

## Provenance of Mudstones

*Like detective work – fingerprinting samples and profiling suspects*

### 7.1. Introduction

How can we determine the immediate source of the constituents in a mudstone or even its ultimate crystalline rock sources (Table 7.1)? A wide range of techniques exist for this endeavor, and, because the kind of provenance information that is obtained is strongly dependent on which of these techniques is brought to bear, we arrange our discussion according to these methods, as outlined in (Table 7.2).

But before we address the questions that these provenance techniques can answer, let's first ask another, "Why bother?" Recalling that the term provenance comes from the French verb *provenir* meaning to supply or provide for, sedimentary geologists use this term to infer the relief, composition, climate and location of the source area of a terrigenous deposit. Such information helps us establish the broad paleogeographic setting of the source and infer

transport paths from source to sink. Achieving these goals also gives us better insights to the tectonic evolution of the source area, perhaps now vanished, or to the original mineralogy of the sedimentary deposit before alteration by burial diagenesis. Moreover, understanding differences in provenance might help explain why two mudstones with similar diagenetic paths have different final compositions.

Historically, these provenance goals were achieved mostly using sandstone petrology and paleocurrent studies, but today there is a growing effort to employ chemical study of the fine fraction of mudstones. Good methods to determine the provenance of both the mudstone and its interbedded siltstones and sandstones would permit us to answer questions such as, "Were both derived from the same source or did the muds come from one source, perhaps far distant, and the sands and silts from another, perhaps nearby?" or "Is there a significant windblown or vol-

**Table 7.1.** Suggested components of muds and sands from different tectonic settings and weathering intensities

Tectonic Setting	Moderate Weathering	Strong Weathering
<b>Igneous Rocks</b>		
Plateau basalts	Fe oxides, smectite, little sand	Fe oxides, some smectite with kaolinite and gibbsite
Island arcs	Smectite with volcanoclastic sands	Smectite and kaolinite with volcanoclastic sands
Continent-margin arcs	Smectite and illite with quartzo-feldspathic and volcanoclastic sands	Smectite, illite and kaolinite with quartzo-feldspathic and volcanoclastic sands
Basement uplifts	Illite with quartzo-feldspathic sands	Kaolinite with quartzose sands
<b>Sedimentary Rocks</b>		
Fold-thrust belts & strike-slip terranes	Recycled illite, chlorite, kaolinite plus some new smectite; quartzo-feldspathic sands	Recycled illite, chlorite and kaolinite plus abundant new kaolinite; quartzose sands
Craton interiors	Recycled illite, chlorite and kaolinite; quartzo-feldspathic sands	Recycled illite, chlorite and kaolinite plus abundant new kaolinite; quartzose sands
<b>Metamorphic Rocks</b>		
Mountain belts	Recycled chlorite, muscovite, illite; quartzo-feldspathic sands	Recycled chlorite, muscovite, illite with new kaolinite; quartzose sands
Precambrian shields	Recycled muscovite, illite; quartzo-feldspathic sands	Recycled muscovite, illite with new kaolinite; quartzose sands

Table 7.2. Common provenance techniques for mudstones

Techniques	Inference ( <i>italics</i> ) and Commentary						
<b>Field properties</b>							
Paleocurrents	<i>Both give direction to source.</i> Sands and mudstones may have different current systems, however, and color of particles may be either acquired in situ (soil) or be detrital.						
Color							
<b>Petrographic study</b>							
Quartz content	<i>Both indicate proximity and direction to source.</i> Fortunately, both are independent of diagenesis. Size gradients in phenocrysts in ash falls identify locations of volcanic arcs and rifts (many studies). Quartz content most rapidly determined by x-ray diffraction and less accurately by gamma ray log (few studies).						
Size gradients of phenocrysts in volcanic ash							
Thin section study	<i>Silt-sized grain types.</i> Special preparation of thin sections required and much petrographic skill. Few studies.						
<b>X-Ray Study</b>							
Kaolinite	<table style="border: none;"> <tr> <td style="border: none;"><i>Weathering intensity</i></td> <td rowspan="4" style="font-size: 3em; padding: 0 10px;">}</td> <td rowspan="4">All techniques widely used in studies of modern muds, but not used extensively in ancient mudstones, because of diagenesis and low-grade metamorphism. X-ray study also separates polytypes such as IIb chlorites.</td> </tr> <tr> <td style="border: none;"><i>Volcanic and other sources</i></td> </tr> <tr> <td style="border: none;"><i>Mechanical vs. chemical weathering</i></td> </tr> <tr> <td style="border: none;"><i>Weathering intensity</i></td> </tr> </table>	<i>Weathering intensity</i>	}	All techniques widely used in studies of modern muds, but not used extensively in ancient mudstones, because of diagenesis and low-grade metamorphism. X-ray study also separates polytypes such as IIb chlorites.	<i>Volcanic and other sources</i>	<i>Mechanical vs. chemical weathering</i>	<i>Weathering intensity</i>
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<i>Volcanic and other sources</i>							
<i>Mechanical vs. chemical weathering</i>							
<i>Weathering intensity</i>							
Smectite							
Chlorite							
Illite crystallinity							
<b>Chemical study</b>							
Major elements	<i>Weathering intensity.</i> Both CIA and Rb/K may be modified by diagenesis such as potassium addition, whereas, the ratios CIW and ICV are less affected by diagenesis. Statistical studies of the whole array of elements are becoming more popular.						
CIA <sup>1)</sup> , Rb/K CIW <sup>2)</sup> , IC <sup>3)</sup>							
Traces	<i>Ratio of felsic to mafic rocks.</i> Selective ratios of both trace elements and the 14 REE's are useful for distinguishing proportions of felsic and mafic rocks – thorium and zirconium indicate a felsic source and scandium and chromium a mafic one.						
Th/Sc							
Zr/Cr							
<b>REE</b>							
Eu/Eu*	A strong negative europium anomaly indicates felsic rocks, as does a high LREE/HREE, often approximated by lanthanum/ytterbium (Caution: ratio may be affected by intense weathering). Many studies since 1990, although still fewer than provenance studies of the sand fraction.						
La/Yb							
Isotopes	<i>Ratio of volcanic to cratonic source rocks.</i> Volcanic rocks tend to be close to mantle values for this ratio, whereas cratonic sources are much more radiogenic. Values tend to be altered by burial diagenesis.						
<sup>87</sup> Sr/ <sup>86</sup> Sr							
$\epsilon_{Nd}$	<i>Model age of initial source terrain.</i> Same advantages of REE's, but gives numerical age of separation of igneous rock from mantle.						

<sup>1)</sup> Chemical index of alteration, <sup>2)</sup> chemical index of weathering, and <sup>3)</sup> index of chemical variability

canic component in the mudstone compared to the sandstone?” or “Has there been chemical exchange between mudstone and sandstone parts of a turbidite bed?” Below we emphasize methods to determine the provenance of mudstones, building upon the long tradition of provenance studies of sandstones. In so doing we recognize that the clay fraction is more likely to be modified chemically and mineralogically by both weathering in the source and by burial diagenesis than is the sand fraction. We also note that some of the provenance techniques below are based on gradients within the depositional basin whereas others are based on the composition of grains (isotopic or REE values obtained from a detrital mineral) derived far from the basin.

Finally, we note that the long transport distances characteristic of muds favor mixing of particles from different sources. Because of this long transport with potential for mixing, the mineralogy and chemistry

of marine mudstones averages provenances from large areas and over extended periods of time compared to sandstones, which tend to reflect more immediate sources. This contrast provides the potential to obtain two somewhat different kinds of provenance information from study of a terrigenous section.

## 7.2. Stratigraphic Methods: Architecture of the Basin Fill

The distribution of facies in a basin, stacking patterns, and the orientation of its clinofolds tell us much about how mud and silt were transported into and across a basin and thus frequently give us an early indication of the location of the source of its terrigenous detritus. This is well shown by a Cretaceous basin in eastern France near Grenoble

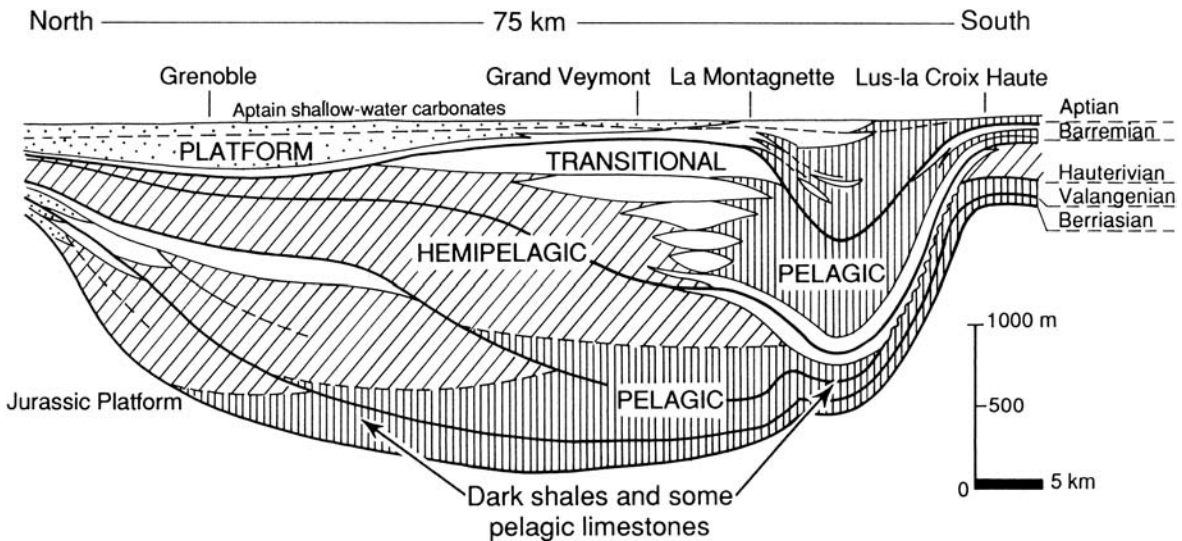


Fig. 7.1. Cross section of a Cretaceous carbonate-rich basin in eastern France has an asymmetrical fill suggesting

progradation and influx of mud from north to south (Arnaud et al. 1984, Fig. 6.21)

(Fig. 7.1). Here basin fill is very asymmetrical from north to south – carbonate pelagics dominate the south side, hemipelagics the north side, and stacking pattern progrades from north to south. Thus, as a *first approximation*, we infer that the basin was filled from north to south. But to be sure, of course, we need to know more – did a land mass exist to the north or was there instead a vast carbonate tidal flat? Or is there reason to believe that longitudinal transport of fines from the east was important? Dip direction of clinoforms, which can be read from seismic sections, and sometimes with good outcrops from the field (Chap. 8), would be most telling here.

### 7.3. Petrographic Methods: Interbedded Sandstones and Siltstones

Much provenance information is carried by the composition of framework grains of interbedded sandstones and siltstones, and there is a long history of efforts to obtain this kind of information (Pettijohn et al. 1987; Zuffa 1985). Insights obtained in this way should always be combined with paleocurrent studies where possible, and ideally every comprehensive provenance study of mudstone should include the paleocurrents of the interbedded siltstones and sandstones. Because this has rarely been done, most sandstone-based provenance studies simply assume that interbedded muds and mudstones were derived from the same source. To see this problem better, think of the Mississippi delta whose muds and sands

are all brought to the Gulf of Mexico by the same river and then think of the far-traveled, Andean-derived, coastal muds of Suriname of northeastern South America interbedded with minor sands derived from the nearby Guyana Shield (Fig. 5.33).

Petrography can also sometimes be applied directly to the mudstone itself. Polished thin sections are especially helpful, as in the Eocene-Oligocene Boom Clay of Belgium, which contains 20 to 40% coarse silt and fine sand (Zimmerle 1993). Strong diagenesis obscured the distinctions between primary and secondary clays, but the coarse fraction contained altered volcanic glass and basalt followed by trachyte as the most abundant rock fragments, indicating a volcanic source that was interpreted as being some 200 to 400 km distant. Petrographic study also helped establish a prodelta marine shelf as the most probable environment of deposition (glauconite, large mica flakes, much fine silt).

In addition to the standard petrographic provenance interpretations of detrital grains of sandstone and siltstone, more and more use is made of single-grain analyses, such as SHRIMP (Sensitive High Resolution Ion Micro-Probe) determinations of  $^{207}\text{Pb}/^{206}\text{Pb}$  to determine ages of detrital zircons to match against known ages of possible source rocks (Santos et al. 2002). A similar application of the ion microprobe is measurement of oxygen isotopes on single silt-sized quartz grains. Aléon et al. (2002) used this procedure to trace dust sampled at the Cape Verde Islands back to sources in the Sahara (Fig. 7.2). Perhaps we will soon see instrumental advances that

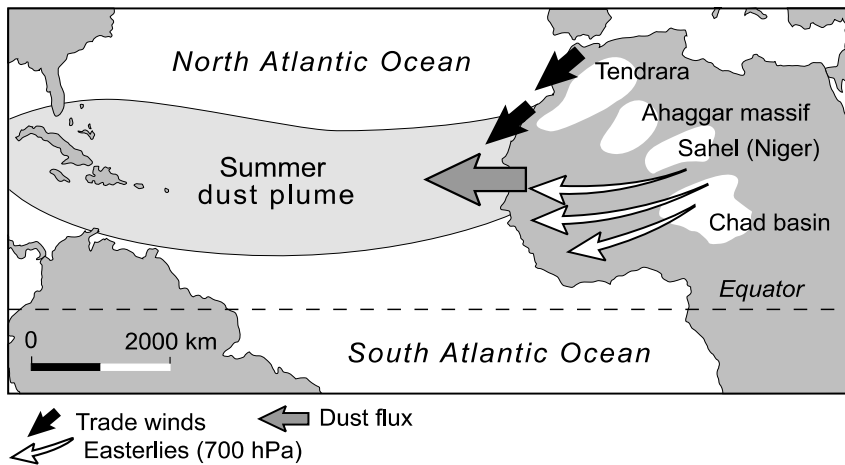


Fig. 7.2. Study of oxygen isotopes of single quartz grains by ion microprobe shows the source for the Saharan dust plume to be mostly from the Niger region (after Aléon et al. 2002). Published by permission of the authors and Pergamon Press

permit this sort of work to be done routinely on fine-grained mudstones.

A very informative component of the silt fraction is the type of particle referred to as a *phytoclast*. These are particles such as wood fragments, pollen

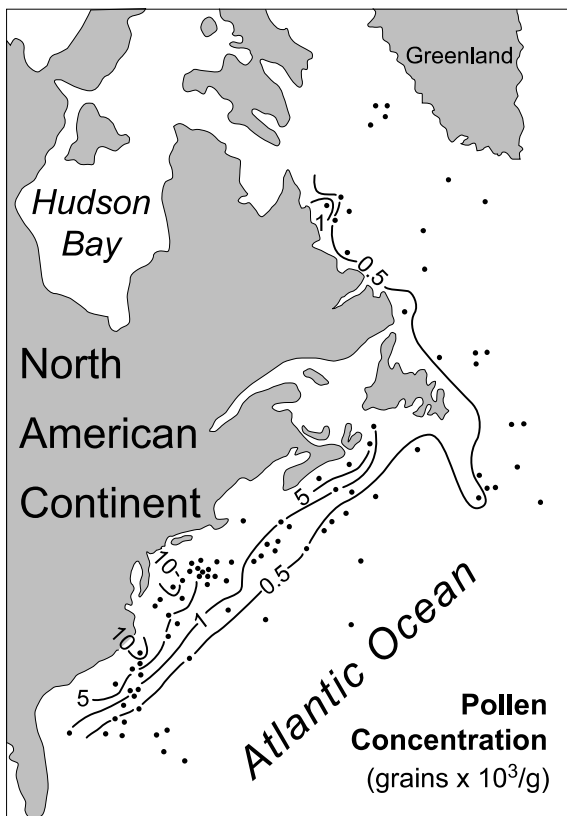
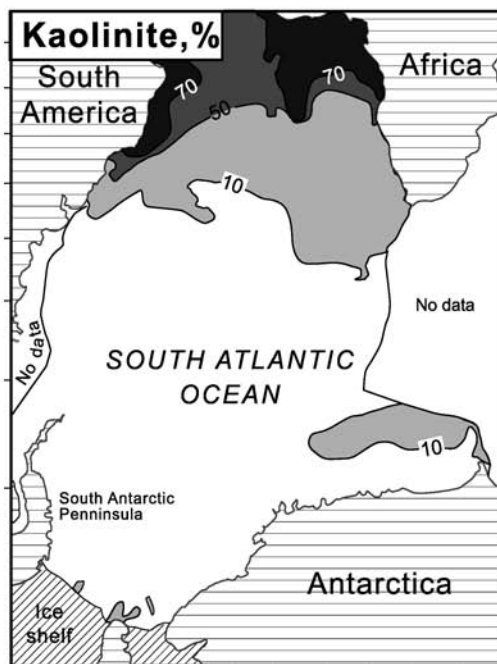
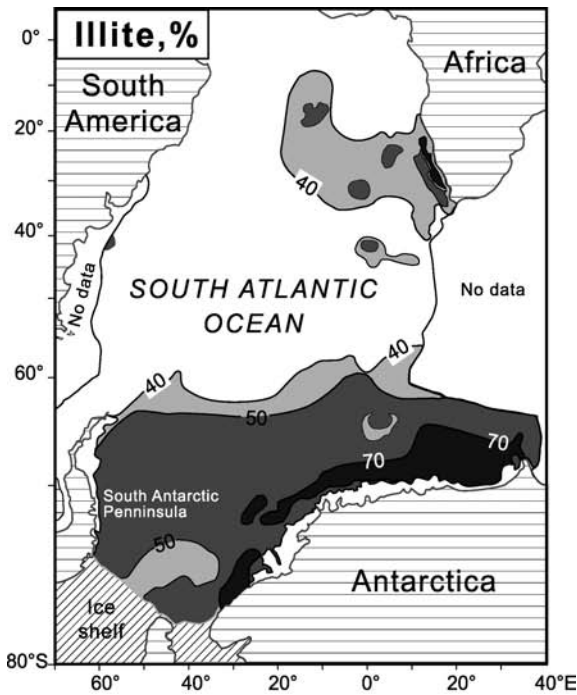


Fig. 7.3. Total pollen grains in sediments from the North Atlantic falls off systematically with distance from the shoreline, except in regions of very cold climate (after Tyson 1995, Fig. 13.13)

grains, or leaf cuticles, and are generally less than 1 mm in size, with the dominant size range 20–50  $\mu\text{m}$ . This material is hydrodynamically equivalent to silt (Tyson 1995, p 215), and commonly is concentrated with the silt fraction, but its lower density makes it more prone to resuspension, so current reworking can lead to organic-rich and organic-poor layers. Mapping of the percent woody fragments can potentially provide a proximal-distal indicator for marine sediments, as was shown in early work by Shepard (1956), but it is more common to use a chemical proxy such as carbon isotopic measurements (see Chemical Methods, below). A phytoclast measurement that is commonly made for modern sediments is the percentage of pollen grains (Fig. 7.3). Pollen falls off rapidly, but more-or-less regularly with distance from the shoreline so it makes a good proximity indicator, except in sub-polar regions where the abundances are vanishingly low. This technique is less used in the ancient and would not apply to rocks older than the Devonian, when land plants were not widely established.

#### 7.4. Mineralogical Methods

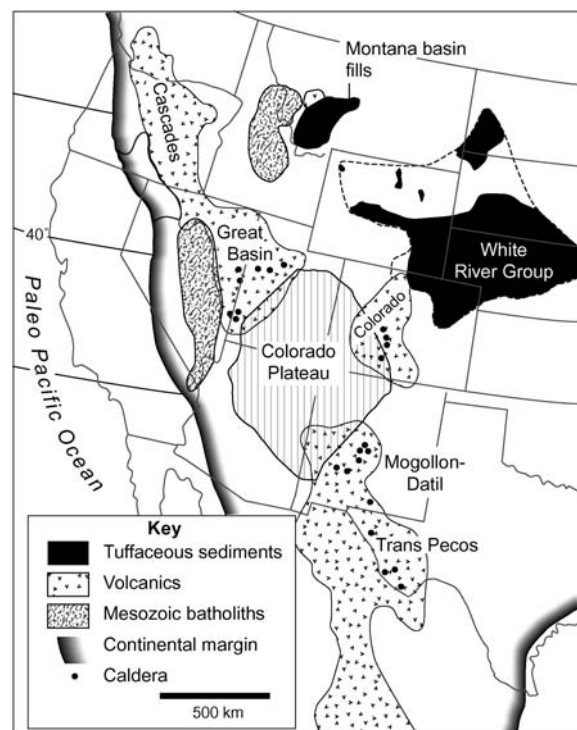
For muds, clay mineralogy has been the mineralogical procedure most often applied to reconstruct provenance. Clay mineral distribution in the South Atlantic Ocean (Fig. 7.4) illustrates well the utility of systematic study of clay distribution in modern muds and in Tertiary and Mesozoic deposits (before appreciable burial diagenesis converts most of the original metastable components into illite-chlorite). In the modern Atlantic, illite and kaolinite have reciprocal abundances: illite predominates off Antarctica (minimal weathering), whereas kaolinite predominates between the tropical coasts of Africa and Brazil



**Fig. 7.4.** Provenance control of illite and kaolinite in the clay fraction of sediments from the South Atlantic Ocean (after Petschick et al. 1996, Figs. 5 and 8). Illite dominates all the coast of Antarctica and the southwest coast of Africa around the mouth of the Orange River because of minimal chemical weathering (frozen or arid conditions). Kaolinite dominates in the low latitudes because of intense weathering under humid tropical conditions. Map patterns based on over 900 analyses. Published by permission of the authors and Elsevier Science

(maximal leaching in the humid tropics). This distribution is the response to two climate extremes and shows well the importance of considering climate when using clay mineralogy as a provenance indicator; if we could reverse the climates of Antarctica and tropical Brazil and Africa, we would only need to switch the labels of the two maps – nothing more.

A volcanic component in the provenance of a mudstone imparts a strong signal to its clay mineralogy. Tertiary volcanism in the western United States has resulted in a series of alluvial deposits rich in fine and coarse volcanogenic debris. A good example is the White River series of mid- to late Tertiary age in Nebraska and adjacent states (Fig. 7.5), which is composed of massive clay- and silt-rich rhyolitic tuffs, now highly altered. These were deposited by streams and wind over a wide area as a thin non-marine “molasse” cap over fine-grained marine Cretaceous rocks. Alteration products such as smectite, opal, zeolites, and calcite dominate the mineralogy of these deposits (Lander and Hay 1993).



**Fig. 7.5.** Tertiary volcanic provinces of western North America and their associated blankets of tuffaceous sediments. Erosion of these sediments contributes much of the suspended load of the Missouri River, and thus imparts a strong volcanic signal to sediments of the Mississippi system (Terry et al. 1998, Fig. 5.). Published by permission of the authors and the Geological Society of America

Because these molasse deposits are easily eroded, they form badlands and are major contributors to fines carried to the Gulf of Mexico by the Missouri and subsequently the Mississippi Rivers. The smectite fraction in the western tributaries of the Mississippi typically varies between 45 and 60%, whereas this clay is notably less abundant in the eastern tributaries (Fig. 7.6). This volcanic provenance persists throughout the > 6,000-kilometer length of the Missouri-Mississippi main stem, despite many cycles of reworking, including strong weathering of alluvial deposits in the lower Mississippi Valley. Another example of long-distance transport of fines is the Amazon River, which carries an Andean signature (mica > quartz > smectite = kaolinite > plagioclase > K-feldspar > chlorite and small metamorphic rock fragments) to its mouth and beyond to the coastal muds of Surinam and the Guayanas (Gibbs 1967; Eisma and Van der Marel 1971). Moral: fine-grained suspension load is easily transported from one side of a continent to another, so that a mineralogical signal can be registered by muds very far from their sources.

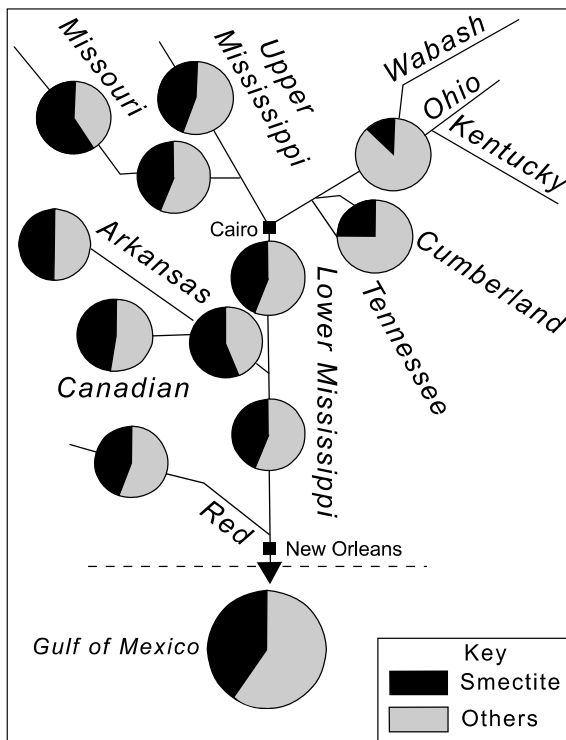


Fig. 7.6. Clay mineralogy of the Mississippi and its tributaries shows abundant smectite in the western tributaries and its lower abundance from the eastern tributaries, with the lower Mississippi and the delta retaining the strong signal of the smectite-rich western sources (after Potter et al. 1975, Fig. 13)

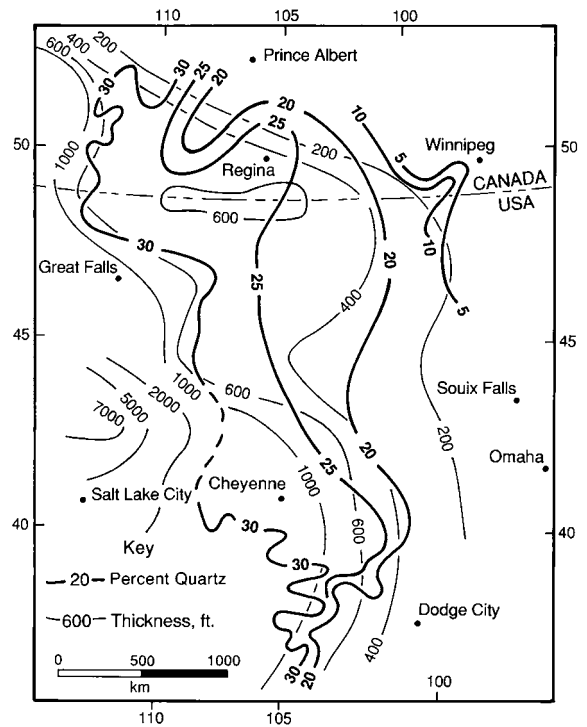


Fig. 7.7. Quartz silt content of Cretaceous Pierre Shale in the High Plains of the United States broadly outlines the source of the mud – the rising Rocky Mountains to the west (Jones and Blatt 1984, Figs. 2 and 3). Published by permission of the authors and the Society for Sedimentary Geology

Measuring the size and amount of quartz grains in the silt fraction of a mud or a mudstone is another approach, although one that has not been widely used because it is so tedious and sampling is not easy in mudstones. In the Cretaceous of the High Plains of United States and southern Canada a map of quartz content clearly identifies the ancestral Rocky Mountains as the source of the mud and silt of the mudstones in the Pierre Shale (Fig. 7.7).

Shoreline indicators such as the systematic mapping of clay mineralogy, palynomorphs, and grain size are all examples of *proximal-distal indicators*. This is the first step to paleogeographic and provenance insight. Below we show that systematic determination of chemical variables in mud and mudstones plays a similar role, but also provides information about the character of the source area.

### 7.5. Chemical Methods

Most of the provenance studies of mudstones use chemical methods, because separation of individual minerals is difficult, although there are a few studies of heavy minerals in mudstones (e. g. Totten and

Hanan 1998). This section presents various chemical methods of provenance determination, which, as pointed out above, always should be accompanied by petrographic study of the companion sandstones and siltstones.

We divide these chemical methods into groups – major elements, trace elements, and radiogenic and stable isotopes – that correspond to their abundance in common rocks and therefore to the instrumentation needed to measure them. Major element chemistry has been a staple of mudstone studies since at least the early 1900s. Today it is done rapidly and inexpensively by X-ray fluorescence (XRF). Some trace elements can also be measured by this technique, but many of those of greatest interest have concentrations too low for this technique, and more expensive methods such as instrumental neutron activation analysis (INAA) or inductively coupled plasma (ICP) must be employed. The neutron activation techniques have the advantage of using the solid sample directly without dissolving it, but have the disadvantage of missing some key elements. ICP, especially when combined with mass spectrometry (ICP-MS), provides very low detection limits for the greatest number of elements, but is correspondingly expensive and requires the sample to be completely dissolved. Some mineral grains such as zircons, which are very rich in heavy rare-earth elements, are extremely difficult to dissolve and extra care must be taken to ensure complete dissolution. Isotopic measurements are the most powerful ways to study geochemistry, but they involve labor-intensive separations and extremely expensive instrumentation.

### 7.5.1. Major Element Chemistry

Provenance studies of mudstones that use major elements as their dominant technique are quite rare, perhaps because of the potential for post-depositional alteration. One promising approach is to use discriminant analysis, as shown by Roser and Korsch (1988). They studied turbidite mudstones and sandstones from New Zealand and found that simple bivariate plots did not separate their samples, but that cross-plotting discriminant functions largely eliminated overlap between populations. Mudstone and corresponding sandstones plot in the same fields, which provides strong evidence that both had the same provenance.

Major element chemistry is perhaps best employed to determine the extent of weathering of the source terrain, once the general tectonic setting has been established by other means. Several chemical

indices have been proposed to quantify weathering effects. The most popular is the *chemical index of alteration* (CIA) defined as

$$[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{K}_2\text{O} + \text{Na}_2\text{O})] \times 100$$

where CaO\* is Ca exclusive of carbonates and the values are in molar proportions to emphasize mineralogical relationships (Nesbitt and Young 1982). High values of the index, greater than 90%, indicate extensive conversion of feldspar to clay and hence intense weathering. Lee (2002) used this parameter to characterize Permo-Triassic mudstones from Korea. These rocks show a trend of decreasing CIA values upwards for each formation, which indicates less weathered detritus upwards. Taken by itself, this trend would indicate progressive unroofing of a weathered granitic source area. However, petrographic study of associated sandstones revealed that those formations with high CIA values also have abundant sedimentary rock fragments, an indication that the high CIA values were produced in part by recycling of older sediments rather than by intense weathering of igneous rocks. The vertical change may reflect mixing of first-cycle and recycled sources as much as a change in weathering intensity. Thus this study provides an object lesson in the value of combining petrographic work with geochemistry.

A limitation of the use of the CIA parameter is the prevalence of post-depositional K addition to older clastic rocks (see Chap. 6). Accordingly some workers have preferred a K-free index, the *chemical index of weathering* (CIW), defined as

$$[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O})] \times 100$$

Harnois (1988).

Both the CIA and the CIW indices reflect mostly the amount of feldspar relative to clay minerals, and therefore neither index is strongly sensitive to the type of parent rock. CIA values for unweathered terrestrial basalts are in the range of 40 to 50 whereas for granites the range is 50 to 55. A better discrimination of parent rock types would include Fe and Mg. Cox et al. (1995) proposed a measure called the *index of compositional variability* (ICV):

$$\begin{aligned} & (\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{Fe}_2\text{O}_3(\text{t}) \\ & + \text{MgO} + \text{MnO} + \text{TiO}_2)/\text{Al}_2\text{O}_3 \end{aligned}$$

where  $\text{Fe}_2\text{O}_3(\text{t})$  = total iron and CaO includes all sources of Ca. In this index, the weight percents of the oxides are used rather than moles, and the values *decrease* with increasing degree of weathering. Average basalt and average granite Li (2000) yield

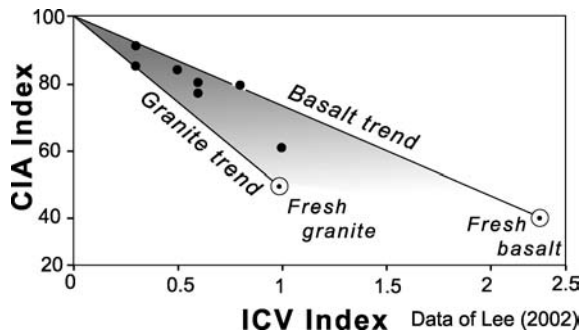


Fig. 7.8. Two indicators of weathering, Chemical Index of Alteration (CIA) and Index of Chemical Variation (ICV) in Late Paleozoic and Early Mesozoic mudstones from Korea (data of Lee 2002)

strongly contrasting ICV values of 2.20 and 0.95. An interesting view of major element chemistry comes from a crossplot of CIA against ICV values. Figure 7.8 shows formation averages from the data of Lee (2002) compared with the rock class averages. Mudstones with the same degree of weathering (the same CIA) commonly have rather different ICV values, indicating differences in the composition of the source area.

7.5.2. Trace Element Chemistry

The ultimate igneous source for a mudstone can usually be categorized easily as relatively mafic or relatively felsic by using trace elements. For example, the elements Ni and Cr are abundant in ultramafic and mafic rocks, but are scarce in rocks of more felsic composition. Thus they are good indicators of ophiolitic sources, and their sudden appearance in a vertical profile may indicate the onset of arc-

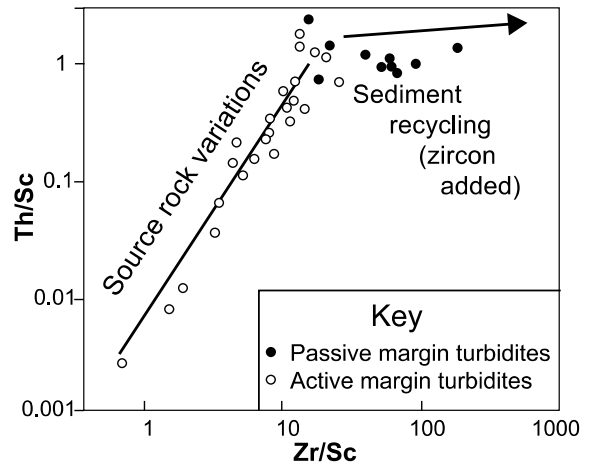


Fig. 7.10. The Th/Sc ratio and the Zr/Sc ratio increase going from mafic to felsic source areas, but passive margin muds show anomalous Zr related to recycling of older sediments (after McLennan et al. 1993, Fig. 3). Published by permission of the authors and Pergamon Press

continent collision in the source area. Also useful is Zr, which is much more abundant in felsic rocks, so plots of Ni/Zr or Cr/Zr are useful to quantify the proportion of mafic material in the source area (Fig. 7.9). Weathering and diagenesis can alter these ratios, however, so it is preferable to use less soluble elements than Ni in provenance studies. Th, Sc, and to a lesser extent Cr, are good indicators of sedimentary provenance, because they are quite insoluble, and thus are transported almost exclusively by terrigenous detritus. Thus they reflect faithfully the chemistry of their sources. They are mostly used in bivariate plots (Fig. 7.10) as aids to detect mixing processes in sediments. For example, Condie and

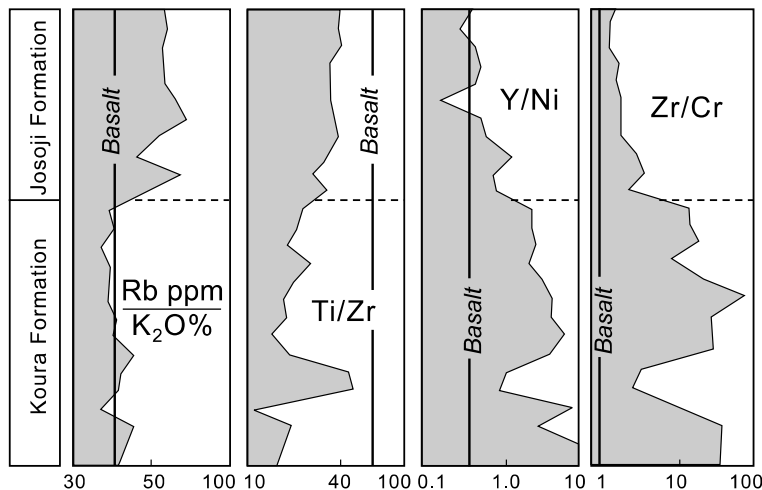


Fig. 7.9. Vertical chemical profile of two Miocene mudstones from the opening of the Sea of Japan shows their changing provenance (after Ishiga et al. 1999, Fig. 7). Interval is about 70 m thick and contains diverse mudstone types with some interbedded sandstones and tuffs. Published by permission of the authors and Pergamon Press



### Box 7.1. Rare-earth elements

Although REE are found in very low concentrations in most natural environments, they are widely used as geochemical tracers. Only rarely do they individually reach concentrations of more than a few parts per million (milligrams per kilogram), as when they were discovered in 1787 by CA Arrhenius in a pegmatite at Ytterby, near Stockholm, Sweden. Lanthanum (La,  $Z = 57$ ) and the remaining *lanthanides* (from cerium, Ce,  $Z = 58$  to lutetium, Lu,  $Z = 71$ ) are the chemical elements known as rare earths. Most have stable trivalent states. The exceptions are Ce, which can also occur as  $Ce^{4+}$  and is used to track oxidation states of water masses and soils, and Eu, which, in igneous processes, can be reduced to  $Eu^{+2}$  and selectively removed compared to its neighbors. Most other chemical properties of all 14 elements, together with lanthanum, are remarkably similar. The “light rare earths” (LREE, La-Sm) are *incompatible* chemical elements (i. e., are elements which, during magmatic crystallization, are not easily included in the structures of principal minerals and thus become progressively enriched in the diminishing amount of residual liquid). Owing to their smaller ionic radii, the “heavy rare earths” (HREE, Gd-Lu) are more easily incorporated into the crystal structures of rock-forming minerals, and these *selectively compatible* REE are hosted by a number of igneous minerals, like feldspars, hornblende, sphene, pyroxenes, garnet, and zircon. Therefore the light to heavy ratio is a useful tracer of igneous differentiation.

REE are commonly reported normalized either to chondrite values or a composite of mudstone analyses (e. g. NASC) and displayed on spider diagrams. The critical provenance parameters that are extracted from these diagrams are the Eu anomaly ( $Eu/Eu^*$ ) and the ratio of the light to the heavy rare-earth elements,  $\sum LREE/\sum HREE$ . The Eu anomaly is calculated from

$$Eu/Eu^* = Eu_N / [(Sm_N)(Gd_N)]^{1/2}$$

where  $N$  refers to the normalized values and

$$La_N/Yb_N$$

is used as a proxy for  $\sum LREE/\sum HREE$ .

Wronkiewicz (1990), McLennan et al. (1990), and McLennan and Taylor (1991) and have favored the use of plots such as Th/Sc against Sc, and Cr/Th against Sc/Th as indicators of the proportions of felsic and mafic source rocks.

Of the trace elements, the most valuable in geochemistry are the *rare earth elements* or REE (Box 7.1), because they are not fractionated from each other by most sedimentary processes. They are largely insoluble under most geological conditions and thus are present in very low concentrations in river water and seawater (typically, from  $10 \times 10^{-7}$  to  $10 \times 10^{-2}$  of the levels found in most rocks). Weathering releases them from primary minerals in the soil, but they are generally retained and concentrated within the weathering profile (Nesbitt 1979) in secondary minerals. Once eroded, these soil minerals then faithfully record the REE signature of the parent material (but watch for Ce variations). Clay minerals typically have much higher total REE concentrations than coarser size-fractions (Cullers et al. 1987), and appear to be the most important mineral fraction in hosting REE in mudstones (Condie 1991).

REE concentrations remain unaffected by most geological post-depositional processes; diagenesis, for instance, typically has little influence on the redistribution of the REE because very large water/rock ratios are required to effect any change in their sedimentary chemistry (but see Lev et al. 1998, for an exception).

REE patterns are shown normalized to either a chondrite meteorite standard or to a composite of mudstone analyses to eliminate the strong differences in cosmic abundance of even vs. odd atomic numbers. Mudstone-normalized patterns (Fig. 7.11) are used for sedimentary rock studies because they emphasize subtle differences among sediments and thus provide a method of identifying specific sources of mud and mudstones (McLennan 1989). Comparison to a shale standard quickly shows the amount of departure, if any, that the mudstone under study shows from typical mudstones, and deviations of specific elements identify slight enrichments and deficiencies that shed light on provenance. Owen et al. (1999) supply an example – among many others – of the potential uses of REE normalized patterns as

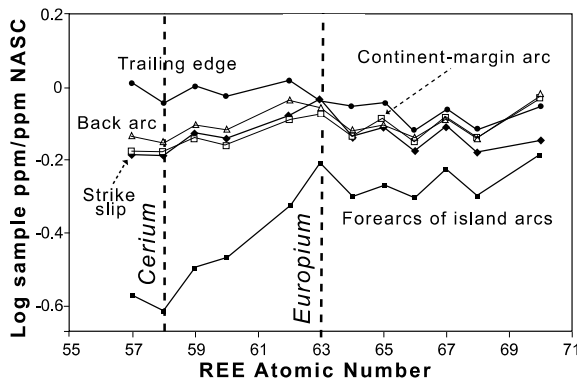


Fig. 7.11. REE profiles for muds from various tectonic settings are similar except for LREE enrichment in Trailing Edge basins and severe LREE depletion in Fore-arc Basins. Back-arc, continental arc, and strike-slip basins are indistinguishable. Data of McLennan et al. (1990) averaged by tectonic setting

provenance indicators. They determined the REE in radiolarian cherts and siliceous mudstones of upper Ordovician age from the Southern Uplands (Scotland) and established that REE signatures can be used as fingerprints to differentiate some of the fault-bounded formations within the study area, and that the provenance for the mudstones had two components: a mature continental block and an andesitic source.

A Precambrian example is provided by Eriksson et al. (1992), who studied the Mt. Isa Basin, an im-

portant host of Pb-Zn mineralization that had at least two phases of rift development. The upward trend in this basin is towards lower values of  $\text{Eu}/\text{Eu}^*$ , increasing Th/Sc, and decreasing concentrations of Cr, Ni and Co. All of these parameters point to an increasing felsic contribution to the fine-grained detritus in the basin fill as the basin developed. The lower part of the succession, where accommodation space in the basin is generated primarily by mechanical subsidence along rift-boundary faults, has more variability in composition, reflecting variable local source rocks. By contrast, the later sag phase, where broad thermal subsidence dominates, has very uniform REE compositions, reflecting long transport under stable tectonic conditions.

### 7.5.3. Isotope Chemistry

**Radiogenic Isotopes.** Isotopes make ideal tracers in the study of sedimentary rock provenance because isotopes of the same element tend to travel together through the sedimentary system, preserving their original source-area signatures. An array of radioactive isotopes has been employed in studies of modern muds, with a somewhat more limited suite used for mudstones (Table 7.1). One that has seen much use in modern sediments is the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (Box 7.2). This application was pioneered by Dasch (1969), who demonstrated that even the finest clays in the deep-sea are not in isotopic equilibrium with

#### Box 7.2. Radioactive Isotopes: Strontium

Strontium isotopes are useful tracers of the sources of modern muds. The method is based on the radioactive decay of  $^{87}\text{Rb}$ , which has a half-life of  $4.88 \times 10^{10}$  years, and produces  $^{87}\text{Sr}$ . The ratio of the concentration of  $^{87}\text{Sr}$  to stable, non-radiogenic  $^{86}\text{Sr}$  is used to infer the source of Sr in muds or mudstones as well as in water (Faure 1986:183–199). The Sr isotopic composition and Sr concentration in fine-grained sediment accumulating in the oceans is controlled by, a) detrital minerals, whose Sr isotopic signature is determined by either the weathering products of predominantly young volcanic rocks ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.704 \pm 0.002$ ), or by those derived from old continental, radiogenic rocks from the crust ( $^{87}\text{Sr}/^{86}\text{Sr}$  generally above 0.730 and commonly as high as 0.800), and b) authigenic minerals (carbonates, sulfides, silicates, etc.), whose  $^{87}\text{Sr}/^{86}\text{Sr}$  is identical to that of the sea water from which they formed. Under advantageous geologic conditions, the noncarbonate fractions can be treated as mixtures of two end-members: the weathering products of young volcanic rocks of basaltic composition at one extreme, and old crustal rocks at the other.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of sea water has varied in the geological past, increasing from 0.7077 about 50 million years ago (Early Tertiary), to its current value in modern oceans, which is bracketed by  $0.709241 \pm 0.00032$  and  $0.709211 \pm 0.00037$  (Elderfield 1986). The continuous increase of the isotopic ratio since the end of the Eocene epoch is used to date samples of marine carbonates or fossil shells of Tertiary age.

Diagenesis tends to reset the Sr isotopic system. Sr is similar to Ca in its chemistry, and its parent Rb closely parallels K in behavior. Because so many mudstones have experienced post-depositional K addition or Ca loss, changes to Sr isotopes are common.

### Box 7.3. Neodymium isotopes

Samarium (Sm) and neodymium (Nd) are rare earth elements linked in a parent-daughter relationship by the alpha decay of  $^{147}\text{Sm}$  to stable  $^{143}\text{Sm}$  with a half-life of  $106 \times 10^9$  years. They are especially useful in geochemistry because these two elements undergo very few changes once a rock has formed. The melting of the Earth's mantle, which forms the more evolved plutonic and volcanic rocks of the exposed continental crust, fractionates Sm from Nd and thus allows for measurable isotopic variations over time. Models of the evolution of this reservoir – CHUR (for “chondritic uniform reservoir”) or DM (“depleted mantle”) – are used to calculate *model ages*, which are a measure of length of time a sample has been separated from the mantle from which it was originally derived.

More useful for mudstones than the model age is  $\epsilon_{\text{Nd}}$  (De Paolo and Wasserburg 1976), which is a measure of the deviation of the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio in a sample from the expected ratio value in a uniform reservoir (CHUR's  $\epsilon_{\text{Nd}} = 0$ ). A positive  $\epsilon_{\text{Nd}}$  implies that the Nd came from depleted sources having a higher Sm/Nd ratio than CHUR (i. e., its source has undergone periods of partial melting or differentiation), whereas negative  $\epsilon_{\text{Nd}}$  values imply derivation from enriched sources with a lower Sm/Nd ratio than CHUR (i. e., a magma source that earlier separated as a liquid from the primary chondritic uniform reservoir).  $\epsilon_{\text{Nd}}$  varies widely among possible source rocks, but is unaffected by most sedimentary processes. Hence it provides a useful fingerprint for choosing among likely sources or for distinguishing one mudstone from another.

seawater, but instead reflect the composition of the rocks on adjacent landmasses. This result had compelling implications for understanding burial as well as provenance of clays, because it established that early diagenesis does little to the chemistry or min-

eralogy of clays, in contrast to the significant changes seen in deeper burial (Chap. 6).

This persistence of  $^{87}\text{Sr}/^{86}\text{Sr}$  values from source to sink has been exploited by a number of workers in provenance studies of modern sediments. For example, Graham et al. (1997) found that oceanic islands in the SW Pacific, which have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7036 to 0.7040, are major sources for clay material only in their immediate vicinity, whereas most of the clays in this region, which have values of 0.7090 or higher, are sourced more remotely from metamorphic rocks on New Zealand.

$^{87}\text{Sr}/^{86}\text{Sr}$  is often used jointly with  $^{143}\text{Nd}/^{144}\text{Nd}$  in provenance studies, because Sr gives information about the composition of the source terrane, whereas Nd gives information about the age at which the source igneous rocks separated from the mantle. Mahoney et al. (1998) used  $^{87}\text{Sr}/^{86}\text{Sr}$ , along with clay mineralogy and  $^{143}\text{Nd}/^{144}\text{Nd}$ , to determine the provenance of Plio-Pleistocene hemipelagic muds in the Shikoku Basin of the Philippine Sea. They established that the isotopic signature of sediment sources from the basin margins is not compatible with the sediment in the basin center and identified an episodic eolian influx of materials with a continental signature (Sino-Korean craton), mixing with other marine sources. Walter et al. (2000) also employed both Nd and Sr isotopic evidence to study the sources and transport mechanisms of terrigenous sediments being delivered to the South Atlantic Ocean (Fig. 7.12). They found that sources varied greatly between glacial and interglacial pe-

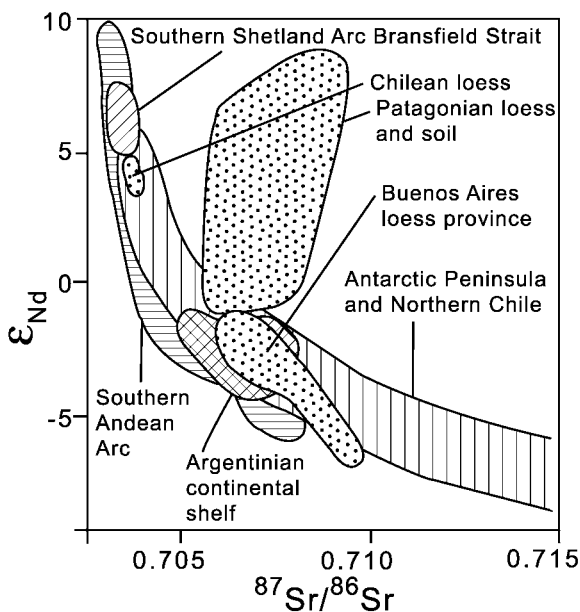


Fig. 7.12. Nd vs. Sr in the southern cone of South America and the adjacent South Atlantic Ocean (after Walter et al. 2000). The complexity of this diagram probably reflects the proximity of fore-arc, back-arc, and passive margin sources. Published by permission of the authors and Pergamon Press

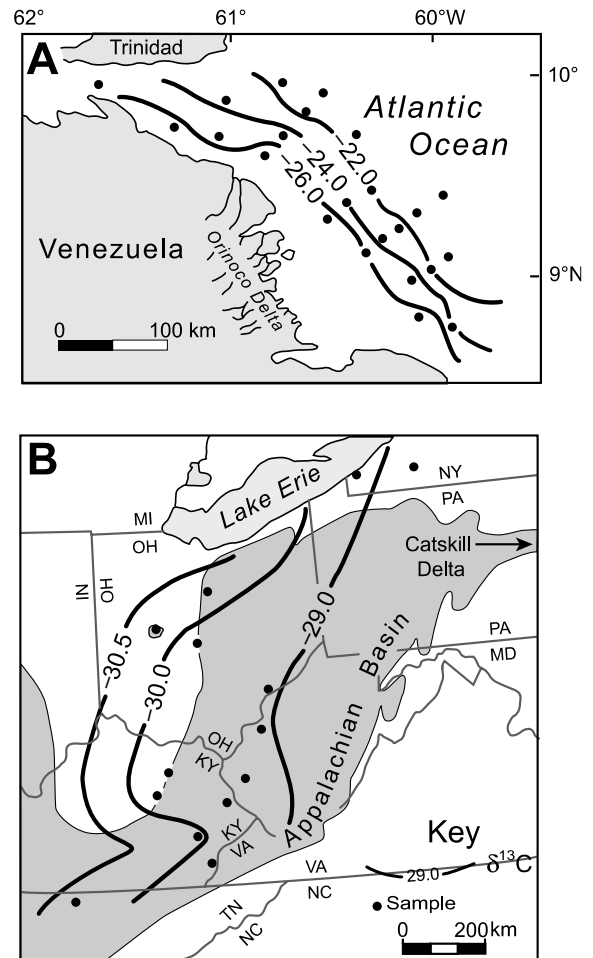
riods, a possibility that needs to be considered in all provenance studies. Nd isotopic methods are so sensitive that they can trace Greenland dust back to sources in China (Borry et al. 2003).

Sr tends to be reset by burial diagenesis because of the high mobility of both Sr and its radioactive parent, Rb. For example Awwiller (1994) found that Rb-Sr ages of Gulf Coast mudstones decrease with increased burial depth, becoming younger than their depositional age. Therefore older rocks present problems for using Sr isotopes in provenance studies, and Nd isotopes accordingly assume more prominence. Gleason et al. (1994) provide an example of use of Nd isotopes to track contributions to the turbidite mudstones and sandstones of the Ouachita Basin. They found that both lithologies share the same Nd signals: a Lower Paleozoic contribution with  $\epsilon_{Nd}$  of  $-16$  to  $-13$ , indicating a source from older rocks on the North American craton, which shifts abruptly in the Late Ordovician to an Appalachian orogen source characterized by younger sources with  $\epsilon_{Nd}$  of  $-10$  to  $-6$ . These changes in source area are consistent with inferences based on the petrography of the interbedded sandstones.

**Stable Isotopes.** Organic chemical indicators are used to provide information about the proportion of terrestrial- to marine-derived organic matter in a mudstone. A map of the values of this proportion would then provide a good picture of the direction to the shoreline. This is a procedure that has been widely used in the modern, but seldom in the ancient, perhaps because of the difficulty of doing detailed sampling of a narrow stratigraphic interval over a large area.

The quickest way to do this analysis is by stable isotope measurements of carbon (see Tyson 1995, Chapter 23 for a thorough review). Land plants today produce particulate organic matter with  $\delta^{13}C$  values of about  $-27$  permil, whereas marine organic carbon is at about  $-20$  permil. Therefore the simple measurement of  $\delta^{13}C$  provides a quick estimate of the relative effect of terrestrial-sourced material in the basin (Fig. 7.13a).

Unfortunately, ancient mudstones are more complicated.  $\delta^{13}C$  of organic matter in Devonian marine shales of the Appalachian Basin indicates that the terrestrial source to the east has values of about  $-26$  permil, but the marine carbon is lighter still, at about  $-32$  permil (Fig. 7.13b). This difference in behavior of the modern and older systems has prompted considerable debate, but the cause seems to be related to higher atmospheric  $CO_2$  levels in the



**Fig. 7.13A,B.** Provenance signal of carbon isotopes in organic matter: (A)  $\delta^{13}C$  in muds off the Orinoco Delta show clearly the contribution of terrestrial carbon,  $\delta^{13}C = -26$  permil, to the marine system with  $\delta^{13}C = -20$  permil (after Kennicutt et al. 1987, p 45), and (B) Devonian black shales of the Appalachian Basin also show a proximal-distal variation in  $\delta^{13}C$ , but with the reverse polarity (after Maynard 1981, Fig. 1). Published by permission of the authors, Pergamon Press and the Geological Society of America

Devonian and at most other times in the Phanerozoic (Lewan 1986; Popp et al. 1989). Their data suggest that the change to modern-style carbon isotopic patterns occurred in the Eocene-Miocene, a time of global lowering of  $CO_2$  and accompanying cooling of the climate. Comparable lowered  $CO_2$  at other times in the geologic past should also have resulted in marine carbon that had heavier  $\delta^{13}C$  values, but there is very little data from the relevant periods, perhaps because these were times of diminished black shale accumulation. Tyson (1995, his appendix B) lists one Permian occurrence with  $\delta^{13}C = -20$  to  $-18$  permil, consistent with this argument. The study of the areal

distribution of carbon isotopes in black shales of various ages would seem to be a fruitful area for future research.

## 7.6. Recycling

An important limitation on the use of mudstones in provenance studies is the extent of recycling, which makes it ambiguous whether the signal observed comes from the immediate source or was inherited from a pre-existing terrane. The problem is more pervasive for muds than for sands because of the greater stability of the clay mineral grains than all but the quartz grains in a sandstone. Does a high CIA value for a mudstone indicate intense weathering in the source area or rather a slightly weathered source made up mostly of older mudstones themselves derived from weathering under wet tropical conditions? Furthermore, how do we know that a particular REE pattern in a mudstone reflects the composition of the parent terrane rather than that of some earlier terrane in the sedimentary recycling history of the material? It turns out that muds and mudstones are commonly the product of the turnover of a pre-existent sedimentary mass because their particles largely consist of stable weathering products, and these particles, like quartz grains in a sandstone, can be recycled through many episodes of burial, uplift and erosion. Veizer and Jansen (1979) estimated that, on a global basis, clastic sediments are 65% recycled. Secondly, most mountainous regions have a high proportion of sedimentary rock exposed, which creates the potential for sedimentary-sourced particles to dominate the suspended load of major rivers. This recycled component of rivers has long been recognized, but it is hard to quantify in the modern and nearly impossible in the ancient for a given deposit.

Gaillardet et al. (1999) provide an initial attempt at estimating the amounts of recycling in individual river basins by comparing the measured suspended load to that predicted from the composition of the dissolved load. The calculations are similar to those developed by Garrels and MacKenzie (1971) for converting average igneous rock into sediment plus ions in solution. For all rivers, there is an excess of suspended load over what would be predicted from the dissolved load if only crystalline rocks are being weathered. The amount of this excess is proportional to the extent of sedimentary rock cover in the source area, and thus provides an estimate of the fraction of recycled material a stream is carrying. The results vary widely for different rivers, with values falling between 45 and 75% recycled material. The overall

conclusion from these calculations is that the amount of recycled material in a mudstone is likely to be very large and highly variable depending on the nature of the river bringing the sediment into the basin of deposition. Therefore provenance studies using mudstones need to somehow take into account this potential for extensive recycling.

Recycling requires knowing the composition of the dissolved load, which we cannot recapture for ancient rocks. In our view, the best key to the amount of recycling in mudstones is found in the petrography of the interbedded sandstones. Abundant volcanic rock fragments in the sandstones indicate a dominantly juvenile source, whereas a pure quartz sand generally indicates a recycled source – be on alert for sandstone rock fragments or for quartz grains with old overgrowths. Pure chemical approaches to recycling, on the other hand, are likely to be less compelling in our view. If a mudstone shows very little evidence of weathering (low CIA + high ICV), then it is likely that the parent terrane contains mostly juvenile igneous rocks. The converse is not true, however. If CIA is high and ICV low, then the cause could be either deep weathering of the source or recycling of previously weathered material. Consider for example a Miocene mudstone, encountered in offshore drilling, that has high CIA values and low Th/Sc, indicating a strongly weathered mafic-rich source. Was the immediate source a weathered basalt or a Paleozoic mudstone itself derived from a basaltic terrane? The tectonic reconstruction of the basin would be radically different depending on the answer to this question.

## 7.7. Ash Fall Mudstones

One component of a mudstone unfailingly reflects primary igneous sources – volcanic ash beds. These come in two main varieties, those deposited in swamps, which become kaolinite-rich *tonsteins*, and those deposited in marine basins, which become smectite-rich *bentonites*. (See Chap. 6 for a discussion of the diagenetic pathways followed by these lithologies, and Chap. 8 for a discussion of their great utility in stratigraphic correlation.) As provenance indicators, these beds are best studied through their trace element chemistry and their phenocryst mineralogy, although some use has been made of tracking the direction to the source by isopach mapping of ash thickness (Huff et al. 1996). A good example of the use of trace elements in tonsteins is Spears and Lyons (1995) who separated sources into rhyodacites and alkali basalts using a plot of  $Zr/TiO_2$  vs.  $Nb/Y$ . Ash

**Table 7.3.** Provenance indicators in volcanic ash beds. Adapted from Bohor and Triplehorn (1993)

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**Feldspars**

Sanidine in rhyolitic ashes, Ca-plagioclase in more mafic ashes, whereas microcline or pure albite indicate a non-volcanic clay or post-depositional alteration; microprobe chemistry of plagioclases a useful fingerprint.

**Quartz**

Euhedral, water-clear beta-form quartz is an unequivocal indicator of a volcanic origin of the clay bed; glass inclusions in the quartz can be probed to give original magma chemistry

**Zircon**

Ideal for ion-microprobe Pb-Pb dates

**Apatite**

Commonly contains glass inclusions useful for magma chemistry

**Biotite**

Has a large compositional variability that can be useful for fingerprinting each ash bed in a series; typically the most abundant phenocryst

**Insoluble trace elements**

Zr, Nb, Y, Ti, Th, Ta, and Hf are commonly used on discrimination diagrams that define magma types

**Rare-earth elements**

REE patterns are good for fingerprinting ashes, and the size of the europium anomaly is an indicator of how felsic the volcano was.

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beds tend to be bimodal in grain size, with coarse phenocryst minerals set in a clay matrix. These phenocrysts come in several types (Table 7.3) and contain much about their parent magmas in the form of mineral chemistries and in the chemistries of their melt inclusions (Huff et al. 1998).

These ashes form *event beds* that span several environments, so they are a powerful contributor to understanding the sequence stratigraphy of a mudstone section. See Sarna-Wojcicki and Davis (1991) for examples of widespread Quaternary continental ashfall deposits in lakes, soils, and on river terraces. The largest covers over 2 million km<sup>2</sup>. In addition, knowledge of the type of volcano that produced the ash is a great help in reconstructing the tectonic setting of the basin of deposition, always a useful step in mineral and petroleum exploration. Numerous thin ash beds, as are found in the Permian of the Paraná and Karoo Basins of Brazil and South Africa, may indicate that the background clay deposition in the surrounding mudstones also had a high volcanogenic input. Such mudstones might be particularly prone to engineering problems or might be especially effective source beds for petroleum because of their capacity for releasing water during hydrocarbon generation.

## 7.8. Provenance of Clays in Archeology

The principles developed above also have application to the sourcing of ceramics in archeological work. Pottery contains two main sets of ingredients, *plastic*, comprising mostly clays, and *aplastic*, coarser materials either native to the clay or added to *temper* the clay and make it easier to work and to give strength to the pottery when fired. The plastic component has provenance characters like mudstone, whereas the aplastic component is analogous to interbedded sandstone, and the strategies for characterizing provenance for these two rock types are also applied to the pottery ingredients.

The aplastic component most commonly consists of quartz-rich sand, carbonate particles, either limestone fragments or broken shells, or *grog*, which is the term for ground up old pottery reused in the new, just like reworked sandstone fragments in a second-cycle sandstone. Petrographic techniques are the method of choice for these sand-sized ingredients (e. g. Ferring and Perttula 1987). Microchemical approaches like the electron probe could be used to study the chemistry of these particles separate from that of the clay matrix, but we know of no such attempts recorded in the archeological literature. For example, some material characterized as grog in thin section may actually be mudstone fragments, and these could be distinguished microchemically from broken pottery, which should have a similar composition to the clay matrix.

Chemical techniques are most appropriate for the plastic component, but whole-sherd analyses have the complication of combining both the clay- and the sand-sized ingredients in the same analysis, when they likely have rather different sources. For example, silicon, being an almost universal temper ingredient, will likely not provide useful information about clay sources. Likewise calcium will reflect mostly the amount of temper if shell or limestone was added to the clay. Within this inherent constraint, some useful results have been obtained by careful study of the chemistry of pottery fragments.

Two kinds of questions are addressed. The simpler is, “Are the pottery sherds at two sites (or from two layers in one site) the same or different from each other?” Simple cluster analysis of all of the chemical data is effective in addressing this type of question. Combining major and trace element data, however, presents problems because of the vast difference in the ranges of concentrations. This is usually overcome by using log-transformed data (or by normalizing each data point to a percentage of

the total range for this particular variable). Statistical analysis of all chemical constituents obviously combines the clay and the temper, but differences in manufacturing procedure may be just as interesting as differences in the sources of the materials, so this “whole-rock” procedure is beneficial.

The second, more difficult type of question to ask is, “What was the geological source of the clay used in this pottery?” Here we have to exclude the temper components. The procedure to follow is again rather similar to provenance studies of mudstones, in that the trace elements give the best provenance discrimination. The elements Si, Ca, P, and Sr should be dropped from the statistical analysis because they are common ingredients of sand or limestone or shells. One might also wish to exclude Al, K, and Na because they are the elements making up the feldspar component of sands, and a quick check of the temper using the petrographic microscope reveals whether grains of feldspar (or feldspathic rock fragments) are sufficiently abundant to warrant the exclusion of these elements. Soltman (2001) shows good illustrations of thin sections of quartz-rich and feldspar-rich tempers. Excluding these temper elements leaves the trace elements and a few less mobile major elements like Fe and Ti to be included in the statistical treatment. The same array of trace element ratios that is useful as bivariate plots in mudstone provenance appears to work best here as well (see for example Rodriguez-Alegria 2003), or multivariate statistical tests such as principal component analysis can be applied.

An interesting example of this approach comes from a study of Roman pottery of Tunisia (Sherriff et

al. 2002). The area contains three likely clay sources, a Miocene marine clay rich in sulfur and gray in color, a Pliocene sandy non-marine brown clay, and a Late Pliocene calcareous non-marine green clay. Principle component analysis defined three distinct fields for the composition of these clays using two linear combinations of chemical variables (Fig. 7.14). The pottery sherds showed a close match to the brown clay, but shifted slightly because of higher Na and Cl, which the authors attributed to seawater added to the mix to harden the pottery.

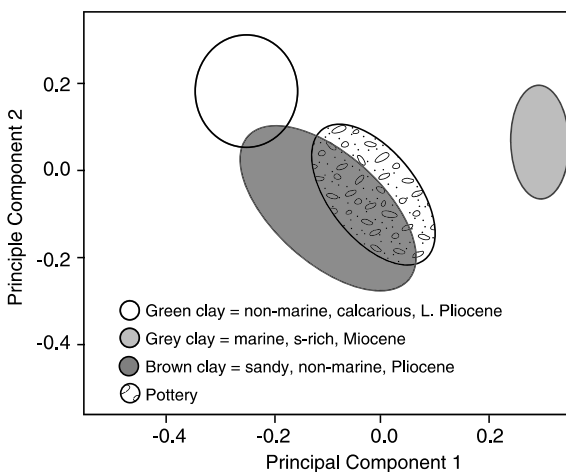
## 7.9. Summary

The determination of provenance of muds and mudstones has many similarities to the better-known procedures for sandstones, but differs in two important ways. Because grain size is so small, petrographic techniques are much less useful, and because transport distances can be so much greater, additional care must be taken to separate local from distant sources. In particular, wind-blown material of sand size cannot be transported long distances, but silt- and clay-size material is easily distributed over the area of an entire continent by the wind. Because petrography is less useful, chemical methods assume greater importance for mudstones compared with sandstones. Major elements are most useful for estimating the degree of weathering of the source, whereas trace elements are best suited to estimating the relative proportions of mafic and felsic rocks in the ultimate source. Radiogenic isotopes are best used to “fingerprint” individual sources, and therefore commonly repay the extra investment required for their use. For all techniques, it is better to compare like types of mudstones. Black shales in particular are prone to enrichments in many trace elements compared to red and green mudstones.

A major source of uncertainty in provenance reconstruction is the proportion of recycled material in the basin fill. An apparently mafic source could instead be an older mudstone that itself had a mafic source, perhaps many million years earlier. For this reason, thin clay beds derived from volcanic ash are particularly good indicators of provenance, but bear in mind that the volcanoes may have been only one of several different sources for the basin fill.

## 7.10. Challenges

**Recycling:** A particle in a mud or mudstone may be derived from weathering of a crystalline rock,



**Fig. 7.14.** Trace elements are also useful for determining sources of clay used in pottery – an example of Roman ceramics from Tunisia (after Sherriff et al. 2002, Fig. 8). Published by permission of the author and John Wiley & Sons

or it may come from weathering of a pre-existing mudstone.

*How does one detect recycling and quantify its effects? Another issue is that our hypothetical particle may have languished along its transport path in alluvial deposits where it was subject to additional alteration. How long does such alluvial storage need to be to change the apparent provenance signal of a mud? How long do particles typically spend in this setting? Is there any way to measure this effect?*

How much of the fine silt in muds and mudstones is added by wind?

*Because wind-blown silt can travel so far, it is quite likely to have a different provenance than water-borne particles in the mud. Is there some combination of chemical variables that can estimate this contribution? The composition of soils on carbonate ocean islands might provide a starting point.*

The amount and composition of muds that are produced by a source area are influenced by both climate and relief, yet it is usually difficult to distinguish the relative importance of these two factors from the resulting mudstone alone.

*This same dilemma has plagued sandstone provenance studies for years. Would detailed comparisons of interbedded sandstones and mudstones help resolve this?*

Many workers have suggested that the Archean weathering environment was much hotter and had much less oxygen than today.

*In what ways would weathering have been different then and how would the provenance signals be changed? Tropical lowland rivers today carry little mud and the little that they carry is mostly kaolinite and quartz, neither of which carries much provenance information. Would Archean rivers have been similar?*

Geochemists have expended much effort assembling global averages of mudstones through time.

*Given that mudstones can be linked geochemically to different tectonic settings, would it not be helpful to separate these analyses by basin type and track the average "rift mudstone" or the average "foreland basin" mudstone through time? Our impression of the "global average shale" may be*

*strongly biased by the vagaries of sampling different plate tectonic settings. Consider also that some settings experience much more recycling than others. Tracking arc-related mudstones through time might provide a better signal than the global average mudstone.*

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### Digging Deeper

Goudie AS, Middleton NJ (2001) Saharan dust storms: nature and consequences. *Earth Sci Rev* 56:179–204.

*Thorough review of information on Saharan dust. Relates clay mineralogy to dust sources. Also gives tables of chemical composition and maps of rate of dust flux to the Atlantic Ocean.*

Lorenz S, Zimmerle W (1993) Miozäne Kaolin-Kohlenstonsteine aus dem Braunkohlen-Tagebau von Bełchatów SW von Łódź Polen. *Zeitschrift Deutschen Geologischen Gesellschaft* 144:187–223.

*A little-known, exceptionally detailed and thorough petrographic and chemical study (Rock-Eval, major and trace elements, electron microprobe) of ash falls in the Miocene lignitic brown coals of Poland. Includes an interesting worldwide summary plus an outstanding compilation of individual components and their diagenetic alteration. See especially their Fig. 7 and plates 1 and 2. Excellent reference when beginning your petrographic examination of a suspected tonstein. See also Throw and Von Rad (1992). Has an extended English abstract and the figure captions are also presented in English.*

McLennan SM, Hemming S, McDaniel DK, Hanson GN (1993) Geochemical approaches to sedimentation, provenance, and tectonics. In: Johnsson MJ, Basu A (eds) *Processes Controlling the Composition of Clastic Sediments*. *Geol Soc Am (Special Paper)* 284, Boulder, pp 21–40.

*Excellent review of the use of immobile trace elements and REE in reconstructing provenance, based mostly on deep-sea turbidite associated muds. Table 1 gives a useful summary of the utility of various petrographic and geochemical techniques.*

Neff H (1992) *Chemical Characterization of Ceramic Pastes in Archeology*. Monographs in World Archeology No. 7, Prehistory Press, Madison, Wisconsin, 289 p.

*Twenty chapters on chemical analysis of pottery from both the Old and the New World. An interesting format of this book is that three of the chapters are critical commentaries on the contributions in each section. Most of the papers employ Principal Components Analysis to compare pottery with potential sources and, just as with mudstones, the REE prove to be the strongest discriminators.*

Taylor SR, McLennan SM (1985) *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific, Oxford, p 312.

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Tyson RV (1995) *Sedimentary Organic Matter*. Chapman and Hall, London, 615 p.

*The premier reference on organic part Comprehensive, well-written treatment with many fine illustrations along with very useful data compilations in the appendix.*