

The redox state of glasses in mantle xenoliths: an EMPA investigation

C. WAGNER^{1,2}, M. FIALIN^{3,4} and M.-L. PASCAL^{1,2}



¹UPMC Univ Paris 06, and ²CNRS, UMR 7193, ISTEP, F-75005, Paris, France. (christiane.wagner_raffin@courriel.upmc.fr)

³UPMC Univ Paris 06, Centre de Microanalyse Camparis and ⁴CNRS, UMR 7094, IPGP, F-75005, Paris, France.



Introduction

Silicate glasses are common in mantle xenoliths from both continental and oceanic settings. Their composition can help understanding processes that occur in the upper mantle or during transport to the surface.

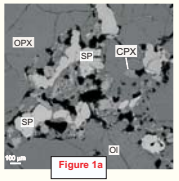
For example, the glass composition has been recently used to trace the nature of metasomatizing agents. Some studies (e.g. [1]) support that these agents are oxidizing relative to primitive lithosphere.

In order to test this possibility, we present here the determination of the redox state of glasses by direct measurements of the ferric/ferrous ratios with the electron microprobe. For this study, we selected anhydrous spinel lherzolites from a subcontinental setting (Massif Central, France). Our previous work has shown that these xenoliths have been cryptically metasomatized, and that the glasses are reaction products between mantle phases and migrating melts [2,3].

1- Petrographic features

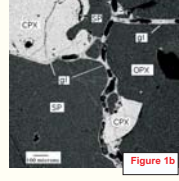
The xenolith is a protogranular anhydrous spinel lherzolite from the French Massif Central (Devès area).

Glass in reactional pockets



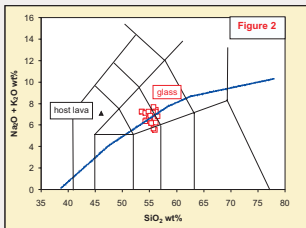
Fresh glass occurs in reactional pockets between spinels and anhydrous silicates (Figure 1a) and as thin veinlets along grain boundaries (Figure 1b). The veinlets are clearly connected to the glassy pockets. The glass contains abundant bubble-like voids, indicative of a former volatile phase.

Glass veinlets



We present here the study of glasses in reactional pockets which contain secondary euhedral to subhedral clinopyroxene, olivine and spinel.

2- Glass composition

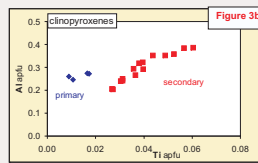
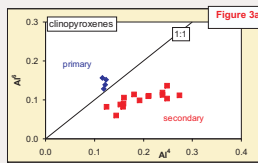


The glass is rich in SiO₂ (54 - 57 wt%), total alkalis (~7 wt%), and Al₂O₃ (~20 wt%). It has a basaltic trachy-andesite composition (Figure 2). It is quartz + orthopyroxene normative.

3- Secondary phases

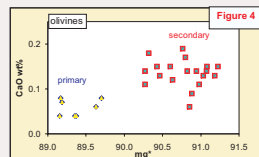
Clinopyroxenes

Compared to primary clinopyroxenes, they are less sodic (0.8 / 1.5 wt% Na₂O), and richer in Ti (up to 1.9 wt% TiO₂ / 0.5) with lower Al^{IV}/Al^{VI} (Figure 3a, b).



Olivines

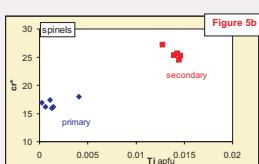
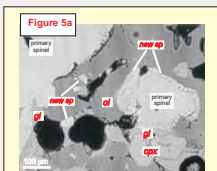
They are Mg- and Ca-richer (mg[#] = 91 and CaO = 0.2 wt% / 89-90 and <0.1 wt% respectively) than primary olivines (Figure 4).



Spinel

They are found in two occurrences: 1) as isolated crystals in the glass or in secondary olivine; 2) in a reactional sieve-textured rim at the glass / primary spinels contact (Figures 5a).

The secondary spinels are Cr- and Ti-richer (cr[#] = 24 and up to 0.99 wt% TiO₂, compared to 17 and 0.2 respectively in the primary spinels) (Figures 5b).



4- Fe³⁺/ΣFe by electron microprobe (EMP)

Method

In the transition metals of the first series, such as Fe, the L-series X-ray emission results from radiative electronic transitions between the unfilled 3d electron shell to the 2p (L_{2,3}) core levels. Distortions of the L emission spectra are caused by large contrasts in the self-absorption coefficients on both sides of the L_{2,3} absorption edges, close to the L_{2,3} peak maxima. In particular, changes in the spectral shape, shifts in the peak position towards lower energies, and changes in the L_{2,3}/L_{2,3} ratios are attributed to X-ray photon self-absorption effects [4,5].

In this study, we use the shift of the L_{2,3} peak position between Fe³⁺ and Fe²⁺ to determine the Fe³⁺/ΣFe ratios in the glasses with total Fe concentration (in wt%) previously determined using the Fe K_α peak. Fe L_{2,3} peak searches were performed at the same spots previously selected for the chemical analyses. All data were obtained with a Cameca SX100 electron microprobe at Centre Camparis, UPMC, Paris.

EMP operating conditions

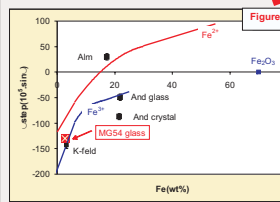
The Fe L_{2,3} peak positions were determined with the peak search routine of the Cameca SX100. Details of the peak search procedure are given in [5,6].

- Rapid spectrometer scan to minimize the beam damage.
- Peak searches carried out simultaneously on two wavelength dispersive spectrometers equipped with enlarged TAP.
- 15 keV, 250 nA, 20 μm beam, 30 s for a single peak search.
- The Fe L_{2,3} peak position of a pure Fe₂O₃ standard was regularly checked by alternating peak searches on the standard and on the glass.

The glass Fe³⁺/ΣFe ratios were determined with a precision of 0.04 (1σ) by cumulating 10 adjacent spots * 8 replicate measurements by spot * 2 TAP monochromators counting simultaneously (for a total time of 40 mn).

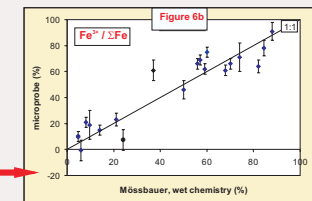
The 8 replicate measurements per spot served as indicator for eventual beam damage which would result in peak shift. Neither oxidation nor reduction (shift towards Fe³⁺ and Fe²⁺ reference curves, respectively) under the beam was detected during the counting time (i.e. 240 s per spot).

Protocol for the EMP analysis



Practically, to prevent any shift due to a mechanical drift of the spectrometer, the Fe L_{2,3} peak position of the unknown is measured relative to the Fe L_{2,3} peak position of Fe₂O₃ taken as a reference position. In Figure 6a, this difference (Δstep (10⁻³ sinθ)) is shown for a series of reference glasses. This gives two calibration lines represented by the solid lines.

Fe³⁺/ΣFe ratio is given by a simple linear relationship between both Fe³⁺ and Fe²⁺ end members, scaled to the related Fe_{total} value at the spot.



Smallest error bars are +/- 4% (1σ). They correspond to the statistical uncertainty for the operating conditions given above. Larger bars as well as data plotting off the 1:1 line may indicate heterogeneous samples (Figure 6b).

5- The redox state of glasses: Results and meaning

2- Calculated melt fO₂

- from the composition of the secondary phases
- at 1080-1100°C and P = 1 ± 0.5 Gpa (P range given by ol- and spinel-glass pairs)

1- EMP results for the glasses

Fe³⁺/ΣFe ratio ~ 0.6-0.8 ± 0.04 (1σ)

fO₂ ~ QFM
⇒ Fe³⁺/ΣFe ratio of 0.15

Remark: due to the low Fe content of the secondary phases, we can only give a range of magnitude for fO₂.

The two results strongly contrast

The high oxidation state of the glass does not reflect the original redox state of the migrating melt.

The redox state of the glass is however consistent with the late-stage reworking of the sample under oxidized conditions, which is locally witnessed by hematite deposition as filling in retraction cracks in spinel and olivine, and as fine overgrowths on secondary olivine and spinels or along the spinel (111) parting planes (e.g. Figure 7).

