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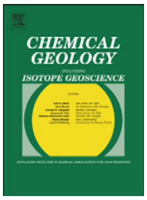

High-resolution LA-ICP-MS trace element mapping of igneous minerals: In search of magma histories

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ABSTRACT

We report experiments on optimisation of LA-ICP-MS mapping as a tool for visualising and quantifying internal structure of trace element concentration in igneous minerals. The experimental design was refined with maps on clinopyroxene and amphibole macrocrysts (mainly antecrysts) from a porphyritic lamprophyre in NE Spain, as well as on a high precision metal wire grid. In terms of spatial resolution, we demonstrate with scanning electron microscope and white light interferometry that a full ablation removes between 0.4 and 0.7 μm of material, depending on ablation parameters. Maps were produced with square laser beam spots of 12 and 24 μm. It was found that complexities can be resolved in the sample even though they are smaller than the beam diameter (e.g., 7–10 μm discontinuities using 12 μm laser beam). Resolution in x and y was found to be identical, probably reflecting the fast washout of the two-volume ablation cell and the short total dwell time of the analyte menu selected. Due to the excellent stage reproducibility and the limited ablation depth, it is feasible to re-ablate the identical map area many times employing different instrument parameters or analyte menus.

On the magmatic crystals, LA-ICP-MS maps define very sharp compositional zoning in trace elements, highlighting complex crystallisation histories where 'normal' magmatic fractionation is not the only process. Events of mafic recharge are easily recognised as zones enriched in compatible metals such as Cr, Ni or Sc. Further, trace element maps reveal complexities in mineral zoning previously undetectable with petrography or major element data. These include resorbed primitive cores and oscillatory zoning within apparently homogeneous mineral zones. Therefore, LA-ICP-MS mapping opens a new window of opportunity for analysis of magmatic histories. The wide combination of instrumental parameters, such as laser beam size, scan speed and repetition rate, make it possible to carry out experiments at different levels of detail. We recommend a two-step approach to mapping. The initial step involves rapid maps to gain an overview of potential complexities in the sample; this enhances representativeness of the analysed materials, as a large number of crystals and trace elements can be tested in little time. Subsequently, detailed maps can be carried out on areas of interest. An additional functionality is to create 1D-profiles from 2D-maps. The potential of the technique to unveil compositional complexities efficiently and at greater detail than traditional microanalysis will help to improve our understanding of processes in the magmatic environment and beyond.

1. Introduction

Compositional variations in geological materials at the microscopic scale can contain a record of geological processes and the evolution of environments. The rich compositional archive has particularly been exploited in igneous petrology, where chemical zoning of individual crystals can be directly related to changes in magmatic environment (Bussweiler et al., 2015; Streck, 2008). Trace element variations during crystal growth bear important information on magma compositions and conditions during crystallisation, complementing petrography and major element studies (Ginibre et al., 2007).

Technological improvements in microanalysis have led to the realisation that magmatic mineral phases are often not in equilibrium with their enclosing groundmass (e.g., Davidson et al., 2007). This has informed the premise that many large crystals, rather than being phenocrysts, should be regarded as antecrysts that formed prior to emplacement at depth (Charlier et al., 2005; Davidson et al., 2007; Gill et al., 2006; Hildreth and Wilson, 2007; Jerram and Martin, 2008; Larrea et al., 2013). The complexity within antecrysts implies the existence of complex magma plumbing systems with episodes of contamination, recharge and magma mixing (Francalanci et al., 2012; Sakyi et al., 2012; Ubide et al., 2014a, 2014b). Events of recharge into deep magma chambers with a more primitive (often fluid-rich) batch of magma have been studied with particular interest as they are considered the main cause for triggering volcanic eruptions (e.g., Kent, 2013;

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Kent et al., 2010; Longpré et al., 2014; Myers et al., 2014; Reubi and Blundy, 2007).

Given the amount of information potentially locked in magmatic crystals, large analytical efforts continue into decoding petrographic textures and microchemical fingerprints (e.g., Saunders et al., 2014). Because high spatial resolution is key to obtaining the maximum amount of information, elemental concentrations are typically measured by in situ analysis. This is achieved via different analytical approaches using scanning electron microscopy (SEM), electron microprobe (EMP), secondary ion mass spectrometry (SIMS), transmission electron microscopy (TEM) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Radiogenic isotope ratios are typically measured from micromilled material (Davidson et al., 2007) but in this field too, SIMS and LA-ICP-MS are starting to permit in situ analysis (e.g., Bellucci et al., 2014; Paul et al., 2011).

In terms of ease of use, analysis time and cost, LA-ICP-MS has rapidly developed in the last decades as an in situ analysis technique of trace element concentrations in geological materials. LA-ICP-MS attains better detection limits (at the ppm level for trace elements in the medium- to high-mass range which are not typically affected by polyatomic interferences) than electron beam techniques and is considerably cheaper than SIMS. The improvement of data reduction schemes (e.g., Hellstrom et al., 2008; Paton et al., 2011) has paved the way for the transition from spot and raster analyses to trace element distribution maps (Woodhead et al., 2007, 2008; Paul et al., 2012, 2014; Rittner and Müller, 2012). Ulrich et al. (2009) explored the possibilities of the LA-ICP-MS mapping and its applications to a variety of geological systems. They highlighted the potential of compositional images to reveal complexities that are not visible under the microscope and were not expected or appreciated from microbeam spot analyses.

In this contribution we explore LA-ICP-MS mapping capabilities for magmatic studies. This includes an investigation of the spatial resolution of the technique, including the size of discontinuities it is able to map and the depth of material it ablates and analyses. Experiments were performed to optimise the analytical set up and to provide recommendations for obtaining the most effective and best detail maps. By way of example, the results of this study are used to interpret better magma evolution pathways, and the method is potentially applicable to any material which can be successfully ablated by the LA-ICP-MS method.

2. Materials

Most LA-ICP-MS mapping experiments in this study were carried out on clinopyroxene and amphibole crystals from a lamprophyre intrusion. Additional analyses were performed on a precision machined grid composed of copper–palladium wires of known dimensions.

The studied magmatic intrusion belongs to the Late Cretaceous alkaline lamprophyre suite in the Catalonian Coastal Ranges (Ubide, 2013; Ubide et al., 2014b, 2014c). Detailed petrography and geochemistry indicated that these lamprophyres were fed by a complex magmatic system, where ascending magmas entrained crystals from disparate crystallisation levels (Ubide et al., 2014b). For the present study, we focused on a ~4 m subhorizontal sheet-like magma body (Molí d'en Ponç lamprophyre: UTM 31T 466218 4629029; Ubide et al., 2014b) that is an ideal target because: i) it has an alkaline composition with high concentrations of trace elements (Ubide et al., 2014b) that help producing small-scale maps; ii) it has large crystals of clinopyroxene and amphibole showing complex zoning patterns (Ubide et al., 2014b); and iii) CaO contents in clinopyroxene and amphibole crystals are homogeneous despite the marked zoning in other elements (see supplementary data Tables E1 and E2 from Ubide et al., 2014b), making Ca suitable for easy internal standardisation.

The analytical work was conducted on one standard 30 μm polished thin section of sample SFB-4 (Fig. 1). The rock is a porphyritic camptonite composed of macrocrysts of clinopyroxene, amphibole, pseudomorphed olivine and opaque minerals standing out from a microcrystalline groundmass with amphibole, feldspars and minor biotite, apatite, analcime, calcite and recrystallised glass. Previous work revealed that most macrocrysts are not cognate phenocrysts but recycled antecrysts, and their growth stratigraphy records an intricate succession of magmatic processes in the plumbing system, including magma recharge, magma mixing and polybaric fractionation during magma ascent and emplacement (Ubide et al., 2014b). Here we present LA-ICP-MS maps of three macrocrysts, named 1) the ‘little clinopyroxene’; 2) the ‘elongated amphibole’ and 3) the ‘little amphibole’ (Fig. 1). These examples represent a range of simple vs. complex zoning patterns and small vs. large size to cover the mapping development goals.

Additionally, a precision machined wire grid was used to investigate the spatial resolution capabilities of the technique (Section 4.1). We used a 300-mesh grid of 3.05 mm diameter, which are commonly used as a sample support mesh in TEM studies. The grid is constructed from wires made of a copper–palladium alloy. It was placed on top of a standard thin section glass and secured with adhesive tape. The orientation of the grid was deliberately aligned at an angle to the edges of the glass slide to avoid potential resolution artefacts from ablating orthogonally. Measurements carried out with SEM confirmed the specified 20 μm wire thickness and 60 μm spacing (Fig. 1). SEM observation also clearly identified the pilot intersection of two wires at the centre of the grid, leading to a distinctive central node that protrudes 7 to 10 μm away from the wires. This area was investigated to help determining the spatial resolution of the method. The wires are also 20 μm deep (they have a square cross section), and this compromises the analysis of the glass substrate between the wires as the focal depth of the laser is less than 20 μm.

3. Methods

3.1. LA-ICP-MS mapping: experimental approach

LA-ICP-MS experiments were carried out in 2014 at the Geochemistry Laboratories of Trinity College Dublin. We used a Photon Machines Excite 193 nm excimer Ar–F laser system with a Helex 2-volume ablation cell and He–Ar carrier gas (ca. 0.8 l/min He and ca. 0.7 l/min Ar). An in-house developed variable volume device was used for signal smoothing between the laser and the mass spectrometer, without compromising spatial resolution significantly. A small volume of N_2 (ca. 7 ml/min) was introduced to the sample-gas mixture via the smoothing device to enhance signal sensitivity and reduce oxide formation. The mass spectrometer used was a quadrupole Thermo iCapQc. The instrument was tuned with scans on NIST612 glass reference material (Jochum et al., 2011) at the beginning of each analytical session.

3.1.1. Laser ablation

The ablation area (i.e., the mapping area) was defined with the Chromium2.1 software (Photon Machines Inc.) in a way that slightly differs from previous approaches (Paul et al., 2012, 2014; Ulrich et al., 2009) as illustrated in Fig. 2. We used a square-shaped laser aperture which was progressively translated by continuous movement of the stage under the fixed ablation site. This generated an evenly ablated line from overlapping squares (Fig. 2b, e). To produce the full map adjacent lines were ablated in a successive manner. The effects of allowing no spacing in between lines were contrasted with those allowing for a small overlap (1 μm; Fig. 2f) to avoid un-ablated gaps. The final ablated area was square- or rectangle-shaped to facilitate production of trace element maps using different data reduction approaches (see Section 4). In the experiments on the thin section, the ablated area included the crystal of interest as well as the immediately surrounding groundmass (Fig. 2a, c). No pre-ablation was found necessary for the elements measured in this study after samples were carefully cleaned with semiconductor grade solvent.