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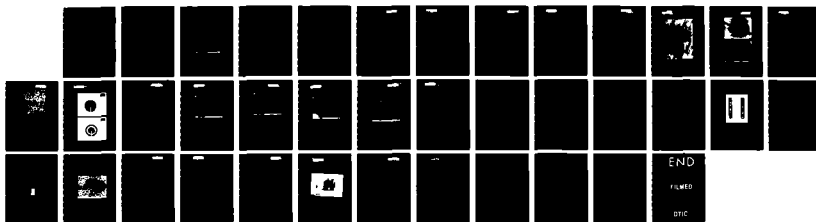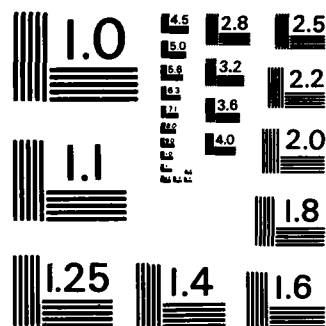   J M HERNDON MAY 85 HSSI-82-0004 AFOSR-TR-85-0728
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TECHNOLOGICAL APPLICATIONS OF

EARTH CORE RESEARCH

Final Report

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June 1985

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes the objectives, states accomplishments and activities during the reporting period relative to contract F49620-82-C-0024.

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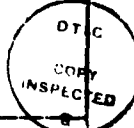
TECHNOLOGICAL APPLICATIONS OF
EARTH CORE RESEARCH

Geophysical phenomenon are inextricably related to the abundances and distribution of elements within the Earth and to the properties of the compounds they form. The discovery of relationships identifying seismologically determined components of the interior of the Earth with petrologically determined components of a particular meteorite, and the introduction for the first time of the concept of a nickel silicide inner core [J.M. Herndon, Proc. Roy. Soc. Lond. A368 (1979) 495; Ibid., A372 (1980) 149; Naturwissenschaften, 69 (1982) 34] afford a fundamentally new understanding of the composition of the interior of the Earth. The research undertaken under the present AFOSR contract is intended to address the question of what elements might be expected to form silicides in the core of the Earth and is aimed at determining and demonstrating the technological feasibility of new concepts originating from the research. Specifically, the research objectives are the following:

a) Prepare a complete bibliography on silicide technology, including the physical and chemical properties.

b) Determine the effects of phosphorous and copper on nickel silicide. Conduct experiments to determine what elements form silicides.

c) Conduct experiments on Earth core type materials to provide new materials and processes.

The schedule for the tasks that are the research objectives and the deliverables is shown in Figure 1.

TASKS/DELIVERABLES	Months After Contract								
	4	8	12	16	20	24	28	32	36

Research Objective a) ▨▨▨

Research Objective b) ▨▨▨▨▨▨▨▨▨▨

Research Objective c)　　　▨▨▨▨▨▨▨▨▨▨▨▨

Reports　　　　　　　▲　　　▲　　　　▲　　　▲

Figure 1.　Schedules

Research Objective a) was completed with the submission in 1982 to AFOSR of a two-volume Interim Report entitled BIBLIOG- RAPHY OF SILICIDE TECHNOLOGY INCLUDING PHYSICAL AND CHEMICAL PROPERTIES.

Research Objective b) consisted of two lines of research: (1) Experiments conducted to determine the effects of phosphorus and copper on nickel silicide; and, (2) Experiments conducted at near ambient pressure to address the question of what elements might be expected to form silicides in the core of the Earth.

Research Objective c) was closely related to and, in certain instances, followed directly from results of experiments under Research Objective b).

The research activities described in this report have led to discoveries that may have technological importance, especially with respect to improving the mechanical properties of nickel silicide, and to discoveries that may have geophysical signifi- cance.　The geophysically important results are related to the chemical state of uranium and thorium within the core of the Earth, and by inference, to the siting of the energy sources responsible for creating the Earth's magnetic field and for moving the continents.

The element silicon forms compounds with most elements (Figure 2 on page 3).　On the surface of the Earth silicon is

Figure 2

combined with oxygen as silica (SiO_2). At the center of the Earth silicon is combined with nickel. The nickel-rich portion of the Ni-Si system contains a number of intermediate phases. Six compounds occur in the system of which only three have open melting points at ambient pressure: Ni_3Si; Ni_5Si_2 (1281°C); Ni_2Si (1319°C); Ni_3Si_2; $NiSi$ (992°C); $NiSi_2$.

Of the various nickel silicides, Ni_2Si was chosen for the present investigation, the rationale being that Ni_2Si occurs in nature in certain meteorites and appears to be the most stable composition.

Experiments were conducted on laboratory prepared nickel silicide samples to determine the effect of additions of phosphorus and copper. The results of the addition of phosphorus is significant: A small amount of phosphorous strengthened and hardened, but kept the ductility of the nickel silicide about

the same. A patent application is planned. The addition of copper resulted in the formation of some unusual microstructures, but their technological utility may be limited.

Silicides have certain technologically important physical properties. For example, silicides are relatively hard and have high melting points. Some even form upon themselves an oxidation resistant coating. However, silicides are quite brittle. The extreme brittleness severely limits their technological applications. The present investigations were undertaken with the hope that the addition of either phosphorous or copper might render the nickel silicide less brittle. The results for phosphorous-containing nickel silicide were certainly gratifying.

Ingots of nickel silicide containing varying amounts of phosphorous or copper were prepared by combining the elements at 1600°C for 24 hours in an argon atmosphere. Because of the volatility of phosphorous, Ni_2P was used as a starting material. Subsequently, the ingots were annealed at 1200°C for 12 hours under argon. The samples were then sectioned and metallurgical mounts were prepared, SEM analyses made and Knoop hardness measurements taken.

Considerable effort was expended in attempting to prepare pure nickel silicide samples for three point and four point bend tests. Samples for three point bending were required to be 40 mils wide and less than 10 mils thick with no chips on the edges. Sample for four point bending could be thicker, i.e. 25-35 mils. Unfortunately, the thicker samples proved stronger than the testing apparatus could tolerate, thus efforts were aimed at preparing thin samples for the three point bending tests.

Early on it became evident that the phosphorous-containing nickel silicide samples were less brittle than the pure nickel silicide samples. This was apparent because, in trying to prepare samples for three point bending tests, extreme difficulty was encountered in preparing the pure nickel silicide samples.

However, the necessity of obtaining quantitative strength data justified the efforts.

The pure nickel silicide material is extremely hard and brittle. Attempts were made to slice samples of the pure material using a Sanford Corporation high speed cut-off saw, but the material cracked and fell apart at thicknesses less than 40 mils. The material seemed to be too brittle to withstand the inherent vibrations. Cutting samples with an abrasive wheel did not work. The nickel silicide heated up and seemed to grip the blade causing it to break. Diamond blades appeared superior, but did not last for more than 10 to 15 cuts. Such extreme blade wear is remarkable: One blade that had been used for years to cut silicon carbide samples wore out with only ten cuts on nickel silicide samples. Attempts were made to cut the nickel silicide samples using a Buehler Ltd. Isomet low speed saw. This saw runs in a kerosene bath. The samples were mounted on a weighted swing arm. It was expected that less vibration would occur, although cutting time would be considerably longer. The diamond blades would actually wear out in three or four cuts. Unfortunately, samples could not be cut into slices thinner than 20 mils with the low speed saw. A Lastec wire saw manufactured by Laser Technology Inc. was also tried. The wire saw seemed to last longer than the diamond blade, but the higher level of vibration would break samples. Also, the wire wandered and not give parallel sides. Moreover, samples chipped. Various schemes were devised. For example, samples of nickel silicide were encapsulated in metallurgical mounts prior to cutting. Unfortunately, the nickel silicide still cracked and fell apart. Attempts were made to thin 40 mil samples by grinding using silicon carbide paper. Nevertheless, chips formed on the edges and cracks would initiate. Also, the grinding would generate heat and dislodge the sample from the holder. Grinding samples down from 40 mils using diamond paste proved too time consuming with almost no results.

Considerable efforts were made to determine whether impurities in the nickel silicide sample might be responsible for the difficulties experienced in sample cutting. Scanning electron microprobe investigations proved negative. Nevertheless, new approaches were adopted using new and, hopefully, more pure chemical starting materials.

Early on in the investigation nickel silicide was made by combining the elements at 1600°C for 24 hours in a silica-containing alumina crucible under an inert atmosphere. At that temperature some interaction between sample and crucible is possible. Crucibles of different compositions were tried, but without observable differences in the sample cutting problem. Finally, nickel silicide samples were made from the elements by radio frequency induction heating on a water cooled copper hearth under an Argon atmosphere. Typically, each sample would be melted ten times to insure homogeniety.

Another potential source of contamination might occur during annealing. Samples were usually annealed at 1200°C for 12 hours and required a protective atmosphere. Early on, the samples were annealed on an alumina boat in an atmosphere of flowing argon. Because of concerns that some contamination might be picked up from the alumina boat, encapsulation in a fused quartz ampule was attempted. It is known that elemental silicon can react with silica to form silicon monoxide. It could not be assumed that nickel silicide would be unreactive with silica. Thus, some means for keeping the sample out of contact with the silica appeared necessary. Initially the samples were wrapped in tantalum foil. That was a failure. The tantalum reacted with the nickel silicide. Some idea of the difficulty in finding a non-reactive surface material can be understood by referring to Figure 2 on page 3. From that figure it is evident that most of the higher melting point elements form silicides. Eventually a solution was arrived at: The interior of the quartz tube was coated with a layer of zirconia using Leecote Solvaset Z.

Despite the extraordinary precautions ░░░░░░ subsequent
synthesis and annealing of nickel silicide, the material was
still extremely brittle. No improvement was noted in the ability
to cut thin slices. It seems therefore a reasonable presumption
that the heretofore mentioned difficulties in cutting were related
not to impurities, but to the nature of the nickel silicide.

During the experiments it became qualitatively evident that
phosphorous containing Ni_2Si appeared less brittle than pure
nickel silicide. Figure 3 on page 8 is a scanning electron
micrograph of phosphorous-containing nickel silicide. Unlike
the pure Ni_2Si material, more than one phase is present. The
phases differ in their relative phosphorous content as indicated
the measured atomic ratios:

area A P/Ni = 0.01

area B P/Ni = 0.04

area C P/Ni = 0.13

The overall sample atomic P/Ni = 0.13 as measured at one-
tenth the magnification shown in Figure 3 is somewhat less than
the P/Ni = 0.21 of the starting materials, indicating some
evaporative loss of phosphorous.

While sectioning the sample shown in Figure 3 it appeared to
the Principal Investigator that the material was less brittle than
the pure Ni_2Si. That observation was supported qualitatively by
a comparison of the microfractures induced during microhardness
measurements. Figure 4 on page 9 shows photo-micrographs compar-
ing the crack propagation in the two samples. Although quali-
tative, these observations served as the basis for committing
considerable effort toward obtaining quantitative results. In
another attempt toward the same end, pieces of samples RO-O and
RG-P were heated in tungsten baskets and thin films were deposited
for transmission electron microscopy. No tungsten was detected in

Figure 3. Scanning electron micrograph of a Ni-Si-P sample. Alloys or compounds of several different compositions are present. Laboratory observations suggest that the addition of phosphorous makes Ni_2Si less brittle.
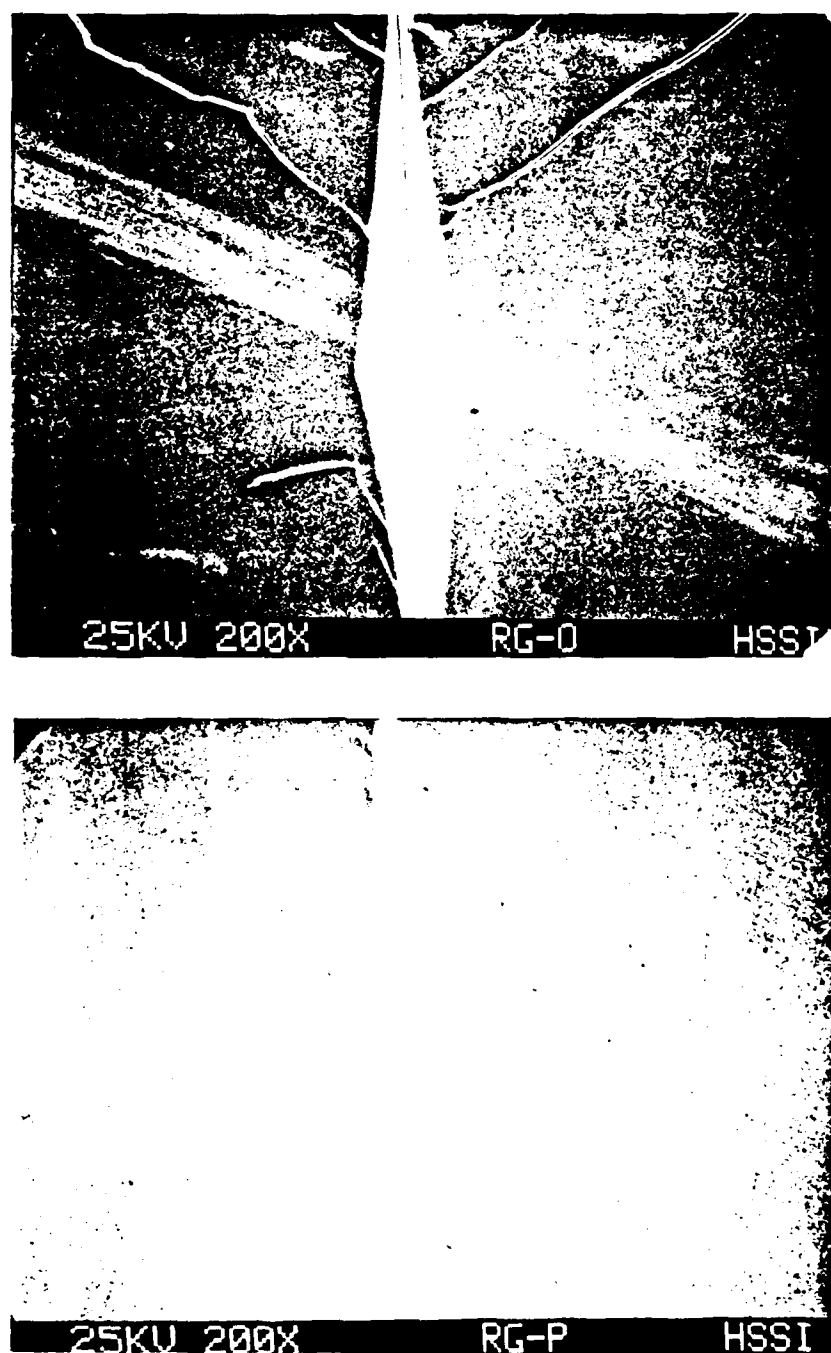
Figure 4. Microcracks originating from indentation. The pure nickel silicide, RG-O, shows large, extending cracks whereas the phosphorous-containing nickel silicide, RG-P, shows small cracks that do not appear to propagate.

the deposit. Figure 5 on page 11 shows a comparison of bright
fields at a magnification of 471,000 (including the photographic
three fold blow-up). Figure 6 on page 12 shows the comparison
of selected area diffraction patterns for the same two samples.
Why the diffraction pattern for RG-P is so diffuse is not known,
perhaps because of smaller grain size. Although interesting,
the thin film experiments did not lead to results useful for
relating to physical properties.

Finally, after many attempts and much expended effort, a
reliable means was found for comparing the mechanical proper-
ties of pure nickel silicide with the phosphorous-containing
nickel silicide. There is good agreement between the hardness
and strength of various metals and alloys. A method to deter-
mine ductility from the hardness impression was suggested by
R. Boklen [The Science of Hardness Testing and its Applications,
J.H. Westbrook and H. Conrad, eds., p. 109, ASM, Metals Park,
OH, 1973] and described and applied by K. Furuya and J. Moteff
[Metall. Trans. 12A, 1303 (1981)]. Booklen's approach is based
on a model of the upward plastic material flow around the inden-
tation. During indenter penetration, the material deforms
plastically near the indenter and a pile-up wall of material is
formed close to the impression. The height of the pile-up wall
may be related to the work-hardening exponent, i.e. uniform
elongation.

Microhardness indentations were made at ambient tempera-
ture by using a Vickers-type indenter with a 200, 300, 400 or
1000 gram load. For evaluation of the ductility, a DEKTAK
profilometer with a diamond stylus was used to measure the
pile-up of metal adjacent to the indentation. Profilometer
traces were obtained across the mid-points of the Vickers im-
pressions along a direction parallel to the indentation edges.
Three indentations were made on each specimen and pile-up
measurements were performed on each of the indentations. Scan-
ning election photomicrographs of the three indentations are

in fused quartz after evacuation and four flushings with helium.
The encapsulated crucible was itself encapsulated together with
an etched tantalum foil in a second quartz ampule. The second
ampule was evacuated and flushed three times with argon. It was
sealed with a slight argon pressure to prevent collapse at
elevated temperature. Figure 14 on page 25 shows the doubly
encapsulated crucible. The encapsulated crucibles were heated
to temperatures as high as 1350°C for twenty-four hours.

Success was attained with the highest temperature run. At
1350 °C the starting materials reacted: Figure 15 on page 26
shows the microstructure obtained. The light components of that
complex structure are nickel-iron-silicon alloys, Significantly,
thorium is concentrated in those nickel-iron-silicon alloys, in-
dicating that thorium changed chemical state. Although conducted
at ambient pressure and not the yet unattainable pressures
characteristic of the center of the Earth, the experiment never-
theless demonstrates the tendency of thorium to form silicides.
It was not clear from analyzing the data whether the uranium had
fully reacted or not. Thus no unambiguous conclusion can be drawn
for the chemical state of that element. Because these results
were obtained so close to the end of the contract, they have not
yet been published. It would be desirable prior to publication
to conduct additional experiments to clarify the chemical state
of uranium.

The nickel-iron-silicon alloy shown in Figure 15 on page 26
is not pure nickel silicide. Evidence from meteorites indicates
that, given sufficient time and temperature, nickel silicide
would precipitate from the alloy,

In most meteorites iron metal occurs containing some nickel.
Observations of the occasional occurrence of nickel silicide
precipitation within the iron metal matrix led the author to
conceive of the idea of the nickel silicide inner core of the
Earth. As no data on the rate of precipitation of nickel silicide
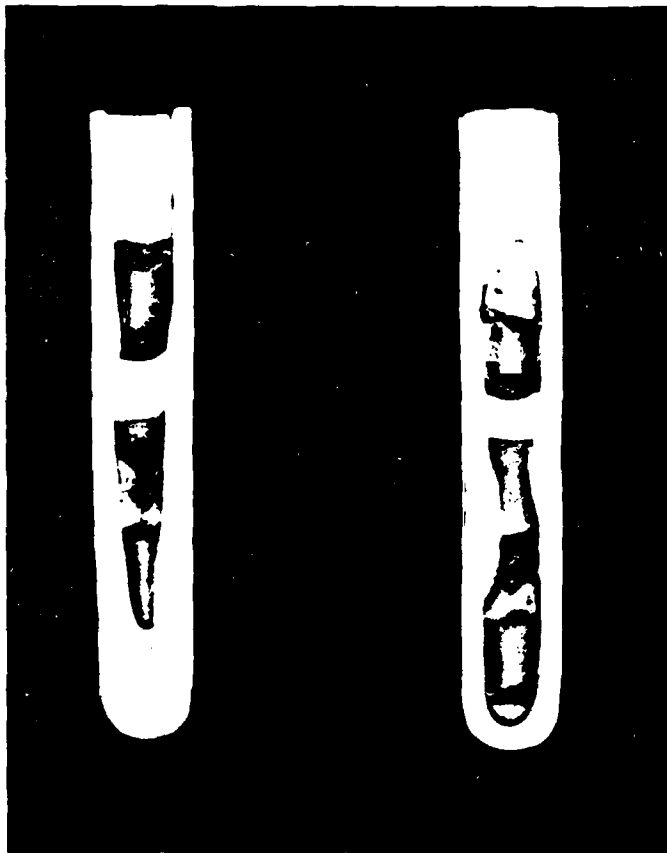could be found in the literature, experiments were undertaken

Figure 13.

determined. An important experimental observation was made by M.T. Murrell and D.S. Burnett [Geochim. Cosmochim. Acta, 46, 2453 (1982)] who found uranium to be concentrated within the sulfide components of enstatite meteorites. Such an enrichment, however, does not prove that the uranium is chalcophile. For example, in the Bustee meteorite titanium nitride (TiN) is found within oldhamite (CaS). Thus, without visual observation one can not say that the uranium exists as a sulfide.

Experiments were undertaken to determine at ambient pressure and at the temperatures attainable whether uranium and thorium would form silicides in a medium similar in composition to the opaque portion of enstatite chondrites, i.e. the portion that corresponds to the core of the Earth.

Initially, experiments were undertaken to determine whether uranium oxide or thorium oxide could be reduced by nickel silicide. An excess of nickel silicide was used. Figure 13 on page 23 shows two of the crucibles from those experiments. The intended reduction did not take place. It is not known whether the reaction thermodynamics were unfavorable or whether the reaction was thermodynamically favorable but slow or unreactive at the relatively low temperature of 1600°C. Figure 13 also illustrates one of the unsuspected phenomenon encountered in such experiments: Although Ni_2Si is dense 7.2 g/cm^3 and the experiment was conducted at almost 300°C above its melting point, the nickel silicide did not settle to a common level in the tube.

Another approach was adopted for the e xperiments. Uranium sulfide (US_2) and thorium sulfide (ThS_2) were mixed with Ni metal, FeSi, FeS and Fe (same relative proportions as in the core of the Earth, except that the amount of actinide sulfide was 0.1% so as to be measurable). The chemical compositions of the starting material were chosen so that there could be no question in analyzing results of whether equilibrium had been approached. The mixture was placed in a cricible composed of zirconia, alumina or enstatite. The crucible was encapsulated
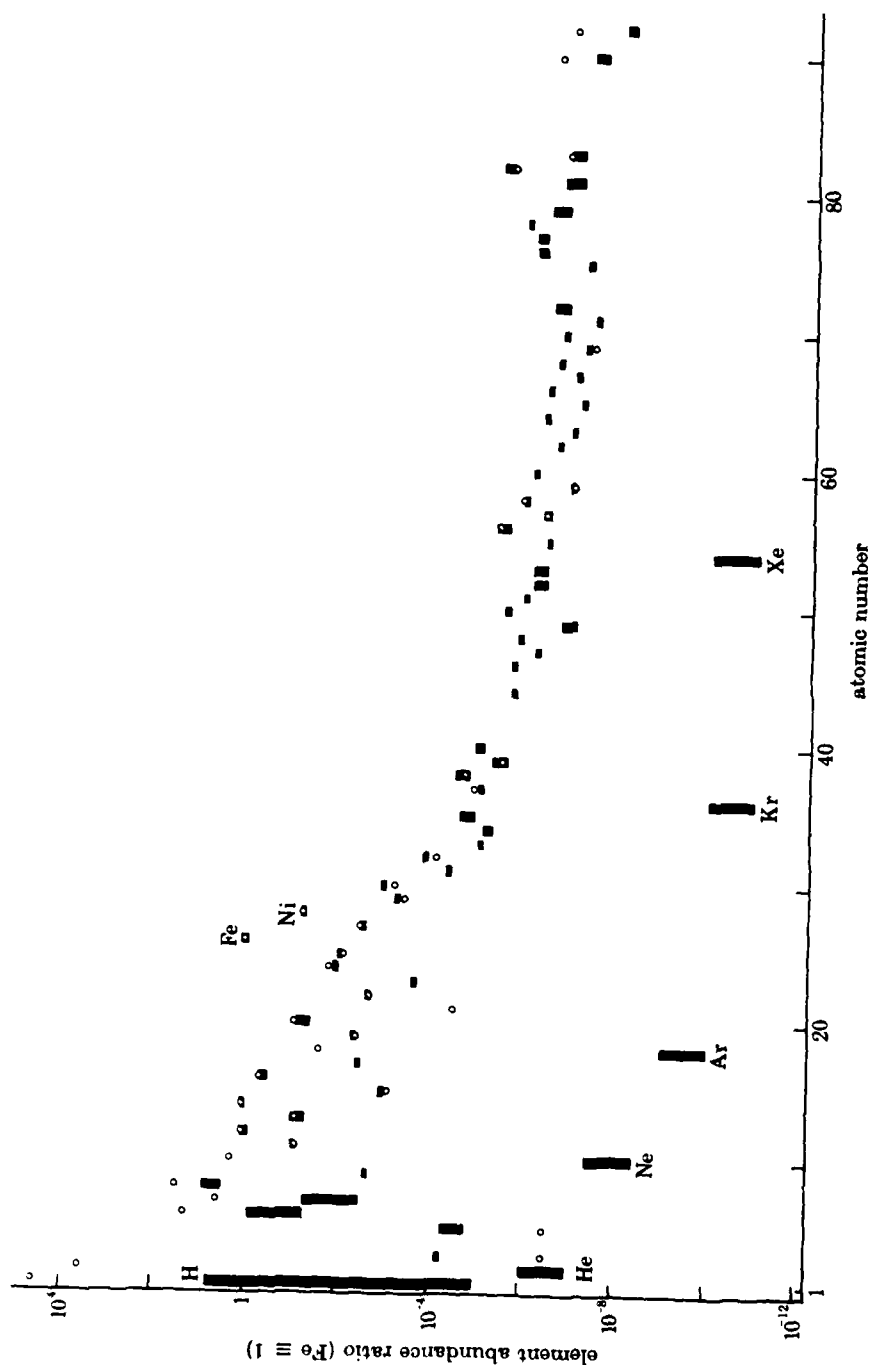
FIGURE 12. Comparison of elemental abundance ratios obtained from spectral analysis of sunlight (O) with corresponding ratios, normalized to iron, obtained from chemical analysis of chondritic meteorites (■): the tops of the bars represent literature values for the hydrated oxygen-rich Orgueil meteorite, the bottoms, those for the anhydrous oxygen-poor Abee enstatite chondrite.
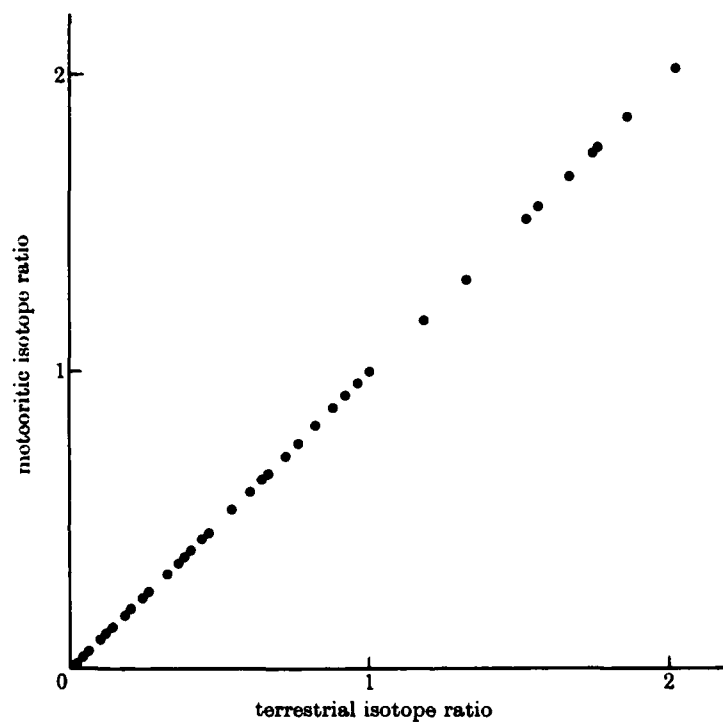
Figure 11. Comparison of meteoritic and terrestrial
isotope ratios of 15 elements. Some of the
52 isotope ratios plotted from literature
values are coincident on this scale.
[From J.M. Herndon, Proc. R. Soc. Lond.
A. 368, 495-500 (1979)]

Most of the energy that heats the surface of the Earth comes from sunlight. However, some heat is produced within the Earth from naturally occurring radioactive isotopes, the most important being ^{235}U, ^{232}Th, and ^{40}K. Knowledge of the presently unknown distribution within the Earth of heat-producing is fundamental to geophysics, for example, as related to the origin of the geo-magnetic field, the driving energy for earthquakes, and the thermal evolution of the Earth as a whole. A decision therefore was made to conduct experiments aimed at determining at near ambient pressure the chemical state of uranium and thorium in matter similar in composition to the core of the Earth. An understanding of the abundances of the elements in nature is important for understanding the experimental approaches under-taken.

The primordial matter from which the Sun, the planets, and other objects in solar system formed had a well defined chemical composition. This follows from astronomical observations, from the essentially constant isotopic compositions of meteoritic and terrestrial elements (Figure 11 on page 20), and from the obser-vation that the abundances of the elements in chondritic meteor-ites are related, although in a complex manner, to the nuclear properties of matter. With the exception of noble gases and light elements (H,C,O,N) which are volatile or from volatile compounds, solar elemental abundance ratios, derived from the spectral analysis of sunlight, are nearly identical to corres-ponding ratios obtained from the chemical analysis of chondritic meteorites (Figure 12 on page 21). The relationships between primordial matter and the chemical composition of the components of the Earth are described in a review article [J.M. Herndon, Naturwissenschafter, 69 (1982) 34] that is reproduced as Appendix I.

In Primordial matter the atomic abundance ratio of uranium to iron is about 1.5×10^{-8}. To date the chemical state of uranium and thorium in chondritic meteorites has not been directly

page 17 are scanning electron photo-micrographs of two of the
copper-containing nickel silicide samples. Following are hard-
ness data and Cu/Ni weight ratios for several samples:

Sample No.	(Cu/Ni) wt	Kroop No.
RG-5	0.01	530
RG-3	0.16	655
RG-1	0.24	156
RG-2	0.35	553
RG-6	0.62	410
RG-4	0.99	309
RG-7	1.55	291

There seems to be no simple relationship between copper content
and hardness. In establishing priorities for continuing efforts,
it would appear that further work on phosphorous additions to
nickel silicide would be a considerably more productive endeavor
than copper additions.

The second line of research under Research Object b) con-
sisted of experiments and theoretical considerations aimed at
determining which elements might be expected to form silicides in
the core of the Earth. From Figure 2 on page 3 it is obvious
that many elements form silicides; too many, in fact, to address
experimentally within the scope of the present project. Initial
efforts, therefore, were directed toward developing criteria to
determine the element or elements most important for experimental
focus. Theoretical considerations based on the Laws of Thermo-
dynamics can in principle be used to determine, at least approxi-
mately, what elements might be expected to dissolve in nickel
silicide. Unfortunately, the measured thermodynamic data neces-
sary, e.g. the heat of solution, are not available in the
literature. Even the JANAF Tables of Thermochemical Data are
totally devoid of data on silicides. Because of the lack of
measured thermochemical data, the theoretical considerations
were abandoned and a different approach for experimental priori-
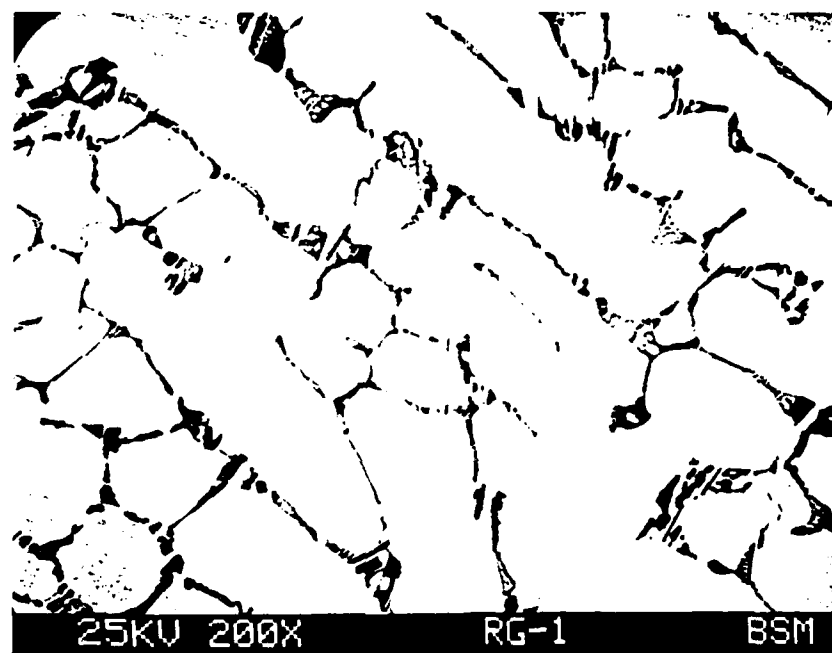tization was adopted, namely, geochemical importance.

Figure 10. Scanning electron photomicrograph
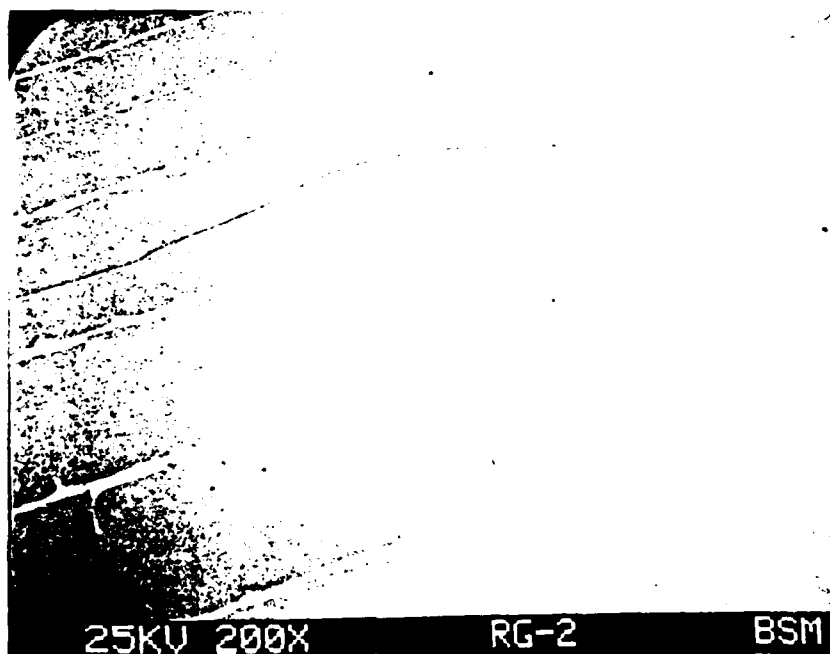showing microstructure of a
Cu-Si-Ni alloy.

Figure 9. Scanning electron photomicrograph
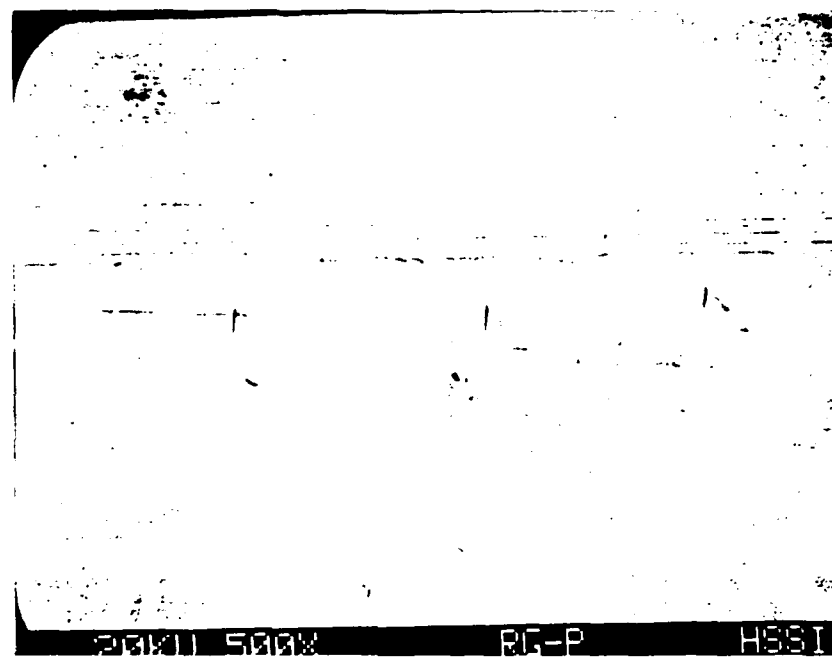showing microstructure of a
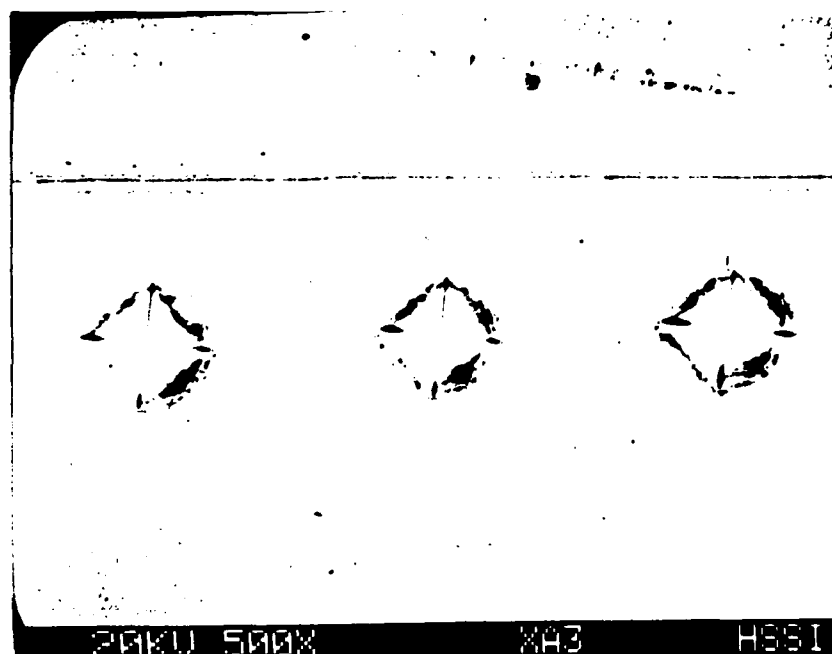Cu-Si-Ni alloy.

Figure 8.

Figure 7.

shown in Figure 7 on page 14 and Figure 8 on page 15. Sample
number XA3 is the pure nickel silicide; Sample number RG-P is
the phosphorous-containing nickel silicide. Hardness data,
expressed as DPH#, i.e. Diamond Pyramind Hardness Number, are
summarized as follows:

Sample No.	Load (Gms.)	DPH#
XA3	200	492
RG-P	200	634
XA3	1000	585
RG-P	1000	705
XA3	400	585
RG-P	300	694

Cracks began to appear at identations with 300 gram load for
sample RG-P and 400 gram load for sample XA3.

From profilometer traces of the microhardness impressions,
the indentation radius, r, and the average pile-up heighth, h,
were obtained. The ratio h/r for the two samples are virtually
identical, indicating similar ductility:

Sample RG-P $\quad\quad$ $h/r = 2.4 \times 10^{-2}$
Sample XA3 $\quad\quad$ $h/r = 2.6 \times 10^{-2}$

From the above data it can be concluded that the addition of
a small amount of phosphorous to nickel silicide has the effect
of increasing the strength and hardness while neither increasing
nor decreasing the ductility significantly. This is an important
result.

Experiments were conducted to determine the effect of copper
addition on nickel silicide. Those experiments produced alloys
with interesting microstructures. However, in no instance did
the addition of copper appear to improve the physical properties.
Indeed, quite to the contrary. Generally, the copper-containing
nickel silicided were considerably less hard. In instances the
separation into lamellar phases was apparent visually, even
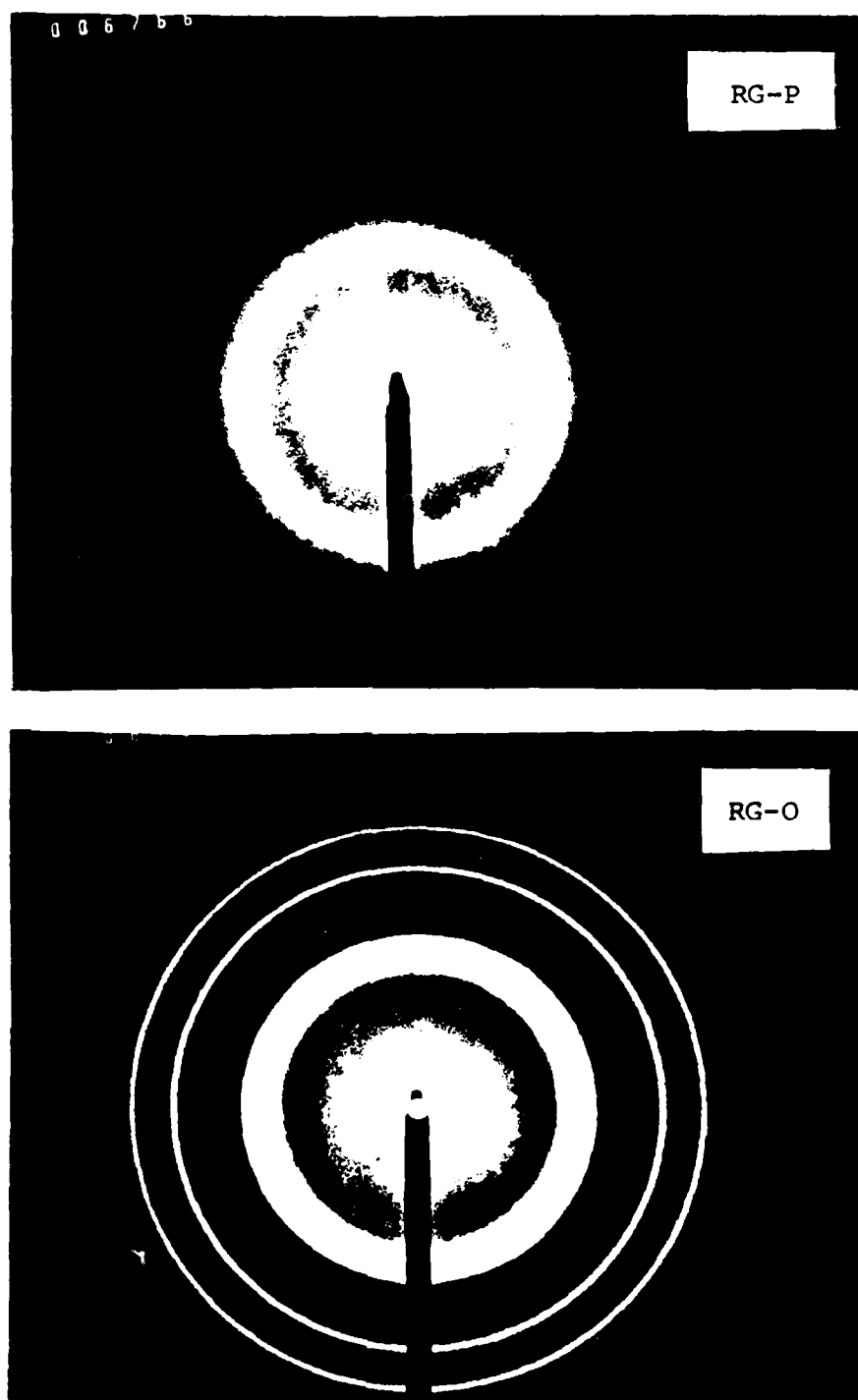without magnification. Figure 9 on page 16 and Figure 10 on
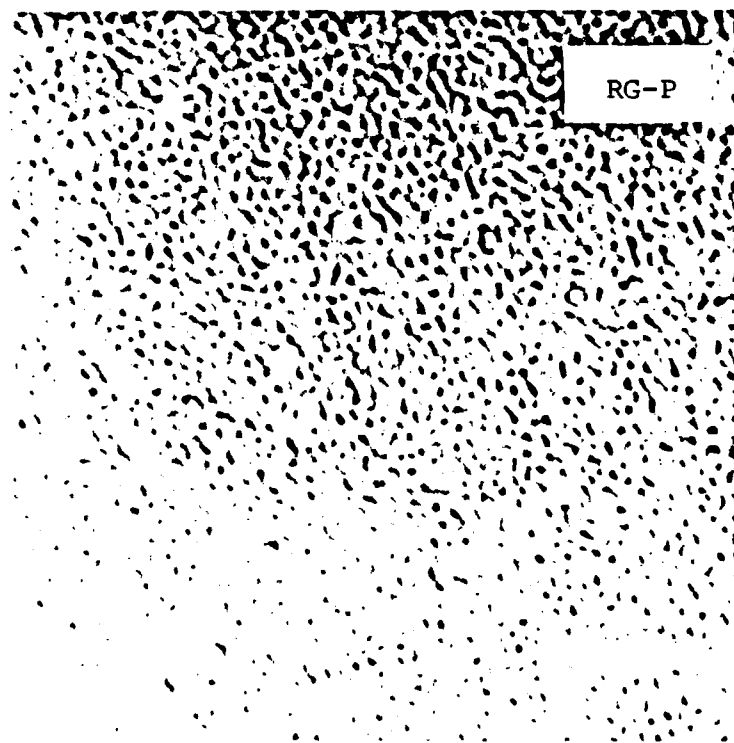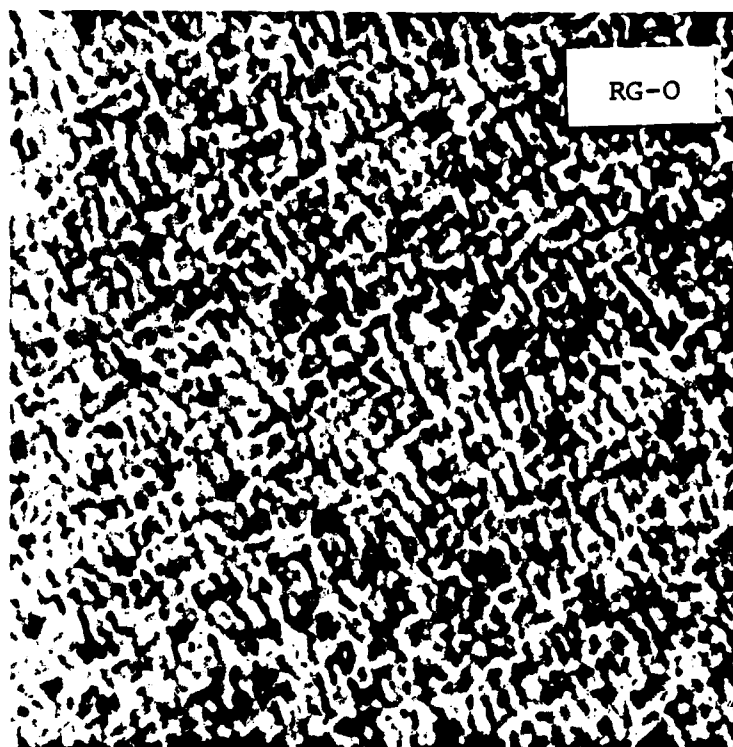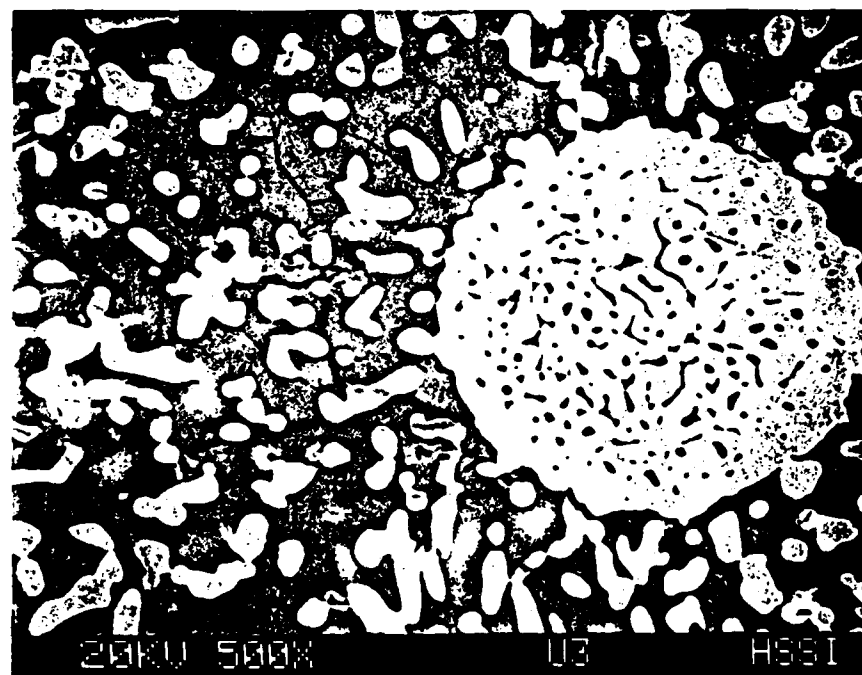
Figure 6.

Figure 5.

Figure 14.

Figure 15.

to determine whether such precipatition might occur within the time and temperature ranges used in the present investigation.

Ingots of Fe, Ni and Si of Earth core relative proportions were prepared from the elements by radio frequency induction heating on a water cooled hearth. The ingots with Ta foil were sealed in quartz ampules after evacuation and argon purge. The encapsulated samples were heated for twelve hour periods at precisely controlled temperatures in the range of 1211°C to 1333°C in platinum wound drop furnaces at the National Bureau of Standards. Subsequently the ingots were sectioned, mounted, and subjected to metallographic observation and SEM analysis. No nickel silicide precipation was observed. Even etching the samples did not reveal nickel silicide precipation. Although it would be interesting to know the time required for precipitation, further efforts would have detracted from the principle aims of the project. The negative results obtained, however, are important as background information for interpreting experimental data.

Research Objective c) was closely related to the results of experiments conducted under the first line of investigation under Research Objective b). The efforts aimed at improving the mechanical properties of nickel silicide by the addition of phosphorous were intended to lead to a new material with technological potential. Because of the problems encountered in that line of investigation, the significant results were obtained near the end of the contract. It was therefore not possible to conduct experiments aimed finding technological applications for that particular raw material.

In addition to seeking technological applications that arise from Research Objective b) investigations, some experiments are being performed with the intention of proving or disproving technologically important possibilities suggested by the literature investigation that is Research Objective a).

Silicides of the alkali earth elements are quite reactive with water and/or acids, but have comparitively high melting points. One series of experiments was undertaken to determine whether calcium silicide could be used, for example, in casting to produce a honeycomb-like structure. The experiments proved that after solidification the calcium silicide could be dissolved away leaving just the metal skeleton. Some reaction was noted, unfortunately limiting the utility of this approach. The method may have value as a way of producing decorative surfaces on gold jewelery, gold being relatively unreactive. A patent application is planned. Further experiments should be conducted.

Calcium silicide, it is known, reacts with halogen-containing acids to form a substance which, when an oxidizing agent is added, causes visible light to be emitted (chemiluminescence). Because of the chemical similarity of calcium, barium, and strontium, it seemed worthwhile to investigate whether the other silicides would chemiluminesce.

The chemiluminescent experiments were conducted using strontium silicide, barium silicide and, for reference, calcium silicide. The compounds were reacted individually with HF, HCl and HBr with constant stirring. The reaction product was hydrolized with boiling water, filtered, washed first with water then with absolute ethyl alcohol and dried. The product thus formed was reacted with the oxidizing agent, ceric ammonium sulfate. In the case of calcium silicide, chemiluminescence was observed as reported [U.S.P. 3,509,062]. The results were negative for strontium silicide. The barium silicide produced a weak chemiluminescence, however, because the color and decay curve of the emitted light was identical to that produced using calcium silicide, contamination of the barium silicide by calcium silicide is almost certain.

Pentlandite, $(Fe,Ni)_9S_8$ is an important ore of nickel in

the Sudbury district. Because iron and ████████ icides have higher melting points than the sulfide pentlandite, thought was given to the idea that by introducing elemental silicon by one of several ways that the nickel iron silicides would precipitate and sink to the bottom and sulfur could be removed as a volatile compound of silicon, e.g. SiS. Some experiments were conducted and a patent application probably will be filed. The potential utility of the method however may be limited due to energy costs to attain the necessary temperatures and the problems associated with the creation of volatile sulfur compounds, some of which were noxious.

The Principal Investigator has previously had experience with a technique employing a high energy pulsed laser to cause melting and/or evaporation in a controlled atmosphere chamber. The condensate from such experiments forms chains and, in instances, individual crystals that are so small as to require scanning transmission electron microscopic analysis. Use of such a system may be of particular value in understanding reactions of high temperature silicides. However, such a system was beyond the budget for the present research effort. The underlying principle, rapid heating to very high temperatures followed by rapid cooling, suggested another experiment.

An experiment was conducted to learn whether an electric arc might be used to produce the requisite high temperatures. The carbon arc was invented in the last century and used to create high temperatures, for example, to produce silicon carbide. An experiment was devised to determine whether a silicon arc could be created and used to form nickel silicide. An apparatus was constructed that would permit the striking of an arc between a nickel electrode and a silicon electrode in an inert atmosphere. Figure 16, page 30 shows the apparatus in operation. Several spherules resulting from the arc were found to contain the following concentrations:

Figure 16.

Sample #	Wt % Ni	Wt % Si
1	66.9	33.1
2	68.8	31.2
3	72.3	27.7

Examination by scanning electron microscopy demonstrated the homogeneous distribution of the two elements. The experiment proved the potential of the silicon arc, but further work beyond the scope of the present project will be required to yield a more controlled environment and to determine possible applications for the technology.

APPENDIX I

The Object at the Centre of the Earth

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The foundation is described for understanding the chemical composition of the inner core, the core and the lower mantle of the Earth.

The Earth consists of concentric shells of matter surrounding a nearly spherical object at the centre. The dimensions of the Earth were first known by the geometry of the ancient Greeks, but knowledge of the matter within the Earth comes from more recent discoveries, primarily arising from investigations of meteorites and earthquake waves.

The mass of the Earth, 6.0×10^{27} g, was determined by Newtonian mechanics after the universal gravitation constant had been measured. The ratio of mass to volume of the Earth, 5.5 g/cm^3, is larger than that of the rocks of its surface regions, 2.9 g/cm^3, by an amount too great to be the result of gravitational compression alone. Having observed that some meteorites are composed almost entirely of a more dense, 7.8 g/cm^3, iron-based alloy, Wiechert suggested in 1897 that the Earth has a core of similar matter [1]. Soon thereafter, in 1906, Oldham found, from studies of the nature and travel times of earthquake waves, evidence for the existence of a fluid core [2]. The Danish seismologist, Inge Lehmann discovered in 1936 that the fluid core was but another mass shell surrounding a solid object at the centre of the Earth, slightly larger than the moon, the so-called inner core [3].

Since the last century, ideas concerning the identification of the substances within the Earth have been evoked by observations of meteorites. Meteorites are rocks of extra-terrestial origin that arrive from space and survive atmospheric entry [4]. The heat of friction developed during flight through the atmosphere causes some surface melting and evaporation. But continuous removal of surface material by atmospheric drag confines thermal damage to the outer few millimeters. The identical nuclear compositions for many corresponding elements of the Earth and the more than two thousand known meteorites attests to their having been derived from primordial matter of common origin [5]. Meteorites formed about 4650 million years ago, only a few million years after the event(s) that created their elements and a few hundred million years before solidification of the oldest known Earth rocks [6]. Meteorites are mineralogically diverse. Some meteorites consist entirely of nickel-iron metal, whereas some are composed of stone and others of stone and metal together. Meteorites are diverse in elemental as well as mineral content [7]. The relative abundances of the elements in certain meteorites, called chondrites, are related to properties of the atomic nuclei [8] and are similar to corresponding abundances obtained from the spectral analysis of sunlight [9]. Some chondrites, called carbonaceous chondrites, contain organic compounds and several percent water by mass [10]. Other chondrites are anhydrous and have constituents that were at some time molten. The anhydrous chondrites consist of two principal components that are readily discerned by the criterion of whether or not light is transmitted through a thin piece of the meteorite. The translucent portion consists of oxygen-containing compounds, primarily silicate minerals. The silicate minerals generally have higher melting points and lower densities than the opaque substances that crystallized from the iron-based alloy.

The idea that the meteoritic silicate and iron-based alloy components are in some way similar to the mantle and core of the Earth has long been in the minds of scientists. But the situation is by no means straightforward. Meteorites display considerable diversity in the relative proportions of their opaque and translucent components, in the elements that comprise those components and in the compounds that crystallized
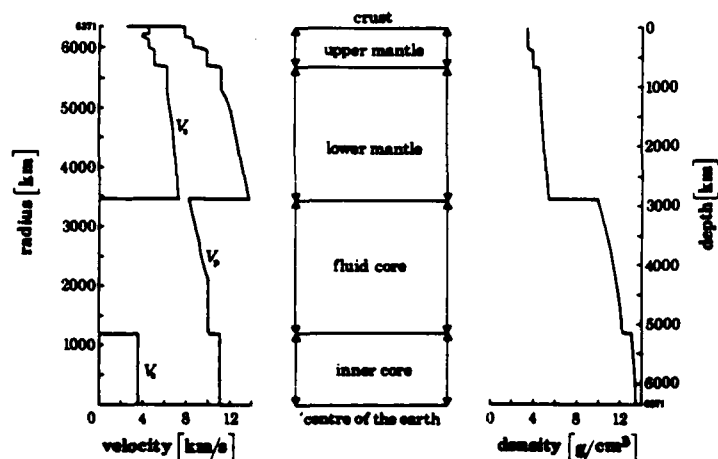
Fig. 1. The principal divisions and physical states of the interior parts of the Earth are indicated by the compressional velocity V_p and the shear velocity V_s of earthquake waves, and the density as a function of depth (from [16], based on the data of [18])

from them. The two principal components of the Earth are also complex. The mantle of the Earth is subdivided into two major parts, the upper and lower mantles, on the basis of the seismic discontinuity that occurs at a depth of about 700 km. The fluid mass shell of the core is bounded by the lower mantle and the solid object at the centre (Fig. 1).

The identification of the composition of the solid object at the centre of the Earth is inextricably related to the abundances of the elements in meteoritic matter. Because iron and nickel are alloyed in most meteorites and because heavier elements are less than one

percent as abundant, it had been thought that the inner core, which has a mass of about five percent that of the total core, consists of partially crystallized, nickel-iron metal [11]. One suggestion not related to abundances, that the inner core is the result of a pressure-induced electronic transition in iron [12, 13], was disqualified by calculations showing the Earth to be insufficiently massive for the required compression [14].

I was first to conceive of the idea that the inner core consists, not of nickel-iron metal, but of nickel silicide [15], a mineral discovered in the 1960's in members of a rare group of enstatite meteorites. Subsequently, I discovered [16], using published data [17–19], a fundamental relationship between the components of a particular type of meteoritic matter and the interior parts of the Earth, expressed as ratios of mass.

Table 1. Atomic abundances of the sixteen most abundant elements relative to iron in the Abee enstatite chondrite and in the H and L group chondrites [20]

	Abee	H group	L group
O	3.18×10^6	4.14×10^6	6.59×10^6
Na	6.05×10^4	5.17×10^4	7.45×10^4
Mg	7.46×10^5	1.19×10^6	1.63×10^6
Al	4.93×10^4	7.52×10^4	1.07×10^5
Si	1.03×10^6	1.23×10^6	1.73×10^6
P	1.20×10^4	7.15×10^3	8.32×10^3
S	3.08×10^5	1.36×10^5	1.73×10^5
Ca	3.66×10^4	6.14×10^4	8.39×10^4
Ti	2.05×10^3	2.59×10^3	3.64×10^3
Cr	1.04×10^4	1.31×10^4	1.89×10^4
Mn	1.03×10^4	8.38×10^3	1.13×10^4
Fe	$\approx 10^6$	$\approx 10^6$	$\approx 10^6$
Co	2.26×10^3	2.96×10^3	2.25×10^3
Ni	5.23×10^4	5.67×10^4	4.85×10^4
Cu	5.13×10^2	2.96×10^2	3.29×10^2
Zn	1.03×10^3	1.60×10^3	2.25×10^3

$$1.49 = \frac{\text{lower mantle mass}}{\text{total core mass}}$$

$$1.43 = \frac{\text{Abee enstatite chondrite silicate mass}}{\text{Abee enstatite chondrite alloy mass}}$$

$$0.0206 = \frac{\text{inner core mass}}{\text{lower mantle-plus-core mass}}$$

$$0.0206 = \frac{\text{Abee nickel silicide mass (theoretical } Ni_2Si)}{\text{Abee meteorite mass}}$$

The relative abundances of the major elements of the Abee meteorite are compared in Table 1 to those of the more oxygen-rich H and L group chondrites. The similarity in their elemental abundances stems from their having formed from primordial matter of

Table 2. Distribution of the elements among the lower mantle and total core (fluid mass shell plus inner core), calculated from the data of [17, 18, 23] (in g)

Lower mantle

O	1.53×10^{27}	Al	3.96×10^{25}	Mn	5.77×10^{24}
Si	7.85×10^{26}	Na	3.36×10^{25}	Fe	5.02×10^{24}
Mg	5.05×10^{26}	Ca	2.38×10^{25}		

Total core

Fe	1.45×10^{27}	Ca	1.84×10^{25}	Ti	2.23×10^{24}
S	2.84×10^{26}	Cr	1.58×10^{25}	Zn	2.09×10^{24}
Ni	8.31×10^{25}	P	9.32×10^{24}	Cu	8.61×10^{23}
Mg	4.75×10^{25}	Mn	5.34×10^{24}		
Si	3.26×10^{25}	Co	4.15×10^{24}		

Table 3. Combinations of light elements previously suggested as being alloyed with nickel and iron in the core of the Earth

C, Si, H [24]	Si [28, 29]
C, S [25]	C, S, Si [30]
Si, O, S [26]	S [31-33]
Mg, O [27]	O [34, 35]

well defined chemical composition. The compounds formed of the elements in Abee and in the rare enstatite meteorites are unlike those found in other types of meteorites or in the surface regions of the Earth. In the more oxygen-rich meteorites all silicon, all magnesium, and some iron, are combined with oxygen as silicate minerals. That results in their having significantly greater silicate to alloy mass ratios than the 1.43 of the Abee meteorite [21], for example:

$$3.58 = \frac{H \text{ group chondrite silicate mass}}{H \text{ group chondrite alloy mass}}$$

$$7.28 = \frac{L \text{ group chondrite silicate mass}}{L \text{ group chondrite alloy mass}}$$

The Abee meteorite and the interior of the Earth formed under conditions of limited available oxygen. The silicate phase, corresponding to the lower mantle of the Earth, consists primarily of enstatite ($MgSiO_3$) that is practically devoid of oxidized iron. During formation, available oxygen was so limited that even some magnesium and some silicon remained uncombined as components of the iron-based alloy [22]. The presence of elemental silicon is a necessary condition for the initial precipitation of nickel silicide.

The distribution of the elements among the lower mantle and total core shown in Table 2 is predicted by analogy with the components of the Abee meteorite. Only those elements are shown whose distribution is known among the silicates and the minerals that crystallized from the iron-based alloy of the Abee meteorite [17].
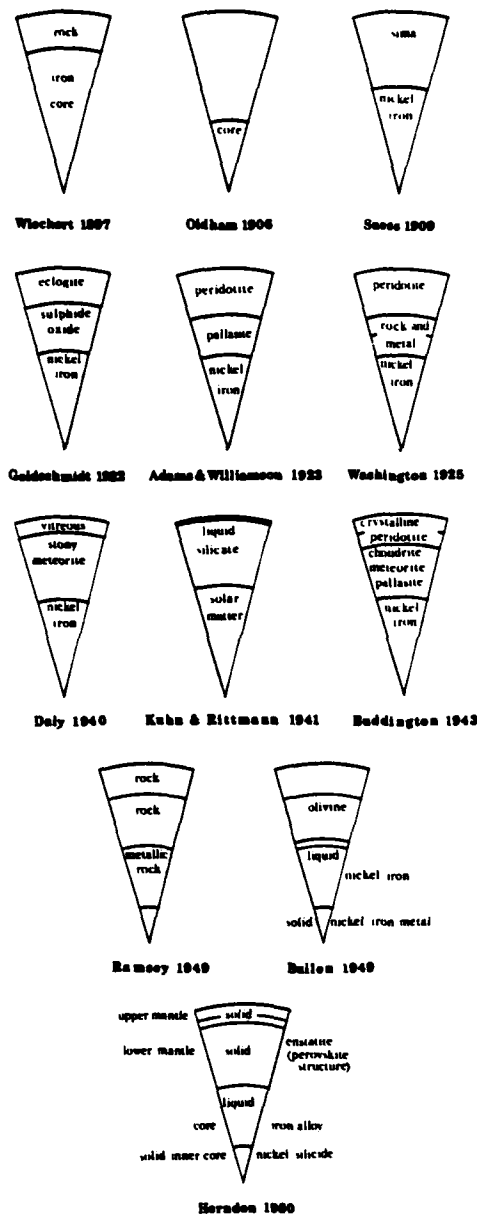
Fig. 2. Schematic representation of the evolution of ideas bearing on the composition of the interior of the Earth [1, 2, 16, 37-45]

Birch [21] found from density distribution calculations that the mean uncompressed density of the total core of the Earth is 5–15% less dense than iron or, alternatively, that the mean atomic mass of the total core is 5-15% lighter than the atomic mass of iron. The mean atomic mass of the iron-based alloy of the Abee meteorite and, hence, of the total core of the Earth, calculated from the abundance distribution shown in Table 2, is 13.9% lighter than the atomic mass of iron. Various combinations of light elements have been suggested as being alloyed with nickel and iron in the core of the Earth (Table 3), but none are like the combination of elements shown in Table 2.

The values for mean atomic number and mean atomic mass of the total core of the Earth found by Knopoff and MacDonald [36] to be consistent with shock wave velocity data and density measurements and with seismic observations are identical to those of the iron-based alloy of the Abee meteorite calculated from the mineralogical data of Keil [17].

	Z	$\bar{M}$
Abee meteorite iron-based alloy	22.8	48.08
Seismologically deduced values	23	48

The evolution of ideas bearing on the composition of the interior of the Earth is schematically represented in Fig. 2.

Whereas determination of the mass distribution or pressure within the Earth is straightforward, estimation of the temperature is not. The idea is invalidated that the temperature at the boundary of the inner core can be obtained by extrapolation of the melting point curve of iron to the respective pressure [46]. Until such a time that melting point measurements as functions of pressure have been made for nickel silicide and until phase relations in the medium of the composition shown in Table 2 have been elucidated, the temperature near the centre of the Earth will remain unknown.

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