Volcanism and its Contribution to Mudrock Genesis

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Abstract: Explosive eruptions from volcanoes are recorded in the stratigraphic record throughout the Phanerozoic. The most visible evidence of these eruptions is generally in the form of preserved tephra layers, and they appear to be concentrated in the stratigraphic record at times of active plate collision and concomitant high stands of sea level. The products of volcanic eruptions are lavas, tephra and gases, and whereas low-silica, anhydrous basaltic magmas are usually erupted in the form of lava flows high-silica, hydrous rhyolitic magmas are commonly explosively erupted as plinian and ultraplinian plumes, and associated pyroclastic flows. Fallout tephras may be preserved in ancient sedimentary sequences as tonsteins, bentonites and K-bentonites, but in many cases they also mix with ambient background sedimentation and thus become simply one of the contributing factors to overall sediment composition. The significance of volcanogenic contributions to mudrocks is easily underestimated since their influence requires detailed study of the fine-grained components by petrographic and X-ray diffraction methods. Volcanogenic sediments react with seawater to produce secondary phases such as zeolites and clay minerals. Typical mudrock clay minerals derived by the alteration of tephra include smectite, illite-smectite and kaolinite, and the most diagnostic non-clay minerals include beta-form quartz, euhedral zircon and apatite, clinopyroxene, amphibole, biotite and sanidine. Further modification of these phases by diagenetic and low-grade metamorphic processes further obscures the nature of their origin.

Key Words: volcanic ash, bentonite, shale, mudstone, clay, siliciclastic, diagenesis

Volkanizma ve Kitaşı Oluşumuna Katkısı

Özet: Şiddetli volkanik patlamalar Fanerozoik boyunca stratigrafik kayıtlarda yer alırlar. Bu kayıtların en iyi gözlenebilenleri iyi korunmuş tefra tabakaları olup, yerkabuğu çarpışma tektoniğinin ve eşzamanlı deniz seviyesi yükselmelerinin yoğunlaştığı evrelerde stratigrafik istifler boyunca sıkça izlenirler. Lav, tefra ve gaz şeklindeki volkanizma ürünleri, bazaltik magmadan kaynaklandığında lav akıntıları, riyolitik magmadan geliştiğinde ise piliniyen ve ultrapiliniyen patlama kolonları ve piroklastik akıntıları meydana getirirler. Atmosferden çökelen tefra, yaşlı tortul istiflerde tonştayn, bentonit ve K-bentonit tabakaları olarak korunabilirler. Ancak birçok durumda, çökelen tefra, çökelme ortamına diğer jeolojik süreçlerle taşınan tortullarla karışarak, toplam tortul bileşimine katkı koyan etkenlerden sadece birini oluşturabilmektedir. Volkanik kökenli malzemenin kiltaşlarının oluşumundaki önemi çoğu zaman, ince taneli malzemenin petrografik ve X-ışını toz difraktometre yöntemleri ile incelenmesi gerektiğinden, anlaşılmamaktadır. Bu tür malzeme deniz suyu ile tepkimeye girerek zeolit ve kil minerallerine dönüşmektedir. Kiltaşlarındaki tefranın bozuşması ile oluşan tipik kil mineralleri simektit, illit-simektit ve kaolinittir. Tefra kökenli en tipik kil dışı mineraller ise beta-kuvars, öz şekilli zirkon ve apatit , klinopiroksen, amfibol, biyotit ve sanidindir. Bu mineral fazlarının diyajenetik ve düşük dereceli metamorfizma ile daha sonraki değişiklikler ise volkanik kökenlerinin belirlenmesini zorlaştırmaktadır.

Anahtar Sözcükler: volkanik kül, bentonit, şeyl, kiltaşı, kil, silisiklastik, diyajenez

Introduction

Mudrocks are fine-grained sedimentary rocks consisting of mostly silt- and clay-size particles. Because of their small particle size, they are difficult to study, even with the petrographic microscope. However, they are important rocks because they are the most abundant sedimentary rocks, making up over 65% all sedimentary rocks, are likely the source rocks for petroleum and natural gas, and locally host valuable ore deposits. In addition, mudrocks are, in many cases, the protoliths for aluminous or pelitic metamorphic rocks.

Among the oldest mudrocks known are tuffaceous mudrocks in the banded iron-formations (BIF) of the Brockman Iron Formation of the Hamersley Range, Western Australia (Pickard 2002). The best estimates of depositional age have been obtained from siliceous

tuffaceous mudrocks in the Joffre Member, which contain 2459±3 Ma and 2454±3 Ma zircon populations most likely derived from felsic volcanism coeval with Banded Iron Formation (BIF) deposition. What makes these sediments all the more interesting is that they contain a significant proportion of volcanic material. In fact, when we look at mudrocks throughout the stratigraphic column, we find that volcanogenic components are almost the rule rather than the exception. These components express themselves in two ways: as phenocrysts of magmatic minerals, such as biotite, zircon, apatite, sanidine, plagioclase, beta-form quartz, amphibole, and clinopyroxene; and as clay minerals, primarily smectite and kaolinite-group minerals. Smectite in sedimentary clays may have formed in place, or it may have been derived from the reworking of older deposits. However, as noted some years ago by Tourtelot (1974, p. 269) '... the accumulation of nearly all the highly montmorillonitic, thick, and widespread shale units that are of recognized engineering, industrial, or agricultural significance has resulted from the deposition of volcanic ash in ocean basins.' Marine smectitic clays are more abundant and extensive than those of fresh-water origin because, throughout geologic history, ocean basins have been the largest repositories of detrital sediments and probably have been the largest areas in which the environment was favourable for the formation of smectite. Smectitic sedimentary beds also have formed in saline alkaline lakes and playas in desert regions of the world. Those deposits generally are not as widespread as marine bentonite beds, but the smectite in them may be highly expansive.

Smectite is formed by the alteration of silica-bearing rocks; the altering solutions are alkaline (pH above 7) and magnesium-rich. Silica-bearing rocks as varied as granite, basalt, serpentine, and graywacke sandstone may alter to smectite under the appropriate conditions. The smectite species formed depends on the conditions of alteration and the chemistry of the parent rock and altering solutions. Glassy rhyolitic volcanic ash is especially susceptible to alteration and is known to be the parent material of many smectite deposits in the form of bentonite and K-bentonite. While bentonites are generally smectite-rich, the clay mineralogy of K-bentonites is typically dominated by a regularly interstratified illite-smectite (I/S) in which the swelling component accounts for 20–40 percent of the total structure. Accessory clays are typically either kaolinite or chlorite.

But beyond the sedimentological and mineralogical controls on mudrock composition, the other major controlling factor is diagenesis, including temperature and pressure effects extending through the range of low-grade metamorphism. We can examine the contrast between recent and ancient mud and mudrock domains by looking first at recent sediments and then at the stratigraphic record.

Recent Sediments

There are two broad realms of recent clay sediments: terrestrial or non-marine, and marine. Terrestrial clay sediments comprise – to varying degrees – most soils, which, in turn, are reflected in the clay content of fluvial and lacustrine systems. The clay-mineral composition of soils is a by-product of several factors including the type of parent material, climate, weathering reactions, topography, and time (Dixon & Weed 1989). Where volcanic sources predominate the soil, clays tend to be smectite-rich and expansive (Figure 1). As an illustration, Olive *et al.* (1989) compiled a map showing the distribution of swelling clays in the conterminous United States (Figure 2). The broad Midcontinent region of the country, between the Rocky Mountains on the west and the Mississippi Valley on the east, has soils that contain more than fifty percent swelling clays. Clays with high smectite content occur in geologic units of Cretaceous, Tertiary, and Quaternary ages and are extensively exposed in areas bordering the Gulf Coast, and in Oklahoma, Nebraska, South and North Dakota, and western Kansas. Those soils that have experienced the most damage due to expansion and/or slope failure are also soils with a high content of swelling clay. They occur in stratigraphic sequences ranging in age from Cretaceous to Quaternary and are exposed in a region extending along the Gulf Coast from east-central Texas to Alabama (Olive *et al.* 1989). The majority of these stratigraphic units are known to contain a high proportion of volcanogenic materials. In the Rocky Mountain region, source rocks are more varied but Cretaceous shale, claystone, and siltstone with abundant swelling clays occur at or near the surface (Tourtelot 1974). Much of this clay is in the form of bentonite or bentonitic materials mixed with detrital sediments (Schultz *et al.* 1980). Similarly, Triassic and Jurassic shales and mudrocks of the western region contain abundant swelling clays, derived largely from the alteration of volcanic debris (Schultz 1963).

Figure 1. Expansive soil in northern Uruguay composed predominantly of smectite from the alteration of volcanic ash.

The inherent swelling potential of aggregates of clay minerals is related to the total internal and external surface area of clay particles and to their ability to adsorb water on those surfaces. Some clay minerals, such as members of the smectite group, are capable of adsorbing appreciable amounts of water between the individual silicate layers, resulting in a very high swelling potential. Clays composed dominantly of Na- and Ca-smectite are generally called bentonites, particularly if they have formed from volcanic rocks. In particular, glassy felsic volcanic ash is highly susceptible to alteration and begins to convert to clay minerals almost immediately upon formation (Fiore 1993). With few exceptions, the Midcontinent soil clays were derived from volcanogenic sources, and this is characteristic of the composition of detrital muds that are transported by regional drainage systems.

Modern marine clays serve as the progenitor materials for mudrocks formed through diagenesis and burial metamorphism in continental-margin sedimentary basins.

One of the first truly comprehensive demonstrations of marine-clay variability was provided by Biscaye (1965) who built on previous studies by Griffin & Goldberg (1963) by analyzing the tops of five hundred deep-sea piston cores from the north and south Atlantic Ocean. His montmorillonite map (Figure 3) shows that some of the highest concentrations occur in areas characterized by active volcanism, such as the region around Madagascar and the Mascareigne Islands in the southwestern Indian Ocean, and that montmorillonite is also a product of continental erosion, particularly in the equatorial Atlantic. Previous studies (Grim & Johns 1954; Murray & Harrison 1956) showed that the western Gulf of Mexico deltaic, shelf, and deep muds are predominantly montmorillonitic, with lesser amounts of illite, chlorite, and kaolinite. The surrounding Cretaceous and Tertiary sediments contain an abundance of montmorillonite, and the detrital clays draining into the western Gulf of Mexico are also predominantly montmorillonitic. Further, the clays in the limestone muds west of the Florida peninsula
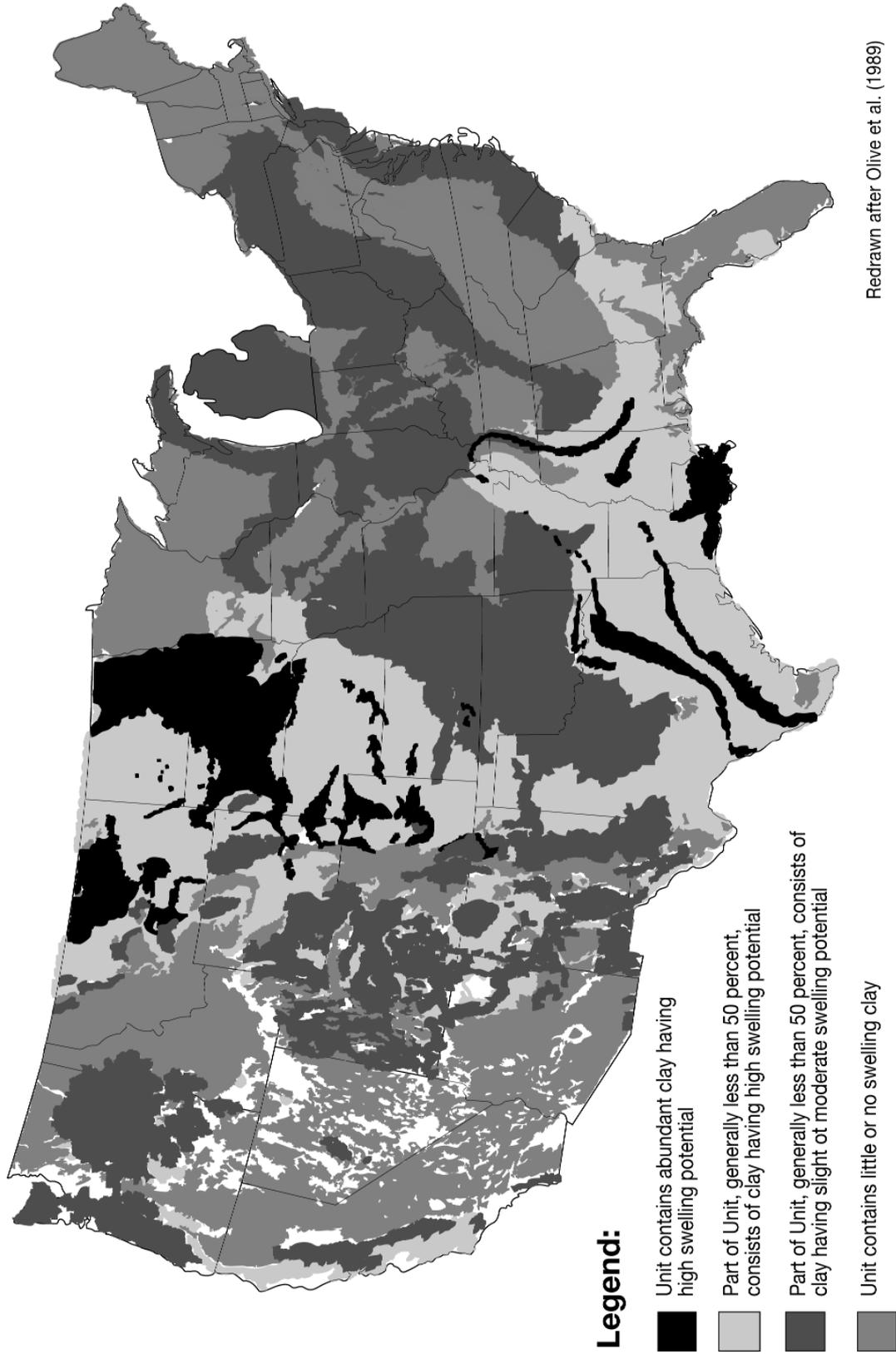
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Legend:

Unit contains abundant clay having high swelling potential

Part of Unit, generally less than 50 percent, consists of clay having high swelling potential

Part of Unit, generally less than 50 percent, consists of clay having slight ot moderate swelling potential

Unit contains little or no swelling clay

Redrawn after Olive et al. (1989)

Figure 2. Swelling clays map of the conterminous United States. The broad Midcontinent region of the country, between the Rocky Mountains on the west and the Mississippi Valley on the east, has soils that contain more than fifty percent swelling clays (Olive *et al.* 1989).
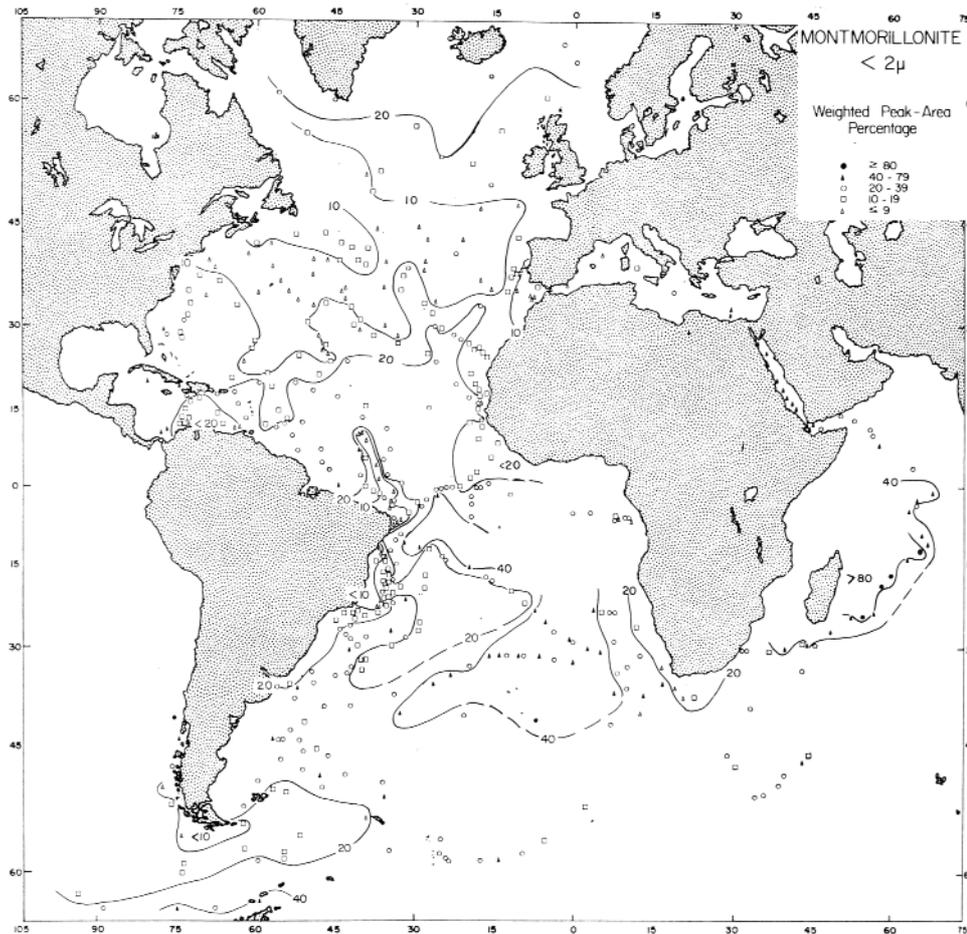
Figure 3. Distribution of montmorillonite in the Atlantic Ocean. Areas of active volcanism, such as the region around Madagascar in the Indian Ocean, are responsible for the high content of swelling clays in nearby sediments (Biscaye 1965).

are predominantly montmorillonitic (Weaver 1958). Figure 4 from Weaver (1958) illustrates the types and amounts of clay minerals found in sediments deposited under similar environmental conditions; it also shows the variety of environments in which the same clay minerals may occur. Most montmorillonite is volcanogenic in origin and, moreover, those deposits formed from one volcanic source tend to be similar in composition, whereas those montmorillonites that originate from diverse volcanic sources are generally quite different in composition. These differences are due to variations in source-material composition rather than in the depositional environments (Weaver 1958). The clear dependence of smectite formation on the presence of volcanic glass in deep-sea sediments was first demonstrated by Peterson & Griffin

(1964) for surficial deposits of the southeastern Pacific Ocean. Smectite appears to form soon after glass deposition in slightly buried sediments. Griffin *et al.* (1967) also demonstrated a close correlation between volcanoclastic debris and smectite abundance in the Lau basin, southwestern Pacific.

Ancient Mudrocks

Clay minerals are the most abundant minerals in mudrocks, making up over 60% of all shales and related mud-dominated rocks. If one looks at mudrocks of various ages, it is observed that Tertiary and younger mudrocks consist mostly of smectites and mixed-layer clays. In older mudrocks, illite begins to become the
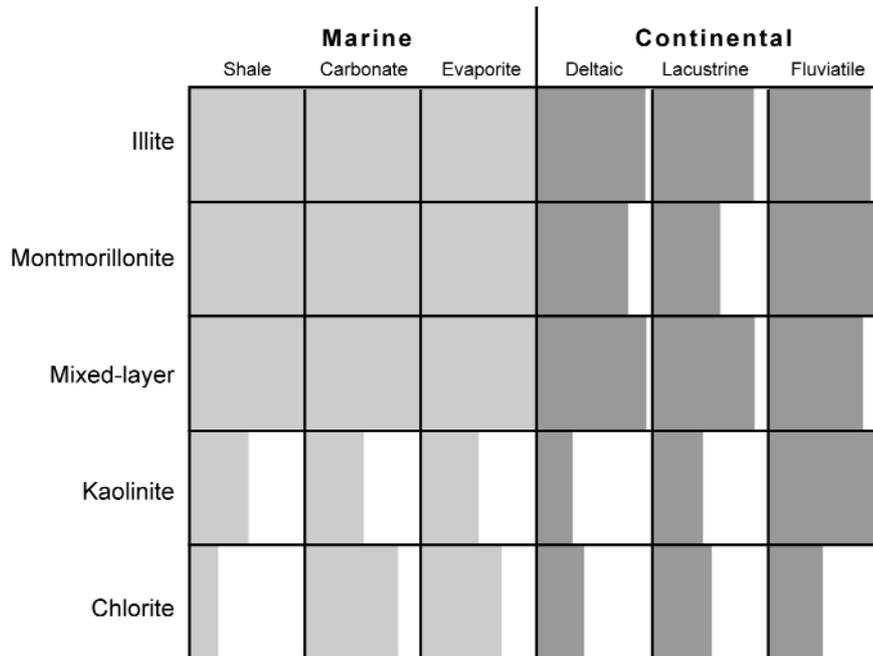
Figure 4. General relationship between marine and terrestrial environments and the types of clay minerals commonly associated with them. The shaded portions represent the approximate percentage of a particular clay mineral in each environmental setting (Weaver 1958).

dominant clay mineral, and in Early Palaeozoic and still older rocks, less than 10% of the clay minerals are smectite clays. Most clays of pre-Late Carboniferous age are composed predominantly of illite and chlorite and contain only small amounts of smectite, whereas younger clays "... have a complex clay-mineral suite with montmorillonite, mixed-layer clay, and kaolinite increasing in importance" (Weaver 1967, p. 2185). Most clays in which smectite is a major constituent are of Mesozoic and Cenozoic ages. Thus, the occurrence of smectite in the stratigraphic column is thus distinctly related to geologic age; this is likely due to diagenetic processes that convert the smectites to illites over time.

Burial diagenesis is seen as one in a series of transformations between a smectite starting material and pure illite. I/S in thick sedimentary sequences develops a rectorite-type interstratification from 100° to 175 °C and can be represented by the reaction: Smectite + K^+ + Al^{3+} = Illite + Si^{4+}. The required Al and K apparently originate from the destruction of detrital K-feldspars and, to a lesser extent, micas. The Al ubstitutes for tetrahedral Si in smectite and thereby generates an overall increase in layer charge, which is compensated for by K-fixation. The application of this model to the interpretation of clay-mineral assemblages in both young and old sediments is made more attractive by the agreement of field evidence (Roberts & Merriman 1990; Srodon 1999) and experimental studies (Eberl & Hower 1976; Eberl et al. 1990; Velde & Vasseur 1992), which supply answers for some of the important thermodynamic and kinetic questions involved. If mixed-layer phases are thermodynamically stable, their stability fields can be illustrated by activity-temperature diagrams. However, if the mixed-layer phases are metastable, their paragenesis can be regarded more as a function of time and temperature (Eberl 1978).

A well-documented example of the early-diagenetic formation of smectite is provided by the study of volcanic-rich oozes deposited near the Santorini archipelago that collapsed into the eastern Mediterranean Sea about 1400 B.C. (Keller et al. 1978). A 720-cm-long core sampled at 280-m water depth within the submerged caldera of Santorini shows a rapid downward change in the nature and abundance of clay minerals and

volcanic debris. Chamley (1971) concluded that the transformation of volcanic glass to smectite is favoured by the presence of very small, porous glass and pumice particles as well as associated siliceous diatoms (Figure 5).

Since the late 1960s a substantial body of literature has developed around the documentation of the diagenetic and metamorphic transformation of smectite to illite through intermediate stages of interstratification of illite/smectite (Meunier & Velde 2004). In Tertiary sediments of the Gulf Coast region of the U.S., for example, Burst (1959) noted a progressive modification in powder X-ray diffraction patterns of the progressive disappearance of smectite with increasing depth of burial. He (Burst 1959, 1969) explained the smectite change as due to a gradual fixation of potassium and magnesium to form illite and chlorite, and to a simple dehydration to one water layer without noticeable chemical conversion. Powers (1959) considered the decrease of smectite with

depth in Gulf Coast sediments as a transformation of Mg for Al in the octahedral sheet, with the consequent fixation of interlayer potassium.

The first truly quantitative data on the mineral chemical evolution in Gulf Coast sediments were reported by Perry & Hower (1970, 1972). They showed (Figure 6) that the smectite-rich layers that dominate the clay mineral component in shallow-buried sediments are progressively replaced by illite-rich interstratified layers down to a depth of 5500 meters. The expandable component of illite-smectite (I/S) ranges from about 80% to 20% with increasing depth. Discrete illite, kaolinite, and chlorite phases are variously present and considered as detrital. Those authors concluded that the diagenetic reaction was constrained more by thermal effects than by geologic age or stratigraphic position. Reynolds & Hower (1970) considered the nature of the interstratification in more detail and identified three types of mixed layering: random, ordered (allevardite-like), and superlattice units described as ISII. Then, in what has become a classic series of studies, Hower and co-workers conducted a detailed examination of Oligocene–Miocene mudrocks in the Gulf Coast region (Aronson & Hower 1976; Hower *et al.* 1976; Yeh & Savin 1977). They looked specifically at
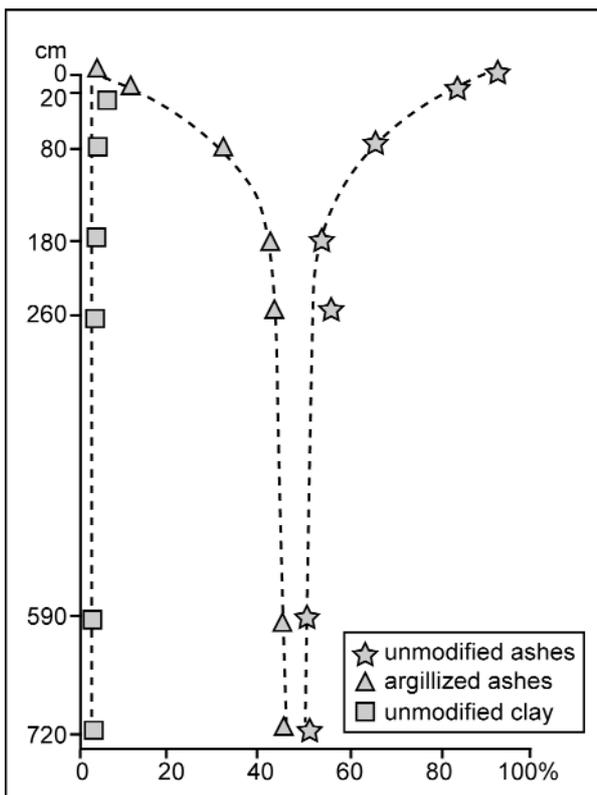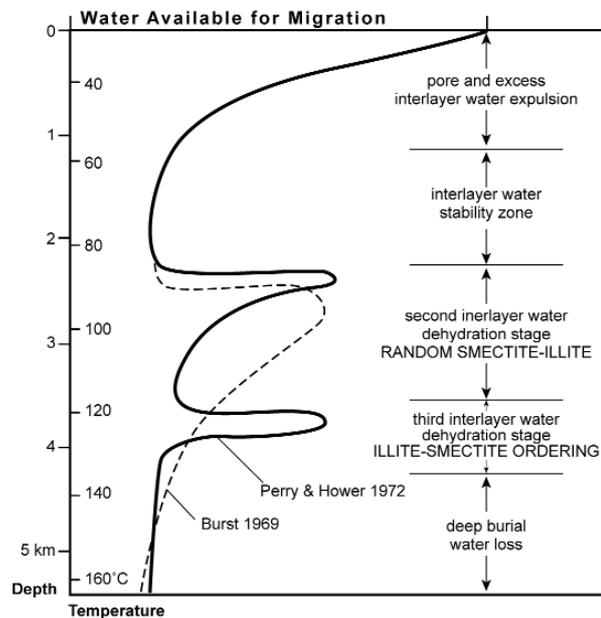

Figure 5. Variation of primary tephra versus secondary clay minerals with depth in modern marine sediments from the Santorini archipelago (Chamley 1971).

Figure 6. Vertical variation of smectite-rich versus illite-rich clay sediments with depth along the U.S. Gulf Coast (Perry & Hower 1972).

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the mineralogy, inorganic chemistry, and the radiogenic- and stable-isotope chemistry of bulk materials as well as different grain-size fractions between depths of 1250 m and 5500 m. The principle transition from smectite to I/S occurs in the interval between 2000 m and 3700 m, after which very little additional change is noted (Figure 7). They concluded that smectite was reacting with K-feldspar (and possibly mica) to produce illite and quartz. Chlorite is an additional by-product in more deeply buried sediments. The systematic decrease of K-Ar ages with depth (Aronson & Hower 1976; Perry 1974) strongly supported their diagenetic model. The measured K-Ar ages of the mixed-layer illite/smectite become progressively younger with increasing depth of burial due to the diagenetic addition of potassium during the conversion of smectite to illite (Figure 8). Subsequent studies of other authors have continued to validate the general conclusions of the Gulf Coast model (Boles & Franks 1979; Srodon & Eberl 1984). The principle differences in interpretation are centered around the concept of clay mineral transformation, as Hower and others imagined it, versus the process of dissolution and reprecipitation (Nadeau 1985).

Data compiled by Weaver (1959) shows that a major change in the composition of clay-mineral suites occurs approximately in mid-Mississippian (Early Carboniferous) time. Data compiled by Weaver (1959) shows that a major change in the composition of clay mineral suites
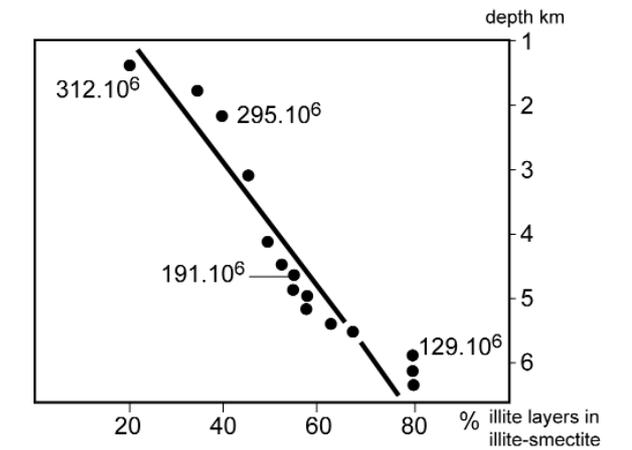

Figure 8. Relation between sample burial depth and percent illite layers in I/S for the <0.5 μm size fraction. Numbers refer to measured K-Ar ages (modified after Perry 1974).

occurs approximately at mid-Mississippian (Early Carboniferous) time. Clay sediments younger than this are much more likely to contain smectite and kaolinite whereas swelling clays in pre-Carboniferous mudrocks are restricted almost entirely to K-bentonites. Kaolinite is rarely described other than as a component, again, in some K-bentonites (Huff *et al.* 1997b). Figure 9, after Weaver & Beck (1977) indicates the relative abundance of various clay minerals in mudrocks as a function of geologic age. Illite, while the predominant clay mineral in all mudrocks, is considerably more abundant in early- and
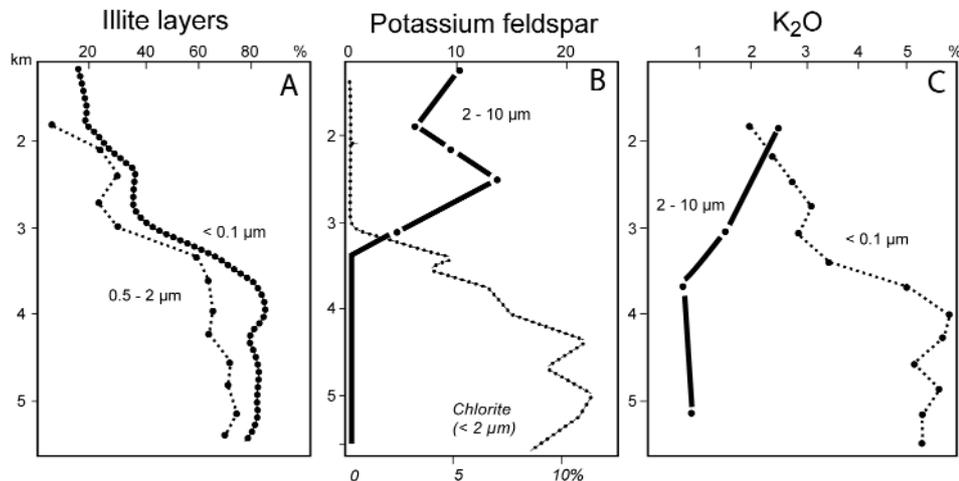

Figure 7. Perry Chemical and mineralogical variations in well CWRU-GC6 as a function of depth. (A) Percent illite in mixed-layer illite-smectite, (B) Chlorite and K-feldspar percent, (C) K2O in both the coarse and fine fractions (after Hower *et al.* 1976).
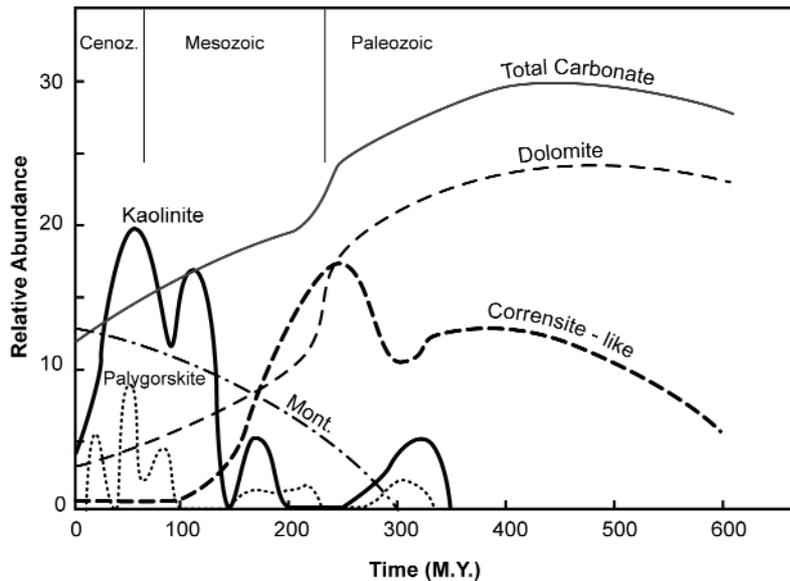
Figure 9. Estimate of the relative abundance of clay minerals in mudrocks as a function of geologic time (modified after Weaver & Beck 1977).

mid-Palaeozoic sediments (Melson *et al.* 1998). Kaolinite occurs only rarely in pre-Carboniferous rocks and then, usually as tonsteins or other volcanogenic deposits (Garcia-Ramos *et al.* 1984; Huff *et al.* 1997b). Bentonites, while common in post-Carboniferous strata are generally K-bentonites in older rocks, the product of smectite alteration to I/S. The principle controlling factors governing this transformation appear to be time, temperature and fluid migration (Elliott & Aronson 1993). Early studies of K-bentonite clay mineralogy by Weaver (1953) and Byström (1956) provided the first detailed insight into the origin of I/S through the alteration of smectite, and led Weaver (1959, p. 181) to conclude that, "much of the mixed-layer illite-montmorillonite in sediments may have been derived from volcanic material deposited in the sea." Since the 1930's K-bentonite beds of Lower Palaeozoic age have been reported from localities throughout eastern North America as well as from parts of South America, Scandinavia and western Europe (Brun & Chagnon 1979; Byström 1956; Huff *et al.* 1998; Kay 1935; Kolata *et al.* 1996; Weaver 1953). Their clay mineralogy is typically dominated by a regularly interstratified illite-smectite (I/S) in which the swelling component accounts for 20–40 percent of the total structure. Accessory clays are

commonly either kaolinite or chlorite. Both siliciclastic and carbonate beds associated with K-bentonite sequences frequently are enriched in volcanogenic debris (Bergström *et al.* 1999) and, as many authors have suggested, the preservation of altered volcanic ash as discrete beds of bentonite or K-bentonite or as admixtures within siliciclastic or carbonate sediments is simply a question of relative rates of sediment accumulation (Huff *et al.* 1999).

Non-clay Minerals

Volcanic debris is recognized as a widespread component of clay-rich deposits, both in recent soils and sediments as well as in ancient consolidated mudrocks (Potter *et al.* 2005). The recognition of these materials is easiest in younger deposits where smectite is a major constituent. But with time and deep burial, smectite-rich sediments undergo a transition to more mixed-layer I/S-rich and illite-rich deposits and the volcanogenic nature of the primary constituents becomes more difficult to distinguish from detrital clays (Nadeau & Reynolds 1981). In such cases, the recognition of primary magmatic phenocrysts can provide clues to their volcanic origin. The principal primary minerals, mostly in the form

of isolated, euhedral phenocrysts, are quartz, biotite, plagioclase and potassium feldspar, ilmenite, apatite, zircon, garnet, and magnetite. Haynes (1992, 1994) has described the characteristics of these minerals in some detail for the Ordovician Deicke and Millbrig K-bentonites in the southern Appalachians. Zircon, in particular, can be a valuable aid in determining the precise ages of the containing beds (Huff *et al.* 1997a). Euhedral to anhedral biotite constitutes up to 30% of the non-clay fraction in some Ordovician K-bentonite in the southern Appalachians, and also serves as a reliable discriminator from otherwise similar appearing beds. In samples where biotite has been well-preserved, it serves as a reliable source of age dates based on the $^{40}Ar/^{39}Ar$ method (Kunk & Sutter 1984; Min *et al.* 2001).

Delano *et al.* (1990) analyzed garnets in Ordovician K-bentonites from New York State and concluded that they represented the influence of a high pressure regime, probably the lower crust, on the composition of the parent magma. They further concluded that this constrained the tectonic setting of the source volcanoes as representing most likely an active plate margin setting. Quartz is particularly abundant in many K-bentonites and may account for as much as 25% of the non-clay fraction (Haynes 1992, 1994). Individual grains are subhedral to anhedral with many showing the remnants of pyramidal faces fractured during the eruption. Quartz grains host numerous melt inclusions whose chemistry provides important insight into the composition of the parental magmac as well as serving as a reliable source of stratigraphic components for chemical fingerprinting (Delano 1992).

Conclusions

Mudrocks throughout the stratigraphic column contain varying amounts of volcanogenic debris. In their most concentrated form, altered volcanic-ash beds appear as bentonites and K-bentonites. In contrast to the clay minerals in Mesozoic and Cenozoic bentonites, which are generally dominated by smectite, Palaeozoic K-bentonites are typified by mixed-layer illite/smectite (I/S) assemblages with illite as the dominant phase. They are generally accompanied by lesser amounts of kaolinite, discrete illite, and mixed-layer chlorite/smectite (C/S). Previous studies have concluded that I/S in K-bentonites, as well as in shales, is a diagenetic product of smectite alteration (Altaner *et al.* 1984; Anwiller 1993; Bethke *et al.* 1986; Brusewitz 1988) and, thus, the recognition of volcanic versus detrital clays in mudrocks becomes more difficult in older strata.

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