Improved imaging and analysis of chlorite in reservoirs and modern day analogues: new insights for reservoir quality and provenance

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Abstract: Chlorite is a key mineral in the control of reservoir quality in many siliciclastic rocks. In deeply buried reservoirs, chlorite coats on sand grains prevent the growth of quartz cements and lead to anomalously good reservoir quality. By contrast, an excess of chlorite – for example, in clay-rich siltstone and sandstone – leads to blocked pore throats and very low permeability. Determining which compositional type is present, how it occurs spatially, and quantifying the many and varied habits of chlorite that are of commercial importance remains a challenge. With the advent of automated techniques based on scanning electron microscopy (SEM), it is possible to provide instant phase identification and mapping of entire thin sections of rock. The resulting quantitative mineralogy and rock fabric data can be compared with well logs and core analysis data. We present here a completely novel Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN®) SEM–energy-dispersive spectrometry (EDS) methodology to differentiate, quantify and image 11 different compositional types of chlorite based on Fe : Mg ratios using thin sections of rocks and grain mounts of cuttings or loose sediment. No other analytical technique, or combination of techniques, is capable of easily quantifying and imaging different compositional types of chlorite. Here we present examples of chlorite from seven different geological settings analysed using QEMSCAN® SEM–EDS. By illustrating the reliability of identification under automated analysis, and the ability to capture realistic textures in a fully digital format, we can clearly visualize the various forms of chlorite. This new approach has led to the creation of a digital chlorite library, in which we have co-registered optical and SEM-based images, and validated the mineral identification with complimentary techniques such as X-ray diffraction. This new methodology will be of interest and use to all those concerned with the identification and formation of chlorite in sandstones and the effects that diagenetic chlorite growth may have had on reservoir quality. The same approach may be adopted for other minerals (e.g. carbonates) with major element compositional variability that may influence the porosity and permeability of sandstone reservoirs.

Chlorite is an important mineral in many different types of sedimentary rock. Chlorite, an aluminosilicate clay mineral with a 2 : 1 : 1 crystal structure (Deer et al. 2013), can vary from Mg-rich chlorite, known as clinochlore (Mg5Al2Si3O10(OH)8), to Fe-rich chlorite, known as chamosite (Fe5Al2Si3O10(OH)8), with all Mg : Fe ratios possible in between these two end-members. Mg-rich chlorite, and other Mg-rich clay minerals such as palygorskite and saponite, have been reported to be primarily associated with clastic sedimentary rocks deposited in semi-arid continental environments (Pay et al. 2000; Worden & Morad 2003). By contrast, Fe-rich chlorite, and other Fe-rich clay minerals such as berthierine and odinite, have been reported to be primarily associated with marine depositional environments (Odin 1990; Ehrenberg 1993; Worden & Morad 2003; Dowey et al. 2012).

The work presented here arose from research by the Chlorite Consortium at the University of...
Liverpool. This research group has focused activity on understanding the origin and distribution of chlorite in sandstones because some types of chlorite can coat sand grains and prevent the growth of pore-occluding quartz cements (Dowey et al. 2012). Our work was primarily undertaken to assess whether all compositions of chlorite inhibit quartz cements, to determine exactly where chlorite sits in sediments and rocks (i.e. as detrital grains, grain coats or patches of cement), and to determine whether different morphological types of chlorite in a given rock have different compositions.

At the University of Liverpool, we have developed a spatially resolved Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN®) technique to uniquely define and map the composition of chlorite in sediments and sedimentary rocks at the scale of a polished thin section or polished pieces of core. QEMSCAN® is an integrated automated mineralogy and petrography solution providing the quantitative analysis of minerals, rocks and artificial materials. This technique should prove to be invaluable to those concerned with characterizing detrital and diagenetic chlorite and different minerals with the same composition, but with different crystal structures, such as berthierine. We show that this innovative technique has numerous advantages over existing techniques, such as light microscopy, X-ray diffraction (XRD), back-scattered scanning electron microscopy (BSEM) and conventional energy-dispersive spectrometry (EDS) using secondary X-rays.

Methods used to study and analyse chlorite in sedimentary rocks

Table 1 presents a summary and comparison of the techniques typically used to study chlorite in sandstones in terms of the type of data output, the cost of equipment, the support equipment requirements, the length of time required for sample preparation, analysis and data processing, the level of operator skill required, the ability to discern the composition of chlorite and the feasibility of discriminating chlorite from other Fe-rich clay minerals.

Light microscopy and optical point counting (Emery & Robinson 1993) can, under favourable circumstances, be used to quantify chlorite and assess where it sits within a sedimentary rock. The reliability of this method is highly dependent on the user’s level of experience, including their ability to identify the presence of clay minerals, as opposed to oxides, organics and fine-grained carbonate minerals (e.g. siderite), and then to discern chlorite from other clay minerals, such as illite and smectite. There is often a considerable statistical uncertainty associated with point counting; however, the uncertainty typically reduces with an increase in the number of points counted. For example, 10% point-counted chlorite has an uncertainty of c. 3.5% for 300 points counted per section and c. 1.8% for 1000 points counted per section (Van der Plas & Tobi 1965). Even for a highly experienced user, it is not possible to determine the composition of the chlorite, or to be completely sure that it is not another distinct type of Fe-rich clay, such as berthierine.

XRD can also be used to determine the mineralogy, and specifically the chlorite concentration, of either a crushed bulk sample (whole sediment) or a physically separated clay-sized fraction (Hillier 2003). XRD can differentiate chlorite from other clay minerals (e.g. illite, smectite, kaolinite or glauconite) by identifying the position and intensity of XRD peaks. XRD can also discriminate Fe-rich clay minerals, such as glauconite, berthierine and odinite. With care and much experience, XRD can also be used to identify the bulk composition of the chlorite and in which part of the crystal structure any elemental substitutions have taken place. However, the chemistry determined from XRD is an average of all the chlorite species in the sample, with little or no chance of ever being able to identify any compositional difference between varying types of detrital (e.g. in lithic grains) and diagenetic (e.g. pore-filling and grain-coating) chlorite. Quantification of chlorite using XRD can be achieved by a variety of approaches, including the reference intensity ratio method (Hillier 2003). Errors are not easy to quantify, but a skilled XRD analyst may, under favourable conditions, be able to repeatedly measure sub-percentage quantities of chlorite. XRD quantification can be influenced strongly by any pre-XRD sample handling steps, such as size separation to concentrate the clay minerals. XRD cannot reveal the location and texture of chlorite within a rock sample — for example, whether chlorite is present as grain coats on sand grains, lithic grains, pore-filling pseudo-matrix or mud-rich laminations.

BSEM has been routinely used to visualize chlorite in polished sections with the brightness of any mineral in a BSEM image being controlled by the average atomic number of the mineral (Emery & Robinson 1993). Thus, in a BSEM image, Fe-chlorite should appear brighter than Mg-chlorite in any rock bearing both types. Note that BSEM does not have any absolute degree of brightness for minerals; the images are controlled in real time by the analyst. Chlorite does not have a unique BSEM brightness and its presence in an image is, initially, suspected by the user based on the morphology of chlorite (e.g. typically as grain coats, pore-filling clusters or in lithic clasts). Most scanning electron microscopes equipped with BSEM detectors have the facility for the EDS analysis of secondary X-rays excited by the primary electron beam. With
Table 1. Comparison of different techniques used for the analysis of chlorite in sandstones

| Sample type | Sample preparation | Representative volume or area | Type of output | Cost of equipment (approximate) | Back-up and laboratory rooms required | Time for sample preparation | Time for analysis | Time for data processing | User skill/experience required | Subtle chemical variants (in this case quantities of Mg v. Fe in chlorite) | Crystallography/polymorphs (e.g. chlorite v. berthierine) |
|-------------|--------------------|-------------------------------|----------------|-------------------------------|--------------------------------------|-------------------------------|------------------|------------------------|-----------------------------|-------------------------------------------------------------------|-------------------------------------------------|
| Transmitted light microscopy, point counting | Thin section | Core plug volume | Descriptions, images, paragenetic sequence and quantitative point counting of grains, cements, pores, matrix, grain size and sorting | £20k–60k | Rock saws, laps, grinding equipment and other thin section making equipment | c. 1 h to cut, grind and finish thin section | c. 1 h to point count 300 | Variable time for image examination | Much training in petrography and some for point counting | Not possible | Not possible |
| X-ray diffraction | Finely ground rock | Core plug volume | Semi-quantitative (at best) mineral proportions. Spatially unresolved data | £130k–250k | Crushing and grinding 'dirty labs', clean room for separating clays | c. 2 h to crush, separate and grind | c. 1 h to examine a polished section | High level of training in sample preparation, analysis and data processing | Much training in petrography, knowledge of mineral chemistry | Can visualize Fe (bright) and Mg (dark) chlorite | Full differentiation of berthierine and chlorite |
| Back-scattered electron imaging | Polished section | Micrometre-resolved images | Images of rock, mineral identification and paragenesis. Can be point-counted for grains, cements, pores, matrix, grain size and sorting using image analysis | £60k–800k | Rock saws, laps, grinding equipment and other thin section making equipment, carbon coater | c. 2 h to crush, grind and polish thin section | c. 1 h minimum to examine a polished section | Time to process mineral chemical data | High level of training in sample preparation, analysis and data processing | Can measure individual points for Fe : Mg ratio | Not possible |
| Electron microprobe, secondary X-ray analysis | Polished section | Cubic micrometre volumes for each analysis | Point (micrometre-scale) analyses of mineral composition | £60k–800k | Rock saws, laps, grinding equipment and other thin section making equipment, carbon coater | c. 2 h to cut, separate and grind | c. 1 h to process | High level of training in sample preparation, analysis and data processing | May be possible | May be possible |
| Infrared spectroscopy | Finely ground rock | Core plug | Semi-quantitative (at best) for minerals, amorphous phases and organics. Spatially unresolved data | £40k–100k | Crushing and grinding 'dirty labs', press to make KBr pellets | c. 2 h to crush, separate and grind | c. 1 h to process spectra | High level of training in sample preparation, analysis and data processing | May be possible | May be possible |

With modification, the comparison can be generally applied to other minerals in other sedimentary rocks.
this approach, the elemental fingerprint of the major elements within a mineral, suspected to be chlorite in a BSEM image, can be determined and the mineralogy confirmed. Energy-dispersive spectra from most scanning electron microscopes, typically collected for 60 or 100 s, can be approximately quantified because the size of the secondary X-ray peaks can be related to the proportions of that element. It is sometimes possible to conclude, in general terms, that chlorite is typically Fe-rich or Mg-rich during BSEM and EDS studies. Quantifying the amount of chlorite in a sedimentary rock in BSEM images is not routine and it is not realistic to manually collect hundreds of secondary X-ray spectra to define the composition of chlorite. BSEM–EDS cannot differentiate chlorite from other Fe–Mg-rich clay minerals, such as berthierine.

Electron microprobe analysis typically uses wavelength-dispersive spectrometry of secondary X-rays. This is an electron beam device dedicated to high-quality chemical analysis, down to parts per million in some instances, of the composition of areas of 1 µm² from polished sections of rocks and minerals, including chlorite (Hillier 1994). Electron microprobe analysis devices typically have BSEM imaging capability and thus can be used to identify chlorite based on morphology and then to exactly measure the Fe : Mg ratio of chlorite in sedimentary rocks. These analyses are slow and labour intensive and not ideal for the estimation of the amounts of minerals in rocks or the relative proportions of different compositions (Fe : Mg ratios) of chlorite in a sedimentary rock. Electron microprobe analysis cannot differentiate chlorite from other Fe–Mg-rich clay minerals, such as berthierine.

Infrared spectroscopy is a bulk technique that can be used on crushed and homogenized rock samples. Different minerals adsorb different parts of the infrared spectrum, with mineral identification and quantification routinely possible if a given laboratory develops its own calibration lines for all minerals, including chlorite (Hillier 1994). Differentiating Fe- from Mg-chlorite is not routinely possible using FTIR sedimentary rocks with a large number of minerals. New infrared-based tools have been developed to analyse whole samples. Different minerals adsorb different parts of the infrared spectrum, with mineral identification and quantification of different compositions (Fe : Mg ratios) of chlorite in a sedimentary rock. Electron microprobe analysis cannot differentiate chlorite from other Fe–Mg-rich clay minerals, such as berthierine.

QEMSCAN® SEM–EDS analysis of sedimentary rocks

QEMSCAN® SEM–EDS gives the spatially resolved mineralogy based on elemental chemistries using polished surfaces of rocks, thin sections, or grain mounts of cuttings or loose sediments, set in resin, and then polished (Pirrie et al. 2004; Armitage et al. 2010). QEMSCAN® is the proprietary name for a rapid, repeatable automated mineralogical analysis technique developed by FEI and now owned by ThermoFisher Scientific. The outputs are detailed mineral identification, quantification and maps of mineral distributions that reveal the fabric of the rock or sediment.

The QEMSCAN® SEM–EDS system is a scanning electron microscope equipped with two or more high-speed EDS detectors. The QEMSCAN® SEM–EDS system uses a tungsten filament unit in the small, portable WellSite system, or a field emission gun in the larger, multi-purpose, laboratory-based Quanta 650 system. Each system is configured to acquire chemical data from secondary X-rays, by single or dual EDS detectors, at spatially pre-defined points across any polished solid sample. The distance between these points, on any given grid, is user-defined depending, primarily, on what the data are to be used for. There is a minimum practical spacing (resolution) of just less than 1 µm due to the physics of the electron beam–sample interaction; the activation volume of the sample that generates secondary X-rays is significantly larger than the area of the focused electron beam, so that the analysis points on a grid with a spacing much less than 1 µm collects data from overlapping volumes of material. However, wider step sizes between the points are possible, resulting in a pixelated image with a lower than optimum spatial resolution. If the QEMSCAN® SEM–EDS data are required to reveal fine details of the texture of a rock, then a high-resolution (1 or 2 µm) spacing should be used. If the QEMSCAN® SEM–EDS data are required to reveal the mineralogy averaged across a whole thin section (e.g. averaging
across graded beds or variably bioturbated sediment), then a much wider spacing (e.g. >20 µm) may be adequate between analysis points. Analysis at systematically varied step sizes for the same sample has shown that the mineral quantities remain credible up to 50 µm spacing between analysis points on a grid across a sample (Pirrie et al. 2004).

Once the elemental concentration has been measured at each point by the EDS detectors, the software automatically matches it with a library of mineral definitions. These mineral definitions are called species identification protocols (SIPs) and are assembled in a SIP list, which is effectively an archived mineral library. Each mineral is assigned a colour and the data points are combined to form a contiguous false colour image of the sample. In addition to the images, the sum of each occurrence of an identified mineral is tabulated so that minerals and groups of minerals may be quantified. Minerals can be grouped, or remain as separate species, and the colour that represents them can be altered to suit the user. This allows users to illustrate, quantify and analyse many complex textures.

QEMSCAN® SEM–EDS analysis can be used to study the mineralogy of sandstones and other rocks in the pursuit of an understanding of, for example, theolithology, stratigraphy, reservoir quality, sediment provenance, the geomechanical properties of reservoirs, caprocks or overburden, and the mineral scale in production equipment. QEMSCAN® SEM–EDS analysis can be used on cores, sidewall cores and cuttings. It can be undertaken on any material that can be polished. The QEMSCAN® SEM–EDS technique is not, on its own, capable of differentiating diverse textural forms of the same mineral – for example, quartz grains and quartz cement (for this, QEMSCAN® SEM–EDS images need to be compared with the output of other techniques, such as optical microscopy or SEM cathodoluminescence images). The QEMSCAN® SEM–EDS technique is also not capable of differentiating minerals with the same composition – for example, rutile and anatase (TiO₂). The QEMSCAN® SEM–EDS technique can be used to define similar minerals with subtle differences in composition – for example, muscovite (KAl₃Si₃O₁₀(OH)₂) may be differentiated from illite primarily by its lower K concentration. Minerals of highly variable composition, such as smectite (McKinley et al. 2003), can have subtle compositional types, which may be identified and quantified if the SIP library has been sufficiently developed. Even so, it is recommended that the occurrence and type of smectite should be independently confirmed using XRD analysis of a glycolated sample; the swelling properties of smectite are primarily related to its crystal structure and so chemistry alone will not provide the necessary degree of certainty.

QEMSCAN® SEM–EDS method for defining chlorite Fe–Mg composition

**Analysis**

The instrument used to gather the data was an FEI WellSite QEMSCAN® system. A tungsten filament produced the focused electron beam, running at 15 kV, with a sample current of 7 nA measured at the Faraday cup. Highly polished, carbon-coated samples were placed in the vacuum chamber. During routine operation, the QEMSCAN® SEM–EDS system was re-calibrated for beam current and back-scattered electron signal every time a new sample block holder was loaded.

The system was programmed to collect chemical data across a pre-defined area of the sample using iMeasure® software. For this work, a 2 µm spacing between data collection points was used for most samples. A smaller spacing leads to only a marginal increase in spatial resolution, but increases the analysis time exponentially. Analysing a 1000 µm area at a 2 µm step size takes one-quarter of the time for the same area analysed at a 1 µm step size for no improvement in mineral quantification and negligible improvement in image quality. The electron beam dwells at each point until sufficient X-rays have been collected by the detectors to allow for successful phase-matching using the reference library. A standard number of 1000 X-ray photons were used in this study and therefore the system did not have to be slowed to achieve the desired results.

**Phase identification**

Two Bruker energy-dispersive X-ray spectrometers recorded the discrete secondary X-rays emitted by the sample excited by the focused electron beam. The X-ray spectrum from each analysis point was processed to identify and quantify the elements present and then output a chemical composition. The recorded chemical composition was matched to the SIP library of pre-defined chemical compositions for various phases, including minerals, glasses and other amorphous materials. The QEMSCAN® SEM–EDS system does not measure or use crystallographic features and therefore cannot discriminate between amorphous and crystalline phases or crystallographic polymorphs. The QEMSCAN® SEM–EDS method relies on the identification of the unique chemical composition of each phase.

Using the iDiscover® software to automatically interpret the X-ray intensity data from each analysis point, the resulting data were stitched to form one colour image of the sample. The number of pixels of each phase were summed and normalized to give the mineral composition in terms of area percentage,
weight per cent or mass per cent depending on the application.

The SIP library containing the chemical definition of each mineral is central to this process. An initial SIP library was supplied by the QEMSCAN® SEM–EDS manufacturers; however, more experienced and suitably trained users can create new and unique SIP libraries to solve specific petrographic problems. Every SIP library defines chemical elements that must be present in a given mineral, elements that may be present and which ranges of elemental concentrations are permitted for a successful match to a mineral in the SIP library. Consideration must be given to the known chemical formula of each mineral, the solid solution series and the precision of the energy-dispersive spectrometer being used. An additional consideration must be given to the contribution of elemental signatures from neighbouring minerals at the edges of grains as a result of the several micrometre diameter activation volume from which secondary X-rays are generated.

Chlorite definition using a modified SIP library

The standard SIP library supplied by FEI contains two types of chlorite with different chemistries: one is Fe-rich and the other is Mg-rich. Both types of chlorite have a wide range of possible elemental concentrations permitted for an admissible match to the SIP library. Chlorite represents a family of minerals that have very similar crystal structures, but with a wide range of possible elemental substitutions. The most common types of chlorite are dominated by Si, Al, O and H, with varying proportions of Fe and Mg. We focused here on the variability of the proportions of Fe and Mg in chlorite. Deer et al. (2013) reported that Mg–Fe substitution occurs over a wide range and natural trioctahedral chlorites can be, to a first approximation, expressed as binary combinations of the clinochlore (\(\text{Mg}_6\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8\)) and chamosite (\(\text{Fe}_{10}\text{Al}_4\text{Si}_6\text{O}_{20}(\text{OH})_{16}\)) end-members.

We developed a range of new SIP libraries for chlorite that categorize it into one of 11 compositionally defined types, including the two chlorite end-members \(\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8\) and \(\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8\). The SIP entry for the Fe-chlorite end-member specifies that no Mg may be present (i.e. no secondary X-rays from Mg picked up by the EDS detectors during data acquisition). The SIP entry for the Mg-chlorite end-member specifies that no Fe may be present (i.e. no secondary X-rays from Fe picked up by the EDS detectors during data acquisition). The SIP library is ordered in ascending Fe content, with chlorite being assigned a compositional type as a function of the specific Fe concentration. The software is flexible enough to allow subdivisions of <10% steps of the Fe : Mg ratio so that we could have defined >11 compositional types of chlorite. However, there is a limited rationale for this approach. The precision of the EDS system, plus the degree of uncertainty resulting from spurious secondary X-ray contributions from neighbouring minerals, both limit the credibility of the use of, for example, 5% steps of Fe : Mg ratios.

There is a small number of relatively rare clay minerals with compositions that fall within the range of compositions defined by the 11 new chlorite SIP files – for example, berthierine and odinite (Odin 1988). These clay minerals can be uniquely differentiated using XRD analysis of crushed sediment samples because they have different crystal structures to chlorite. XRD analysis also allows the identification of specific sites in the chlorite crystal lattice where elemental substitutions have occurred. A crystallographic technique such as XRD can be used in conjunction with a QEMSCAN® SEM–EDS system to confirm the mineral identification in rocks where polymorphism is possible or suspected.

Importantly, these 11 new compositional subdivisions of the chlorite group have been developed and used, but this extra level of sophistication has not slowed either the operation of the device or the rate of automatic interrogation of the output data. With the new SIP files developed by the University of Liverpool, the QEMSCAN® SEM–EDS system can identify, compositionally categorize and quantify chlorite in reservoir rocks and show the detailed spatial distributions of different types of chlorite. This fast and user-independent process will allow new insights into clay mineral composition, abundance and distribution in a wide range of rock types.

Results and interpretation

Chlorite compositions are presented and interpreted from a range of rock types to illustrate the capability of the new SIP files.

Garnet–mica schist

We wanted to start testing the capability of this new chlorite analysis technique with rocks that we expected would contain chlorite of different compositions. The early stages of prograde metamorphism of clastic sedimentary rocks typically involve the development of chlorite and evolution towards a schistose texture. Garnet starts to develop during the middle stages of prograde metamorphism. As a function of thermodynamic equilibrium, chlorite in the schist matrix tends to have a lower Fe : Mg ratio than the coexisting garnet (Atherton 1977; Yardley 1989). Metamorphic rocks routinely undergo some degree of retrograde alteration during the long
and slow uplift and cooling cycle. In the case of garnet, the edges of garnet porphyroblasts tend to experience some degree of alteration to chlorite. As the parent garnet has a higher Fe : Mg ratio than the chlorite matrix, it might be expected that the garnet-replacive chlorite has a higher Fe : Mg ratio than the matrix chlorite. A sample of Dalradian garnet–mica schist from the Scottish Highlands was analysed with the QEMSCAN® SEM–EDS system (Fig. 1a). The matrix chlorite is typically \( \text{c. Fe}_{40}\text{Mg}_{60} \) or \( \text{Fe}_{50}\text{Mg}_{50} \) (Fig. 1b–d). Garnet has undergone some retrogressive alteration to chlorite, as predicted, and this replacive chlorite has a composition of \( \text{Fe}_{80}\text{Mg}_{20} \) (Fig. 1b–d). Not only has our bespoke collection of chlorite SIP files and QEMSCAN® SEM–EDS analysis revealed that there are two compositionally different types of chlorite present in this rock, but it also has shown exactly where the different types of chlorite exist within the rock.

**Chlorite from the Lower Jurassic Cook Formation, North Sea basin**

Some Lower and Mid Jurassic sandstones from the eastern side of the North Sea basin have been reported to be rich in chlorite. Deeply buried and relatively high-temperature reservoirs of the Lower Jurassic Cook Formation have been reported to contain chlorite grain coats that have locally inhibited the growth of quartz cement (Gupta & Johnson 2001; Skarpeid et al. 2017). Light optical examination showed that Cook Formation sandstones do contain clay coats (Figs 2 & 3a) but, of course, there was no way to discern the compositional type of chlorite.

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**Fig. 1.** Data from a garnet–chlorite–mica schist from the Dalradian of Scotland. (a) Light optical image showing equant garnet, with a hint of a retrogressive alteration halo, sitting in a chlorite-bearing schistose matrix. (b) QEMSCAN® SEM–EDS image of the same area as part (a) with the colour scheme selected to illustrate the compositional variations of chlorite for this image shown in part (c). This QEMSCAN® SEM–EDS image shows the \( \text{Fe}_{60}\text{Mg}_{40} \) chlorite in the matrix, with the darker green, more Fe-rich chlorite (\( \text{Fe}_{80}\text{Mg}_{20} \)) in the retrogressive alteration halo at the margin of the garnet. (c) Enlargement of part (b) showing the difference in composition and morphology of the two types of chlorite in a partially retrogressed garnet–chlorite–mica schist. (d) Histogram representing the subtly bimodal proportions of the types of chlorite in the garnet–chlorite–mica schist. The dominant peak shows that most of the chlorite (in the schistose matrix) is slightly Fe-depleted, but the minor garnet alteration is distinctly Fe-rich, as expected given that the parent garnet tends to be Fe-rich relative to chlorite according to standard metamorphic AFM phase diagrams.
QEMSCAN® SEM–EDS analysis showed that much chlorite is present in these rocks, with many samples enriched in by slightly Fe-dominated chlorite (Fe_{60}Mg_{40}, Fig. 3b). Some chlorite is slightly Mg-dominated (Fe_{40}Mg_{60}, Fig. 3b). Some samples have roughly equal amounts of Fe_{60}Mg_{40} and Fe_{70}Mg_{30} chlorite (Fig. 3b). Examination of the QEMSCAN® SEM–EDS images collected at a 1 µm spacing showed that there are several textural types of chlorite in these sandstones (Figs 3c, d), each with their own composition. The first is patches of pore-filling chlorite that is slightly Fe-dominated (Fe_{60}Mg_{40}); the second is chlorite that has partially replaced mica, which is slightly Mg-dominated (Fe_{40}Mg_{60}); the third is grain-rimming chlorite, which is relatively Fe-enriched (Fe_{70}Mg_{30}). This new approach to chlorite in sandstones has, for the first time, shown that different genetic types of this mineral exist in different parts of the same sandstone (i.e. grain-replacive, pore-filling and grain-coating chlorite) and that different textural types of chlorite have discrete compositions.

Lower Jurassic Cleveland Ironstone Formation

The Lower Jurassic Cleveland Ironstone Formation from an onshore ore exploration borehole in North Yorkshire (Myers 1989) was analysed using the QEMSCAN® SEM–EDS method and the new SIP files to assess the types of clay minerals present. Optical microscopy showed a complex pattern of pores, millimetre-sized grains and a green–brown filling material; unequivocal mineral determination proved impossible using light optical microscopy (Fig. 4a). Back-scattered electron imaging, together with point secondary X-ray analysis, better revealed the porosity and predominance of the ‘granular’ siderite (FeCO_3) and pore-filling Fe-rich clay. QEMSCAN® SEM–EDS analysis with the new SIP categories further showed the siderite and its pores and identified the pore-filling clay as Fe-rich chlorite (Fe_{80}Mg_{20}). However, subsequent XRD analysis showed that the filling clay is the 7 Å 1 : 1 clay mineral berthierine and not 14 Å 2 : 1 : 1 chlorite. QEMSCAN® SEM–EDS analysis is not suitable for the differentiation of berthierine from chlorite, but has value in revealing the location, amount and composition of these minerals in sedimentary rocks.

Upper Jurassic Corallian Group hybrid sandstone–limestone

The stratigraphically complex Upper Jurassic Corallian Formation from the Weald and Wessex basins in southern England is composed of interbedded sandstones and carbonates with reported local iron enrichment (Williams 2003). Optical microscopy of

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**Fig. 2.** Standard colour scheme for QEMSCAN® SEM–EDS derived mineralogy. In porous sedimentary rocks, the mineral name, ‘background’ refers to the pores between (and in) grains, so that QEMSCAN® SEM–EDS can be used to define porosity for pores larger than c. 1 µm in size. The finite range of colours means that it can be difficult to represent all the minerals present in a rock, especially the non-equilibrium assemblages typical of sedimentary rocks. Minerals can be grouped, explaining our mineral here named ‘other clays’, which includes illite, kaolinite, smectite and glauconite. The grouping of clays other than chlorite into one term is simply to allow chlorite to occupy the full range of green colours. Pure Fe-chlorite, known as chamosite, represents one end-member; pure Mg-chlorite, known as clinohlore, represents the other end-member. The Species Identification Protocol has been tailored to identify nine intermediate types of Fe–Mg-chlorite.
a carbonate-dominated sample from an onshore oil exploration borehole in the Weald basin, SE England showed millimetre-sized iron-rich grains, 400 µm ooids with quartz, calcite or porous cores and poikilotopic, pore-filling calcite cement (Fig. 5a, b). Optical microscopy examination was largely unhelpful for the identification of clay minerals in these rocks. QEMSCAN® SEM–EDS analysis using the new SIP files showed the presence of Fe-rich chlorite (Fe$_{70}$Mg$_{30}$) with small amounts of slightly less Fe-rich clay (Fig. 5c). A QEMSCAN® SEM–EDS image of the areas imaged with optical microscopy showed that the ooids are predominantly iron ooids (Fig. 5d). QEMSCAN® SEM–EDS imaging also showed apatite grains and unusual apatite coats on detrital quartz grains and pore-filling siderite. Subsequent XRD analysis showed that the Fe-rich clay is berthierine, analogous to the Cleveland Iron Formation (Fig. 4).

**Sherwood Sandstone Group and Skagerrak Formation sandstones**

Analysis of sandstones from the semi-arid, continental sandstone deposits of the Lower Triassic Sherwood Group from the west of Ireland (Schmid et al. 2004) and the Lower Triassic Skagerrak Formation from the Central North Sea (Stricker et al. 2016) showed that chlorite can be present in continental as well as marine clastic sediments. Chlorite...
is present as a variety of different types of grain in the continental sediments, including detrital chlorite flakes and chlorite-bearing lithic grains, and can be present as a pore-filling matrix and even as rare grain coats (in the Skaggerak Formation, but not the Sherwood Sandstone).

Skaggerak Formation sandstones contain some of the more Mg-rich chlorite in the study, with some detrital chlorite flakes approaching clinochlore in composition (Fe$_{20}$Mg$_{80}$) (Fig. 6a). The chlorite matrix in Skaggerak Formation sandstones was more Fe-rich (Fe$_{50}$Mg$_{50}$), suggesting a different sediment provenance for the coarse chlorite flakes and the finer chlorite matrix. There are traces of grain-coating chlorite in the Skaggerak Formation sandstones, but QEMSCAN® SEM–EDS analysis showed that pyrite is the dominant grain-coating mineral in this sample (Fig. 6b). The QEMSCAN® SEM–EDS chlorite compositional histograms from the Skaggerak Formation sandstones display a wide range of compositions (Fig. 6d), confirming what is evident in the images and supporting multiple chlorite sources of chlorite grains in the primary sediment.

The Sherwood Group sandstones contain more Fe-rich chlorite (Fe$_{60}$Mg$_{40}$) than the Skaggerak Formation sandstones (Fig. 6d). Chlorite in the Sherwood sandstones is predominantly found within lithic grains, with negligible amounts found in the clay matrix and none present as grain-coating material (Fig. 6c).

Modern sediment from the Ravenglass estuary

Liverpool’s Chlorite Consortium has undertaken detailed studies of mineral and grain coat...
distributions in modern (younger than 11 000 years),
marginal marine sedimentary systems as analogues
to ancient and deeply buried chlorite-bearing estu-
mineralogy of sand and medium to coarse silt grains and the mineralogy of the coating material and clusters of matrix material. The limited spatial resolution of the QEMSCAN® SEM–EDS analysis means that the approach is not useful for analysing individual and isolated crystals less than $c. 1–2 \mu m$ in size. Analysis of grain mounts of whole-sediment samples from the Ravenglass estuary show that most of the grain-coating material is illite-dominated, but chlorite represents up to 30% of the grain coats. The detrital chlorite flakes are relatively Fe-poor ($Fe_20Mg_80$). In Skaggerak Formation sample. (c) Sherwood Sandstone sandstones in which all the chlorite is in the form of lithic grains. (d) Histograms ($n = 6$) representing the compositions of detrital chlorite in lithic grains, micas and detrital chlorite in the Lower Triassic Sherwood Sandstone and Skaggerak Formation. The Sherwood Sandstone has a more Fe-rich detrital chlorite than the Skaggerak Formation, presumably the result of the completely different provenance of these two roughly coeval rocks.

Discussion

Any mineral that has a known major element composition can be identified, imaged and quantified using...
QEMSCAN® SEM–EDS. For relatively pure minerals such as quartz, there is negligible solid solution with elements other than Si (Kraishan et al. 2000) and its identification and quantification using QEMSCAN® SEM–EDS is straightforward. For minerals that have substantial degrees of major element substitution, such as Fe replacing Mg (or Ca) in dolomite, it is possible to identify, image and quantify different compositional types of dolomite using QEMSCAN® SEM–EDS. To achieve this, each QEMSCAN® SEM–EDS user needs to develop their own suite of compositional definitions of different sub-types of a given mineral (with major element substitutions). These are known as SIP files.

We have focused here on chlorite, which has variable Fe : Mg ratios, and developed 11 compositional definitions of chlorite on this basis. Our new suite of SIP definitions have been applied to seven different rock samples suspected to have compositionally different types of chlorite.

We initially demonstrated the value of the new QEMSCAN® SEM–EDS chlorite analysis by confirming our expectation that, in metapsammites, chlorite that is retrograde after garnet is distinctly more Fe-rich than the matrix chlorite (Fig. 1). Although we are delighted to demonstrate the value of our new approach, we are also aware that this level of quantification and imaging of different types of chlorite in metamorphic rocks has not previously been achieved. The new QEMSCAN® SEM–EDS SIP files were developed for sedimentary rock analysis, but can be applied equally well to metamorphic rocks.
and hydrothermally altered igneous chlorite-bearing rocks.

We have demonstrated that grain-coating chlorite in sandstones can have a distinctly higher Fe : Mg ratio than chlorite sitting within detrital grains (Fig. 3). Although it is not the purpose of this paper to develop new models of clastic diagenesis, Figure 3 and the displayed difference in Fe : Mg ratios between some types of detrital chlorite and chlorite grain coats hints strongly that some compositional and textural types of detrital chlorite are more susceptible to creating grain coats than others. It seems now that there is a strong lithic provenance control on the development of chlorite grain coats.

We have also shown that quartz-inhibiting chlorite grain coats have grown on top of a root layer of another clay mineral. This suggests that the development of burial diagenetic, Fe-rich chlorite coats was facilitated by a non-chlorite grain coat, formed earlier, possibly in the sedimentary depositional environment, such as those identified in the Raven glass estuary (Fig. 7) (Wooldridge et al. 2017a, b; Griffiths et al. in press).

Although QEMSCAN® SEM–EDS cannot differentiate between minerals of the same composition, we have been able to demonstrate that two different ironstones contain a strongly Fe-enriched chlorite-like mineral (Figs 4 & 5). In these cases, XRD analysis has shown that the Fe-rich clay is 7 Å 1 : 1 berthierine, reported to be a precursor of chlorite that grows during burial diagenesis (mesodiagenesis) (Worden & Morad 2003). The two examples illustrated here have not been deeply buried (probable maximum burial 2000 m and maximum temperature 60 or 70°C); if the rocks achieved higher temperatures, then berthierine would isochemically convert into Fe-rich chlorite.

Detrital chlorite in sediments and sedimentary rocks reflects the provenance of the hinterland and the degree of chemical weathering between the site of initial bedrock exposure and the site of ultimate deposition (transport history (Worden et al. 2018)). We have shown that detrital grains can have widely variable compositions within the same host sediment (Figs 3, 6 & 7). On this basis, the identification, quantification and imaging of chlorite compositions based on QEMSCAN can now be used as a novel provenance tool and to help decipher sediment transport routes.

Conclusions

(1) We report a novel, SEM–EDS-based method for the identification, imaging (mapping) and quantification of different compositional types of chlorite in thin section via a newly developed bespoke QEMSCAN® SEM–EDS analysis protocol (new SIP libraries).

(2) With this approach, chlorite compositions have been subdivided into 11 types based on 10% steps from pure Mg-chlorite to pure Fe-chlorite.

(3) QEMSCAN® SEM–EDS analysis can now show not just the average composition (Fe : Mg ratio) of chlorite in a rock or sediment, but also the proportions of different compositional types of chlorite in a single sample.

(4) QEMSCAN® SEM–EDS imaging can be used to show where different compositional types of chlorite sit texturally within a sedimentary rock, e.g. chlorite detrital grains, chlorite-bearing lithic grains, chlorite-rich matrices, chlorite-bearing autochthonous grains (i.e. created in situ in sedimentary environments) or chlorite coats on sand grains.

(5) No other analytical technique, or combination of techniques, can easily replicate QEMSCAN® SEM–EDS’s ability to identify, image and quantify different compositional types of chlorite in thin sections.

(6) Examples of the analysis of chlorite in a range of sedimentary and metamorphic rocks and modern sediments have shown that QEMSCAN® SEM–EDS’s ability to identify, image and quantify different compositional types of chlorite can be used to great effect to appreciate hitherto unsuspected subtleties in chlorite chemistry and texture.

(7) Berthierine, a low-temperature clay mineral, cannot be differentiated from chlorite using QEMSCAN® SEM–EDS because they have the same composition. Berthierine and chlorite can be differentiated using XRD analysis of powdered rock samples.

(8) In sedimentary rocks, Fe-rich chlorite preferentially occurs as complex autochthonous Fe ooids and grains and in ironstones, but is also the type of chlorite that preferentially forms continuous grain coats, which prevent the growth of quartz cements in sandstones.

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