Investigating oxygen fugacity changes as results of subduction metamorphism and metasomatism

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Introduction

- Arc magmas have higher oxygen fugacity than other magmas, although the cause of this high fO2 is poorly understood.
- One possible explanation is that oxidization potential is transferred from a subducting slab to arc magma via fluids (Kelley and Cottrell, 2009)
- Vanadium (V) is a redox-sensitive element and can be used as an indicator of the oxygen fugacity recorded by natural rocks. Minerals containing V, such as pyroxene and rutile in eclogites, record the oxygen fugacity of the rock as it experiences metamorphism (Aulbach and Stagno, 2016).
- Vanadium partitioning in these minerals can also be affected by pressure, temperature and bulk-rock V concentration.
- In this study, I investigate the changes in V content of rutile and omphacite using two different approaches on two eclogites from the Franciscan Complex, California, and the Monviso Complex, Italy.

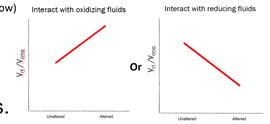
- **First approach**: comparing the V content of earlier-formed inclusions inside of garnets with the V content of later-formed matrix minerals to investigate changes in oxygen fugacity during prograde metamorphism.
- **Second approach**: investigating the V content of minerals in an unaltered metamorphic rock and compares those to the V content of the same minerals in a part of the same rock that was altered by metamorphic fluids to investigate changes in oxygen fugacity due to fluid-rock Interaction.

Hypotheses

- **First hypothesis:** if the oxygen fugacity decreased throughout the prograde metamorphism, V concentration ratio of rutile and omphacite would decrease from the inclusion to the matrix phases.

Figure 1: Expected vanadium concentration ratio trends for the first hypothesis (above) and for the second hypothesis (below)

- **Second hypothesis:** the rock-fluid interaction would cause changes in the V concentration ratio of rutile and omphacite from unaltered to altered regions.



Geologic background of samples

Franciscan Complex

- The eclogite sample was collected at Jenner Beach near Jenner, CA, north of San Francisco
- Proves prograde metamorphism therefore the garnets of this sample contain inclusions that formed earlier on the prograde path than matrix .
- Peak metamorphic conditions of about 1.5 GPa and 560°C (Krogh et al., 1994).

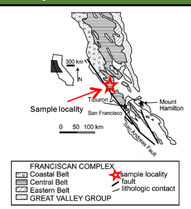


Figure 2: Geologic map of the Franciscan Complex and the sample locality. Source: Modified from Catlos and Sorensen (2003).

Monviso Ophiolite Complex

- The eclogite sample was collected from within the Lower Shear Zone (LSZ) sub-unit, Lago Superiore Unit, Monviso Metaophiolite complex (W. Alps).
- Covered by reaction rind that was altered by rock-fluid interaction.
- Peak metamorphic conditions of about 550˚C and 2.6 GPa (Angiboust et al., 2014).

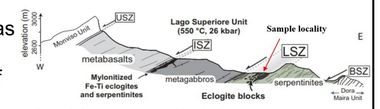
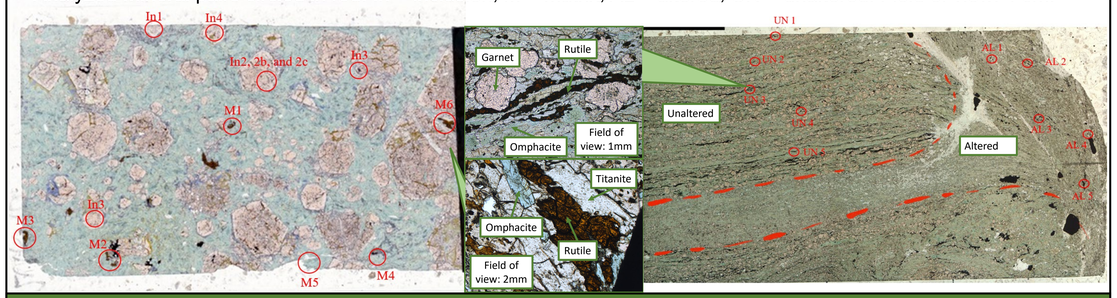


Figure 3: Cross-section of the Monviso Complex and the sample locality. Source: Modified from Angiboust et al. (2014).

Thin section

Figure 4: Thin sections of the Franciscan (Left) and the Monviso(Right) samples

- Analyzed mineral pairs circled in red. In = inclusion; M = matrix; AL = altered; UN = unaltered. Field of view: 4 cm.



Results

Figure 5: Vanadium concentration (Left) and ratio (Right) of the matrix and inclusion phases in the Franciscan sample

- Distinct V concentration difference between matrix and inclusion rutile. However, V concentration in omphacite between two phases are indistinguishable and calculated V ratio based on this data also are not distinguishable.
- Error bars in concentration figure represent analytical uncertainties to 2 sigma, and 2 sigma propagated uncertainty in ratio figure

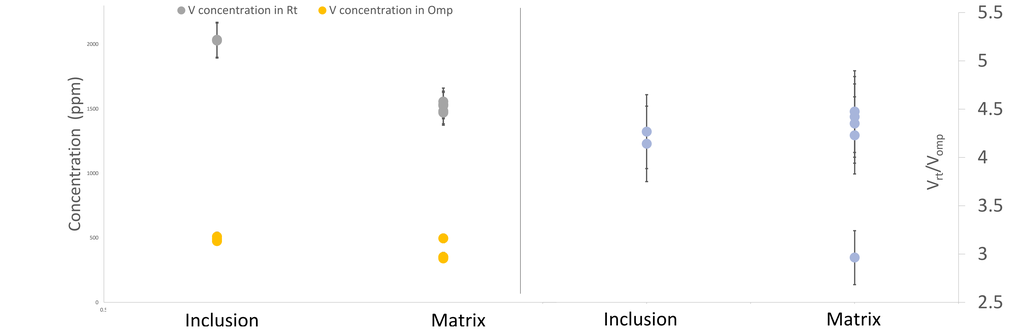
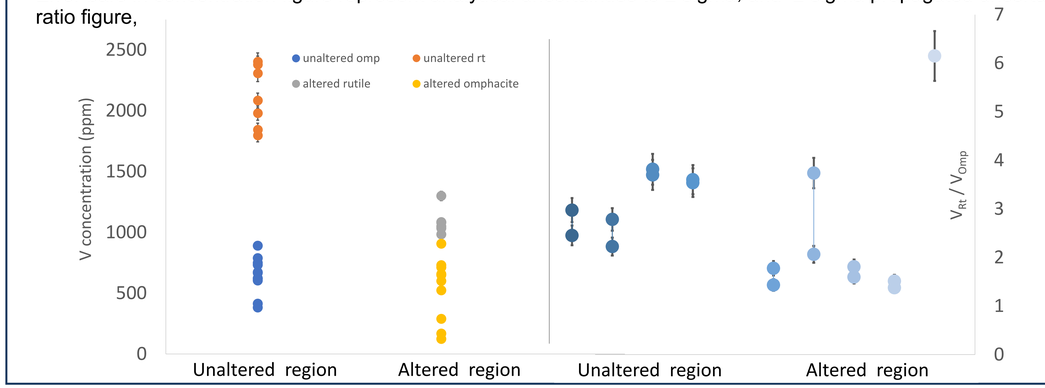


Figure 6: Vanadium concentration (Left) and ratio (Right) of the unaltered and altered region in the Monviso sample

- Rutile has higher V in unaltered rock compared to altered rock while omphacite compositions overlap.
- Vanadium ratio decreases from the unaltered to altered regions, with two outliers.
- Error bars in concentration figure represent analytical uncertainties to 2 sigma, and 2 sigma propagated uncertainty in ratio figure,



Results

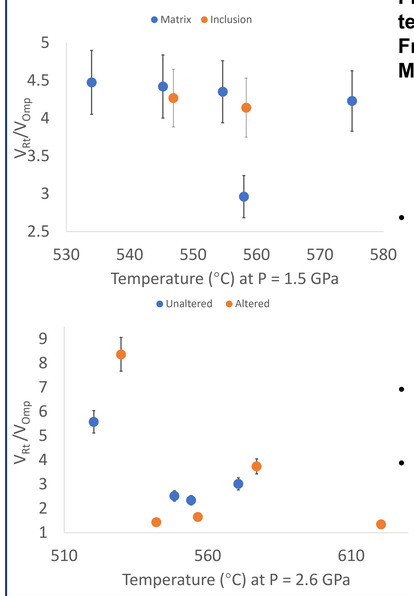


Figure 7: Estimated temperatures for the Franciscan (above) and the Monviso (below) samples

$$T(°C) = \frac{83.9 + 0.410P}{0.1428 - Rln\phi} - 273$$

R = gas constant, 0.0083144 (kJ K^{-1})
P = pressure (kbar)
ϕ = Zr concentration in rutile (ppm)
Equation sourced from Tomkins et al., 2007.

- Average temperatures (with 2 sigma) of
  Matrix phase = 553 ± 31°C;
  Inclusion phase = 553 ± 16 °C;
  Unaltered region = 565 ± 71 °C;
  Altered region = 548 ± 42 °C.
- 2 standard of average reflects the variation in Zr throughout the sample.
- Phases/regions of each sample were formed in similar *P-T* conditions.

Discussion

- Vanadium concentration in rutile of the Franciscan sample is higher in the inclusion phase than the matrix phase. However, the V ratio that based on these data is not different between matrix phases and inclusions. This suggests either that fO_2 did not change during metamorphism or that the two phases are recording the same metamorphic event.
- Distinct V differences between rutile and the resulting differences in the V ratio in the unaltered and altered regions in the Monviso sample indicate these regions were formed in different environments. In addition to that, the decreasing V ratio between the unaltered and altered regions supports the hypothesis that the oxidation state of the rock was changed by the altering fluid.
- Temperature differences can not explain V partitioning variations.
- Studies on other eclogite that formed under different P-T conditions might help us understand the observed V variations.

Acknowledgements

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References

Angiboust, S., Pettke, T., Hoog, J. C. M. D., Caron, B., & Oncken, O. (2014). Channelized Fluid Flow and Eclogite-facies Metasomatism along the Subduction Shear Zone. *Journal of Petrology*, *55*(5), 883–916. doi: 10.1093/petrology/egu010

Aulbach, S., & Stagno, V. *(2016). Evidence for a reducing Archean ambient mantle and its effects on the carbon cycle. Geology, 44(9), 751–754. doi: 10.1130/g38070.1*

Catlos, E. J. (2003). Phengite-Based Chronology of K- and Ba-Rich Fluid Flow in Two Paleosubduction Zones. *Science*, *299*(5603), 92–95. doi: 10.1126/science.1076977

Kelley, K. A., & Cottrell, E. (2009). Water and the Oxidation State of Subduction Zone Magmas. *Science*, *325*(5940), 605–607. doi: 10.1126/science.1174156

Krogh, E. J., Oh, C. W., & Liou, J. C. (1994). Polyphase and anticlockwise P-T evolution for Franciscan eclogites and blueschists from Jenner, California, USA. *Journal of Metamorphic Geology*, *12*(2), 121–134. doi: 10.1111/j.1525-1314.1994.tb00008.x

Tomkins, H. S., Powell, R. and Ellis, D. J. 2007. The pressure dependence of the zirconium-in-rutile thermometer. Journal of Metamorphic Geology, 25: 703-713. doi:10.1111/j.1525-1314.2007.00724.x