



## Nanoscale characterisation of crystal zoning



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### ABSTRACT

Advances in analytical techniques are fundamental to the enhanced understandings of many geological processes. Zoned volcanic crystals have been analysed by low (5) kV field emission gun electron probe micro-analyser (FEG-EPMA) and NanoSIMS to obtain sub-micrometre chemical profiles and compared to time-of-flight SIMS (TOF-SIMS) and high (15–20) kV EPMA profiles. Plagioclase and orthopyroxene crystals have been analysed by FEG-EPMA, at accelerating voltages of 5 kV providing a spatial resolution (step size) of  $\leq 350$  nm (the resolution of the lowest energy X-ray) for orthopyroxene crystals using a 30 nm beam and ca. 750 nm for plagioclase crystals which at low voltages are unstable and require a 500 nm defocused beam. Step sizes are comparable in size to interaction volumes. Analytical protocols are detailed that permit quantitative major and minor element compositions to be acquired at similar precision and accuracy as traditional EPMA analyses at 15–20 kV. NanoSIMS analysis of the same crystals provides a greater spatial resolution of up to 200 nm and allows the measurement of Li also. The NanoSIMS profiles, however, cannot currently be quantified. The ability to analyse crystals at sub-micrometre scales is demonstrated by the good agreement between NanoSIMS, FEG-EPMA, conventional EPMA and TOF-SIMS data. FEG-EPMA, NanoSIMS and TOF-SIMS techniques have broad applications within the earth sciences. In petrologic studies for example, these methods have the ability to analyse small crystals in experimental charges and provide chemical profiles of crystal zoning at a spatial resolution of ca. 200–300 nm. Such profiles are important in crystal forensics and diffusion chronometry studies. The implications for the latter application are that timescales of volcanic processes that occur in the days–years immediately prior to the eruption can now be studied.

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## 1. Introduction

Fundamental to our understanding of volcanic eruptions are the timescales over which magmatic processes occur in the lead up to eruption. The evolution of a magmatic system may occur over millennia (e.g. Charlier et al., 2005, 2008; Claiborne et al., 2010), whilst the final stages of magma evolution may occur over much shorter timescales immediately prior to eruption (e.g. Morgan et al., 2004; Martin et al., 2008; Saunders et al., 2010; Kahl et al., 2011; Druit et al., 2012; Saunders et al., 2012a). Many conventional radiometric dating techniques do not have the resolution to interrogate timescales of magmatic processes that occur in the days–years immediately prior to eruption, as the half-lives of elements are greater than the time scales of interest. An alternative method and one that is increasingly used in volcanic studies is diffusion chronometry (e.g. Costa et al., 2003; Morgan et al., 2004; Costa et al., 2008; Druit et al., 2012; Saunders et al., 2012a), which uses the diffusive relaxation of chemical zoning in igneous crystals to

retrieve timescales of magmatic processes. Different elements have the potential to record different magmatic processes such that by studying several different elements within a crystal it is possible to gain insights into several different components of the magma genesis. Conversely, because different elements diffuse through crystals at different rates their diffusive relaxation can be used to extract timescales from minutes to millennia. The chemical zonation of minerals that provide the basis of diffusion chronometry can vary from 10's of micrometres to less than a few nanometres.

Diffusion serves to modify the elemental concentration of adjacent crystal zones as crystals attempt to obtain equilibrium internally and with the external melt. On eruption, diffusion effectively ceases due to rapid decrease in temperature (quenching). However, the timescales that can be calculated using diffusional methods are limited by the diffusivity of the element of interest and resolution of the measured chemical profile that is dependent on the analytical methods employed to obtain the profile. The rate of diffusion depends on the chemical potential gradient and the diffusion coefficient at the conditions of interest. Diffusion coefficients are specific to the mineral and element of interest. If the characteristic diffusion length is shorter than the analytical length scale, no temporal information can be obtained. To avoid complications from convolution and overlapping analyses, four analytical points clear

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of the adjacent background chemical composition on either side of the chemical profile are required to extract diffusion profiles that can be modelled (Costa and Morgan, 2010). Thus in order to investigate time-scales that occur in days–months prior to eruption, for all but the most rapidly diffusing elements, sub-micrometre spatial resolution is required.

Recent studies have exploited the high-resolution of backscattered electron (BSE) images and cathodoluminescence images (Morgan et al., 2004; Wark et al., 2007; Saunders et al., 2010; Saunders et al., 2012a) to increase the spatial resolution of chemical profiles for diffusion studies. The intensity of the images reflects specific aspects of the chemical composition of the crystal. Thus, the intensity of each pixel can be used as a proxy for the chemical composition at a spatial resolution of 200–400 nm (Saunders et al., 2012a,b). This technique, however, is limited to a few specific elements that due to their atomic structure are disproportionately represented in BSE images (Reed, 1996). These may be major elements of a solid solution or elements with high atomic number relative to their crystal matrix. For example, BSE images of pyroxene crystals display information predominantly on the Fe–Mg content of the crystal (e.g. Morgan et al., 2004; Saunders et al., 2012b). As the BSE images cannot be used to obtain any information on the chemical gradient of any other minor or trace elements across interfaces within crystals, an alternative analytical technique is required if other elements are to be modelled. Ideally these techniques would allow quantification of the composition. However, diffusion modelling relies on a concentration gradient without the need for absolute concentration; this allows us to exploit analytical techniques that can only achieve a relative concentration profile, even though the long-standing problem of quantification remains.

In the last few years, several techniques have emerged that can potentially obtain chemical profiles at the nanoscale (used to describe sub-micrometre resolution). These include NanoSIMS, field emission gun (FEG)–EPMA and time-of-flight (TOF) SIMS (see Saunders et al., 2012b). Depth profiling with a conventional SIMS also has the ability to achieve a 100 nm spatial resolution (Genareau et al., 2007), although it requires very careful crystal orientation during analysis such that the chemical profile is exactly perpendicular to the interface of interest. As the location (depth) and shape of this interface may not be known, obtained profiles may not be perpendicular. Consequently, any chemical profile obtained may be artificially lengthened resulting in overestimation of any calculated timescale (Costa and Morgan, 2010), whereas EPMA, NanoSIMS and TOF-SIMS allow us to observe the crystal zonation in 2D prior to analysis, allowing the most vertical boundaries to be chosen for analysis and to perform complementary analyses.

### 1.1. Developments in EPMA

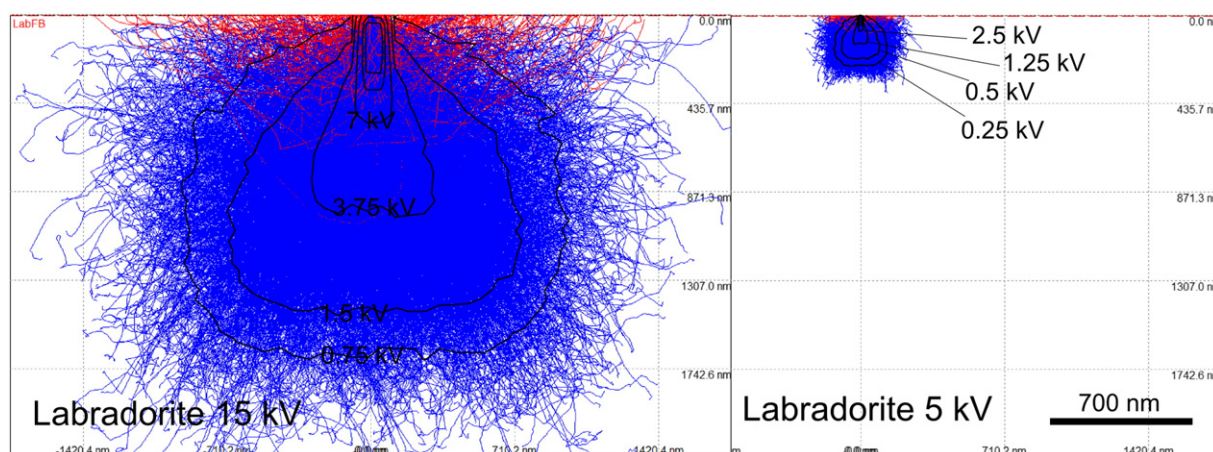
Since the 1960's the EPMA has been routinely used to determine the chemical composition of minerals on a micrometre scale. Typical operating conditions for mineral analyses are an accelerating voltage of 15–20 kV and a beam current of 5–20 nA. Thus, the approximate spatial resolution attainable is 2–3  $\mu\text{m}$  for a silicate mineral with a density of ca. 2700  $\text{kg}/\text{m}^3$  (Fig. 1). The spatial resolution is governed by the interaction volume (the volume in which beam electrons interact with the sample to produce secondary radiation) with most x-rays analysed having a large overvoltage (ratio of beam energy to critical excitation energy, typically <2) and generated from a large fraction of the total interaction volume (Goldstein et al., 1992). The interaction volume is therefore used as an approximation of the total spatial resolution. In situations where particular elements for which the x-ray analysed has a small overvoltage (e.g. Ca K at 5 kV, overvoltage 1.2) the actual spatial resolution will be much smaller. This results from beam electrons losing energy as they penetrate into the sample restricting the x-rays which they can excite (Fig. 1).

Reducing the spatial resolution is possible by decreasing the accelerating voltage which in turn decreases the interaction volume by reducing the beam penetration (Merlet and Llovet, 2012); however, this also increases the beam spot size thus offsetting any improvement in resolution. At low accelerating voltages and modest beam currents (5–20 nA) using a tungsten or LaB<sub>6</sub> sourced EPMA the large increase in spot size with decreasing accelerating voltage limits the lateral resolution to a minimum of about 1  $\mu\text{m}$  at 10 kV for silicate minerals. Using a FEG source the primary beam intensity is much higher and the increase in beam size constrained to tens of nanometres (McSwiggen, 2013). As the X-ray generation is significantly reduced at low accelerating potentials it is necessary to increase beam currents to give a sufficient count rate. The rise in beam currents further reduces lateral spatial resolution. Even so, the instrument specification for a JEOL 8530 FEG-EPMA is that the spot size will be no more than 100 nm at 10 kV with a beam current of 100 nA.

With these advances, the FEG-EPMA is well facilitated to allow the quantitative chemical analysis of nanoscale volumes of material. A Monte Carlo simulation (Fig. 1) predicts that at an accelerating voltage of 5 kV and a beam current of 10 nA, a spot size of about 30 nm (smallest observable feature measured in SE) will yield a spatial resolution of ca. 350 nm; considerably smaller than at higher accelerating voltages.

### 1.2. Developments in in-situ mass spectrometry techniques

With advances in the last 30 years, in-situ mass spectrometry techniques have allowed the analysis of trace elements in crystals and melt



**Fig. 1.** Monte Carlo simulation for labradorite plagioclase at 15 kV and 5 kV accelerating voltage. Electron interaction volume is shown (with red lines displaying backscattered electrons). Contours give modelled beam electrons energy showing the energy loss away from point of beam impact.

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