Observation of Non-lithophile Behavior for U

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Abstract. In the Hvittis enstatite chondrite
fission track radiography shows that U is highly
concentrated in CaS (oldhamite), with a concen-
tration of 400±50 ppb. The oldhamite U concen-
trations are equilibrated, although intergrain
concentration variations of less than 15% would
not be detected. Various approaches to a U
material balance do not agree, but at least 50%
and, more likely, nearly 100% of the U is con-
centrated in CaS. It is likely that CaS is the
major reservoir for other actinide and lanthan-
ide elements as well. Consequently, enstatite
chondrites may provide reliable Pu/U abundance
ratios. The highly reducing formation con-
ditions for enstatite chondrites have caused U
to deviate from lithophile behaviour, but K is
observed to remain lithophile. Although this
observation may not be generalizable, we propose
that discussions of radioactive heating of
planetary cores should include U and Th and
not focus exclusively on K.

Introduction

In essentially all natural occurrences U ex-
hibits strongly lithophile character, concentrat-
ing in silicate, oxide or phosphate minerals.
Deviations from lithophile character are impor-
tant because incorporation of U into sulfide or
metallic phases would potentially serve as a
heat source for planetary cores. Heating of
metal or metal-sulfide cores is necessary for a
variety of reasons, e.g. to generate fluid mo-
tions to produce planetary magnetic fields (Ja-
cobs, 1975; Gubbins and Masters, 1979; Stevenson,
1981). Although radioactive heating may not be
necessary, K is usually taken as the important
radioactive element in discussions of core
heating by radioactive decay (relevant litera-
ture reviewed in Jacobs, 1975; Brett, 1976). An
exception is Ruff and Anderson (1980) who also
considered heating by U and Th. Laboratory
experiments have shown that Pu, U and to a lesser
degree Th can be reduced from a silicate melt to
dissolve in Pt-metal alloys but very low limits
were set on the partitioning of U into FeSi and
FeC alloys (Jones and Burnett, 1980). This
paper demonstrates that in the Hvittis E6 enstat-
ite chondrite, extremely reducing formation
conditions have caused U no longer to be litho-
phile, but rather to assume chalcophile character

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and concentrate in CaS. However, K has remained
lithophile.

Experimental

Quantitative U fission track radiography, as
described in Stapanian (1980) or Jones and Bur-
nett (1979), was performed on three polished
sections of Hvittis. Muscovite mica track detec-
tors were clamped on the sections during irradia-
tion by $\sim 2 \times 10^{18}/cm^2$ thermal neutrons. The dist-
ribution of ^{235}U fission tracks on the mica
provides an image of the distribution of U in
the meteorite. By comparison of the densities
(tracks/cm^2) of tracks with the densities of a
standard, U concentrations can be determined for
regions (phases) which are large compared to the
fission fragment ranges (10-20 microns).

Results

The fission track images of the Hvittis
sections showed an unusually high degree of track
localization. Mapping of the locations of the
track clusters back onto the sections showed that
U was highly concentrated in CaS (oldhamite).
The sources of 42 track localizations were in-
vestigated with an SEM plus semiconductor X-ray
detector, yielding 39 CaS grains, two holes
(either plucked CaS or contamination U) and one
K-Al-Si-rich region. Despite a deliberate
search, no U-poor CaS grains were located. U
concentrations, based on the track density in
the center of the grain, were measured for the
larger CaS grains (usually >50 microns since
the calculated fission fragment range in CaS is
20 microns). U concentrations were uni-
form within counting statistics (50-200 tracks/
grain) within a given section. For the three
sections the U concentrations are 387, 351 and
323 ppb U with a precision (standard deviation
of mean) of ±4% for each measurement. The dif-
ferences are significant and cannot be explained
by reactor flux gradients. The U concentrations
include a 30% correction for the fission fragment
range difference between CaS and our glass U
standard. Microprobe analyses of CaS grains
after irradiation indicate S loss, probably due
to oxidation (CaS is a metastable phase under
terrestrial conditions). Assuming no U volatili-
zation, this could lead to underestimation of U
concentrations by up to 30%, because of overcor-
rection for range differences, if complete oxida-
tion has occured. Variations in the degree of
oxidation among sections could explain the varia-
tions in average U content in CaS for different
sections. Other sources of systematic error
(poor sample -detector contact, track counting
at high track densities, etc.) will also lead to
low concentrations, although these should not
be significant. Consequently the best estimate
of the U concentration of Hvittis CaS is 400±50
ppb. Random scans over 0.6 mm^2 of one mica

detector gave a total rock concentration of
4.4±0.2 ppb in reasonable agreement with
the neutron activation U content (6.2ppb) by
Morgan and Lovering (1968), but, more important-
ly, documented that at least 80% of the tracks
are not randomly distributed but are localized
in regions of dimensions of 10 microns or
larger. Because the large (50-100 micron) track
localizations were shown to correspond to CaS,
the observed localization down to ~10 microns
suggests that essentially all of the U in Hvittis
is found in CaS. Coupled with the uniform U
concentrations among CaS grains, this is suggest-
ive of an equilibrium distribution of U. In
this sense E6 chondrites may be more equilibrat-
ed than type 6 ordinary chondrites, for which U
may not have an equilibrium distribution among
the various phases (Jones and Burnett, 1979).
However, modal estimates of CaS do not account
for all of the 6 ppb total rock U: Keil (1968)
gives 0.2% by weight CaS based on petrographic
point counting of 6 cm^2 of section; however,
this seems low for our sections since the
area of large CaS grains investigated for tracks
alone corresponds roughly to this much CaS.
Using total rock Ca, Al, Mg concentrations
(Von Michaelis et al., 1969), and microprobe
mineral concentrations (Keil, 1968), a CaS modal
abundance of 0.7% is obtained from mass balance.
This would still only account for ~50% of the
U in CaS. Plagioclase and enstatite are ruled
out because they would be required to have 20
and 5 ppb U respectively to account for the
missing U. Enrichments of this magnitude would
have been readily recognized in the track distri-
butions. Large metal or FeS grains have at least
an order of magnitude less U than CaS. In other
E6 chondrites MnS has ~1/20 the U of CaS (Murrell
and Burnett, 1981) but this is an insignificant
contribution to the total rock U. Subsequent
work will investigate the material balance fur-
ther, but it is likely that these discrepancies
simply represent a very inhomogenous distribu-
tion of CaS.

For comparison with U, one of our sections
was carefully searched for K-bearing phases.
Since plagioclase is the only Al-bearing phase,
comparison of the total rock K/Al (Von Michaelis,
et al., 1969) with the average plagioclase K/Al
(Keil, 1968) indicates that 75-85% of the K is
accounted for by plagioclase. We observed small
(<10 micron) K-Al-Si-rich areas, primarily as in-
clusions in plagioclase. An analysis of the lar-
gest area gave ~80% SiO$_2$, too high for K-feld-
spar, suggestive of either residual glass or
fine SiO$_2$, K-feldspar intergrowths. A quantita-
tive assessment of these K-rich areas is diffi-
cult, but they seem sufficiently abundant to
account for the 15-25% of K not accounted for by
plagioclase. No other K-rich phases were found.
Djerfisherite (a K-Fe-Cu-sulfide) is found in
some unequilibrated enstatite chondrites (see,
for example, El Goresy et al., 1971) but has not
been reported in equilibrated enstatite chon-
drites.

Discussion

Our data indicate that CaS in E-chondrites is
the analog of the Ca-phosphates in ordinary chon-
drites in being an important U-bearing reservoir.

Subsequent work has shown Th concentration in CaS
(Murrell and Burnett, 1981). Oldhamite is also
likely to be an important reservoir of Pu and the
rare earths, although laboratory observations of
U and Pu reduction and alloying from silicate
melts were not accompanied by similar behaviour
for Sm (Jones and Burnett, 1980). If the highly
reducing conditions during the formation of
E-chondrites have produced trivalent U as well
as Pu (Benjamin et al., 1978), then minimal
chemical fractionation of these elements may
result. Even if CaS does not contain all of the
actinide and lanthanide elements in equilibrated
E chondrites, the same valence state (+3) for Pu
and U would make these meteorites the best avail-
able source for solar system Pu/U ratios.

As with all other geochemical data, our re-
sults do not yield unambiguous, model-independent
conclusions about the possibility of radioactive
heating of planetary cores. Our direct observa-
tion is that under low pressure, highly reducing,
metamorphic (800-1000°C?) conditions, U loses
lithophile character but K does not. Even avoid-
ing the semantic discussion of whether "chalco-
phile" should be restricted to FeS, our results
show no tendency for U to be incorporated into
metal (consistent with Jones and Burnett, 1980)
or FeS, although reasonably high U concentra-
tions (4-17ppb) have been reported in FeS from
iron meteorites (as tabulated by Morgan, 1971).
Whether or not significant quantities of highly
reduced, E-chondrite-like, materials were accret-
ed into the Earth is unknown. Also, the degree
of solubility of CaS or miscibility of liquid
CaS with molten Fe-FeS at higher temperatures
is unknown. However, if solubility or miscibili-
ty is negligible, then, barring transitions to
denser phases, the low density of CaS would tend
to keep it near the surface if it were a signifi-
cant constituent in the accreting earth mater-
ials. The observation of djerfisherite in some
unequilibrated E chondrites and aubrites is a
complication to the generality of our observa-
tion; however the disappearance of djerfisherite
in equilibrated E-chondrites suggests that it is
a disequilibrium phase. It has been argued that
K-sulfides are stable phases only at high temper-
atures (Goettel, 1975; Goettel and Lewis, 1973);
thus the djerfisherite alternatively could be
interpreted as part of a high temperature compo-
nent in unequilibrated E chondrites which disap-
pears at metamorphic temperatures. However, we
speculate that djerfisherite is an alteration
product of a K, S, Cu-rich vapor (impact pro-
duced?) reacting with Fe-Ni metal or Fe-Ni sul-
fide. Vapor phase alteration, probably impact-
derived, is a very plausible mechanism to explain
ultra-fine-grained Pb, Bi-rich metals and co-
existing magnetite in some unequilibrated ordi-
nary chondrite (Woolum et al., 1981). Clarke
et al. (1977) have found K-sulfide in a kimber-
lite nodule, but formation as a vapor-phase
alteration product was the favored origin by
these authors (Clarke, 1977).

Consequently, we consider it entirely possi-
ble that under all conditions where K would tend
to be partitioned significantly into non-oxygen-
bearing phases, U (and Th) would be partitioned
more strongly into such phases and perhaps be
incorporated under less extreme (e.g. fO$_2$) cond-
itions. Thus it is not clear to us that the

effect of partitioning of radioactive elements
into the core would favor K and thus would lower
the K/U of the earth relative to chondrites as
has been generally assumed. Measurable K parti-
tioning into Fe-FeS has been reported in several
synthesis experiments (Goettel, 1972, 1975;
Oversby and Ringwood, 1973; Ganguly and Kennedy,
1977) but, except for Goettel (1972), these are
basically qualitative observations. The measured
amounts of K in all these experiments would be
significant for core heating. The behaviour of
U and Th in similar experiments has not been
studied. We conclude that, at present, discus-
sions of radioactive heating of planetary cores
should not focus exclusively on K, although
the necessity for radioactive heating, in gener-
al, has not been established.

Bukowinski (1979) has calculated that at high
pressures the outer electrons in atomic K will
be in predominently d states and thus K will
become a transition metal and alloy more readily
with Fe. This could invalidate our hypothesis,
but similar calculations do not exist for U.
Thus, it is possible that U would also show
metallic character at high pressures as well.
Also, it is not clear that the calculations are
valid for K-Fe-S alloys (as opposed to K metal).
Finally, Somerville and Ahrens (1980) failed to
observe transitions of $KFeS_2$ to a metallic
state for pressures up to 110 GPa.

For some specific models, stronger conclusions
are possible. For example, if S is not an impor-
tant constituent of the Earth's core and if the
metal separated near the surface at low pressure,
then the present Hvittis results suggest (but
certainly do not prove) that U would be more
easily reduced and alloyed than K. However the
laboratory studies of Jones and Burnett (1980)
indicate that the partition coefficients of U
between FeC and FeSi alloys and a silicate melt
are very small, <10^{-4}, suggesting that neither
U nor K would be incorporated into the core in
this model and that radioactive heating would be
insignificant. An alternative model is that the
Earth's core formed at high pressure with insig-
nificant S. Although strong arguments exist
against this model (Stevenson, 1981), it cannot
be be ruled out. In this case our results along
with Jones and Burnett (1980) indicate that
hypothetical pressure effects would have to
reverse the relative partitioning behavior of K
and U or increase metal-silicate partition coe-
fficients by 2-3 orders of magnitude for radio-
active heating to be important.

In summary, we emphasize the important point
that data in the literature suggest that a S-rich
core will dissolve enough K to produce signifi-
cant radioactive heating, although additional
experiments are desirable. What we have suggest-
ed is that U and Th might also be important.

References

Benjamin, T.M., W.R. Heuser and D.S. Burnett,
Laboratory studies of actinide partitioning

relevant to ^{244}Pu chronometry. 9th Lunar
Planetary Conf. Proceedings, 1393-1406, 1978.

Bukowinski, M.S.T., Potassium: a siderophile
element in, High Pressure Science and Tech-
nology, K.D. Timmerhaus and M.S. Barber,
ed., Plenum Press, 2, 237-244, 1979.

Brett, R., The current status of speculations on
the composition of the core of the earth,
Rev. Geophys. Space Phys., 14, 375-384, 1976.

Clarke, D.B., G.G. Pe, R.M. MacKay, K.R. Gill,
M.J. O'Hara and J.A. Gard, A new K-Fe-Ni-
sulphide from a nodule in kimberlite, Earth,
Plan. Sci. Lett., 35, 421-428, 1977.

Clarke, D.B., Synthesis of nickelon djerfisher-
ites and the origin of potassic sulphides at
the Frank Smith Mine, in The mantle sample:
Inclusions in kimberlites and other volcan-
ics, F. Boyd and H.O.A. Meyer, eds., Am.
Geophys. Union, Washington, 2, 300-308, 1977.

El Goresy, A., N. Grogler and J. O'Hermann, Djer-
fisherite composition in Bishopville, Pena
Blanca Springs, St. Marks, and Toluca meteor-
ites, Chemie der Erde, 30, 77-82, 1971.

Ganguly, J. and G.C. Kennedy, Solubility of K in
FeS liquid; silicate(Fe-S) equilibria and
their planetary implications, Earth, Plan.
Sci. Lett, 35, 411-420, 1977.

Goettel, K.A., Partitioning of K between silicate
and sulphide melts: Experiement relevant to
the earth's core, Phys., Earth, Planet.
Interiors, 6, 161-166, 1972.

Goettel, K.A. Potassium in the earth's core,
Thesis, Mass. Inst. of Technology, Cambridge,
Mass., 1975.

Goettel, K.A. and J.S. Lewis, Comments on a paper
by Oversby and Ringwood, Earth, Plan. Sci.
Lett., 18, 148-150, 1973.

Gubbins, D. and T.G. Masters, Driving mechanisms
for the earth's dynamo, Advances in Geo-
physics, 21, 1-50, 1979.

Jacobs, J.A., The Earth's Core, Academic Press,
London, 1975.

Jones, J.H. and D.S. Burnett, The distribution of
U and Pu in the St. Severin chondrite, Geo-
chim. Cosmochim. Acta, 43, 1895-1905, 1979.

Jones, J.H. and D.S. Burnett, Laboratory studies
of actinide metal-silicate fractionation,
Proc. 11th Lunar Plan. Sci. Conf., 995-1001,
1980.

Keil, K., Mineralogical and chemical relation-
ships among enstatite chondrites, J. Geophys.
Res., 73, 6945-6976, 1968.

Morgan, J.W. and J.F. Lovering, U and Th abundan-
ces in chondritic meteorites, Talanta, 15,
1079-1095, 1968.

Morgan, J.W., Uranium, in Handbook of elemental
abundances in meteorites, B. Mason, ed.,
Gordon and Breach, 1971.

Murrell, M.T. and D.S. Burnett, Actinide micro-
distributions in enstatite chondrites (abs.)
in Lunar and Planetary Science XII, Lunar,
Planetary Institute, Houston, 741-743, 1981.

Oversby, V.M. and A.E. Ringwood, Potassium dis-
tribution between metal and silicate and its
bearing on the occurrence of potassium in the
earth's core, Earth, Planet. Sci. Lett., 14,
345-347, 1972, ibid, 18, 151-152, 1973.

Ruff, L. and D.L. Anderson, Core formation, evo-
lution and convection: A geophysical model,
Phys. Earth Planet Interiors, 21, 181-201,
1980.

Somerville, M. and T.J. Ahrens, Shock
  compression of KFeS$_2$ and the question of K in
  the core, J. Geophys. Res. 85, 7016-7024, 1980.
Stapanian, M. I., Induced fission track measure-
  ,ments of carbonaceous chondrite Th/U ratios
  and Th/U microdistributions in Allende in-
  clusions, Thesis, Calif. Inst. Technology,
  Pasadena, CA, 1980.
Stevenson, D.J., Models of the earth's core,
  Science, 214, 611-618, 1981.

Von Michaelis, H., L.H. Ahrens and J.P. Willis,
  The composition of stony meteorites II,
  Earth, Planet. Sci. Lett., 5, 327-394, 1969.
Woolum D.S. and D.S. Burnett, Metal and Bi/Pb
  microdistribution studies of an L3 chondrite:
  The implications for a meteorite parent body,
  Geochim. Cosmochim. Acta, 45, 1619-1632, 1981.