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Serpentinite dehydration leads to a release of oxygen

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Introduction

Serpentinite rocks composing ~70% of the oceanic crust [1] and carrying ~12 wt.% H_2O sink into subduction zone and introduce large amount of water in the upper mantle during their dehydration [2]. Release of aqueous fluid is an important process regarding generation of earthquakes above the subducting slab, partial melting in a mantle wedge, formation of arc magmas.

In addition, serpentinites are known to contain such minerals as magnetite Fe_3O_4 and pyrite FeS_2 in the amounts of ~5 wt.% [3] and 1.5 wt.% [4], respectively. During metamorphic reactions speciations of Fe and S are tended to change and affect oxygen fugacity. In turn, released oxygen may influence the mobility of fluid mobile elements and metals [5].

Materials and Methods

Conditions of experiments

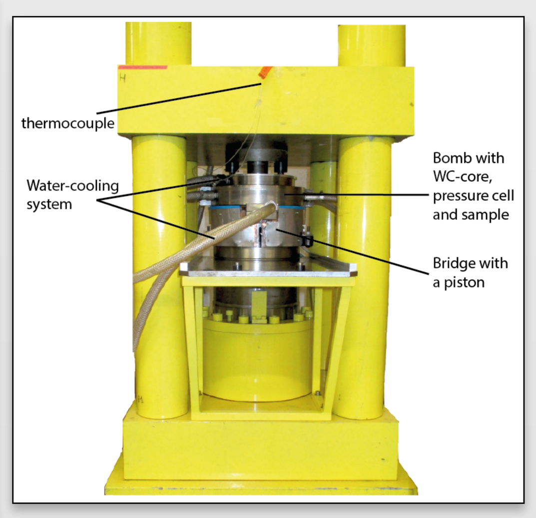
T = 450 - 900°C, P = 2 GPa

Duration - 7 days

fO_2 of the experiments ~ QFM - QFM-2

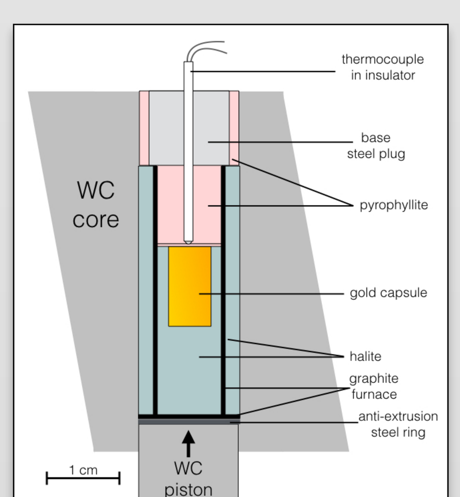
Three starting material mixtures were used for experiments:

1. Antigorite 100 wt%
2. Antigorite + 5 wt% Magnetite
3. Antigorite + 1.5 wt% Pyrite



Piston cylinder apparatus

- **Electron microprobe** was used to analyse mineral compositions of experimental products.
- Phase abundances and water amount in each experimental product were estimated using **mass balance calculations** using the average individual mineral compositions measured by EPMA.
- Bulk K-edge **XANES** measurements were performed (SOLEIL and SLS synchrotrons) to determine Fe and S speciation.
- **Fe^{3+}/Fe_{total}** ratios were derived from the analysis of pre-edge peaks [6].

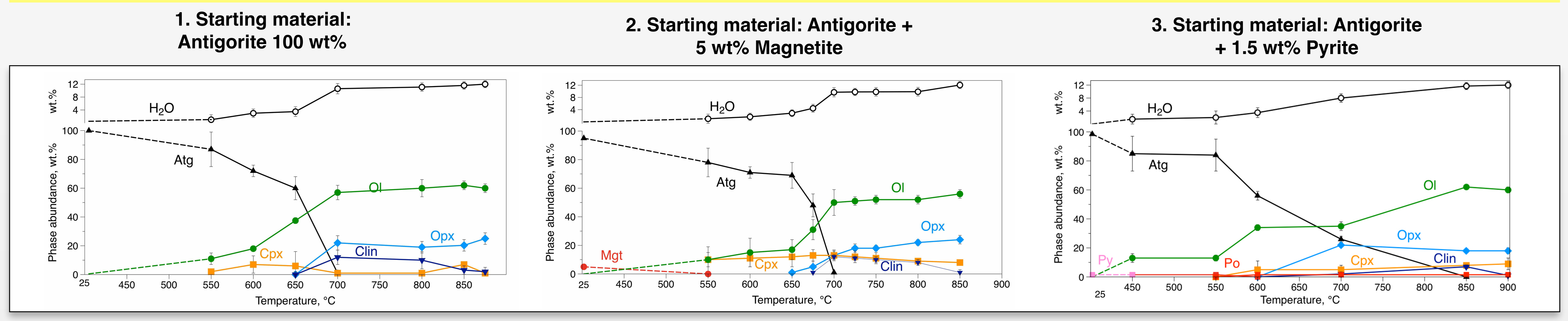


Cross-section of the pressure cell and the solid media piston cylinder assembly

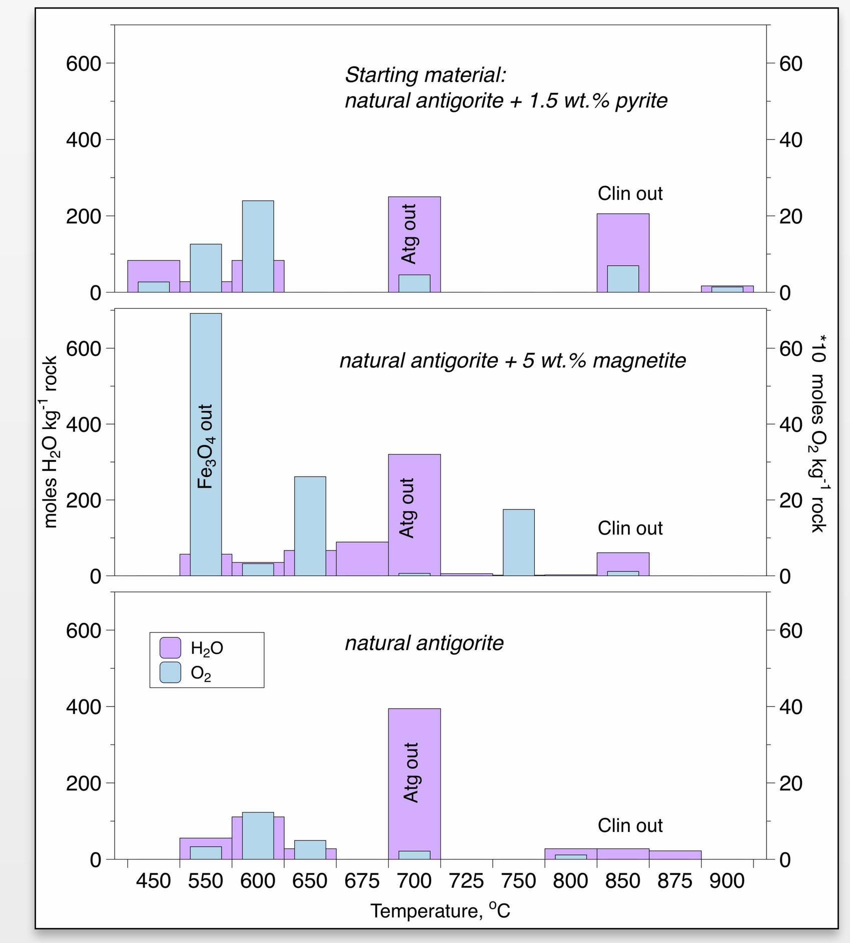
References

[1] Hacker et al. (2003) J. Geophys. Res. 108, article number 2029. [2] Ulmer & Trommsdorff (1995) Science 268, 858-861. [3] Debret et al. (2014) EPSL 400, 206-218. [4] Alt et al. (2013) Lithos 178, 40-54. [5] Pokrovski & Dubrovinsky (2011) Science 331, 1052-1056. [6] Wilke et al. (2001) Am. Mineral. 86, 714-730

Mineral assemblages of experimental products



The decrease in the amount of **antigorite** is observed in three experimental sets. **Olivine** and **orthopyroxene** are the most abundant phases at high T assemblages, between 800 and 900°C, in all experimental sets. Slight differences in the amounts of **clinochlore** and **clinopyroxene** are observed depending on starting material at temperatures between 600 and 850°C. **Pyrite** is replaced by pyrrhotite in the experimental set#3 at 600°C. **Magnetite** destabilizes at T<550°C and does not present in any experimental product in the set#2.

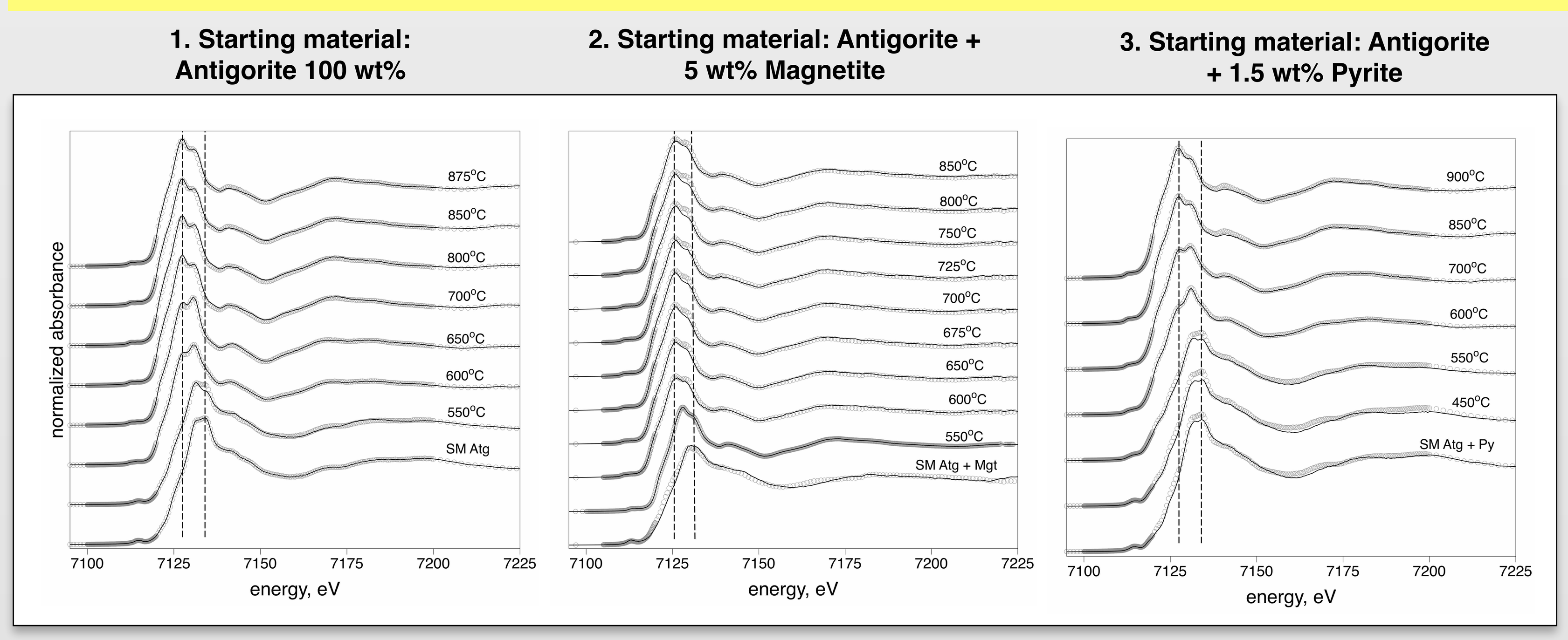


Dehydration of Mgt-bearing serpentinite leads to a release of **great amount of oxygen** at temperatures < 550°C.

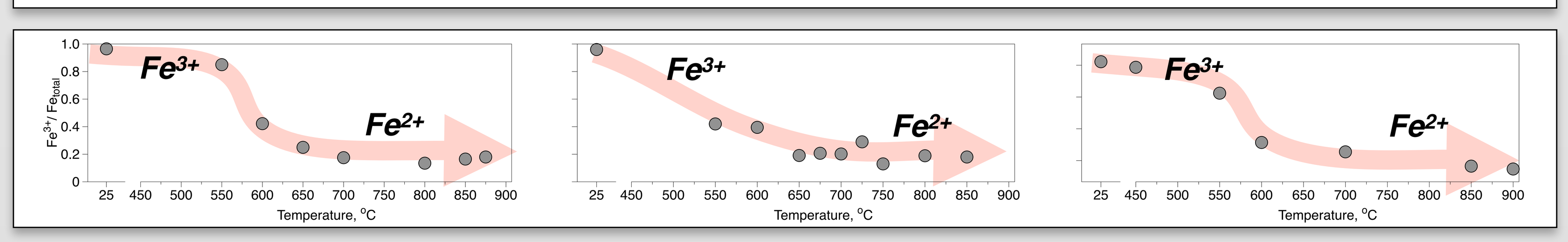
In total Mgt-bearing serpentinites release about 5 times more O_2 than Mgt-free assemblages.

Whereas amount of released **H_2O** is the same in all three experimental systems.

Fe *K-edge* XANES

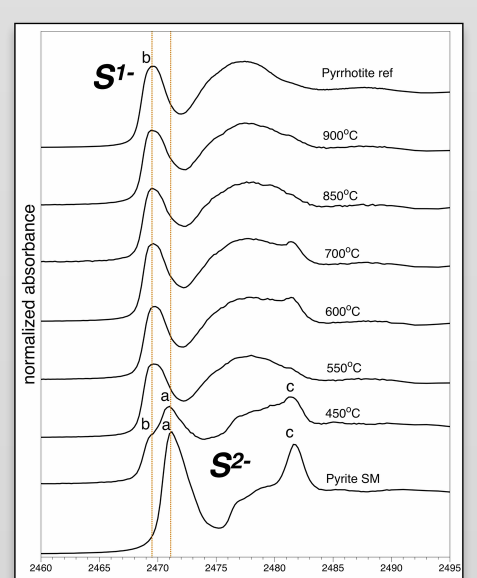


The normalized **XANES** spectra of Fe shows clear **shift** of energies from starting material to the high temperature experiment patterns.



Fe^{3+}/Fe_{total} ratios of dehydrating serpentinites display a drastic reduction of iron from ambient to high P-T conditions.

S *K-edge* XANES

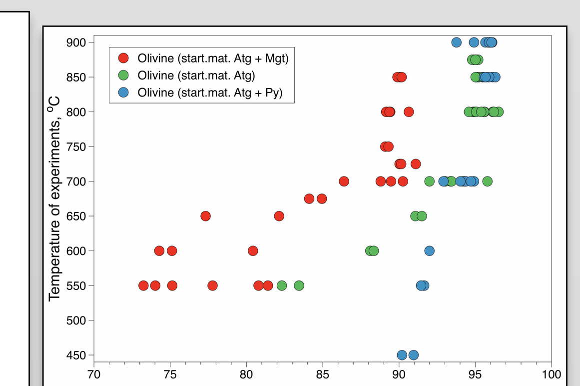


XANES spectra at **S K-edge** of run products from third experimental set (pyrite in starting material) revealed reduction of S by formation of **pyrrhotite from pyrite** between 450 and 550°C at 2 GPa.

Pyrite-pyrrhotite transition occurs coincidently with olivine crystallization and depletion in Fe of coexisting silicates, mostly olivine.

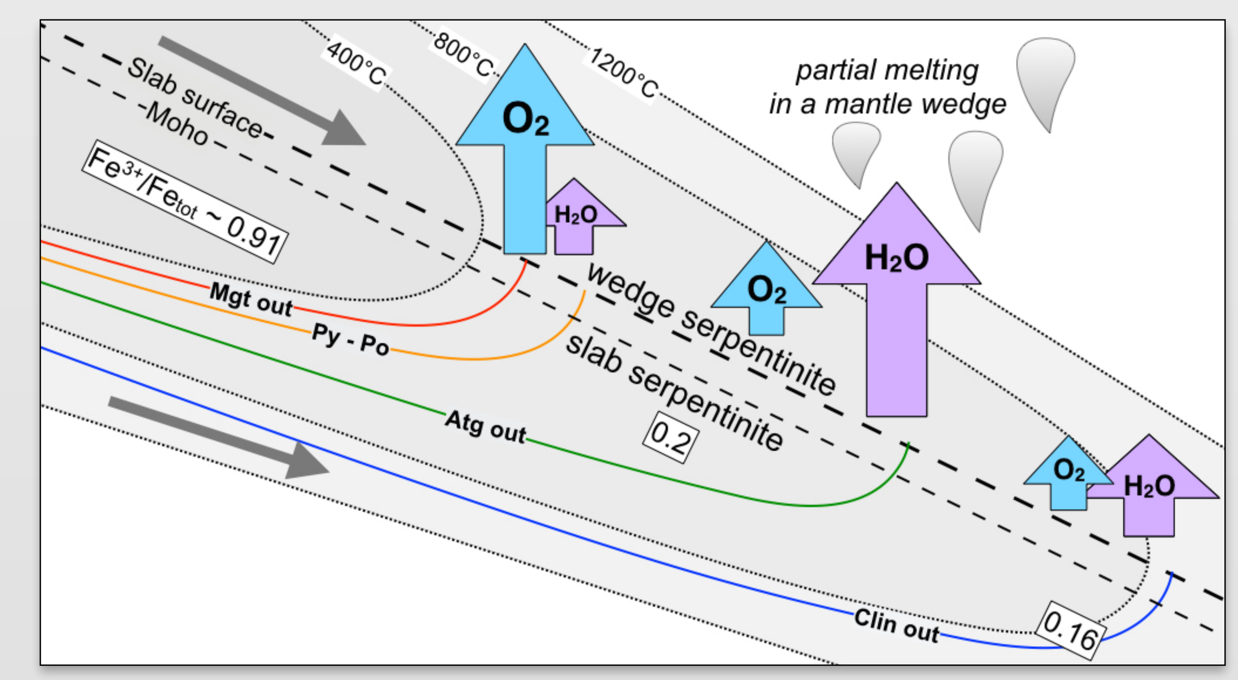
$$2(Mg_2Fe)(FeSi)O_5(OH)_4 + 4FeS_2 = 2Mg_2SiO_4 + 4H_2O + 3O_2 + 8FeS$$

antigorite *pyrite* *olivine* *water* *oxygen* *pyrrhotite*



Mg# of olivines from three different sets of experiments.

Conclusions



- The dehydration of serpentinites results in **continuous water release** between 450°C and 900°C;
- Dehydration is accompanied by **reduction of Fe and S** below 550°C and therefore, release of **O_2**;
- The **main portion of water** is released around 700°C due to complete breakdown of antigorite;
- The reduction of sulfur revealed that most probably **sulfur is not mobile** and stays in the rock in form of pyrrhotite;
- **What is the fate of released oxygen in subduction zones?**