

Mineral characterisation of industrial mineral deposits at the Geological Survey of Norway: a short introduction

NIGEL J. COOK

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Mineral characterisation involves the study of minerals in terms of their size, habit, chemical composition, morphology, textural position, association and other attributes. There is an established and increasingly important need for this type of study applied to deposits of industrial minerals. This is due to increasing specification requirements for raw materials and mineral products to compete in the marketplace and the realisation that mineral characterisation can ensure optimisation of mineral processing, thus maximising profit. Developments in micro-analytical technology in recent years have made it possible to characterise minerals in an increasingly comprehensive manner. This paper briefly summarises some of the methods used by the Geological Survey of Norway in routine investigations carried out in partnership with the industrial minerals industry. Characterisation of minerals has become an increasingly important part of Survey activities, simultaneous with a relative decline in field-based studies. X-ray diffraction analysis (XRD), image analysis, quantitative electron probe microanalysis (EPMA) and scanning electron microscopy (SEM) are becoming routine methods and supplement traditional microscopic studies and geochemical analysis. Other innovative micro-beam techniques such as laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) are likely to become important in the future, as the need for microanalysis at lower detection limits intensifies. The resource industry is becoming increasingly aware of the importance of this type of information and the value of mineral characterisation data. This trend is likely to increase in future.

Nigel John Cook, Geological Survey of Norway, N-7491 Trondheim, Norway.

Introduction

The characterisation of minerals in terms of their size, habit, chemical composition, morphology, texture, association with other minerals and other physical attributes is important in studies of mineral deposits of all types. The growing need for detailed information about the mineralogical composition of a mineral deposit determines that mineral characterisation studies form an integral and often critical part of investigations of deposits. This is true both for metal ores and deposits of industrial minerals and covers both deposits under active exploitation and prospects being evaluated for future exploitation. As far as industrial minerals are concerned, the reasons for this are many-fold. Firstly, there is a recognised increasing need for specification of raw materials and products to meet market demands, a continued need to achieve optimisation of mineral processing and motivation to achieve maximum economic benefit from resource exploitation. Secondly, rapid developments in micro-analytical technology have made it possible to characterise materials, and therefore identify and potentially address and solve problems unthinkable a generation ago. The Geological Survey of Norway (NGU) is extensively involved in partnership projects with an expanding domestic industrial minerals industry in Norway and the characterisation of minerals is becoming increasingly important in our investigations of mineral resources. This is true in cases in which the investigation is carried out on a contractual basis for industrial end-users and also in research projects aimed at a deeper under-

standing of formation and distribution of industrial mineral resources in Norway.

Application of research tools such as X-ray diffraction analysis (XRD), image analysis, quantitative electron probe microanalysis (EPMA) and scanning electron microscopy (SEM) on a routine basis are valuable supplements to traditional microscopic studies and geochemical analysis, although it should be stressed that these traditional methods remain essential in any study. More recently, other innovative micro-beam techniques such as laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) are playing an increasingly important role. Such techniques permit detection limits for trace elements in minerals not believed possible some years ago, and with increasingly good resolution, precision and accuracy. This trend is likely to intensify in coming years as new techniques are developed and become available commercially. Also, as industry becomes increasingly aware of the kind of information that can be generated, still greater emphasis will be placed upon mineral characterisation in studies of industrial mineral deposits.

This paper briefly reviews some of the techniques used in mineral characterisation procedures currently used by NGU and applied in studies in the industrial minerals sector. The reader is referred to the references on each technique for details of principles and applications. In an effort to meet the growing needs of industry and the researcher, NGU is continuously developing methodologies and upgrading applications of routine characterisation techniques. Moreover, we are continuing to develop our mineral characterisation capabilities still further and to design approaches for specific end-

users of the data. Several other papers in this volume discuss the type of data generated and its interpretation in more detail.

The need for mineral characterisation data

In order to exploit any mineral deposit, it is necessary to provide comprehensive data on all minerals present and their respective proportions in the ore as well as in waste and concentrate products, in addition to the spatial distributions of those minerals on the scale of the deposit. A comprehensive mineralogical investigation should encompass not only those minerals of economic value (e.g., carbonate, talc, rutile, ilmenite; i.e. the ore itself), but also harmful minerals, whose presence may negatively impact upon exploitation, processing or saleability of end products. Furthermore, the chemical composition of the minerals, their size, morphology and association are all factors influencing the attractiveness of a deposit or products produced from it, and therefore its success as a commercial venture. These and other factors, such as local variations in composition, grain size, modal mineralogy or the mineralogical distribution of harmful trace elements, can influence profitability or can affect the selection of processing routines to be employed. In short, a comprehensive mineral characterisation of a deposit is an indispensable advantage, which can guide exploitation of the deposit for maximum profit. The required investment for undertaking such a study can readily pay for itself by allowing for an optimisation of recovery or, for example, by the early recognition of problems of an environmental or marketing character not realised by chemical analysis alone.

Methodology of mineral characterisation

The starting point in investigations of all types of samples is an adequate characterisation of bulk chemistry to assess concentrations of major and minor elements present. The analytical methods used should be selected on the basis of established practice and suitability to the type of sample and desired accuracy and precision and minimum levels of detection. In some rare cases, subsequent mineralogical analysis may provide data that makes repetition of geochemical analysis necessary; for example, if minerals are found to be present which are insoluble in the acids used for sample digestion. Equally important in the early stages of any mineral characterisation is examination of representative samples using conventional optical microscopy in transmitted light. Reflected light microscopy should be carried out in cases where oxides, sulphides or other opaque minerals are present. Although common sense, the importance of sufficient optical microscopy at applicable magnifications, in any mineral characterisation, is commonly underplayed. Much fundamental mineralogical information can be gained at minimal expense from optical examination of suitable samples. Such information may be critical in subsequent interpretation of micro-analytical data.

Image analysis

Image management systems open up a wide range of new possibilities in the field of mineral characterisation and are now relatively commonplace in mineralogical laboratories. The capability to analyse images from SEM or microscope images on a routine, systematised basis has been possible through the development of user-friendly and compatible software coupled with increasingly powerful computers. The type of information provided can be configured to meet the needs of the individual researcher, but can include details of grain size and distribution of grain size, grain morphology and association and the relative abundance of minerals in the investigated sample. Providing that individual minerals have different appearances in the optical image, their physical attributes can be qualitatively or quantitatively identified. The image can range from an optical transmitted-light microscope image to a back-scattered electron SEM image in which individual minerals appear at different brightness intensities depending on the average atomic weight of component elements. False-colour tagging of minerals of interest (for example, deleterious amounts of quartz in carbonate or products, or minor quantities of sulphide minerals in a magnetite concentrate) allows presentation of the scale of the problem and also offers an effective means to communicate the problem to interested parties in reports. Image analysis is particularly effective when coupled with quantitative or semi-quantitative microanalysis, allowing rapid estimation of elemental distributions between mineral phases present in a given sample, and for assessment of characteristics and distribution of compositionally distinct varieties of the same mineral in a sample (e.g., two co-existing white micas in a concentrate).

X-ray diffraction analysis

X-ray diffraction (XRD) analysis is a mineralogical identification method that permits semi- to full-quantitative assessment of the minerals present in a given sample and in what relative proportions they occur. The sample may be a pulverised bulk sample, a processing product or a pure, separated mineral fraction. The method is especially suitable for the study of material containing significant small-scale variation in mineralogy (e.g., carbonates), or in mineral chemistry of component minerals or an exceptionally coarse-grained sample, inhibiting the reliability of image analysis studies of thin-sections. Reliable information can be obtained from XRD analysis of a split of a larger representative sample. XRD is thus a standard method and one that is of key importance in many investigations of industrial mineral deposits and products. Furthermore, changes in mineral composition are reflected in the diffraction properties, allowing small changes in composition within, for example, carbonate from different parts of a given deposit to be identified. Information on crystal structure can be obtained if the necessary software is available, allowing, for example, rapid discrimination of calcite from aragonite or identification of clay minerals or zeolites. The XRD method has its advantage in being a rapid technique involving only minimal sample preparation and is therefore a convenient starting point in mineral characterisation.

tion procedures. It may be used to complement microscopic study of thin-sections and may be followed up by other supplementary techniques where more information is required.

Scanning electron microscopy

Investigation of samples by scanning electron microscopy (SEM) allows detailed identification of individual minerals, either *in situ* within a polished thin-section prepared from a rock sample, or a sample mount prepared from concentrate or other processing product. SEM also provides an optical image that can be processed and treated by image analysis techniques, permitting characterisation of size, morphology, habit and association. Back-scattered electron imaging adds the possibility to search for minor or trace phases of interest, which are otherwise difficult to recognise using conventional microscopic procedures, and to map their distribution. Back-scattered scanning electron microscopy can also be used to reveal morphological attributes and mineral fabrics in appreciably more detail than conventional optical microscopy (e.g., Kringsley et al. 1998) and is an indispensable tool for the investigation of many types of industrial mineral deposits. The application of cathode luminescence is a further tool for the study of microfabrics in structurally complex rocks.

Electron probe microanalysis

Quantitative microanalysis is attainable by using an energy-dispersive system (EDS) or wavelength-dispersive system (WDS) as an add-on to an existing SEM or, ideally, by using a dedicated electron probe and a suitable set of elemental standards. Such quantitative methods are often the only way to acquire the necessary data to solve key questions concerning mineralogical distribution patterns and to achieve full mineralogical characterisation of a given sample. The techniques involved have been described in detail in several reference texts (Reed 1993, 1995, 1996, Scott & Love 1994). The current generation of electron probe instrumentation, coupled with user-friendly operating software, has opened up the possibility to obtain rapid and reliable non-destructive analyses of mineral phases *in situ*. Automatic operation, now a standard feature of today's microprobes, allows analysis to be carried out rapidly and at relatively low cost, enabling a statistically valid database to be assembled in a short time. Minerals can be identified and, in cases where the mineral in question is part of a solid solution series, the precise chemical composition can be defined with excellent accuracy and precision. The high spatial resolution in the range of 1 to 3 μm also permits for quantitative measurement of the finest samples, crystal-scale variations in mineral chemistry, chemical mapping of zoned crystals and identification of small trace phase inclusions.

Knowledge of mineral chemistry is critical to the characterisation of a mineral, whether for quantification of product or for petrologically oriented research on the genesis of an industrial mineral deposit. The detection limits offered by electron probe microanalysis are reasonably low (on the order of 0.1 wt. %, but depending on operating conditions and the mineral being analysed) using normal count times.

This may, however, be reduced by an order of magnitude by using longer counting times, thus making the method useful for determination of trace and minor element concentrations. Robinson and co-workers (1998) recently reviewed the application of electron probe microanalysis to quantification of elements at the trace element levels. Precision of the electron microprobe is typically $\pm 1\%$ with an accuracy of about 3% relative, although a relative accuracy of 1% is readily achievable for major elements in silicate minerals.

One of the few disadvantages of the microprobe method is that the lightest elements ($Z < 4$) cannot be analysed. Furthermore, analysis of elements with Z between 5 and 10 is not possible using many microprobes in service today without the addition of synthetic multi-layer diffraction devices enabling analysis of some of these elements (e.g., O; Nash 1992). Thus, Li and F (both constituents of some micas), B, Be, H, C, N and O are missing in most analyses. The H_2O content of minerals is normally estimated as being the difference between the sum of the oxides and 100%, but this may be subject to considerable error. An additional problem is that microprobe techniques cannot measure the oxidation-state of Fe (and other elements such as Mn). This can lead to uncertainties in the calculation of mineral formulae, for example in the case of minerals such as magnetite. Electron probe microanalysis is also dependent upon the sample material being mounted and polished, making analysis of some types of materials problematic and adding to preparation times. However, such problems are, in general, not insurmountable.

The electron microprobe allows the rapid accumulation of a large body of quantitative data in a relatively short time period. However, the manner in which the technique is applied will depend on the type and depth of information required. In simplest terms, analysis of representative points can be used to assess the range of compositions in a given sample that can then be compared to other samples. The electron beam may also be enlarged to give an average composition across a given area. If the objective is to quantify inhomogeneities on the scale of a single crystal or thin-section, a scanning technique can be applied, giving a distribution map. Alternatively, analyses can be made along a traverse across the area of interest. If greater detail is required, inhomogeneities can be further studied on a point-by-point basis. Careful optical microscopy and/or use of the scanning electron microscope are an essential prerequisite for efficient use of microprobe time.

It should be stressed that not all electron microprobe data obtained and/or published are of acceptable quality. For successful use of electron probe microanalysis, the user should be well informed and trained in mineralogy and have relevant prior knowledge of the sample material, allowing the appropriate type of data to be obtained and sensibly interpreted. Successful microprobe analysis also depends on an interplay between the user and trained technical personnel, whose appreciation of the instrument and inherent limitations is sufficient to select suitable operating conditions for the task concerned and thus reduce the danger of producing poor or misleading data.

Laser ablation inductively-coupled plasma mass spectrometry

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS; 'laser ablation microprobe analysis' or 'laser probe analysis') has rapidly evolved during the past decade as a powerful technique that complements, but does not replace the electron microprobe. Like other relatively new techniques (proton and ion microprobes), LA-ICP-MS allows *in situ* analysis with appreciably lower detection limits (a few tens of ppm or lower) albeit with a reduced spatial resolution compared to the electron microprobe. The method is rapidly establishing itself as an efficient method for determination of trace element concentrations *in situ* within mineral samples. Application of the method to industrial minerals can include determination of harmful elements in ilmenite, rutile, talc or other minerals, e.g., REE concentrations at the ppm level within carbonates. Larsen et al. have discussed the determination of impurities in 'ultra-pure' quartz in this volume.

The LA-ICP-MS method, described by Perkins et al. (1995), allows quantitative analysis of nearly all elements in the periodic table, including most of the light elements within all types of minerals. The method also allows determination of the abundance of individual isotopes and has found considerable application among geoscientists as a tool for determination of stable isotopes (Wright 1995) and notably for Ar-Ar dating of minerals (Kelley 1995). Matrix effects, although far from as serious as in ion probe analysis, infer that the ability to obtain precise and accurate quantitative analysis depends on careful selection of suitable standards with comparable if not exactly the same matrix. Unlike the electron microprobe, however, the method is destructive and the volume of sample analysed is larger; ablation craters have a typical size of 20-80 µm in diameter. Rapid technical development of LA-ICP-MS methods, as well as an expanding catalogue of suitable mineral standards, is likely in the coming decade and the method will undoubtedly play an increasingly important role as a mineral characterisation tool in the future.

Concluding statements

Various other methods are available which have application to mineral deposits, including stable and radiogenic isotopes, microanalysis using Micro-PIXE or SIMS methods and fluid inclusions. Several reviews of these and other microanalytical methods are available (e.g. Cabri & Vaughan 1998, McKibben et al. 1998). Transmission electron microscopy (TEM) is also used extensively as a diagnostic tool in the study of minerals at the sub-microscopic scale (Buseck 1992), e.g., in cases involving mineral polytypism and stacking disorders. Application of TEM is also standard practice in the investigation of asbestos mineralogy.

The number and combination of techniques used in a given study will vary from case to case and will depend upon the questions requiring resolution. The type of information obtained can be individually tailored to meet the requirements of the end-user. Typical end results include identification of a particular mineral or range of minerals as the host for a particular useful or harmful element, depiction of compositional variation in a particular mineral across a given spatial

area, or a full determination of mineralogical balances in ore and their corresponding mineral products. In many cases, an integrated approach is necessary, involving several of the methods referred to above in order to give the fullest mineralogical characterisation possible. For example, electron probe microanalysis, LA-ICP-MS and image analysis can be combined to provide information on the mineralogical distribution of harmful elements (e.g. Ni) in different types of ore.

In all cases, selection of a statistically valid number of representative samples is a prerequisite for obtaining meaningful data. Furthermore, since mineral deposits, like other geological objects, are almost never homogeneous, it may be necessary to repeat the mineral characterisation procedures during the lifetime of a mineral deposit, in order to recognise changes in mineralogy within the deposit as it undergoes successive exploitation.

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