CHAPTER 9: ANALYSIS OF HEAVY MINERALS IN SEDIMENTS BY COMPUTER-CONTROLLED SCANNING ELECTRON MICROSCOPY (CCSEM): PRINCIPLES AND APPLICATIONS

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INTRODUCTION

Computer-controlled scanning electron microscopy (CCSEM) is an automatic particle analysis technique for which a standard model scanning electron microscope (SEM) is used. This automated mineralogy technique combines the advantages of two SEM functions: energy dispersive X-ray spectrometry (EDX) for chemical measurements and digital image analysis of back-scattered electron (BSE) micrographs. CCSEM analysis of a wide range of geological and non-geological materials has been introduced at the Geological Survey of Denmark and Greenland (GEUS) as a fast and reliable method to determine the chemistry of both individual grains and bulk samples. The chemical analysis is combined with measurements of the two-dimensional size and morphology features of every single grain by advanced image analysis. The CCSEM technique is an alternative to the mineral liberation analysis (MLA) and QEMSCAN techniques, discussed elsewhere in this volume (Sylvester 2012; Pirrie et al. 2004). Results of the CCSEM analyses at GEUS are stored and visualized in a web-accessible Oracle database.

The CCSEM technique was developed at the beginning of the 1980s for the characterization of impurities in coal (Lee & Kelly 1980, Huggins et al. 1980) and the study of synthetic crystals for superconductors and catalysts (Lin & Barnes 1984). Soon CCSEM, and the similar techniques MLA and QEMSCAN, found a broader application in the study of dust particles and fibers in lung tissue of mine workers (Friedrichs 1987), in the analyses of aerosols for air quality control and source emission characterization (e.g., Heasman & Watt 1989, Martin et al. 2008), and the degree of sintering and consolidation of coal ash deposits (e.g., Huffman et al. 1994). In earth sciences CCSEM has been used for example in the determination of the sediment budget of a lake (Yin & Johnson 1984), in mining studies (Gu 2003, Rollinson et al. 2011), for the characterization of soil and dust (Pirrie et al. 2004), for provenance analysis of coastal sands (Knudsen et al. 2005, 2009, Bernstein et al. 2008), characterization of Ti beach placer deposits (Frei et al. 2005a), for provenance studies on sandstone in oil-bearing basins (Frei et al. 2005b), for the analysis of kimberlite indicator minerals (Keulen et al. 2009) and for distinguishing fluvio-deltaic facies (Olivarius et al. 2011). Other areas where CCSEM has been applied range widely and include characterization of small inclusions, e.g., impurities in metal alloys or steel (Schwoebel et al. 1988), analyses of gun-shot residues (e.g., Lundrigan 2004, Steffen et al. 2007), archaeological studies of

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cosmetics ceramics (e.g., Hardy & Rollison 2009, Knapp et al. 2011) or the grain size distribution of raw materials in the cement industry (Keulen et al. 2008).

**ANALYTICAL TECHNIQUES**

**Sample preparation**

Sample material may consist for example of (1) a representative part of a bulk sample, (2) carefully selected grains held on double-sided sticky tape, or (3) a heavy mineral separate representative of a bulk sample. Grains, beads, crushed rock material, and powders of both geological and non-geological origin can be analyzed as long as the majority of the examined grains have a grain size larger than ca. 10 \( \mu \)m. For most studies conducted in GEUS CCSEM laboratory, approximately 1 g of sample material was mounted in epoxy resin, using a technique developed at the DuPont Experimental Station, Wilmington, DE, that ensures that almost every grain is completely embedded in the epoxy, without touching any neighboring grains (e.g., McLimans et al. 1999). The epoxy mounts are cut to show a representative part of the mount, subsequently polished, and coated with carbon to enhance their conductivity (Fig. 9-1). However, it is also possible to use thin sections of sample material, like sandstone or sprayed separates, prepared in a similar way.

**CCSEM analysis**

The CCSEM analyses at GEUS were undertaken using a Philips XL40 SEM equipped with two EDX detectors: a Thermo Nanotrace 30 mm\(^2\) window and a Pioneer Voyager 2.7 10 mm\(^2\) window Si(Li) detector. The tungsten filament of the SEM was operated with an acceleration voltage of 17 kV, a filament current of typically 50–70 \( \mu \)A, and the sample was placed at a working distance of 10 mm. The Thermo Noran System SIX software package was used to automatically collect X-ray spectra, grain size and morphology of all particles and to recalculate the data following the Proza \((\phi\rho\Sigma)\) data correction and the filtering quantification technique. The technique has previously been described in detail by Keulen et al. (2008) and is an improvement of the method reported by Frei et al. (2005b) that was based on the now outdated Noran Vantage software package.

The samples were studied in the BSE contrast mode of the electron microscope; the individual particles appear as different shades of grey in their black epoxy matrix (Fig. 9-1). Grey-level intensity

![Fig. 9-1: A: CCSEM sample of beach sediment from Jutland, Denmark, divided into a number of frames in a grid. Part of the grid is outlined in white. Grains of different chemical compositions (different grey values) are embedded in epoxy resin. B: Enlargement of one of the frames of the grid (indicated in red in A). The guard region (yellow) and analyzed grains (red) are shown; the image represents a snapshot of the CCSEM procedure [used by permission of GEUS, from Keulen et al., 2008].](image-url)
thresholding by the image analysis function integrated in the software creates a binary image of the BSE micrograph and allows for the separation and selection of individual grains (Fig. 9-1B). A grid of image frames covering the whole sample area is defined by feeding the end-coordinates of the sample to the computer and by setting the required magnification (typically 30–100x) for the analyses (Fig. 9-1A). Grids consist of 15 to 60 frames with approximately 20–50 grains per frame. A guard region between each frame avoids the double measurement of very large particles in the sample and ensures that only grains that lie completely within the image frame are included for analysis and thus record the true shape of grains. A ‘hole-fill’ function enables more precise measurement of the grain size (e.g., diameter, perimeter, width) and the grain shape (e.g., circularity, aspect ratio) from the binary image. Since the grains are mounted in epoxy resin in such a fashion that they do not touch each other, no digital grain separation techniques, as commonly applied in automatic particle analysis software, have to be used. Thus, the original 2D grain shape and grain size are completely available for analysis, without the introduction of artifacts by grain erosion and dilation or median filtering. Most standard grain shape factors can be measured. The smallest grains in the sample can be excluded from the analysis to avoid the measurement of particles that are only a few pixels in size, especially if a good grain morphology resolution is required.

The binary image created forms the basis for the measurements of the grain chemistry. The software forces the microscope to scan within the perimeter of each grain to obtain the chemistry of either the whole grain area by using the SEM’s scanning function, or from a single point in the center of the grain mass by using the focused beam function. The mineral chemistry is thus determined on the basis of EDX analyses only, not on the grey-level intensity of the BSE-contrast micrographs. As opposed to MLA and QEMSCAN, CCSEM does not provide a visual representation of the mineralogy of each analyzed particle; it yields only a spectrum providing the chemistry of the particle. A typical spectrum for one particle contains 2000 counts for the highest peak, however for special studies the amount of counts in the highest peak can be increased. Spectra with a very low number of counts can be removed to ensure good measurement statistics. Commonly, 800–1200 grains were measured in approximately three to four hours.

The Noran software produces a results table (.csv file) that lists grain shape, grain size and grain chemistry for each individual grain. All spectrum files and image frames, with a typical size of 1024 x 774 pixels are stored after analysis. Spectrum files can be reprocessed to include accidentally omitted elements retrospectively, without the need to physically reanalyze the sample.

**Nomenclature used in the discussion of CCSEM results for heavy minerals**

All results discussed in this contribution are solely based on the geochemistry of grains in mounts that were analyzed with CCSEM and no additional petrological investigations were carried out. Only grains in the size fraction 45–500 or 45–710 micrometres that fell through the heavy liquid have been mounted for subsequent CCSEM analysis. Hence, all results and interpretation are only based on this grain fraction (which usually comprises ca. 200–1200 individual grains). The density of the heavy liquid used is 2.9 g/cm³, which removes quartz and feldspar, but does not remove minerals like hornblende (3–3.4 g/cm³), dolomite (2.9 g/cm³), and white mica (ca. 2.9 g/cm³), which are strictly speaking not heavy minerals. In this contribution, however, all analyzed minerals, except quartz and feldspars, will be referred to as heavy minerals. Only a small fraction, usually one or a few percent for most sediment samples, of the grains remains after heavy liquid treatment. For brevity, we will refer to the analyzed mounts as “the sample” and not always as “the heavy mineral suite of the sample”. Terms like “abundant” or “rare” should be read in perspective, as they reflect the composition of the heavy mineral suite, unless stated differently.

The mineral classification is automatic and purely based on the chemical composition of the measured grains. No further mineralogical or crystallographic investigations are involved in the classification. Therefore, the TiO₂ (i.e., rutile, anatase and brookite) and Al₂SiO₅ (andalusite, sillimanite and kyanite) polymorphs cannot be distinguished and are grouped as one mineral species (rutile and sillimanite, respectively). The distinction between ilmenite, leucoxene and rutile, for example, is entirely based on the measured TiO₂ wt.% content only. The boundaries in the automatic CCSEM classification scheme applied at GEUS for Ti-minerals lie at: magnetite < 21 wt.% TiO₂, Ti-magnetite < 46 wt.% TiO₂, ilmenite < 70 wt.% TiO₂, leucoxene < 87.5 wt.% TiO₂ < rutile.
The amount of water in the crystal lattice cannot be determined with EDX analyses (and consequently not with CCSEM) for two reasons: 1) it is not possible to measure light elements, like B, C, or O, precisely and very light elements, like H, at all, and thus, it cannot be determined whether water is present or not; 2) the EDX software automatically recalculates the obtained concentrations to 100%, since analyses are based on standard-less analysis. Therefore, it is not possible to evaluate if certain elements are not represented in the analysis. As a result it is not possible to distinguish between pyroxenes and hornblende. A large compositional overlap exists between these two mineral groups if water in the hornblende crystal lattice is not taken into account. Therefore, the mineral classification scheme lists both minerals together: clinoamphibole/pyroxene and orthoamphibole/pyroxene, or clino-pyribole and orthopyribole for short. For the same reasons, no distinction can be made between magnetite and hematite.

DATABASE AND INTERACTIVE WEB ACCESS

The GEUS CCSEM data are stored in a relational database, allowing safe storage as well as fast querying and retrieval of the data. The amount of CCSEM data is large, considering that a typical CCSEM sample consists of roughly one thousand grains and for each grain circa 30 analytical parameters are measured, including elemental composition, grain size and shape. All analytical parameters are stored in the database, together with the energy dispersive X-ray spectrum for each grain (from which the elemental composition of the grain is determined), and back-scatter mode SEM images of the sample. At the time of writing the database contains 2140 CCSEM samples, with altogether 2 341 337 grains analyzed, and a total of 76 854 938 analyses. Each grain is classified according to a mineral classification scheme based on the measured concentration of elements in the grain. It is possible to choose between different classification schemes depending on the type of sample.

The CCSEM data are accessed through an interactive web application (Fig. 9-2). The database can be searched using interactive map functionality and/or alphanumerical search criteria. Once a sample is found, a wide array of interactive diagrams allows the user to analyze the data. It is, for example, possible to interact with the following diagrams: (i) a pie-chart showing the modal composition of the sample; (ii) a grain size plot allowing the user to compare grain sizes of the various minerals; (iii) histograms showing the Ti distribution along with any element the user chooses; (iv) an element scatter plot where the user defines the elements and the minerals s/he wants on the plot (shown on Fig. 9-2) and; (iv) a ternary plot where specific element concentrations are plotted against each other for...
garnet grains. All plots can be exported in vector-graphics file formats. In addition to the interactive diagrams both raw and recalculated CCSEM data are listed in various table formats, and can be exported to Microsoft Excel. All backscatter images are available in the application and can be viewed online and/or downloaded.

The central point is that users have the option to retrieve the data easily and interact with the data so that the desired analyses can be performed within the web application in a time-efficient manner. The online access has the added benefit that users around the globe always have live access to the database, meaning that as soon as new data are uploaded the user can start interacting with them immediately.

**VALIDATION OF CCSEM ANALYSIS**

**Analysis of the major element composition of garnet: comparison of electron microprobe (EMPA) and CCSEM**

Detrital garnet is one of the most common heavy minerals in clastic sediments, especially in northwest Europe. Because garnet has a wide range in potential major element compositions that are strongly dependent on paragenesis, garnet geochemical studies have proved particularly useful in identifying and characterizing the provenance of clastic sediments (e.g., Morton 1985, Hutchison & Oliver 1998, Morton et al. 2004).

Garnet major element compositions are conventionally acquired from hand-picked grains by wavelength dispersive (WDS) or energy dispersive (EDS) X-ray electron microprobe analysis (EMPA). Data are usually acquired by spot analysis on grain surfaces of garnet mounted on sample stubs (e.g., Morton et al. 2004) or on embedded, sectioned, and polished grain mounts. In either way, analysis is tedious and time-consuming because all analyses have to be pre-set manually by an operator. In contrast, all data are acquired fully automatically in CCSEM analysis without the need for pre-setting analysis points manually. Consequently, CCSEM analyses are much more time- and cost-efficient compared to conventional analysis.

In order to test the reliability of the garnet major element data that CCSEM analysis provides, Frei et al. (2012) have determined the major element chemistry of 2835 detrital garnet grains separated from 37 samples (collected in the Kangerlussuaq area, Southeast Greenland, and in wells in the UK sector of the Faroe–Shetland Basin) by WDS analysis using EMPA (at Copenhagen University and the Natural History Museum, Humboldt University, Berlin). All samples were subsequently re-analyzed by CCSEM using the same polished mounts prepared from garnet separates that were previously used for EMPA analyses.

The study of Frei et al. (2012) shows an excellent agreement between the datasets obtained by EMPA and CCSEM analysis. Three representative samples are shown in Figure 9-3, where the compositional variation of the garnet assemblages is depicted in ternary diagrams using the molecular proportions of Fe$^{2+}$+Mn (almandine+spessartine), Mg (pyrope), and Ca (grossular) – i.e., $X_{Fe^{2+}+Mn}$, $X_{Mg}$, and $X_{Ca}$, respectively – as poles. Following Morton et al. (2004), three different garnet assemblages (Fig. 9-4) are interpreted as follows: type A garnet (low Ca, high Mg) is believed to be derived from high-grade granulite facies metasedimentary rocks or charnockite; type C garnet (high Ca, high Mg) is from metabasic rocks; and type B garnet (low Mg, variable Ca and Mn) is predominantly from low- to medium-grade metasedimentary rocks or from intermediate to felsic gneiss and granite.

The garnet population from sample 459682 shows a very uniform distribution. Virtually all garnet grains are Fe–Mn rich and Mg–Ca poor and fall into field A of the ternary plot. The results from EMPA and CCSEM are in excellent agreement (Fig. 9-3A). The only minor differences are one single grain with slightly higher Mg content detected by EMPA and one single grain with slightly higher Ca-content detected by CCSEM.

The garnet in sample W4629 is continuously distributed along the Fe rich part of the pyrope–almandine+spessartine join with Mg contents varying between ~10 and 40%, and Ca contents that are generally below 10% (Fig. 9-3B). Virtually all garnet plots into fields A or B of the ternary diagram. The results from EMPA and CCSEM for this slightly more complex population are in remarkable agreement and only insignificant differences are observed.

In sample 459679 the compositional distribution resembles those observed in sample W4629, with the bulk of the garnet plotting with Mg contents between 10 and 40% along the pyrope–almandine+spessartine join (Fig. 9-3C). However, a small additional population of garnet with elevated Ca content (between 10 and 20% Ca) plots into field C of the ternary diagram. The presence of this small garnet fraction with elevated Ca contents is confidently detected by CCSEM.
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Fig. 9.3. Garnet compositions in sample 459682 (A), W4629 (B) and 459679 (C) as determined by EMPA (open symbols; left side) and CCSEM (solid symbols; right side) [after Frei et al. 2012]. X\textsubscript{Fe}, X\textsubscript{Mn}, X\textsubscript{Mg} and X\textsubscript{Ca} are molecular proportions of Fe, Mn, Mg, and Ca, respectively. All Fe was calculated as Fe\textsuperscript{2+}.

The apparent minor deviations observed between the results for major elements obtained by the EMPA and CCSEM methods might be explained with a fundamental analytical difference between the two techniques: all EMPA analyses were obtained by analyzing a single spot in the core of each grain using a focused beam with a spot size of 1 µm. Hence, EMPA analysis neglects potential chemical zoning of garnet grains. In contrast, CCSEM analysis is obtained by scanning the complete grain and therefore represents a “bulk” composition for the entire garnet grain.

Additionally, for EMPA analysis clean, inclusion-free and intergrowth-free regions can be selected manually for spot analysis by the operator. The presence of inclusions, intergrowths, and unliberated, agglomerated grains in the garnet separates used by Frei et al. (2012) is apparent. These grains cannot be avoided, even if utmost care is taken during hand-picking using a binocular microscope. CCSEM does not resolve these features while scanning the entire garnet grain during EDX analysis and these features can be regarded as the most likely source for the minor differences between EMPA and CCSEM results.

Analysis of the minor element composition of garnet: comparison of electron microprobe (EMPA) and CCSEM

Determinations of the elemental composition of macrocrystalline phases in kimberlitic rocks or in detrital sediment samples are an important tool in diamond exploration. Classification schemes have been devised for several minerals where fields of major and minor element compositions present a defined probability that the phases in question have crystallized under conditions where diamond is stable. For example, the relationships between Cr, Ca and Mn contents of pyrope garnet and the Cr, Ca and Na content of eclogitic garnet define such probability fields (Grütter et al., 2004). Other minerals, which are routinely used in this way are
e.g., olivine and ilmenite (Mitchell 1995, Wyatt et al., 2004). The accuracy of the CCSEM analyses with respect for minor elements was shown in a study by Keulen et al., (2008, 2009) where the kimberlite indicator minerals ilmenite, olivine and garnet were analyzed with CCSEM. Here, we will summarize the results for minor elements in garnet.

To test the accuracy of the CCSEM analyses, indicator minerals from the ‘Garnet Lake’ kimberlite body in West Greenland, a known source of diamond, were used. A series of hand-picked pyrope (garnet) grains were mounted in epoxy resin. The sample was analyzed using CCSEM, with extended counting times (5000 counts in the highest peak) to ensure good statistics. The accuracy of CCSEM was tested by comparing the results with compositional data obtained from electron microprobe (EMP) analyses for the same minerals, as reported by Hutchison (2005) and Hutchison & Heaman (2008).

A good reproduction of the EMP measurements was achieved by CCSEM for the Cr and Ca concentration in garnet (Fig. 9-5); the statistical correlation coefficient between the two methods for these elements is 0.70. The relative error in the reproducibility of the measurements is ca. 1–2% for major elements and ca. 4–8% for minor elements and the average R² value for analyses on MgO, Al₂O₃, SiO₂, CaO, Cr₂O₃ and FeO in the grains measured with both methods is 0.8. The ratio between EMP and CCSEM measurements for garnet and olivine is excellent with values between 0.97 and 1.06 for on MgO, Al₂O₃, SiO₂, CaO, Cr₂O₃ and FeO. However, the scatter in the CCSEM data is much larger and therefore a relatively low R² value between both methods has been obtained. The measurements on the discussed indicator minerals demonstrate a good reproduction of the EMP analyses with the CCSEM and the ability of the CCSEM to put the measured minerals into the right category (Keulen et al., 2009). We are confident that this validity of the data can also be achieved for many other minerals.

APPLICATIONS OF CCSEM
Characterization of individual heavy mineral populations
Characterization of Ti minerals

The world’s most important source of Ti, used in a plethora of industrial applications, are the Ti minerals ilmenite, leucoxene, pseudorutile and rutile mined from heavy mineral beach placer deposits. Determination of the average TiO₂ content of the Ti minerals in a heavy mineral beach placer deposit is essential to the assessment of quality and economics of a potential deposit. Conventionally, this parameter is determined by using mineral separates obtained by size, gravity, magnetic, and/or other separation methods, followed by XRF or electron microprobe analysis. These methods are generally tedious, time-consuming, and labor-intensive resulting in high cost.

The TiO₂ content of primary ilmenite ranges from about 45 wt.% to the ideal stochiometric value of 52.6 wt.% (Deer et al. 1992). The continuous alteration of primary ilmenite via pseudorutile to leucoxene is attributed to complex processes of oxidation and hydroxylation associated with leaching of Fe leading to a significant increase in the TiO₂ grade of the Ti mineral fraction (e.g., Grey & Reid 1975, Frost et al. 1983, Grey et al. 1994, Mücke & Bhadra Chaudhuri 1991). Therefore, the average TiO₂ content of the ilmenite fraction of sediment is a very sensitive proxy for the sediment’s
maturity (Mücke & Bhadra Chaudhuri 1991), with immature sediments showing TiO$_2$ contents of the ilmenite fraction around or a little below the stoichiometric value (around 50 wt.%), while the ilmenite fraction in mature sediments show elevated TiO$_2$ contents (>53 wt.%). Because CCSEM provides the average chemical compositions of all minerals present in a given sample, the TiO$_2$ distribution of the Ti mineral fraction can be easily calculated without the need for tedious and time-consuming mineral separation.

The average TiO$_2$ contents of the Ti mineral fraction of beach sands from southwest India, as determined by CCSEM, are shown in frequency distribution diagrams in Figure 9-6. Sample 2000212 (Fig. 9-6A), displays a pronounced bimodal distribution with the majority of the data forming a sharp peak at an average TiO$_2$ content of about 48 wt.% and a pronounced peak at 95 wt.%.

These features are characteristic of primary, unleached ilmenite and are pointing to immature sediment with only a modally subordinate presence of rutile. In contrast, the beach sand from sample 2000227 (Fig. 9-7B) is characterized by a unimodal distribution that peaks at an average TiO$_2$ content of 62 wt.% characteristic for a more mature sediment. The distribution is slightly skewed towards higher TiO$_2$ contents indicating the progressive leaching of Fe from primary ilmenite. Rutile is only present as a modally insignificant phase.

The modal distribution in the heavy mineral fraction in samples 2000212 and 2000227 are shown in Figure 9-7. Sample 2000212 (Fig. 9-7A) contains a large proportion of mafic silicate minerals, that are vulnerable to dissolution during alteration at ambient conditions (e.g. Weibel 2003). This sample yielded ilmenite with a low TiO$_2$ content (Fig. 9-6A). In contrast, the modal distribution in sample 2000227 (Fig. 9-7B) is dominated by environmentally stable minerals (e.g., zircon, kyanite/sillimanite, rutile, leucoxene, and garnet; cf. Morton & Hallsworth 1994) and it contains only an insignificant proportion of mafic silicate minerals. The TiO$_2$ content in this sample is high (Fig. 9-6B).

Clearly, the modal abundances reflect the different degrees of maturity of the sands investigated and point to a high degree of maturity of the beach sand from Chavara. The TiO$_2$ content in ilmenite can be used as a proxy to indicate the sediment maturity.

**Characterization of garnet compositions**

Garnet is a mineral that is observed in many types of metamorphic and igneous rocks. It is relatively stable under most weathering conditions and inert to most diagenetic processes up to a few kilometres overburden. Information on the original composition and metamorphic grade of the garnet-bearing source rocks are lost in most cases. However, the composition of garnet can be used to get a crude estimate of the chemistry (felsic, mafic or calc-silicate) and metamorphic facies $...$
The cation composition of garnet varies widely in garnet from felsic, mafic, and calc-silicate rocks (such as siliceous marble). The garnet composition also depends on the pressure \((P)\) and temperature \((T)\) conditions under which it was formed or recrystallized. This property has been known for a long time and it forms the basis for the development of many geothermometers and geobarometers. For Al-rich garnets, especially Mg, Fe and Ca are indicative of host rock composition and \(P-T\) conditions of metamorphism. This type of garnet includes a large majority of garnet in igneous and metamorphic rocks.

To set up an automated garnet classification system, garnet compositions of metamorphic rocks were taken from 46 publications that cover many different geological settings. A maximum of fifteen measurements from each publication was used to avoid generating a bias with respect to a certain area or rock type. From each publication the metamorphic facies or \(P-T\) conditions, which were calculated using pseudosections, geothermometers and geobarometers, and the rock type were copied. All garnet compositions were plotted in a triangular diagram, using pyrope \((X_{\text{Mg}})\), almandine + spessartine \((X_{\text{FeMn}})\), and grossular \((X_{\text{Ca}})\) as end-member compositions. The diagrams were divided into seven different groups based on their metamorphic facies and their chemistry (Fig. 9-8).

Garnet plotting in group 1 includes kimberlitic garnet and other garnet that underwent ultra-high pressure metamorphism. Garnet in group 2 is mainly from felsic granulite rocks. “Felsic” includes all source rocks with a pelitic, semipelitic, metasedimentary, granitic, or granodioritic composition. Group 3 comprises garnet mainly from felsic amphibolite; these garnet samples are the lower temperature equivalents of group 2. The boundary between these two groups is set at \(X_{\text{Mg}} = 25\), which corresponds to a temperature of ca. 700–750°C.
Group 4 consists of garnet from a) felsic amphibolite that either has a more Ca-rich or more intermediate composition, like Ca-rich semipelite, b) felsic rocks that underwent eclogite-facies metamorphism, or c) charnockite. Group 5 includes garnet from intermediate and mafic amphibolite, and eclogite that was formed at relatively low temperature. Group 6 comprises garnet from garnet-amphibolite, mafic granulite and higher temperature mafic eclogite. Garnet derived from calc-silicate and anorthositic rocks comprise Group 7. CCSEM can thus be applied to automatically classify aluminous garnet grains and with this classification, conclusions on the provenance of the garnet grains can be drawn.

Provenance of Ti beach placer deposits

The Chavara heavy mineral sand deposit in Kerala State of southwest India is one of the world’s best known heavy mineral beach placer deposits and has been exploited since the early 1900s. A primary ore mineral in this placer deposits is ilmenite, which is of particular interest because it occurs in high concentrations and has elevated TiO₂ content (>60 wt.%, Ali et al. 2001). The heavy mineral deposits at Chavara are part of a long shoreline of coastal sands containing altered, high TiO₂ ilmenite that begins near the town of Manavalakurichi in the south and stretches north for approximately 130 km (Fig. 9-9).

Outside this stretch of coastline, there are several occurrences of beach sand with high concentrations of heavy minerals. However, in these ilmenite is generally unaltered and has an average TiO₂ of 53.0 wt.% or less (Fig. 9-9). The similar climatic conditions and geomorphology along the Kerala State coast suggest that the differences in degree of ilmenite alteration, and hence TiO₂ content, may in large part be related to the primary ilmenite geochemistry and ultimately to the source of the ilmenite. Alternatively, sediment containing altered ilmenite could have passed through a geochemical cycle with a history distinctly different from sediment containing unaltered ilmenite (e.g., Lloyd et al. 2005).

In order to place constraints on the processes that led to the formation of heavy mineral sand deposits containing high TiO₂ ilmenite, Bernstein et al. (2008) addressed the issue of heavy mineral provenance in beach and river sediments along a nearly 800 km long portion of the Indian coast in the states of Kerala and Tamil Nadu. They employed CCSEM to study a large number of beach sediment samples as well as river and Teri sediment samples.

![Fig. 9-9: Map of southern India, showing locations and sample numbers of beach and river sediments studied by Bernstein et al., (2008). The shape of symbols indicates the sediment type. The shading of symbols indicates the average TiO₂ contents in ilmenite of individual samples [used by permission of Elsevier, from Bernstein et al., 2008].](image-url)
from all across the catchment area to the beach samples (Teri refers to red elastic sediment known as ‘Teri sand’ now found in most of the areas between the Precambrian basement and the east-facing coastline). The CCSEM data document a marked variation in Ti content of ilmenite in the beach and river sediments (Fig. 9-9). The most striking feature is that in general all high TiO$_2$ ilmenite beach sands are linked with catchment areas predominantly in the khondalite belt of high-grade metasedimentary rocks in the hinterland.

This link between high-TiO$_2$ ilmenite beach sands and the high-grade metasedimentary rocks of the khondalite belt is further substantiated by correlations with minor element contents in the ilmenite, garnet chemistry of the sediments, and typical mineral assemblages (such as the occurrence of hypersthene and sillimanite). Beach sediment samples with high TiO$_2$ ilmenite and sediment samples from all rivers draining the khondalite belt show low MnO contents (<0.6 wt.%) and high MgO contents (>0.8 wt.%; Fig. 9-10A). Garnet from beach sediment samples with high TiO$_2$ ilmenite and sediments from rivers draining the khondalite belt are typically low grossular (<5%) garnet plotting close to the pyrope to almandine–spessartine join (Fig. 9-11). Samples with high-grossular garnet come from sediments north of the Chavara Mineral Province, and from sediments northeast of Tuticorin (Fig. 9-9 and 9-11). Furthermore, all beach sediment samples containing ilmenite with high TiO$_2$ content have garnet with low average grossular component (Fig. 9-10B). Other samples with similar average garnet compositions are all river sands from khondalite belt drainages. The mineral assemblages of high-TiO$_2$ ilmenite beach sands and those of river sediments draining the khondalite belt are characterized by the dominance of Al-silicate minerals (andalusite, sillimanite and kyanite, which cannot be distinguished by CCSEM), whereas sediments with low-TiO$_2$ ilmenite are dominated by enstatite–ferrosilite (hypersthene; Fig. 9-12). The regional variations in mineral assemblages determined by CCSEM are in very good agreement with those reported by Mallik et al., (1987).

The mineral compositional data and heavy mineral assemblages determined by CCSEM thus place tight constraints on the source for high Ti heavy sand deposits in SW India. Based on these observations Bernstein et al. (2008) concluded that high-Ti ilmenite from Chavara beaches originated in the khondalite belt of high-grade metasedimentary rocks. This study demonstrates that CCSEM can be

![Figure 9-10: A. Average MgO vs. TiO$_2$ in ilmenite from individual samples studied by Bernstein et al., (2008), showing the restricted range of average MgO in altered ilmenite. B. Correlation between average TiO$_2$ in ilmenite and average grossular component in garnets from individual samples. Sample numbers are those displayed in Fig. 9-9 [used by permission of Elsevier, from Bernstein et al., 2008].](image)

used for the identification of possible source regions of beach placer and other sediment-hosted deposits and thus ultimately in the exploration for industrial mineral resources.

**Characterization of basement regions using stream sediment samples**

For basin reconstructions, studies of sediment transport patterns and provenance analyses in scientific and applied (e.g., oil industry) studies, a
Fig. 9-11: Garnet compositions in ternary compositional space with the end-member components pyrope (Py: Mg$_3$Al$_2$Si$_3$O$_{12}$), grossular (Gr: Ca$_3$(Al, Fe)$_2$Si$_3$O$_{12}$), and almandine-spessartine (AS: (Fe,Mn)$_3$Al$_2$Si$_3$O$_{12}$), as shown in the inset empty triangle. The data points are for individual garnet grains in a given sample as noted by the sample number in the triangle [used by permission of Elsevier, from Bernstein et al., 2008].

Fig. 9-12: Variations in modal abundances of Al-silicate minerals and hypersthene in the heavy mineral fraction of sediment samples studied by Bernstein et al., (2008). Sample numbers marked with circles indicate >3% modal Al-silicate for the present sample collection. Also given are results from Mallik et al., (1987) on the modal composition of sediments from beaches and rivers of Kerala State indicated with S (abundant sillimanite) and H (abundant hypersthene) [used by permission of Elsevier, from Bernstein et al., 2008].
characterization of the basement in possible sediment source areas is of great importance and of increasing interest. Here, we demonstrate how CCSEM can be applied as one of the tools in such characterization studies.

Stream sediment samples were collected from the basement rock in western Greenland between ca. 66 and 71.5° N. The area can be divided into four different zones (Fig. 9-13). 1) The Paleozoic metasedimentary rocks east of Nuussuaq and Svartenhuk Halvo; these stream sediment samples show abundant dark and white mica, relatively low amounts of clinopyroxene/clinoamphibole, sillimanite/kyanite, ilmenite, magnetite and garnet in their heavy mineral separates. 2) Samples from the Proterozoic basement between ca. 70° and 69°N (roughly between Maarmorilik and Anup Nunaa); these samples are rich in clinopyroxene/clinoamphibole, and dark mica, they yield some epidote, but hardly any white mica or orthopyroxene/orthoamphibole. They show sillimanite/kyanite, garnet and some titanite. 3) Samples from the Proterozoic basement between ca. 69° and 68°N (roughly between Anap Nunaa and Aforsiorfik); these samples are rich in clinopyroxene/clinoamphibole and epidote, but yield hardly any dark or white mica or orthopyroxene/orthoamphibole. They show some titanite. 4) The samples from the Paleozoic and Archean basement south of ca. 68°N; this group of samples has abundant clinopyroxene/clinoamphibole, orthopyroxene/orthoamphibole, and small amounts of biotite, epidote, garnet, titanite, and sillimanite/kyanite. The sample from the Archean granite at Søndre Strømfjord cannot be included in this sample set.

The composition of the garnet roughly follows this grouping (Fig. 9-13). If we take the garnet classification as discussed above, with its seven groups, we see that the stream sediments in the northernmost zone (north of Maarmorilik, derived from the Proterozoic metasedimentary rocks) abundantly yield group 2 garnet (high temperature metamorphosed felsic rock), with some group 1 and group 3 garnet. The garnet in zone 2, between ca. 70° and 69°N (roughly between Maarmorilik and Anup Nunaa) are also dominated by group 2 garnet, but yield in addition some group 4 and 6 garnet, which are derived from more intermediate to mafic rock types metamorphosed at intermediate to high metamorphic temperatures. The garnet in zone 3 is the most diverse, with garnet from groups 2, 3, 4, and 6. Groups 3 and 4 are indicative of intermediate temperatures during metamorphism, while groups 4 and 6 imply intermediate to mafic rock types. The samples from the southernmost studied zone, including the granite intrusion at Søndre Strømfjord, show many garnet grains that are derived from an intermediate to mafic rock type that was metamorphosed under intermediate temperature conditions (group 4).

If we compare these results for the modal heavy mineral suite and the garnet composition to field evidence from mapping in the area (Fig. 9-13) the division into four different zones can be justified from the geological map. The northernmost zone is characterized by samples collected from Proterozoic metasedimentary rocks. These rocks were metamorphosed at high grade conditions and are rich in Al-bearing minerals, such as mica and sillimanite (Garde & Steenfelt 1999). These minerals are observed in the heavy mineral suite and are in accordance with a felsic high temperature rock type in the area, as indicated by the garnet.

The second zone is still characterized by high-grade basement rocks. Metasedimentary enclaves occur in some areas and these enclaves are also the richest in garnet, which shows their signature. A stronger presence of clinopyroxene/clinoamphibole (probably hornblende) shows that intermediate gneiss is more abundant here than in the area with metasedimentary rocks. Dark mica might be indicative for a metasedimentary rock or for an intermediate composition orthogneiss, thus no conclusions can be drawn on the presence of this mineral.

Zone 3 shows the lowest metamorphic conditions: much of the garnet was formed at intermediate temperature conditions (group 3 and 4) and epidote (a retrograde mineral) is present in abundance, while magnetite, garnet and sillimanite–kyanite are mainly absent or only present in small quantities.

The last zone (zone 4, the area south of Aforsiorfik) is identified on the geological map (Fig. 9-13) as having orthopyroxene in the basement rocks. The orthopyroxene, in many areas mapped as hypersthene, is often taken as an indicator of granulite-facies metamorphic conditions. Even though granulite-facies conditions cannot be proven, higher temperature minerals like magnetite and sillimanite–kyanite are more abundant in these samples, as is orthopyroxene/orthoamphibole. The garnet however, does not indicate high-temperature metamorphism, but is more of an intermediate metamorphic grade.
Fig. 9-13: Basement of Western Greenland between ca. 72 and 66° N (after Henriksen et al., 1995, 2009), with data for the garnet composition (a) and the heavy mineral suite (b) of representative stream sediment samples. Garnet composition and heavy mineral modal compositions were downloaded from the web-interface with the CCSEM database. (a) Garnet grouping as discussed in text and in Figure X-8. (b) Modal heavy mineral distribution, where pyrobole is a short form for pyroxene and/or amphibole. See section of Nomenclature for restrictions. Background map Copyright: Geological Survey of Denmark and Greenland [used by permission of GEUS].
These four different groups of minerals can be used to identify the provenance of sedimentary rocks derived from this basement, as for example the Mesozoic–Paleogene sediments on Svartenhuk Halvø, western Nuussuaq and Disko (see Fig. 9-13 for localities) or sediment from drillcores in the Davis Strait between Canada and Greenland.

SUMMARY AND CONCLUSIONS

CCSEM is a fully automated technique that allows analysis of the chemistry and grain morphology of a large number of individual minerals in sediment and sedimentary rocks. The technique is based on a combination of digital image analysis of BSE images and EDX analysis and can be set-up on each standard off-the-shelf scanning electron microscope that is equipped with at least one EDX detector and commercially available software packages for EDX analysis that allow automated particle analysis to be performed (e.g., the Noran Vantage or the Thermo Noran System SIX software packages).

CCSEM allows the accurate and precise determination of the modal abundances of individual mineral fractions (e.g., garnet, ilmenite, rutile, zircon, monazite, or apatite) and their average chemical composition as well as compositional variation. Furthermore, CCSEM provides information about their size (e.g., diameter and perimeter length) and shape (e.g., aspect ratio and circularity). Because the sample preparation is simple and the chemical and physical properties are determined in one fully automated analytical session, CCSEM is a powerful and cost-efficient tool for research in sedimentology. Although the technique has a wide range of applications ranging from quality control of feedstock of industrial minerals to exploration of sediment-hosted mineral deposits, it is especially beneficial for the mineralogical characterization of sand and sandstone, and hence for provenance studies that address the generation and transport paths of sand through geological time.

Similar to other SEM-based automated particle analysis platforms, such as the Mineral Liberation Analyzer (see Sylvester, 2012) and QEMSCAN (Pirrie et al. 2004), CCSEM offers great potential for qualitative and quantitative mineralogical analysis of sediments and sedimentary rocks and its widespread application will open new avenues of research for all scientists interested in sedimentology. The advantage of CCSEM over MLA and QEMSCAN is the ability to produce a chemical analysis of each individual grain.

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HEAVY MINERALS IN SEDIMENTS BY COMPUTER-CONTROLLED SCANNING ELECTRON MICROSCOPY


http://www.geus.dk/program-areas/raw-materials/greenl-map/greenl-map/kostart-dk.htm


