WDS

Strontium in plagioclase revealed by QUANTAX WDS for SEM

Application Note # WDS-03

Introduction

Trace elements and their spatial distribution in rocks and minerals are of substantial interest to geoscientists: for example in igneous rocks, trace elements are valuable tracers for magma sources and geological processes affecting the subsequent evolution of magma. Electronbeam techniques using WDS are state-of-the-art tools for such in-situ investigations [1].

Here we present a study on major and trace element distributions in plagioclase (sodium-calcium feldspar), the commonest rock-forming mineral series. Strontium (Sr), a trace element in plagioclases, is of special interest since it can be used for diffusion chronometry or for studies of crystal-melt evolution [2], [3].

The analytical challenge in this specific case is not only related to the low concentration of the element of interest (Sr < 1000 ppm), but also to the distinct EDS peak overlap of Si Kα and Sr Lα.

Sample

The investigated sample is a volcanic rock from Savo in the Solomon Islands [4]. Savo is an island arc stratovolcano, with two thirds of the cone below the sea and one third exposed as the island. The sample is a trachyte (crystal rich volcanic rock with a sodium-dominated intermediate composition) from the main crater. Though the exact age of the sample is not known, much of the exposed material at Savo would have been erupted in the last 400 years.

The eruption style is that water-rich magmas ascend through the crust, crystallizing across a range of pressures and temperatures. In the shallow subsurface they presumably degas and have a final period of crystal growth, before they are “squeezed out” as crystal-rich lavas into domes which commonly collapse or explode to produce large debris flows.

Measurement conditions

The measurements were performed on a FE-SEM equipped with both, a Bruker XFlash® ED spectrometer and a Bruker XSense® WD spectrometer using a grazing incidence parallel beam optic. The trace element Sr was determined by WDS, all other (major) elements were determined by EDS. Matrix corrections were made by φ(ρZ). Table 1 compiles the measurement conditions.

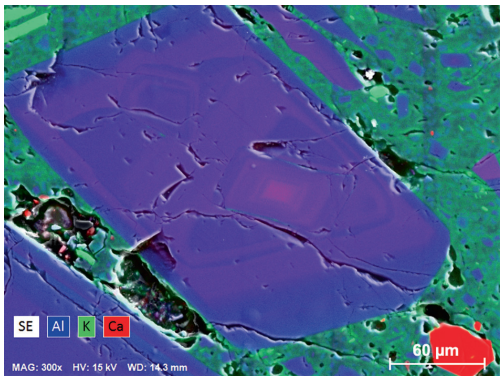

Figure 1
Element distribution map for Al, K and P in the investigated sample. High Al contents characterize the plagioclases, whereas K indicates the surrounding matrix and some biotites. Apatite is obvious due to its high Ca content. The EDS data was acquired simultaneously with WDS.

Results

The porphyritic volcanic rock contains abundant feldspars, varying from sodium-rich (albite, $NaAlSi_3O_8$) to relatively calcium-rich (labradorite, $Na_{0.4}Ca_{0.6}Al_{1.6}Si_{2.4}O_8$) plagioclase compositions. Figure 1 gives an impression of the porphyritic texture with plagioclase as dominant phenocryst phase.

EDS spectra of such plagioclases show prominent peaks for Si, Al and O besides minor, variably high peaks for Na and Ca (Figure 2a). Although Sr may partition in trace amounts into plagioclases, it cannot be determined from the EDS spectra.

This predicament is due to the coincidence of:

- (I) Very close X-ray lines of Si and Sr: The X-ray lines of Si Kα (1.740 keV) and Sr Lα (1.806 keV) are only 66 eV apart from each other.
- (II) Extreme intensity differences of these X-ray lines: Sr Lα is a peak of low relative intensity within the tail of the major Si Kα peak which is 170 times more intense in a spectrum of plagioclase.
- (III) Restricted EDS resolution: The EDS resolution defined as FWHM (full width of the peak at half peak maximum) is of the order of 70 eV for Si Kα. Consequently, the small peaks of Sr L cannot be resolved from the major Si K peaks using EDS.

Using elaborate peak deconvolution methods, EDS is, however, able to detect Sr upon manual interaction of the skilled analyst. Nevertheless, count rates are very low and quantification of a trace element such as Sr overlapping with a major element such as Si yields inaccurate results with large errors.

Table 1
Measurement conditions

Measurement parameter	Value
Acceleration voltage	15 kV
Probe current	90 nA
EDS detector	XFlash® 6 I 10
Outgoing count rate	480 kcps
WDS detector	XSense®
X-ray line by WDS	Sr Kα
Diffractor crystal	PET
Acquisition time	10 h

In contrast, WDS is able to detect even Sr L peaks of low intensity in the X-ray spectra of plagioclase (Figure 2b). The energy range scan obtained with WDS clearly shows the Sr Lα peak (1.806 keV) right inbetween Si Kα (1.740 keV) and Si Kβ (1.837 keV).

The resolution of the applied QUANTAX WDS at the energy region of interest is 3.5 eV (FWHM of Si Kα) which means an improvement in resolution by a factor of 20 relative to EDS. The intensity ratio of the Sr La and Si Kα peaks is 1:170 for the present WDS spectrum in Figure 1b. The small peak at 1.819 keV is Si Kβ', a low energy satellite line of Si Kβ.

Applying a peak-background method and SrF_2 as reference material for standard-based quantification of selected point analyses, Sr concentrations of up to 0.1 wt.% were determined by WDS for the most calcic plagioclases.

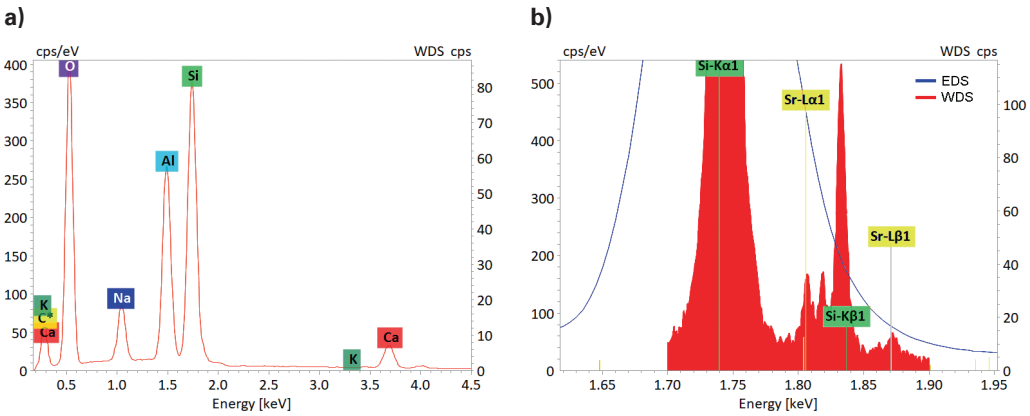

Figure 2
X-ray spectra of a plagioclase in the investigated sample derived by (a) EDS and (b) combined EDS-WDS analysis. Figure 2b shows an enlarged section of the X-ray spectrum in the region of interest between 1.6 – 1.95 keV, where the EDS spectrum is presented in light red and the WDS energy range scan in brown.

Plagioclase phenocrysts within the studied rock frequently show multiple and sometime complex zoning (Figure 3). High contents of Ca (labradorite, $Na_{0.4}Ca_{0.6}Al_{1.6}Si_{2.4}O_8$) are characteristic for the crystals core and may recur repeatedly throughout the zoned crystals. The plagioclases get more Na-rich (albite, $NaAlSi_3O_8$) towards their rim. Zones with high contents of Na or Ca are inevitably inverse.

Spatial distribution of the trace element Sr within the plagioclases was determined by WDS mapping. The respective compositional maps (Figure 3a, b) consistently show that the highest Sr concentrations correlate well with the Ca-rich zones in the plagioclase crystals.

Discussion

The plagioclases in the present sample record crystal growth during magma evolution and ascent, and are often spectacularly zoned from calcic to sodic compositions. Disequilibrium compositional zonation of igneous minerals are commonly explained by derivation from a long-lived magma system with multiple replenishment by mafic mantle melts [1]. Whereas high contents of Ca indicate juvenile magma injected into the magma chamber and contributing to the growth of the plagioclase crystals, the crystals get more Na-rich during subsequent fractional crystallization [5].

The present results on the distribution of Sr substantiate that trace amounts of strontium can substitute for calcium in the crystal lattice of plagioclases. Moreover, the findings indicate that the juvenile magma which was involved in the formation of the present volcanic rock was fairly enriched in Sr.

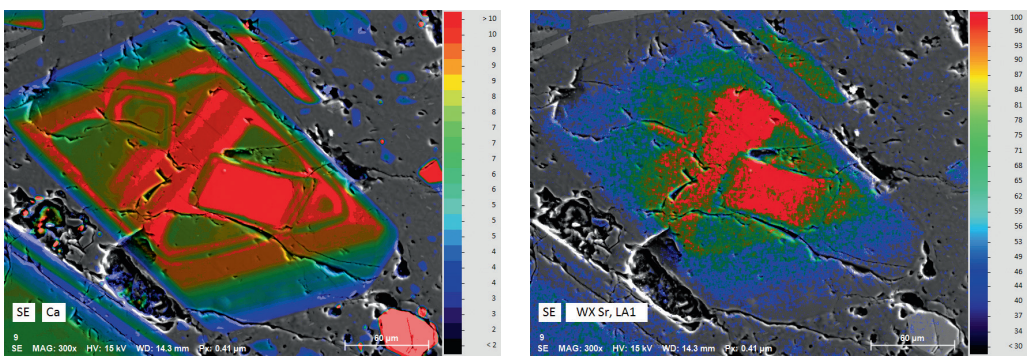

Figure 3
Qualitative compositional maps of a complexly zoned plagioclase presented in palette colors (map size 314 µm x 245 µm). Map (a) shows the distribution of the major element calcium derived from EDS data. Map (b) shows the distribution of the trace element strontium simultaneously acquired by WDS.

Conclusion

Electron-beam techniques allow high-resolution imaging and quantitative analysis of compositional zoning in minerals. The results clearly show that QUANTAX EDS and QUANTAX WDS are powerful tools for the analysis of geological samples, such as plagioclases.

Installed on the same (FE-)SEM, both spectrometers (EDS and WDS) ideally complement each other. QUANTAX WDS is perfectly suited for mapping and in-situ analyses of the trace element Sr in silicates. The WDS technique is indispensable especially under such analytical circumstances where the close proximity of X-ray lines coincides with pronounced differences in line intensities.

References

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