New Opportunities for Nanomineralogy using FIB, STEM/EDX and TEM

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INTRODUCTION
Since its development during the late 1980s and 1990s, the focused ion-beam (FIB) microscope has been used extensively for the characterisation of synthetic materials such as semiconductors [1-3]. Its utility comes from the coupling of high-resolution (~7 nm) imaging with the ability to machine the sample surface using a gallium ion beam. As FIB microscopes are becoming more readily available, and now in combination with electron guns (dual-beam instruments), they are finding a much wider range of applications including the machining of natural materials, often with the purpose of producing site-specific electron-transparent samples for subsequent investigation by transmission electron microscopy (TEM) [4-6].

We have carried out a pathfinder investigation to evaluate the use of the FIB microscope to prepare electron-transparent samples of Earth and planetary materials. These samples have been characterised by conventional high-voltage TEM imaging and also by scanning transmission electron microscopy in a scanning electron microscope (SEM-STEM), also known as 'low-voltage' STEM. Here we describe our methodology for preparing FIB samples of rocks and minerals and present two case studies that illustrate the huge potential of combining FIB with TEM and SEM-STEM techniques and some of the challenges faced when working with Earth and planetary materials.

MATERIALS AND METHODS

Firstly, we studied the debris-covered weathered surfaces of K-rich feldspar grains collected from <10,000 year-old soils in northern England and Scotland. Mineral surfaces and associated weathering products have been especially difficult to prepare for TEM investigation using conventional Ar ion milling, but FIB techniques offer the opportunity to prepare electron-transparent cross-sections that preserve the delicate surfaces and associated weathering products.

In addition to imaging grain surfaces, this study sought to determine whether the outermost parts of the feldspar minerals are crystalline or amorphous. This question is especially important because results of many previous laboratory experiments designed to simulate natural weathering have shown that reaction of crystalline silicate minerals with acidic solutions leads to selective leaching of some ions, such as Na, Al, K and Ca, leaving a residual silicon-enriched amorphous layer tens to hundreds of nm thick [e.g. 7-9]. Significantly, the experimentally produced ‘leached layers’ have rarely been found within naturally weathered minerals [10,11]. Although TEM is an obvious technique to use in order to determine whether such amorphous layers can form naturally, the preparation of samples using conventional Ar ion milling has been very challenging. FIB techniques may provide an ideal way in which to prepare cross-sections of weathered minerals for study at the nanoscale.

The second set of samples studied were meteorites, most of which come to Earth from the asteroid belt. Many of these rocks are very finely crystalline and mineralogically heterogeneous on a micrometre to submicrometre scale and so TEM has again been extensively used in studies of their composition and origin. However as meteorites, by their very nature, are rare and precious, it is imperative that the volume of material that is damaged or destroyed during sample preparation is minimised. In addition, owing to the very fine grain size of these rocks, the electron-transparent sample must be precisely located, for example within a micrometre-wide vein or a submicrometre-sized mineral grain. To date most samples for TEM have been manufactured by Ar ion milling, but this technique destroys relatively large volumes of material, the thin areas are difficult to precisely locate.

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and differential thinning of mineralogically heterogeneous samples can be a problem. FIB milling offers an attractive alternative, with damage to very little material and site-specific sampling.

The meteorites studied were the CM2 carbonaceous chondrite Murchison and the ureilite Hajmah(a). Murchison is composed of a very finely crystalline and mineralogically complex mixture of anhydrous silicate minerals that formed at high temperatures and hydrous silicates produced by lower temperature water-mediated alteration. The two groups of minerals are often juxtaposed, with the hydrous minerals forming a rim around millimetre-sized aggregates of anhydrous mineral grain called chondrules. Owing to the millimetre-sized aggregates of anhydrous silicates produced by lower temperature water-mediated alteration, the hydrous minerals forming a rim around millimetre-sized aggregates of anhydrous silicate minerals is one of the most controversial topics in meteorite science as they display many seemingly paradoxical mineralogical, petrological and chemical features; the origin of the carbon-rich matrix is one of the major issues of contention. As with the fine-grained material in Murchison, the inherent difficulties in preparing samples of this rock for study has meant that the origin and history of ureilites is not well understood.

Figure 1 is a flow chart summarising the various steps in preparation of the feldspar and meteorite samples for FIB, TEM and SEM-STEM work. Prior to FIB milling all samples were imaged and chemically analysed using a FEI Quanta 200F field-emission SEM equipped with an EDAX Pegasus X-ray microanalysis system. The weathered feldspar were handpicked from the soils and attached to SEM stubs using carbon adhesive tabs. Secondary electron images and chemical analyses of uncoated grains were acquired in low-vacuum mode (0.45 torr), but where samples were charging a very thin (<10 nm) sputtered coat of gold was applied. Areas selected for FIB work were relatively flat but showed signs of weathering by the presence of etch pits, and/or had a covering of organic material including bacteria and fungi or inorganic weathering products such as day minerals. Grains selected using the above criteria were carefully removed from the carbon tab and remounted onto SEM stubs using a fine layer of epoxy resin. Most samples were sputter coated with 30-50 nm of gold followed by an additional 100 nm of evaporated gold in order to protect the surface from ion damage during FIB work. Uncoated polished thin sections of the meteorites were characterised by SEM backscattered electron imaging and prior to FIB milling the area of interest was coated with 30-50 nm of gold.

The FIB work used a FEI Strata 200-TEM. The first steps were performed automatically using a preprogrammed script, with later steps carried out manually. A 30 kV Ga+ ion beam was used throughout and the beam current was altered during the different steps as required. The first step was to mill two crosses either side of the site of interest which the instrument used as a recognition tool whilst carrying out the automated milling. In the next step a 1-μm thick strip of Pt was deposited on the sample surface between the crosses using a 300 pA beam (Figure 2a). The Pt strip is important, especially for the weathered feldspar surfaces, because it prevents the area of interest from being eroded during subsequent milling. Two trenches were then cut either side of the Pt strip, using a 1.5 nA beam, until the remaining slice was ~800-1000 nm thick (Figure 2b-d). The microscope stage was then tilted to 45° and the slice cut free apart from the Pt strip, which held it in place (Figure 2e). Whilst tilting between -1.2° and +1.2° a 7.5 μm wide by 150-200 nm thick ‘window’ was cut into the middle of the slice using a 10-300 pA beam (Figure 2f). During final polishing a 5 μm wide by 110 nm thick inner window was cut using a 10 pA beam (Figure 2g). The two small pieces of Pt strip holding the sample in place were then cut (Figure 2h) and the slice was extracted from its trench using an ex-situ micromanipulator and placed on a holey carbon film supported by a Cu grid.

The FIB-produced cross-sections were studied by both conventional TEM diffraction-contrast imaging and SEM-STEM microscopy. TEM imaging used a FEI Tecnai F20 TEM/STEM and a Tecnai T20 TEM whereas the SEM-STEM work was carried out on the Quanta SEM. For SEM-STEM the Cu grid containing the FIB sample was secured in a holder containing two solid-state electron detectors positioned below the sample. Interaction of the primary electron beam was then tilted to 45° and the slice cut free apart from the Pt strip, which held it in place. The slice was then tilted to 45° and the slice cut free apart from the Pt strip, which held it in place.
electron beam with the sample produces secondary and backscattered electrons that can be used to form images with conventional detectors above the sample and X-rays that can be collected for chemical analyses. The detector directly beneath the sample forms brightfield (BF) images using electrons scattered at low angles from the direct beam, whereas the detector that is offset from the sample can form a darkfield (DF) image using electrons that have been scattered at relatively high angles (Figure 3a,b). Most contrast in SEM-STEM images arises from differences in thickness and atomic number with a relatively small component of Bragg diffraction. In this study the best results were obtained using an accelerating voltage of 20 kV and a small probe size.

RESULTS

Using the FIB we were readily able to produce electron-transparent cross-sections of rough weathered mineral surfaces that preserved weakly-adhering organic and inorganic materials intact.

Imaging of these samples by SEM-STEM gave mixed results. Figure 4a-d shows SEM-STEM images of two samples, one of a feldspar grain that is overlain by a diatom and the other of a debris-free etched surface. The SEM-STEM images proved especially useful for an overview of the structure of the sample, and the topography of weathered surfaces is particularly clearly defined by the difference in electron scattering between the feldspar and overlying gold and platinum (Figure 4c). However, the SEM-STEM gave poor images of any structure within the feldspar crystal itself and any amorphous layers that may potentially be present. Similarly, the sample with the diatom (Figure 4d) clearly showed the internal structure of its skeleton, although there was relatively little contrast between the diatom and the underlying feldspar.

Bright-field diffraction contrast TEM images were better for exploring microstructures within the feldspars (compare Figures 4a-c with 5a,b and 4d with 5c,d) and additionally showed that thin amorphous layers do indeed occur immediately below the weathered surfaces of some grains (Figure 5a-d). Imaging of feldspar grains on which different thicknesses of gold had been applied prior to FIB milling showed that those with the thinner coats of gold (30-50 nm) had an ~80 nm thick amorphous layer, whereas the samples with thicker gold coats (30-50 nm of sputtered Au plus 100 nm of evaporated Au) only displayed a very narrow (≤5 nm) layer. We also found that feldspar directly beneath the diatom was crystalline but an amorphous layer ~70-80 nm in thickness was present where the Pt strip had been deposited directly on top of the uncoated feldspar (Figure 5d).

In contrast to results from the interiors of weathered mineral grains, SEM-STEM proved a highly effective technique for studying FIB-produced samples of the meteorites. Figure 6 shows images of part of a chondrule rim. Relatively low magnification BF and DF SEM-STEM and BF TEM images of the rim are remarkably similar in both contrast and the level of detail (Figure 6a-d) and show that the rim is composed of a very fine-grained mixture of individual mineral grains and mineral aggregates.

The chemical composition of different areas of these samples were determined by qualitative X-ray analyses which, owing to the thickness of the section (~110 nm), have a spatial resolution of a few tens of nanometres. Results show that the bright areas in the DF images are Fe-rich silicates whereas the darker areas are Mg-rich silicates (Figure 6a), demonstrating that much of the contrast in these images comes from differences in mean atomic number.

Despite the good level of detail in the SEM-STEM images, TEM provided far superior images of the very finely crystalline phyllosilicates that comprise the sample (Figure 6d). By comparison, FIB milling of Hajmah(a) proved to be challenging owing to differential rates of milling between the amorphous carbon, graphite, diamond, metals, carbides and silicates within the carbon-rich matrix. We were able to manufacture one FIB slice but it broke during the ex-situ lift out.

Similar difficulties were experienced in a preliminary study of the formation of clay mineral veins within silicate grains from the Martian meteorite Y000593. In cases where the FIB-produced slice incorporated both clay and the adjacent silicate it could be successfully extracted and studied. To date however we have not been able to successfully mill a slice solely within the clay owing to disintegration during early stages of milling.

DISCUSSION

Our results have shown that FIB in combination with TEM and SEM-STEM are powerful tools for the preparation and high-resolution
imaging of rock and mineral samples. Using the FIB we have been able to manufacture electron transparent slices from very rough surfaces including the diatom on the feldspar grain, and also very specific sites, including the Murchison rims.

However, damage to the crystal structure of these samples during FIB milling and subsequent imaging is a significant problem. The amorphous layers directly below those feldspar grain surfaces with a thin coating of gold are interpreted to be an artifact produced by implantation of Ga⁺ ions, especially during initial deposition of the platinum strip. Previous work on silicon has shown that at least 60 nm of gold must be applied to a sample surface in order to prevent Ga⁺ beam damage [12]. These results are supported by conclusions from our work that beam damage can only be eliminated by using more than 50 nm of gold or by machining parts of the sample over lain by objects such as the diatom. Importantly, FIB-produced slices of those naturally weathered grains that had sufficient protection from beam damage lack any evidence for a naturally formed amorphous layer at the grain surface.

Imaging of the FIB-produced slices by SEM-STEM gave mixed results. The technique was very useful for preliminary characterisation of the slice owing to significant differences in electron scattering, and so good contrast, between regions of different thickness and between the mineral/rock and overlying gold and platinum layers. Darkfield SEM-STEM also produced excellent high-resolution and high-contrast images of the Murchison rim. The close correspondence between differences in chemical composition of the rim constituents and their contrast in DF images indicates that much of this contrast comes from differences in mean atomic number.

With regard to imaging of internal structures within the feldspar grains and the distribution of crystalline and amorphous feldspar, diffraction contrast TEM imaging produced the best results. However these images also demonstrated that feldspar is highly susceptible to electron beam damage in the TEM, which produces layers that enlarge inwards from grain surfaces and are almost indistinguishable from the FIB-produced amorphous layers.

CONCLUSIONS
Focused ion beam techniques have the potential to revolutionise the preparation of Earth and planetary materials for high-resolution imaging and chemical analysis. However, great care must be used during the FIB work and subsequent imaging to avoid, or at least minimise, ion and electron beam damage. This problem is especially relevant to studies of experimentally and naturally weathered materials and has implications for the analysis of very small samples of extraterrestrial materials, such as cometary dust particles, which may be turned completely amorphous during FIB preparation.

SEM-STEM is a quick and easy method for the initial characterisation of samples produced by FIB and results for some Earth and planetary materials can even rival bright-field TEM images.

We predict that SEM-STEM may find many future applications for the imaging of natural materials and especially those within which the features of interest are defined by differences in mean atomic number, although TEM will remain the technique of choice for high-resolution and diffraction-contrast imaging.

REFERENCES

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