New constraints on the Sulfur isotope signature of the sub-continental lithospheric mantle wedge: *in situ* $\delta^{34}S$ analyses of pentlandite from orogenic garnet-bearing peridotite of the Ulten Zone, Eastern Italian Alps

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Big Picture

- **Exhumed (ultra-)HP rocks** provide a tangible material to directly study the elements cycles in subduction settings
- **S behaviour** is complex during slab metamorphism and metasomatism
- Still significant **uncertainties** on the speciation, flux and isotopic composition of S (Li et al. 2020)
- S isotope composition of **mantle wedge** is poorly constrained

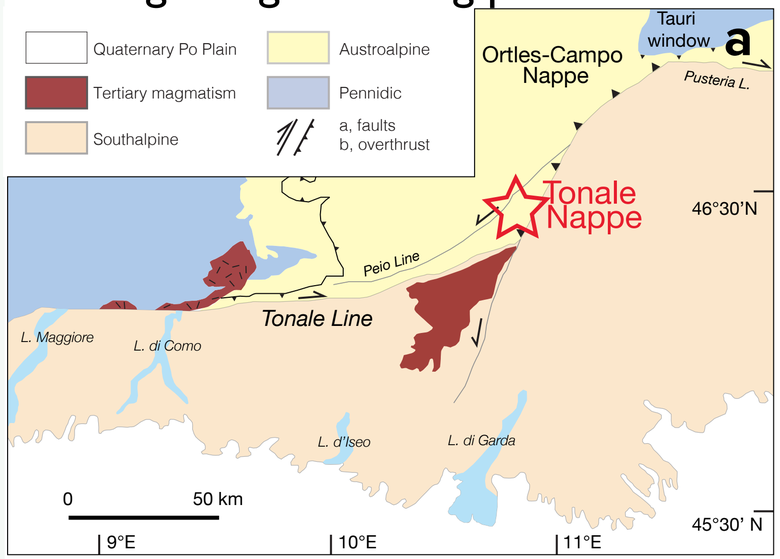
Goals:

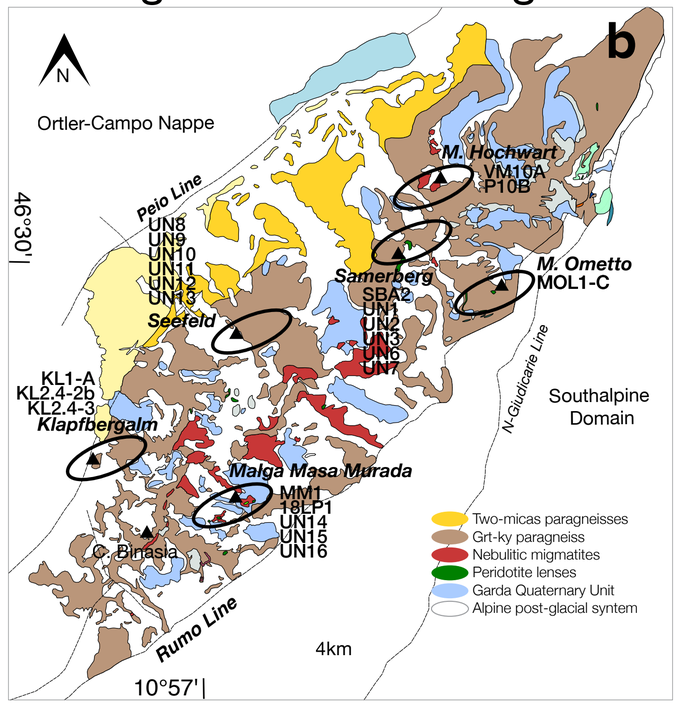
➪ **Unravel S sources of sulfides locally associated with carbonates occurring in the Ulten Zone peridotites**

➪ **Provide constraints on the S isotope signature of the orogenic mantle**

Geological Setting

Ulten Zone (UZ) is an exhumed tectonic mélange of Variscan age, composed by grt-ky-bearing gneisses and migmatites embedding lenses of orogenic grt-bearing peridotites





(a) UZ is part of the Tonale Nappe in the Italian Alps and (b) simplified sketch of the Ulten Zone and sample location after Langone et al. (2001) and Consuma et al. (2020)

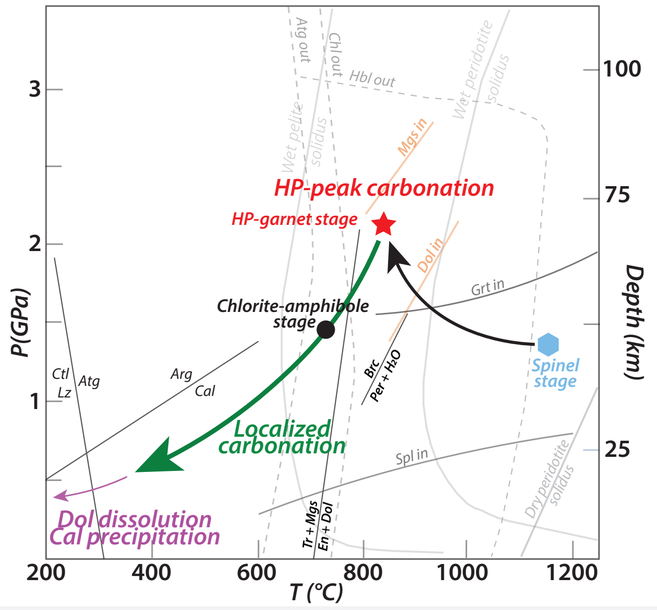
Sulfur Isotopes

- Base metal sulphides (**BMS**), within mantle-derived peridotite are largely composed of monosulphide solid solution (**MSS**) and intermediate solid solution (**ISS**)
- Sulfides solid solutions forming at high-T are not stable at lower temperatures and tend to re-equilibrate to polymineralic sulfide assemblages
- **Sulfur isotopes** provide an excellent geochemical tool to investigate HT-mantle processes due to minimal isotope fractionation at HT and large differences between mantle and crustal reservoirs

➪ **In-situ ^{34}S analyses of multiple generations of sulfides with a well-constrained petrography is necessary to understand the evolution of S throughout the metamorphic evolution of UZ peridotites**

Ulten peridotites: good to investigate the deep S cycling

- 3 main lithotypes: **coarse-grained spinel peridotite** (*CP*), **fine-grained garnet-amphibole peridotite** (*FGP*), **fine-grained chlorite-amphibole peridotite** (*FCP*).
- *FGP-FCP* interpreted as derivatives of *CP*. Serpentinization increases from *CP* to to *FCP*.
- Hydrous phases + carbonates + sulfides assemblages in multiple textural positions suggest **several stages of metasomatism** involving **H_2O-C-S liquids** throughout the UZ metamorphic evolution.



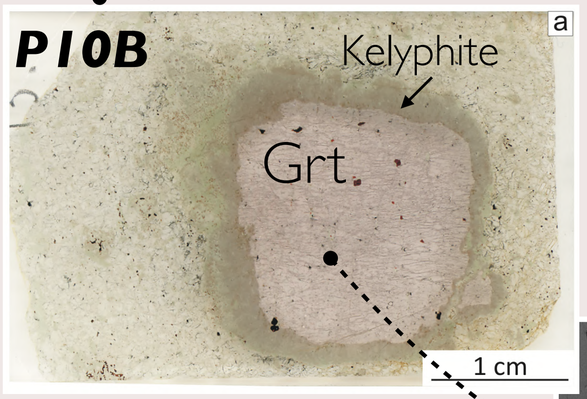
P-T path of the UZ peridotites and carbonate formation stages related to influxes of liquids into the peridotites. See Consuma et al. (2020) for a detailed explanation.

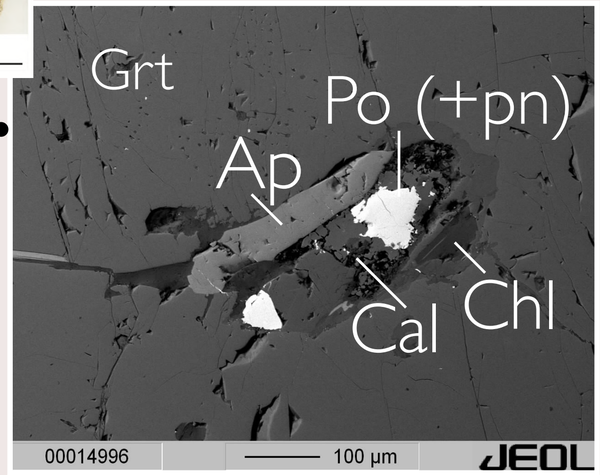
➪ **Provenance of C-S-bearing fluids still uncertain**

Petrography of sulfides: polycristalline inclusions (PI) in garnet

"Huge" cm-sized garnet from M. Hochwart

Figure modified after Lo Po' et al. 2020.





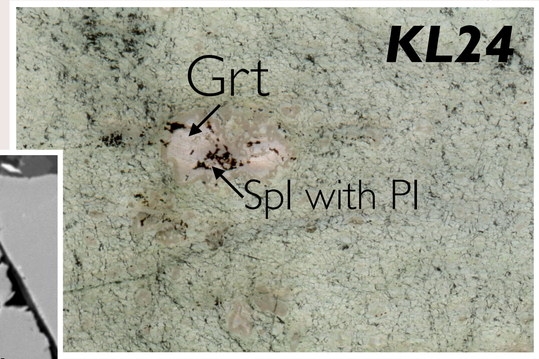
- **Pyrrhotite** (Po) grains were predominantly found in P10B garnet as PI
- Outside garnet, only **pentlandite** (Pn) have been found interstitial in the matrix

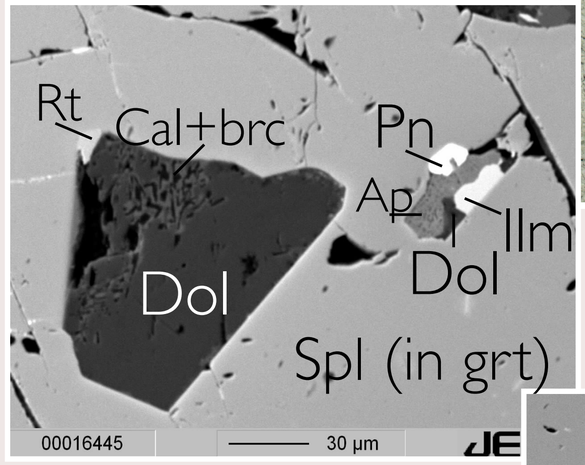
Two hypotheses:

➪ 1) Large garnet may have preserved HT-sulfide assemblages (but here not negative shapes!)

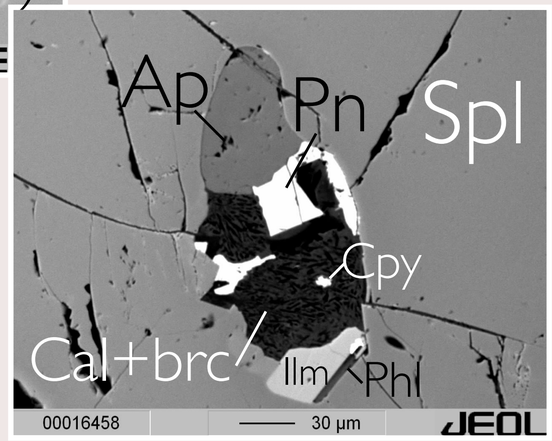
➪ 2) Po (+Pn) is related to local garnet-fluids reaction at the initial stage of exhumation (following Lo Po' et al. 2020)

Mm-sized garnet from Klapfbergalm



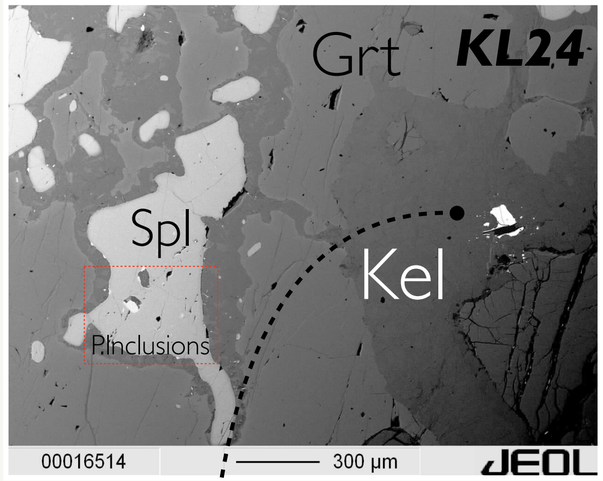


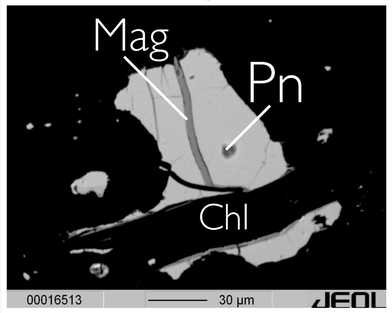
- PI in mm-sized garnet consists of Pn with occasionally **chalcopyrite** (cpy) or **chalcocite** (cc)
- **No Po** have been found in garnet nor in the matrix



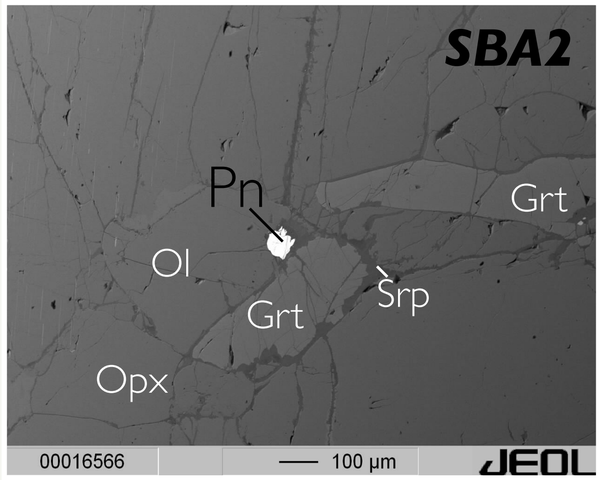
Petrography of sulfides

In kelyphitic corona

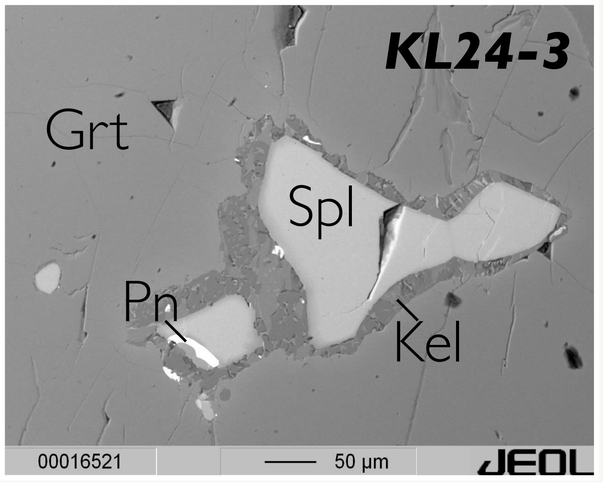




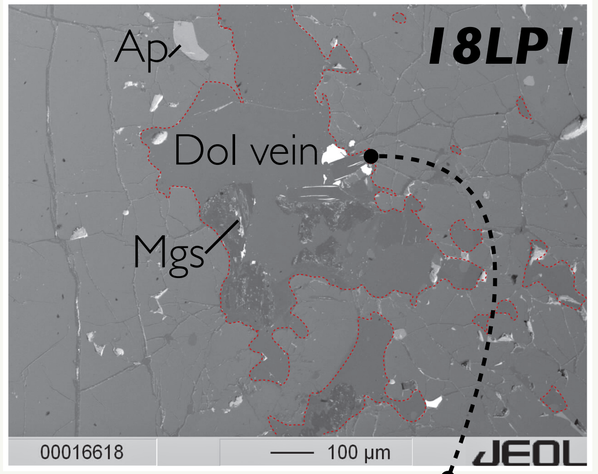
Interstitial in matrix

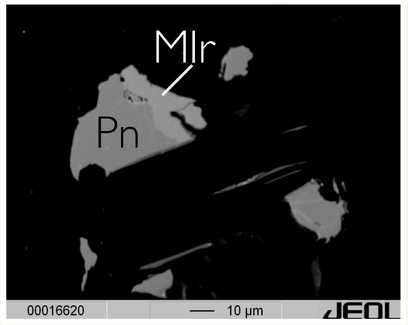


In spinel, orthopyroxene (not Pl)



In carbonates/ serpentine veins

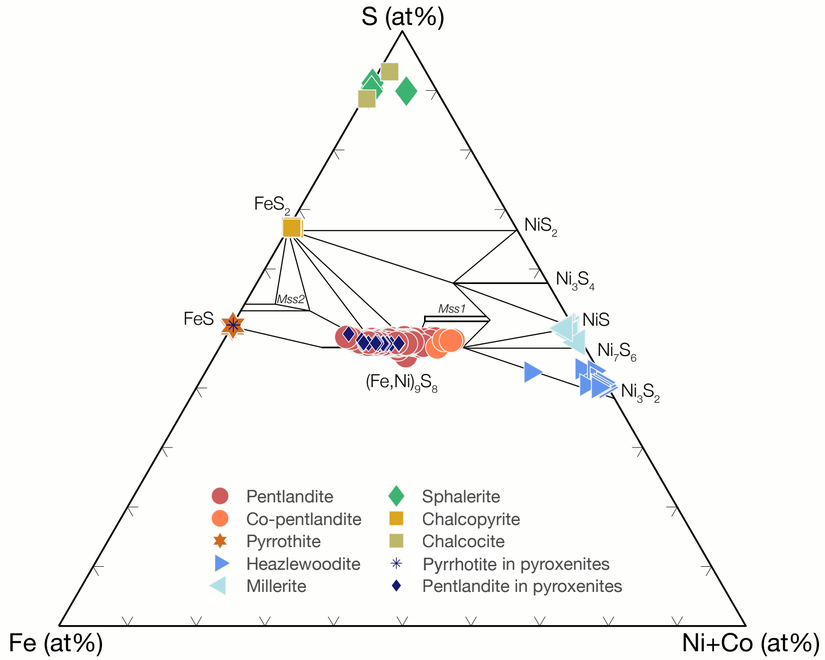




petrographic summary

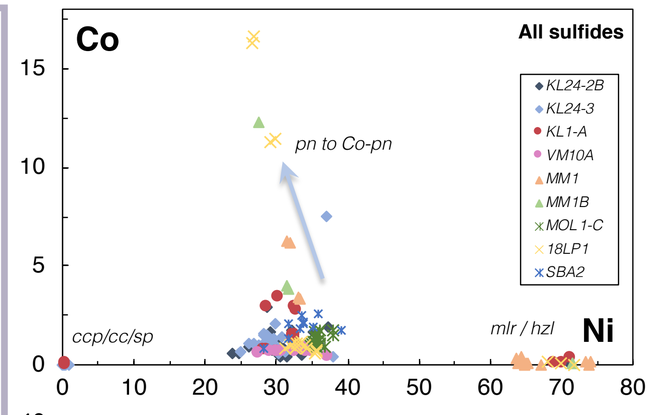
- **Pn** is the dominant sulfide phase of UZ peridotites
- **Rare Po** grains as Pl found in cm-sized garnet
- Pn ±**heazlewoodite** ±**millerite** in *FCP*
- **Cpy**, **Cc** and **Sphalerite** were found only in porphyroclastic *FGP* in association with garnet and its kelyphitic corona
- Occasionally, **nickeline** (Ni,As) **blebs** (3-5µm on average) were found within interstitial Pn grains or Pn associated with serpentine

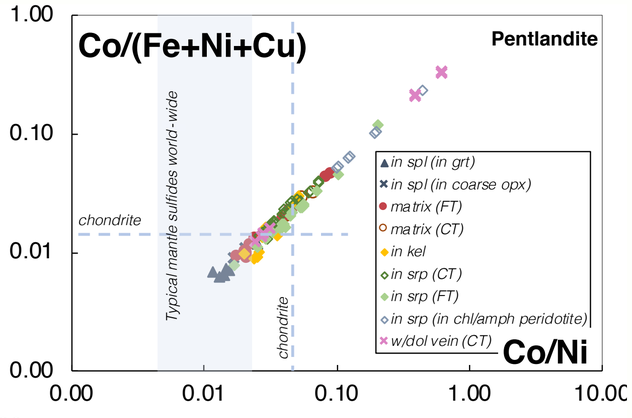
Major Element Compositions

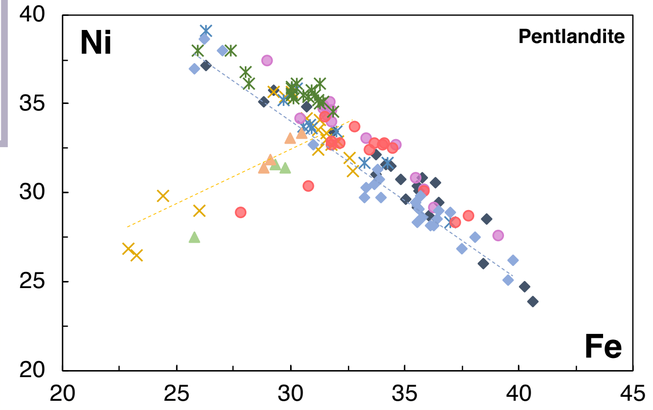


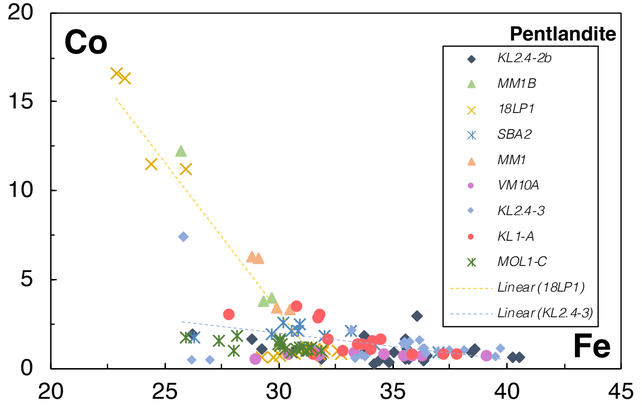
Compositions of BMS from UZ peridotites in the Fe-Ni-S system at 250°C and atmospheric pressure. Phase relationships and Mss1 and Mss2 compositional fields after Craig (1973)

Lithotype
FGP:
KL24-2B
KL24-3
KL1-A
VM10A
FCP:
MM1
MM1B
CP:
MOL1-C
18LP1
SBA2





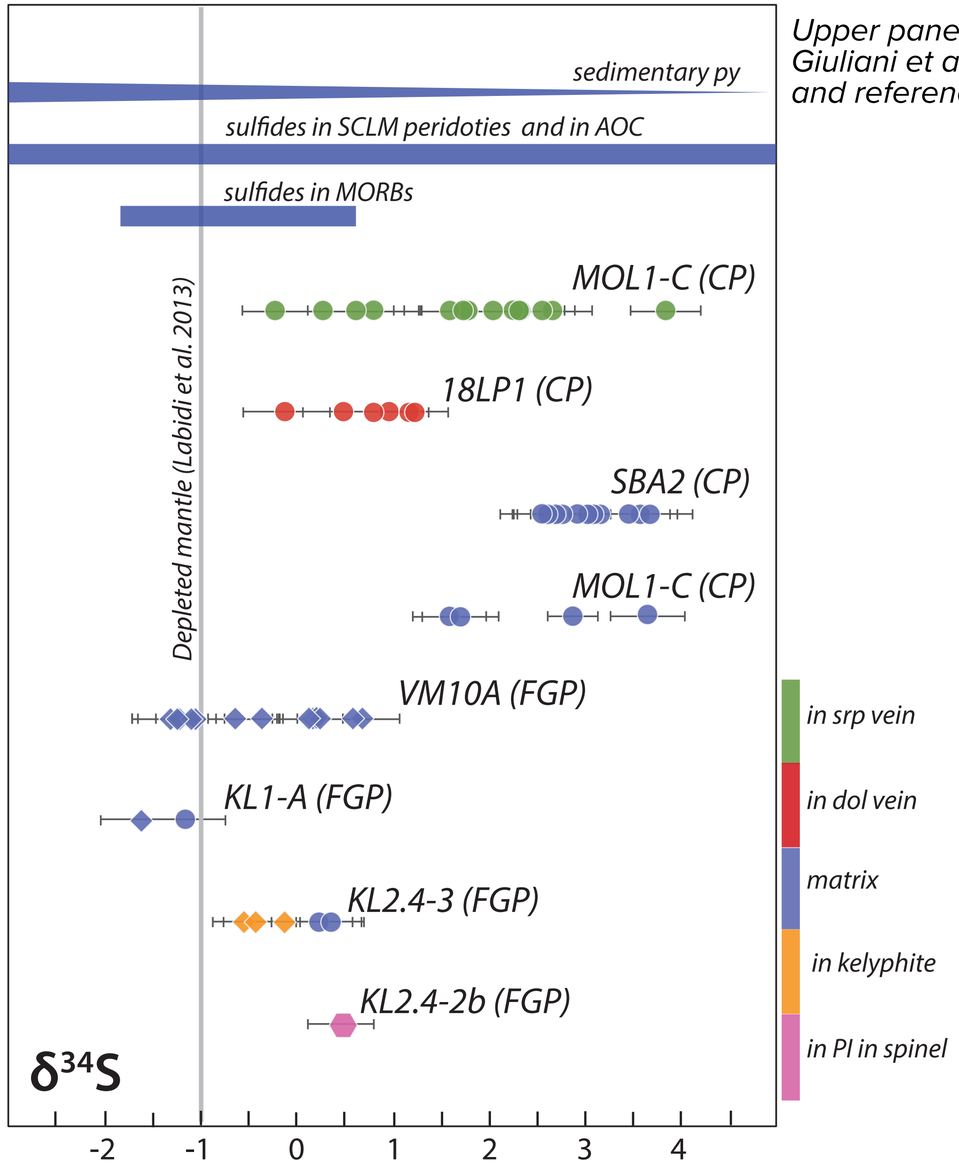




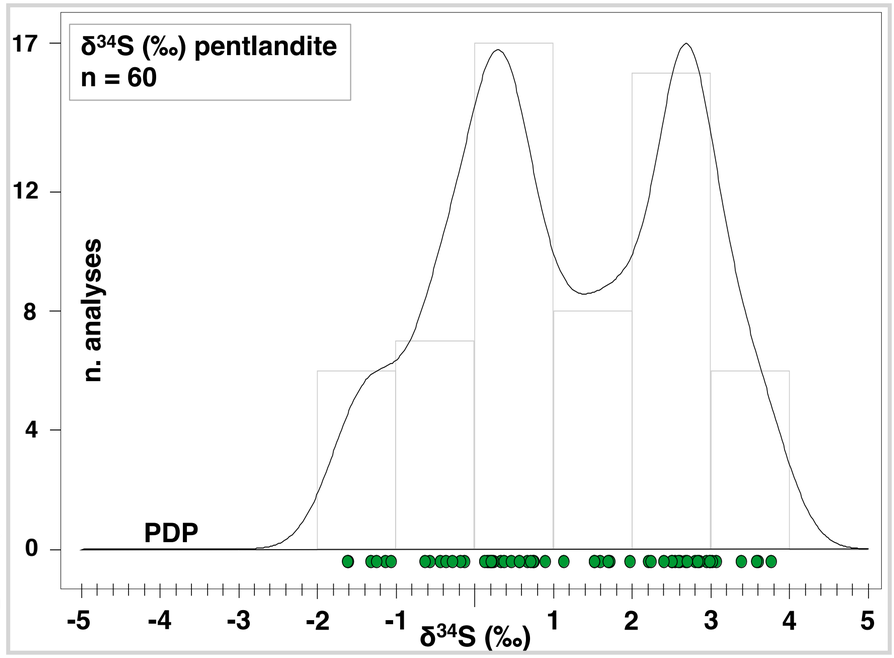
microstructural positions from samples UNx and P10B currently unavailable (office inaccessibility!)

- Pentlandite is ubiquitous with variable composition:
  Fe: 22.8-39.5 wt%; Ni: 28.8-37.8 wt%; Co: 0.4-16.5wt%
- **Pn in Pl and other grains fall in the typical mantle sulfides range**

Sulfur isotopes as geochemical tracer: SIMS analyses of pentlandite grains



Upper panel: Reservoirs data from Giuliani et al. (2016), Walters et al. (2019), and references therein



Frequency of measured $\delta^{34}S$ of pentlandite grains with probability denser curve (PDP)

- **Limited isotope signature variation for *in situ* analyses of Pn ($\delta^{34}S$ ~ −1.6 to 3.8 ‰)** with an average of $\delta^{34}S$= -0.11 (n=15) for matrix Pn in fine-grained peridotites and $\delta^{34}S$= 2.83 (n=20) in coarse-grained peridotites
- Isotopic variability of Pn in a serpentine vein is due to isotopic fractionation coupled with the removal of light S during serpentinization at T<600°C

For Methods see LaFlamme et al. (2016)

Conclusion Remarks

- The **rare preservation of Po** and the overall occurrence of Pn suggests that Pn ±Po probably derive from re-equilibration of mss to low-T, whereas Ni-rich sulfides may have formed from $(Ni,Fe)_{3\pm x}S_2$
- Assuming **limited S isotope fractionation** during re-equilibration of high-T mantle sulfides to pentlandite-bearing assemblages at T of about 600°C (see discussion in Lorand and Gregoire, 2006) we suggest that our Pn grains mostly preserve a mantle-like isotopic signature
- **Mantle-like sources** are required for S-bearing fluids (as also suggested for C-bearing fluids by using in situ Sr isotope of associated carbonates, Consuma et al. 2020). Mantle-like signature for both S-C is a key finding for the UZ peridotites and unexpected considering the strong interaction with crustal fluids
- The overall occurrence of Pn and occasional Nickeline blebs suggest a late influx of hydrothermal fluids capable to **remobilize Ni** from a sulfide source

Future Directions

- *PGE analyses of sulfides*
- *Build a model based on textural observations, compositional-isotopic data for the source, medium, and timing of introduction of volatiles into the mantle wedge*

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Thank you!
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