The Earth as a Thermal Engine

- Important Radioactive Heat Sources in the Earth
  - Uranium - ^{235}U, ^{238}U
  - Thorium - ^{232}Th
  - Potassium - ^{40}K

- Traditionally, radioactive heat production exclusively in the Crust and Mantle of the Earth (Bulk Silicate Earth - BSE)

- My talk is about possible ^{40}K radioactivity in the Core

Experimental Evidence for Potassium Radioactivity in the Earth's Core

V. Rama Murthy
Department of Geology and Geophysics
University of Minnesota

Co-Investigators

Wim van Westrenen and Yingwei Fei
Geophysical Laboratory
Carnegie Institution of Washington

Potassium in the Core!

- Conventional Wisdom
  - Classification of elements based on geochemical affinity
    - lithophile : affinity for silicates
    - chalcophile: affinity for sulfur
    - siderophile: affinity for iron metal
  - Potassium is strongly lithophile, hence only in the silicate mantle and crust (Bulk Silicate Earth-BSE)
  - No known chalcophile or siderophile affinity
    - Cannot be in the metallic core of the Earth

Geochemical Behavior

- Recent understanding
  - Geochemical affinity depends on a number of variables - pressure, temperature, composition etc.
  - Lithophile, chalcophile and siderophile affinities are not fixed
- Can potassium have had a different geochemical affinity under core forming conditions?

The Core of the Earth

- The core is less dense by ~10%(?) than pure Fe-Ni metal
  - Must be alloyed with light element(s)
- Required characteristics of alloying element(s)
  - sufficiently abundant in the Earth
  - alloy easily with Fe
- Clues from Cosmochemistry, Meteoritics, Experimental investigations, Equation of State
- Candidates: C, O, S and Si

Reprinted from:
1970, *Phys. Earth Planet. Interiors* **2**, 276–282. North-Holland Publishing Company, Amsterdam
Printed in the Netherlands

THE CHEMICAL COMPOSITION OF THE EARTH'S CORE: POSSIBILITY OF SULPHUR IN THE CORE

V. RAMA MURTHY and H. T. HALL

Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

- The idea that Sulfur is the dominant light element, alloyed with Fe-metal in the Core.
- Eutectic melting of Fe-FeS
- But, how much sulfur?

How much Sulfur in the metallic Core?

- A crucial study by Holzheid and Grove, 2002
  - Solubility of S in FeO-containing silicates in equilibrium with a Fe-melt as a function of T, P and silicate melt structure
  - S-content of metal in equilibrium with silicate melt containing ~200 ppm of S will be in the range 6-12 wt%.
  - BSE Mantle S-content : 250±50 ppm
  - So, core S about 10 wt% is reasonable

EARTH AND PLANETARY SCIENCE LETTERS 11 (1971) 239–244. NORTH-HOLLAND PUBLISHING COMPANY

THE EARLY CHEMICAL HISTORY OF THE EARTH: SOME CRITICAL ELEMENTAL FRACTIONATIONS

Henry T. HALL and V. RAMA MURTHY

Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455, USA

+

Lewis, J.S., EPSL. 1971

- a heretic point of view
  - Potassium can be chalcophile and may be sequestered into a sulfur bearing core
  - Significant implications both for the Mantle and the Core

Chemical Model of K entry into Core

- In the presence of S in the core
- based on stability and solubility of K_2S in FeS

Lewis, EPSL.,1971

MO + FeS = MS + FeO

Hall and Murthy, EPSL.,1971

MO + FeS = MS + FeO

$MSiO_3$ + FeS = MS + $FeSiO_3$

M_2SiO_4 + FeS = MS + 1/2 Fe_2SiO_4

where M = metal

A 3-decade saga!

Potassium in the Core: "Now you see it; now you don't!"

		K in Core?
Theoretical Suggestions		
V. M Goldschmidt, 1930's?	stability of K_2S	-
Geochemical Studies		
Hall and Murthy, 1971	behavior of alkali sulfides	YES
Lewis, 1971	K with S in core	YES
Molecular Dynamics Calculations		
Bukowinski, 1976		YES
Sherman, 1990		NO
Parker et al, 1996		YES

A 3-decade saga!

Potassium in the Core: “Now you see it; now you don’t!”

		K in Core?
An aborted suggestion		
V. M Goldschmidt, 1930’s?	stability of K_2S	-
Geochemical Studies		
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Molecular Dynamics Calculations		
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A 3-decade saga!

Potassium in the Core: "Now you see it; now you don't!"

Experiments

Low P (~ 20kb) and T(< 2000 C)

Oversby and Ringwood, 1972	$4x10^{-2}$ to $2x10^{-2}$ at 15kb, 1450 ^{0}C	NO
Goettel, 1972	Roedderite-FeS equilibrium	YES
Murrell and Burnett, 1986	$2.7x10^{-3}$ at 15kb, 1450 ^{0}C	NO
Chabot and Drake, 1999	$1.3x10^{-4}$ to $3.7x10^{-2}$ at 15kb, 1900 ^{0}C	NO

High P(>20GPa) and T(>2000 C)

Ito and Morooka, 1993	0.015 at 26 GPa	NO
Ohtani, et al.,1993	0.08 to 0.36 at 47GPa	NO, MAY BE
Ohtani and Yurimoto, 1996	0.0098 at 20GPa, 2500 ^{0}C	NO
Ohtani, et al., 1997	0.24 at 20 GPa; 2500 ^{0}C	MAY BE

Our Experiments

- Measurements of:

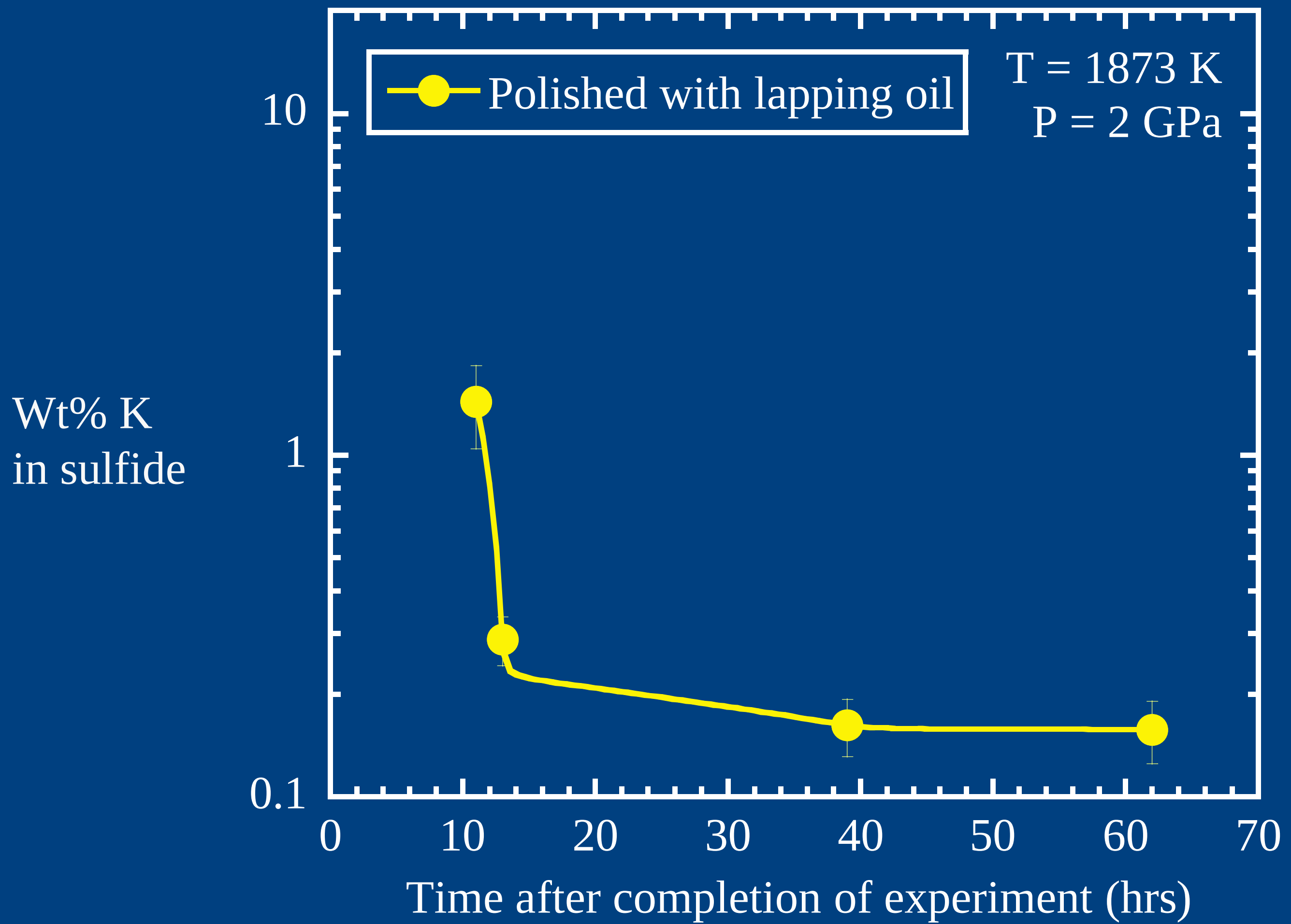
$$\text{K Distribution Coefficient, } D_K = \frac{\text{Concentration in sulfide}}{\text{Concentration in silicate}}$$

as a function of Temperature, Pressure and Composition at redox conditions applicable to core formation in the Earth

Unsuspected Experimental Difficulties

- Murphy's Law Prevails!
  - High data scatter and poor reproducibility
  - Lack of mass-balance for potassium
  - Potassium loss from graphite capsules
  - Potassium loss due to use of liquid lubricants in polishing

Unsuspected analytical problems!



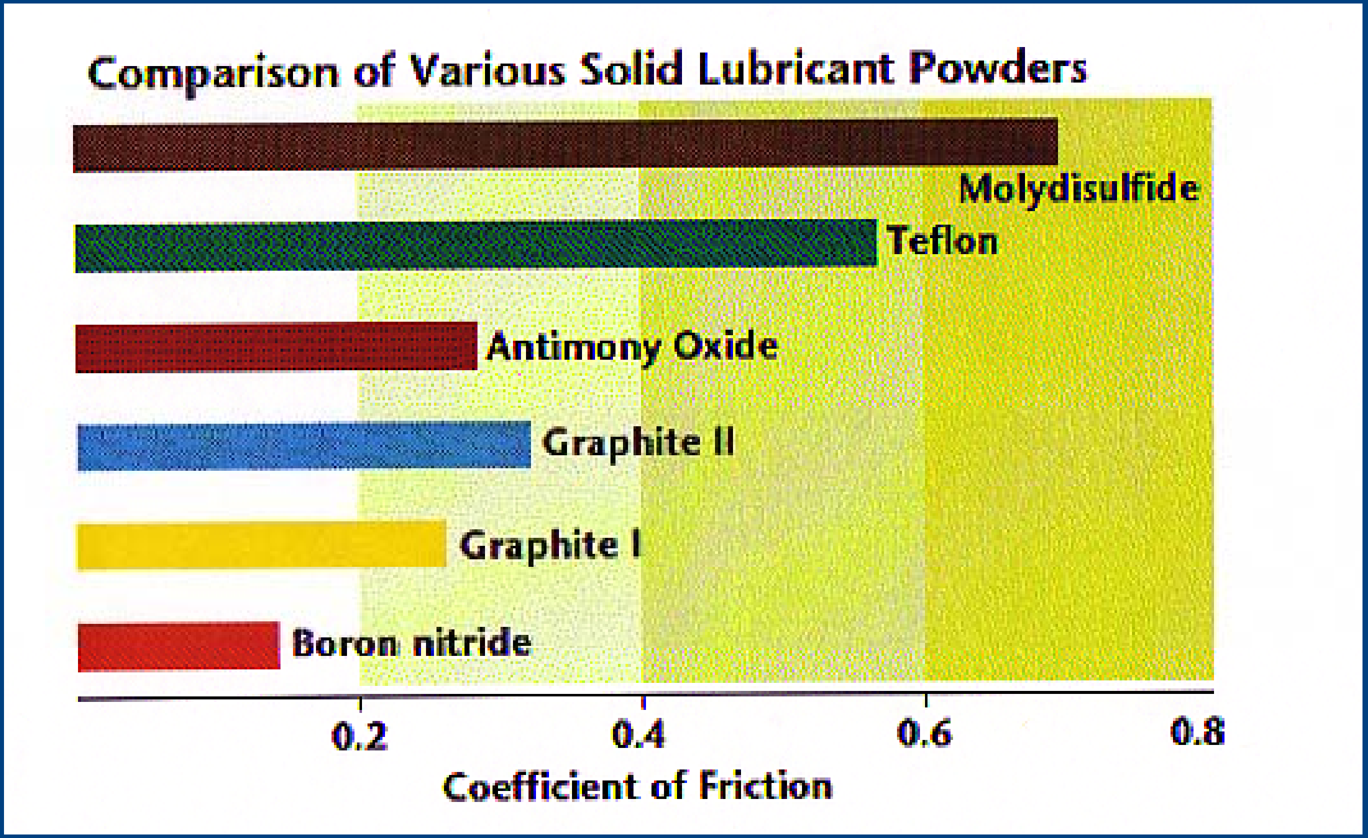
K-loss due to liquids used in polishing

Unsuspected Experimental Difficulties

- Murphy's Law Prevails!
  - High data scatter and poor reproducibility
  - Lack of mass-balance for potassium
  - Potassium loss from graphite capsules
  - Potassium loss due to liquid lubricants

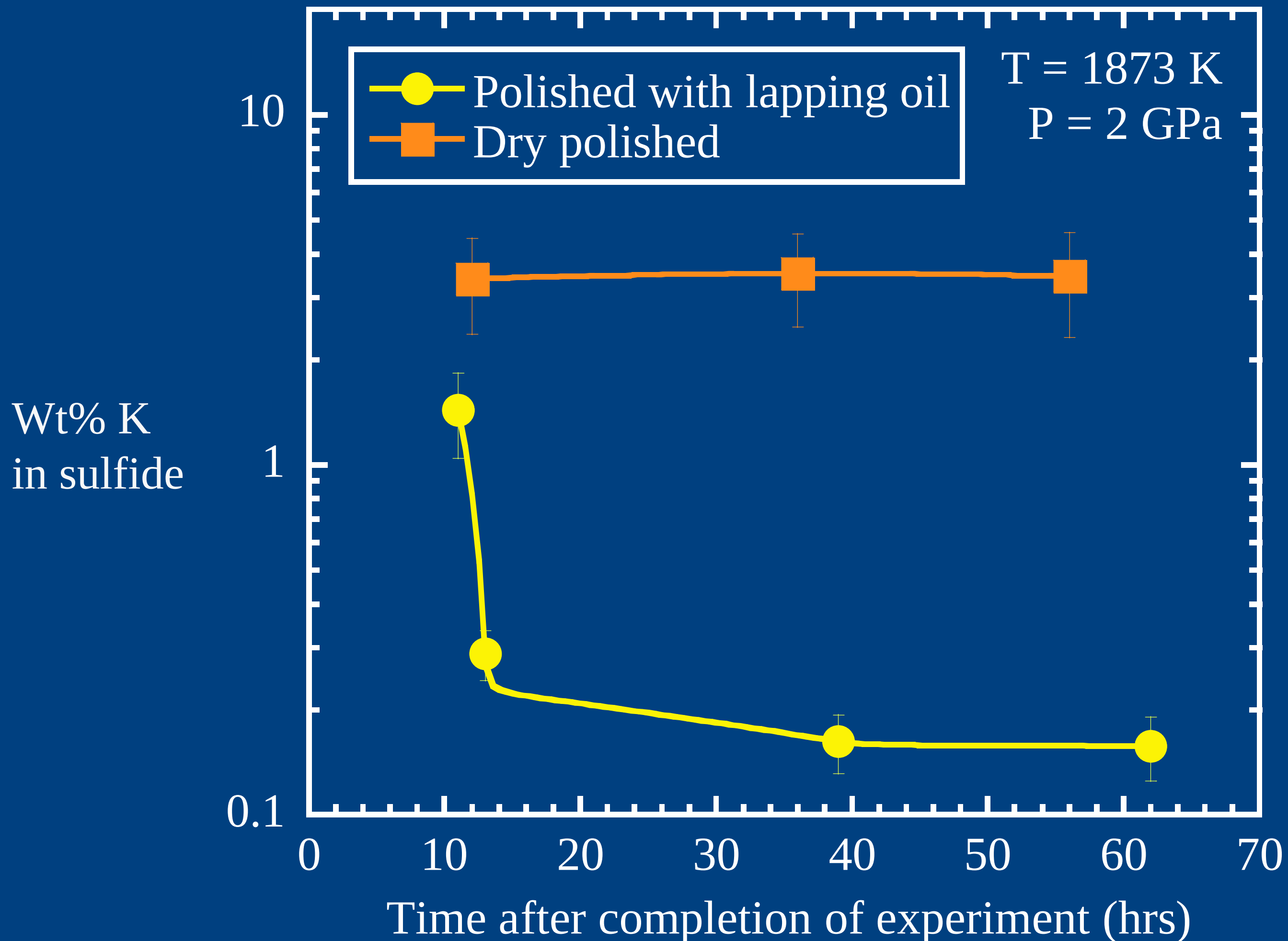
- 8 months and over 60 experiments later
  - Double capsules with graphite inside sealed platinum
  - 'Beauty-polish' with dry lubricants

“Beauty” polishing agent - Boron Nitride Powder



Unsuspected analytical problems!

Mystery resolved!



Techniques

Experimental

Starting Material-Fe, FeS, K-silicate and/or KLB-1

Graphite in sealed Pt-capsule

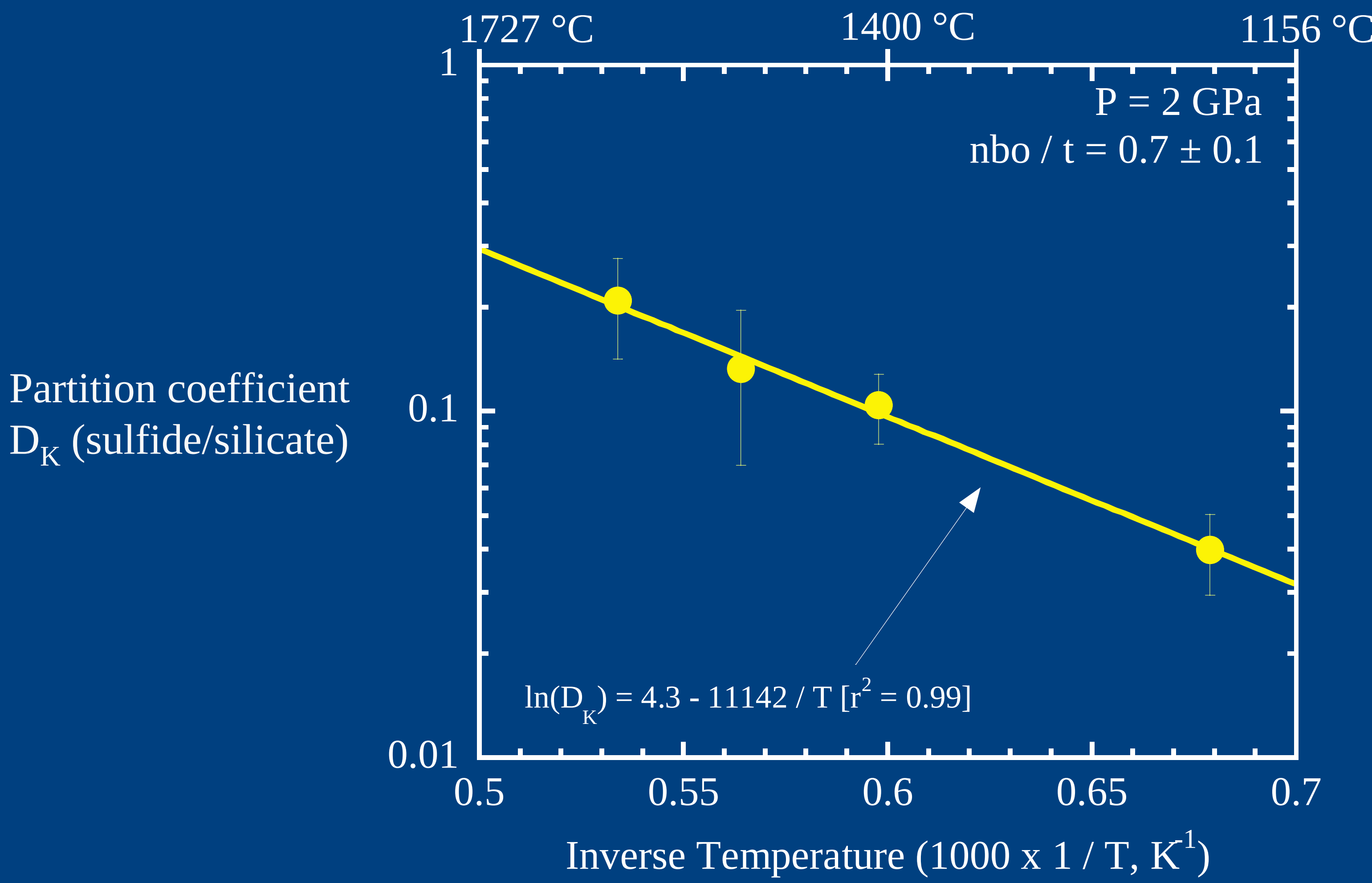
1-3 GPa,1200-1700 C

Analytical

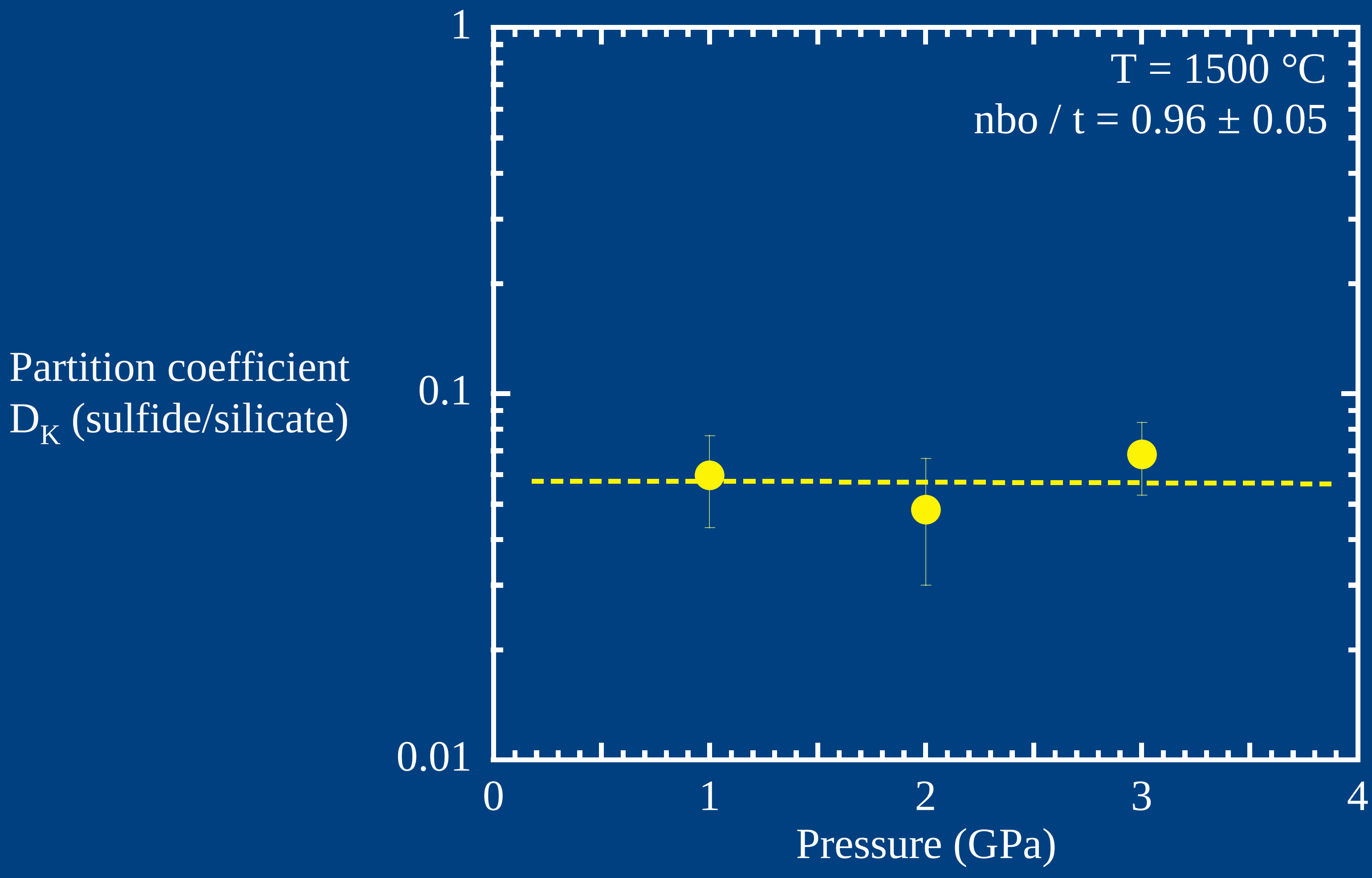
Electron Microprobe
K ± 20 ppm detection

Contamination Monitor
Si in Sulfide

T dependence of D_K at constant silicate composition



D_K as a function of Pressure

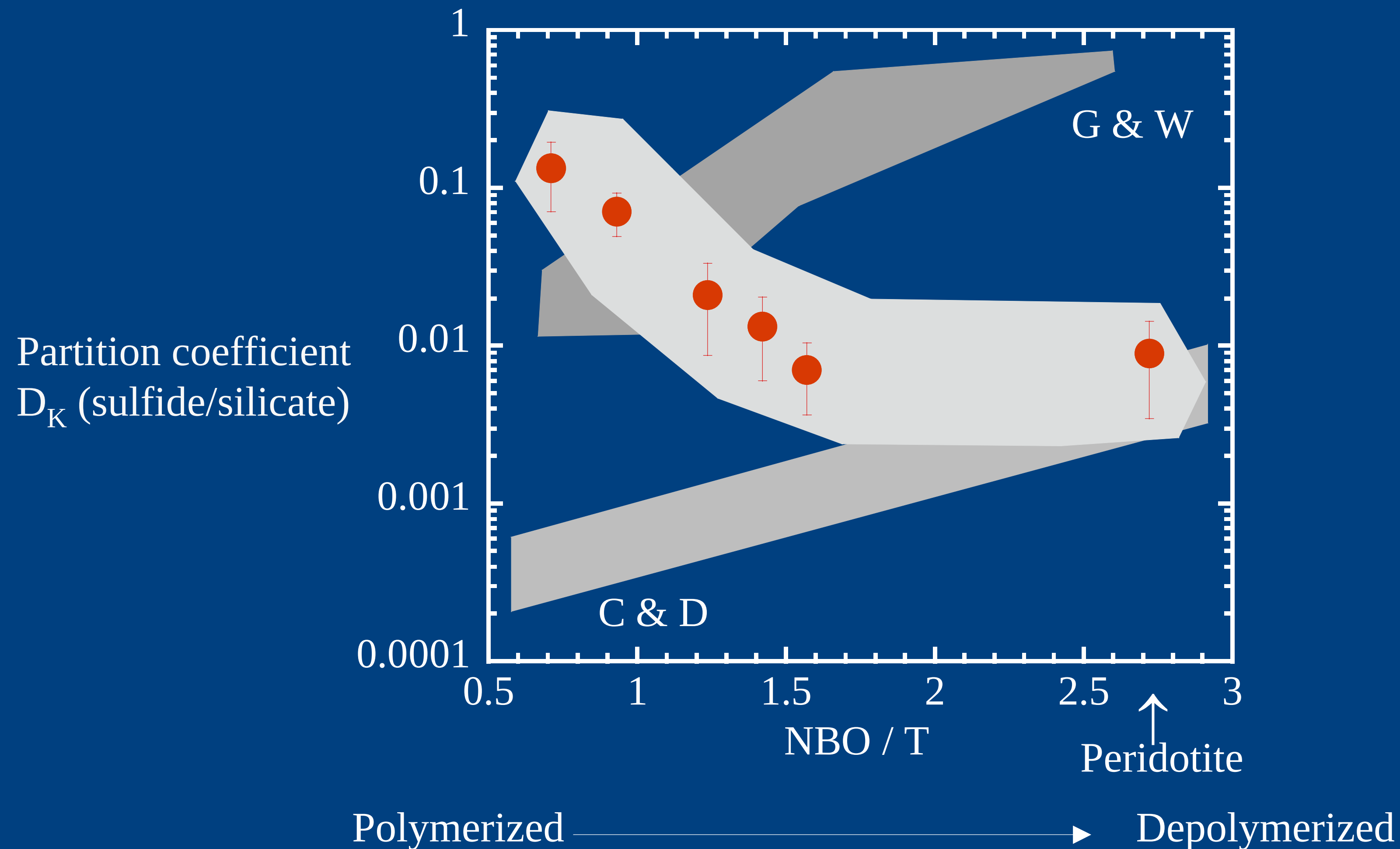


Effect of silicate composition on D_K

This study: P = 2 GPa, T = 1500 ^{0}C

C & D: P = 2.5 GPa, T = 1900 ^{0}C

G & W: Polybaric, Polythermal



Potassium in Sulfur-bearing Cores of Planets

- Our experiments unambiguously confirm that K can be chalcophile
  - enter the sulfur-bearing cores of planets
  - act as an additional heat source in the core
- Consequent planetological implications
- How much potassium?
  - How much sulfur is in the Core
  - Mantle-Core equilibration temperature
  - The initial Earth inventory of Potassium

Some Heuristic Estimates

- Assumptions
  - Composition and Temperature dependence of D_K as in our experiments

<u>Earth</u>

- Sulfur content of Core ~10 wt%
- Core mantle equilibration at 3000-4000 K

<u>Mars</u>

- Sulfur content of Core ~15 wt %
- Core mantle equilibration at 2000-2500 K
- Mars Core - 15% by mass of the planet

^{40}K Heat Production Scenarios

Earth

Present CMB heat flux ~ 8-10 TW

^{40}K Heat Production in Core: 0.4 - 0.8 TW

4 billion years ago : ~ 6-13 TW

Mars

^{40}K Heat Production in Core ~ 1.5 - 4.5 x10^{10} W

4 billion years ago : ~ 0.2 - 0.7 TW

Additional New Experimental and Theoretical Studies

Gessman and Wood (2002)	2-24 GPa	silicate-sulfide	YES
Murthy et al., (2003)	1-3 GPa	silicate-sulfide	YES
Lee and Jeanloz (2003)	26 GPa	K-Fe metal	YES
Lee et al., 2003	*ab initio* calculation		YES
Hirao, et al., 2005	134 GPa	K-Fe metal	YES

- K can enter both Fe-metal and Fe-FeS Core

Additional New Experimental and Theoretical Studies

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- K can enter both Fe-metal and Fe-FeS Core

Planetary Implications of K in Core

- Additional source of heat in the Earth's Core
  - Substantial heat production in early history of the planet
  - Implications for global processes:
    - Maintaining a core dynamo for ~3.5 b.y.
    - The size and age of the inner core
    - Mantle dynamics and convection

Geochemical Arguments to sort out!

1. What is the significance of the lithophile volatile element trend in BSE relative to C1 chondrite?
2. Condensation temperatures of elements or compounds?
3. Do the BSE estimates apply for the whole Earth or just the Upper Mantle?
4. What is the effect of the chemical and dynamic linkage of the Upper Mantle with the Crust?
5. What is the trace-element inventory of the Lower Mantle?
6. What is the relevance of C1 chondrite or any chondrite when the O-isotopic composition of the Earth is considered?
7. What are the controls for refractory element (Ca, REE etc) sulfides in meteorites and the Earth?

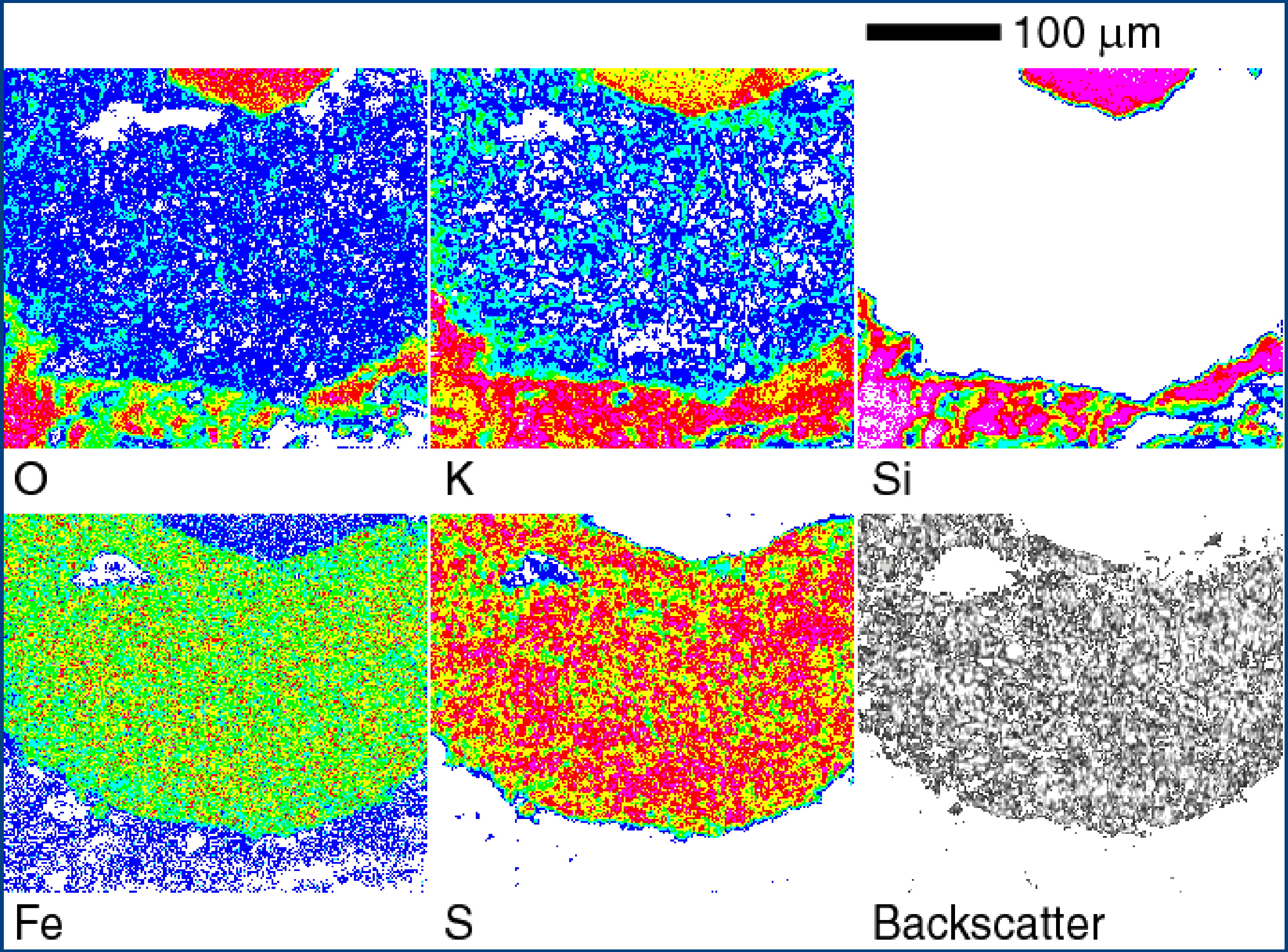
Conclusions

1. Radiogenic heat is the major driving force of the dynamics of the planet

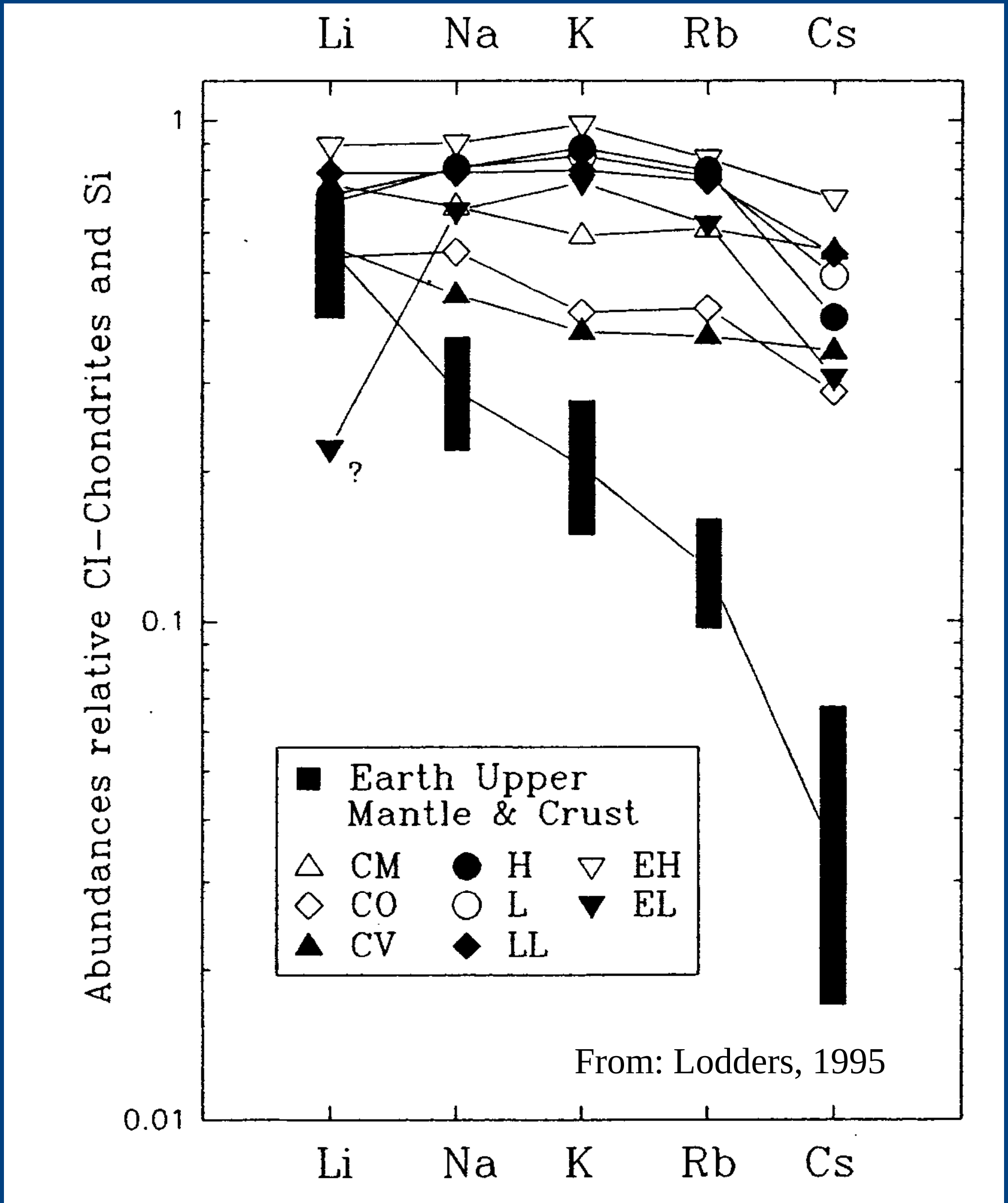
2. Geochemical and Geophysical models are not yet adequate enough to precisely define the radioactivity of the Mantle and Core.

3. A totally independent approach, such as the geoneutrino flux determination, will have a great impact in advancing our knowledge of many global scale phenomena in the Earth.

Thank you all !



Alkali Element Patterns in Chondrites and the Silicate Earth



Geochemical Arguments against K in Core!

- Volatile lithophile element trend of BSE relative to C1 chondrite
  - BSE basically constructed from the Upper Mantle samples
  - Upper mantle dynamically linked and in chemical exchange with the Crust
  - Assumes the Lower Mantle (nearly half the mass of the Earth) is compositionally similar to the Upper Mantle, a question by no means settled by either geophysics or geochemistry