

C0020 **Identification and Quantitative Analysis of Clay Minerals**

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p0005 Because of their great structural diversity, clay minerals are difficult to identify and quantify. Powder X-ray diffraction (XRD) remains the standard technique for clay mineral identification, although transmission electron microscopy (TEM) has played an increasingly important role in this regard during the past two decades. [Au1]

p0010 The identification of clay minerals by XRD has been described in a number of textbooks, three of which are of particular importance and relevance. The monograph edited by Brindley and Brown (1980) remains the most

comprehensive data source, although the user-friendly textbook by [Moore and Reynolds \(1997\)](#) provides adequate information for routine analysis. Most students of clays or soils consult [Jackson's \(1975\)](#) book for chemical methods of treating clay prior to clay mineral separation and fractionation.

p0015 The Mineralogical Society (UK), the Mineralogical Society of America, and the Clay Minerals Society (USA) have also published several monographs on techniques of clay mineral analysis and identification. The book edited by [Wilson \(1994\)](#) concentrates on spectroscopic methods of clay mineral analysis, while that by [Amonette and Zelazny \(1994\)](#) is dedicated to the quantitative analysis of soil clay minerals. The theoretical principles behind the identification of interstratified clay minerals were presented in detail by [Drits and Tchoubar \(1990\)](#). [Środoń \(2002\)](#) reviewed a range of techniques of quantitative analysis of clay-rich rocks. Simplified analytical methods have long been able to provide semi-quantitative data. Over the past decade, some XRD techniques have produced satisfactory quantitative results and further progress is expected in this field.

p0020 This chapter provides a brief introduction into the world of clay mineral identification and quantification and is a guide to the corresponding literature.

s0005 2.2.1 IDENTIFICATION TECHNIQUES

s0010 2.2.1.1 Sample Size

p0025 If sufficient material is available, the best identification strategy is to start with XRD and apply other supplementary techniques as required. Such a course of action is followed in this chapter. XRD allows the most precise identification and provides very representative data, as each measurement represents an average over millions of clay mineral particles. If sample size is limited (mg), however, the identification may have to be done by electron microscopy (EM) techniques, allowing observation and measurement to be made of individual particles. This investigative approach has many advantages, but special care must be taken to ensure that the observations are representative, even if the studied rock appears very homogeneous ([Środoń et al., 1992](#)).

s0015 2.2.1.2 Clay Mineral Separation

p0030 Clay minerals are most often identified by reflection powder XRD of both oriented and random preparations. Identification is greatly facilitated if the clay fraction is first separated from the rock (bulk sample), to minimize contamination by non-clay minerals.

p0035 It is common practice to separate and study either the <2 , or <0.2 μm fractions or both. Besides being more representative of the clay minerals present in the rock, the <2 μm fraction corresponds to the widely accepted granulometric definition of 'clay' (see [Chapter 1](#)). The <2 μm fraction is also

better suited for studying coarser grained clay minerals such as kaolinite and chlorite. Being more abundant, this fraction is also generally easier to separate from the rock by gravitational settling in a column of water. The advantages of using the $<0.2\ \mu\text{m}$ fraction are twofold: (i) common mixed-layer clay minerals (in particular illite–smectite, hereafter I–Sm), making up the finest grained components of rocks, are concentrated in this fraction and (ii) a superior orientation of particles can be achieved when preparing sedimented samples for XRD. As a result, a series of $00l$ reflections, free of hk reflections, are obtained with an order of magnitude stronger intensities as compared with the $<2\ \mu\text{m}$ material. This effect is related to the nature of clay grains in the two fractions: the dominance of aggregates in the $<2\ \mu\text{m}$ fraction and the dominance of individual clay mineral particles in the $<0.2\ \mu\text{m}$ fraction (see Chapter 1 for definitions of ‘aggregate’ and ‘particle’). Separation of the $<0.2\ \mu\text{m}$ fraction is usually carried by centrifugation at a few thousand rpm (e.g. 3000 rpm for about 45 min) using large centrifuge bottles (~ 1 L capacity). Two conditions must be met for a successful fractionation: (i) the clay mineral particles have to be liberated from the rock and (ii) the clay mineral dispersion has to be stable (no coagulation). To achieve these ends, a variety of procedures are used, depending on the degree of consolidation of the rock, as well as the presence of coagulating substances (e.g. salt or acid solutions, sulphates and carbonates that dissolve easily in distilled water) and cementing agents (e.g. carbonates, sulphates, Fe (hydr)oxides and organic matter) (see Chapter 7.1 in Volume A). If the rock is unconsolidated and free of coagulating and cementing agents, simple soaking in water and stirring plus sonification with an ultrasonic probe may produce a stable dispersion. Some kaolins (weathering products), bentonites (sedimentary rocks) and many hydrothermally altered volcanic rocks fall into this category. On the other hand, if the rock contains salts, the dispersion will tend to coagulate. In such cases, the salts must be removed (by repeated centrifugation in distilled water until the dispersion becomes stable). However, even such mild treatment (dispersion in a volume of distilled water) would change the composition of exchangeable cations (towards divalent species) because the exchange coefficients depend on the solution concentration (Sayles and Mangelsdorf, 1977).

p0040 Sedimentary rocks commonly contain some carbonates. Besides acting as binding agents, carbonates dissolve during centrifugation causing clay mineral coagulation. Digestion in an acetic acid–sodium acetate buffer (pH 5.5) is the most commonly used technique for carbonate removal (Jackson, 1975). The mild pH of this buffer causes only minimal damage to the clay minerals, but the original exchangeable cations are replaced by Na^+ . This is an added advantage, however, since Na^+ promotes clay mineral dispersion and the formation of a stable dispersion. For this reason, the acetate buffer treatment is often routinely applied. However, the excess electrolyte has to be removed prior to separation because of its flocculating effect. The acetate treatment is effective even for carbonate-rich rocks (see Chapter 7.1 in Volume A).

- p0045 If the rock is organic-rich, it should be reacted with hydrogen peroxide (H_2O_2) after treatment with acetate buffer. The removal of organic matter by H_2O_2 is a standard procedure in studying soil clays (Jackson, 1975). The above order of treatment is important because a carbonate-free and slightly acidic environment is required for effective peroxide action without side effects (see Chapter 7.1 in Volume A). The effectiveness of this treatment and alternative treatments (e.g. employing sodium hypochlorite) decreases significantly with increasing degree of diagenesis (Środoń and Paszkowski, 2011).
- p0050 If the colour of the rocks is reddish, brownish or yellow after the buffer or peroxide treatment, free iron (hydr)oxide removal is required. This step is performed under slightly alkaline conditions using sodium dithionite as reducing agent (Jackson, 1975). The amount of dithionite used should be kept to a minimum if the presence of iron-rich clay minerals is suspected because the treatment may reduce some structural iron in clay minerals. On the other hand, dithionite treatment is often a key to success in clay mineral separation because iron oxides are very effective cementing agents (see Chapter 7.1 in Volume A).
- p0055 Soils often contain measurable amounts of X-ray-amorphous Si and Al oxides that can be removed using various alkaline extraction techniques without damaging the clay minerals (Jackson, 1975; Smith, 1994). This issue is not important when dealing with common rocks.
- p0060 Soaking in water is usually not sufficient to achieve disintegration of consolidated rocks. Crushing or even grinding may have to be applied. However, grinding should be avoided unless absolutely necessary (e.g. deep burial) since this treatment changes the particle size distribution, contaminating finer fractions with fragments of coarser minerals. Applying cycles of freeze and thaw is a safer technique as it forces a rock to disintegrate along natural grain boundaries. A special instrument is needed, and the procedure is very time-consuming. It is only worth pursuing if required by the nature of the study, for example, isotope dating or crystal thickness measurements (Liewig et al., 1987). In any case, a few minutes of sonication with an ultrasonic probe in a small volume of water should follow other procedures of disintegration before proper separation is performed. Ultrasonication is not harmful to clay minerals, helps break aggregates and liberates clay mineral particles.
- p0065 The separated clay fractions are voluminous dispersions and contain salts added during the pre-treatments. The excess salt should be removed before drying. A practical way of achieving this goal involves three steps: (i) coagulation with an appropriate 1 M chloride salt to introduce the required exchangeable cation, followed by at least two further washings (additions) to complete the exchange; (ii) removal of the excess electrolyte by washing with distilled water and centrifuging (2–3 times) and (iii) dialysis until all the electrolyte is removed.
- p0070 Dialysis is performed after dispersing the sediment (in the centrifuge bottle) in a small amount of water using an ultrasonic probe, and pouring

the dispersion into a dialysis tube. The tube is closed and hung in a beaker filled with deionized water. By connecting a series of beakers and flowing deionized water through them, the dialysis period can be greatly shortened. Dialysis is stopped when the conductivity of water in the beakers approaches that of deionized water (the reference pure water should be in contact with atmospheric CO₂ as long as dialysis proceeds, because dissolved CO₂ affects the conductivity of water).

p0075 As some time can be saved if clay minerals are in the Na⁺ form, the final coagulation with NaCl has long been a standard practice in shale studies. From today's perspective, Ca²⁺ saturation seems preferable if smectites or mixed-layer clay minerals involving smectite are being studied. This is because at low humidity, typical of dry climates, I-Sm in the Na⁺ form may behave like illite-vermiculites during standard XRD tests, whereas I-Sm in the Ca²⁺ form preserve their characteristics (Eberl et al., 1987). Studies by Sakharov et al. (1999) indicated that this behaviour is also detectable at high humidity. Mixed-layer clay minerals identified routinely as I-Sm often display I-Sm-vermiculite characteristics when studied more precisely in the Na⁺ form. Yet these mixed-layer minerals can be modelled as a two-component I-Sm system in the Ca²⁺ form. Since two-component systems are much easier to analyze, Ca²⁺ is the exchange cation of choice in XRD work.

p0080 The dialyzed clay dispersion has to be dried. This is commonly done by drying in an oven after placing the dispersion in a disposable plastic dish or a ceramic dish, covered with a plastic foil. The disadvantage of this technique is clay segregation during drying. Hand-grinding has to be applied as a final step to homogenize the clay. Soft, homogeneous clay can be obtained by freeze-drying (see Chapter 7.1 in Volume A), which is today the technique of choice.

s0020 2.2.1.3 Sample Preparation

p0085 Oriented preparations enable the 00 l series of reflections to be obtained, providing identification of groups, information about mixed-layering, chemistry (some species) and crystal thickness distribution. There are numerous techniques for preparing oriented samples for XRD examination (Moore and Reynolds, 1997). Sedimentation onto a glass slide, performed using a dispenser, is commonly applied for identifying clay minerals (from the 00 l series of reflections), but this technique is often inappropriate for quantitative analysis because of clay mineral segregation during sedimentation on the slide, in particular when coarser clay fractions are used. An ultrasonic probe should be used for a few seconds in order to completely disperse the clay, just before making the slide. Frosted glass offers better adhesion of the clay than a smooth glass surface, but some disorientation may occur if the film is too thin. The clay mineral film should be sufficiently thick (10 mg/cm²) to ensure 'infinite thickness' for X-rays. When this condition is fulfilled, relative reflection

intensities become independent of the clay mineral film thickness and can be modelled using computer programs (see later), in order to evaluate layer chemistry. If the clay mineral film is too thin, a broad band from glass centred at about 0.34 nm becomes visible.

p0090 Random preparations provide *hkl* (*hk*) reflections, enabling di- and tri-octahedral minerals (sub-groups) to be distinguished, polytypes to be identified and stacking faults to be assessed. Side loading, described in detail by Moore and Reynolds (1997), is the most practical technique for making random preparation for identification purposes. The procedure includes sieving the sample through a screen (ca. 0.4 mm) just before loading it into the holder, covering the front of the holder opening with frosted glass (never a plastic) and tapping or vibrating in order to pack the powder (using a tamper to pack may produce orientation). Spray-drying is even more effective in producing reproducible and completely randomized clay samples (Hillier, 1999). This technique, however, is not very practical for routine identification work, as it is time-consuming and requires relatively large samples. Vertical goniometers are better suited for studying such random preparations than horizontal goniometers, as random preparations may not be stable enough for recording in the vertical position.

p0095 An alternative XRD strategy of studying *hkl* reflections is to use an oriented clay mineral film in the transmission mode. The film is prepared by sedimenting a clay dispersion on a plastic foil, separating the dried material from the foil and mounting in a transmission goniometer. In such a configuration, 00*l* reflections are eliminated from the XRD pattern, and *hkl* reflections are maximized (Wiewióra, 1985).

s0025 2.2.1.4 Pure Versus Mixed-Layer Clay Minerals

p0100 The official classification of layer silicates by the International Mineralogical Association deals only with pure end-member minerals, dividing them into groups, sub-groups and species. In nature, however, pure species are rare while interstratified clay minerals are common (Środoń, 1999). Thus, any scheme of clay mineral identification has to start by choosing between pure clay mineral and mixed-layer clay mineral. Only after carrying out this step should the identification of group, sub-group and species be attempted.

p0105 Pure clay minerals, like all other minerals, are characterized by one type of unit cell. They display an integral series of 00*l* reflections with similar broadening, controlled mostly by crystal thickness (Sherrer equation; for details, see Drits et al., 1997). On the other hand, particles of mixed-layer clay minerals contain two or more types of layers (different unit cells), giving rise to a non-integral series of 00*l* reflections (Bragg Law does not apply). The positions of the reflections are intermediate between those of the pure end-members, and the reflection broadening can be highly variable, depending on the distance between the corresponding end-member reflections (Méring

rule; Moore and Reynolds, 1997). The so-called ‘regular mixed-layer clay minerals’ are the exception to this rule. The particles of these minerals are composed of two alternating layer types (ABABAB...), and hence may be considered to comprise AB unit cells. Such minerals are rare in nature, although seven species have been identified and recognized as separate minerals and given individual names (Środoń, 1999). They show integral series of 00 l reflections with similar broadening; including the so-called superstructure 001/001 reflections that correspond to $d_A + d_B$ values (where d_A and d_B are basal spacing values of the component layers). To summarize, the identification criteria are the following: (i) integral series of 00 l reflections with similar broadening identify pure clay minerals (or regular mixed-layer clay minerals if the superstructure reflection is present) and (ii) non-integral series of reflections with variable broadening indicate an irregular mixed-layer clay mineral. These criteria also apply to electron diffraction studies.

p0110 In most cases, the distinction is straightforward. Doubts may arise as to whether a clay mineral is strictly pure or contains <5% layers of a different type. In the latter instance, the peak displacements and broadening due to interstratification are so small that special care must be taken to distinguish them from minute irregularities related to other factors. This reservation also applies to regular interstratifications. Serpentine–chlorite interstratification is another special case. In this case, the peaks are not displaced relative to the positions of pure chlorite because the 001 serpentine reflection (ca. 0.7 nm) is very close to the 002 chlorite reflection. Only the reflection broadening serves as an identification criterion. Both subjects are described in the following section.

s0030 2.2.1.5 Identification of Pure Clay Minerals

s0035 2.2.1.5.1 General Rules

p0115 The criteria used to classify phyllosilicates (see Chapter 1) often are not very useful for their identification. In particular, groups are identified according to (though not exclusively by) their layer charge, a property that is directly measurable only in monomineral samples. Operational definitions were therefore proposed. The books by Brindley and Brown (1980) and Moore and Reynolds (1997) should be consulted for more details.

p0120 The commonly used operational XRD definitions of clay mineral groups are based on the positions of the 00 l reflections of samples in four different states: air-dry, saturated with ethylene glycol (EG), and heated at 300 and 550 °C. Clay mineral groups are identified by applying combinations of these tests. Tri- and di-octahedral sub-groups are differentiated using the position of 06 reflection (the b_0 parameter is much larger for tri- than di-octahedral clay minerals and this difference manifests clearly at high 2θ angles) and/or the stretching region in the infrared spectrum (3500–3700 cm^{-1}). Except for

species in the serpentine–kaolin group (mostly representing different structural modifications), all other species are defined solely by their chemical compositions. In some cases, different tests based only on XRD can produce positive identification but often chemical methods have to be applied to identify clay mineral species. If the concentration of clay minerals in the clay fraction is substantial (>10%), identification can be made by XRD, at least to the sub-group level, supported in some cases by IR spectroscopy. At lower concentrations, and in some particularly difficult cases, one has to resort to EM techniques.

s0040 **2.2.1.5.2 Kaolin–Serpentine Group**

p0125 A ~0.7-nm spacing in the air-dry state identifies kaolin–serpentine minerals with the exception of halloysite. If halloysite is a possibility, the preparations should first be recorded air-dry and then heated at 350 °C for a few hours to ensure full dehydration of this mineral. Halloysite in its natural, fully hydrated state has a basal spacing of ~1 nm, so occasionally it has been mis-identified as illite. Halloysite that was partially dehydrated during sample preparation, or storage, exhibits spacings between 1 and 0.7 nm (Moore and Reynolds, 1997), indicative of partial removal of one of two types of interlayer water. Sometimes, it develops well-defined 0.86 nm spacing (complete removal of one type of water; Giese, 1988). In such an intermediate state, the hydrated halloysite may resemble mixed-layer kaolinite-2:1 clay minerals but the total dehydration test (350 °C) distinguishes between the two, as the mixed layer involving a 2:1 layer will not collapse to 0.7 nm.

p0130 Churchman et al. (1984) developed a simple test to differentiate halloysite from kaolinite in mixtures by intercalation of formamide. Intercalation into halloysite is rapid (<1 h) and complete, whereas intercalation into kaolinite requires at least 4 h of contact with formamide, and even then the process is incomplete. The formamide test also allows the proportion of halloysite in the mixture to be estimated from changes in the intensity of the XRD peaks near 0.7 and 1.0 nm. However, formamide intercalation is influenced by particle size, crystallinity and iron content. Prior air-drying and mild heating also tend to inhibit layer expansion. The quantitative analysis of kaolin minerals in mixtures would therefore require the application of a combination of chemical and instrumental techniques, such as XRD, differential thermal analysis and EM studies (Joussein et al., 2005).

p0135 Kaolin and serpentine sub-groups can be distinguished by their respective XRD reflections in the 06 region (0.149 nm for all kaolin minerals and 0.153–0.156 nm for serpentines). The Fourier transform infrared spectroscopy (FTIR) spectra of kaolins and serpentines are also clearly different (Russell and Fraser, 1994). If Mg serpentines are excluded, a strong and narrow band near 3700–3697 cm⁻¹ allows kaolin layers (both discrete and mixed-layered) to be detected at a level of 1–2% of the sample mass. This is also the most

effective technique of detecting small amounts of kaolin minerals in the dominant presence of chlorite. If kaolin minerals are abundant, a clear splitting of the 002 kaolin (0.354 nm) and 004 chlorite (0.356 nm) reflections is observable with narrow slits. The 06 region also differentiates the two minerals (0.154–0.155 nm for chlorites vs. 0.149 nm for kaolins). However, all these tests fail to detect serpentine when chlorite with a similar chemical composition is dominant, in which case the inspection of high-resolution TEM images may be the only reliable means of identification.

p0140 Identification of kaolin species is based on diagnostic reflections from random preparations (Moore and Reynolds, 1997). To detect halloysite in mixtures dominated by kaolinite (no separate 00 l reflections visible), intercalation tests are applied as described earlier (see also Giese, 1988). Careful comparison of peak profiles between air-dry and heated preparations is also helpful.

p0145 Mg-rich serpentine minerals (lizardite, chrysotile, antigorite), characteristic of metamorphic serpentinite rocks, are usually coarse-grained minerals (not clay-size). These species show different structural modifications, and their XRD identification was described in detail by Wicks and O'Hanley (1988). Amesite and cronstedtite are Al- and Fe-rich analogues of lizardite, respectively; both were characterized in detail by Bailey (1988).

p0150 Berthierine and odinite are two genuine clay-size serpentines encountered with other clay minerals in marine sedimentary rocks. Their structures are so similar (Bailey, 1988) that they cannot be distinguished without chemical analysis (main difference in Fe²⁺/Fe³⁺).

s0045 2.2.1.5.3 Talc–Pyrophyllite Group

p0155 These coarse-crystalline minerals, characteristic of metamorphic environments, are identified in air-dry preparations by distinct basal spacings (0.92 nm for pyrophyllite and 0.93 nm for talc) in combination with 060 (0.1493 nm for pyrophyllite and 0.1527 nm for talc). In surface environments (weathering of ultrabasic rocks, saline lakes), clay-size analogues of talc called kerolite or pimelite (Ni-rich species) can be found. Kerolites are characterized by a basal (d_{001}) spacing of 0.96 nm, but the 001 reflection is displaced to 1.0–1.01 nm because the particles are very thin (Evans and Guggenheim, 1988). Thus, the distinction between kerolite and illite is based on higher order 00 l reflections. The 06 reflection (0.1527 nm for talc vs. 0.150 nm for illite) or the vibration band in the FTIR spectrum (3676 cm⁻¹ for talc vs. 3620 cm⁻¹ for illite) can provide further confirmation.

s0050 2.2.1.5.4 Smectite Group

p0160 Since smectites are expandable, their 00 l spacings depend on the interplay of several factors: layer charge, charge location, nature of interlayer cations, humidity and type of polar molecules introduced between the layers. All known smectites, including Otay montmorillonite (with a layer charge of

0.6/O₁₀(OH)₂), after saturation with EG at medium relative humidities, show a rational series of 00 l reflections, and the basal (d_{001}) spacing of the sodium form is 1.66–1.72 nm (Środoń, 1980). At low humidity, some glycolated Na⁺-smectites may display characteristics of vermiculite ($d_{001} \sim 1.45$ nm), while the Ca²⁺-exchanged forms retain their smectitic character. Thus, the operational definition of smectite, applicable to the full range of relative humidity, should include glycol saturation and Ca²⁺ as the exchangeable cation. Using this test, smectite cannot be mistaken for any other mineral, provided that the 00 l series is rational. Rationality should be checked using higher order reflections because the positions of the 001 and 002 reflections are displaced towards lower angles, as a result of small particle thickness. It should be stressed that the 001 reflection alone cannot be used as evidence for smectite, because randomly interstratified clay minerals such as 1-Sm or kaolinite-smectite have reflections at exactly the same position. If higher order reflections cannot be measured, the identification is less precise and mixed-layering is possible. In such a case, a narrow 001 reflection is indicative of pure smectite, as mixed-layer clay minerals have reflections at 1.7 nm that are substantially broader than those of pure smectite. After K-saturation followed by heating at 300 °C for 1 h, a pure smectite should produce an XRD pattern resembling that of illite (basal spacing ~ 1 nm). If the 00 l reflections after heating correspond to a higher spacing, the presence of isolated brucite or gibbsite ‘islands’ in the smectitic interlayer spaces is indicated. This ‘incipient chloritization’ (see later) does not inhibit swelling but can prevent full collapse of the interlayer spaces on heating. Infrared analysis can be used to detect small amounts of kaolinite layers in kaolin-smectite (Madejová et al., 2002).

p0165 The position of the 06 reflection uniquely distinguishes di-octahedral smectites (0.149–0.152 nm) from their trioctahedral counterparts (0.152–0.153 nm). The overlapping 0.152 nm value of di-octahedral clay minerals is characteristic of nontronite. This mineral is distinguishable from tri-octahedral clay minerals by very weak 002 and 003 reflections, thermogravimetric analysis (nontronite dehydroxylates at 300–400 °C, while tri-octahedral clay minerals require temperatures above 700 °C), FTIR (3556 vs. 3677 cm⁻¹) and, of course, by chemical analysis. Most pure bentonitic smectites are low in Fe (0.149–0.150 nm), while Fe-rich smectites, characteristic of soil weathering, show intermediate 06 values. The Greene–Kelly test (saturation with Li⁺ ions and heating at 300 °C) can be used to distinguish beidellite from montmorillonite: montmorillonite does not re-expand while beidellite does (Moore and Reynolds, 1997). Chemical analysis is always required to confirm the identity of tri-octahedral species (saponite, stevensite, hectorite).

s0055 2.2.1.5.5 Vermiculite Group

p0170 Like smectite, vermiculite is an expandable mineral. However, the expansion of vermiculite is more restricted because its layer charge is higher than that of

smectite, and this charge is largely located in the tetrahedral sheet. The distinction of vermiculite from smectite is arbitrary, based on a layer charge of 0.6 eq/O₁₀(OH)₂ (see Chapter 1). Some clay mineralogists argue that both groups of minerals should be treated as one continuous series. Extensive work has been done on tri-octahedral vermiculites (de la Calle and Suquet, 1988), but data on the di-octahedral counterparts are very scarce (see for instance, Malla and Douglas, 1987). The most widely accepted operational definition of vermiculite is based on its ca. 1.45 nm basal spacing for the Mg²⁺-exchanged form after treatment with glycerol, and the collapse of the K⁺-form to 1.0 nm on heating at 300 °C for 1 h. Of course, pure vermiculite should display a rational series of very narrow reflections, but such minerals are very rare. The glycerol test distinguishes vermiculite from smectite, and the heating test distinguishes vermiculite from chlorite (the 1.4-nm basal spacing of chlorite is not affected by heating in such conditions). The heating test can be used to detect vermiculite in the presence of chlorite. The application of different tests to soil vermiculites has been described in detail by Malla and Douglas (1987).

s0060 2.2.1.5.6 Illite Group

p0175 The classification scheme (see Chapter 1) does not provide criteria for distinguishing illite from vermiculite. Indeed, illite is regarded as a species in the true (flexible) mica group. Both illite and vermiculite have a closely similar range of layer charge, but illite is non-expandable and has fixed instead of exchangeable cations in the interlayer space. In reality, illites are exclusively di-octahedral and of clay-size, while vermiculites are most commonly tri-octahedral and often of mica-size. The charge of illite layer is 0.95/O₁₀(OH)₂, but the overall charge calculated in the structural formula is often lower because illite particles are very thin and their external basal surfaces are smectitic (Środoń et al., 1992, 2009).

p0180 Operationally, illite can be defined as a clay-size material, exhibiting a rational series of reflections with a d_{001} value of about 1.0 nm that does not change on EG saturation or heating to 300 °C. Swelling tests detect mixed-layering with expandable layers, and heating discriminates between illite and hydrated halloysite. This definition includes micro-divided mica, if it is present in the <2 μm fraction. Short of calculating the structural formula from chemical analysis of uncontaminated specimens, there is no way to distinguish illite from di-octahedral mica.

p0185 The positions, shapes and relative intensities of 00 l reflections of an illitic material often change slightly after EG treatment, indicating some mixed-layering. The most sensitive indicator of mixed-layering is based on the intensities, rather than the positions, of the 00 l reflections (Środoń, 1984):

$$I_r = (001/003_{\text{air-dry}}) / (001/003_{\text{glycol}})$$

where Ir denotes the intensity ratio of the 001 and 003 reflections from air-dry and glycolated samples. A value of $Ir = 1 \pm 0.1$ is indicative of pure illite.

p0190 End-member species of the illite group are illite proper and aluminoceladonite, ferruginous illite, glauconite and celadonite (K^+ -illite), brammalite (Na^+ -illite), and tobellite (NH_4^+ -illite). Solid solutions are common. In illite proper–aluminoceladonite series, d_{001} decreases from 1.0024 to 0.9898 nm and in glauconite–celadonite series from 1.0002 to 0.9961 nm (Drits et al., 2010). Au3

p0195 The presence of some iron species should be suspected if the 002 reflection is clearly weaker than in typical Al^{3+} -illites, and an admixture of tri-octahedral micas can be ruled out. Such a hypothesis can be verified in the 06 region if smectites are absent: 0.150-nm reflections identify Al^{3+} -illite, 0.151-nm reflections indicate ferruginous illite and glauconite, and 0.154 nm is typical of tri-octahedral micas. The FTIR spectrum is equally conclusive: 3630 cm^{-1} for Al^{3+} -illite, $3530\text{--}3560\text{ cm}^{-1}$ for glauconite, $3605\text{--}3580\text{ cm}^{-1}$ for ferruginous illite, 3594 cm^{-1} for biotite and 3796 cm^{-1} for phlogopite. The celadonite spectrum is very distinctive, with four sharp bands in the $3533\text{--}3601\text{ cm}^{-1}$ region (Wilson, 1994). Only chemical analysis enables indisputable discrimination to be made between ferruginous illite and glauconite.

p0200 Na^+ -illite is not a well-documented species. Most non-expandable sodium phyllosilicates are coarse grained and correspond to sodium mica (paragonite) in composition. Only detailed chemistry can differentiate the two. The data on rectorites (regular mixed-layer clay minerals) provided by Brown and Weir (1963) indicate that the illitic component of the interstratification is a genuine brammalite. Paragonite and brammalite can be easily distinguished from K^+ -illite and micas as well as from pyrophyllite and talc by the 00l series based on $d_{001} = 0.96\text{ nm}$. The 060 region is equally conclusive: 0.148 nm. Commonly K^+ -illite contains very small substitution of K^+ by Na^+ , detectable only by chemical analysis (Środoń et al., 2009).

p0205 NH_4^+ -illite is a well-documented species (Środoń and Eberl, 1984; Šucha et al., 1994). Distinction from K^+ -illite is based on 00l series with $d_{001} = 1.033\text{ nm}$. Solid solution between K^+ and NH_4^+ forms occurs, and their ratio can be evaluated from the position of the 005 reflection (Lindgreen et al., 2000). FTIR can also be used to detect NH_4^+ in illite; NH_4^+ ions give rise to a band at 1400 cm^{-1} (Šucha et al., 1998). In sedimentary rocks, 10–20% substitution of NH_4^+ for K^+ is common (Środoń et al., 2009; Środoń and Paszkowski, 2011).

p0210 Polytypic varieties and types of structural defects in illite are well recognized. Moore and Reynolds (1997) gave a guide to their identification and quantification by means of computer modelling of XRD patterns, the application of which was reviewed by Środoń (2002). *Cis-* versus *trans*-vacant layers in illite can be quantified by thermal analysis (Drits et al., 1998a,b). Au4

s0065 2.2.1.5.7 Chlorite Group

p0215 The unique dehydroxylation behaviour of chlorite allows this mineral to be indisputably identified in any clay mineral mixture. On heating at $550\text{ }^\circ\text{C}$

for 1 h, the d_{001} value of chlorite decreases from slightly above 1.4 nm to 1.38–1.39 nm. At the same time, the intensity of the 001 reflection strongly increases, while the intensity of the higher order reflections decreases. This test distinguishes chlorite from vermiculite and minerals with incomplete chlorite layers, all of which collapse to 1.0 nm. It also differentiates chlorite from mixed-layer minerals involving chlorite and incomplete chlorite layers, showing mixed-layer 1.4/1.0-nm reflections. Chlorite may also be distinguished from mixed-layer chlorite–serpentine since the even-numbered reflections of the latter are broader (Reynolds et al., 1992).

p0220 Common chlorites are tri-octahedral minerals with $d_{060} > 1.53$ nm. This distinguishes them from di–tri-octahedral and di-octahedral species, which themselves can be discriminated only by chemical analysis.

p0225 Tri-octahedral chlorites display a range of iron contents and also a variable distribution of iron between the octahedral sheet and the interlayer space. Both the iron content and its distribution can be quantified from the relative intensities of 00 l peaks, using the technique of Moore and Reynolds (1997). In order to perform such determinations in mixtures, the overlapping vermiculite reflections have to be removed by heating at 300 °C, while the kaolinite reflections are shifted by intercalation (op. cit.). The measurement is not possible in the presence of serpentine without detailed computer modelling of the XRD pattern. The chemical composition of tri-octahedral chlorites can also be evaluated from the d_{001} and 060 values (Wiewióra et al., 1998).

p0230 Moore and Reynolds (1997) have described methods for identifying chlorite polytypes. This may be difficult in mixtures with other clay minerals, and magnetic separation of chlorite may be required (Amonette and Zelazny, 1994).

s0070 2.2.1.5.8 *Sepiolite and Palygorskite Group*

p0235 These minerals have clay-size particles and a fibrous morphology. In oriented preparations, they do not display a series of 00 l reflections. If present in sufficient quantity, their identification can be based on several reflections (Moore and Reynolds, 1997). A small admixture is marked only by the presence of strong 110 reflections at 1.20–1.29 nm (sepiolite) and 1.03–1.05 nm (palygorskite), which are insensitive to EG or glycerol treatment. When sepiolite is heated at 300 °C, the reflection at 1.2 nm disappears and new reflections appear at 1.04 and 0.82 nm (these changes are reversible upon hydration). When palygorskite is heated, the intensity of the 1.03 nm reflection decreases, and a new reflection at 0.92 nm appears (Jones and Galán, 1988). These tests distinguish sepiolite and palygorskite from mixed-layer clay minerals. IR spectroscopy (Russell and Fraser, 1994) may also aid identification, while the fibrous particle morphology can be observed by SEM and TEM.

s0075 **2.2.2 IDENTIFICATION OF MIXED-LAYER CLAY MINERALS**

s0080 **2.2.2.1 Peak Position Approach**

p0240 The identification of rare regular mixed-layer clay minerals involves recognizing the nature of the component layers. The same criteria as used for pure minerals can be applied. For example, smectite layers are expected to swell to ~ 1.7 nm with EG and to collapse to ~ 1.0 nm on heating, while illite layers remain stable. Thus rectorite, a regularly interstratified I–Sm, should show a rational series of 00 l reflections, based on a 2.7-nm spacing for a glycolated sample and a 2.0-nm spacing when heated. Specified criteria of integrity (Bailey, 1982) have to be met in order to classify a clay mineral as a regularly interstratified species. The 06 reflections and IR spectra can be used to distinguish di- from tri-octahedral species.

p0245 An irrational series of 00 l reflections indicates irregular mixed-layering. The nature of the component layers, their proportions, and the pattern of interstratification should be identified. A practical identification scheme starts from considering two-component systems, because they are the most common and easiest to recognize. Firstly, the low-angle region is inspected for the superstructure reflection (corresponding to A + B basal spacing). This reflection appears if interstratification is ordered, that is, the layers are not arranged in a random array but the alternation of component layers (AB sequence) is favoured. The superstructure reflection is relatively strong if the ratio of the component layers is close to 1:1. A lack of superstructure reflection indicates that the interstratification is either random or dominated by one type of layer. The presence of a superstructure reflection and its behaviour during standard treatments may be very helpful in identifying the component layers.

p0250 In both ordered and random cases, the identification is based on Méring's rules, as explained in detail by Moore and Reynolds (1997). The glycosylation and heating tests should be performed before identification is attempted, because these tests help narrow the range of possibilities (e.g. no change after glycosylation eliminates smectite). If a chosen model is correct, all mixed layer reflections of random clay mineral particles should be located between the corresponding reflections of pure component minerals. In case of an ordered mineral, its regular version serves as one of the end-members (e.g. rectorite for ordered I–Sm) and the dominant layer as the other end-member. Broadening of the mixed-layer reflections depends on the distance between the reflections of pure end-members, and may serve as an additional identification criterion. In extreme cases, when the distance is very large (as between the 001 reflection of glycolated smectite and the 001 reflection of illite), only broadening and decreased intensity of the 1.7-nm peak (smectite 001) are observed in randomly interstratified I–Sm but the position of this peak does not change.

p0255 If several reflections of a sample are recorded under test conditions appropriate for a given case, and all have followed Méring's rules, the identification

of a two-component mineral can be achieved. Otherwise, an alternative model consisting of more than two components has to be investigated.

p0260 If the clay mineral is identified as a two-component system, either random or ordered, the layer ratio can be measured. Several techniques are in use, based on the positions of selected reflections, on their broadening, or on the computer simulation of entire XRD patterns.

p0265 Drits et al. (1994) published an approximate but universal technique as an extension of the Méring approach. Layer ratios are calculated from peak positions on the assumption of their linear migration from one end-member position to another as a function of layer ratio. Au5

p0270 Reynolds and Hower (1970) introduced a similar approach, but based on peak migration curves, constructed from computer-generated XRD patterns. They proposed measuring the layer ratio in I–Sm from the 002/003 peak positions in the glycolated state. Since then, numerous plots of this nature, dedicated to the identification of various mixed-layer minerals, have been published (see review in Środoń, 2002). The problems associated with identifying minerals involving chlorite have been discussed by Reynolds (1988), while the identification of all common mixed-layer minerals has been reviewed by Moore and Reynolds (1997).

p0275 The identification techniques for I–Sm are the most detailed because this mixed-layer clay mineral is the most frequently studied. It is also the most abundant mineral and is useful for geological interpretations such as dating and deriving paleo-temperatures. Środoń (1980) and Watanabe (1981) used pairs of reflections to minimize the effect of particle thickness and of variable thickness of the glycol–water interlayer complex, while Dudek and Środoń (1996) applied realistic (log-normal) distributions of the thickness of the mixed-layer particles. Special techniques were proposed for dealing with the most common case of I–Sm in mixtures with discrete illite (Środoń, 1981, 1984). They allow the layer ratio to be measured until ca. 90% illite in the mixed-layer clay mineral if the latter is relatively abundant.

s0085 2.2.2.2 Peak-Broadening Approach

p0280 The techniques based on peak positions fail if

- o0005 i. the admixture of another type of layer is very low (a few per cent). In this case, the Q technique of Moore and Reynolds (1997) based on peak broadening can be applied;
- o0010 ii. the peak positions of the two components coincide (as in the case of serpentine-chlorite). In this case, the serpentine/chlorite ratio can be measured from the broadening of 004 versus 005 peaks (Reynolds et al., 1992); and
- o0015 iii. a mixed-layer clay mineral having a composition dominated by one end-member is a minor component of a mixture with that end-member as a

discrete phase. A well-known example of this case is the illitic fraction of clastic rocks from the zone of advanced diagenesis and anchimetamorphism. There is no simple technique for measuring the I–Sm ratio in such materials. Instead, broadening of the 1.0 nm peak (overlapping illite and I–Sm reflection) is used most often as the diagenetic/metamorphic grade indicator (Kübler index; Kish, 1987).

p0300 The Kübler index is a complex function of the illite/swelling layer ratio in the mixed-layer clay mineral, the state (spacing) of the swelling layer (which itself depends on several factors), the mass ratio between the mixed-layer clay mineral and discrete illite, and the particle thickness distributions of the two minerals. This measurement can be made more rigorous if a modified Scherrer equation is applied to the 1.0 nm reflection of a K^+ -exchanged and heated (dehydrated) sample (Drits et al., 1997). Under such experimental conditions, the 1.0-nm peak broadening becomes a function of crystal thickness distribution exclusively, and the mean crystal thickness of the mixture can be measured by the Scherrer equation modified to account for the log-normal shape of crystal thickness distribution.

p0305 Another alternative to the Kübler index is the XRD measurement of crystal thickness distribution by the Bertaut–Warren–Averbach (BWA) method, adapted to clay minerals by Drits et al. (1998a,b) using the MudMaster computer program. In this approach, information on crystal thickness distribution is extracted from the shape of the 1.0-nm reflection. Pure non-swelling illite can be studied by this technique in its natural state. If swelling is detectable, its effect has to be eliminated before the measurement (peak broadening should not be affected by mixed-layering). It can be done either by K^+ saturation and heating (collapsing swelling layers to 1.0 nm; Kotarba and Środoń, 2000), or by dispersing the I–Sm component of the mixture into fundamental illite particles using polyvinylpyrrolidone (PVP) (Eberl et al., 1998). The PVP technique is potentially capable of providing a sensitive grade indicator of deep diagenesis and anchimetamorphism. The MudMaster program can also be used to study crystal thickness distributions of other clay minerals, such as smectites (Mystkowski et al., 2000).

s0090 2.2.2.3 Expert Systems

p0310 A computer can guide the student of mixed-layer clay minerals through mineral identification procedures. Two such expert systems are available: INTERSTRAT by Garvie (1994), and the program of Plançon and Drits (1994). In identifying mixed-layer clay minerals, INTERSTRAT relies on a series of patterns calculated with NEWMOD, whereas Plançon and Drits' program relies on published techniques based on selected reflection characteristics.

s0095 **2.2.2.4 Integrated Approach: Computer Modelling**

p0315 The identification based on peak position and broadening can be verified by direct modelling of the 00 l XRD pattern using existing computer programs (review in Środoń, 2002). Also, computer modelling is the only technique capable of identifying and quantifying mixed-layering if more than two components are present. The most complete statistical description of interstratification and theoretical treatment of the XRD by disordered particles, underpinning computer modelling, were published by Drits and Tchoubar (1990). A practical guide to modelling two-component mixed-layer clay minerals using the NEWMOD computer program is also available (Moore and Reynolds, 1997).

p0320 Modelling is usually very time consuming because it uses a trial-and-error approach: input data are adjusted manually until a satisfactory fit of peak positions, shapes, and intensities in the entire XRD profile is reached. The use of a log-normal shape of crystal thickness distribution, discovered by Drits et al. (1997) for illites, simplifies modelling. Nevertheless, the number of variables is so large that solutions are often non-unique. For this reason, Sakharov et al. (1999)—who conducted an intensive study to model complex clay mineral mixtures involving mixed-layer clay minerals—proposed that the model should be judged reliable if it provides a satisfactory fit for at least two states of a sample (e.g. air-dry and glycolated for clay minerals involving a smectite layer). No generally accepted strict criteria of ‘satisfactory fit’ exist. Commonly, the least-squares criterion of the quality of fit of the entire pattern is used. In the author’s opinion, such a criterion is adequate if quantitative analysis of a mixture is the target of a fitting exercise (see below). If the layer ratio of a mixed-layer clay mineral is the main goal, the criterion of fit should be based in most cases on peak positions, as they are usually most sensitive to the layer ratio. As an example, a 0.1° 2θ error in peak position changes the evaluation of illite layers in randomly interstratified I–Sm by about 15% (absolute values). It would be appropriate to specify the criterion of fit for a case under study.

p0325 The modelling procedure can be automated using available optimization techniques. At least two such approaches are in use, both of which are proprietary of oil companies. At Exxon, Pevear and Schuette (1993) used genetic algorithms and NEWMOD to model XRD patterns of clay mineral mixtures. The SYBILLA program, developed at ChevronTexaco (McCarty et al., 2008), applies evolutionary programming and the modelling program of Drits and Sakharov (1976). SYBILLA can handle not only two-component but also multi-component mixed-layering, and automatically models all clay mineral components of a mixture that were identified by the operator. The application of XRD pattern modelling to sedimentary samples revealed that their clay mineral composition is often more complex than previously assumed (e.g. McCarty et al., 2008).

s0100 **2.2.3 QUANTITATIVE ANALYSIS**

p0330 Quantitative analysis is performed to obtain the contents of clay minerals either in the bulk rock or in the clay fraction. XRD is the most commonly used technique, but IR spectroscopy and major element analysis, combined with qualitative XRD, have also been applied. All these methods have been reviewed by Środoń (2002).

p0335 Clay minerals are very difficult to quantify, and large analytical errors have to be expected. This is because their particles have varied chemical compositions and structures, and tend to adopt a preferred orientation. In most cases the results are semi-quantitative. However, recent worldwide contests in the quantitative analysis of artificial rocks containing clay minerals (McCarty, 2002; Kleeberg, 2005) would indicate that some XRD techniques are capable of providing very accurate results (below 10% of cumulative error from actual values for samples composed of 13 minerals, including four clay minerals). It is not certain at present whether techniques other than XRD can achieve this level of accuracy. Further comments will be therefore restricted to XRD techniques.

p0340 The overall success of quantitative analysis strongly depends on sample preparation, data processing, and selection of standards. These aspects will be briefly characterized below, separating bulk rock from clay fraction analysis.

s0105 **2.2.3.1 Bulk Rock Quantitative Mineral Analysis**

s0110 **2.2.3.1.1 Sample Preparation**

p0345 Because of their platy habit, clay mineral particles have a strong tendency for preferred orientation, enhancing the 00l reflections and weakening the hk reflections as compared with a fully random preparation. Most XRD methods of quantitative analysis require perfectly random preparations. Methods based on Rietveld refinement can correct for orientation, although this adds variables that have to be dealt with. Most techniques use an internal standard in order to avoid normalization to 100%. Thus, sample preparation generally aims at achieving three goals: randomness, homogenization with a known amount of internal standard, and reduction in the size of coarse grained minerals below ca. 20 μm, in order to assure good reproducibility of reflection intensities. Size reduction should not cause measurable damage to the crystal structures.

p0350 The required reduction in size can be achieved by 5 min of wet grinding of a 3-g sample in a McCrone micronizing mill. This particular grinding process produces narrow grain-size distributions (O'Connor and Chang, 1986) without a coarse-grained 'tail' characteristic of other grinding techniques. The sample mass (3 g) ensures that there is enough material between the corundum rollers, so the corundum contamination is negligible. Water, methanol, or hexane can be used as grinding fluids (Środoń et al., 2001).

p0355 Wet grinding also ensures perfect homogenization of the sample and the standard. Al_2O_3 , advocated by Chung (1974), is the most commonly used internal standard. Środoń et al. (2001) introduced ZnO, which can be used in smaller quantities (10%), and which produces less coincidence with the reflections of common rock-forming minerals.

p0360 The techniques of producing random preparations from powders of samples containing clay minerals have been described in Section 2.2.1.3. For quantitative analysis, care should be taken to produce, as far as possible, a similar degree of packing, which is important for the reproducibility of XRD patterns (peak displacement and broadening due to variations in sample density).

s0115 2.2.3.1.2 Data Collection, Processing, and Selection of Standards

p0365 The data collection procedure should ensure high peak/background ratios, low sensitivity to sample density variations, and good counting statistics, while the strongest reflections (e.g. 0.334 nm quartz) stay within the linearity range of the counter, and the beam stays entirely within the preparation for the lowest 2θ angle, from which the analysis is performed.

p0370 Numerous strategies of data processing are in use. They all rely upon measuring the intensity of diffraction of a given mineral in the investigated sample and comparing it with the intensity of a pure standard of this mineral. The matrix effect on the intensity is taken into account by using an internal standard and experimentally established mineral/standard peak ratios called 'RIR or MIF'¹ (Hubbard and Snyder, 1988; Reynolds, 1989) to calculate directly the contents of each crystalline phase (for details, see, e.g. Środoń et al., 2001). Three main groups of techniques are currently in use. They differ by what they measure, how they carry out the measurement, and what they use for standards. All require *a priori* knowledge of the qualitative mineral composition of the sample. Thus detailed mineral identification is pre-requisite for a successful quantitative analysis.

p0375 The first group of techniques, which could be called single-reflection/natural standard, relies upon a selected individual reflection as a measure of the mineral concentration and upon natural specimens as standards (e.g. Hillier, 2000; Środoń et al., 2001). The second group (whole pattern/natural standard) obtains intensities of the components of a mixture by fitting the entire XRD pattern of a sample with patterns of pre-registered pure standards (e.g. Smith et al., 1987; Batchelder and Cressey, 1998). The third group (whole pattern/computed standard) fits the experimental pattern with the patterns of pure components calculated from the crystallographic data. Elaborate procedures are used for refining line widths and shapes of the calculated patterns, correcting for absorption contrast, orientation, amorphous material

np0005 1. RIR stands for reference intensity ratio and MIF for mineral intensity factor. RIR is most commonly used.

content and several intensity aberrations, and the fit is maximized by the Rietveld technique (Taylor, 1991; Bergmann et al., 1998).

p0380 All three types of techniques were used by top contestants during recent world competitions in quantitative analysis of rocks (Reynolds Cup organized at every second Clay Mineral Society conference since 2002). The main advantages of the Rietveld-based techniques are the calculation of standards and the correction for instrumental errors, which makes this technique easily transferable from one instrument to another, less dependent on the quality of sample preparation, and independent on the availability of pure standards. The first advantage does not apply fully to clay minerals at the present stage of the development of these techniques, despite a remarkable progress in modelling defective structures (e.g. Ufer et al., 2008). Natural clay mineral standards are used instead, because of the complexity of clay mineral structures (mixed-layering, polytypes, tri-dimensional defects), making them unsuitable for Rietveld refinement. Calcium dolomites, which are quite common components of sedimentary rocks, pose the same problem (Drits et al., 2005). For such variable minerals, the problem of possibly good correspondence between the standard and the analyzed mineral remains very important. The error related to the selection of standards can be minimized in the single-peak technique by choosing analytical reflections possibly insensitive to structural variations, but at the expense of the convenience of automated whole pattern fitting.

p0385 A technique combining both advantages uses evolutionary programming to perform the fit with natural standard patterns, but assigns different weights to fitting different portions of the pattern (Mystkowski et al., 2002). Weights are radically increased for the portions containing selected analytical reflections. For the analysis, 06 reflections are used, allowing the following clay minerals to be quantified: Fe-chlorite + berthierine, Mg-chlorite, tri-octahedral 2:1 clay minerals, di-octahedral 2:1 Fe clay minerals (nontronite + glauconite), di-octahedral 2:1 Al-rich clay minerals (illite + smectite + I-Sm + mica) and kaolinite. In particular cases, polytypes can also be quantified (e.g. 2M₁, 1M and 1Md for 2:1 clay minerals).

p0390 Clay mineral reflections are relatively broad and weak. For this reason, the analysis of clay minerals in the bulk rock is feasible provided that the clay mineral contents are not too low. If the clay mineral content is low (e.g. relatively clean sandstones or carbonates), a better strategy is to remove quantitatively most of the dominant mineral (e.g. to dissolve carbonates) and to apply the random preparation analysis to the residue.

p0395 Chemical analyses can aid quantitative XRD analysis of rocks in certain instances. If an element can be assigned only to one mineral, the content of this mineral can be calculated from the chemical analysis more precisely than from the XRD data, for example, zircon from Zr, barite from Ba, pyrite from S, apatite from P, etc. (e.g. Środoń and Kawiak, 2012). CEC and K₂O + (NH₄)₂O contents can often be used to calculate smectite and illite + mica contents separately (Środoń, 2009), which is important for many practical issues.

p0400 This is probably as good as anybody can do today in the field of clay analysis from random preparations. If more detailed quantification of clay mineral species is required, the analysis of oriented preparations has to follow.

s0120 **2.2.3.2 Quantitative Mineral Analysis of the Clay Fraction**

s0125 *2.2.3.2.1 Sample Preparation*

p0405 The 00 l series of reflections contains information on the clay mineral species present in a sample. The preparation technique for quantitative analysis should ensure, as much as possible, good orientation in order to intensify these reflections and avoid segregation of clay mineral particles during sample preparation. The sedimentation technique, which is commonly used in clay mineral identification, may produce segregation with respect to grain size. Quantitative analysis of such preparations would therefore overestimate fine-grained clay minerals. The technique of smearing a clay paste on to a glass slide and the use of a 'Millipore' transfer filter are apparently well suited for quantitative analysis (Moore and Reynolds, 1997). They also ensure 'infinite thickness' of the preparation.

s0130 *2.2.3.2.2 Data Processing*

p0410 Simplified techniques, based on assigning 'weighting factors' to different clay mineral reflections (Schultz, 1964; Biscaye, 1965), were commonly used until quite recently. The results generated by such techniques should be considered semi-quantitative. Moore and Reynolds (1997) proposed a more rigorous single-peak technique, based on the standard intensities calculated by NEWMOD. In assuming the same degree of orientation for all analyzed clay minerals, this technique shares one drawback with the old ones. In reality, the orientations may be different because of differences in the shape of clay mineral particles (in particular, curled shape of swelling clay mineral particles versus flat shape of common non-swelling clay minerals). Such differences in orientation have been recorded for fresh marine sediments (Zeelmaekers, 2011).

p0415 Fitting the entire experimental patterns with computer-generated patterns of identified clay minerals offers the best chance of accurate quantification of clay mineral species. In this approach, the orientation of different clay minerals can be modelled individually. Manual fitting was performed originally (e.g. Sakharov et al., 1999; Lindgreen et al., 2000), but this approach is too time consuming for routine applications. The future of quantitative clay analysis using oriented preparations lies with the automated fitting techniques. Verification of such analyses was performed recently (Zeelmaekers, 2011) using independent data sets (CEC, K₂O content), and it demonstrated that the modelling produces realistic quantitative data, at least at the level of clay mineral groups (e.g. kaolinite vs. 2:1 clay minerals).

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