The High-pO2 Method to Prevent U-Loss During Single-Aliquot Hematite (U-Th)/He Measurement: Development, Implementation, and Automation

Florian Hofmann[1]

[1]University of Southern California

November 23, 2022

Abstract

Single-aliquot (U-Th)/He dating of iron-oxides requires less mass and has a higher spatial resolution than the two-aliquot approach, and is, therefore, a more reliable tool for quantifying the timescales of weathering processes, fault activity, and the development of soils and surfaces. Highly helium-retentive hematite samples must be heated to 1000-1100 °C to completely degas He, but we show that U is lost progressively during laser-heating starting at ˜900 °C, with major U-loss at ˜980 °C and complete U-loss at 1050-1100 °C. This partial or complete loss of U leads to incorrect (U-Th)/He ages that appear older than the true ages. We performed a series of heating tests on hematite and goethite aliquots with independently determined (U-Th)/He ages of 10-1761 Ma in which the helium release was determined by isotope-dilution mass spectrometry and phase change was monitored by infrared spectroscopy. As hematite is heated, reduction of Fe3+ causes a phase change to magnetite and then to elemental Fe. We correlate the onset of U-loss to the phase change from hematite to magnetite. By raising the temperature of this phase transition using a high oxygen partial pressure (pO2) in the sample chamber during laser-heating, we show that the onset temperature of U-loss is equally raised. Samples can therefore be safely degassed at higher temperatures without any detectable U-loss. In our implementation of this technique, the O2 in the sample chamber is being withdrawn from a tank using a pipette and it is being released before and captured after the degassing process on activated charcoal in a cold finger with a movable LN2 Dewar flask. We describe the automation of this process for routine degassing of hematite samples. We show that an average age calculated on a reference hematite sample from replicate aliquots (n=12), which were analyzed using this procedure, has a relative uncertainty of 2% (1σ), and is within uncertainty of the previously measured two-aliquot age. We suggest this high-pO2 degassing procedure as a way to precisely and reproducibly determine single-aliquot hematite and goethite (U-Th)/He ages.

The high-pO_2 method to prevent U-loss during single-aliquot hematite (U-Th)/He measurement: Development, implementation, and automation

Florian Hofmann
University of Southern California

Jonathan Treffkorn
Ken Farley
California Institute of Technology

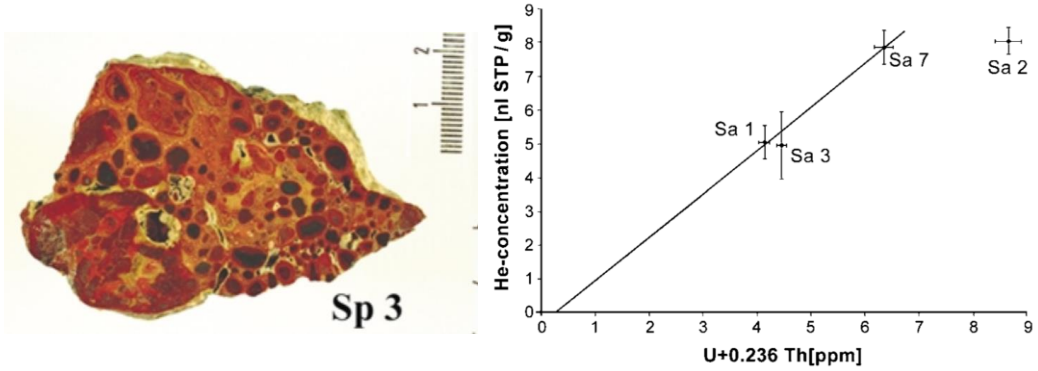
Thermo2021

September 13, 2021

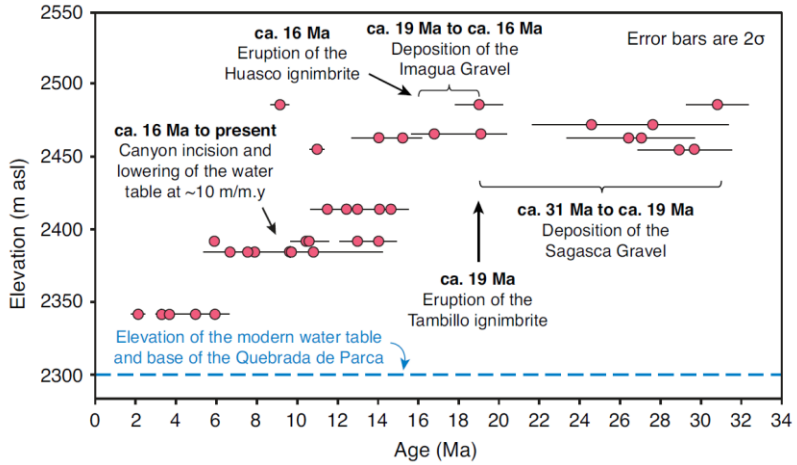
Utility of hematite (U-Th)/He

Geochronology

Pidgeon et al. (2004) – formation age of ferruginous nodules from lateritic duricrusts

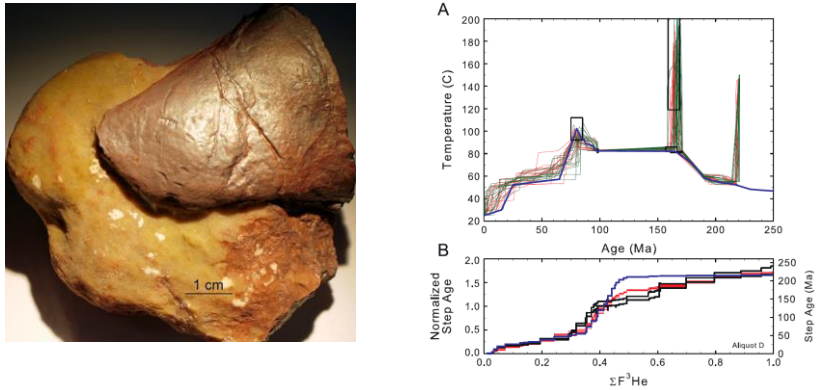


Cooper et al. (2016) – downward migration of water table resulting from incision

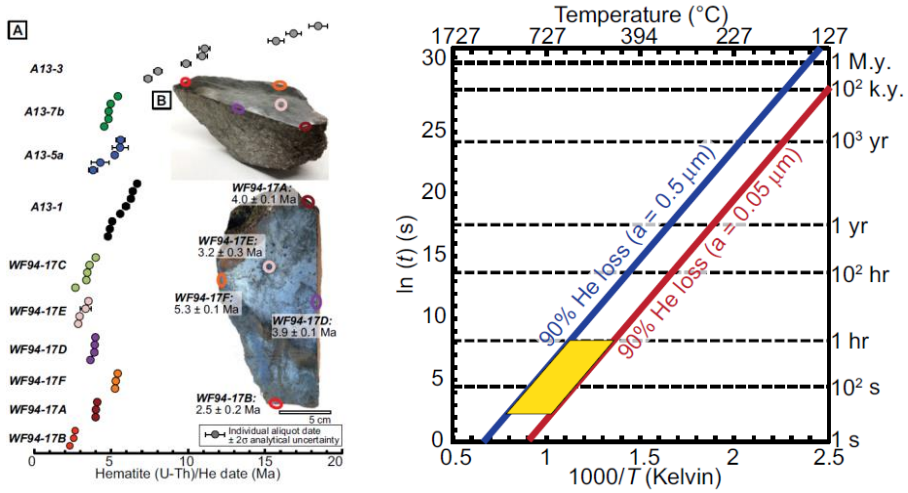


Thermochronology

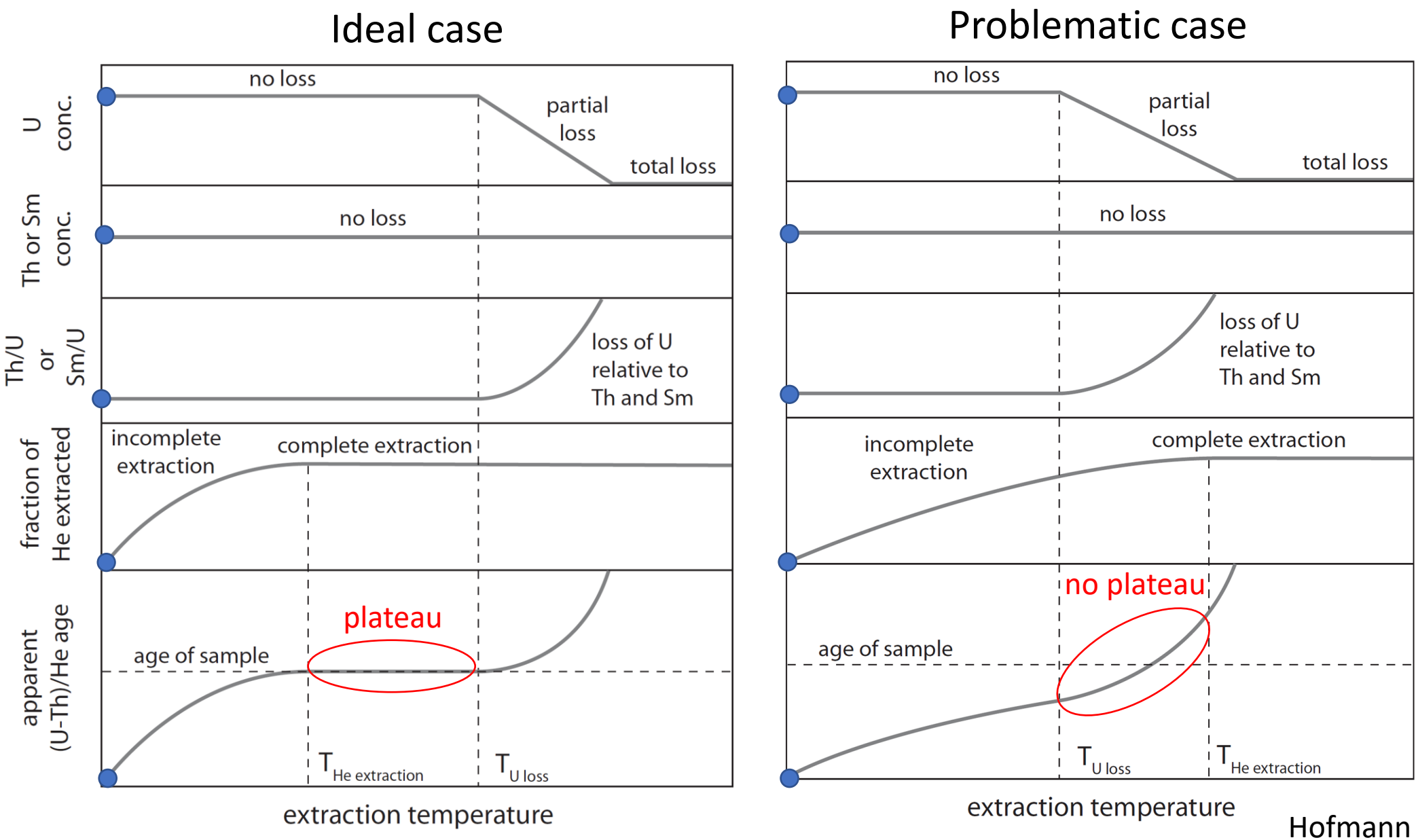
Farley and Flowers (2013) – temperature history modeling of polycrystalline aggregates



Ault et al. (2015) – resetting of hematite crystallites due to shear-heating

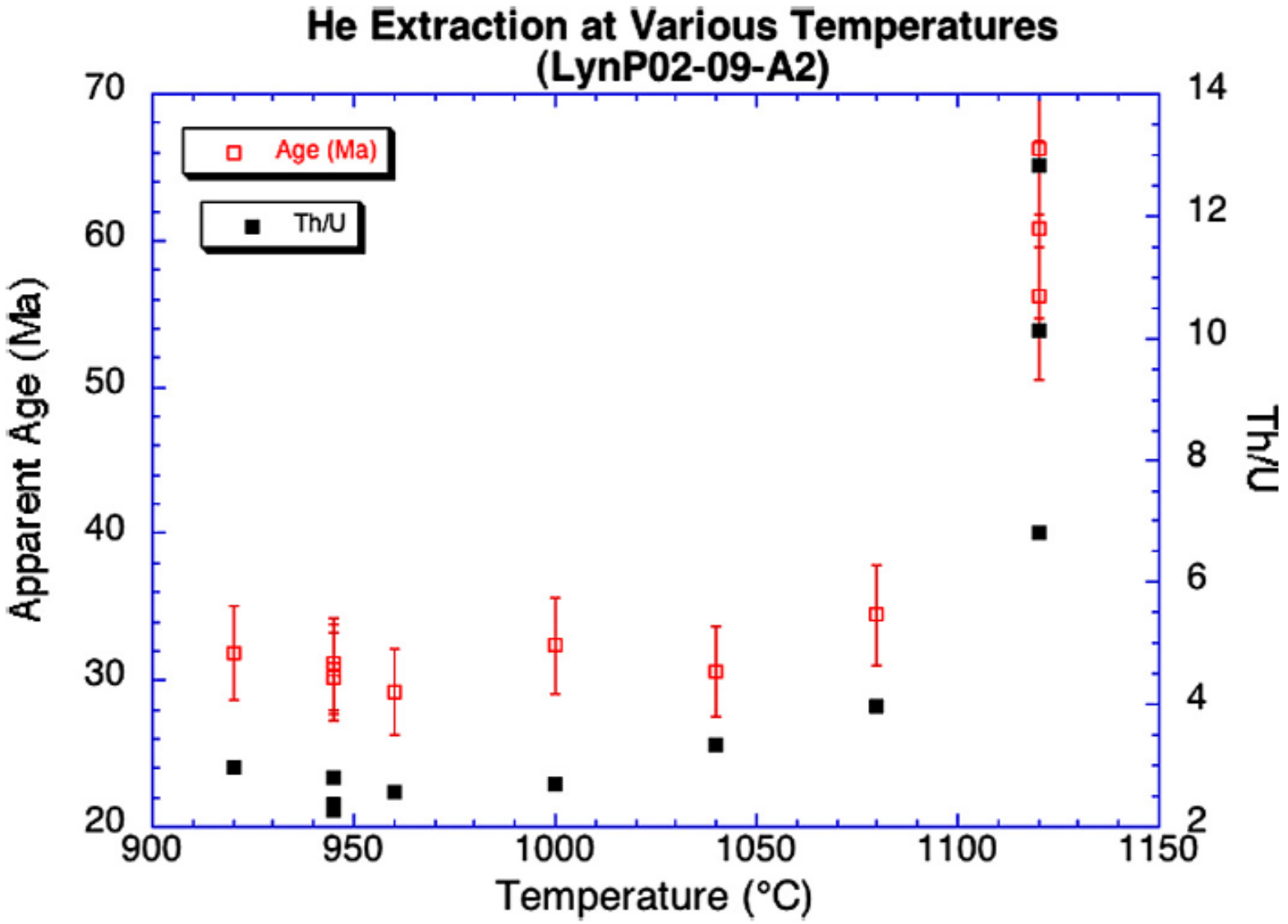


Loss of U during laser-heating



Hofmann et al. (2020)

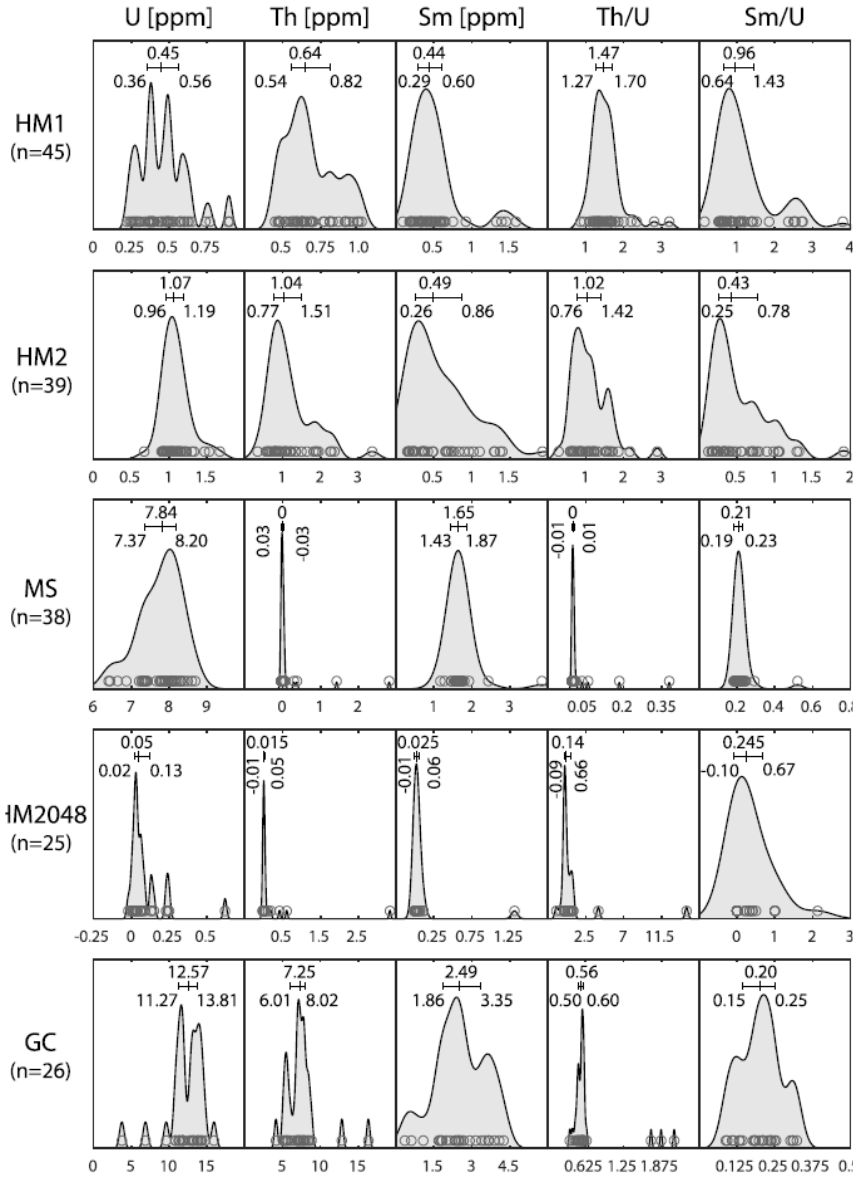
Loss of U during laser-heating



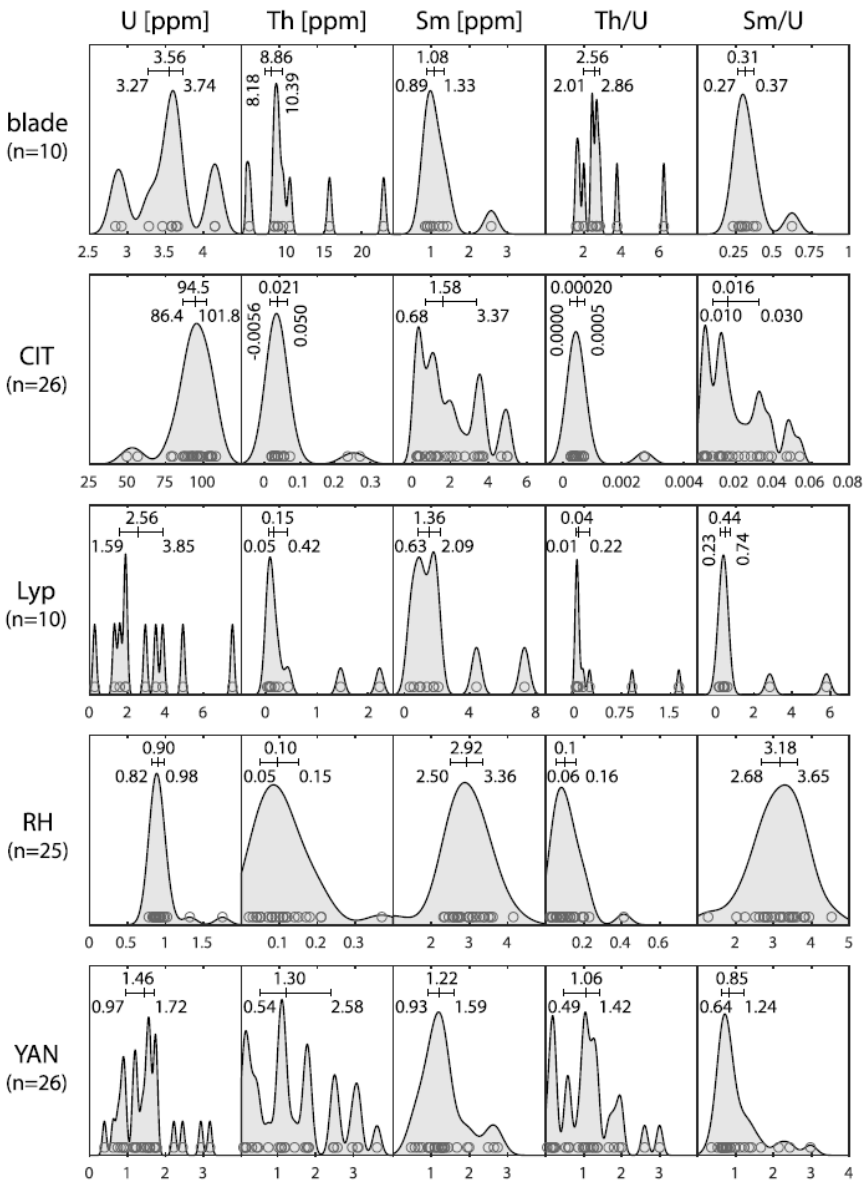
Vasconcelos et al. (2013)

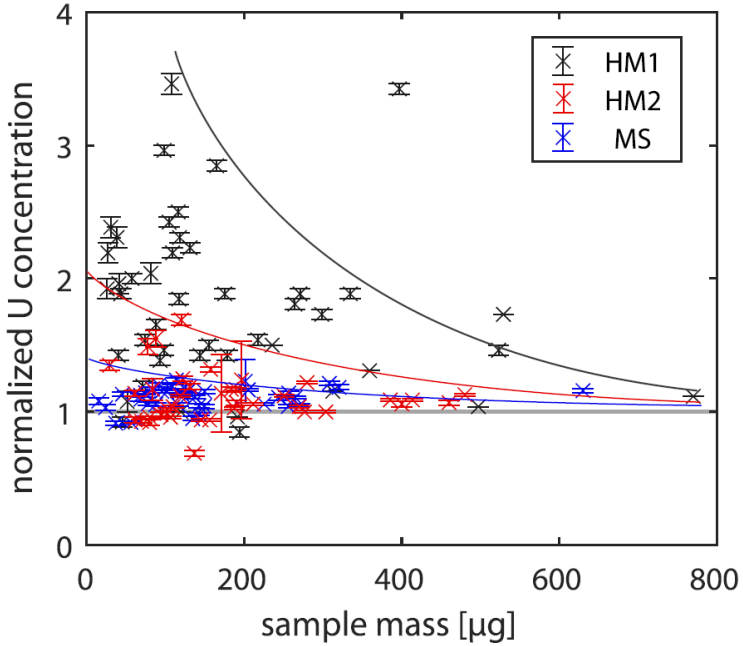
Natural variability in hematite and goethite samples

Hematite



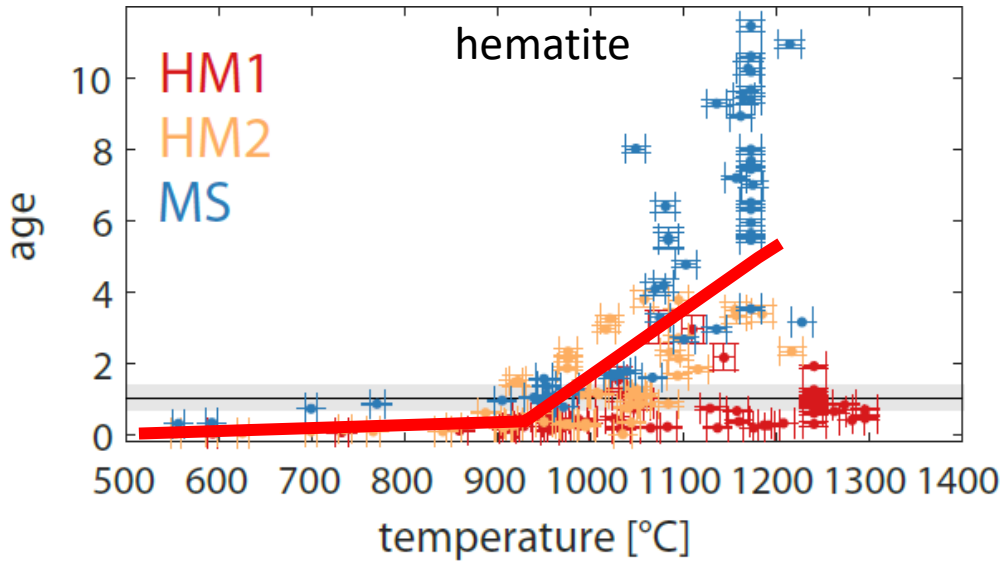
Goethite

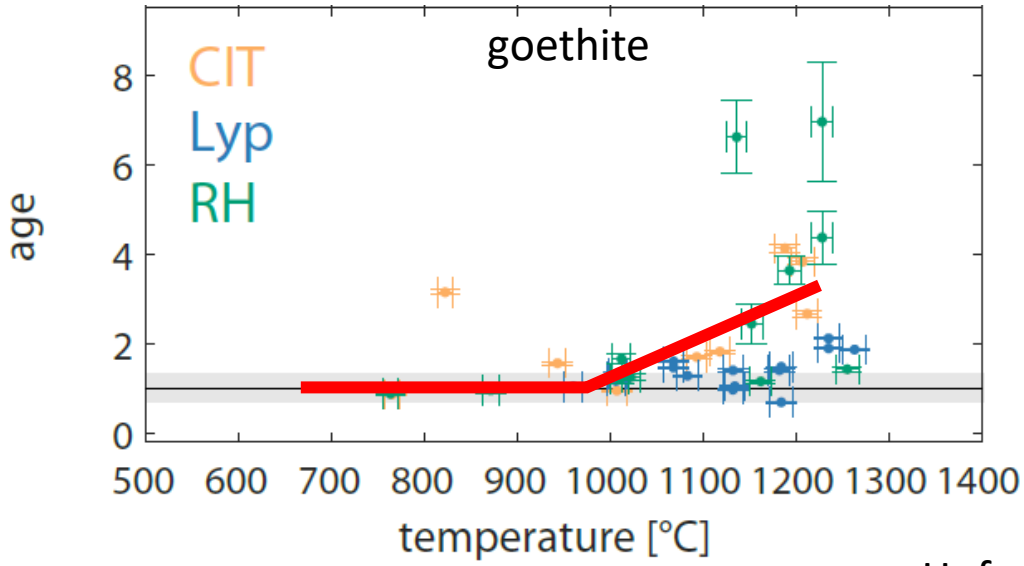


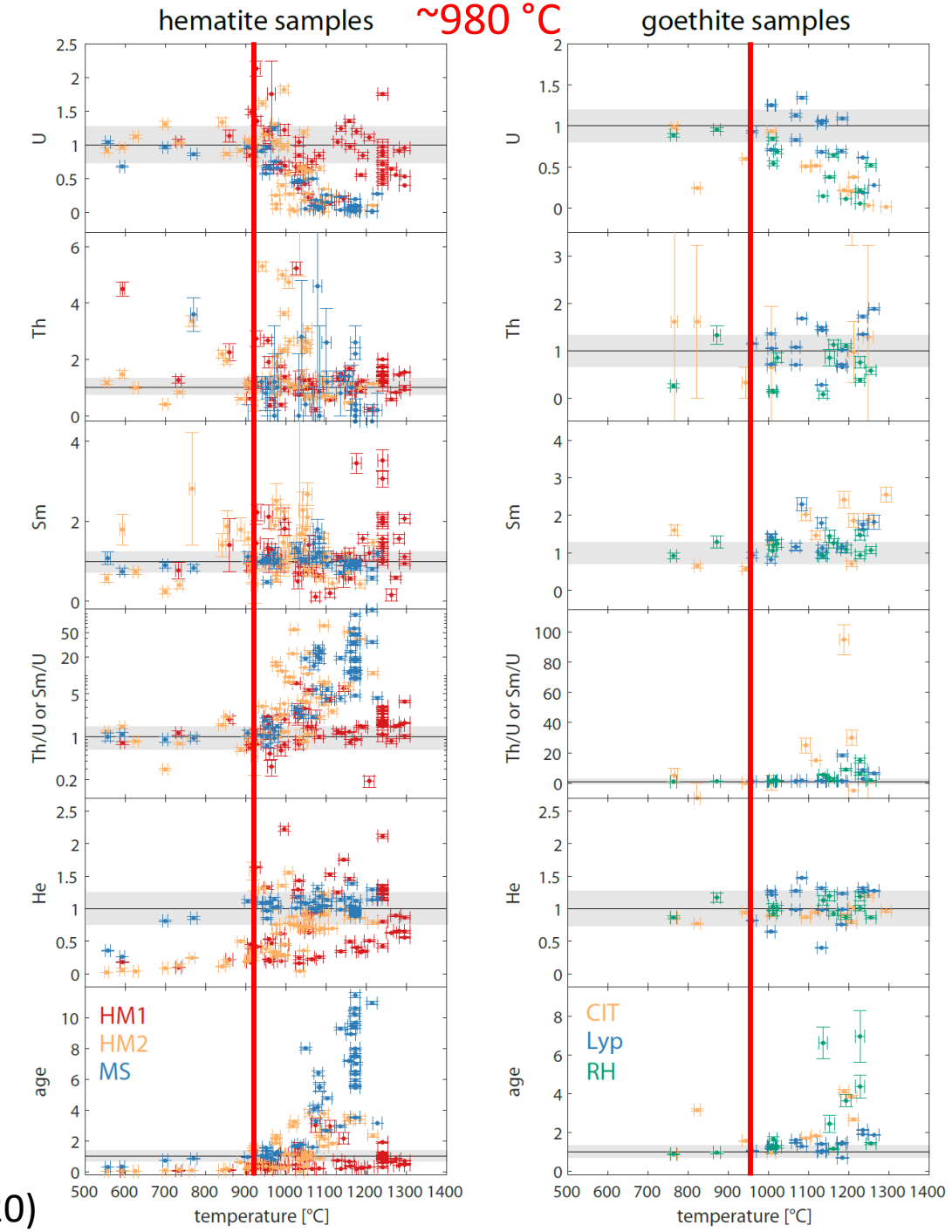


Hofmann et al. (2020)

Heating tests of multiple samples

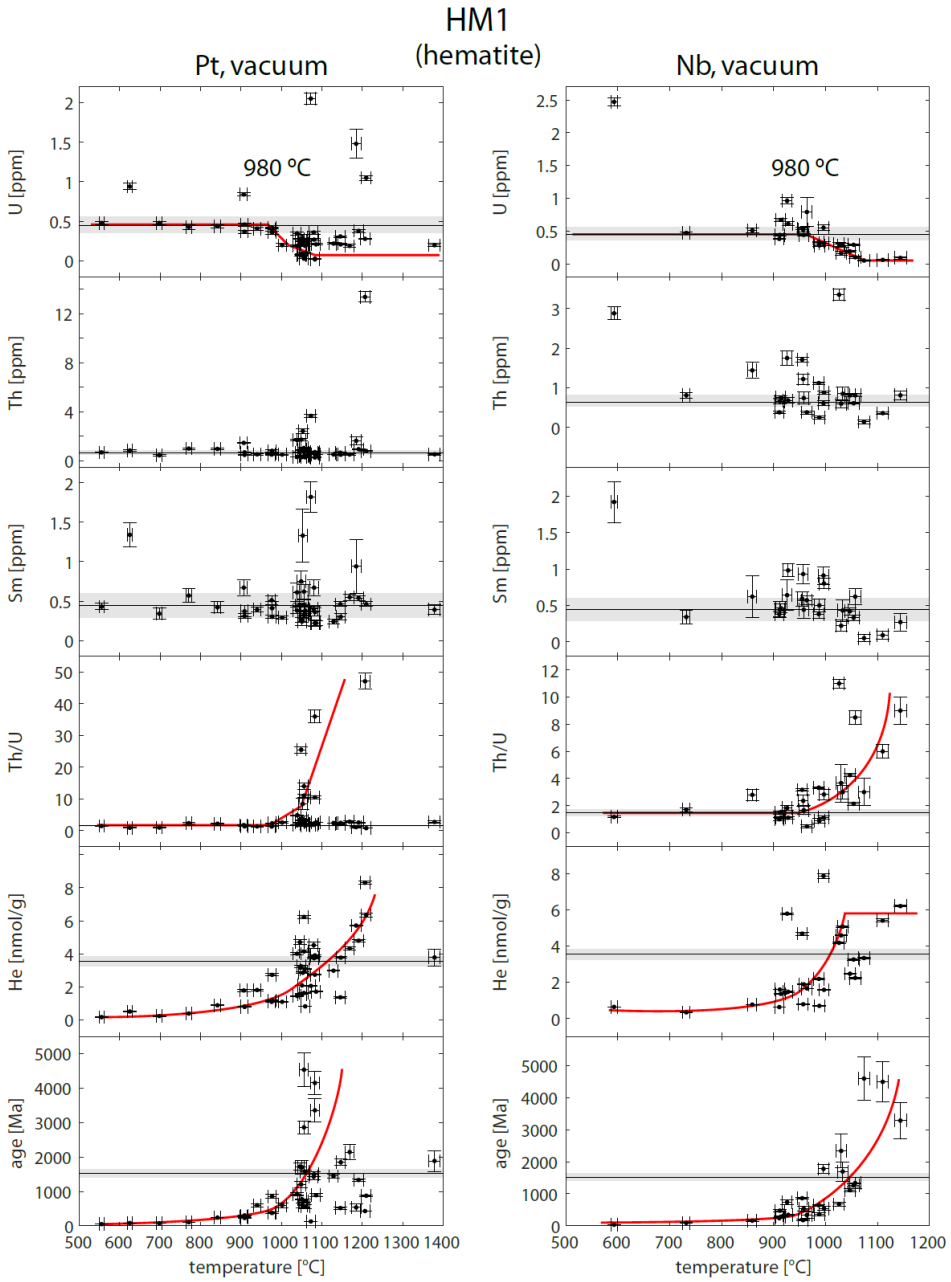






Hofmann et al. (2020)

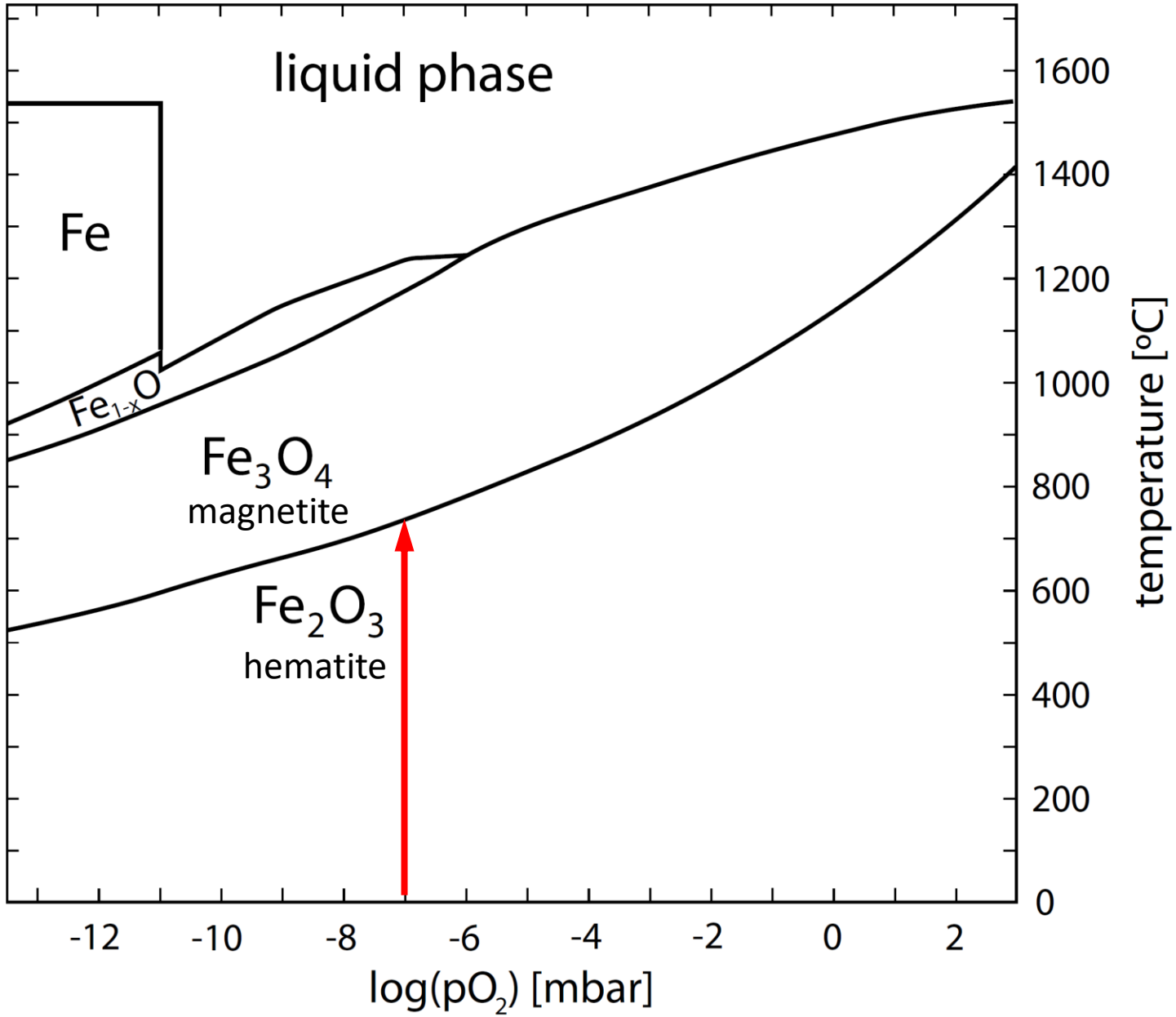
No difference between Pt and Nb tubes



Hofmann et al. (2020)

What happens during laser-heating?

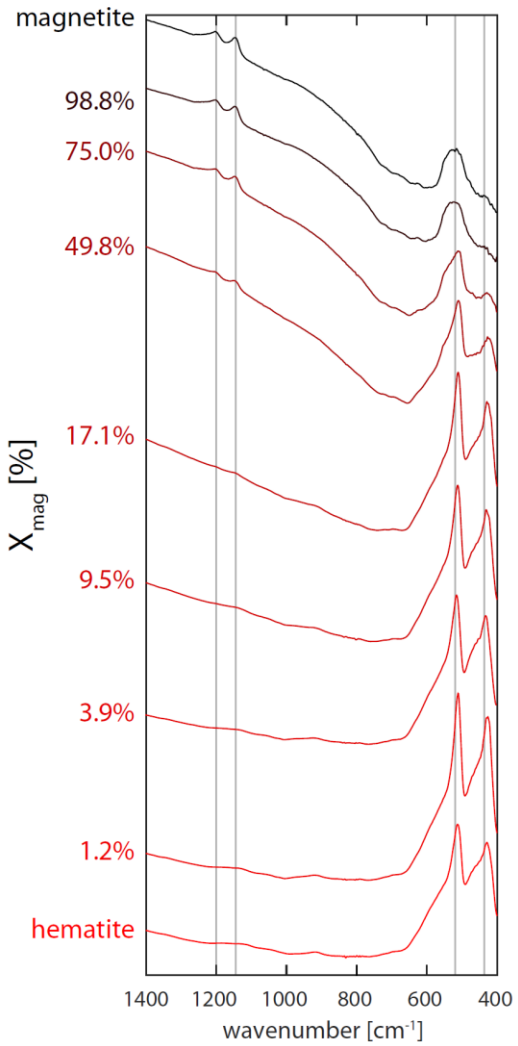
Reduction of hematite:
$3Fe_2O_3 \rightarrow 2Fe_3O_4 + O_2$

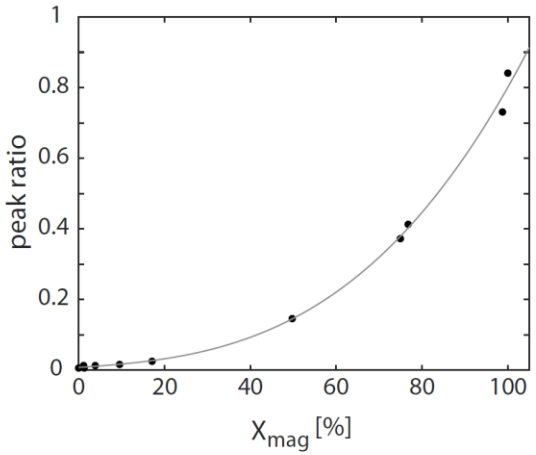


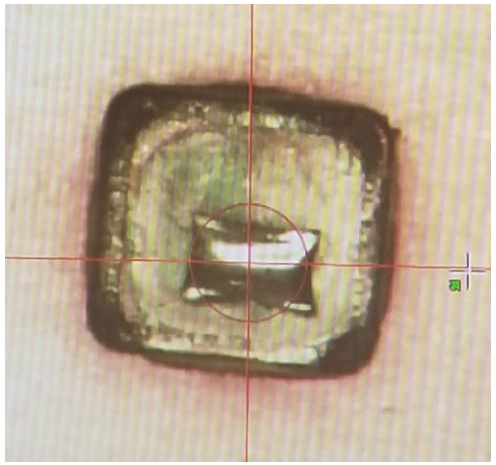
Phase diagram after Ketteler et al. (2001)

Monitoring phase changes during laser-heating with FTIR

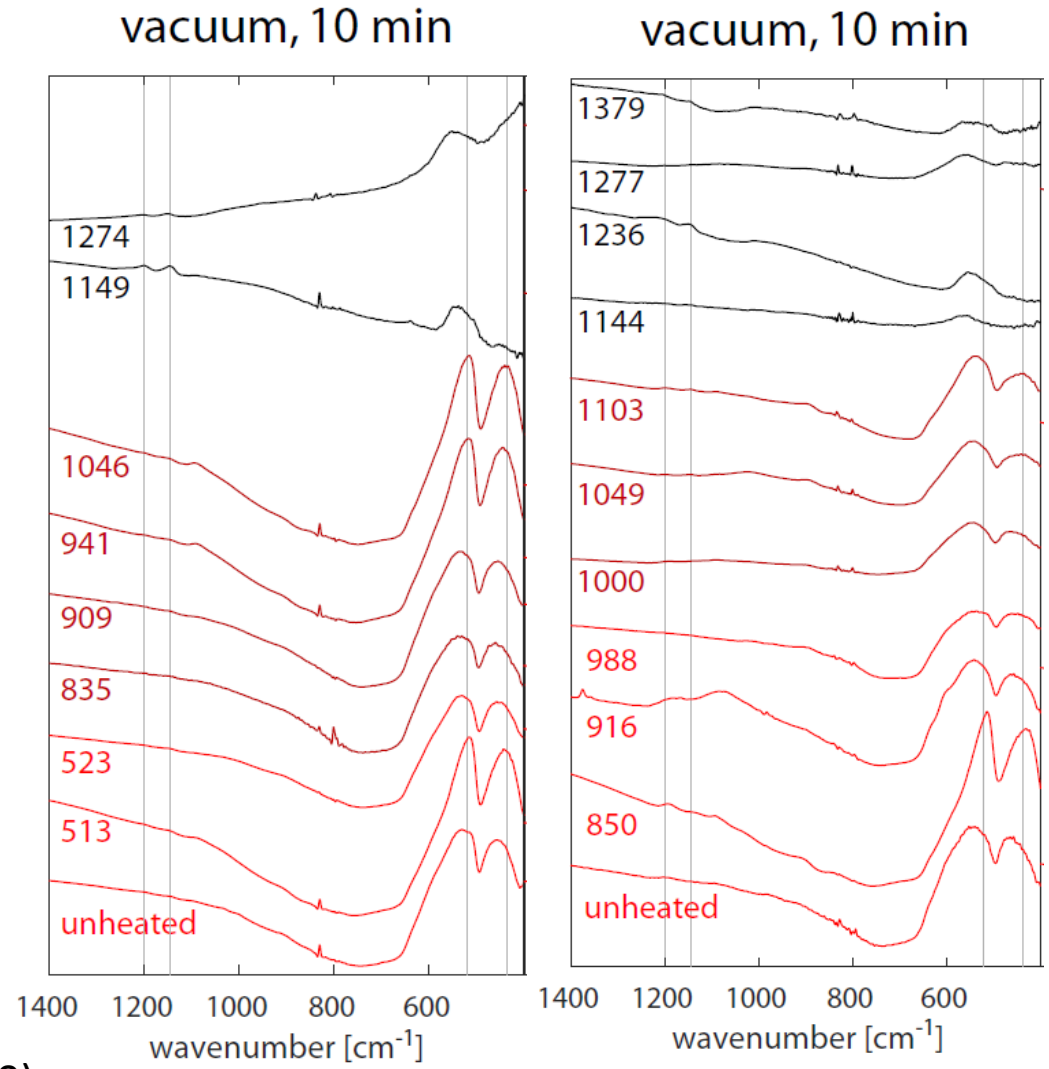
Calibration of FTIR spectra
with known mixtures of hematite and magnetite





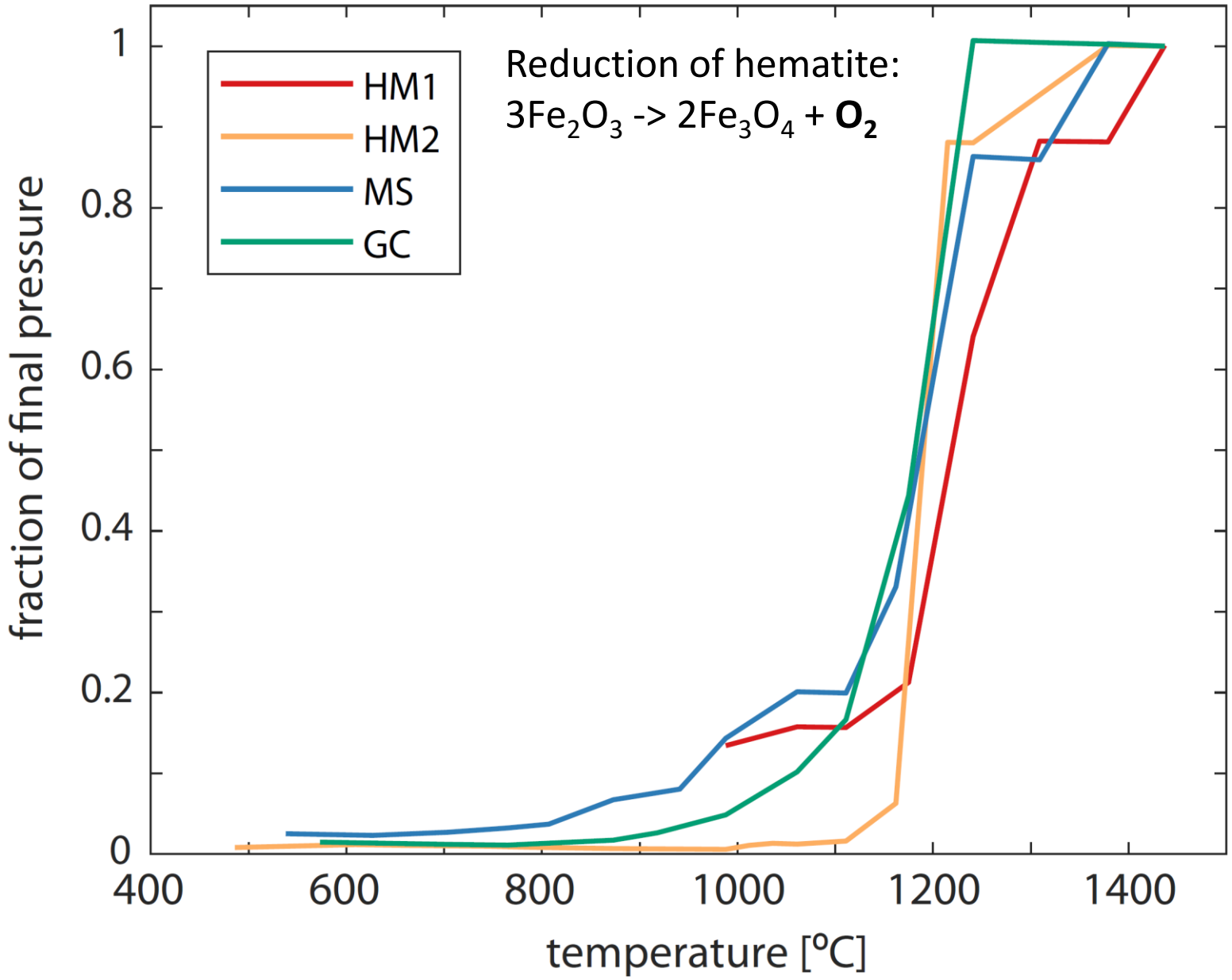


FTIR measurements of heated hematite samples



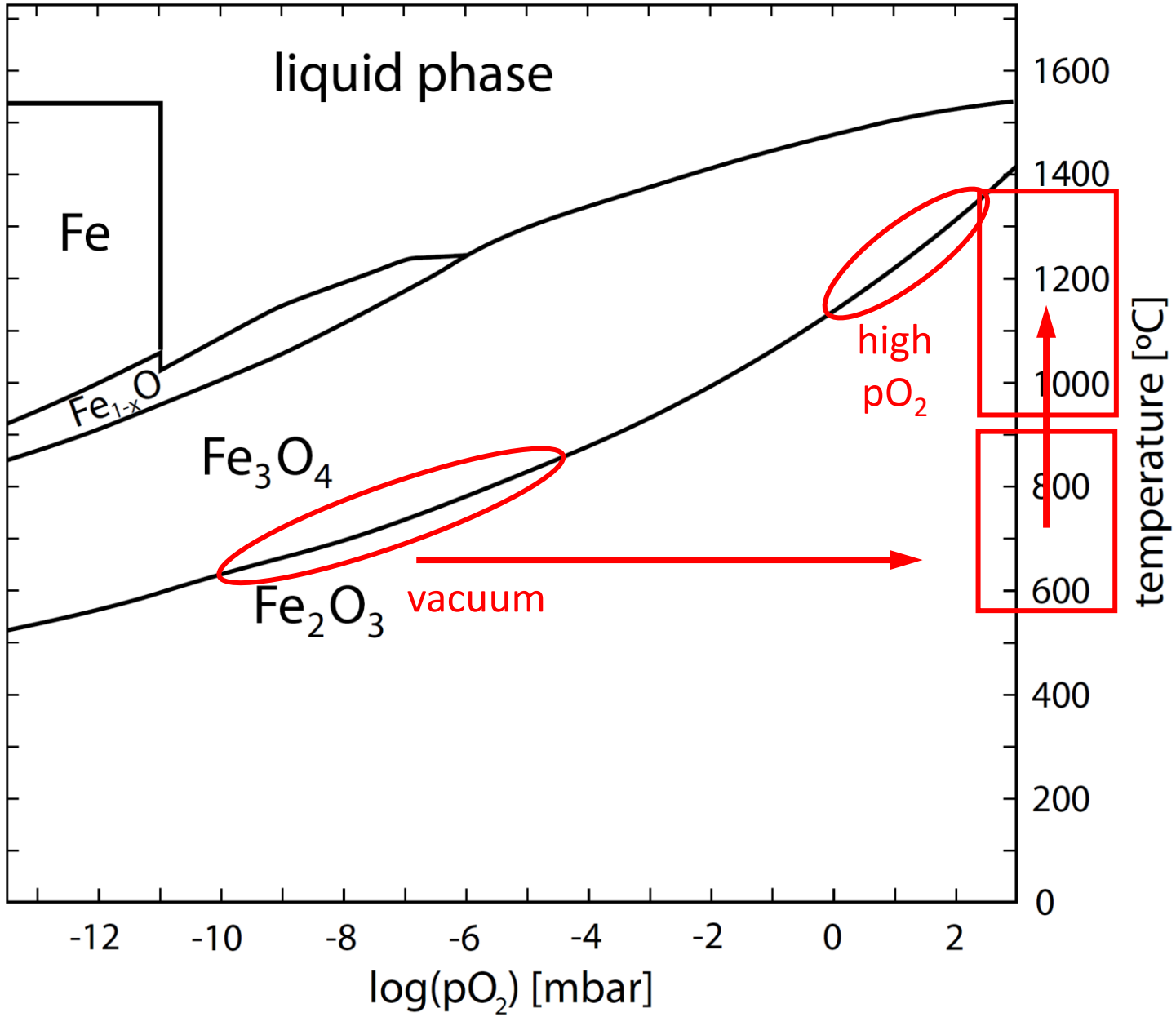
Hofmann et al. (2020)

Hematite to magnetite transition detected by pressure increase



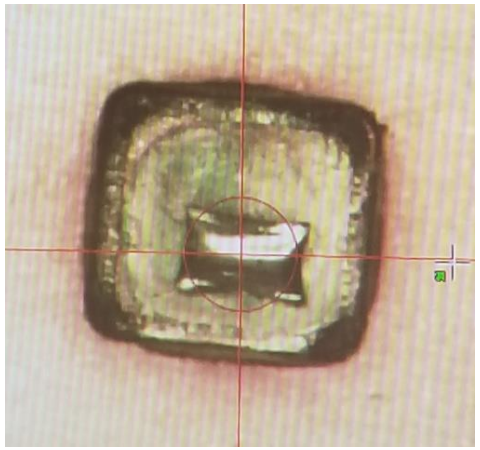
Hofmann et al. (2020)

Delaying phase change (and U-loss?) to higher temperatures

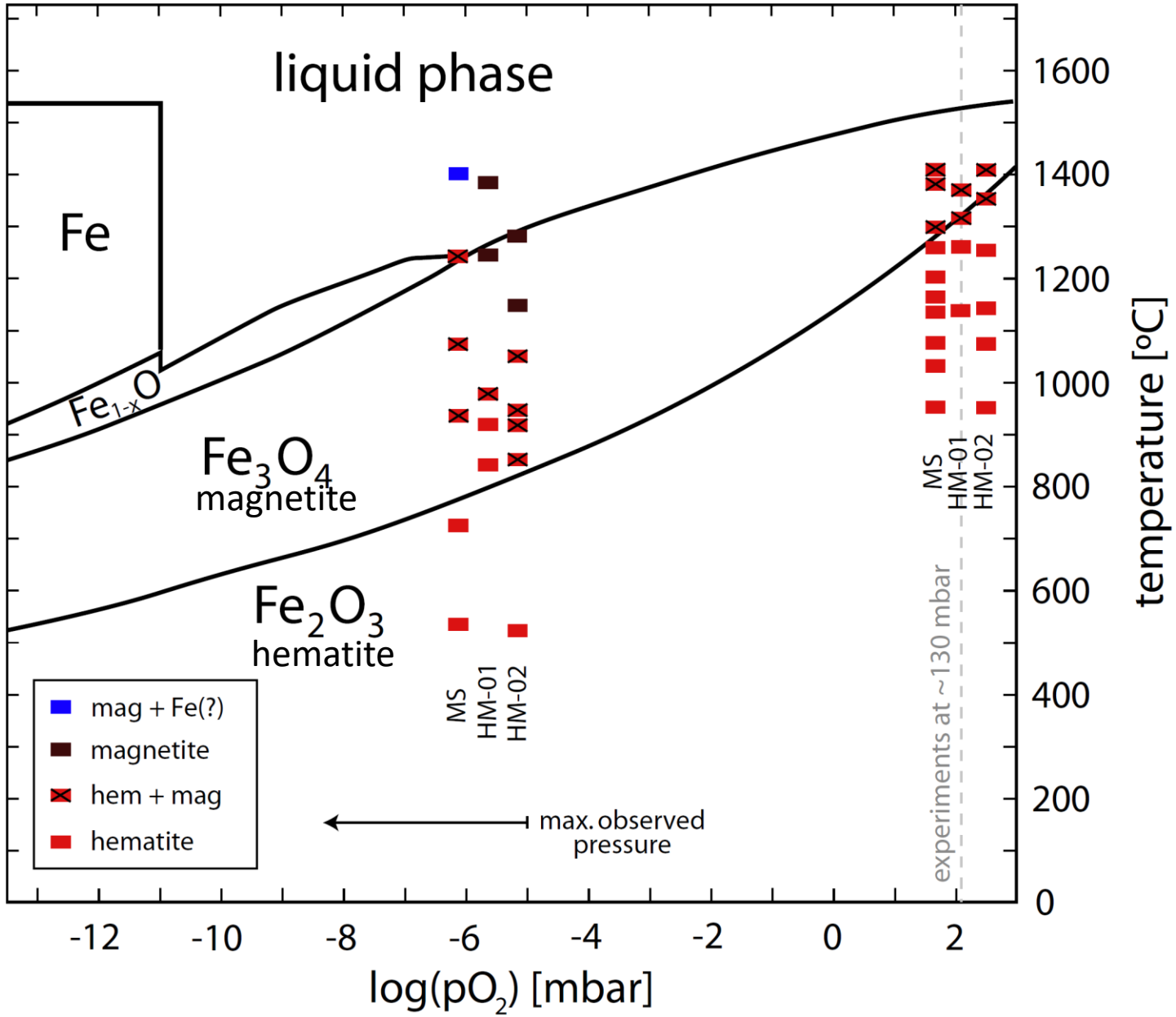


Phase diagram after Ketteler et al. (2001)

Data from laser-heating experiments vs. prediction



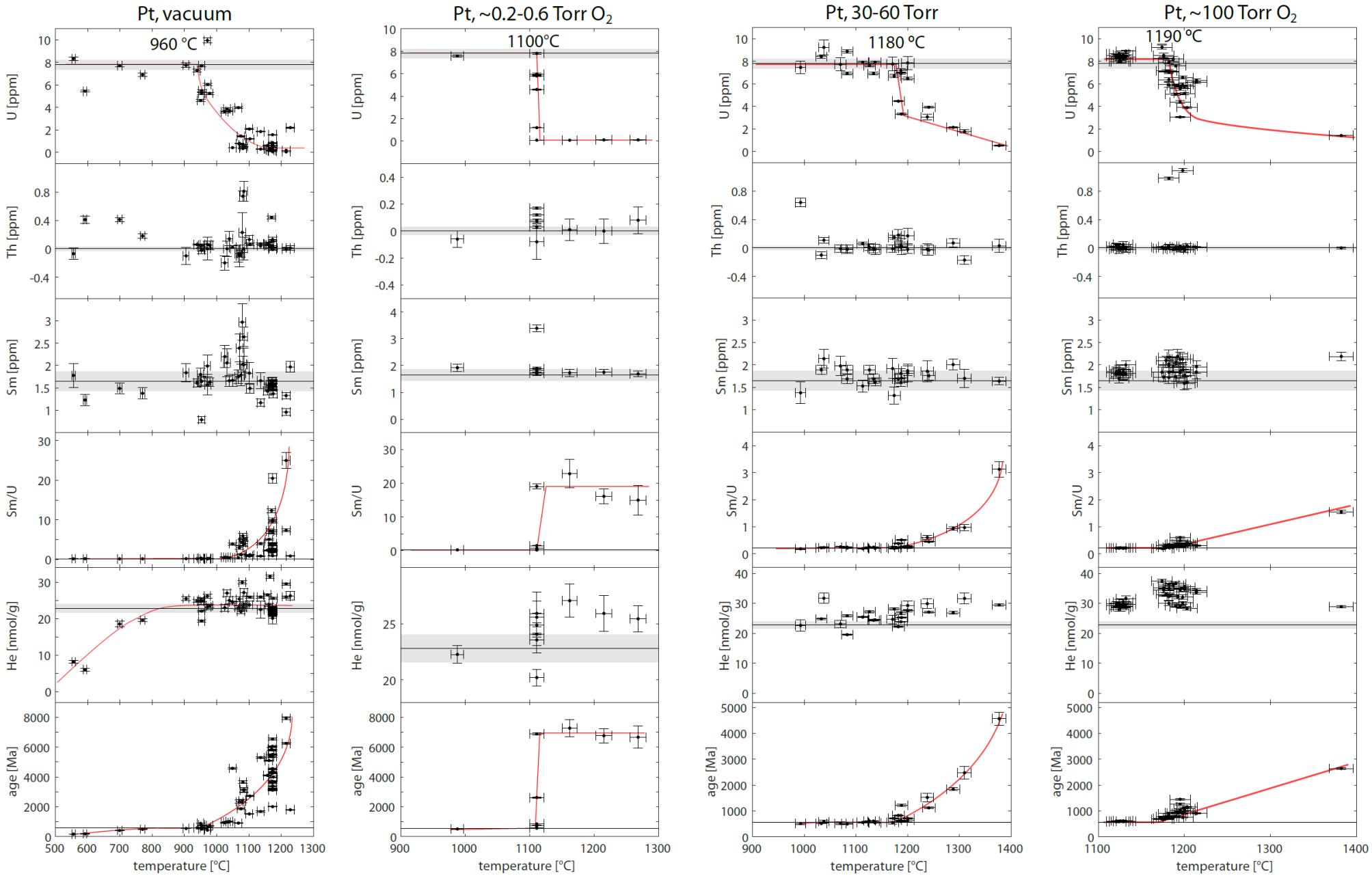
- Laser-heating of Pt packets
- FTIR on powdered sample



Hofmann et al. (2020)

Phase diagram after Ketteler et al. (2001)

Effect of increasing pO_2 on U-loss temperature

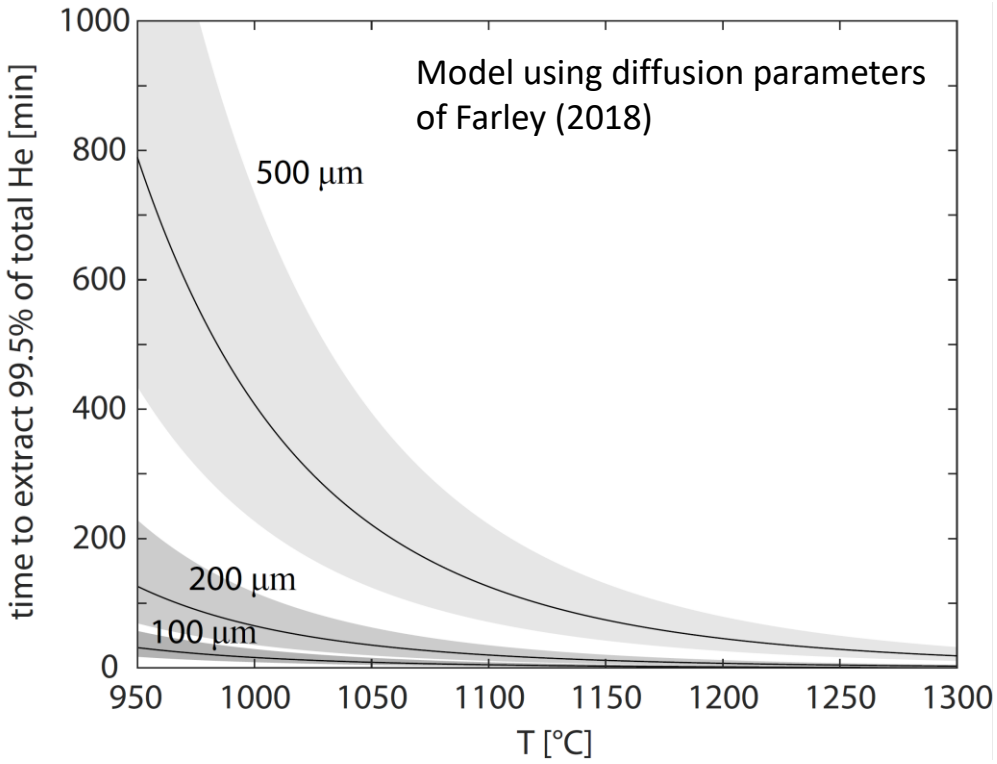


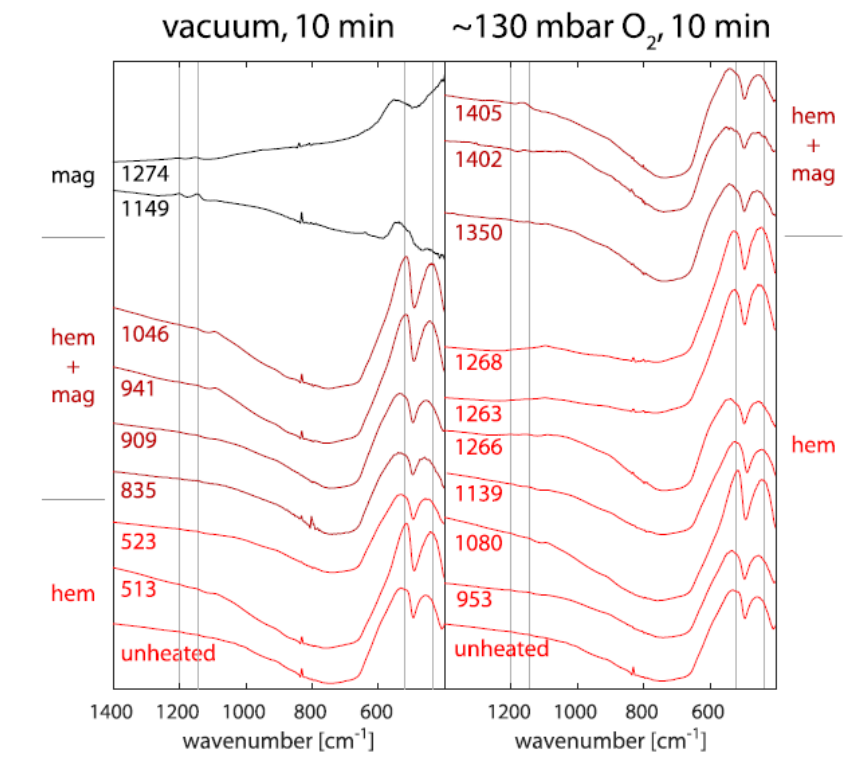
Correlation of U-loss and phase change

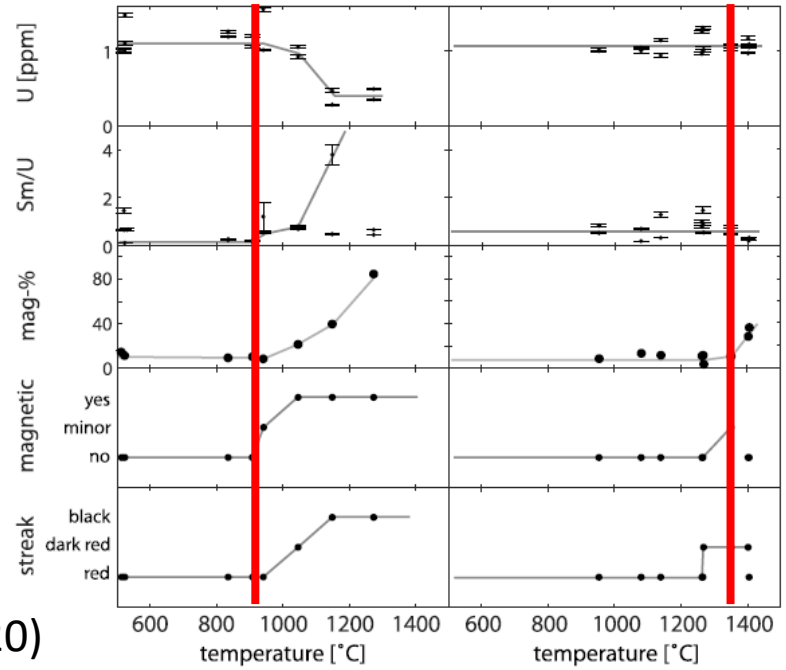
Delay of phase change/U-loss:

~980 °C → 1200-1300 °C

with ~100 Torr (130 mbar) O_2

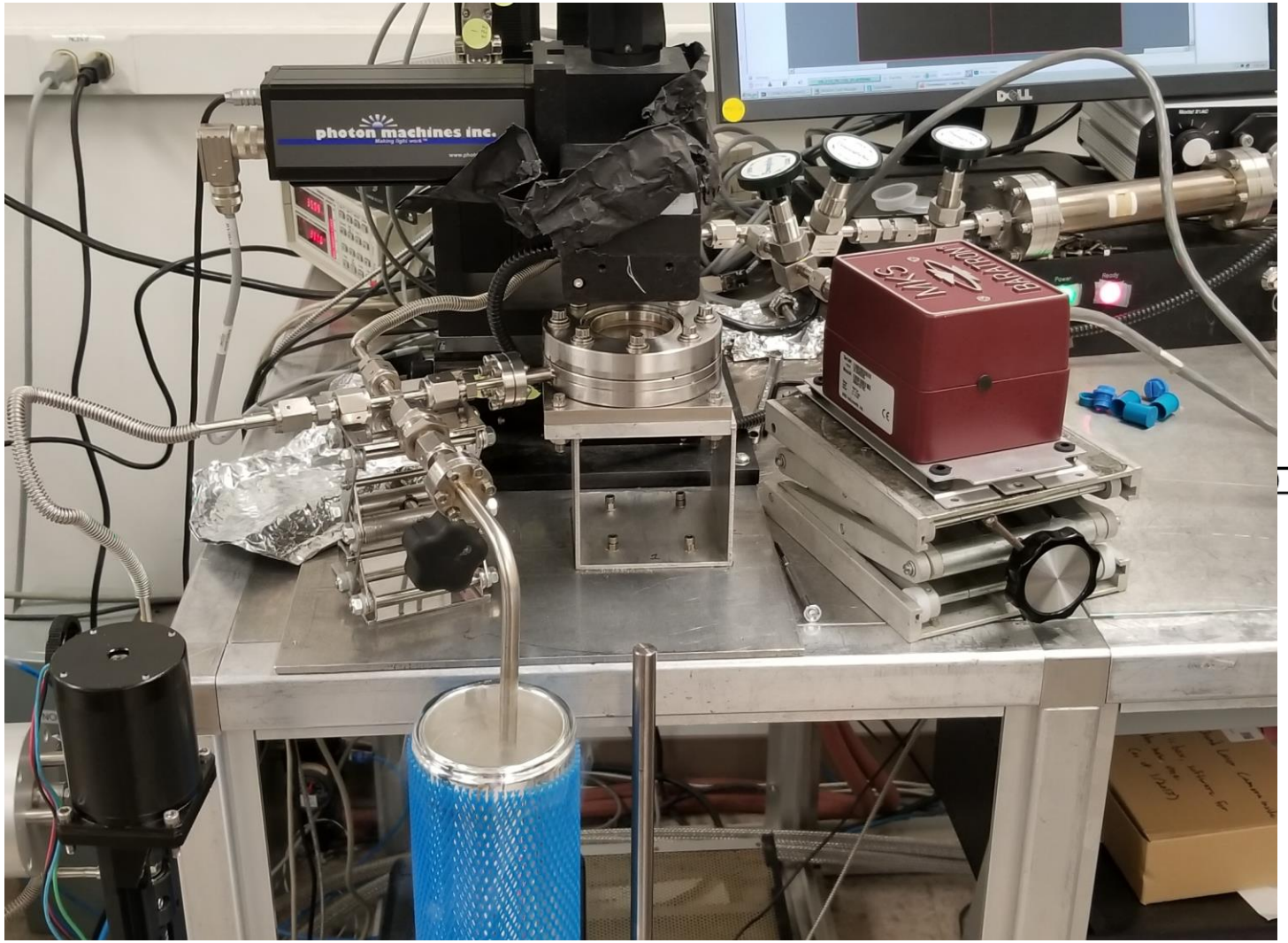


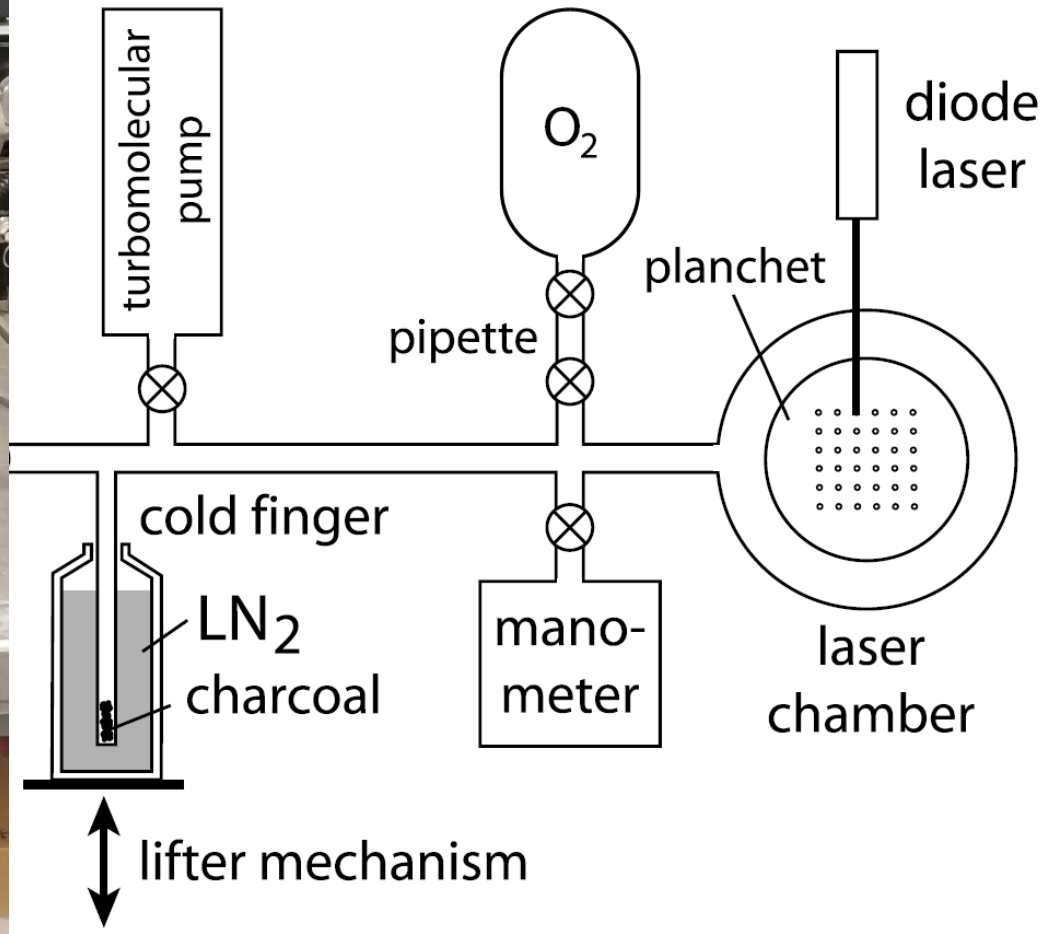




Hofmann et al. (2020)

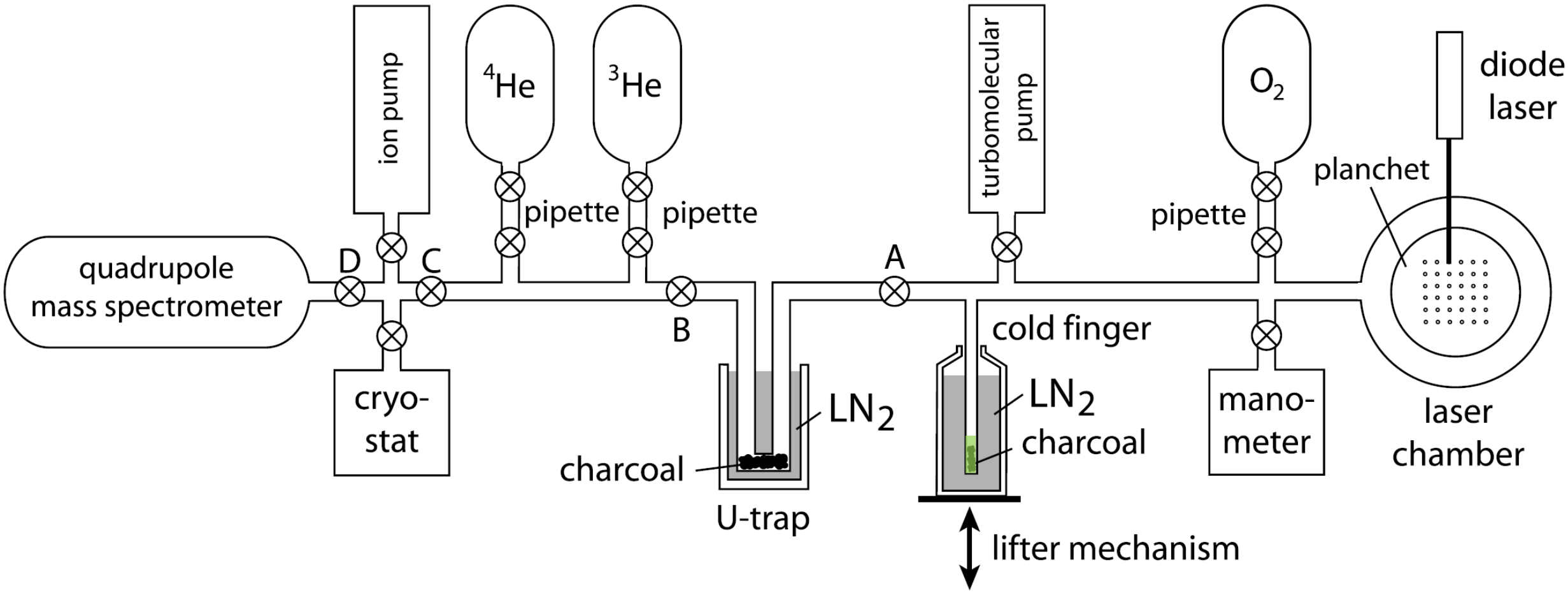
Modifications to the quad line to automate this method





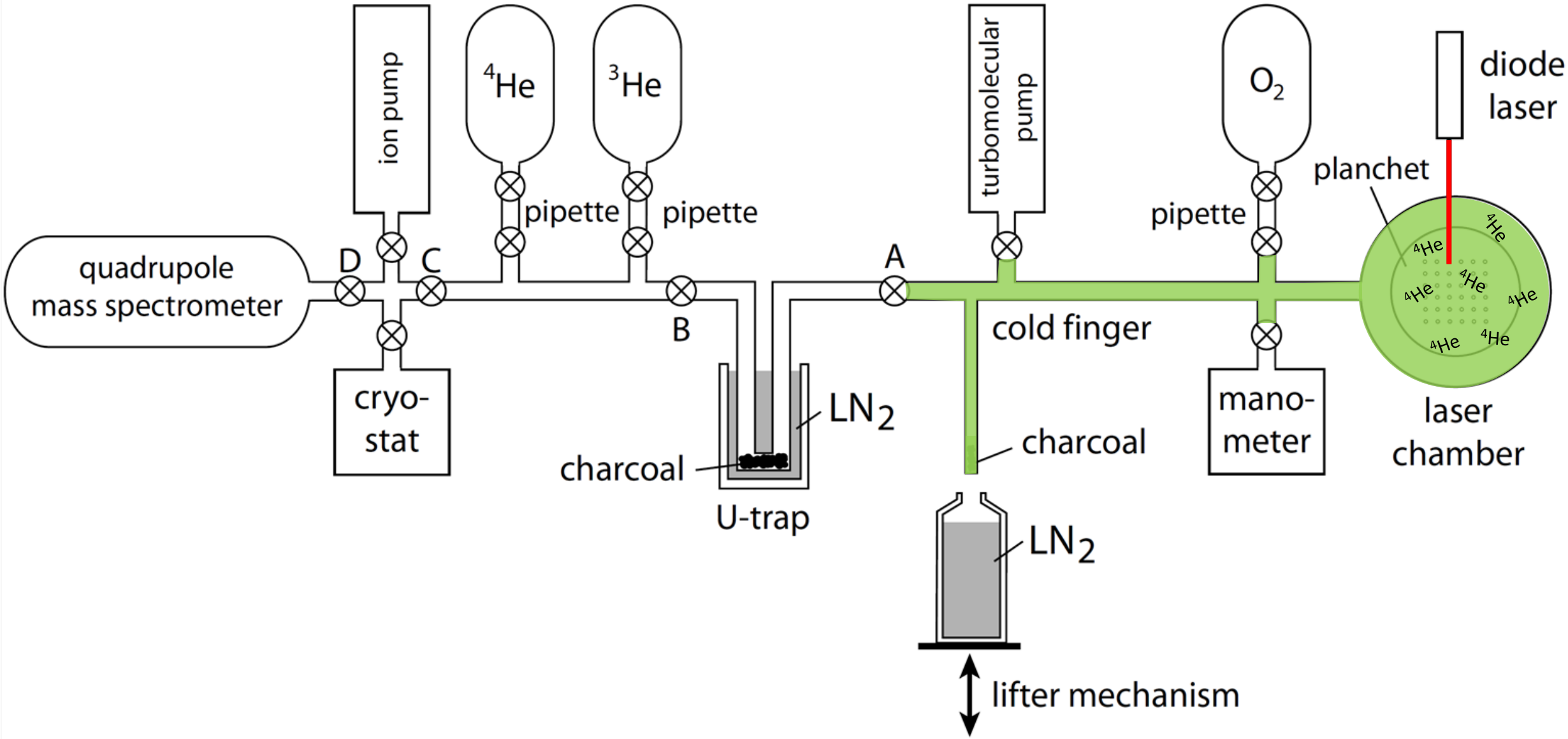
Hofmann et al. (2020)

High-pO_2 degassing procedure



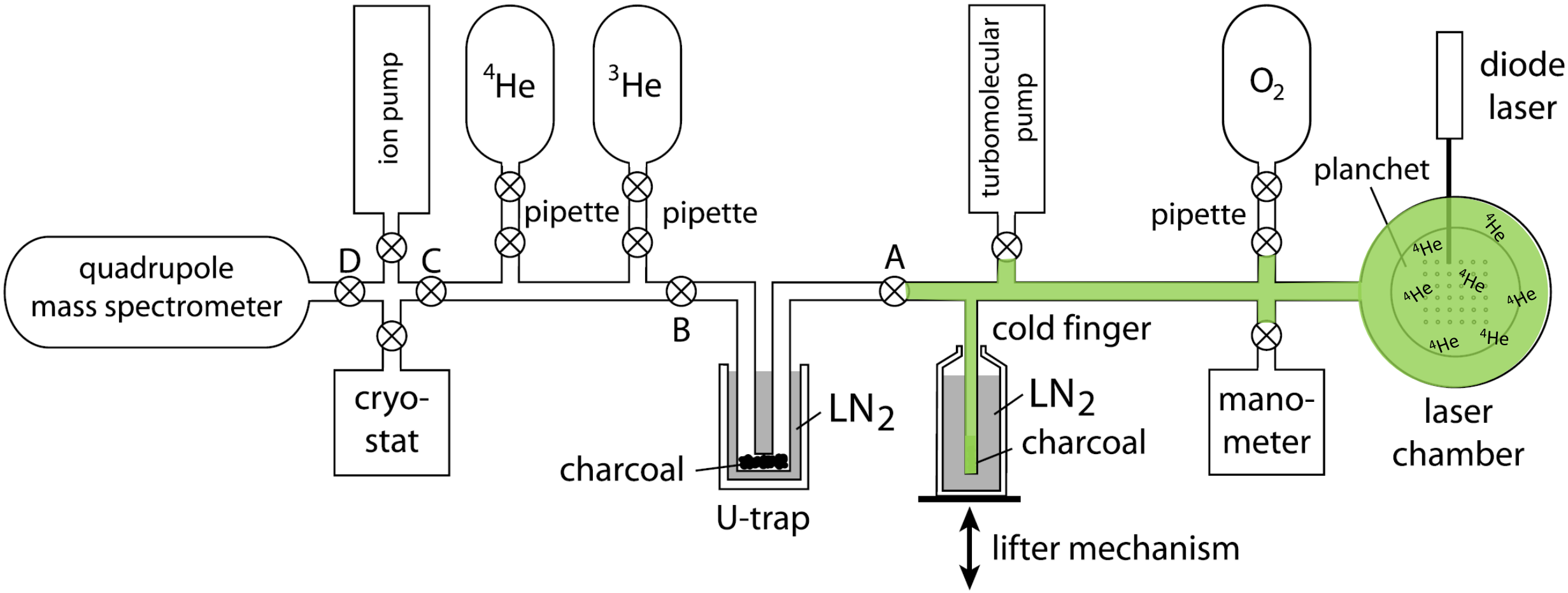
Hofmann et al. (2020)

High-pO_2 degassing procedure



Hofmann et al. (2020)

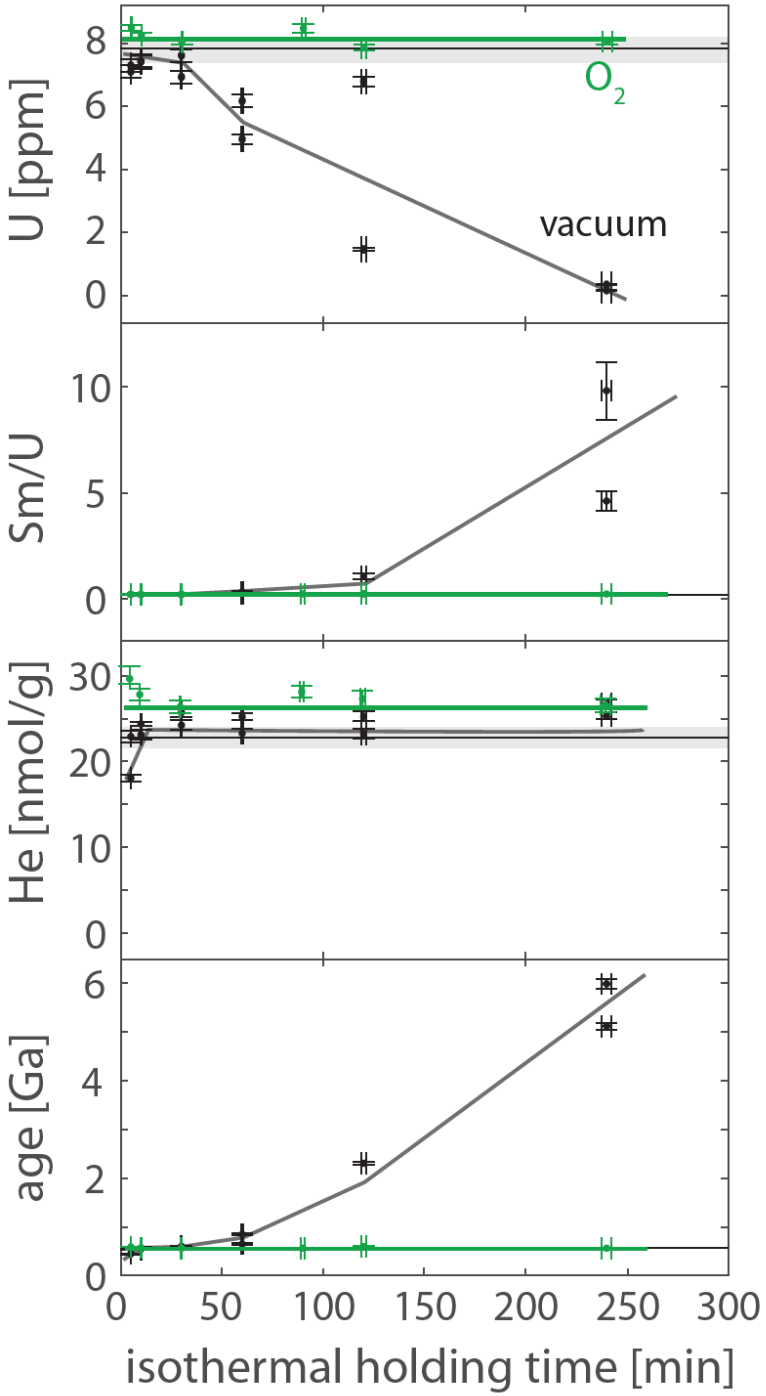
High-pO_2 degassing procedure



Hofmann et al. (2020)

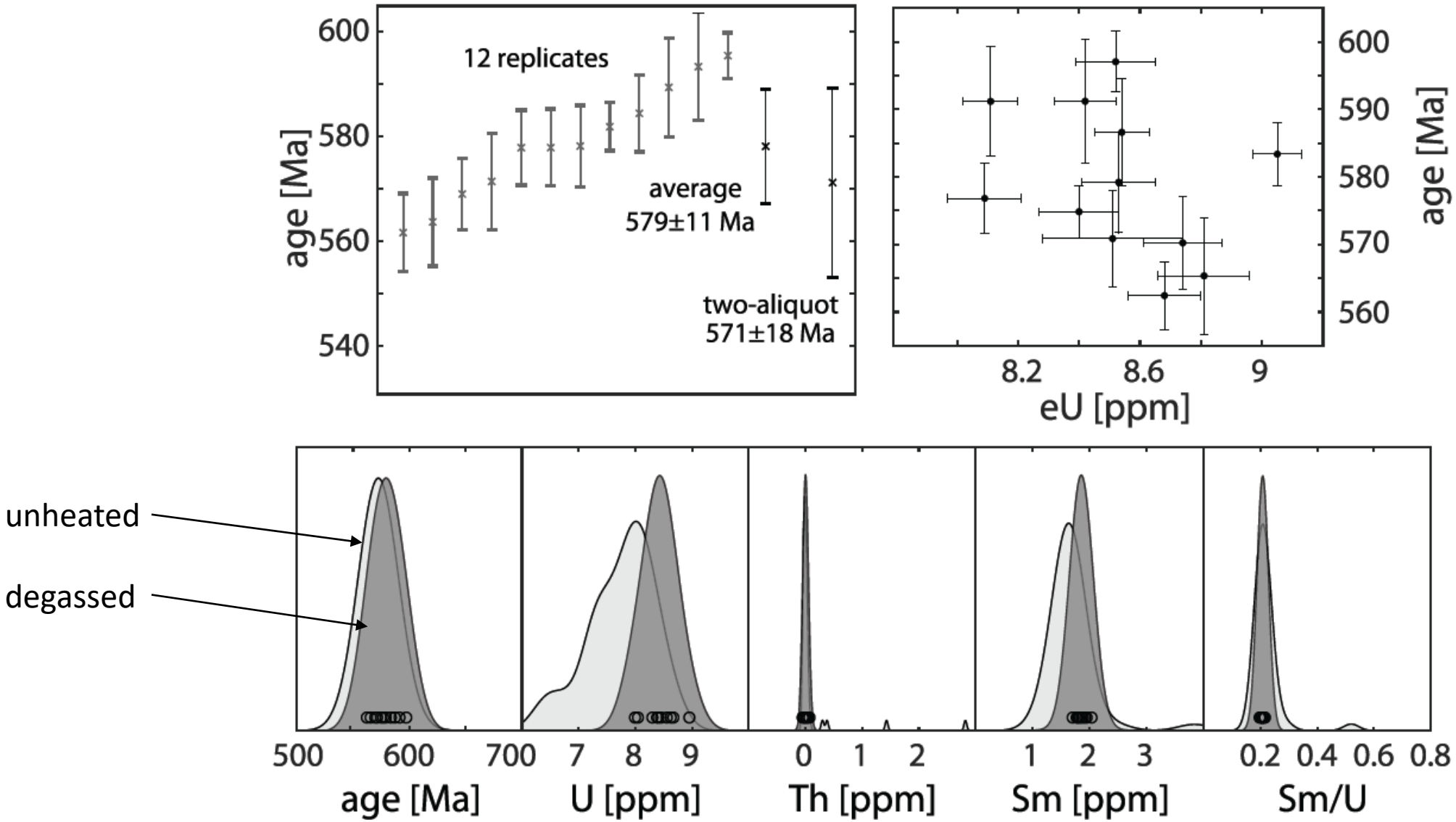
Isothermal holding at 1000 °C in vacuum and O_2

- Loss of U in vacuum increases with holding time
- No detectable loss of U with high-pO_2 at 4 h of holding



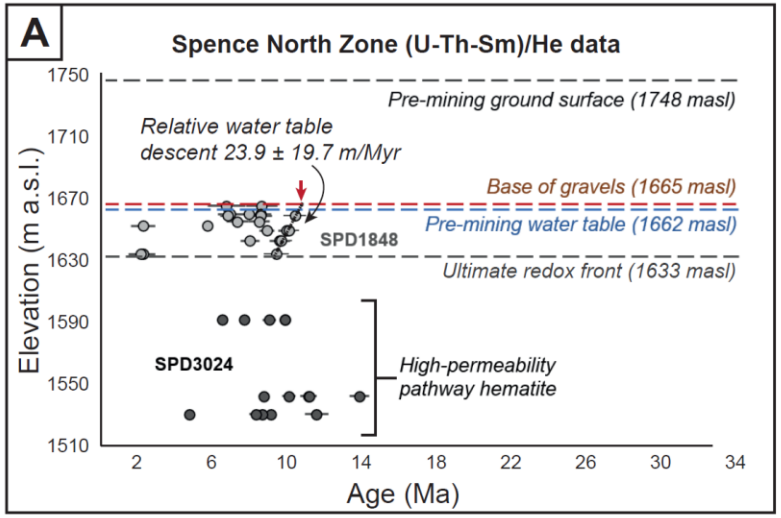
Hofmann et al. (2020)

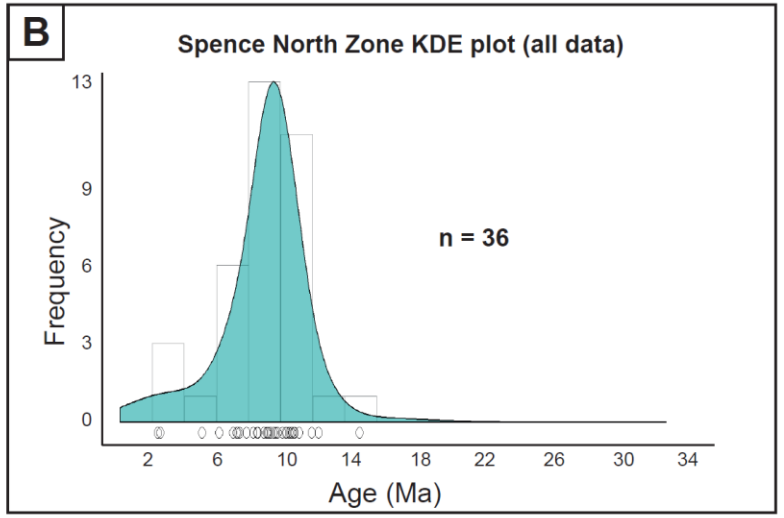
Analysis of highly-retentive hematite sample using high-pO_2 method

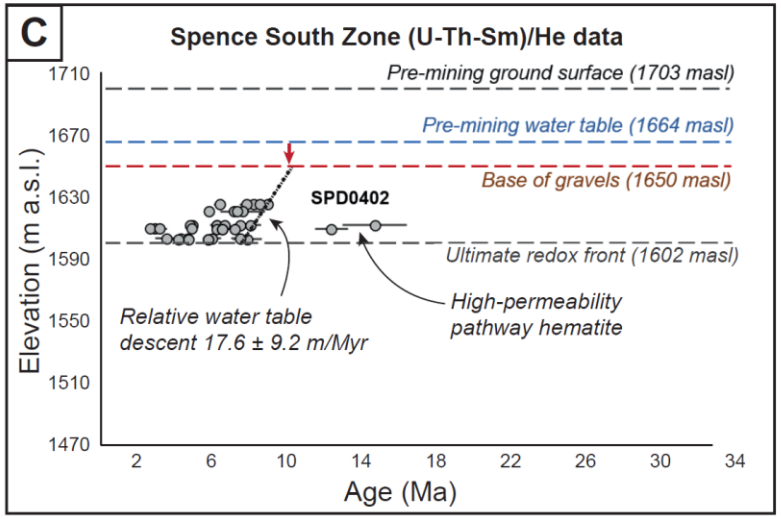


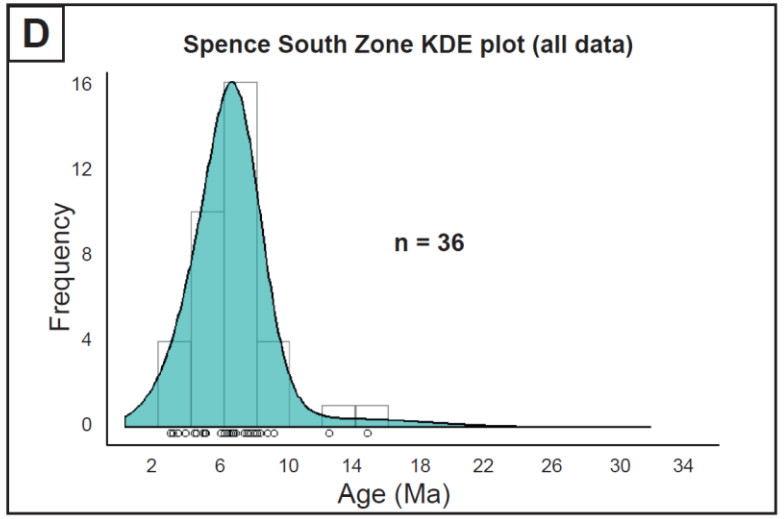
Hofmann et al. (2020)

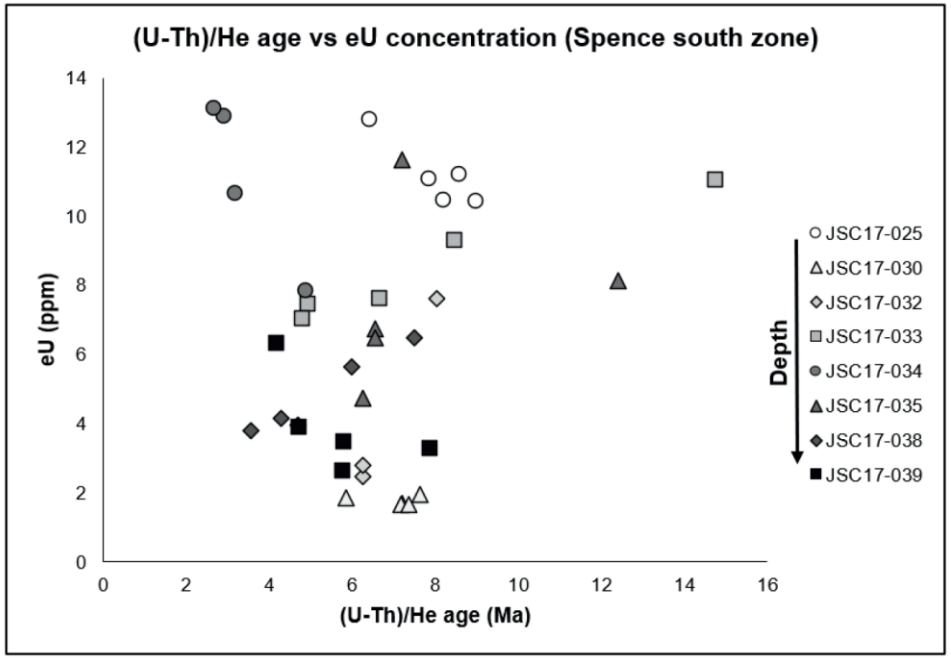
Recent paper on weathering and groundwater in the Andes using this method







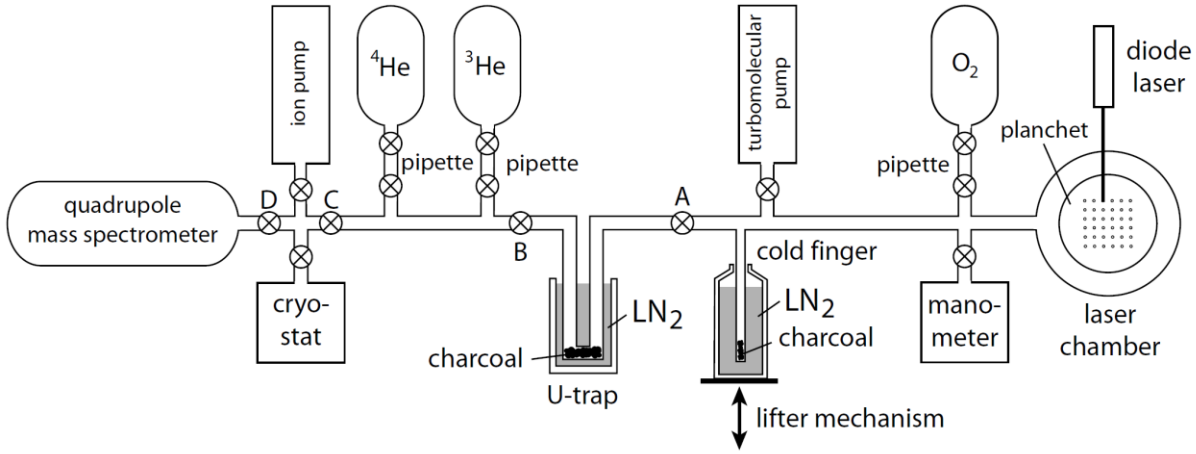




Shaw et al. (2021)

Conclusions

- Hematite and goethite show detectable U-loss at ~980 °C, massive loss at 1050-1100 °C
  → Pyrometric feedback during laser-heating is important!
- Th/U or Sm/U can indicate major loss of U, but intra-sample variability (usually 10-20%) can make it hard to detect small but significant loss
- Some hematites must be heated to 1000-1100 °C to be completely degassed
- U-loss correlates with phase change from hematite to magnetite
- This phase change and U-loss can be delayed to higher temperatures with an increased oxygen partial pressure (pO_2) during laser-heating
- This procedure can be automated for routine hematite (U-Th)/He dating



Chemical Geology 532 (2020) 119350

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

U-loss associated with laser-heating of hematite and goethite in vacuum during (U–Th)/He dating and prevention using high O_2 partial pressure

Florian Hofmann*, Jonathan Treffkorn, Kenneth A. Farley

California Institute of Technology, 1200 E California Blvd, Pasadena, CA 91125, United States