Mapping Geochemical Zoning with Quantitative EDS

ZEISS Mineralogic

Seeing beyond

Authors: Richard J M Taylor, Ph.D
           Carl Zeiss Microscopy Ltd
           Cambourne, Cambridge CB23 6DW, UK

Date: June 2021

Introduction

Many geological processes occur over timescales and temperatures that do not allow for chemical equilibration, with mineral assemblages captured as a snapshot of an ongoing process. Such petrological studies form an integral part of geoscience research and interpreting their textures and geochemical variation is key to unlocking the evolution of geological terrains. The internal geochemical zoning of partially equilibrated minerals is a key aspect of the studies. Multiple or complex geological events can be identified through chemical zoning as either stepped or diffusive profiles. Extraction of all the data available from the profiles requires a correlative approach as information exists at many levels and resolutions. For example, use of a light microscope (LM) may reveal crystallographic zonation but not fine chemical variations for which a Scanning Electron Microscope (SEM) with an Energy Dispersive Spectroscopy (EDS) detector may be used.

The SEM is a highly versatile instrument that can identify geochemical zoning with both a qualitative and quantitative analysis. Backscattered Electron (BSE) analysis allows SEM images to capture variation based on the average atomic number of the elements present within an analytical volume. This qualitative approach is useful for distinguishing mineral phases and can be used to identify internal zoning. However, many common geochemical zoning signatures, such as the diffusion of Fe and Mg in silicates can be hard to distinguish with BSE imaging alone. Geochemical zoning is more clearly defined by direct chemical measurements using Energy Dispersive Spectroscopy (EDS) detectors on the SEM. The characteristic X-rays produced by each excited element within the microscopic beam-sample interaction volume can be used to determine quantitative geochemistry using the EDS measurements. This is a key workflow for geochemistry and petrology, directly linking mineral textural observations (imaging) with geochemical measurements (analysis) on the SEM.

ZEISS Mineralogic

ZEISS Mineralogic (ML) is an analytical SEM with automated mineralogical mapping using quantitative geochemical analysis through Energy Dispersive Spectroscopy (EDS). ML is an SEM system designed specifically to obtain quantitative chemistry and automatically classify mineral phases direct from thin sections. The result is a unique system that can combine the two key aspects of quantitative EDS – rapid phase mapping, and geochemical analysis.

The results can be visualized as a CHEMera map, where minerals are automatically identified by ML and phases of interest have their internal geochemical zonation exposed. ML is versatile, with a variety of imaging detectors that can be applied alongside the EDS capability. In this instance we present the capabilities of ZEISS Mineralogic based on ZEISS Sigma VP FE-SEM equipped with Back Scattered Electron (BSE) imaging and two Oxford Instruments Ultim Max 65 EDS detectors.

Ultim Max EDS detectors have been designed for accuracy and ease of use under all analytical conditions, including at the high count rates often used in automated mineralogy. This is made possible by Oxford Instruments' TruQ spectrum processing technology, which combines a series of dedicated algorithms to process and quantify every spectrum in real time to ensure that the right results are calculated every time. This means that a high level of confidence can immediately be attached to the results without the need for manual review of acquired spectra.

Analysis of geochemical zoning

The following examples demonstrate how the rapid chemical imaging of zoned minerals can be used to interrogate research samples from metamorphic and igneous petrology. Each example takes a slightly different approach, from simple observations of zonation, incorporating phase ID with chemical data, and streamlining a research workflow.

Figure 1 shows four images of a garnet from a high-grade metamorphic rock from the Glenelg region of NW Scotland. These basement gneisses have seen a multistage history, that while cryptic from field observations of the rocks them-selves, is recorded by the chemical zonation of the garnet within the gneiss. Using the quantitative EDS capabilities of ZEISS Mineralogic we can obtain multiple sets of correlated information.
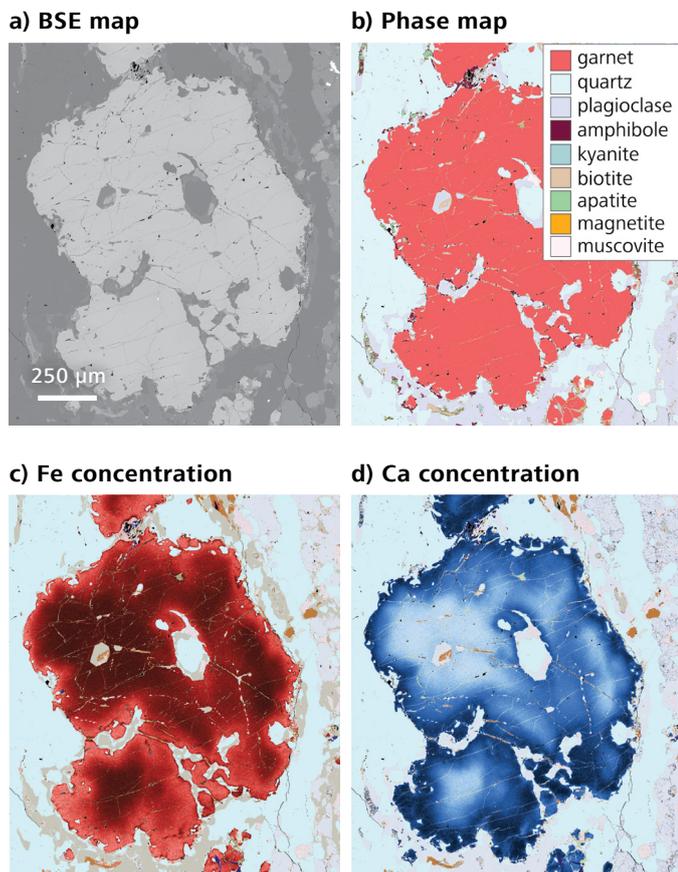
a) BSE map

b) Phase map

- garnet
- quartz
- plagioclase
- amphibole
- kyanite
- biotite
- apatite
- magnetite
- muscovite

c) Fe concentration

d) Ca concentration

Figure 1 *ZEISS Mineralogic images for a chemically zoned garnet from Glenelg, Scotland. These rocks have undergone high pressure metamorphism coincident with the formation of local eclogite pods.*

a) BSE image of a 1.5 mm garnet in a deformed felsic gneiss.

b) ZEISS Mineralogic phase map identifying my minerals present in the BSE image based on quantitative geochemistry.

c and d) ZEISS Mineralogic CHEMera map of garnet zonation in Fe and Ca respectively at 2 μm pixel size. CHEMera maps replace the phase of interest (in this case garnet) with the quantitative geochemistry that the original phase map was based on. Here the dramatic increase in Ca (grossular component) charts the transition from a HT to HP crustal setting during the evolution of the rock.

Figure 1a shows the BSE image of a 1.5 mm garnet; no internal zoning is visible in the BSE image. Figure 1b shows a 2 μm pixel step size ZEISS Mineralogic phase map of the same field of view (FoV), clearly showing the central garnet in a quartzofeldspathic matrix with minor phyllosilicates, kyanite, amphibole and accessory minerals. In Figure 1c-d the garnet classification in the phase map has been replaced with pixel-by-pixel geochemical data. Figure 1c shows the Fe concentration measured using the quantitative EDS data that underpin ZEISS Mineralogic, while Figure 1d shows the equivalent map for Ca. These images highlight the flexibility of the quantitative Mineralogic approach for petrology.

All images in Figure 1 are produced from the same data collection and so no additional time is required to obtain the geochemical information, they simply visualize the data in a different way. Such quantitative zoning information charts the geological history of the sample.

The increase in garnet Ca content (grossular component) toward the rim of the grain charts burial of this rock deep in the crust to a higher pressure environment, coinciding with the formation of the kyanite and rutile. The quantitative EDS chemistry can be incorporated into thermodynamic modelling of the sample to chart the pressure and temperature conditions the rock experienced during its evolution.

Figure 2 shows the Fe zonation at a 5 μm pixel size in a garnet from the Loch Lomond area of Scotland. The map demonstrates the real power of CHEMera maps, utilizing all the data available from automated, quantitative EDS for the interpretation of geological histories. As this garnet grew during prograde metamorphism the pressure and temperature (P-T) conditions changed: this is recorded in both the garnet chemistry (Fe increase), and the inclusions trapped by the garnet as it grew. Cordierite, tourmaline and ilmenite are present in the low-Fe core, while rutile and apatite dominate the high-Fe rim of the garnet. By seamlessly correlating both the chemistry of a key mineral, and the phase identification of the inclusion assemblage, detailed geological interpretations can be made.

Garnet CHEMera map

- tourmaline
- cordierite
- ilmenite
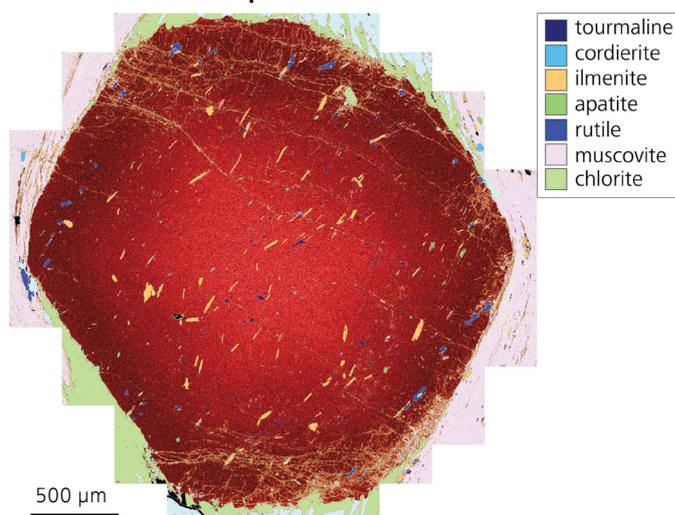- apatite
- rutile
- muscovite
- chlorite

Figure 2 *Garnet CHEMera map from Loch Lomond area of Scotland. This example clearly demonstrates how the two components of the EDS data can be used for geological interpretation. Variation in Fe in garnet can be compared to the evolving inclusion assemblage within the garnet as it grew. By combining the information from both geochemistry and phase ID, greater detail can be obtained from an single dataset.*
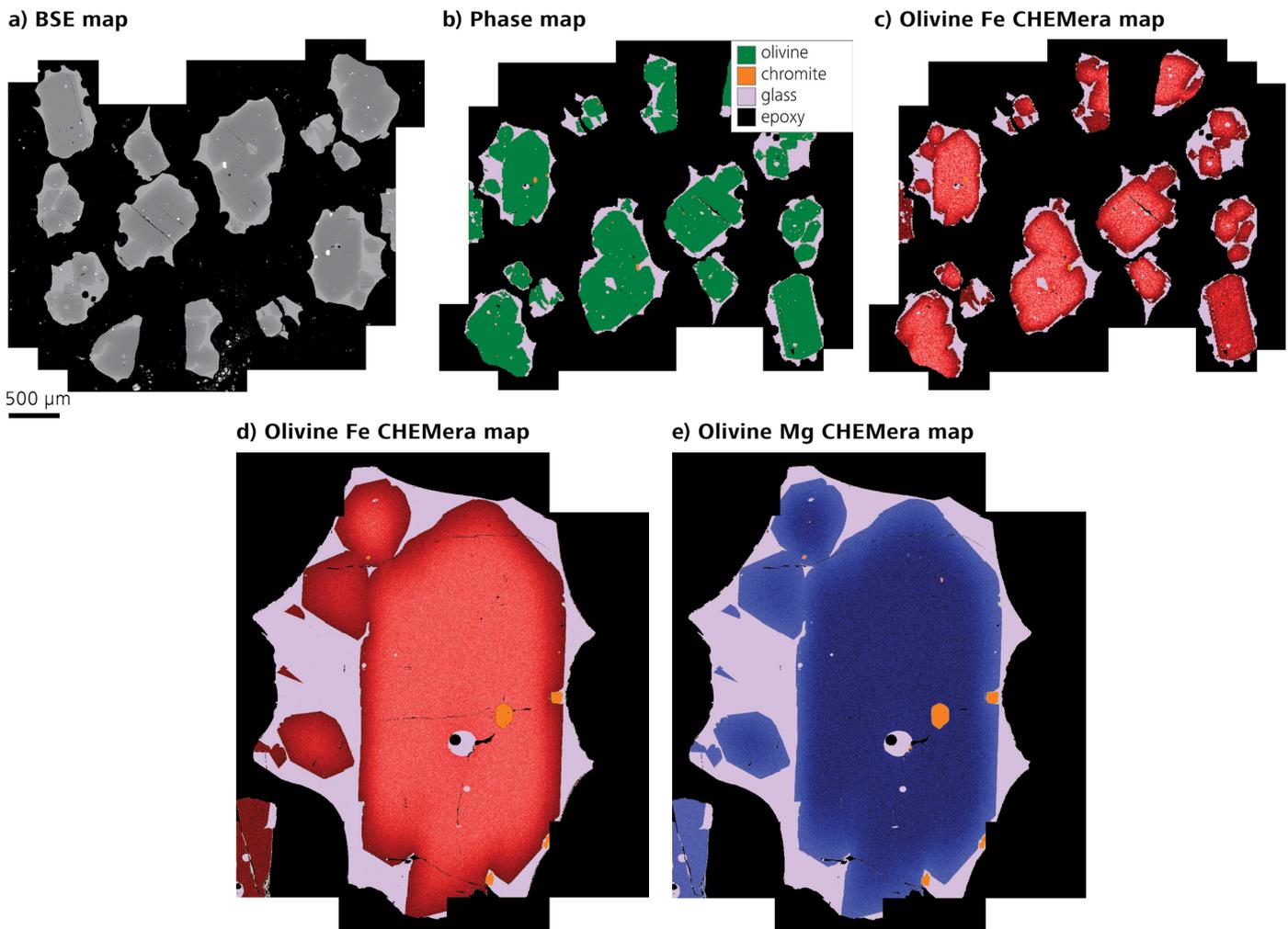
a) BSE map

b) Phase map

- olivine
- chromite
- glass
- epoxy

c) Olivine Fe CHEMera map

500 μm

d) Olivine Fe CHEMera map

e) Olivine Mg CHEMera map

Figure 3 Example of using the CHEMera mapping approach as a workflow for sample interpretation.

a) BSE image of a grain mount containing olivine in basaltic glass.

b) ZEISS Mineralogic phase map of the same grain mount identifying the key minerals.

c) ZEISS Mineralogic CHEMera map produced from the same dataset as b, clearly showing the disequilibrium chemical zoning within the olivine grains.

d and e) ZEISS Mineralogic CHEMera map of garnet zonation in Fe and Mg respectively at 2 μm pixel size. Using the grain mount to identify a key grain for a more detailed scan, the quantitative zoning profiles of the olivine rims can be used to determine processes such as magma storage and eruption rates.

Figure 3 shows an example workflow from igneous petrology, in this case a grain mount of large olivines in basaltic glass, mounted in an epoxy disk. These primitive, forsteritic olivine grains were stored in a mush pile beneath the Hawaiian volcano Kilauea for possibly hundreds of thousands of years. The olivine grains have then been disturbed by the injection of new magma into the system, and chemically altered as they were scavenged by the more evolved carrier melt. Figures 3a and 3b show the BSE and Mineralogic phase map respectively, in this case the phase map has been collected at 20 μm step with the epoxy ignored, enabling a very rapid initial assessment of the ZEISS Mineralogic dataset. Figure 3c shows the same ZEISS Mineralogic data as a CHEMera map, with the olivine classification replaced by the Fe chemistry. Even at a relatively coarse pixel size, this rapid scan of the mount, undertaken in less than an hour, highlights that many grains are strongly zoned.

Following this an individual olivine 1 x 0.5 mm was scanned at a smaller pixel step size of 2 μm in order to better define the chemical zoning. Figures 3d and 3e show a CHEMera map of this single grain displaying Fe and Mg respectively. At this pixel resolution the diffusion of Fe and Mg can be visualised within the outer 500-600 μm of the large grain. These quantitative diffusion profiles, showing ~8-10 wt% variation in Fe and 6-7 wt% variation in Mg, can be used to chart the timescales of the 2018 eruption at Kilauea.

Summary

Quantification of geochemical zoning is an essential part of many petrological studies. ZEISS Mineralogic offers a unique capability as a research tool providing both automated mineralogical scans of samples up to full thin sections and core, with all the information underpinned by quantitative geochemical data. These data can be accessed in informative ways to highlight key processes at the mineral scale.