

Electron Microprobe Analysis of Minor and Trace Elements in Beam Sensitive Materials: How Far Can We Go?

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Minor and trace elements analysis by electron microprobe (EMP) requires a long counting time at high beam current (≥ 50 -100 nA) in order to increase precision. The challenge is usually the accuracy, which depends essentially on the correctness of background and peak interference corrections [1,2]. Such an analysis becomes more challenging in beam sensitive materials, like carbonate, phosphate, glass, and alkali-rich materials, due to the beam damage induced by the high electron dose. As the latter can yield (very) inaccurate results if not properly accounted for, it is necessary to find an optimum analytical protocol that will minimize or correct the beam damage effect, while keeping the detection limit low enough. The question then arises: how far can we go in terms of detectability in such materials?

Here we explore this problem with the analysis of apatite and melt inclusions. The studied samples are rhyolites from the Nisyros-Yali volcanic center (South Aegean Sea). These phases are important in linking the role of volatiles exsolving in the magma chamber and the eruptive style with the hypothesis that a volatile supersaturated reservoir will favor effusive events, whereas the opposite will lead to explosive events [3]. Two potential saturometers are investigated: the Cl-F-OH exchange in apatite [4] and the Cl in melt inclusions [5]. In addition, the analysis of trace elements in melt is a better proxy than major elements alone to determine the differentiation level of the melt. It is imperative to analyze apatite and glass inclusions rather than apatite phenocrysts or matrix glass, as the latter are more likely to re-equilibrate their F- and Cl-content during cooling. Preliminary results are presented for the analysis of (1) F and Cl in apatite inclusions, and (2) Rb, Ba, and Zr trace elements (50-400 ppm range) in glass inclusions. In both cases, the analyzed inclusions are ~ 5 -10 μm in size, which prevents the use of other *in situ* technique such as LA-ICP-MS. Thus, EMP analysis with a maximum beam size of 5 μm remains the best option. Several techniques exist to mediate beam damage effects. For instance, damage is more limited with the use of a cold stage or with a conductive coating with higher thermal and electrical conductivity (e.g., Al instead of C). Here we explore the feasibility of EMP analysis using software-based corrections; two distinct methods are considered: (a) a Time Dependent Intensity (TDI) correction to account from the change in count rate together with a Mean Atomic Number (MAN) background correction [6], and (b) a method alternating the peak and background measurements over several time intervals to compensate for the change of peak and background count rates. In each case, only C-coating is applied on the sample without the use of a cold stage. All analyses are performed at 15 keV on a JEOL-8200 EMP equipped with three high-sensitivity spectrometers and two regular spectrometers. Data are acquired and processed using the software Probe for EPMA (ProbeSoftware, Inc.). In addition, separate EDS analyses are acquired on a JEOL-6390 SEM equipped with a Thermo UltraDry 30 mm² SDD EDS detector.

The analysis of F and Cl in apatite is difficult as the beam damage effect depends on the analytical conditions, and the composition and orientation of the grain [7]. Here, accuracy is of the utmost importance, as the results are used to recalculate the OH-content as accurately as possible. Tests are first made in several F-rich apatite grains of random orientation to determine the point at which the beam

damage cannot be corrected using a TDI correction. This test reveals that the maximum electron dose cannot exceed $40 \text{ nA} \cdot \text{s}/\mu\text{m}^2$, which translates into an adopted analytical condition of 80 s measurement at 10 nA with a $5 \mu\text{m}$ defocused beam. To maximize the peak acquisition time, the MAN background correction is applied. For this study, such a correction is acceptable, as the measured contents are expected to be relatively high ($\geq 0.1 \text{ wt}\%$), and reaching a low detection limit is not absolutely required, although desirable. The TDI correction adds some extra time, and therefore the total counting time on the peak is set to 60 s in order to keep the total analysis time around 80 s. F $K\alpha$ and Cl $K\alpha$ are measured on two spectrometers (LDE1 + TAP-H and two PET-H, respectively), and the fifth spectrometer is used to measure P $K\alpha$ and Ca $K\alpha$. At these conditions, detection limits for F and Cl are ca. 310 and 50 ppm, respectively. The method is validated with the analysis of F- or Cl-free apatite (blank tests), and of two synthetic F-OH and F-Cl apatite materials provided by D. Harlov. The apatite inclusions are very close to the ideal end-member of apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$ with a maximum of 2 to 3 wt% total of non-analyzed elements such as Si, Na, S, REE, U and Th. When those additional components are specified, the results on Cl are identical within the error, and only the F-content changes slightly between +1.2 to -3.5% relative.

Data acquisition on the glass inclusion is still a work in progress, and only preliminary data in reference materials are currently available. The analysis of Rb $L\alpha$ (on TAP) and Ba $L\alpha$ (on PET-H) is complicated by the interference of Si $K\alpha$ and Ti $K\alpha$, respectively, and by the fact that the low background position is at the low spectrometer limit. Zr $L\alpha$ is measured using two spectrometers (PET and PET-H). A two-fold approach is necessary to yield the best results. First, the major elements are determined by EDS or WDS at $\sim 2 \text{ nA}$. The accuracy of the EDS measurements is ascertained by comparing EDS and WDS analyses of several synthetic glasses with compositions varying from basaltic to rhyodacitic, with both analyses yielding identical results within the error. The EDS even outperforms WDS in terms of accuracy as the effect of beam damage is less pronounced (shorter analysis time). Second, the trace elements are analyzed by WDS using a $5\text{-}\mu\text{m}$ beam and a variable beam current (10, 20, 40 and 100 nA) and peak counting time (1 to 5 min; doubled when the background is acquired). Analyses using the MAN background correction and a TDI correction are inadequate, as the accuracy would necessitate a blank correction using a reference glass standard of very similar composition to the glass inclusion being analyzed, which is impossible to obtain for each specific glass composition. Instead, the most promising results are obtained using the alternate peak and background measurement. In order to yield a low detection limit (goal: 50 ppm), a current above 40 nA and a counting time of at least 5 min is required. Blank tests yield accurate zero values, suggesting an accurate compensation for beam damage, yet small discrepancy on the accuracy still remains with regard especially to Rb analysis (overcorrection from Si) and Ba (background problem). Although more work is required to improve the accuracy, these preliminary results suggest that a detection limit as low as 50-100 ppm can be achieved in hydrous glass for these elements.

References:

- [1] M Fialin et al, *American Mineralogist* **84** (1999), p. 70-77.
- [2] MJ Jercinovic et al, *IOP Conference Series: Materials Science and Engineering* **32** (2012), 012012.
- [3] RG Popa et al, *Journal of Volcanology and Geothermal Research* (under review).
- [4] JD Webster et al, *American Mineralogist* **100** (2015), p. 522-535.
- [5] MJ Stock et al, *Nature Geosciences* **9** (2016), p. 249-255.
- [6] J Donovan and TN Tingle, *Journal of Microscopy and Microanalysis* **2** (1996), p. 1-7.
- [7] B Goloff, JD Webster and D Harlov, *American Mineralogist* **97** (2012), p. 1103-15.