Electron backscatter diffraction from unpolished particulate specimens: Examples of particle identification and application to inhalable mineral particulate identification‡ⓐ

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ABSTRACT

By simply crushing mineral grains, suspending the powder in a liquid, and dispersing the suspension on a suitable substrate, it is possible to collect adequate compositional and structural information to identify an unknown phase using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS) and an electron backscatter diffraction system (EBSD). This technique could have important applications in the identification of inhalable particulate material. A simple test is presented to show how SEM/EDS/EBSD data are used to accurately determine the identity of mineral particles. Individual EBSD patterns contain more useful structural information and can be collected and interpreted more quickly than individual selected-area electron diffraction patterns collected with a transmission electron microscope. A case study is presented as an example of how EBSD is able to determine the phase identity of a potentially asbestiform mineral.

Keywords: Electron backscatter diffraction, scanning electron microscopy, particulate matter, phase identification

INTRODUCTION

Electron backscatter diffraction (EBSD) using a scanning electron microscope (SEM) provides the analyst with a wealth of diffraction information from a single pattern that in most cases can, in conjunction with compositional information provided by EDS, unambiguously determine the identity of an unknown phase. The electron diffraction technique in transmission electron microscopy (TEM) is selected-area electron diffraction (SAED). The TEM/SAED technique has limitations with structurally similar phases (e.g., pyroxenes and amphiboles) (Ring 1980). While a single SAED pattern contains information from a single zone axis (one interplanar angle and two *d*-spacings), a single EBSD pattern contains information from multiple zone axes and lattice planes. EBSD provides an analyst with a wealth of information that can allow a much more rapid determination of crystallographic parameters useful for phase discrimination.

EBSD has been thoroughly described in several works (Prior et al. 2009; Schwarzer et al. 2009 and references therein). EBSD occurs when a focused electron beam is incident on a steeply inclined crystalline specimen and a portion of those electrons are elastically scattered. This produces electrons that are scat-

tered at high angles (i.e., backscattered) which in turn produces a quasi-omnidirectional point source of electron illumination within the specimen. When the electron beam is held at a point on the specimen, diffraction of these backscattered electrons can occur if the Bragg condition is satisfied for a lattice plane. These diffracted electrons form a pair of cones centered on each lattice plane and the point of the incident electron beam. Because the source of backscattered electrons within the sample is omnidirectional, diffraction occurs from all lattice planes simultaneously. The diffracted electrons that leave the specimen are collected on a phosphor-coated screen, which is imaged by a high-speed CCD digital camera system. The resulting diffraction pattern is comprised of Kikuchi diffraction bands, and several crystallographic parameters can be determined by analysis of these patterns (Michael and Eades 2000). The widths of bands are determined by the interplanar spacing of the diffracting plane. The points where multiple bands intersect show the location of zone axes. It is possible to determine the unit-cell dimensions and space group symmetry from the information contained in a single EBSD pattern (Dingley and Wright 2009). When used for phase discrimination, chemical composition and measured interplanar angles are used for comparison to a database of previously characterized phases, similar to the phase identification process used in powder X-ray diffraction. This indexing process can be performed either in a fully automated or manual process (Dingley 2004).

When EBSD is used to determine the lattice preferred orientation of a bulk polycrystalline material, the speed with which the analysis can be performed is the primary concern. The accuracy of automated algorithms for image analysis and pattern indexing depend on consistent pattern quality. Because of this, high-quality

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EBSD patterns are required from each data collection point. When preparing a bulk specimen for automated EBSD mapping, great care is taken to produce a polished surface with as little lattice deformation as possible to provide the highest quality diffraction patterns. Even small amounts of near-surface lattice deformation significantly degrade pattern quality. With fine particulates, the surfaces of the particles are typically deformation free and are a result of fracture or cleavage of a larger particle or crystal growth. By using the chemical composition, determined qualitatively with EDS, it is possible to narrow the number of candidate phases to relatively few (<50). The Kikuchi bands observed in an EBSD pattern are used to determine interplanar angles. This list of angles is compared against those for each of the candidate phases. With this type of analysis, there is always an opportunity for a human operator to intervene and reject incorrect solutions and adjust the image analysis parameters or manually identify diffraction bands in the collected pattern to produce an accurate indexing solution. Because of this, patterns of even marginal quality are still useful. Pattern quality in particles may be negatively affected by, for example, weathering or internal strain. In most particulate samples, there will be an abundance of grains, and an operator can quickly and easily reposition the electron beam if a usable diffraction pattern is not readily obtainable from a specific particle.

While the majority of studies use EBSD to examine bulk materials, it is possible to use EBSD methods on particulate samples. The use of EBSD for the identification of small particles of a limited number of synthetic and natural phases has been previously investigated (Small et al. 2002; Small and Michael 2001). In the decade since the publications of these papers, to our knowledge, there have been no published studies using EBSD for the identification of inhalable particles of concern to human health; Raanes and Hjelen (1997) present EBSD results for asbestos minerals, but only from polished specimens. Analysis of airborne particulate samples to identify inhalable asbestos particles by TEM has been commonplace for over 40 yr (e.g., Millette and Bandli 2005). TEM has been preferred over SEM in part because the TEM was the only tool capable of determining both the composition and structure of a microscopic particle of a crystalline material (Millette 2006). Recent advances in EBSD technology have made it possible to easily obtain diffraction data useful for phase discrimination using a SEM. Through the addition of an EBSD system to a SEM equipped with EDS, phase discrimination capabilities of the SEM approach that of a TEM for the discrimination of inhalable particles with less sample preparation and more crystallographic information from a single diffraction pattern. Because EBSD patterns capture the orientations of a large number of diffracting lattice planes, it is possible to quickly differentiate structurally similar phases (e.g., pyroxenes and amphiboles). To perform the same differentiation with TEM/SAED is time consuming and requires a high level of operator proficiency.

The purpose of our study is to show that the methodology that is routinely employed on polished bulk specimens can also be used on natural occurring particulate specimens. To test the utility of EBSD for phase discrimination of inhalable mineral particulates, two sample groups were analyzed: a pair of polymorph phases and a pair of phases with subtle differences in composition and crystal structure. The first case was tested using calcite and aragonite particles. The second case was tested using diopside and tremolite particles. The samples were analyzed as individual phases to assess the reliability of this technique to identify each phase individually. Sample groups were also prepared as binary mixtures to test the ability of the technique to discriminate these phases in a mixture.

The end goal of this and our ongoing work is to demonstrate that EBSD could be a powerful addition to the standard asbestos analytical methods currently employing TEM/SAED instrumentation. The successful adaptation of EBSD to asbestos analysis methods may provide significant economy in the time required for sample preparation, data collection and interpretation, as well as accuracy improvements when non-asbestos fibers are observed, particularly from non-occupational settings.

MATERIALS AND METHODS

Samples selected from the University of Minnesota, Duluth (calcite, aragonite, and diopside), and University of Idaho teaching collections were identified by hand sample properties and visually homogenous crystals were selected for this study. The tremolite specimen from the University of Idaho had been previously characterized by Brown and Gunter (2003). Powder X-ray diffraction was used to verify the hand sample identification of the above materials and to identify any possible impurities present in them. Each material was examined by SEM/EDS/EBSD individually and as a binary mixture at approximately 1:1 ratio by volume. All samples were prepared for analysis by hand in an agate mortar and pestle.

An additional case study sample was obtained as a small amount of loose powder from an undisclosed locality. The material was observed to be byssolitic to asbestiform habit in hand sample. The material had been previously analyzed by TEM/SAED and polarized light microscopy using standard asbestos methods by an undisclosed commercial laboratory.

For SEM examination, a portion of each powdered specimen was suspended in approximately 10 mL of isopropanol and placed in an ultrasonic bath for approximately 30 s. A 10 μL drop of the suspension was placed on a 12.5 mm diameter 0.2 μm pore size polycarbonate membrane filter fixed onto an aluminum SEM specimen stub and allowed to dry at room temperature (modified from Bern et al. 2009). The subsample of the case study suspension was placed on a gold-coated polycarbonate membrane filter. All samples were observed uncoated. All particles analyzed were less than 100 μm in diameter with the majority being less than 20 μm.

A JEOL model JSM-6490LV scanning electron microscope equipped with an Oxford Instruments xAct energy-dispersive X-ray spectrometer and a NordlysII, Channel5 EBSD system (HKL Technologies, 2004, ver. 5.0.6.3) was used. Samples were analyzed at 15 kV accelerating voltage and approximately 4 nA probe current, and the sample substrate surface was tilted 70° toward the EBSD phosphor screen. The calcite, aragonite, diopside, and tremolite samples were observed in variable pressure mode at a chamber pressure of 30 Pa to minimize sample charging. Variable pressure operation can introduce significant artifacts into EDS data. For this study, samples were analyzed both at high vacuum and variable pressure conditions and the qualitative elemental identification results were observed to be indistinguishable. EBSD patterns were collected at 100 ms frame time with 2 × 2 binning. Bands were detected automatically by digitally processing the collected EBSD patterns; the detected bands were verified manually and adjusted where necessary. Indexing was performed by the system software, inspected manually, and either verified or rejected. Rejected results were re-indexed using manually selected bands. Commercially available phase databases were used for comparison to the minerals analyzed (HKL Technologies, 2004, Inorganic Crystal Structure Database, 2000, FIZ-Karlsruhe, ver. 5.0.6.2) as well as the MSA Crystal Structure database (www.minsocam.org/MSA/Crystal_Database.html; accessed 2012-05-09 http://www.webcitation.org/67X6O6fRu).

RESULTS AND DISCUSSION

Polymorph case (calcite and aragonite)

Selection of known phases from the available databases was made on the basis of qualitative composition determined by EDS. For the calcite and aragonite group, 13 phases were found

that contained carbon, oxygen, and calcium. The full list of 13 phases was used for the examination of the calcite and aragonite prepared as individual phases. When the binary mixtures were examined, only a single calcite and a single aragonite reference phase were used for comparison. Representative images and EBSD patterns collected from calcite and aragonite particles are shown in Figures 1a–1b.

A total of 87 particles of the calcite sample were indexed—a significant number, approximately 1/3 of the analyzed particles from each sample, did not produce usable diffraction patterns. The majority of the indexed particles (76) were identified as calcite. Several collected patterns produced automated indexing results that matched other phases: calcite III (high-pressure polymorph) and monohydrocalcite. Both of these phases are monoclinic with pseudohexagonal symmetries, which require careful manual examination of patterns to provide an accurate indexing result.

It is important to note that not every particle analyzed for this study produced an indexable diffraction pattern. Several variables related to sample geometry and lattice deformation can lead to the degradation of pattern quality. Approximately 1/3 of all particles analyzed failed to produce indexable patterns. For the calcite case above, this would effectively reduce the indexing success from 87% (76 correctly indexed as calcite out of 87 total particles indexed) to 58% (2/3 of 87%).

A total of 87 particles of the aragonite sample were indexed: all matched an aragonite phase from the database. There were no interferences from other phases observed during the analysis. Of the 13 reference calcium-, carbon-, and oxygen-containing phases, aragonite was the only orthorhombic phase.

Of the 93 particles examined from the calcite and aragonite mixture, 43 matched with calcite, and 50 matched with aragonite. Because of the different symmetries of these phases, it is possible to unambiguously and rapidly differentiate these two phases using EBSD alone. Average band contrast, which is a qualitative measure of the quality of individual EBSD patterns, was 63 (0–255 scale). This shows that patterns of marginal quality can be used for phase discrimination from particulate samples.

Pyroxene/amphibole case

Selection of known phases from the available databases was made on the basis of qualitative composition determined by EDS. For the diopside-only sample, Ca, Mg, Al, Si, and O were used to search the databases for candidate phases. This resulted in 55 total phases for comparison, including tremolite. For the tremolite-only sample, Ca, Mg, Si, and O were used to search the databases for candidate phases. This resulted in 17 total phases, including diopside. Representative images and EBSD patterns from diopside and tremolite particles are shown in Figures 1c–1d.

Of the 95 particles analyzed from the diopside sample, all but one was identified as diopside. The other phase observed was calcite. This was not unexpected as the diopside crystals were obtained from a diopside marble specimen.

Of the 101 particles analyzed from the tremolite sample, all matched tremolite. Only a single particle produced a pattern with a solution that may have been misinterpreted as a diopside solution (Fig. 2). However, it is still clear that tremolite is the correct phase match to the band positions present in the pattern in Figure 2.

Of the 63 particles examined from the diopside and tremolite mixture, 33% matched with diopside, and 65% matched with tremolite. A single calcite particle, accounting for the remaining 2%, was observed. Because diopside and tremolite have similar symmetries (i.e., they have the same point group, $2/m$), significantly more time was required to determine if the phase indexing was correct (5–10 min per particle, compared to less than one minute for the calcite/aragonite case), and generally higher quality patterns were required (average band contrast 83).

Unknown sample

A single sample was analyzed as a case study to show the utility of EBSD for phase identification of possibly asbestiform minerals. A deposit being explored for precious metals was found to contain a potentially asbestiform gangue mineral. The loose crystals were pale green in color and byssolitic to asbestiform in habit. Transmission electron microscopy and polarized light microscopy (performed by another laboratory) had produced inconclusive results. TEM/EDS/SAED results were consistent
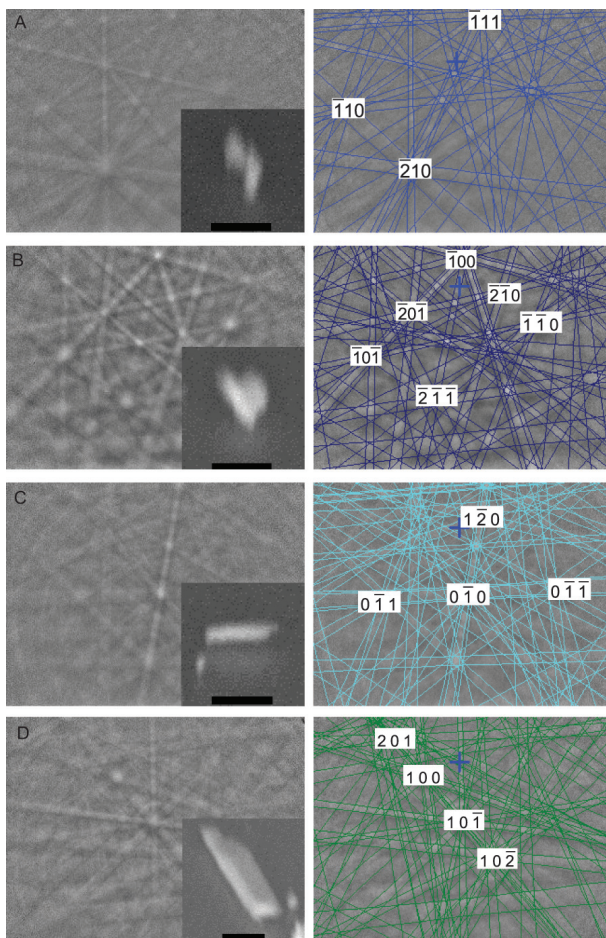

FIGURE 1. Representative EBSD patterns (observed left, indexed right) and backscattered electron micrographs (insets, scale bars 5 μm) of calcite (**a**), aragonite (**b**), diopside (**c**), and tremolite (**d**).
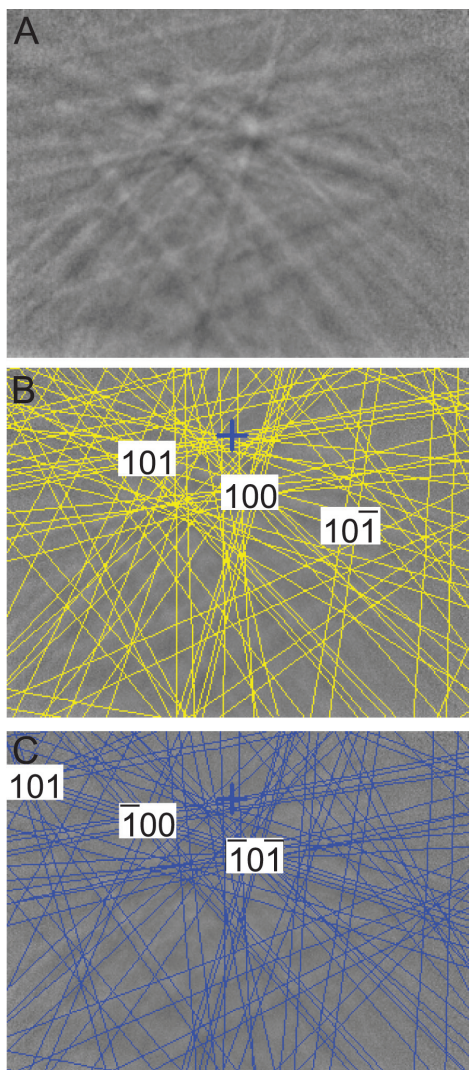
FIGURE 2. Example of inaccurate phase indexing. (**a**) Observed EBSD pattern. (**b**) Pattern indexed as diopside, note presence of bands in pattern not shown in indexed overlay (yellow) and bands in indexed overlay not present in pattern. (**c**) Pattern correctly indexed as tremolite.

FIGURE 3. (**a**) Secondary electron micrograph of representative particle of case study material. Horizontal and vertical scale bars are both 20 μm (foreshortening of the vertical scale due to sample tilt). (**b**) Observed EBSD pattern collected at cross in **a**. (**c**) Actinolite indexing result from pattern in **b**.

with either a pyroxene or amphibole. Optical properties (refractive index and extinction angle) of the material were found to be consistent with either an amphibole or pyroxene. A small portion of the material was examined by SEM/EDS/EBSD. By using EBSD and quantitative EDS analysis, it was determined that the material was an amphibole with composition between actinolite and ferro-actinolite $[Na_{0.2}Ca_{1.8}Fe_{2.8}Mg_{2.4}Al_{0.6}Si_{7.5}O_{22}(OH)_2]$ and a representative particle (byssolitic morphology) is presented in Figure 3. The total time required to make this determination using SEM/EDS/EBSD was less than 1 h, including sample preparation. TEM sample preparation for airborne samples collected on polycarbonate membrane filters requires approximately one hour to produce a sample ready for analysis. EBSD can examine the same filters directly without the need for additional preparation, aside from mounting the filter on a specimen stub. This may be
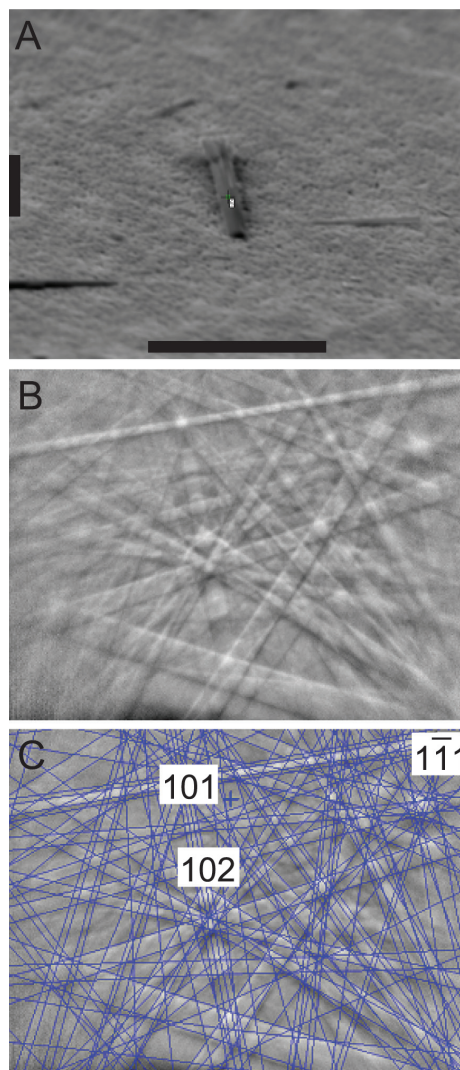
advantageous as it would minimize the potential for particle loss or addition during the sample preparation steps and would provide time savings.

This work shows that EBSD can be used for phase discrimination on mineral particulate specimens. More work is ongoing to explore the limits of the technique in terms of mineral habit and minimum particle size. The work done thus far provides a more direct sample preparation route when compared to the polishing required for EBSD on bulk specimens or carbon support film preparations from membrane filter samples for TEM. By isolating a few grains of an unknown, creating a suspension of crushed material and dispersing on a substrate it is possible to accurately determine the identity of an unknown phase in a matter of minutes. In contrast, preparing an adequately polished surface from a bulk material can require up to several hours.

Furthermore, it is possible to collect adequate EDS/EBSD data from particles of inhalable size (less than 100 μm) on polycarbonate membrane filter surfaces.

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