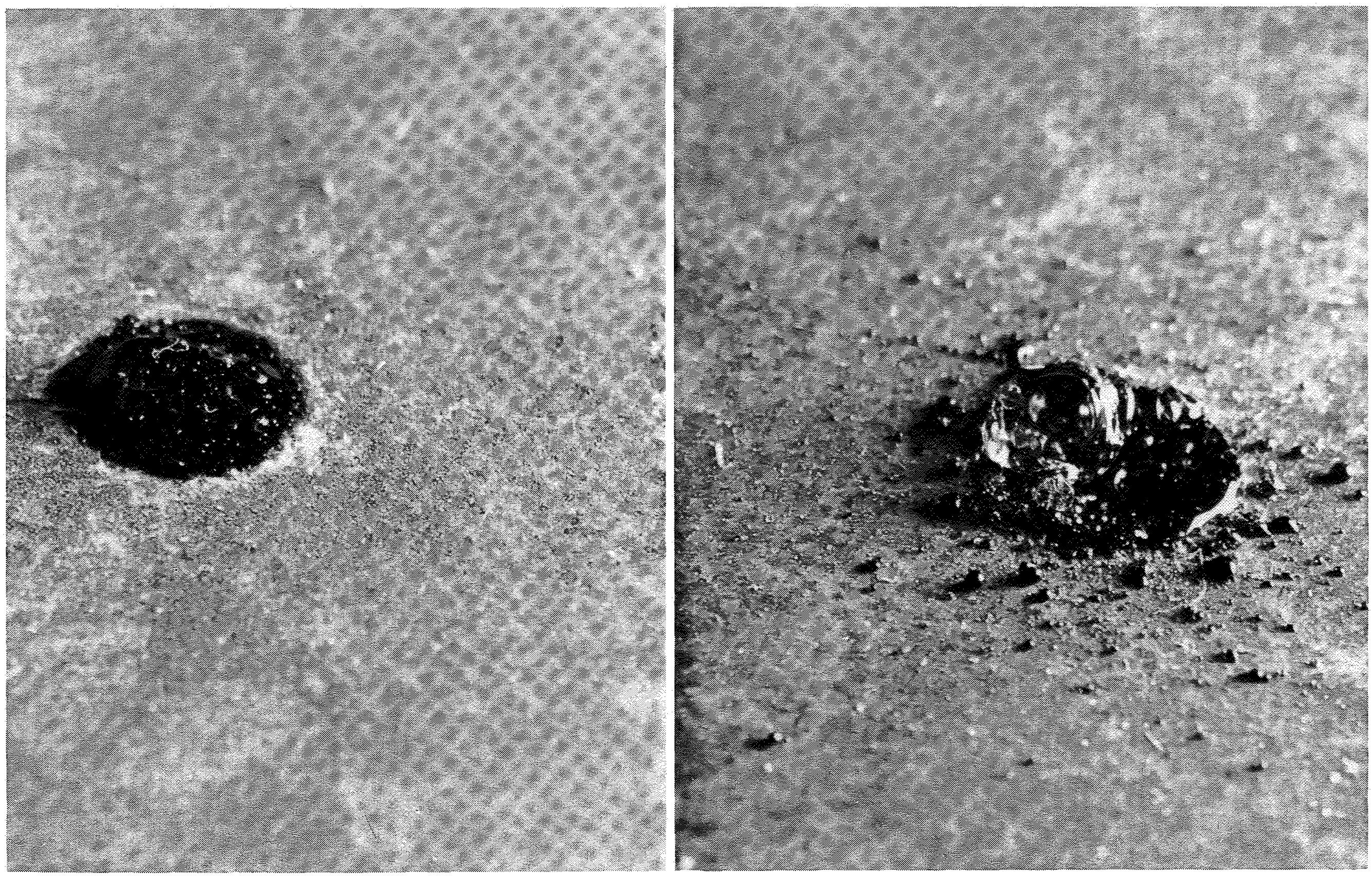

FIGURE 3. - A Comparison of Rock Disintegration by Melting in Atmosphere and Vacuum (10^{-6} Torr).

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Thermophysical properties of rock over lunar temperature range
Investigator:	David P. Lindroth, Project Leader
Location:	Twin Cities Mining Research Center Minneapolis, Minnesota
Date begun:	October 1966 To be completed: June 1969
Personnel:	Joseph M. Pugliese, Supervisory Geophysicist Russell E. Griffin, Electronic Research Engineer David P. Lindroth, Physicist Carl F. Wingquist, Physicist Walter G. Krawza, Engineering Technician

PROGRESS REPORT

Objective

The objective of this work is to extend current studies of the effect of temperature on thermophysical properties of rocks at atmospheric pressure to cover the lunar temperature range.

Summary

Work during the year dealt with the completion of the thermal expansion measurements and the adoption and development of a new method for measuring the thermal properties, conductivity, diffusivity, and heat capacity. The investigation of thermophysical properties will be extended to ultrahigh vacuum as a part of a new task beginning next fiscal year.

Progress During the Year

Early in the year the flash method was adopted for measuring thermal diffusivity. Measurements were performed on Sioux Quartzite using a 100-watt CO_2 laser as the heat source and microminiature grid thermocouples as the detectors. Similar measurements were made later on Al_2O_3 disks. When compared with literature values the two sets of measurements showed significant scattering and were therefore unacceptable. We found the source of scatter to be mainly poor thermal contact between the thermocouples and the specimens. We then made a decision to abandon the use of thermocouples and introduce remote sensing techniques to obtain the temperature history at the rear face of the specimen.

Arrangements were made to obtain a radiometer which will be used to remotely measure the rear surface temperature history. The radiometer will cover a temperature range from -20° to +3,200° C and will be used for the determination of thermal diffusivity at elevated temperatures. The instrument is expected to arrive in the first quarter of FY 1970, and diffusivity work will continue at that time.

The first phase of the study of thermophysical properties of simulated lunar rocks has ended and is summarized in this and succeeding paragraphs. Figure 1 shows the properties of coefficient of expansion, conductivity, specific heat, and diffusivity for the different rock types at atmospheric pressure and room temperature. The rocks are listed in order of decreasing density. A large portion of the conductivity and specific heat data was obtained from the literature and thus represents a range of rocks categorized under the type names rather than rock from the specific sites selected for the Bureau's simulated lunar rocks. The thermal diffusivity was computed from values of conductivity, specific heat, and density. The coefficient of expansion data represent values measured on our own specific rocks, averaged over the range from 37° to 69° C.

Because diffusivity is proportional to thermal conductivity, thermal diffusivity will be smaller at lower pressures. At the same time conductivity is dependent upon the mineral composition, crystal orientation, the degree and size of microcracks in the material, temperature, and in the more porous rocks, the fluid filling the pores. Thus, because of dependence on these wide ranging variables, both conductivity and diffusivity may vary considerably for the same general rock type. In the denser rock types, for example. conductivity tends to decrease with increasing temperature. Also in the porous rocks conductivity is lower at lower pressure.

Specific heat is dependent on the chemical or mineralogical composition of the specimen and its temperature. Since most minerals have a value for specific heat between 0.18 and 0.20 cal/g °C, and since rock is an aggregate of minerals, the range of specific heat for a particular rock type will be small as seen in figure 1. The total range of specific heat for the different rock types (excluding serpentinite) is also fairly small. Serpentinite has a higher range of values for specific heat than the other rock types mainly because of its higher moisture content. The average water content for serpentinite is 12 percent as compared to the other rock types which range up to only 3 percent in water content.

Figure 2 shows the percent expansion range for the 14 simulated lunar rocks as a function of temperature from 136° K to 420° K. Table 1 shows the percent expansion measurements on which figure 2 is based. These are preliminary data covering a short temperature range and a more complete set will be presented in a forthcoming journal article. The thermal expansion of the simulated lunar rock types ranges from -0.080 to +0.120 percent over the temperature span indicated with the reference point at room temperature. In the final report the temperature range will extend to 1,200° K and curves showing the dynamic coefficient of thermal expansion will be presented.

Processing of the remeasured dissipation factor data for the 14 simulated lunar rock types has started. Here, again, other priority needs have prevented its completion. However, at the request of Jane de Wys, formerly

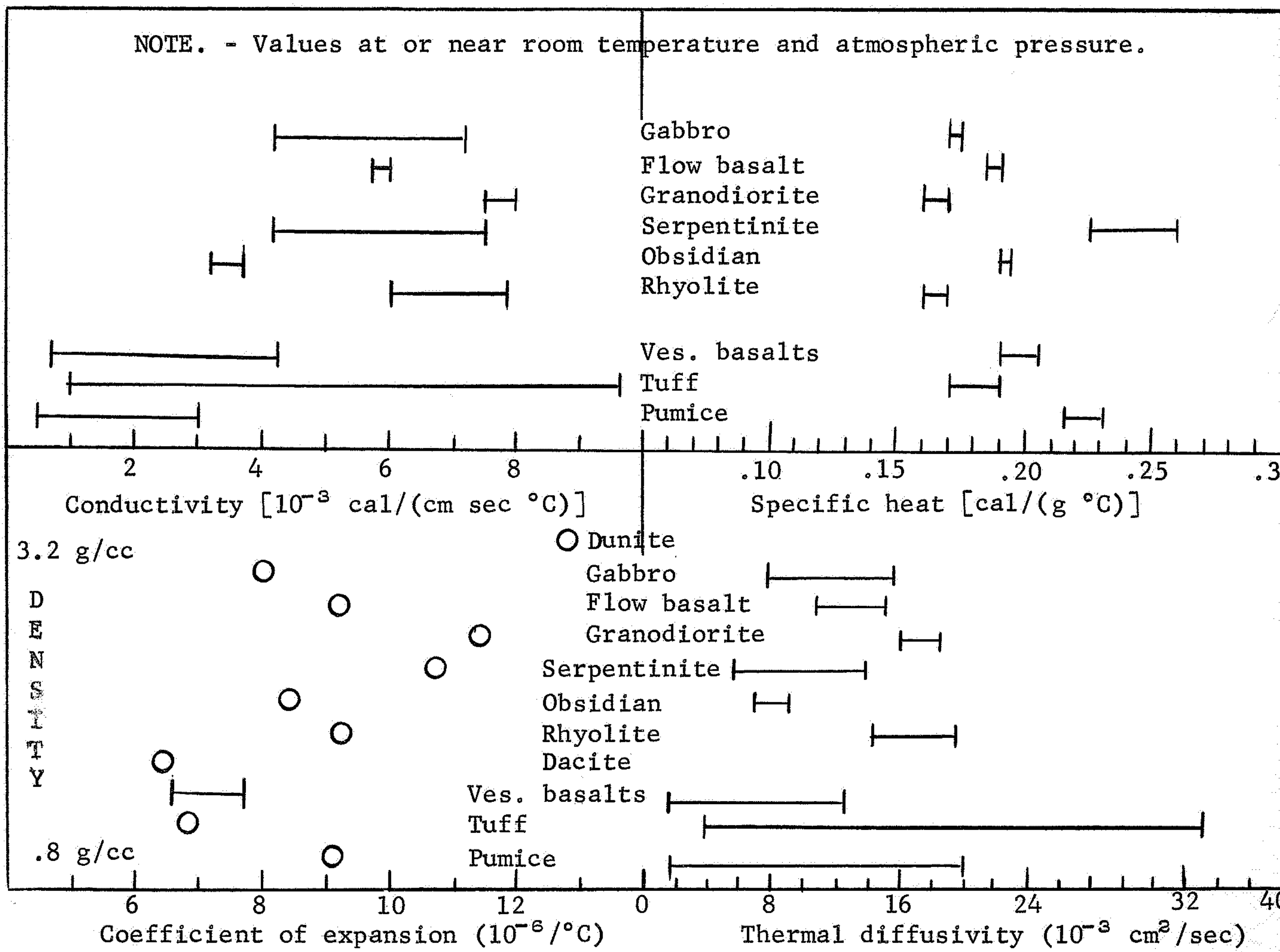

FIGURE 1. - Summary of Rock Thermophysical Properties in Earth Environment.

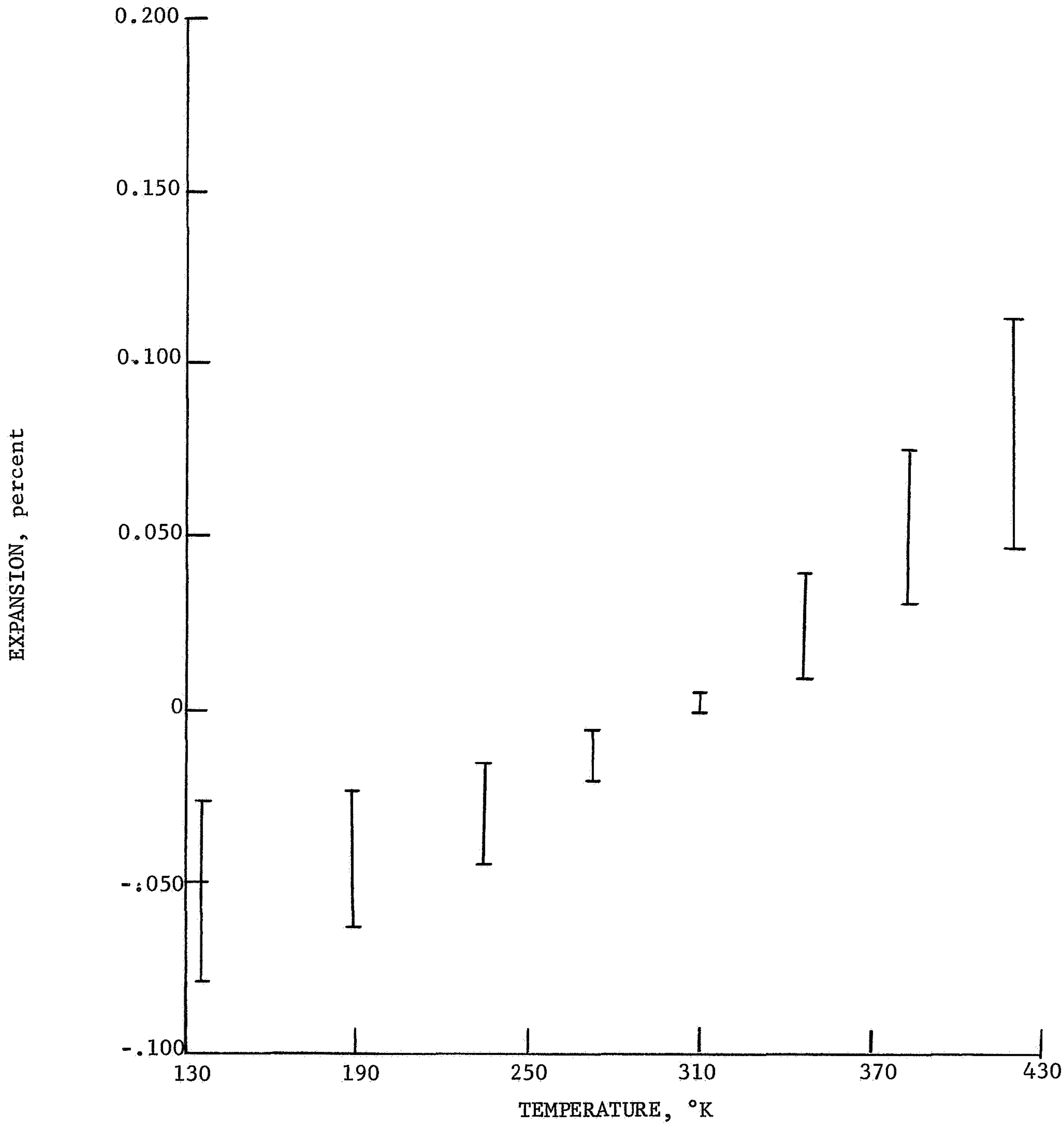

FIGURE 2. - Thermal Expansion Range of 14 Simulated Lunar Rocks in Earth Environment.

TABLE 1. - Thermal expansion measurements

Rock	Thermal expansion (percent)							
	136° K	189° K	233° K	273° K	310° K	347° K	383° K	420° K
Dunite	-0.064	-0.062	-0.046	-0.021	0.004	0.039	0.074	0.113
Gabbro	-.037	-.034	-.022	-.009	.001	.018	.048	.083
Tholeiitic basalt	-.080	-.062	-.044	-.020	.002	.023	.050	.079
Granodiorite	-.036	-.040	-.034	-.020	0	.018	.056	.100
Serpentinite	-.065	-.059	-.039	-.020	.004	.027	.056	.092
Obsidian	-.062	-.056	-.039	-.018	.0005	.016	.037	.059
Altered rhyolite	-.078	-.059	-.039	-.012	.005	.030	.067	.104
Rhyolite	-.062	-.049	-.031	-.016	0	.021	.053	.096
Vesicular basalt #1	-.028	-.024	-.017	-.007	.001	.014	.031	.046
Vesicular basalt #2	-.031	-.029	-.024	-.013	.001	.019	.040	.067
Dacite	-.055	-.042	-.030	-.013	.002	.014	.034	.053
Vesicular basalt #3	-.037	-.034	-.030	-.016	.002	.021	.042	.067
Tuff	-.044	-.045	-.035	-.016	-.0005	.009	.032	.056
Pumice	-.048	-.042	-.024	-.020	.0007	.016	.041	.065

of the Jet Propulsion Laboratory, Pasadena, Calif., dielectric constant and apparent density measurements were made on fine particle samples of gabbro, flow basalt, and vesicular basalt #1. These measurements are of interest in connection with simulated footpad magnet experiments. The experimental results are being compared with Surveyor V, VI, and VII lunar landing results. These dielectric constant and apparent density measurements were then expanded to include fine particle samples of the rest of the 14 simulated lunar rocks. The measurements were made at a frequency of 30 MHz at room temperature and a relative humidity range of 25 to 33 percent. Details of the dielectric constant and dissipation factor studies will be summarized in a manuscript.

Status of Manuscripts

Dielectric Constants and Dissipation Factors for Fourteen Rock Types Between 20 and 100 Megahertz, by R. E. Griffin, is under preparation as a journal article.

Thermal Expansion Measurements of Simulated Lunar Rocks, by R. E. Griffin and S. G. Demou, is under preparation as a journal article.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Basic problems of drilling in lunar environment
Investigator:	Robert L. Schmidt, Project Leader
Location:	Twin Cities Mining Research Center Minneapolis, Minnesota
Date begun:	January 1967 To be completed: December 1969
Personnel:	William E. Bruce, Supervisory Mining Engineer Robert L. Schmidt, Mining Engineer Carl F. Anderson, Electronic Engineer Robert R. Fumanti, Engineering Technician

PROGRESS REPORT

Objective

The objective is to study the basic problems of particle adhesion, heat removal, and bit lubrication associated with drilling in a lunar environment.

Summary

During fiscal year 1969, the work associated with heat removal and bit lubrication has been held in abeyance so maximum funding and personnel effort could be directed toward the study of the effect of vacuum particle adhesion on a mechanical cuttings-removal system. Completion of the ultrahigh vacuum tests and any further work on basic drilling problems will be carried out as part of a new consolidated surface properties task beginning next fiscal year.

Progress During the Year

The first two quarters of fiscal year 1969 were devoted to feasibility study and engineering design of the vacuum drilling apparatus. Construction began during the third quarter, and at the time of this writing the apparatus is about 90 percent complete (figure 1).

Previous experiments in vacuum chambers have demonstrated the tendency of rock particles to adhere to metal surfaces in ultrahigh vacuum. The technical report, "Ultrahigh Vacuum Adhesion of Comminuted Basalt Rock Metals," by Selheimer and Johnson, reports an adhesive force between basalt particles and stainless steel on the order of 100 to 150 dynes per square centimeter. The report attributes this cohesive force to static attraction and Van der Walls' forces, the latter having the predominant effect. The report also infers that ". . . soil to soil cohesive forces are greater than adhesive forces between metals and soils . . . ." This suggests that the primary obstacle to mechanical cuttings removal in vacuum will be the agglomeration of the cuttings, rather than adhesion between cuttings and drill rod.

FIGURE 1. - Ultrahigh Vacuum Drill Apparatus Mounted on Test Bench.

Although vacuum drilling tests have been conducted by others in the past, these experiments were in a pressure range of 1 x 10^{-7} torr or higher. The experiment designed during the year is intended to accomplish for the first time drilling in ultrahigh vacuum. A comparison of drilling torque between drilling in atmosphere and in ultrahigh vacuum will determine the extent of vacuum adhesion. This will be accomplished by means of an externally mounted torque sensor. A supplementary comparison will be made by high-speed movies taken while drilling both in atmosphere and ultrahigh vacuum. A mass spectrometer will be used to record partial pressures of gases emitted during drilling.

Status of Manuscripts

Developing a Lunar Drill: A 1969 Status Report, by R. L. Schmidt, was presented as a part of a panel discussion at the Seventh Annual Meeting of the Working Group on Extraterrestrial Resources in Denver in June.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Use of explosives on the Moon
Investigator:	Frank C. Gibson, Project Coordinator, Explosives Physics
Location:	Explosives Research Center Pittsburgh, Pennsylvania
Date begun:	July 1966 To be completed: June 1971
Personnel:	Frank C. Gibson, Supervisory Research Physicist Richard W. Watson, Research Physicist J. Edmund Hay, Research Physicist Charles R. Summers, Research Physicist John J. Mahoney, Laboratory Electrician Elva M. Guastini, Explosives Equipment Operator

PROGRESS REPORT

Objective

The task objective is the acquisition of basic knowledge leading to the solution of potential problems involved in the use of chemical high explosives in the lunar environment, specifically: (1) the stability of explosives and explosive devices in the lunar environment; (2) the problem of exposure of explosives and explosive devices to (micro)meteoroid impact; and (3) the propagation characteristics of the blast wave (products cloud) in the lunar atmosphere.

Summary

During fiscal year 1969 preliminary studies of explosive initiation by small, high velocity particles were completed, but extension of the experiments to higher velocities was deferred to enable concentration on blast wave studies. Techniques were developed and experiments carried out with small charges in expendable glass chambers at pressures as low as 10^{-7} torr. Progress was made in developing a facility for large-scale studies. Work on this task will continue next fiscal year with Richard W. Watson assuming the role of principal investigator.

Progress During the Fourth Quarter

Emphasis was placed on obtaining measurements of the pressures developed by the expanding products cloud from solid explosives detonated in vacuum. The initial work in this area was conducted with 1.0-inch diameter spheres of RDX detonated by an exploding bridge wire. However, electrical noise from the initiation system led to ambiguities in the interpretation of the pressure gage records. The use of lower voltage in the bridge-wire circuit resulted in erratic initiation. For these reasons a new charge design was selected for further experimentation. The current charge consists of a 2.0-inch diameter sphere of Composition B initiated by a 1/2-inch diameter by 1/2-inch long tetryl pellet placed near the center of the sphere. The tetryl is detonated with either a military type, M-36, or a conventional No. 6 electric detonator. Framing camera photographs of this type of charge detonated in air showed that the products expansion envelope was reasonably spherical.

In order to gain confidence in the reliability of the pressure measurements, a number of firings were conducted in air for the purpose of measuring air shock pressures at various distances from the Composition B sphere. The resistance gage, utilizing the normal gage circuit,[1] proved unsatisfactory at distances greater than about 4.0 cm from the periphery of the charge; this was due to the fact that the signal-to-noise ratio approached unity at greater distances. In view of this an attempt was made to use a commercial piezoelectric gage which has a considerably greater output than the resistance gage for a given pressure level. Although widely varying results were obtained with the new gage, due to signal overshoot and gage ringing, the gage signal did have a very short rise time, making it useful for time-of-arrival measurements at relatively large distances from the charge. Since accurate shock velocity measurements can be used to compute the shock pressure in air, a calibration for the 2.0-inch diameter Composition B sphere was established using two gages with a fixed spacing of 10 cm placed at distances from 10 to 100 cm from the charge. Resistance gages were employed in the same fashion at shorter distances; the resistance gages had a fixed spacing of 5.0 cm. The data from this series of trials are presented in table 1 in terms of the measured shock velocity (averaged over the gage-spacing interval), the Mach number and the calculated values of shock overpressure and reflected shock overpressure. Having obtained these data the resistance gage was recalibrated using a modified gage circuit employing a higher operating voltage (20.0 volts) and a larger current viewing resistor ($\approx 470\ \Omega$) than are normally used. This results in a substantial increase in the signal output and permits the gage to be used at distances greater than 30 cm from the charge which is more than the maximum distance available in our present high vacuum test chamber. The data from the resistive gage calibration are also presented in table 1 in terms of the ratio of the gage resistance under dynamic load to the static gage resistance.

A few preliminary firings have been conducted at 2.0×10^{-6} torr with resistance gages spaced at 2.5, 5.0, 7.5, and 10.0 cm, measured from the periphery of the charge. The initial results lead to the tentative conclusions that the peak stagnation pressure in vacuum is roughly one-half that of the reflected shock pressure in air at the same distance from the charge. In addition, the pressure rise is gradual, taking about 5.0 μsec to reach peak, at the distance employed. The rise time appears to increase with increasing distances from the charge according to expectations. Work in this area is being continued.

[1]Watson, Richard W. Gauge for Determining Shock Pressures. Review of Scientific Instruments, v. 38, No. 7, July 1967, pp. 978-980.

Status of Manuscripts

None in progress.

TABLE 1. - Summary of air shock pressure measurements using 2.0-inch diameter Composition B sphere

Distance (cm)	U_s (m/sec)	M	P_s (psi)	P_r (psi)	R_p/R_o
5.0	5,280	15.35	4,023	31,619	0.587
7.5	4,770	13.87	3,282	25,518	.784
10.0	4,190	12.18	2,527	19,521	.877
15.0	3,290	9.56	1,550	11,671	.921
20.0	2,580	7.50	947	6,805	.954
25.0	2,123	6.17	636	4,468	.967
30.0	1,810	5.26	457	3,263	.976
35.0	1,480	4.30	300	1,852	-
45.0	1,201	3.49	191	1,055	-
55.0	935	2.71	109	492	-
65.0	808	2.35	77	300	-
75.0	693	2.01	52	163	-
85.0	665	1.93	47	139	-
95.0	615	1.79	38	98	-

NOTES. - Distance measured from periphery of charge.
U_s = shock velocity.
M = shock Mach number.
P_s = shock overpressure.
P_r = reflected shock overpressure.
R_p/R_o = dynamic/static gage resistance ratio.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Effect of lunar environment on behavior of fine particles
Investigator:	David E. Nicholson, Project Leader
Location:	Spokane Mining Research Laboratory Spokane, Washington
Date begun:	April 1966 To be completed: June 1971
Personnel:	William R. Wayment, Supervisory Mining Engineer David E. Nicholson, Mining Engineer David F. Stafford, Physicist Maynard D. Serbousek, Structural Engineer Robert W. Carnes, Engineering Technician

PROGRESS REPORT

Objective

The primary objective is to determine basic physical properties which may influence the handling and transportation of fine particles in a lunar environment, as an extension of current studies of fine particle behavior in mine backfill applications. Intergranular static and dynamic coefficient of friction and energy loss will be measured. Flow rates and shear strength at various states of particle packing and at various particle sizes will be determined and correlated with friction and energy loss properties. This work will initially be performed under conditions of normal earth atmosphere, but will be extended to include selected tests in ultrahigh vacuum. The work will be correlated with the study of electrostatic properties of granular particles being conducted at College Park and the study of frictional properties of mineral surfaces being conducted at Minneapolis.

Summary

Major accomplishments during the year included completion of the crushing and sizing circuit for producing uncontaminated fine particle samples of simulated lunar materials and design of the vane shear testing device for studying fine particle behavior in ultrahigh vacuum. Moderate vacuum experiments were conducted to study gross flow characteristics of simulated lunar basalt and theoretical analysis of the frictional behavior of fine particles was continued. Work under this task will continue next year with emphasis on the ultrahigh vacuum studies of fine particle material in cooperation with the Twin Cities Mining Research Center.

Progress During the Year

Improvements in the layout of the crushing and grinding circuit were completed during the year. The Vortec air classifier has been lined with tungsten carbide to reduce contamination and a high-speed tachometer has been installed on the impact mill to control the effects of feed rate on the mill operating speed. Fine powder samples of 14 simulated lunar rocks were provided for several NASA contractors during the year, including the Jet Propulsion Laboratory, North American Rockwell, General Dynamics, and the U.S. Geological Survey.

A moderate vacuum experiment was performed at Spokane to determine the gross flow behavior of our simulated lunar basalt powder. A small glass vacuum vessel was blown for this test. A flask-shaped powder container was attached through a restricted orifice to a long tubular chamber. An evacuation port with a movable glass swivel fitting, a thermocouple vacuum gage, and a cold trap were attached to the vacuum line. Thermal tape was wrapped around the container vessel during bakeout. Our simulated lunar basalt powder usually has a no-flow characteristic through the orifice at normal atmospheric conditions. Under light evacuation to the 1 torr range, the material became free flowing. After extended bakeout at about 150° C and tumbling the powder in the tube and flask, the pressure was stabilized at about 1 micron and the material again became nonflowing.

These gross flow properties along with results from frictional tests done by other investigators indicate that studies of lunar adhesion will need to be done under realistic vacuum conditions. The data can be interpreted to indicate that under normal atmosphere absorbed water layers are increasing the friction or creating surface tension effects in the material creating a no-flow condition. During intermediate bakeout and evacuation stages sufficient water layers have been removed from the particle surfaces to reduce the surface tension effects and the material becomes free flowing. After extended bakeout and evacuation the contamination is reduced sufficiently to start increasing the friction and cohesion of the material toward what we might expect in the lunar environment. These results indicate there should be some thought given to utilization of moist powder samples to simulate lunar adhesion effects by substitution of surface tension effects of absorbed water layers.

A small torsion or vane shear test apparatus has been designed during the past year to be utilized in the Twin Cities Mining Research Center ultrahigh vacuum system by attachment to the lunar drill feedthrough mechanism. A view of the modified tester is shown in figure 1. This torsional tester, having infinite shear strain or rotation, will allow us to test repeatedly a powder sample in a vacuum under many conditions of consolidation and normal load to determine the so-called "effective angle of internal friction" and the unconfined yield strengths of the powder.

Considerable theoretical study was performed during the year on Mohr-Coulomb failure criteria and Duffy-Mindlin theory as applied to low stress conditions and cohesion of lunar powdered material. We feel that some

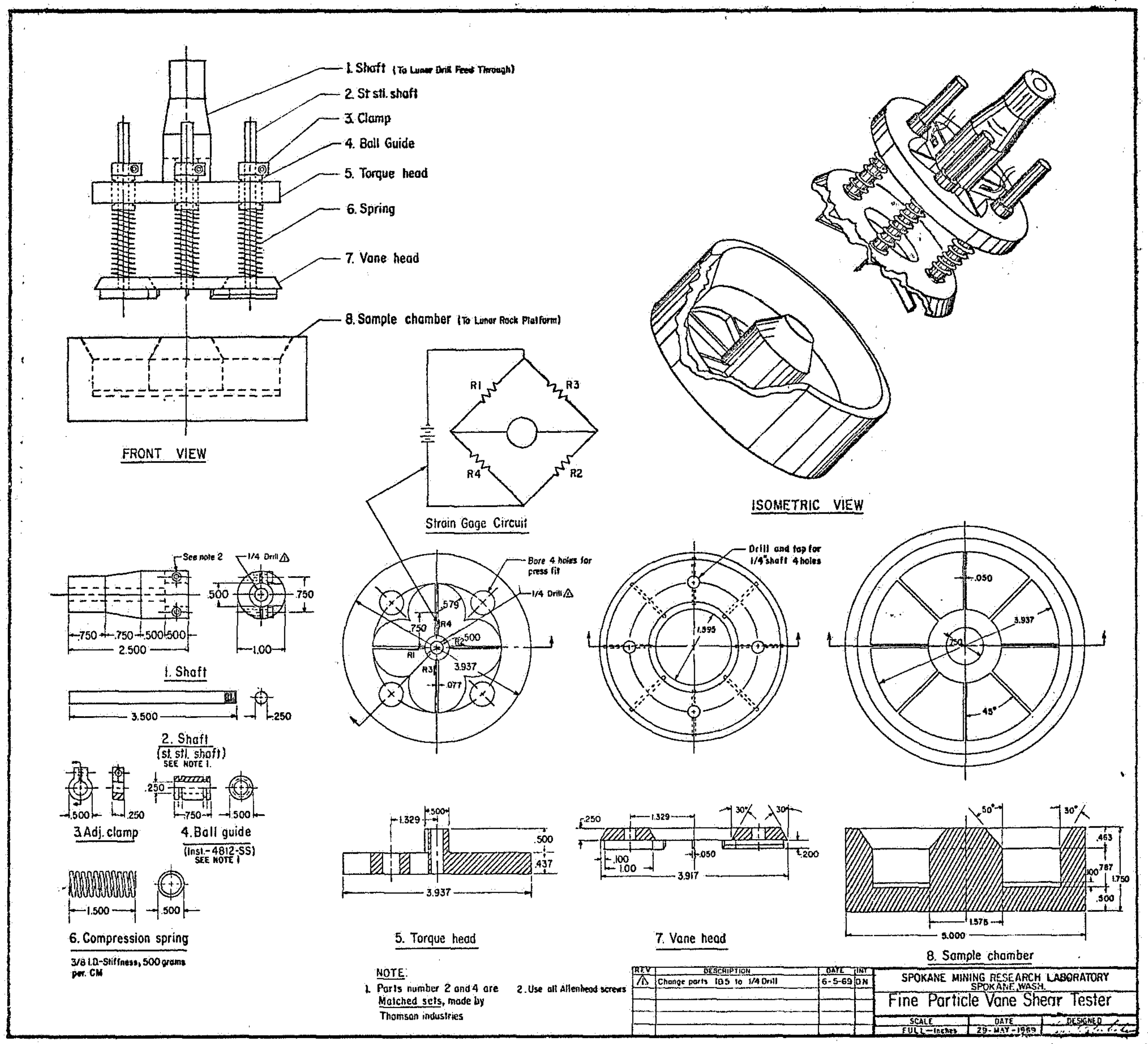

FIGURE 1. - Vane Shear Tester for Testing Simulated Lunar Rock Powders Under Ultrahigh Vacuum.

special form of the general Mohr-Coulomb failure theory will be required to correctly define the failure envelope of a granular material in the lunar environment. In standard Coulomb theory, a pure frictional material is represented by the formula:

$$\tau = \sigma \tan \Phi$$

where the shear strength, τ, is related to the applied stress, σ, through the friction angle, Φ.

Another form of the Coulomb equation treating both frictional and cohesion effects is:

$$\tau = c + f(\sigma)$$

The effect of volume change during the shear process in this equation is included in the frictional term, $f(\sigma)$. The cohesion, c, is constant for a given material. However, we feel that the cohesion developed in the vacuum conditions on the lunar surface will not be constant, but will also need to be treated as a function of applied stress. Thus, we would have a shear equation of the following form:

$$\tau = g(\sigma) + f(\sigma)$$

where g is the expression for cohesion as function of applied stress and f is the standard frictional function. In effect, we are setting a condition of work hardening in a lunar soil material when compressed under any type of load.

An example of defining a material with these failure characteristics can be shown on a standard Mohr failure plot. The lunar powder to be represented in the plot is assumed to have an angle of internal friction of 45°. Normal loads are applied in 1 psi increments to 6 psi. Both the cohesion intercept on the shear axis and the tensile strength of the powder are equal for the assumed 45° envelope shape. It is assumed that for every 1 psi increase in the normal stress, the cohesion or tensile strength will increase at a linear rate of 0.3 psi. Assuming we are performing a direct shear test on this material, we would develop a relationship from the method of Mohr which would indicate a material with zero cohesion at the origin and an "effective angle of internal friction" of 51-1/2°.

Another plotting method which we proposed in the third quarter progress report is the compound stress concept, where the tensile strength can be plotted as an additive stress to the applied normal stress. This plotting method would show the compound stress failure plot and indicate the correct angle of friction of 45° for the material.

Status of Manuscripts

Progress Report on Lunar Fine Particle Project, by David E. Nicholson, was submitted as an informal written report to the NASA Review Panel at the Twin Cities Mining Research Center in May.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Support for underground lunar shelter
Investigator:	Robert C. Bates, Project Leader
Location:	Spokane Mining Research Laboratory Spokane, Washington
Date begun:	April 1966 To be completed: June 1969
Personnel:	Robert C. Bates, Mining Engineer Lester J. Crow, Mining Engineer Edward W. Parsons, Mining Engineer Colen S. Smith, Mining Engineer

PROGRESS REPORT

Objective

The objective is to advance ground support technology in areas having both terrestrial and extraterrestrial application. Research will be conducted on ground support materials which have potential for utilization both on the Earth and the Moon.

Summary

Excellent results were obtained in the development of a sulfur-basalt aggregate grout having an average unconfined compressive strength of 8,000 psi. An additive was found that expanded the grout enough to compensate for the shrinkage of the sulfur. Unconfined compressive strengths of the expanded grouts were about 5,000 psi.

An analysis of the problem of sublimation of sulfur in a vacuum was carried out. Protective coatings would be required except at low temperatures. Some research was done on sodium silicate as a bonding agent and a nonsublimating coating. Sodium silicate did not appear to have the desired characteristics.

A laboratory model of a machine for delivering sulfur-basalt aggregate grout into void spaces was designing fabricated, and tested. Reasonable success was attained.

A report describing the sulfur-basalt concrete development work is nearly ready for publication. A summary of the past work and current ideas on underground lunar shelters resulting from this task is being assembled as a basis for possible resumption of the work at some appropriate time in the future.

Progress During the Year

Investigation of sulfur-basalt aggregates using combinations of coarse and fine grain sizes was completed. Manufactured samples of basalt aggregate gradations, with selected average grain sizes and coefficients of uniformity, did not produce compressive strengths exceeding those already obtained (10,700 psi) from natural grades of crushed basalt. Increased emphasis on smaller particles that could be used as a grout yielded excellent results. A series of experiments on combinations of fine basalt particles with sulfur were made. The unconfined compressive strengths averaged around 8,000 psi. In addition, an expansive additive was found for the grout. In experimenting with a number of hydrocarbons and oxidizing agents, it was found that some forms of hydrocarbons would react with the sulfur at elevated temperatures forming hydrogen sulfide gas which expanded the grout. The grout expanded enough to offset the shrinkage of the sulfur. The unconfined compressive strengths of the expanded grouts were about 5,000 psi.

A number of experiments were made with sodium silicate plus additives as a bonding agent and by itself as a sealant. As a bonding agent it did not cement the particles together well enough to develop any reasonable strengths. As a sealing agent it was not stable at room temperatures. Sodium silicate is deliquescent and sensitive to the changes of moisture in the air. Depending on the moisture content in the air, the silicate either absorbed moisture and turned wet on the surface or dried out and cracked.

In the study of other materials for use as supports, plastics were examined. Some plastics degrade quickly in a space environment because of radiation and evaporation effects. Others, such as phenolic laminates, epoxy laminates, polyester laminates, and polyurethane appear stable. They could possibly furnish the bonding and sealing qualities needed for an underground lunar shelter. If time had been available experimental work would have been done on these materials.

Design concepts for supports of shelters using sulfur and other materials were formulated. Coarse double graded sulfur-basalt aggregate concrete could be used to make high strength building blocks for construction of either supports or shelters. The blocks can be cemented together with a coating of sulfur. Fine-particle basalt and sulfur grouts could be extruded into a form to furnish supports or any shaped structure. The sulfur materials should be sealed inside and out with a nonsublimating material. However, if the temperature a few feet below the lunar surface is below -30° C as expected, the outside of a buried shelter would not have to be sealed as sublimation rates of sulfur are insignificantly low at this temperature.

A model mechanical device was designed and fabricated to test injection of sulfur grout into an aggregate by means of air pressure. The device was completely heated while in use to maintain the surface grout in a fluid state. The first experiments were made with sulfur alone. It is transferred easily under pressures of 2 psi or more, and readily penetrated aggregate of minus 30 to plus 50 mesh at room temperature. To penetrate aggregates less than 50 mesh it was necessary to elevate the temperature of the aggregate above room temperature; at 150° F minus 100 plus 200 mesh aggregate was penetrated. Some difficulty was experienced in transferring sulfur with aggregate particles of any size. The material tends to segregate, with the larger particles settling out.

To study the effect of particle shapes on compressive strength in sulfur-aggregate mixtures, cylinders were poured comparing round and crushed basalt aggregate particles of the same gradation. There was very little difference in the unconfined compressive strengths. Round particles of basalt are very hard to find in a natural state. The particles used came from the area of the Coulee Dam and the Grande Rounde River in Washington.

Status of Manuscripts

Strengths of Sulfur-Basalt Concrete, by Lester J. Crow and Robert C. Bates, is being prepared as a Bureau of Mines Report of Investigations.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title: Electrowinning of oxygen from silicate rocks
Investigator: Donald G. Kesterke, Project Coordinator
Location: Reno Metallurgy Research Center
Reno, Nevada
Date begun: June 1966 To be completed: May 1970

Personnel: Donald G. Kesterke, Metallurgist
Freddy B. Holloway, Physical Science Technician

PROGRESS REPORT

Objective

The objective is to determine the feasibility of electrowinning elemental oxygen from silicate rocks, as one phase of multidisciplinary efforts to develop basic knowledge for using lunar mineral resources in support of space missions.

Summary

A cell and insulation system was constructed of refractory materials which are inert to free oxygen at elevated temperatures. The design incorporated a hot-pressed boron nitride crucible, with heat furnished by silicon carbide resistors. Thermal insulation around the cell consisted of alumina, boron nitride powder, and conventional firebrick.

Evaluation of various refractory materials for use as electrodes showed that iridium exhibited the best corrosion resistance of all materials investigated for use as an anode. Silicon carbide proved to be a satisfactory cathode material.

Electrolysis conducted at 1,150° to 1,200° C in a bath composed, in weight-percent, of 69.4 BaF_2, 5.6 LiF, and 25.0 basalt-plus-sinter yielded up to 5.0 volume-percent oxygen in the cell gases. Subsequent experiments were conducted in the same temperature range, using a bath in which the silicate content was increased to 35.0 weight-percent. However, no improvement in cell performance was achieved, and fuming was excessive. Improved results and decreased fuming were attained using baths composed of 48.5 weight-percent BaF_2, 16.5 weight-percent LiF, and 35.0 weight-percent basalt-plus-sinter. The higher LiF content permitted electrolysis at lower temperatures, with no significant change in the voltage-amperage characteristics. Experiments were conducted at 1,050° to 1,100° C using anodes having an immersed surface

area of about 0.85 sq in. Electrolysis current was 40 to 50 amperes, and the voltage was 17 to 19. Oxygen contents over the cell of about 7 percent were attained. Electrolysis at the same temperature, using anodes with double the surface area, resulted in more than 10 volume-percent oxygen in the cell gases.

Progress During the Fourth Quarter

Objectives for the quarter were to continue experiments to electrowin elemental oxygen from silicate-bearing mixtures. Emphasis was directed toward eliminating the adverse effect on cell performance due to interference between the cathode deposit and anode.

Investigations were continued to electrowin oxygen from a mixture composed of 48.5 weight-percent BaF_2, 16.5 weight-percent LiF, and 35.0 weight-percent basalt-plus-sinter. Electrolysis was conducted at 1,050° to 1,150° C, using 50 to 70 amperes and 19 volts. In some experiments, 30 to 40 dc ampere-hours were applied to the cell without interruption. Oxygen contents in the cell gas as high as 12.3 volume-percent were achieved; however, the cathode deposit often grew so large that contact between it and the anode occurred. This caused embrittlement of the iridium and anode loss rates which sometimes exceeded 100 mg per ampere hour. Because of the small size of the electrolytic cell, there is no practical way of removing the deposit, other than by replacing the cathode. To ensure that short circuiting would not occur, electrolysis was limited to 18 to 20 ampere-hours per cathode. Electrolysis was then stopped, and the cathode was replaced with a new one. Using this procedure, an oxygen content of almost 14 volume-percent was achieved in two experiments, and more than 11 percent was attained in several other experiments. Typical anode loss rates during these electrolyses were 25 to 35 mg per ampere hour.

The investigations will be extended during the coming fiscal year to include design and operation of a larger cell which will permit evaluation of the problems and potential for practical application of the electrowinning technique.

Status of Manuscripts

Electrowinning of Oxygen from Silicate Rocks, by Donald G. Kesterke, was presented at the Seventh Annual Meeting of the Working Group on Extraterrestrial Resources in Denver in June.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Reduction of silicates with carbon		
Investigator:	Larry A. Haas, Project Leader		
Location:	Twin Cities Metallurgy Research Center Minneapolis, Minnesota		
Date begun:	June 1966	To be completed:	May 1969
Personnel:	Sanaa E. Khalafalla, Supervisory Research Chemist Larry A. Haas, Research Chemist Howard W. Kilau, Chemist Thomas H. McCormick, Physical Science Aid		

PROGRESS REPORT

Objective

The objective is to determine the optimum reaction rate criteria for extracting oxygen from possible lunar materials in a simulated lunar environment. The major emphasis of this research is to determine the kinetics and mechanism of the carbothermal reduction of siliceous materials in a high temperature vacuum furnace.

Summary

The extraction of oxygen from possible lunar raw materials is of prime concern to the Nation's space program for generating rocket fuel and establishing life survival stations on extraterrestrial bodies. Attention is focused here on gasifying silicate oxygen in the form of CO which can then be processed via CO_2 and photosynthesis to molecular oxygen. In metallurgical practice, silicon carbide is also made by reacting silica with carbon at a temperature above 1,500° C. The same reaction under varying conditions can be made to prepare silicon metal and ferrosilicon. The carbon-silica reaction is also important in iron and steelmaking as an optimum silicon content in pig iron promotes the removal of sulfur.

The kinetics and mechanism of oxide reduction by solid reductants have received little attention compared to gaseous reductants because of the greater difficulties encountered in solid/solid interactions. Analyses of heterogeneous solid reactions are further complicated when gaseous products are formed which could react with the reactants. In this investigation, the possibility of gaseous side reactions was reduced by studying the reaction in vacuum.

Results showed carbothermal reducibility of siliceous minerals was correlated more with the chemical constitution than with the mineral structure. The reducibility of aluminum, calcium, and magnesium silicates

increased with their silicon dioxide content, provided the minerals remain in the solid state at the reaction temperature. Aluminum silicates rich in alkali liquify at 1,400° C and hence reduced less readily. Reducibility of liquid sodium-aluminum silicates exhibited a systematic increase with sodium content. Reducibility (at 1,400° C) of solid silicates appeared to decrease inversely, not only with the melting point of the component oxides, but also with the melting point of the mineral.

Mixed siliceous minerals (igneous rocks) reduced more readily if the silicate remained in the solid state at 1,400° C. Reducibility of 10 simulated lunar rocks exhibited a systematic increase with the iron oxide content. Iron silicate was readily reduced at temperatures as low as 1,200° C. It was concluded that the reducibility of iron-containing minerals or rocks can be correlated with their iron oxide concentration and that silica content is of secondary importance. Alkali metal oxide at concentrations greater than 1 percent in minerals or rocks retard the SiO_2 reduction reaction.

The rate of carbothermal reduction of silica is very sensitive to the furnace pressure, being 30 times faster at 10^{-4} torr than at 0.25 torr. At pressures less than 10^{-4} torr, the reaction starts by an initial sluggish period and after 1 hour at 1,450° C, an accelerating period develops. This induction accelerating phenomenon has been tentatively explained by germination of surface nuclei and their two-dimensional growth.

Progress During the Fourth Quarter

The effect of small amounts of oxide impurities on the carbothermal reducibility of 70/100 mesh silica gel was studied. With 5-percent lime the results were compared to those previously obtained with 70/100 agglomerated silica pellets and 70/100 mesh silica particles. It is evident from figure 1 that silica pellets had the highest activity in carbothermal reducibility. This may be due to the more uniform distribution of powdered CaO in pelletized silica as compared with CaO impregnated silica or silica gel particles. The effect of lime concentration on the carbothermal reducibility of silica gel at 1,400° C is shown in figure 2. Curves b and c show the beneficial effect of 0.5 and 5-percent CaO, respectively, on increasing the reduction rate of lime-impregnated silica as compared to the blank of pure silica given in curve a.

The effect of small additions of alkaline earth metal oxides, other than CaO, as well as those of the alkali metals was studied during the quarter and the results are shown in figure 3. Curves b, c, d, e, f and g represent the kinetic carbothermic reduction of silica gel at 1,400° C in presence of 5-percent MgO, CaO, SrO, BaO, Na_2O, and Al_2O_3, respectively. Although no specific correlations can be made within the same group in the periodic table, it can be concluded that alkaline earth metals promote the carbothermal reducibility of silica while the alkali metals retard it. This can be easily attested to from the duration of the induction period, which was decreased from 480 minutes with pure silica gel to 75, 95, 210, 295, and 385 minutes in the presence of 5-percent CaO, BaO, MgO, Al_2O_3, and SrO, respectively. The induction time in presence of alkali metals

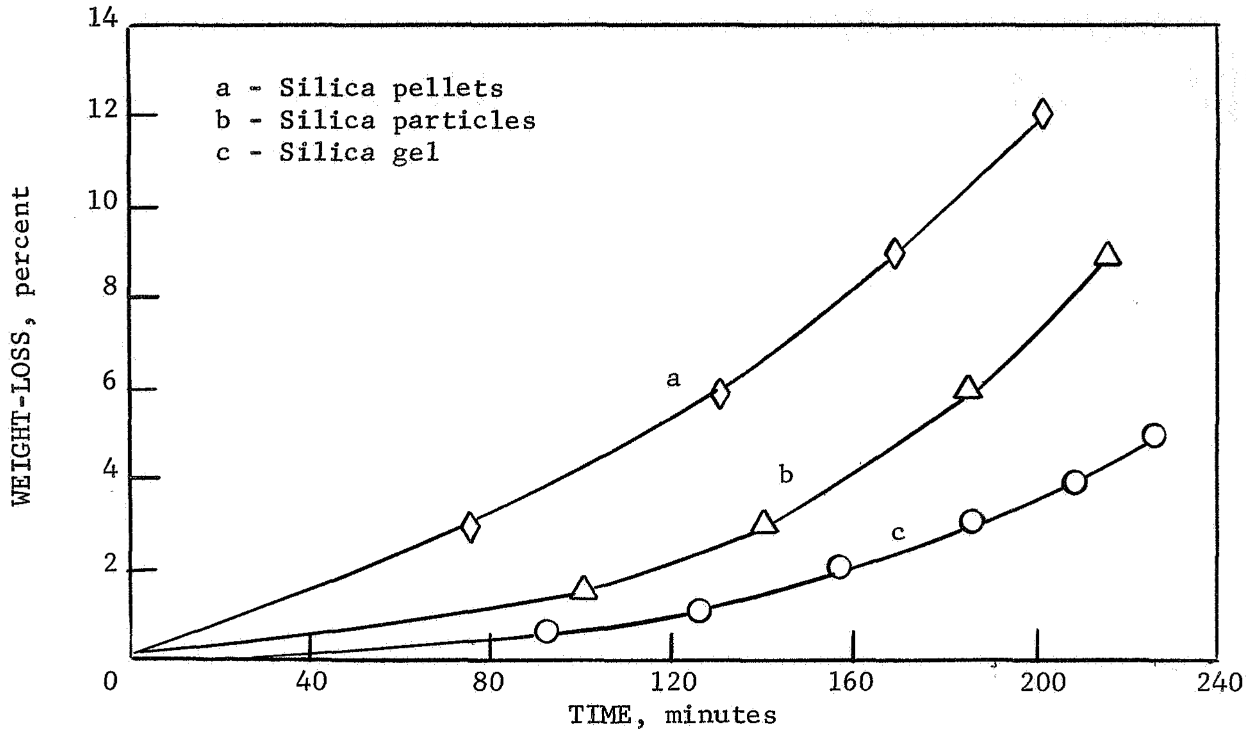

FIGURE 1. - Effect of 5-Percent CaO on the Vacuum Carbothermic Reduction of Different Forms of Silica at 1,400° C.

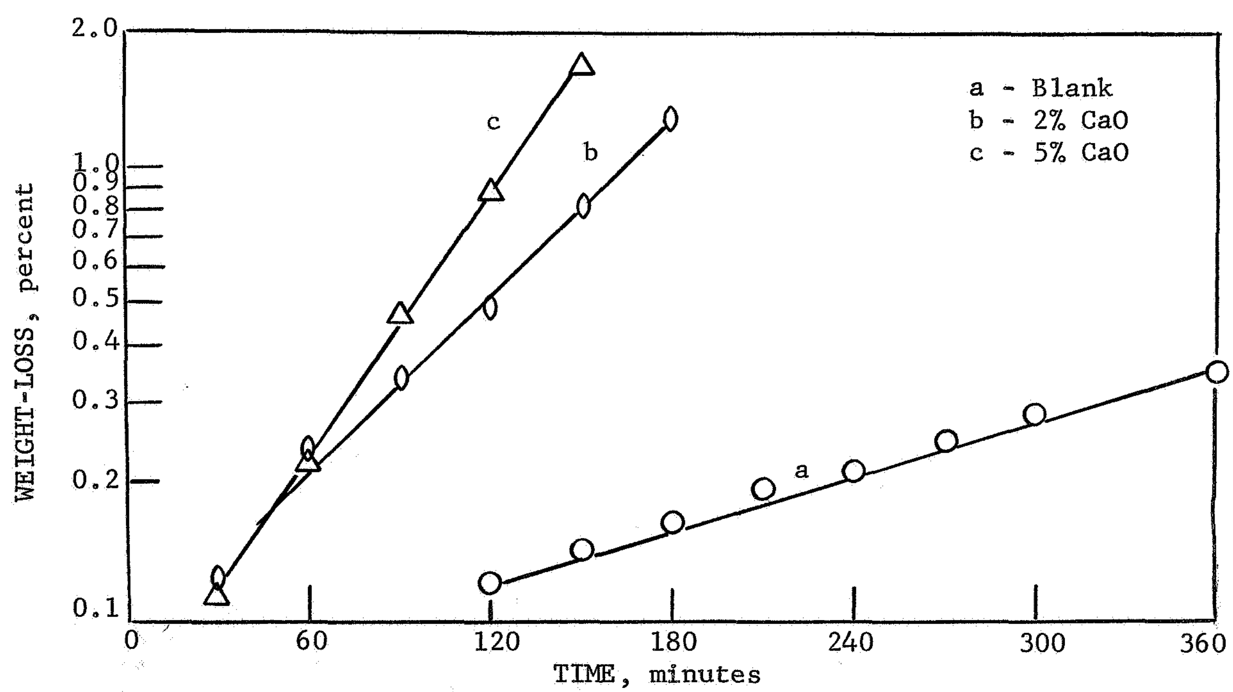

FIGURE 2. - Effect of Lime Percentage on the Vacuum Carbothermic Reduction of Silica at 1,400° C.

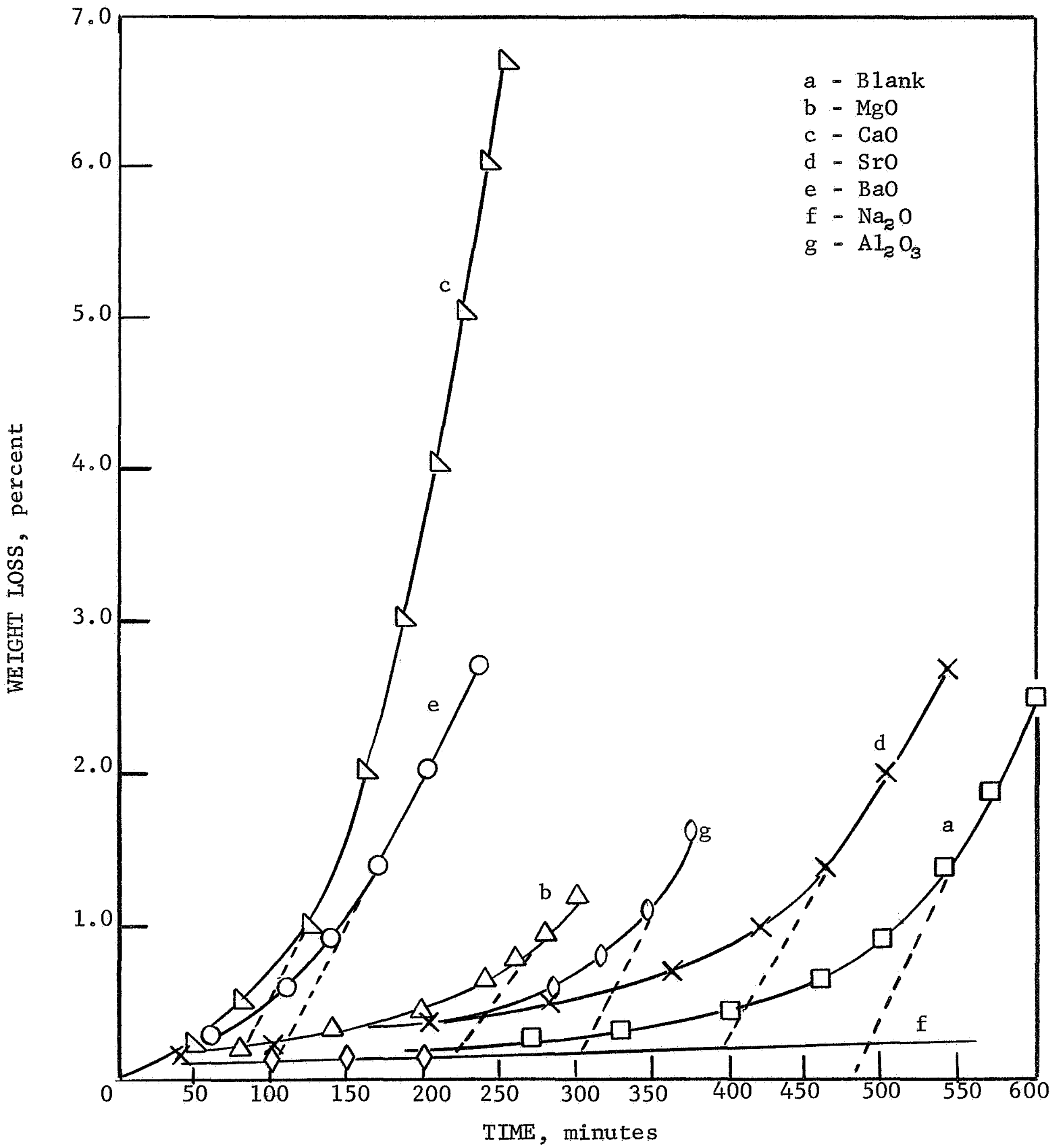

FIGURE 3. - Effect of 5-Percent Metal Oxide Additions on the Vacuum Carbothermic Reduction of Silica at 1,400° C.

was so large that it cannot be measured within the usual experimental time. In cases in which the acceleratory period was determined, its slope was approximately the same in presence of impurities as in their absence. Thus it appears that the impurity effect on silica reduction is limited to its influence on the initial number of germ nuclei but not on their rate of propagation and growth. When this effect is superimposed on the changes of the melting points expected on mixing with the impurity, the difficulty of obtaining significant correlations with the physical parameters of the additive becomes apparent. The results of previous research in this project indicated that the reducibility of silicates decreases inversely, not only with the melting point of basic oxide constituents of the silicate, but also with the melting point of the mineral. It was also reported that silicates that melt at the reduction temperature react slower with graphite when compared with silicates that retain their solid state of aggregation.

The opposing effects of structural promotion versus lowering of the melting point are exemplified by a study of the effect of sodium oxide concentration on the carbothermal reduction of silica. The reduction curve of silica gel at 1,400° C in presence of 0.5 and 5-percent sodium oxide are shown in curves b and c of figure 4. Thus, while 5-percent Na_2O retards the reduction because of its effect on lowering the melting point of silica, smaller amounts of that additive that do not significantly lower the melting point will be able to expound their structural promoting effect. Hence the presence of 0.5-percent Na_2O promotes the silica reduction reaction. Based on the melting point effect alone, MgO would be expected to be the most efficient promoter in the alkaline earth oxides. Its low atomic volume, on the other hand, tends to nullify this effect by making it inferior to other more voluminous ions, such as calcium, strontium, and barium in its structural promotion. Strontium and barium are expected to top the list in structural promotion, yet the increased basicity of their oxides tends to make them flux easily with silica, and hence undesirably lower the melting point. A striking balance of these opposing effects appears to be reached in the case of CaO. The atomic volume of calcium is large enough, and the melting point of its oxide is high enough so as to render lime the most efficient promoter for the carbothermal reduction of silica.

The kinetics of reduction of silica gel with graphite was studied with various weights of the reactants and at a series of temperatures. An Ainsworth recording electrobalance was used to follow the weight of the sample as the reaction progresses. With larger sample size, the volume of carbon monoxide produced was so large that the pumping rate was not sufficient to maintain the desired vacuum in the furnace. Pumping rate control of the kinetics was overcome by reducing the sample size. It was found that sufficient reproducibility was obtained with sample sizes between 0.60 and 7.2 grams. The kinetic curve at 1,460° C was carefully determined with a 0.90-gram sample of 5 to 1 silica gel to graphite weight ratio and the data are recorded in table 1 as percent weight-loss versus time in the first two columns. Previous investigations showed

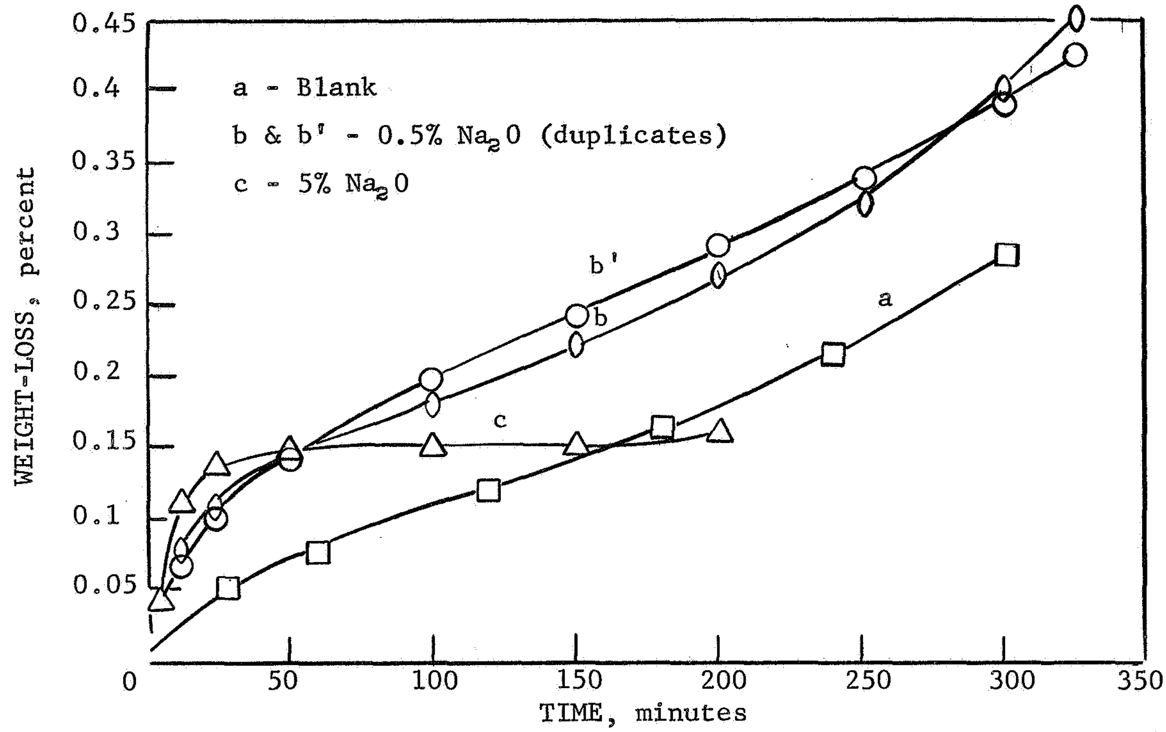

FIGURE 4. - Effect of Soda Percentage on the Vacuum Carbothermal Reduction of Silica at 1,400° C.

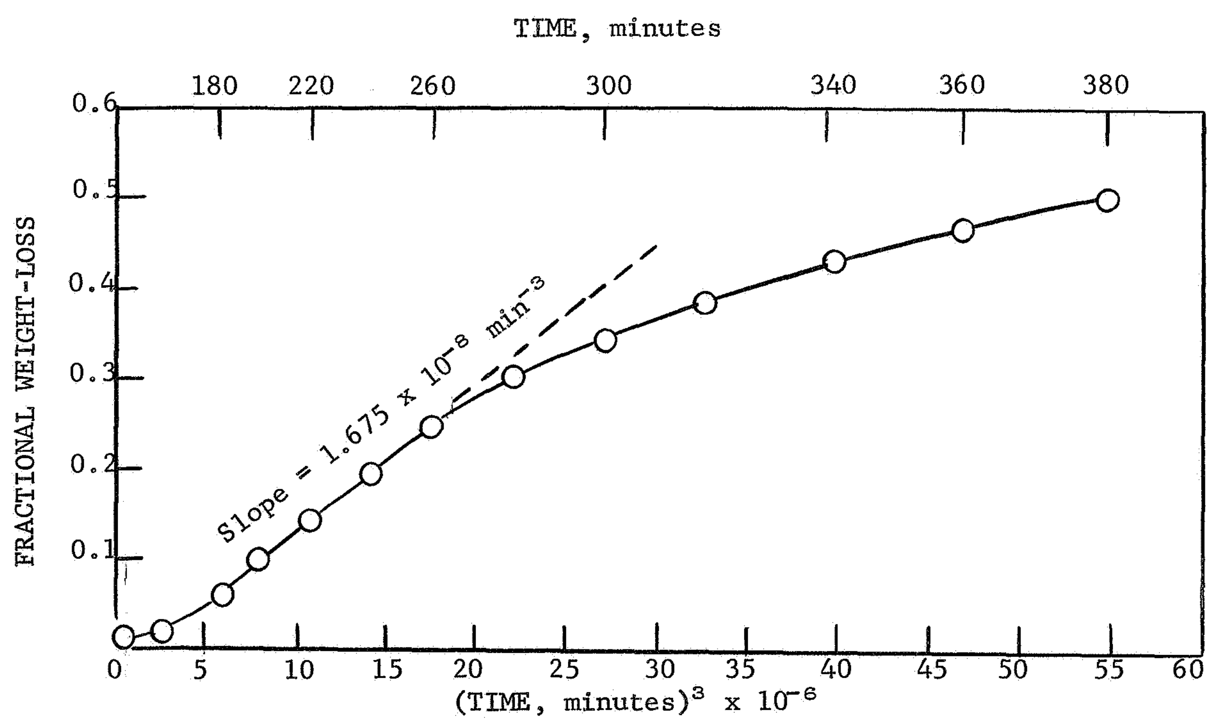

FIGURE 5. - Variation of Fractional Weight-Loss With the Cube of Time.

TABLE 1. - Carbothermal reduction data for 0.9-gram sample of an equimolar mixture of silica gel and graphite at 1,460° C

Time min, t	Fractional weight-loss, y	y/(1 - y)	$\varphi(t) = s\ N_0\ k^2 t^2\ (1 - e^{-kt})$
20	0.0010	0.0010	0.0001
40	.0021	.0021	.0009
60	.0032	.0032	.0029
80	.0048	.0048	.0063
100	.0070	.0071	.0115
120	.0111	.0112	.0186
140	.0200	.0204	.0276
160	.0356	.0369	.0387
180	.0599	.0637	.0517
200	.0946	.1045	.0668
210	.1160	.1312	.0751
220	.1394	.1620	.0839
230	.1650	.1976	.0931
240	.1922	.2379	.1029
250	.2183	.2793	.1131
260	.2462	.3265	.1238
270	.2736	.3767	.1350
280	.3038	.4364	.1466
290	.3233	.4777	.1587
300	.3440	.5243	.1713
310	.3662	.5779	.1843
320	.3870	.6314	.1977
330	.4085	.6907	.2116
340	.4296	.7530	.2260
350	.4489	.8146	.2408
360	.4680	.8795	.2560
370	.4861	.9459	.2717
380	.5022	1.0089	.2877
390	.5188	1.0782	.3043
400	.5333	1.1426	.3212
420	.5659	1.3035	.3563
440	.5906	1.4425	.3932
460	.6123	1.5792	.4317
480	.6313	1.7123	.4718
500	.6490	1.8491	.5136
520	.6653	1.9874	.5571
540	.6792	2.1169	.6021
560	.6919	2.2452	.6489
580	.7034	2.3719	.6972
600	.7133	2.4883	.7472
620	.7221	2.5987	.7988
640	.7300	2.7040	.8521
660	.7367	2.7980	.9070

that the carbothermal reduction of silica at 1,400° C followed a third order power law with respect to time for the first 15 percent of the reaction. Last quarter a kinetic equation based on the lateral growth of germ nuclei was derived. The term germ nuclei refers to a number of unique points with highly localized activity which can germinate in a crystalline specimen. These nuclei are situated at regions of disorder, such as the points of emergence of dislocations, at vacancy, interstitial or impurity clusters. The derived kinetic equation can be approximated for very small reaction times, t, to

$$y \simeq s\ N_0\ k^3 t^3 \tag{1}$$

where y is the fractional reaction, s is a shape factor defining the number of sites per unit area at which a new atom can be added to a nucleus, N_0 is the total number of the initial germ nuclei, and k is the rate-constant for the radial growth of the nuclei.

In order to test the validity of the proposed kinetic equation and the mechanism upon which it is based, the experimental data in table 1 were analyzed in terms of this equation. To perform this analysis, the values of the parameters s, N_0 and k must be retrieved by some semi-independent methods. One easy way of linearizing the reduction curve in its initial segments is obtained by plotting y against the cube of the elapsed time. This plot for the reduction of silica gel at 1,460° C is shown in figure 5. The slope of the initial significantly linear segments of that curve is estimated to be 1.675×10^{-8} min^{-3}, which according to equation (1) should be the value of $s\ N_0\ k^3$. We have no means of estimating these parameters separately, except for s, which is expected to be $4\pi/3$ for spherical nuclei, 8 for cubical nuclei, and 4 for compact two-dimensional nuclei. The method of trial and error was used to apportion the slope value of 1.675×10^{-8} among the two quantities $s\ N_0$ and k^3. Preliminary trials showed that the assignments of $s\ N_0 = 0.0327$ and $k = 8 \times 10^{-3}$ min^{-1} gave reasonable agreement between theory and experiment. Based on these two parameters, values of the functions $\varphi\ (t) = s\ N_0\ k^2 t^2\ (1 - e^{-kt})$ and $y/(1 - y)$ were calculated and are given in the third and fourth columns of table 1. When $y/(1 - y)$ was plotted against $\varphi(t)$, a reasonably straight line, shown in curve b of figure 6, was obtained. The original reduction curve with its sigmoidal shape is shown as curve a in the same figure. The empirical kinetic law for the carbothermal reduction of silica appears, therefore, to be of the form

$$y/(1 - y) = a\varphi(t) \tag{2}$$

where a is a constant determining the slope of line b in figure 6. In order to derive a mathematical expression consistent with equation (2), some mechanistic assumptions must be made. Thus, if N_0 germ nuclei are available for activation at the start of the reaction, the number of nuclei at time t will be given by

$$N_t = N_0\ (1 - e^{-kt}) \tag{3}$$

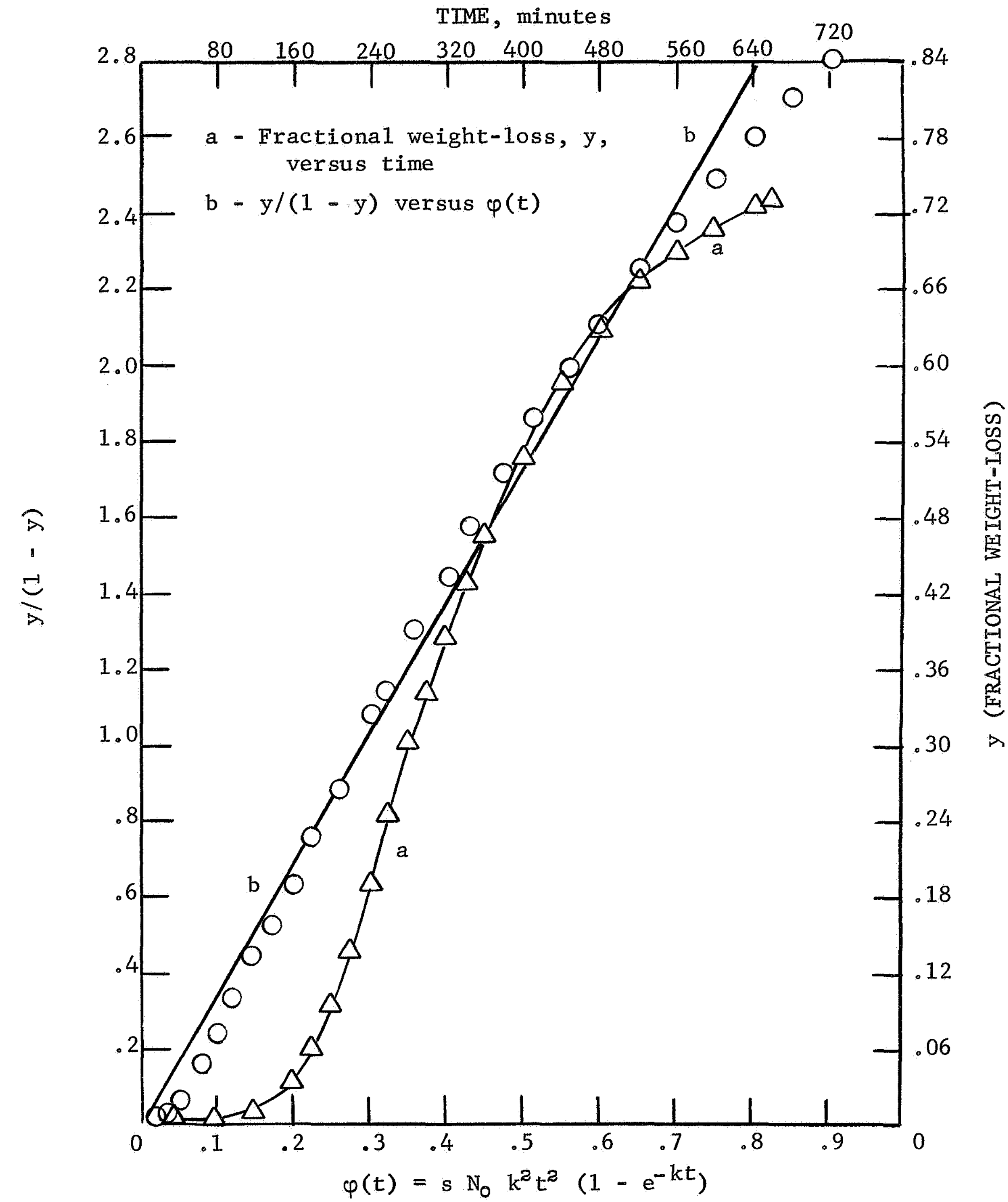

FIGURE 6. - Variation of the Ratio of Fraction Reacted to Fraction Unreacted With $\varphi(t)$ for the Vacuum Carbothermal Reduction of Silica at 1,460° C.

where N_t is the number of reaction nuclei present at time t. Assuming compact or two-dimensional nuclei on the reaction interface, the functional relationship for the growth of nuclei at time t will be of the form $s\ N_t\ k^2t^2$. The fractional reaction, y, will therefore be given by

$$y = s\ N_t\ k^2t^2$$

$$= s\ N_0\ k^2t^2\ (1 - e^{-kt}). \qquad (4)$$

The rate of carbothermal reduction at time t will be given by

$$dy/dt = 2s\ N_0\ k^2t\ (1 - e^{-kt}) + s\ N_0\ k^3t^2\ e^{-kt}. \qquad (5)$$

For a random distribution of nuclei, the effective area is assumed to be a fraction $(1 - y)^2$ of the total area. The significance of this assumption in elucidating the reaction mechanism is that the reaction nuclei appear to germinate on both sides of the reaction interface; i.e., on the silica as well as the graphite planes. Were the nuclei to grow on one surface only, then the effective nucleation area will be a fraction (1 - y) of the total area. Allowing for this nuclei interpenetration, the rate of reaction will be given by

$$dy/dt = s\ N_0\ k^3t^2\ (1 - y)^2\ e^{-kt} + 2s\ N_0\ k^2t\ (1 - y)^2\ (1 - e^{-kt}). \qquad (6)$$

Replacing the parameter kt by τ to facilitate integration, and letting $s\ N_0 = m$, then

$$dy/(1 - y)^2 = m\tau^2\ e^{-\tau}\ d\tau + 2m\ \tau\ d\tau - 2m\ \tau\ e^{-\tau}\ d\tau. \qquad (7)$$

Integrating equation (7), one obtains

$$1/(1 - y) = me^{-\tau}\ (\tau^2 + 2\tau + 2) + m\tau^2 + me^{-\tau}\ (\tau + 1) + I$$

$$= m\tau^2\ [1 - e^{-\tau}] + I$$

$$= s\ N_0\ k^2t^2\ [1 - e^{-kt}] + I \qquad (8)$$

where I is the constant of integration. When t = 0, y = 0, and hence I = 1. With this initial condition fulfilled, the kinetic equation becomes

$$1/(1 - y) - 1 = y/(1 - y) = s\ N_0\ k^2t^2\ [1 - e^{-kt}]. \qquad (9)$$

Equation (9) predicts that the plot of y/(1 - y) against $\varphi(t)$ should give a straight line. This is supported by curve b of figure 6 which follows a straight line up to about 70 percent reduction (560 min). Deviation from any kinetic equation is expected at very high reaction percents when the reactants are nearly consumed and the model of contacting spheres, where the reaction occurs at sites on the interparticle contacts, is no longer valid. The linear form of the kinetic data up to these high percents of reaction can be considered as a proof of the suggested carbothermal reduction mechanism.

Expanding the exponential term in the right-hand side of equation (9) yields

$$y/(1 - y) = s\ N_0\ k^2 t^2\ [1 - 1 + kt - k^2 t^2/2 + \ldots.] \qquad (10)$$

For small values of the product kt, that is for small reaction times and/or lower temperatures where the rate of nucleation, k, is small, the right-hand side of equation (10) reduces to $s\ N_0\ k^3 t^3$. Remembering that under these limiting conditions, y is also small and can be neglected relative to unity, then equation (10) will reduce to the cubic law given by equation (1) except for the proportionality constant α.

Status of Manuscripts

The Effect of Physical Parameters on the Reaction of Graphite with Silica in Vacuum, by L. A. Haas and S. E. Khalafalla, was published as Bureau of Mines Report of Investigations 7207 in December.

Carbothermal Reduction of Solid and Liquid Siliceous Minerals in Vacuum, by S. E. Khalafalla and L. A. Haas, was presented at the Annual Meeting of AIME in Washington, D. C. in February and is being prepared for journal publication.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Stability of hydrous silicates and oxides in lunar environment
Investigator:	Hal J. Kelly, Project Coordinator
Location:	Albany Metallurgy Research Center Albany, Oregon
Date begun:	April 1966 To be completed: May 1969
Personnel:	Hal J. Kelly, Supervisory Ceramic Research Engineer Ray L. Carpenter, Research Physicist

PROGRESS REPORT

Objective

The objective of this project is to investigate by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) the stability of some silicate and oxide minerals in air and under high vacuum at elevated temperatures. The determination of the energies required to dissociate oxide and silicate minerals and recover oxygen and water is the long-range objective.

Summary

One of the principal uncertainties in the composition of the lunar surface arises from lack of knowledge of the stability of minerals in the lunar environment. Accordingly, to design methods of processing lunar rocks to recover their useful components, the problem of elevated temperature stability under vacuum of hydrous silicates and oxide-bearing silicates must be solved. To assist in establishing solutions to these problems, high temperature, high vacuum DTA and TGA determinations were made on oxygen-containing and hydrous silicates to establish (1) their probable stability on the lunar surface, and (2) the thermal energy necessary to remove the oxygen or water from common rock-forming minerals by thermal decomposition. This research provides data on the rate of removal of oxygen and/or water and delineates the conditions under which removal may be accomplished by thermal dissociation in a high vacuum environment.

Minerals of four groups - zeolites, epidotes, bauxites, and amphiboles - and several miscellaneous minerals were obtained, purified, and used in thermal analyses. Of these only those in the epidote and amphibole groups have been found to be compatible with differential thermal analyses in vacuum.

A platinum calorimeter was installed. Improvements in circuit design have reduced noise and made it possible to use the platinum calorimeter

in vacuum as well as air. The X-Y recorder used previously has been replaced with an X-X-T recorder which is being used for all quantitative differential analyses. A source of bucking potential has been installed in the temperature measuring circuit of the DTA equipment so that higher temperatures can be recorded. Tests of the heating rate of the samples showed that the heating rate over the temperature range of interest is 11.2 ± 0.4° C minute.

A series of runs were made on the epidote and amphibole minerals in air and in a vacuum of 10^{-5} torr. The sample used in each run was weighed before and after the run and both series of runs were bracketed with calibration runs. From the data, the weight loss and the energy of decomposition in air and in vacuum were obtained. The results show there is a small decrease of energy required for decomposition in vacuum. Comparison of the weight-loss data with the results of TGA shows that the total weight loss in air is the same as obtained in vacuum except for the amphibole minerals which showed a slightly larger weight loss in vacuum, largely due to loss of sample during decomposition.

Progress During the Fourth Quarter

Differential thermal analyses were made on epidote, zoisite, tremolite, and actinolite in air and in a vacuum of 10^{-5} torr. Calibration runs were made before and after the minerals were run in air and then again before and after the minerals were run in vacuum. The average of the two values for each series of runs was used to calculate the heat of decomposition for the minerals under the two experimental conditions. The values obtained are given in table 1. The data show that there is a small decrease of heat of decomposition in a vacuum environment.

TABLE 1. - Heats of decomposition of minerals in air and vacuum

Mineral	Heat of decomposition, cal/g	
	Air	Vacuum
Epidote	32.3	31.6
Zoisite	32.5	30.7
Actinolite	31.0	30.0
Tremolite	32.1	31.2

The characteristic DTA temperatures for decomposition in air and vacuum were determined from the thermographs for the four minerals. These are compared in table 2. The temperatures for the start of decomposition, the departure temperatures, are lower in vacuum than in air for the minerals zoisite and tremolite, but the departure temperatures for epidote and actinolite are the same in air as in vacuum. The minerals which show a decrease of initiation temperature in vacuum are the ones which are end members of their group and do not contain iron. The intercept temperatures are lowered by decomposition in vacuum except for the mineral actinolite. The peak temperatures are not decreased to any extent by decomposition in vacuum.

TABLE 2. - Decomposition temperature of minerals in air and vacuum

Mineral	Condition	Departure temp., °C	Intercept temp., °C	Peak temp., °C
Epidote	Air	923	942	986
Epidote	Vacuum	922	926	986
Zoisite	Air	916	950	976
Zoisite	Vacuum	894	931	969
Actinolite	Air	974	1,008	1,059
Actinolite	Vacuum	979	1,004	1,057
Tremolite	Air	1,001	1,040	-
Tremolite	Vacuum	938	1,028	1,074

The sample weight before and after each DTA run was determined and from these data the weight losses were calculated. Thermogravimetric analyses (TGA) were run on the four minerals in air. The weight losses determined for the various experimental conditions are listed in table 3. The weight losses for epidote and zoisite are in agreement for the three methods but actinolite and tremolite show larger weight losses in vacuum than in air. The increase in weight loss in vacuum shown for actinolite and tremolite is due to a small loss of sample during decomposition.

TABLE 3. - Weight loss of minerals in air and vacuum

Mineral	Weight loss (percent)		
	Air (DTA)	Vac (DTA)	Air (TGA)
Epidote	2.15	2.18	2.18
Zoisite	2.14	2.20	2.24
Actinolite	1.95	3.16	1.99
Tremolite	2.30	4.11	2.46

Status of Manuscripts

A report summarizing the work is being prepared for presentation at the Western Regional Meeting of the American Ceramic Society at Seattle, Washington, October 15-17, 1969, and for publication as a Bureau of Mines Report of Investigations.

ANNUAL STATUS REPORT FISCAL YEAR 1969

Bureau of Mines NASA Program of Multidisciplinary Research

Task title:	Magnetic and electrostatic properties of minerals in a vacuum
Investigator:	Foster Fraas, Project Leader
Location:	College Park Metallurgy Research Center College Park, Maryland
Date begun:	June 1966 To be completed: May 1969
Personnel:	Ronald A. Munson, Research Chemist Foster Fraas, Metallurgist Anderson Walls, Laboratory Technician

PROGRESS REPORT

Objective

The objective is to study adsorption and contact electrification in a vacuum and determine their effect on the separability of nonconducting minerals.

Summary

Under a very high vacuum of 10^{-8} torr and in the particle size range of 104 to 420 microns, suitable for the electrostatic and magnetic separation of ores, there is no adhesion of particles produced by crushing and grinding due to the limited contact area, and for repeated contacts, area size has a frequency of occurrence in agreement with the normal law. At a temperature of 102° C, the maximum of the lunar environment, contact electrification is reversible upon return to atmosphere. Vacuum operation has a number of advantages over operation in air. Calculations which are described in detail in the manuscript being prepared for publication show that the lack of air viscosity permits magnetic and electrostatic separation at high feed rates, while the absence of sound transmission results in the extension of particle vibration to small sizes. Vibration applications, particularly with piezoelectric minerals by electromechanical coupling, provide for particle agglomerate dispersion, removal of surface dust, and particle size reduction by fracture. The unrestricted transmission of electromagnetic radiation and atomic particles has further advantages. It permits more extensive application of the photoelectric effect to mineral separation, and the use of electron and ion deposition for the dispersion of particle agglomerates and the electrostatic separation of conductors from nonconductors.

Progress During the Fourth Quarter

The ratio of the particle vibration energy lost in air to the energy stored in the particle was studied further, resulting in an integrated form of the equation developed in the last quarter,

$$W/W_o = e^{-(\rho_a/\rho_s)(2c/z)t}$$

where W is the energy after an elapse of time, t, W_o is the stored energy at zero time, z is the dimension of a cubical particle radiating from two faces, and ρ_a and ρ_s are the densities of air and the particle, and c is the velocity of sound in air. This equation provides similar but more striking information, namely, an exponential increase in energy loss in air for decreasing particle diameter, z. The large difference between the air and vacuum response of small particles is thus emphasized.

Although application of electromechanical coupling to the vibration of piezoelectric particles may result in a narrow frequency range for resonance, a sweep frequency generator could be used to cover a range of modes and particle diameters. An inverse effect is the electromagnetic radiation generated by the vibrating particle.

An approximately 1,200 Å ultraviolet lamp was constructed for use within the limited confines of the vacuum chamber. Photoconductivity data are reported in the manuscript. Final work on the manuscript was completed.

Status of Manuscripts

Factors Related to Mineral Separation in a Vacuum, by F. Fraas, was completed for publication as a journal article.