(NASA-CR-153980) VOLATILE TRACE ELEMENTS IN PRIMITIVE METEORITES (Purdue Research Foundation) 12 p

N77-83596

Unclas

00/91 42028

Twelfth Semiannual Progress Report

March, 1977 - August, 1977

for

National Aeronautics and Space Administration

Grant NGL 15-005-140

entitled

Volatile Trace Elements in Primitive Meteorites

awarded to

Purdue Research Foundation

Purdue University

West Lafayette, Indiana 47907

prepared by

Michael E. Lipschutz, Principal Investigator

Professor of Chemistry and Geosciences

Purdue University

West Lafayette, Indiana 47907

Date of Report: September 1, 1977

I. General Remarks

Since submission of our Eleventh Semiannual Progress Report (September, 1976 - February, 1977) the following papers have been published, are still in press, or have been submitted:

(a) Thermal Metamorphism of Primitive Meteorites-III. Ten Trace Elements in Krymka L3 Chondrite Heated at 400-1000°C.
M. Ikramuddin, C. M. Binz and M. E. Lipschutz
Geochimica et Cosmochimica Acta, 41, 393-401 (1977).

(b) Condensation and/or Metamorphism: Genesis of E- and L-Group Chondrites from Studies on Artificially Heated Primitive Congeners.
M. E. Lipschutz and M. Ikramuddin
Proceedings of Colloquium No. 39, International Astronomical Union (Lyon, France), in press (1977).

(c) Thermal Metamorphism of Primitive Meteorites-V. Ten Trace Elements in Tieschitz H3 Chondrite Heated at 400-1000°C.
M. Ikramuddin, S. Matza and M. E. Lipschutz
Geochimica et Cosmochimica Acta, in press (1977).

(d) Thermal Metamorphism of Primitive Meteorites-VI. Eleven Trace Elements in Murchison C2 Chondrite Heated at 400-1000°C.
S. D. Matza and M. E. Lipschutz
Proceedings of the Eighth Lunar Science Conference, in press (1977).

(e) Volatile/Mobile Trace Elements in Karoonda (C4) Chondrite.
S. D. Matza and M. E. Lipschutz
Geochimica et Cosmochimica Acta, in press (1977).

(f) Further Mobile Element Studies in Heated Abee (E4).
M. Ikramuddin, M. E. Lipschutz and E. K. Gibson, Jr.
Geochimica et Cosmochimica Acta, submitted (1977).

II Status of Projects

During the period covered by this Report we have devoted most of our efforts to studies of various chemical and physical changes induced in primitive meteorites heated under conditions simulating open-system, thermal metamorphism in early parent bodies. In most cases to be discussed (except under items IIA1, IIA2 and IIB) samples were heated under standardized conditions, i.e. at 100°C increments for 1 week under a low pressure (initially $\sim 10^{-5}$ atm) H_2 atmosphere. In the past few years we concentrated upon determination of 10-11 mobile trace elements in various primitive chondrites by destructive neutron activation analysis to conduct a comparative survey at temperatures $\leq$ 1000°C; we are continuing these productive studies but have expanded into other areas as discussed below. In effect this has created a broad consortium study, the results of which are now beginning to become apparent.

Below, we summarize our progress during the past 6 months in categories subdivided according to the very different techniques used: mobile trace elements in unheated chondrites and samples heated from 400-1000°C; mobile trace elements in samples heated from 1000°-1500°C; mobile trace element transport mechanisms; mineralogic and petrologic studies; major and minor elements in samples heated from 1000-1500°C; noble gas measurements; carbon and sulfur measurements.

A. Trace Element Studies

1. Unheated Chondrite - Karoonda (C4)

As discussed in the Eleventh (September, 1976 - February, 1977) Progress Report our measurements of mobile Ag, Bi, Cd, Cs, Ga, In, Se, Te, Tl and Zn and non-volatile Co are consistent with the suggestion by McSween that

Karoonda represents a C3 chondrite thermally metamorphosed in an open system in a parent body at temperatures of 500-600°C. During the period covered by this Report we extensively revised the paper describing these results and it is now in press (cf. paper (c) in part I). These results and those to be described in parts IIA2c and IIC1 below also bear upon a common question: whether C3(0) chondrites represent a suite of chondrites thermally metamorphosed in a parent body.

2. Chondrites Heated at 400-1000°C

In the studies to be described in this part and in part IIA3, samples are heated at temperatures $\geq$ 400°C under our standardized conditions; the nature of the apparatus differs above and below 1000°C, however. We study trace element retentivity as a function of temperature in each primitive chondrite heated under this standardized set of conditions so as to simulate open-system thermal metamorphism in a parent object. For each set of samples we use the retentivity data to calculate apparent trace element bond energies in the host phases. We compare trace element trends (including statistical evaluations of the raw abundance data) in a suite of heated primitive chondrite samples with those in unheated congeners to assess whether metamorphism could have played an important role in the evolution of that chondritic type. At times (as in part IIA1 above) we must also determine the volatile/mobile trace element content of such unheated samples. Finally, we compare trace element trends in heated samples of chondrites of different types which nonetheless apparently share a related origin; we note specific instances below in summarizing advances achieved since submission of our Eleventh Report.

a. Krymka (L3)

Our results from study of Ag, Bi, Co, Cs, Ga, In, Se, Te, Tl and Zn in this chondrite were described in the Tenth (March, 1976 - August, 1976) Progress Report. This paper has now been published (cf. paper (a) in part I). A comparison of results for this chondrite with those for Abee (E4) has not yet appeared (cf. paper (b) in part I). This comparison points to differences in the genetic histories of E3-6 and L3-6 chondrites; results for the former are consistent with an episode of open-system thermal metamorphism in a parent object while the latter apparently escaped such an event.

b. Tieschitz (H3)

Our study of Ag, Bi, Co, Cs, Ga, In, Se, Te, Tl and Zn in this chondrite was described in the Eleventh Progress Report. This paper - which has now been accepted and is in press (cf. paper (c) in part I) - leads to the conclusion that H3-6 chondrites, like L3-6 chondrites but unlike E3-6 chondrites and Karoonda, escaped an episode of open-system thermal metamorphism.

c. Murchison (C2)

Our study of Ag, Bi, Cd, Co, Cs, Ga, In, Se, Te, Tl and Zn was summarized in the Eleventh Progress Report. Since that time the manuscript was submitted to the Proceedings of the Eighth Lunar Science Conference and was revised; it is now in press (cf. paper (d) in part I). As noted, comparison between trends in Allende (C3) and Murchison indicates differences in the genetic histories of these carbonaceous chondrites, possibly including a low-temperature sintering by mild, closed-system metamorphism of Allende parent material. Thus carbonaceous chondrites are not merely simple mixtures of material differing in thermal history, but in some cases suffered post-accretion processing. Furthermore Murchison may act as a prototype for previously unprocessed material in view of differences in its response to thermal treatment compared with other chondrites. Trace element data for Karoonda (section IIA1) and heated Murchison samples and mineralogy/petrology results (section IIC1) re-enforce McSween's suggestion that C3O chondrites acquired many mineralogic/petrologic properties by low-temperature sintering.

d. Allende (C3O)

As noted in the Eleventh Progress Report, our original feasibility study involved but 6 elements in this chondrite (Bi, Co, Ga, In, Se and Tl) compared with the 10-11 elements included in subsequent investigations (e.g. parts IIA2 a-c) and it would be helpful for genetic comparisons if all chondrite studies included the same elements. Furthermore, experiments at temperatures > 1000°C indicate that retention of some of these elements at higher temperatures might be below our detection limits. Accordingly we broadened our scope to include determination of additional elements - Ag, As, Cd, Cs, Cu, Rb, Sb, Te and Zn (plus Co and Tl as internal comparison monitors) - in this meteorite.

During the period covered by this Report we completed testing of our analytical methods by completing analysis of 11 unheated samples to reduce the precision to reasonable levels and establish accurate values for initial contents. Heating experiments at three temperatures have been completed and analysis of the 600°C sample is in progress.

e. Orgueil (C1)

Of all meteorites, C1 chondrites are closest compositionally to unfractionated solar material. Study of the response of this chondrite to heating should yield unique information on the response of primitive material to early heating episodes and will allow comparison of trends among C1-3 chondrites. Subsequent experiments (cf. part IIA3) on samples heated > 1000°C suggest the wisdom of expanding coverage and we decided to determine 15 trace elements - Ag, As, Bi, Cd, Co, Cs, Cu, Ga, In, Rb, Sb, Se, Te, Tl and Zn.

We have designed an analytical procedure for these elements and are now beginning to test it. By March 1978 we hope to begin analysis of unheated samples to assess precision and accuracy.

f. Abee (E4)

This study involved two aspects: determination of C and S (in cooperation with Dr. E. K. Gibson, Jr.) in samples heated under standardized conditions from 400-1000°C; determination of Ag, Bi, Co, Cs, Ga, In, Se, Te, Tl and Zn in samples heated at 700°C for 1 week under pressures of $\sim 10^{-5}$, 10^{-4} and 10^{-3} atm Ne. The latter experiments were performed to determine whether the increased trace element retention in runs in which large quantities of gas were evolved from the samples was due to physical interactions in the gas phase.

We found that eight trace elements are retained or lost more easily from Abee (E4) heated at 700°C for 1 week in 10^{-5} - 10^{-3} atm Ne than in 10^{-5} H_2. Mobile Zn and In are exceptional; their retention varies inversely with ambient Ne pressure and both are better retained in Ne than in H_2. Thus physical interactions in the gas phase do not affect mobile element transport. During week-long heating at low pressures (initially $\sim 10^{-5}$ atm H_2) S is mobilized only at 1000°C while C contents decrease progressively from 600-1000°C. Apparent activation energies for C are 60 and 16 kcal/mole below and above 700°C; as for In but not Bi, Tl or Zn these values are consistent with diffusive loss from different hosts in different temperature intervals. In E4-6 chondrites C and S contents largely reflect nebular fractionation and condensation processes.

As noted in part I (cf. paper (f)) this manuscript has been submitted to a journal for consideration.

3. Chondrites Heated at 1000-1500°C

As discussed in the Eighth (March, 1975 - August, 1975), Ninth

(September, 1975 - February, 1976), Tenth and Eleventh Reports we have been interested in extending our studies to temperatures above 1000°C; this temperature region would extend into the formation region of achondrites and iron meteorites, a zone of great interest because geochemical fractionation effects can be anticipated. Furthermore, results from experiments in this temperature region would be useful for characterizing the genetic process of the high-temperature portion of carbonaceous chondrites, i.e. whether this portion represents material condensed directly from the nebula at high temperature or low-temperature material melted in a transient episode in the nebula or on parent objects. To a considerable extent there could also be a time-temperature trade-off so that such experiments could be used to study chondritic mineral equilibration.

The major problem in extending our studies to these high temperatures was one of materials; to design an apparatus that would survive at high temperature and low vacuum, would be inert to attack by molten chondrite, would not contaminate the chondritic charge and would be inert in affecting trace element retentivity. As reported in the Eleventh Report, most of these containment problems were apparently solved - at least at temperatures $\leq$ 1200°C. Since then some problems arose which we solved; we are now analyzing the first suite of samples.

a. Allende

We have completed heating runs at 1000, 1100, 1200, 1270, 1315 and 1400°C and completed analysis of Ag, Bi, Cd, Co, Cs, Ga, In, Se, Te, Tl and Zn in homogenized powder from the 1000, 1100 and 1270°C runs; we have also analyzed chips from the 1270°C run to assess contamination problems at these ultra-trace levels. Analysis of homogenized powder from the 1200 and 1315°C are in progress. While it is premature to describe our results in detail we report loss of <u>all</u> elements is more facile and progresses to extremes of well over 99.9% at 1270°C with a steepening of the slopes on Arrhenius diagrams. We modified our chemical and counting techniques slightly so that all elements should be detectable even in the highest temperature heating run. By March, 1978, we intend to have completed all experimental work on this project and to have completed a manuscript describing this project.

b. Murchison

Heating runs at 1100, 1315 and 1400°C are completed and analysis of Ag, Bi, Cd, Co, Cs, Ga, In, Se, Te, Tl and Zn in homogenized powder is in progress. We hope to be nearly finished with experimental work on this project by March, 1978.

c. Abee

Heating runs at 1100 and 1270°C are completed. Two unheated powder samples and one heated at 1270°C have been analyzed for Ag, Bi, Cd, Co, Cs, Ga, In, Se, Te, Tl and Zn; analysis of a powder sample heated at 1100°C is in progress.

B. Theoretical Modeling

During the period covered by this Report we have begun to evaluate various models for mobile element siting in relation to expected trends for loss. Included thus far are consideration of desorption versus volume diffusion and siting in two chemically different hosts; thus far these do not markedly alter any conclusion obtained previously. We plan to complete this study after March, 1978 using several elements - probably In, Se and Tl - in Allende heated at 400-1400°C as model elements.

C. Mineralogy/Petrology

1. Murchison

W. R. Van Schmus had no ready access to a microprobe and could not therefore devote the necessary time to mineralogic/petrologic investigations of heated meteorites; we decided to undertake study of the simpler carbonaceous chondrites ourselves. Murchison is being studied in polished section and its study is farthest along: unheated, 800, 900, 1000, 1100 and 1315°C samples are completed; and other samples are in various stages of preparation (cf. part IIA 3b). Among changes noted are that the matrix becomes more coarsely crystalline and sulfides begin to decompose at ∿ 800°C; by 1315°C the chondrite is entirely altered to olivine and chromite. Up to 900°C the heterogeneity of olivine in the matrix is unaltered, but from 900 to 1100°C the mean fayalite content increases progressively from 14.0 to 27.9% and the percent mean deviation decreases progressively from 124 to 42%. By 1315° the olivine is nearly uniform in composition. We plan to complete detailed study of this chondrite by March 1978.

2. Allende

Sections of this meteorite from all temperature runs (cf. part IIA 3a) have been prepared: polished thin sections from those at ≤ 1000°C and polished sections from those > 1000°C. We plan to begin study of these samples shortly; this will be completed only after March 1978. A cursory look at the samples indicates only minor textural changes ≤ 1100°C but at ≥ 1200°C the structure is entirely altered.

3. Krymka

Polished thin sections from all heating runs at temperatures ≤ 1000°C (and unheated material) have been prepared and sent to Professor H. Y. McSween (University of Tennessee) who is very interested in working on these samples. Professor McSween has had extensive experience with C30 chondrites and has argued very persuasively that these constitute a metamorphic sequence, a conclusion which our experiments on Murchison support (cf. part IIC1). He is interested in extending his studies to heated ordinary chondrites, like Krymka.

D. Major and Minor Elements

During the period covered by this Report we found that trace element losses from Allende heated > 1000°C are severe, indeed even Co is lost to some extent. (Unpublished data indicate loss of Fe, Ni, Ca, K, Ti, Al and Na from Murchison at 1315°C). This suggests that instrumental neutron activation analysis (INAA) of heated chondrites - especially those heated > 1000°C - would be useful to examine the mobility of major and minor elements. Furthermore, since these form discrete compounds (minerals) with known thermodynamic properties, calculated apparent activation energies can be compared with known thermodynamic data to check mobilization models.

Since March 1977 we have carried out experiments on BCR-1 and Allende using a low flux ($\sim 10^9$ n/cm^2/sec), swimming pool reactor at Purdue to test out the feasibility for INAA. The preliminary results are encouraging and we will probably be able to determine numerous elements including Al, Ba, Ca, Cl, Cr, Fe, K, Mg, Mn, Na, Sc and some rare earths. Since INAA is a fairly standard technique we hope to complete all preliminary experiments and replicate analyses of unheated samples to assess accuracy and precision by March 1978.

E. Noble Gases

During the period covered by this Report Dr. G. Herzog completed measurement of all He, Ne, Ar, Kr and Xe isotopes in Allende samples heated at 400-1000°C during his sabbatical stay at Heidelberg. We have only just begun to examine the results both intrinsically and in comparison with data from short-term step-heating experiments by Manuel and co-workers. The most obvious results are that ^{3,4}He decrease progressively starting at 400°C - to extremes of > 100x. Loss of ^{20,21,22}Ne begins at 600°C while ^{40}Ar begins at 400°C; ^{36,38}Ar, ^{84}Kr and ^{132}Xe are lost only $\geq$ 900°C while other Kr and Xe isotopes are retained even at 1000°C. Extreme losses of all noble gases but He are $\leq$ 10x. Apparent activation energies are ordered as $^{3,4}He \sim {}^{40}Ar < {}^{20,21,22}Ne$

$< {}^{36,38}Ar \sim {}^{84}Kr \sim {}^{132}Xe$. We plan to begin a paper describing our results after Dr. Herzog returns and hope to complete this by March 1978. The results suggest that it would be worthwhile continuing measurements on ordinary chondrites at least and Dr. Herzog indicated his interest in carrying this out on his return.

F. Carbon, Sulfur

Dr. E. K. Gibson has completed C, S measurements of Abee (cf. part IIA2e and will shortly begin on Murchison - both sets of samples having been heated at 400-1000°C. These experiments should be completed by March, 1978.

III Administrative Information

The following individuals are co-workers at Purdue currently doing research on this grant:

A. Dr. G. Bart, Postdoctoral Research Associate

B. Mr. S. Matza, Graduate Assistant in Research

C. Mr. H. Ngo-The, Graduate Assistant in Research

D. Mr. J. Carvalho, Graduate Research Assistant

E. Mr. C. Neal, Graduate Assistant in Research

The NASA Technical Officer for this grant is Dr. B. French, NASA Headquarters, Lunar Programs Office, Code SL, Washington, D. C. 20546.

Michael E. Lipschutz

Michael E. Lipschutz

cc. Dr. French, NASA
Prof. Benkeser, Purdue
Dr. Waling, Purdue

MEL:JHB