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Oxidation state of the lithospheric mantle beneath the Massif Central, France: the message from clinopyroxene

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Oxidation state is an important parameter that influences many geochemical processes. By controlling the speciation of volatiles, the oxygen fugacity (fO_2) directly affects partial melting and the resulting magma composition. The oxidation state of mantle peridotite can also be modified through metasomatic interactions involving migrating melts or fluids (e.g. [1]). As such, fO_2 can reveal the extent and type(s) of metasomatism that have occurred in the subcontinental lithospheric mantle (SCLM). The oxidation state of mantle peridotite is usually determined from the equilibrium between Fe-bearing endmembers of olivine, orthopyroxene and spinel [2]. On the other hand, metasomatic interactions in the SCLM are generally assessed from the trace element composition of coexisting clinopyroxene. This opens the possibility that the oxidation state recorded by spinel may not represent the conditions related to the observed metasomatic signatures, especially if there is evidence that clinopyroxene was introduced by the metasomatic process. In recent years, multi-valence trace elements such as V have been proposed as redox proxies, which opens a new avenue for determining oxidation state where clinopyroxene is a key player in this type of assessment.

We have determined the oxidation state of a suite of perdiotite xenoliths from the French Massif Central by measuring $Fe^{3+}/\sum Fe$ in clinopyroxene by Mössbauer spectroscopy and applying the oxygen barometer of Luth & Canil [3]. Fe^{3+} contents are elevated with $Fe^{3+}/\sum Fe$ ranging from 0.15-0.35. $\Delta log fO_2$ values calculated relative to the fayalite-magnetite-quartz buffer (FMQ) range from FMQ-0.7 to FMQ+1.1. These results are in very good agreement with values determined from the spinel-based equilibrium reported by Uenver-Thiele et al. [4]. This indicates a general redox equilibrium within the mantle assemblage independent of the degree or type of metasomatic overprinting. Fe^{3+} contents in clinopyroxene do not correlate with the likely substitution partners Na or $^{[IV]}Al$. However, the partitioning of Fe^{3+} between clinopyroxene and spinel is observed to be a strong function of Cr# in spinel. $D_{Fe3+}^{sp/cpx}$ changes from 3-6 in lherzolitic compositions (spinel Cr# = 0.1-0.15) to 12 in harzburgites (Cr# = 0.35). Thus, Fe^{3+} is more strongly partitioned into spinel in more refractory bulk compositions than in fertile peridotite. In any case, metasomatism appears to be generally an oxidizing process that leads to elevated Fe^{3+} contents in both spinel and clinopyroxene.

We have also measured V and Sc concentrations in our clinopyroxenes to investigate their behaviour during metasomatism. Lee et al. [5] proposed the use of V/Sc as a redox proxy for mantle-derived magmas and residual peridotites, claiming that this ratio reflected the partial melting process and was insensitive to metasomatic interactions. However, clinopyroxenes in our suite exhibit distinctly lower V/Sc in the more strongly overprinted samples. We observe selective removal of V during metasomatism (Sc contents are more or less the same as in less metasomatized samples). This change in V concentration can be understood in terms of a shift in $D_V^{cpx/melt}$ due to the migrating melt being more oxidized, causing V extraction from the host peridotite. Thus, our results indicate that V/Sc can be reset

during metasomatism and should be used with caution as a redox proxy when working with strongly metsomatized peridotites from the SCLM.

References:

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