Petrography of Shales: A Survey of Techniques

by

Jürgen Schieber[1] and Winfried Zimmerle[2]
[1]Department of Geology, The University of Texas at Arlington, Arlington, Texas 76019, USA; [2]Prinzengarten 6, D-29223 Celle, Germany

Introduction

With clays typically being the most abundant constituent of shales, their study and identification has long figured prominently in the petrographic study of shales. Useful texts are those by Correns (1938), Müller, 1967, Grim (1968), Millot (1970), Weaver (1989), Serra (1990), Jasmund and Lagaly (1991), and Blatt (1992). They cover aspects such as classical clay mineralogy, applied clay mineralogy, clay geology, clay deposition, clay in engineering geology, geochemistry, clay diagenesis and logging responses. When dealing with clay minerals one has to keep in mind that they are typically metastable (Lippmann, 1979), a circumstance that makes precise determination often difficult (e.g. mixed-layer clays, glauconite group).

Besides the composition-centered, general classification schemes mentioned in the introduction to this book (e.g. Ingram, 1953; Dunbar and Rodgers, 1957; Folk, 1965; Picard, 1971; Lewan, 1979; Blatt, Middleton, and Murray; 1980; Lundegard and Samuels, 1980; Potter et al, 1980), several authors have presented classification schemes that were designed to meet specific needs of a region, basin, or stratigraphic unit. Conze (1984) defined six types of fine-grained sediments in the Upper Carboniferous of the Ruhr basin, based on grain size, sedimentary structures, and organic carbon content. Nuhfer et al. (1979) presented a classification Devonian shales of the eastern US that relies heavily on features observed in X-radiographs. Mineralogical-geochemical classifications of some genetic kaolinite types, resulting from bedrock weathering and recycling of clays from older sediments, were presented by Lasch and Thiergärtner (1981). Classifications in which textural characteristics are emphasized over compositional parameters were presented by Schieber (1989, 1994b) for shale successions with comparatively small compositional variations.

Methods

In the past, macroscopic appearance, X-ray diffraction data, and chemical composition have been the primary parameters in the petrographic descriptions of many shale and mudstone successions. Improved methodologies, however, are now available and have been summarized by Fripiat (1982) and Zimmerle (1993). It is useful to distinguish between microscopic and non-microscopic methods.

Microscopic Methods

Examination of standard and polished thin sections is the mainstay of microscopic petrographic analysis. Because of the general softness of shales and mudstones, preparation of good thin sections often poses a challenge. The difficulty of preparing good petrographic thin sections of shales and mudstones is one of the reasons why acceptance and application of thin section microscopy of these rocks has been long delayed. Various methods of thin section preparation, utilizing special epoxy resins, multiple epoxy impregnation, diamond laps instead of loose grit, double polish, etc., have been developed (e.g. Altemüller, 1974; Catt and Robinson, 1961; Murphy, 1986; Lindholm, 1987; Miller, 1988). Thin sectioning of very soft materials, such as varved clays, requires special care (Junge and Magnus, 1994). Polished thin sections are ideal because they are amenable to a variety of microscopic analyses, such as transmitted light microscopy, reflected light microscopy, fluorescence microscopy (FL), cathodoluminescence microscopy (CL), scanning electron microscopy (SEM), and backscattered electron microscopy (BSE). The latter two are combined with X-ray fluorescence spectroscopy (XRF). To prepare polished thin sections of shales and mudstones, however, is labor intensive because of a wide range in hardness of constituent minerals, the difficulties in polishing soft clay minerals, the general lack of cementation, and the difficulties of injecting stabilizing epoxy into the tiny pores of these rocks. Thus, although they are ideal to work with, cost factors usually demand judicious application of this type of sample preparation.

Thin section petrography of soils deals with similar aspects as thin section petrography of shales and mudstones. Methods, terminology, and fabrics differ slightly, but artifacts observed in soil thin sections, particle

shape graphs, surface roughness descriptors, and alteration sequences may inspire the student of shale petrography. Thus, the handbook for soil thin section description (Bullock et al., 1985) is a handy and compact supplement to other texts on thin section description. Although there have been sustained efforts by a few individuals to communicate the benefits of thin section petrography of shales (Zimmerle, 1982, 1994), overall, detailed microscope descriptions of shales are surprisingly rare (Schieber, 1989). Nonetheless, examination of petrographic thin sections is in our opinion the most readily available source of a wide range of aspects of shale geology, including sedimentary and microfabric features, mineralogy, diagenesis, and fossil content.

Electron-optical methods include scanning electron microscopy (SEM, e.g. O'Brien, 1981), transmission electron microscopy (TEM, e.g. Chiou et al., 1991), scanning transmission electron microscopy (STEM; e.g. Hover et al., 1996), and backscattered electron microscopy (BSE, e.g. Krinsley et al., 1983). SEM and BSE methodology and their application to sedimentary rocks have been summarized by Trewin (1988). Their successful application to shale petrography has been demonstrated by a large number of investigators (e.g. Pye and Krinsley, 1984; Nöltner, 1988; O'Brien and Slatt, 1990; Davies et al., 1991; Macquaker and Gawthorpe, 1993; Hover et al., 1996). Using these methods, resolution can be extended down to 0.1 microns, allowing for more detailed study of submicroscopic aspects, such as mineral composition, grain contacts, grain orientation, grain deformation, pore spaces, and interstitial cements. For mineral identification the SEM Petrology Atlas of Welton (1984) can be quite useful. On freshly fractured surfaces, features such as mineral orientation, shape and size, and organic content are readily observed, and freeze-drying techniques allow examination of microtextures and pore spaces of recent sediments (Bryant et al., 1991). Nonetheless, interpretation of electron microscope images requires experience, because the novice is often bedeviled by artifacts of sample preparation.

Sample preparation is easiest and least problematic for SEM/SE (secondary electron) observation (e.g. O'Brien and Slatt, 1990). SEM/BSE studies, on the other hand, require high quality polished thin sections. The softness of shales, and the tendency of hard grains to pluck during polishing, pose a considerable challenge in the manufacture of polished thin sections for BSE (Pye and Krinsley, 1984). To prepare shale samples for TEM and STEM studies is quite tedious. The aim is to present a slice of sample to the microscope that is only about 10^{-4}mm thick. Whereas standard techniques to prepare TEM samples from modern muds are well established (e.g. Baerwald et al., 1991), the same can not be said for their fully consolidated ancient equivalents. The hardness of the material in general, as well as plucking and tearing by quartz grains, make preparation of TEM samples from ancient shales and mudstones extremely challenging. This is one of the main reasons why there a so few TEM studies of shales. In recent years ion-milling has been introduced as an alternative method to thin samples for TEM and STEM (Jiang et al., 1990). Because the aforementioned problems of plucking and tearing are eliminated with this method, it is likely that we will see a gradual increase of TEM and STEM studies of shales.

An extension of electron microscopic techniques that shows considerable promise for provenance studies in shales and mudstones is scanned cathodoluminescence (CL). Basically, polished thin sections are examined with a CL detector installed on an SEM. Milliken (1994) showed that CL textures observed in quartz silt grains of Oligocene mudstones of south Texas were most likely inherited from rhyolitic source rocks. Once a systematic inventory of CL textures for quartz from a variety of igneous, metamorphic, and sedimentary rocks has been acquired, scanned CL of quartz silt is likely to become widely employed in provenance studies of shales and mudstones.

Whereas electron microscopic techniques are ideal to study individual mineral grains, grain relationships, pore spaces, and interstitial cements of shales, the majority of sedimentologically relevant textural features are most easily studied under the petrographic microscope. When polished slabs and petrographic thin sections are examined, many seemingly drab shales show a wide range of sedimentary features (e.g. Schieber, 1986, 1989, 1990a, 1990b, 1994a, 1994b, 1996) that can be used to determine sedimentary conditions. Furthermore, studies by Zimmerle (1982, 1991, and this volume) indicate that there is still a great deal to be learned about shale provenance from careful examination of petrographic thin sections.

Phase contrast microscopy (PCM) utilizes the phase difference of light rays transmitted by different portions of an object to create an image in which the details of the object are distinct, despite their near uniformity of refractive index (Correns and Piller, 1955). PCM can be used in thin sections and grain mounts to observe fine morphological details, such as crystal edges, cleavage fragments, and crystal overgrowth. Unfortunately, PCM is not widely utilized any longer. An example of its application to argillaceous rocks is given by Strübel et al. (1991) and Zimmerle (1993).

Wherever possible, the examination of polished thin sections should be supplemented by X-ray diffraction analysis (XRD) and chemical analyses of major and trace elements. If feasible, examination of selected samples by auto-radiographs, X-radiographs, differential thermal analysis (DTA), infrared adsorption spectroscopy (IR), and transmission electron microscopy (TEM), might provide additional valuable information. Studies of the diagenesis

of shales, typically based on interpretation of bulk mineralogical and chemical analyses, can be much better understood with the help of electron-microscopic analysis of polished thin sections (e.g. Pye and Krinsley, 1984; Primmer and Shaw, 1985; Nöltner, 1988: Huggett, 1989). Beyond smear-slide and X-ray diffraction evaluation, the mostly soft sediment cores from ODP and other operations in marine geology would greatly benefit from thin section petrography.

Ultrathin sections (UTS) are recommended to make microfabric features more easily visible (e.g. Bowles, 1968; Weaver, 1989). This is desirable because the detrital particles in shales and mudstones are typically smaller than the 30 micron thickness of the standard thin section, in which case grains and grain contacts may be masked or obscured. UTS should allow better evaluation of fabric parameters of shales, and may possibly lead to a classification of grain contacts within shales. One drawback of this approach is the need to double-polish the thin section, which increases the cost considerably.

Another microscopic approach to shale petrography is the examination of silt and sand-sized constituents in grain mounts after separation from the shale matrix. This furnishes additional information on the provenance of the fine-grained sediment and the diagenetic alteration of grains. Separation of this grain population by means of heavy liquids and/or magnetic separators allows a further split into light and heavy minerals, and facilitates the study of rare constituents which are not manifest in conventional thin sections. Auxiliary methods for analysis are SEM with an attached energy dispersive X-ray analysis system (EDS), or microprobe.

Light Minerals in Shales

Light-mineral analysis of shales deals with the insoluble wash residue of silt- to sand-size (after heavy mineral separation). Typically, the spectrum of grain sizes, grain shapes, grain types, and grain surface features is surprisingly large. Within the light-mineral crop, rare components are more likely to be detected. Examples of the examination of light-mineral crops in shales are studies of tuffaceous clays and tuffs (Gaida et al., 1978; Kemper and Zimmerle, 1978, 1982; Zimmerle, 1989; Keller et al., 1989), of Albian claystones from North Germany (Zimmerle, 1982), of the Oligocene Boom Clay of Belgium (Zimmerle, 1994, and this volume), and of the Oligocene Septarian Clay of NW Poland (Cedro et al. 1995).

Sodium bisulfite fusion is a rather useful technique when one wants to examine the quartz and feldspar fraction of mudstones and shales. The technique is described in detail by Blatt et al. (1982), and in essence consists of the fusion of pea-size shale fragments with sodium bisulfite over a Bunsen burner. Quartz and feldspar are the only minerals that survive this treatment, although caution needs to be exercised because altered and partially altered feldspars are liable to be destroyed in the process (Blatt and Caprara, 1985). The isolated quartz and feldspar grains can then be further examined with binocular microscopes, petrographic microscopes (grain mounts), and the SEM. One can also utilize the quartz and feldspar residues for further geochemical investigations (e.g. Charles and Blatt, 1978).

Heavy Minerals in Shales

Pertinent methods to study heavy minerals of fine-grained terrigenous clastics are:

(1) separation with heavy liquids, or heavy liquids in combination with centrifuging.
(2) SEM examination of polished thin sections in combination with an energy dispersive X-ray analysis system (EDS).
(3) radiographs of heavy minerals as high-density components (e.g. siderite layers).
(4) autoradiographs of radioactive minerals.
(5) fluorescence spectra of fluorescent heavy minerals (Aoki, Lorenc, and Zimmerle, 1987).
(6) cathodoluminescence spectra (Marshall, 1988).

Heavy mineral analyses of shales are rare, because conventional heavy mineral analysis within the 0.063-0.3 mm range is not adequate for fine-grained terrigenous clastics. Finer particle sizes (smaller than 0.063 mm) are difficult to separate by means of heavy liquids and this is the reason why silt- and clay-size heavy minerals never have been analyzed routinely. Nonetheless, further grain size fractionation of heavy minerals is recommended, either by means of polished thin section study down to 0.001 mm (Nöltner, 1988), or by time-consuming separation procedures (e.g. centrifuges). Examination of mineral separates by SEM is most practicable.

The entire heavy mineral spectrum between 0.001 and 0.5 mm has to be studied (Zimmerle, 1991) in order to cover all the heavy minerals and their varietal features. The reason for this is ,in part at least, the fact that certain heavy minerals may occur primarily in certain size fractions within their source rocks. The classical study of primary grain sizes and shapes of various minerals in igneous rocks by Feniak (1944) clearly demonstrated that igneous rocks of plutonic and volcanic origin display marked differences in primary grain size. Certain heavy minerals, such as brown spinel (picotite) occur primarily as accessory minerals in the extremely fine grain-size

fraction (Kubanek et al., 1988). In the Pleistocene diatomites of Lower Saxony, volcanic glass particles and volcanic augite are found mainly in grain-size fractions smaller than 0.053 mm (Riezebos and Zimmerle, 1988). Likewise, garnet and other metamorphic minerals abound in the coarser sand fraction, whereas zircon and apatite are dominant in the fine sand to silt fraction (Feniak, 1944). This complication has to be kept in mind when analyzing heavy minerals of shales. To rely on data from only one or a few size fractions could lead to erroneous conclusions.

Another marked difference between the heavy mineral composition of sandstones and fine-grained terrigenous clastics is the following: siltstones and shales commonly contain a larger amount of unstable heavy minerals than sandstones, because a high clay content protects heavy minerals from intrastratal solution and weathering. Not much has been published on this important aspect of heavy mineral analysis.

Moreover, small changes in heavy mineral contents can profoundly influence the bulk rock trace element composition for those elements that are strongly enriched in certain heavy minerals (e.g. Zr, Hf, REE). This is clearly demonstrated in the contribution by Totten and Hanan to this volume.

Certain heavy minerals, such as leucoxene, are quite common in mudstones and shales. Leucoxene is a collective term for very fine-grained, semiopaque to opaque alteration products of opaque titaniferous ore minerals, such as ilmenite. It typically consists of submicroscopic anatase, brookite, sphene, or rutile, or mixtures thereof (Zimmerle and Tietze, 1971). The so-called "Tonschiefernädelchen" of early petrographers (Rosenbusch and Wülfing, 1921) turn out to be very minute dispersed rutile prisms derived from the breakdown of biotite. They occur in varying amounts in most shales, but are normally not recognized or overlooked. Exceptionally high amounts of titanium bearing minerals are commonly derived from the weathering of basic volcanic rocks (e.g. basalt). According to the experience of one of the authors (W. Zimmerle), sphene is not as frequent among the alteration products of opaque titanium ores as commonly inferred. Brown spinel (picotite), either as thin translucent flakes or as minute octahedrons, occurs down to a grain size of a few microns. It indicates basic to ultrabasic (plutonic or volcanic) source rocks (Zimmerle, 1984; Kubanek et al., 1988). It is likely that with new separation methods accessory minerals of minute grain size, as yet undescribed, will be detected. In the following paragraphs we summarize results of some selected heavy mineral studies of shales, in order to show the potential of such an approach.

On of the earliest publication on heavy minerals in shales is by Schlünz (1935), who described heavy minerals (>0.02 mm) from a sample of the Toarcian Posidonia Shale of Mecklenburg/Germany. He reported opaque ore minerals, biotite, tourmaline, epidote, zircon, garnet, rutile, apatite, and small amounts of unstable heavy minerals, such as olivine, enstatite, hypersthene, and hornblende. The unstable minerals are very uncommon in sedimentary rocks of that age. They were probably only preserved because of enclosure in the very fine-grained matrix (74% of grains <0.001 mm) of a highly impermeable shale.

Another pioneering study is that by Blatt and Sutherland (1969), who found appreciable amounts of silt- and fine sand-sized non-opaque heavy minerals in Tertiary shales of the Texas Gulf Coastal Plain. The authors suggested that non-opaque heavy minerals in shales may be very important for correlation of down-dip basinal sections where diagnostic fossils are absent.

Heavy minerals in the 0.005-0.01 mm range of the lowermost Carboniferous of the Harz Mountains/Germany include zircon, apatite, monazite, various Ti-oxides, pyrite, marcasite, barite, chalcopyrite, galena, argentite, and gold (Nöltner, 1986). Of course, not all of these minerals were necessarily derived from an allochthonous source area. The sulfide and sulfate minerals are most likely of diagenetic origin (Maynard, 1983), and the gold may have been the result of complex organometallic reactions (e.g. Kucha, 1982; Parnell, 1988).

Non-Microscopic Methods

X-ray powder diffraction (XRD) is a basic tool in the mineralogical analysis of shales. Modern instrumentation and advanced automation give fast, but only semiquantitative results. Quantitative XRD analysis requires careful calibration and is more time consuming. Even then, results are sensitive to variations in sample preparation and presentation, as well as to irregularities in the powder matrix. For those reasons, "quantitative" XRD data of shales, although giving the impression of high accuracy through their numerical presentation, can be quite deceptive as every experienced crystallographer will admit. Nonetheless, the literature abounds with "quantitative" XRD data. Hardy and Tucker (1988) summarize the various techniques and their applications. Knowing the clay mineral composition can be useful for provenance studies (e.g. Starke, 1968, 1970; Morton, 1972) and for reconstruction of the burial history of shales (e.g. Weaver, 1980).

Recent studies suggest that application of the Rietveld method to XRD data of sediments can provide us with improved petrological modal analyses from X-ray powder diffraction data (Mumme et al., 1996). Mumme et al. (1996) report that depending on mineral assemblage, up to eight mineral components can be determined with a detection limit of about 0.5 weight percent.

Infrared absorption spectroscopy (IR), i.e. the observation of an absorbtion spectrum in the infrared range (0.0007 to 1 mm), is an auxiliary tool to better discriminate certain clay minerals, such as minerals of the kaolin group. In the same manner, differential thermal analysis (DTA), carried out by uniformly heating or cooling a sample, gives characteristic heating curves that are diagnostic of endothermic and exothermic chemical and physical changes within a given clay mineral (Langier-Kuzniarowa, 1973). Thermoluminescence (TL), successfully applied by Charlet (1971) in the study of sandstone provenance, might also be applicable in provenance studies of argillaceous rocks.

X-radiography (Hamblin, 1971) and autoradiographs are additional methods for studying textures of shales and differences in mineral composition and distribution. Best results in X-radiography are obtained with relatively uncompacted muds and clays. Under those circumstances they may reveal features that would otherwise go unnoticed. With increasing degree of consolidation, however, the amount of detail diminishes. In the authors' experience, in fully consolidated shales thin section study tends to reveal more features than X-radiography. An interesting variant of X-radiography, where a traveling core stage is used to ensure uniform exposure and resolution, has been developed by Algeo et al. (1994). Contributions by Jaminski et al. (this volume) and Hoffman et al. (this volume) demonstrate how this method can be applied successfully to the analysis of small scale compositional variations in black shales.

Color is an important but much neglected topic in the study of shales. It is a scalar property, and shales display a large range of colors, predominantly shades and hues of blacks and grays, greens, browns, yellows and reds. Unfortunately, color determinations are always biased by environmental conditions and human insufficiencies. They depend on the moisture content of the rock, whether observation was made with natural or artificial light, and on the smoothness of the observed surface. Human factors include the color sense of the observer and the state of eye fatigue (e.g. during continuous logging of drill cuttings). More objective color determinations can be made with comparison charts. A variety of these is available (Potter et al., 1980), but the Munsell color chart (Munsell Color Co., 1975) is probably most widely used. Physical measurements by means of normed equipment are superior to comparison charts, but cumbersome and time consuming.

Shale color reflects the sum of the color spectra of its constituents. Potter et al. (1980) consider the amount of iron, its oxidation state, and the amount of organic carbon, the dominant factors that determine shale color. Many geologists have associated certain shale colors with particular depositional environments (e.g. Conybeare, 1979), and that for example greenish-gray shales are often shallow marine, whereas red colors are indicative of fluvial settings is pointed out in many textbooks (e.g. Boggs, 1987). Color, however, is usually not a direct product of the depositional environment, but rather a result of diagenetic processes. Thus, there are numerous exceptions to the standard interpretations one commonly hears concerning the environmental significance of shale color (e.g. Conybeare, 1979). Regional case studies where color figured significantly in the final conclusions are e.g. those of Morad (1983; Proterozoic sediments of Sweden), Hosterman (1994; Devonian black shales of Appalachian basin), Schünke (1984; Triassic of SW Germany), McBride (1974; Difunta Group, NE Mexico), and Stehli et al. (1972).

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