Stable Isotope Geochemistry, Sulfur, and My Research on Iron Meteorites

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Outline

1. Stable Isotope Fractionation

2. Methods

3. Iron Meteorites

3. Preliminary Results

5. Possible Implications

6. Conclusion

Stable isotope Fractionation

Equilibrium fractionation

$$H_2{}^{18}O + C^{16}O \leftarrow\rightarrow H_2{}^{16}O + C^{18}O$$

- Isotope Exchange reactions have K values different than one (*eg.* 1.008)
- Due to vibrational frequency differences of different "isotopologues"
- Lower free energy for heavier isotopes in tighter bonds
- Temp dependent, can do isotope thermometry in rocks to find equilibration temperatures

Stable isotope Fractionation

Kinetic fractionation

$$H_2{}^{18}O_{(l)} + H_2{}^{16}O_{(l)} \rightarrow H_2{}^{16}O_{(g)} + H_2{}^{18}O_{(g)}$$

- Lighter isotopologues react FASTER
- In non-equilibrium reactions the light version will dominate on the product side
- Can quantify extent of reactions in rocks (*eg.* Evaporation in chondrules, lunar formation)
- Bacteria preferentially take in light isotopes... commonly used as signs of first life in rock record.

"The Terrestrial Reference Array"
(holy music)

- For all these reactions involving sulfur it is almost always observed that:

$$\delta^{33}S = (\delta^{34}S)^{0.515} \text{ And } \delta^{36}S = (\delta^{34}S)^{1.91}$$

- The logarithmic relationships describe a curve known as the "Mass-Dependent Reference Array" (Terrestrial is a slight misnomer)

Natural Abundances

^{32}S=94.93% ^{34}S=4.29% ^{33}S =0.76% ^{36}S=0.02%

“The Terrestrial Reference Array”

(holy music)

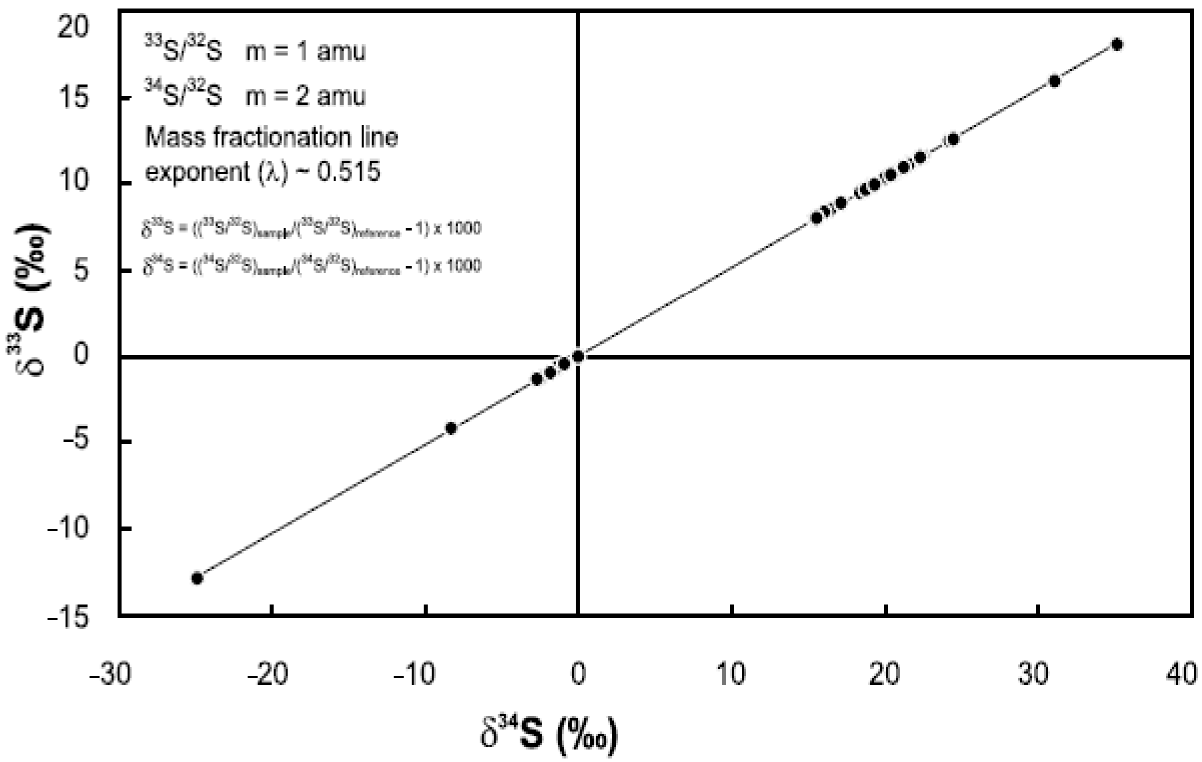


Fig. 2. Plot of $\delta^{33}S$ vs. $\delta^{34}S$ for terrestrial sulfide and sulfate younger than 2.0 Ga [7–9,26,50]. The array defines a tightly constrained curve with $^{33}\lambda = 0.515$. This terrestrial mass fractionation line does not reflect a single fractionation process but represents the average effects of the various mass-dependent fractionation processes that have operated over Earth's history. The slope

Mass Independent Fractionation

(Scary music)

- certain isotope systems (O, S, Hg) have observed departures from classical physics in natural samples.
- Exotic mechanisms of fractionation discovered as a result include:
  - UV photolysis (PES shifts, symmetry)
  - nucleus effects (size/odd *vs.* even)
  - high energy particle interactions
  - nucleosynthetic anomalies

Mass Independent Fractionation

(Scary music)

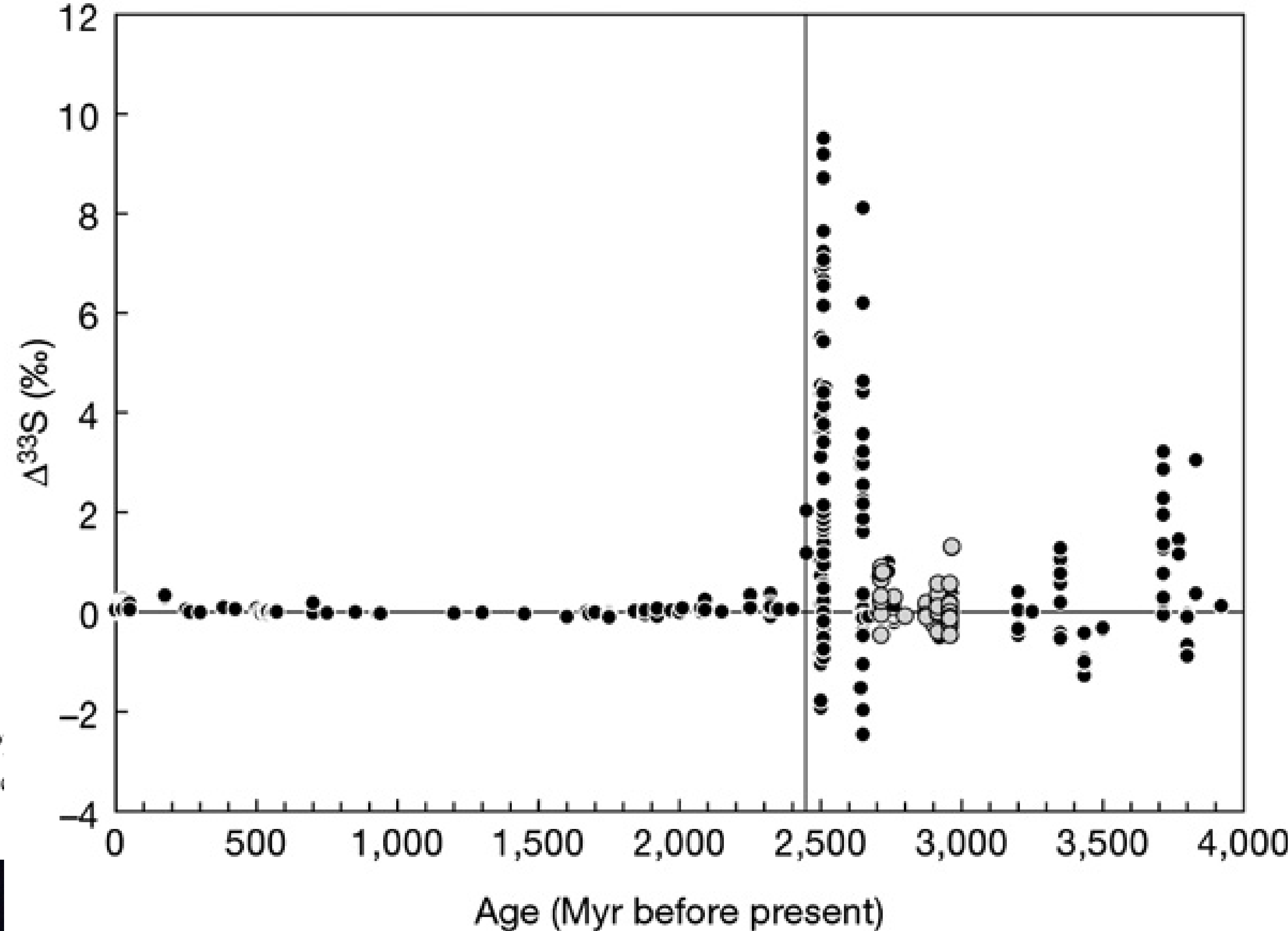


Fig. 2. P... tightly con-
strained ... ss but repre-
sents the ... ry. The slope

Methods of analysis

- Crushed Rock + Acid → $H_2S_{(g)}$
- $H_2S_{(g)}$ + $AgNO_{3(l)}$ → $Ag_2S_{(s)}$
- $Ag_2S_{(s)}$ + $F_{2(g)}$ ----HEAT---> $SF_{6(g)}$
- SF_6 Purified (Gas Chromatography)
- SF_6 + Mass Spectrometer → 4 separate ion Beams
- Measure electrical currents from $^{32}SF_5^+$, $^{33}SF_5^+$, $^{34}SF_5^+$, $^{36}SF_5^+$
- fancier methods are being fine-tuned (SIMS)

- All measurements are ratios and are reported with respect to a known standard

Iron meteorite types

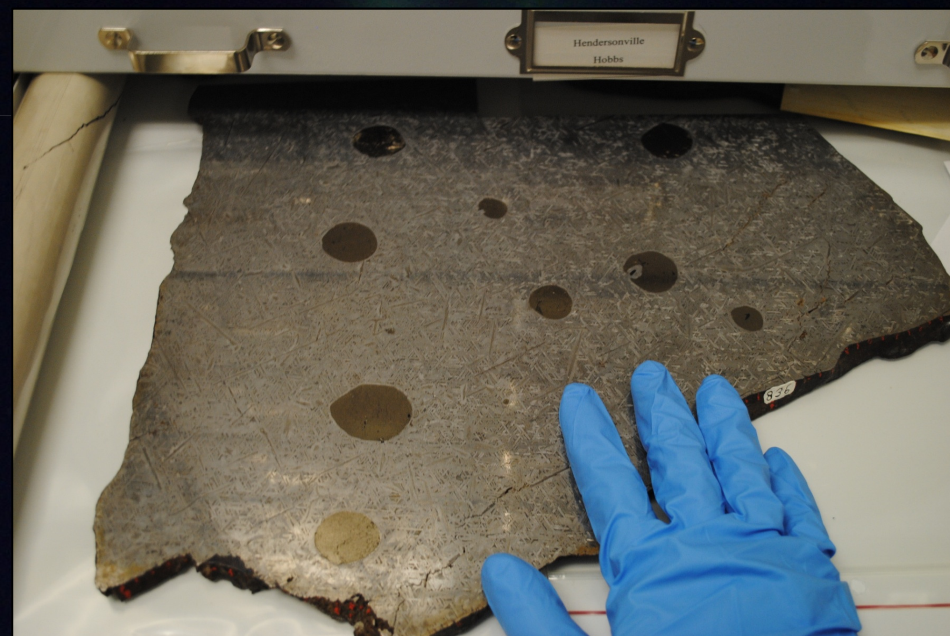
- Separated into chemical groups
- Each chemical group has to come from a separate parent body (according to chemical modelling).
- Dichotomy between "Magmatic" and "Non-Magmatic" iron meteorite groups
  - "Non-Magmatic" irons didn't have enough heat to fully segregate cores, and therefore contain abundant silicate (basaltic) inclusions.
  - "Magmatic" irons are thought to come from fully segregated cores and lack rock inclusions

Iron meteorite types

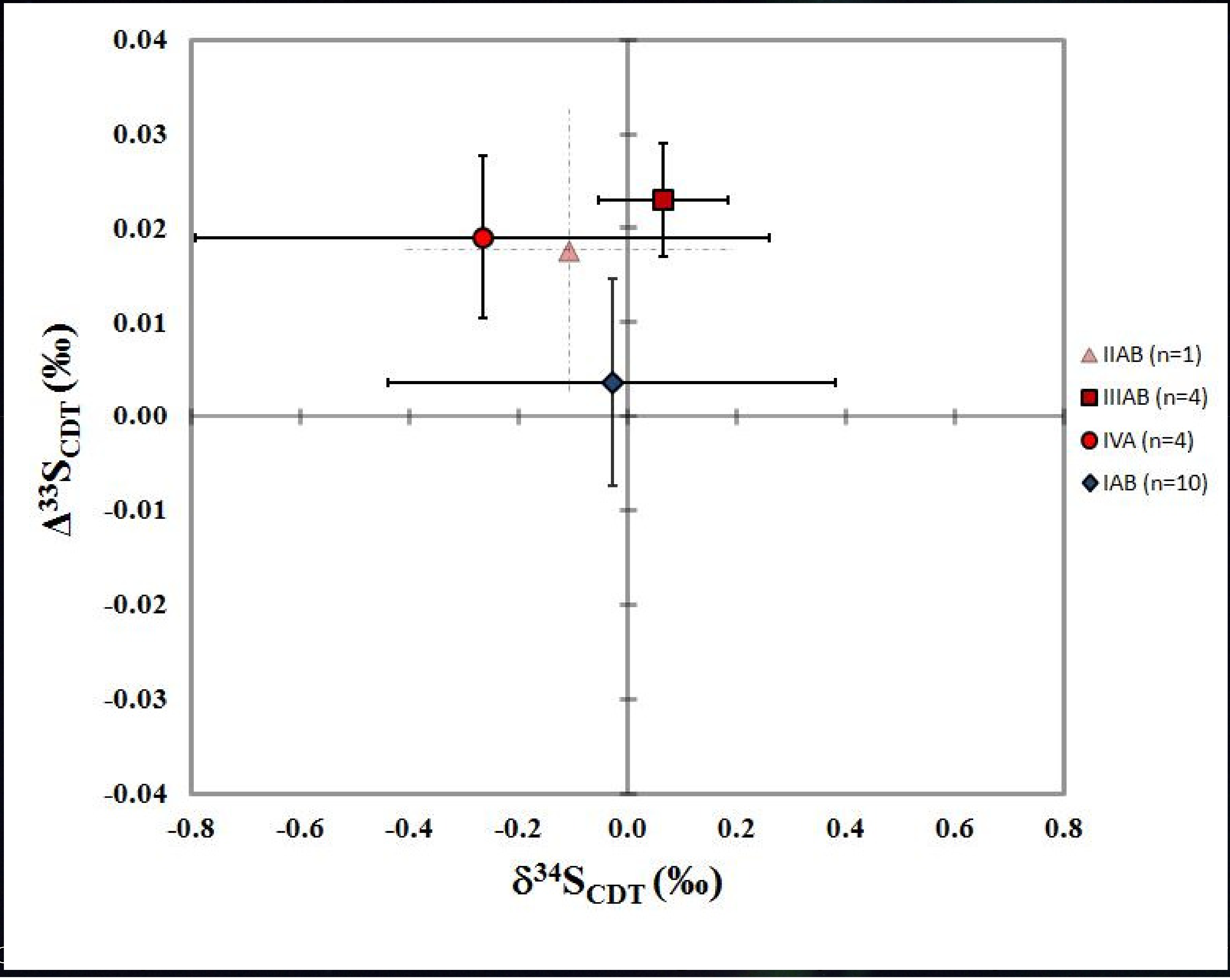
NON-MAGMATIC

LATER
(younger)

MAGMATIC



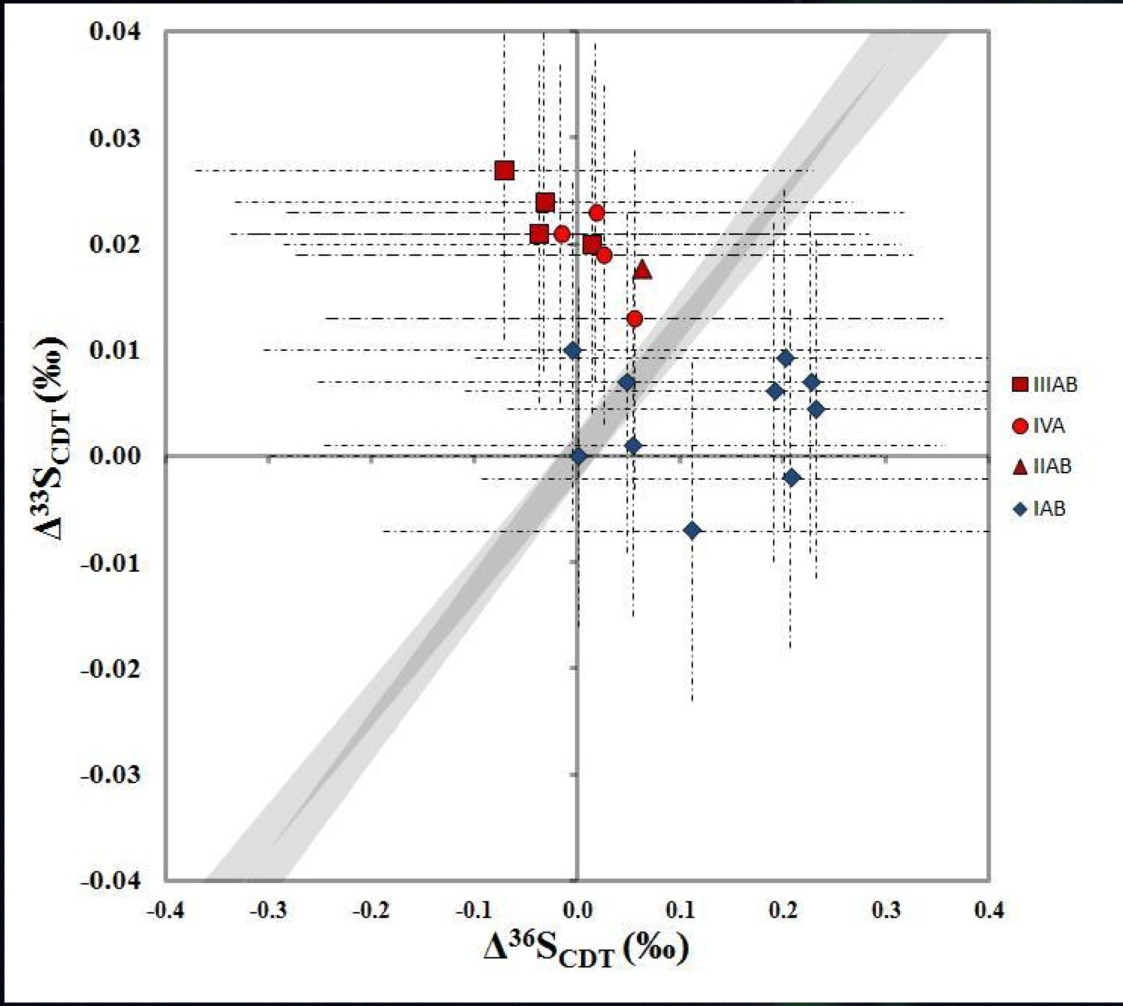
EARLIER
(older)



*All err… …ements

$\Delta^{33}S$ *vs.* $\Delta^{36}S$

Can distinguish between exotic fractionation mechanisms based on the relative enrichments in ^{33}S and ^{36}S



Possible implications

- Magmatic Iron meteorites inherited their sulfur from a region with more intense UV bombardment, earlier in solar system evolution
- Non-Magmatic irons inherited sulfur from sources without mass-independent processes later in solar system evolution

- Could Reflect:

- evolution of sun (transition out of T-Tauri phase)
- Progressive loss of gas phase sulfur over time

Questions?

Institute for Sulfur Isotope Studies, University of Maryland

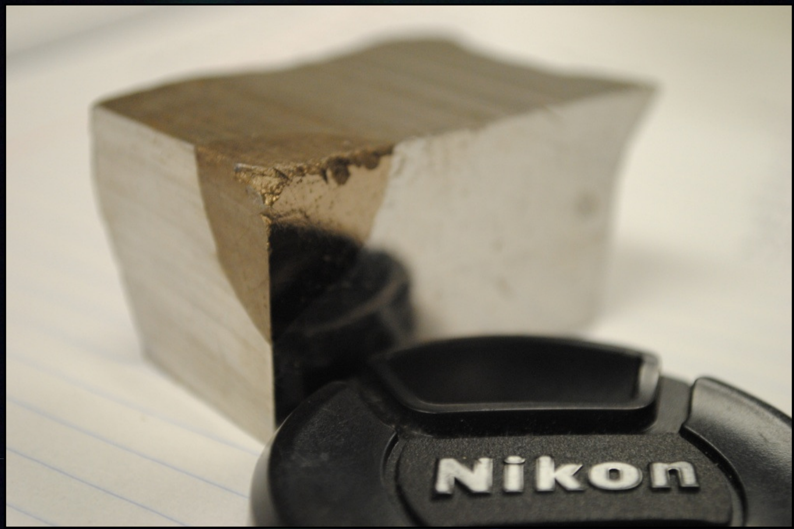
Smithsonian Institution

Linda Welzenbach

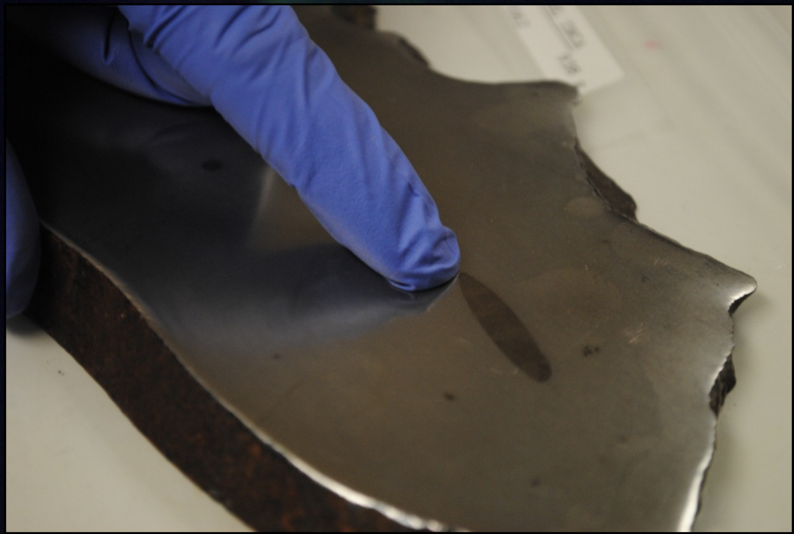
The American Museum of Natural History, NY

Naturhistoriches Museum, Austria

NASA

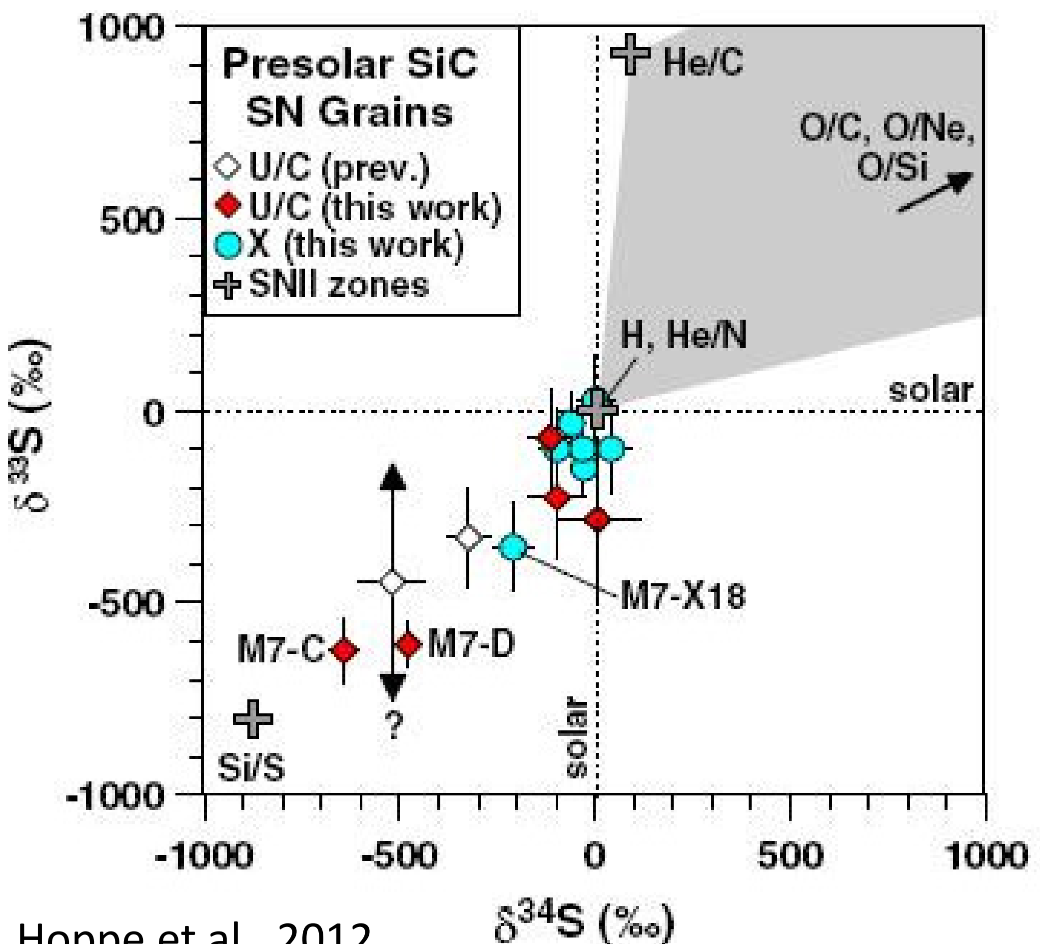


Troilite nodule, Thule IIIAB



Troilite nodule, Cerro del Inca IIIF

Supplemental



Hoppe et al., 2012