

EUG XI



Symposium PCM5

High Spatial Resolution Microanalysis in the
Transmission Electron Microscope
and Related Techniques:
Applications for the Geosciences

Convenors

Rik Brydson
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PCM5

Electron Microscopy and Spectroscopy

Thursday AM Session

PCM5 : THam02 : G3 Quantitative Compositional Imaging with Energy-Filtering TEM

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Since many mineral samples are too fine grained and heterogeneous to be studied by standard methods such as electron microprobe or wet chemistry, advanced microscopy techniques are indispensable for their characterization. The spatial resolution problem can be overcome by using electron energy-loss spectrometry (EELS) combined with transmission electron microscopy. In particular energy-filtering TEM (EFTEM) enables a full chemical characterization from the μm to the sub-nm range. Although the first experimental energy-filtering prototype microscopes were already built during the sixties, the technique's wide-spread success started only during the last few years with the commercial availability of more sophisticated filter designs. Equipping a TEM with an energy-filter offers extraordinary advantages for the characterization of both materials science, mineralogical and biological samples: Besides improvements for TEM imaging and electron diffraction like better contrast or thickness mapping, the most important application of EFTEM is to derive the two dimensional distribution of a particular element by making use of the element-specific ionisation edges. EFTEM enables the mapping of the elements ranging from lithium to uranium by taking a series of energy-filtered images around an edge in about a minute. Elemental maps with resolution well below 1 nm [1] and elemental sensitivities down to a single monolayer have been reported [2]. The signal in the EFTEM elemental maps is related to the concentration of the corresponding element, however, it also depends on a number of other factors like crystal orientation, mass thickness and collection angle. Thus, the EFTEM elemental maps are an efficient tool for qualitative characterization, but have not been considered to be readily amenable to quantitative analysis. However, recently it could be shown that these EFTEM elemental maps can be used to extract quantitative information, e.g. elemental concentration maps or chemical phase maps [3,4,5]. In this work we will compare these methods for typical mineralogical samples and discuss their particular advantages for practical work. Additionally, we will show how related sets of elemental maps can be examined and combined by using correlation techniques such as scatter diagrams, thus yielding chemical phase distribution maps. Another important advantage of EFTEM is that it can be used for chemical bonding mapping by utilizing the near edge fine structures of the ionisation edges (ELNES). This procedure is efficient for mapping the valence states of minor and major amounts of elements on a scale heretofore impossible and allows to be obtained not only from ultra-fine grains but also, for example, at reaction fronts in minerals. Over the last years numerous and wide-ranging applications of EFTEM elemental mapping have been reported [6]. For example, EFTEM allows for the detailed analysis of mineral intergrowths, inclusions, oscillatory zoning, exsolution textures and grain boundaries on the scale of nanometres.

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PCM5 : THam04 : G3 Investigation of Exsolution in Minerals by Valence State Mapping, Electron Spectroscopic Imaging, Electron Loss Spectroscopy and EDX

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Microstructure and its development due to exsolution, cation ordering and oxidation processes plays an important role in mineral physics. The main topic of this contribution is the investigation of exsolution phenomena in the solid solutions hematite (Fe_2O_3) – ilmenite (FeTiO_3) and magnetite (Fe_3O_4) – hercynite (FeAl_2O_4) by using energy filtered TEM.

Exsolution in the titanohematite solid solution was studied in natural samples in which exsolution lamellae can be seen by optical microscopy, but which also contain much finer lamellae. Conventional bright field TEM studies of the fine-scale exsolution are made difficult due to the strong strain contrast. Using energy filtered TEM avoids these artefacts and shows two different scales of exsolution: exsolution lamellae on the scale of 100nm surrounded by a precipitation free zone and precipitates with dimensions of a few nm in between exsolution lamellae. With valence state and elemental mapping we determined the spatial distribution of Fe^{2+} and Fe^{3+} as well as the chemical distribution of hematite and ilmenite. Quantification by using EDX, EELS, valence state of Fe (van Aken et al., 1998) and elemental mapping results in compositions of approximately $\text{hem}_{0.4}\text{ilm}_{0.6}$ for the exsolution lamellae and the small precipitates and $\text{hem}_{0.8}\text{ilm}_{0.2}$ for the precipitation free zone (Golla et al.).

For the system magnetite-hercynite we first investigated the magnetic susceptibility of synthetic samples of the solid solution using a Kappabridge. The Kappabridge is extremely sensitive to small amounts of material with different Curie temperatures, such as would be produced by exsolution or oxidation processes. With increasing hercynite concentration, both oxidation and exsolution processes took place during one heating and cooling cycle of the Kappabridge. We found three different temperature ranges over which these processes take place on the time scale of the experiment. In the first range the heating and cooling cycles are reversible i.e. the sample is unchanged. We interpret the behaviour in the second range to be caused by oxidation processes and the third range can be explained as exsolution. Using energy filtered TEM we have verified that exsolution occurs during the higher temperature Kappabridge experiments. Compositional modulations, interpreted as spinodal decomposition on a scale of 5-10 nm have been mapped using energy filtered imaging.

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PCM5 : THam05 : G3 Element Distribution in and between Minerals: Detection via Drift-Compensated EDX-STEM Mapping

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The increasing use of transmission electron microscopy (TEM) in earth sciences has brought to our attention that much of the information on global earth processes is reflected at the submicroscopic scale, in the microstructures of minerals. The structural and chemical signatures of minerals reflect the physicochemical changes they underwent in their geological environments. The focus is here on the microchemical signature of minerals, which can be mapped with nanometre resolution using scanning transmission electron microscopy (STEM) combined with energy-dispersive microanalysis (EDX).

The new generation of STEMs with field-emission guns (FEG) allows us to acquire bright-field or dark-field STEM images with a high spatial resolution of ~ 1 nm. The X-rays generated in a mineral during the scanning process can be simultaneously detected using modern EDX systems. This simultaneous detection in dynamical scanning mode has two major advantages over a point-by-point acquisition of X-ray spectra: (a) sample contamination can be largely avoided, especially if a cooling stage is employed and (b) the irradiation damage in beam-sensitive minerals can

be distinctly reduced. The spatial resolution of such dynamically acquired X-ray maps is however often limited by sample drift occurring during the relatively long detection times (minutes to hours). To circumvent this problem, drift can be compensated via an algorithm that involves the repetitive acquisition and comparison of STEM images with a reference image. In case of sufficiently high chemical gradients, mineral precipitates with a size on the order of 10 nm can be routinely imaged with EDX mapping. Even better resolution can be achieved in case of planar exsolution lamellae. Compared to energy-filtered imaging, STEM-EDX mapping has the important advantage that all elements in a sample can be detected in parallel. Therefore, minerals in polyphasic systems can be quickly distinguished and assigned by comparison of all elemental maps. Such comparisons of elemental maps also help to recognise diffusion profiles and substitution mechanisms in and between minerals. Examples will be given to demonstrate these strengths of drift-compensated STEM-EDX mapping.

PCM5 : THam06 : G3 Precision TEM Sample Preparation using Focused Ion Beam Thinning (FIB)

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Focused ion beam thinning FIB makes it possible to prepare a TEM foil from just the volume you are interested in, without destroying the mineral or the object you want to investigate. This method allows the preparation of TEM foils of tiny inclusions in minerals ($< 1 \mu\text{m}$), very small mineral grains and microfossils for TEM investigations. Thin foils can be prepared directly out of the inclusions, which remain inside their container mineral. Oriented sections can be cut out of tiny mineral grains. Cross sections of reaction rims are easily prepared.

FIB using a FEI FIB200 at the FEI application laboratories in Cambridge and München has been successfully applied to TEM specimen preparation of olivine ($\text{Mg, Fe}_2\text{SiO}_4$) and wollastonite reaction rims.

TEM foils with a thickness of about 100 nm have been prepared in two different manners. Single crystals of 1 mm in diameter and a thickness of about 30 μm were glued onto a copper disc with a hole of 1 mm in diameter in the centre. Prior to fixing the specimen onto the disc, a sector of about 60-90 degree was cut out of the disc. This specimen setup allows the preparation of a thin foil, 15 μm wide, 10 μm deep and 100 nm thick, at the edge of the specimen or cutting several foils of similar size at different selected locations from the surface of the specimen disc.

The advantage of preparing the thin foil starting from the edge of the sample is that the area of interest must not be removed from the specimen and placed onto a separate TEM support grid. Disadvantage is that the area of interest must be near the edge of the foil. Cutting the foil from the surface of the specimen allows the free selection of the area of interest. In this case the foil is removed from the specimen and placed onto a copper grid covered with a Formvar film by using a manipulator with a thin glass fibre. The transfer occurs by using an optical microscope. Applying the FIB technique results in TEM foils of 15-20 μm in width and 7-12 μm in depth with a homogeneous thickness of about 100 nm. Thinner specimens are possible, and depends on the ability of the operator. The amount of implanted Ga that is used as ion beam material is very low and does not affect the chemical analysis of the olivine. The specimen is thin enough even for HREM imaging or EELS spectroscopy.

In the future FIB will open a new and wide field for TEM investigation of very small mineral inclusions, synthesis products and microfossils.

PCMS

Electron Microscopy and Spectroscopy

PCMS : THam07 : G3 Chemistry and Structure of Leached Layers Formed on Labradorite Feldspar

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Leached layers in the near-surface of labradorite feldspar were formed by hydrolyzing samples at 25°C in a pH 3.0 solution. Electron transparent thin sections of reacted samples were prepared by ultramicrotomy and examined by conventional TEM and HRTEM. Electron diffraction diagrams confirm that preferential leaching leads to the formation of leached layers that have an amorphous structure. The amorphous/crystalline boundary is in all cases well-defined and sharp. The thickness of the leached layers is variable, ranging from = 300-1000 nm. The variation in the thickness of the leached layers occurs over lateral distances of ~500 nm. The individual lamellae (an artefact of the ultramicrotome technique) that extend from the surface to the unaltered bulk material are often broken at the amorphous/crystalline boundary, this suggesting a boundary with elevated strain is created during the structural transformation. EELS analyses (at intervals of ~50 nm) along individual lamellae indicate that the amorphous/crystalline boundary is associated with a sharp, step-change in the counts of Al, Si, and Ca, whereas the change in O is more gradual. Al and Ca counts are lower in the amorphous zone, whereas Si and O counts are lower in the crystalline zone.

PCMS : THam11 : G3 Comparison of Different Quantification Methods of Fe³⁺/ΣFe-Ratios using Electron Energy-Loss Spectroscopy

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In the last few years, different quantification methods of Fe³⁺/ΣFe ratios have been developed using electron energy-loss spectroscopy (EELS). These methods are based on the analysis of Fe L_{2,3}- and Fe M_{2,3}-energy-loss near-edge fine structure (ELNES) and combined with transmission electron microscopy enable routine investigations of the Fe³⁺/ΣFe ratio at high lateral resolution on a scale of a few 10 nm (van Aken, 1995; van Aken et al., 1998; van Aken et al., 1999; Garvie & Buseck, 1998). The following Fe³⁺/ΣFe quantification methods will be compared and the size of the absolute error discussed. The integral intensity ratio of the Fe L_{2,3} white lines show a linear dependence as a function of Fe³⁺/ΣFe ratio. Straight lines arise with different slopes for different mineral groups (garnets, pyroxenes, spinels), which can be explained by the different crystal structures and concomitant variable crystal field splitting. The method of the modified integral intensity of the Fe L_{2,3} white lines employs two 2 eV-wide integration windows centring around both the Fe L_{2,3}-maximum for Fe³⁺ and the Fe L_{2,3}-maximum for Fe²⁺. This method leads to a universal curve with acceptable absolute errors of about ±0.05 for Fe³⁺/ΣFe ratio (van Aken et al., 1998). The Fe L_{2,3}-ELNES can also be modelled with the help of standard spectra (van Aken, 1995; Garvie & Buseck, 1998). The method used by Garvie & Buseck (1998) can be improved considerably through an appropriate choice of standard spectra, whereby the Fe³⁺/ΣFe ratio can be determined with an absolute error of about ±0.03, depending on the quality of measured spectra. Another method employs a simple mathematical description of the valence-depending splitting of Fe L_{2,3}-ELNES by fitting several Gaussian functions and an ArcTan function. The systematic analysis of the integral portions of the individual Gaussian curves for different mineral groups provides a further Fe³⁺/ΣFe quantification method with an absolute error of about ±0.03.

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Garvie LAJ & Buseck PR, *Nature*, **396**, 667-670, (1998).

PCMS : THam12 : G3 EELS Study of Iron Valency at Nanometer Scale in Perovskite-Structured Materials

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We present the study of the iron valencies at nanometer scale in cements and high-pressure assemblages. In these two geomaterials, crystals appear as sub-micronic or nanometric phases, requiring the use of highly spatially resolved spectroscopies. In this case, Electron Energy Loss Spectroscopy (EELS) attached to a Transmission Electron Microscope (TEM), provides a unique tool to investigate the bonding in these materials. Indeed, EELS provides a nanometer scale spectroscopy of the unoccupied electron states, allowing for instance, the study of the iron d band occupations in 10 nm wide crystals. First, we will show how the study of the EELS Fe L_{2,3} edges enables a quantitative determination of the Fe³⁺/ΣFe ratio. The limitations in the accuracy of the methods proposed in the literature (Garvie & Buseck 1998, van Aken et al. 1998), inherent to the solid state effects (for instance, crystal field interaction or magnetic ordering) are also discussed. Then, we applied this valence quantification technique in combination with TEM images and local composition measurements in order to assess the charge compensation processes occurring in brownmillerite crystals which can constitute as far as 30% of calcium aluminium cements. We applied the same technique in order to measure the valency of iron in silicate perovskite-magnesiowüstite biphasic assemblages synthesized from natural olivine in multi-anvil press and diamond-anvil cell. In this case, the technique of line spectra ensuring a minimized electronic dose allows spectra to be collected from crystalline silicate perovskite prior to its amorphization. This technique is also particularly well suited to measure chemical shifts or evolutions of fine structures, since all spectra are acquired under the same experimental conditions. In magnesiowüstite and silicate perovskite observed in contact in these samples, Fe³⁺ is strongly partitioned into the silicate phase. In addition, spectra at the Si L_{2,3} edge measured in the thin amorphous layer between crystalline silicate perovskite and magnesiowüstite confirm that amorphization of silicate perovskite is accompanied by a change from 6-fold to 4-fold oxygen coordination of silicon atoms.

van Aken P.A., Liebscher B. and Styrsky VJ, *Phys. Chem. Mineral.*, **25**, 323, (1998).

Garvie L.A.J. and Buseck P.R., *Nature*, **396**, 667, (1998).

PCMS : THam13 : G3 Geochemical Applications of EELS: Quantification of Fe-Oxidation State in Mixed Valency Minerals

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Geochemical applications of Electron Energy-Loss Spectroscopy (EELS) in the Transmission Electron Microscopy (TEM) are uncommon despite its considerable potential. EELS has a wide range of applications, including determination of oxidation state, valence and elemental quantification and co-ordination of atomic species. Of these, determination and quantification of Fe oxidation state is of particular geochemical significance. The current methods of determining Fe³⁺ include X-ray Absorption Spectroscopy or Mössbauer Spectroscopy which are bulk techniques and cannot give the spatial resolution of EELS. Alternatively Electron Probe Micro-Analysis (EPMA) has a spatial resolution on the micron scale but uses stoichiometric determination of oxygen to calculate Fe³⁺ and hence can suffer from validity problems. The use of a Field Emission Gun (FEG) TEM in EELS produces higher

spatial and energy resolution (~0.8eV) than conventional TEM. The increase in energy resolution produces better peak separation of the Fe L_{2,3} edge and allows for quantification of Fe²⁺ and Fe³⁺ in mixed valency minerals. Using the current quantification methods (Garvie and Buseck, 1998 and van Aken *et al.*, 1998) it is possible to quantify Fe³⁺/ΣFe in a range of silicates and oxides. Our current work concentrates on two applications: 1. Valency determination and quantification of Fe in mantle xenoliths; and 2. Co-ordination fingerprinting of Fe bearing sulphides. In the former, EELS data for Fe³⁺ and thermobarometry calculations (Harley, 1984a and b) are used to recalculate P-T data for a range of well characterised mantle xenoliths to provide tighter constraints on their depth of formation. In the latter, EELS analysis of Fe L_{2,3} and S L_{2,3} edges of Fe sulphides has been carried out to provide a range of data on the speciation and precipitation kinetics of microcrystalline sulphides in sediments.

van Aken PA, Liebscher B & Styrsky VJ, *Phys. Chem. Mineral.*, **25**, 323-327, (1998).

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PCMS : THam14 : G3 EELS Analysis of Micas

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Electron energy loss spectroscopy (EELS) in the TEM has matured to the point that it can be used as a probe into the unoccupied states of elements within micas. Sheet silicates are particularly well-suited for EELS since simple grinding produces large thin areas. In addition, the modular nature of sheet silicates make them amenable to systematic investigations of structural end members. An effort has begun to catalogue the EELS spectra of numerous sheet silicates, in order to determine the fingerprints of O, Mg, Al, Si, Fe, and K core-loss edges. Preliminary results are very promising. EELS spectra for Al and Si L_{2,3} edges show clearly distinguishable tetrahedral and octahedral shapes. The Al L_{2,3} edge for margarite containing equal amounts of ^{IV}Al and ^{VI}Al can be modeled by weighted sums of microcline and pyrophyllite or gibbsite spectra. The same analysis can also be applied to the Al K edge. This technique has been applied to white micas from low-grade metamorphic (LGM) rocks. When comparing LGM white micas (including illite/smectite) with higher-grade muscovite, the LGM white micas appear to have distinctly ^{IV}Al character in both the L_{2,3} and K lines. This is in contrast to pyrophyllite, which shows typical ^{VI}Al character. However, the high Si content of LGM micas requires that most (~75%) of the Al be octahedrally coordinated. The difference between LGM micas and pyrophyllite spectra may be due to distortions of the octahedra in illite/smectite mixtures or some other structural factor.

An extra peak occurs in O K edges 10 eV above the main peak onset (i.e., at greater energy loss) in trioctahedral sheet silicates and is most pronounced in brucite. This peak is missing in dioctahedral sheet silicates. The peak is also present in lepidolite (aluminous trioctahedral), suggesting that it is related to octahedral vacancy content and not simply due to the presence of Al. Future work will include sheet silicates with intermediate octahedral vacancy content. The O K edge prepeak also was observed in most sheet silicates and apparently differs in intensity between di- and trioctahedral species. However, this peak rapidly diminishes as beam damage progresses. Under the conditions of our analyses, the prepeak is not considered a reliable measure of OH content.

Light elements important to micas, such as Li and N, can be detected by EELS. Spectra of lepidolite and tobelite demonstrate that these light elements can be easily identified. Calculated energy dispersive spectra (EDS) show that end member tobelite produces only a small N peak, which is easily swamped by neighboring C and O peaks. The ability of EELS to detect compositional and structural features on the nanometer scale gives us a more complete description of mica crystal chemistry than previously possible.

