

DIAGENETIC CLINOPTILOLITE AND OPAL-CT FROM THE MIDDLE EOCENE WITTERING FORMATION, ISLE OF WIGHT, U.K.

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ABSTRACT: Thinly interbedded estuarine sandstones and mudstones in the middle Eocene Wittering Formation (Bracklesham Group), Isle of Wight, contain authigenic clinoptilolite, opal-CT, and possibly authigenic smectite over a thickness of 8.5 m. The clinoptilolite and opal-CT cements have resulted in these beds being the only ones tightly cemented in the Wittering Formation, the rest being soft sands and muds. The unit contains abundant siliceous sponge spicules, many of which are preserved as voids and were the likely source of the opal-CT. The presence of an organic-rich, rooted paleosol (histosol) immediately overlying the unit is believed to have contributed significantly to the early diagenetic history of the estuarine sediments, in particular the formation of zeolite. Although the pH and dissolved silica of unmodified seawater are too low for zeolite formation, high concentrations of dissolved silica are believed to have resulted from dissolution of siliceous sponge spicules (opal-A) and formation of silica-organic acid complexes. Organic-acid dissolution of feldspars (absent from the zeolite-bearing interval) is the most probable source of alumina and cations for zeolite formation. REE data show that volcanic ash was never present and cannot therefore have been the source of the zeolite. This investigation therefore demonstrates a novel route by which the pore-fluid chemistry required for zeolite formation can be achieved.

INTRODUCTION

Zeolites are an important group of silicate minerals consisting of a hydrated aluminosilicate framework with interstitial cations of the alkali and alkaline earth metals. In marine environments they form during burial diagenesis. The specific conditions for zeolite formation are relatively uncommon, especially the high aSiO₂ required. As a result zeolites are quantitatively uncommon cements of sandstones compared with quartz or calcite. Their formation and composition depends on the chemistry of the mineralogical precursor, the chemistry of interstitial waters, the temperature, and the composition of the host sediments (Kastner and Stonecipher 1978). Consequently, the occurrence of zeolites in sandstones has been recognized to be important to understanding the diagenetic evolution and reservoir characteristics of sandstones in hydrocarbon exploration (e.g., Surdam and Boles 1979; Crossey et al. 1984; Noh and Boles 1993). Formation of zeolites (especially heulandite and clinoptilolite), is widespread in shallow-buried sediments with either abundant biogenic silica (e.g., Coombs et al. 1959; Berger and von Rad 1972; Reich and von Rad 1979; Bohrmann et al. 1989; Gingele and Schulz 1993; Diester-Haass 1995) or volcanic ash (e.g., Read and Eisbacher 1974; Barrows 1980; Tsolis-Katagas and Katagas 1990; Pablo-Galan and Chavez-Garcia 1996; Noh and Boles 1993; De Ros

et al. 1997; Jeans et al. 1997; Noh 1998; Ogihara 2000), or both (Aoki and Kohyama 1998). Where only ash is involved, the ash is silica-rich; where both ash and biogenic silica are involved, the ash can be basaltic (e.g., Hathaway and Sachs 1965; Weaver 1968; Zemmels et al. 1975). Clinoptilolite is also commonly found in pelagic sediments, mostly in brown clays with trace amounts of volcanoclastic debris and microfossil-rich siliceous sediment (40–60% of occurrences), volcanoclastic sediment (20–25% of occurrences), and also in calcareous sediments (Kastner and Stonecipher 1978). Clinoptilolite is seldom found in shallow marine (Noh and Boles 1993; Jeans et al. 1997) or nonmarine (Manville 1997) sediments, though from the above it is evident that the environment of deposition need not be a controlling factor in clinoptilolite formation. In pelagic sediments clinoptilolite is typically found at > 1 m burial depth, with maxima at 7–12 m (Kastner and Stonecipher 1978; Stonecipher 1976 and 1978).

Formation of opal-CT is also widespread in shallowly buried sediments with either abundant volcanic ash (e.g., Heath 1974; De Ros et al. 1997; Matyskiela 1997) or biogenic silica (e.g., Gibson and Towe 1971; Reynolds 1970; Weaver and Wise 1974). Opal-CT or microquartz can result in preservation of high porosity in deeply buried sandstone (Aase et al. 2001). Hence an understanding of the factors controlling distribution of these minerals is of economic interest. The formation of biosiliceous deposits occurs in a wide range of environments and is typically associated with either upwelling or input of terrestrial organic matter supplied by rivers. It is also possible that siliceous organism “blooms” may occur as a result of nutrient enrichment in the form of dissolved volcanic ash. The vast majority of these deposits are diatom-rich. Fracture-surface scanning electron microscope studies (Weaver and Wise 1974; Kastner et al. 1977; Rouchy et al. 1995; Michaelopoulos et al. 2000) have demonstrated the direct replacement of biogenic silica (opal-A) by opal-CT. However, most siliceous sediments are not associated with detectable volcanic ash, and include only minor, if any, zeolite or authigenic smectite (Weaver and Wise 1974; Rouchy et al. 1995). This suggests that other factors are critical to the formation of these minerals. A potential source of solutes for zeolite or smectite precipitation is dissolution of feldspars and silica minerals by organic acids produced by roots (Bennett et al. 1991).

The presence of zeolite in the Wittering Formation (Bracklesham Group, middle Eocene) on the Isle of Wight was previously reported by Gilkes (1968), but this is the first study to consider the noncarbonate diagenesis of the Wittering Formation. The presence of zeolite has been confirmed during a recent systematic study of the clay mineralogy of the entire Tertiary section at Whitecliff Bay (Huggett in press). Published accounts of zeolite in shallow marine sediments with biogenic silica are very few, compared with those for deeper-water deposits. This presented an opportunity to investigate an unusual zeolite mode of occurrence, in as much as the

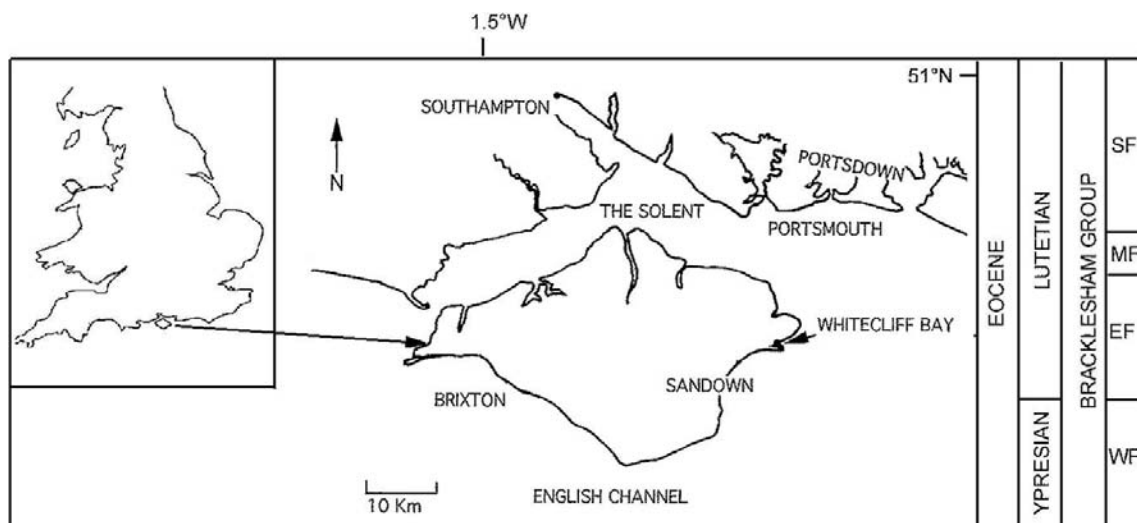


FIG. 1.—Map showing the location of Whitecliff Bay. The sampled interval of the Wittering Formation is shaded gray on the stratigraphic summary log. WF = Wittering Formation, EF = Earnley Formation, MF = Marsh Farm Formation, SF = Selsey Formation.

Wittering Formation was deposited in an estuarine environment, is overlain by nonmarine sediment, and there is no direct evidence in the form of ash falls for volcanoclastic sediment in the Wittering Formation. This investigation set out to show the geochemical requirements for zeolite formation could have been met during diagenesis of the Wittering Formation.

GEOLOGICAL SETTING

During the middle Eocene the Hampshire Basin in southern England (Fig. 1) was a center of shallow marine and estuarine sedimentation in the region adjacent to the proto-Solent estuary (Plint 1983; Huggett and Gale 1997). The Wittering Formation (NP12–13, Ypresian, Bracklesham Group) is a 53 m thick interval comprising mostly uncemented glauconitic sandstones, siltstones, and mudstones. The interval we have studied here (Fig. 1) lies in the higher part of the Wittering Formation, between a marked erosional surface cut in highly glauconitic sandstones (E3 of Plint 1988) and the prominent rooted coal called the Whitecliff Bay Bed. This part of the succession contains a major hiatus that includes magnetic Chron 22. This gap lies either in the E3 erosional surface or at the level of the Whitecliff Bay Bed (Aubry et al. 1986).

At the base of the sampled interval is a glauconitic sandstone (zone A), overlain by an interval of flaser-bedded silty clays and lensoid sandstones (zone B), which increase in thickness and induration between -0.75 and -2.2 m (Fig. 2A). These medium to coarse glauconitic sandstones have erosional bases, are 0.05–0.2 m thick, and contain abundant truncated current ripples and gutter casts (Plint 1983). The sandstones are unique in the Eocene of the region in that they contain sponge spicules and are silica cemented. Above zone B is a bioturbated glauconitic sandstone with an erosional base, and containing carbonate-cemented concretions and shark's teeth (zone C). This passes upwards into several meters of flaser-bedded silty clays and fine sandstones (zone D), with abundant carbonized roots descending from the Whitecliff Bay Bed (zone E). The density of roots increases upwards, progressively obliterating primary sedimentary lamination.

Plint (1983) placed our study interval entirely within his L2 lagoonal facies, which he interpreted as having formed from suspension in quiet water, interrupted episodically by wave agitation and storms which deposited the sandstones and formed the ripples and gutter casts (cf. Reineck and Singh 1973). Limited faunal and floral evidence suggests a mixed-salinity, brackish environment. The overlying coal represents a freshwater marsh, and the subjacent peaty, rooted soil is a buried histosol (Retallack

2001). In Plint's facies model, these dominantly intertidal sediments formed in a coastal area sheltered by an offshore barrier bar (Plint 1988). Plint (1988), Huggett and Gale (1997), and Amorosi (1995) all placed this unit within the transgressive systems tract of a sequence that includes most of the upper Wittering Formation. However, the unit is equally likely to form part of a lowstand, because the deposits infill an incised valley, the base of which is defined by the erosion surface E3 (Jan Hardenbol, personal communication). The Bracklesham Group of the Isle of Wight was probably never buried more deeply than a few hundred meters (Gale et al. 1999), and has therefore not undergone significant burial diagenesis.

There is circumstantial evidence of a basaltic volcanic sediment source for the Wittering Formation. Volcanic activity was occurring at, or about, this time in both Northern Ireland (Old 1975) and in the Faroe–Greenland Province (Knox and Morton 1988). The stratigraphic equivalent to the Wittering Formation in Denmark, the top of the Rosnæs Clay Formation and the base of the Lillebælt Clay Formation, is an interval with ash layers attributed to the Faroe–Greenland pyroclastic phase.

SAMPLING AND METHODS

Our unpublished data from above and below this interval show zeolite and opal-CT to be absent from outside the sampled interval of the Wittering Formation. For this investigation we sampled at 0.05–0.2 m intervals through the main zeolite and opal-CT bearing interval, taking care to include every sandstone and mudstone bed (Fig. 2B). For a further 2 m above and 2.5 m below, samples were taken at 0.5 m intervals. This range was sufficient to include all cemented sandstone beds in the Wittering Formation and many uncemented ones. Samples of mudstone from 2 m above the coal, and from the Glauconitic sandstone A, were included for thin-section analysis (Appendix I) and bulk rock XRD (Table 1). Sample positions are described as plus or minus their height above or below a central point that is the burrowed base of glauconitic sandstone C (Fig. 2).

Bulk-rock quantitative X-ray diffraction (XRD) analyses samples were obtained using a Enraf–Nonius diffractometer with PSD (Position Sensitive Detector) 120 (Table 1), Cu K α radiation and Ge monochromator. The samples were crushed with acetone, and a thin film of the powder was mounted on a quartz substrate and analyzed at approximately 7 degrees between surface sample and beam. The quantitative analysis was done using a whole-pattern fitting method (Batchelder and Cressey 1998). Cristobalite was used as a proxy for opal-CT. Two zeolite-rich samples were re-scanned after heating at 500°C for 4 hours. The $< 4 \mu\text{m}$ fraction of each

sample was analyzed by XRD. A portion of each sample was gently crushed, mixed with distilled water plus a few drops of $\text{NH}_4(\text{OH})$ as a dispersant, and placed in an ultrasonic bath (at 20°C) for 10 minutes to release the maximum amount of clay into suspension. The suspended material was centrifuged to leave only the clay fraction in suspension (800 revolutions/minute for 3 minutes); this was then centrifuged at 4000 revolutions/minute for 30 minutes to deposit the entire $< 4 \mu\text{m}$ fraction, which was filtered (mixed with a little distilled water to make a thick slurry) onto an unglazed ceramic tile. The samples were scanned on a Phillips 1820 automated X-ray diffractometer using Ni-filtered CuK radiation. The clay tiles were scanned at a rate of 5 seconds per 0.02° step width, using 0.3 mm slits from 2 to $40^\circ 2\theta$. After spraying with glycol they were re-scanned from 2 to 26° and again after heating at 400°C for 4 hours, and if necessary, after heating at 550°C , also for 4 hours. Using weighting factors calculated from known mixtures of clays, opal-CT, and clinoptilolite, semiquantitative percentages of these components were calculated.

Thin sections (stained with sodium cobaltinitrate) of 9 sandstones were point-counted (500 points) to determine the proportion of sponge spicules (Appendix I, see Acknowledgments). Polished thin sections of 15 mudstone beds were also examined optically. Three sandstone thin sections with $> 10\%$ zeolite and three with only trace amounts were carbon coated and examined in greater detail by back-scattered electron microscopy. The sections were examined in a Jeol LV3510 electron microscope with an Oxford instruments ISIS energy dispersive X-ray analysis system. Gold-coated fracture surfaces of selected zeolite and opal-CT-rich samples were examined in secondary electron imaging mode.

Major-element, trace-element, and rare-earth-element (REE) geochemical analysis was performed on five samples spanning an interval with both high and low zeolite content. Samples were ground using an agate ball mill, dried at 105°C overnight, and subjected to LiBO_2 fusion to effect a total dissolution; analysis was undertaken using a combination of inductively coupled plasma-optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS) (see Wray and Wood 1998). Rare-earth element data for all samples have been normalized to chondrite and to the USGS reference material Cody Shale (SCO-1), which was prepared and analyzed as part of the batch (see Jarvis and Jarvis 1985).

RESULTS

Petrology

The glauconitic sandstones A and C are very fine to fine grained, well sorted, quartz arenite with minor pyrite and calcite cements. Zone B siltstones and very fine grained sandstones are also glauconitic and well sorted, and have variable proportions of clay matrix. Several zone B siltstone and sandstone beds are rich in sponge spicules, with up to 10% point counted at -2.65 m (Figs. 2B, 3). Zone B mudstones are planar bedded with occasional siltstone or sandstone-filled burrows. They are dominated by clay, with 20–35% quartz silt, 4–6% organic matter (visible in thin section), $< 5\%$ pyrite, and occasional reworked glauconite. Zone D is similar to B but finer grained overall, and with many more carbonized roots extending down from the coal. Variable proportions of a microcrystalline silica mineral were observed by optical microscopy of zones B–D siltstones and sandstones (Fig. 3). XRD analyses show that the silica mineral is opal-CT (it has a pair of reflections between 4.04 and 4.09\AA , or less often, one broad reflection). Opal-CT is most abundant (up to 15% point counted) in the beds with least clay and pyrite. The lithified samples are those with the most opal-CT. Overall, sandstones analyzed by bulk-rock quantitative XRD have 3–8% zeolite and $\leq 11\%$ opal-CT, whereas the mudstones have $\leq 2\%$ zeolite and $\leq 3\%$ opal-CT (Table 1). Insufficient K feldspar was detected in thin section from zones B–E to register in any of the point-counts or bulk rock XRD. This is in contrast to the rest of the formation (including the point counted mudstone from 2 m above the coal and glauconitic sand-

stone A), where $\sim 4\%$ feldspar is the norm in mudrock and $\sim 10\%$ in sandstone (Table 1, Fig. 4E, F).

Opal-CT and zeolite in the Wittering Formation occur over an interval approximately 8.5 m thick, but mostly in zones B–D (Fig. 2B). Both minerals are absent from the rest of the Bracklesham Group (Huggett and Gale 1997). Zeolite reflections detected by XRD (Table 2) are intermediate in relative intensities between heulandite and clinoptilolite (Mumpton 1960; Bish and Boak 2001). Reflection positions are closest to clinoptilolite, but relative intensities are intermediate between clinoptilolite and heulandite. Heating at 500°C resulted in a slight shift of reflection positions to lower values but an insignificant change in relative intensities. This stability on heating confirms that the mineral is clinoptilolite. The Si/Al ratio > 4 (based on quantitative EDS analyses) also indicates that the mineral is clinoptilolite (Boles 1972). The cations are principally Ca, with minor Na, K, and Mg (Table 3). The content of alkali metal and alkaline earth metal cations of the Wittering Formation clinoptilolite is low compared with many published analyses (Kastner and Stonecipher 1978; Ogihara and Ijima 1989; Sameshima 1987; Sheppard 1989; Ogihara 2000). The reason for this is not apparent. Scanning electron microscopy revealed euhedral prismatic crystals of clinoptilolite up to $50 \mu\text{m}$ long and $25 \mu\text{m}$ wide, marginally overgrown by spheres of opal-CT platelets (Fig. 4A). The opal-CT forms coatings on quartz grains and clay-coated grains, it is also intergrown with clinoptilolite, and it infills moldic porosity in sponge spicules (Fig. 4B).

Both the zeolite and the opal-CT are concentrated in the siltstone and sandstone beds, though they have dissimilar distribution patterns: opal-CT is distributed more widely across the sampled interval and not all the clinoptilolite maxima coincide with opal-CT maxima (Fig. 2B). Both minerals have their maximum abundances between -0.7 m and -1.45 m, but opal-CT is almost as abundant between -2 m and -4 m, and does not increase between -0.1 m and $+0.5$ m as does the clinoptilolite. The zeolite occurs between -3.75 m and $+2.50$ m (zones B–D) and opal-CT occurs between -4.75 m and $+4$ m (Fig. 2B). The zeolite is estimated to form up to 25% of the clay fraction (7% of the whole rock).

The clays of the $< 4 \mu\text{m}$ fraction are predominantly smectite and illite with minor kaolinite and chlorite. Semiquantitative XRD analysis indicates that smectite typically forms 40–70% of the clay fraction. Illite values are typically 20–60%. Chlorite and kaolinite are typically $< 5\%$ of the clay fraction. Kaolinite was not detected in about half the samples. In this respect the sampled interval is no different from the rest of the Wittering Formation (Huggett and Gale 1997). In BSEM images of samples without zeolite, the clay matrix typically has a compacted texture (Fig. 4C), whereas in the zeolite-bearing samples occasional patches of open textured smectite were noted, with or without opal-CT in the interstices (Fig. 4D).

Major-element and trace-element data are broadly similar to those found in clays and shales (Wedepohl 1969; Gromet et al. 1984). All geochemical data are tabulated in Appendix II (see Acknowledgments). Chondrite and Cody Shale normalized REE data are plotted in Figure 5, and REE are plotted stratigraphically in Figure 2B.

Sponge Spicules

Marine siliceous sponges were widespread and abundant worldwide in shallow water during the middle and late Eocene (Gammon et al. 2000). Sponge spicules occur throughout the middle part of the sampled interval, and are common from -2.5 to -3.0 m in zone B, where they constitute up to 10% of the total sediment. The spicules are entirely disarticulated, indicating that they have been transported. Sponge spicules have three discrete preservational styles: (1) hollow external molds formed by opal-CT lepispheres which are found in the lithified sandstones (Fig. 4A), (2) solid structureless pseudomorphs (quartz) which are found in the unconsolidated sandstones, and (3) pyritized spicules, recorded by King and Kemp (1982). Pyritized spicules are known from other parts of the Bracklesham and Bar-

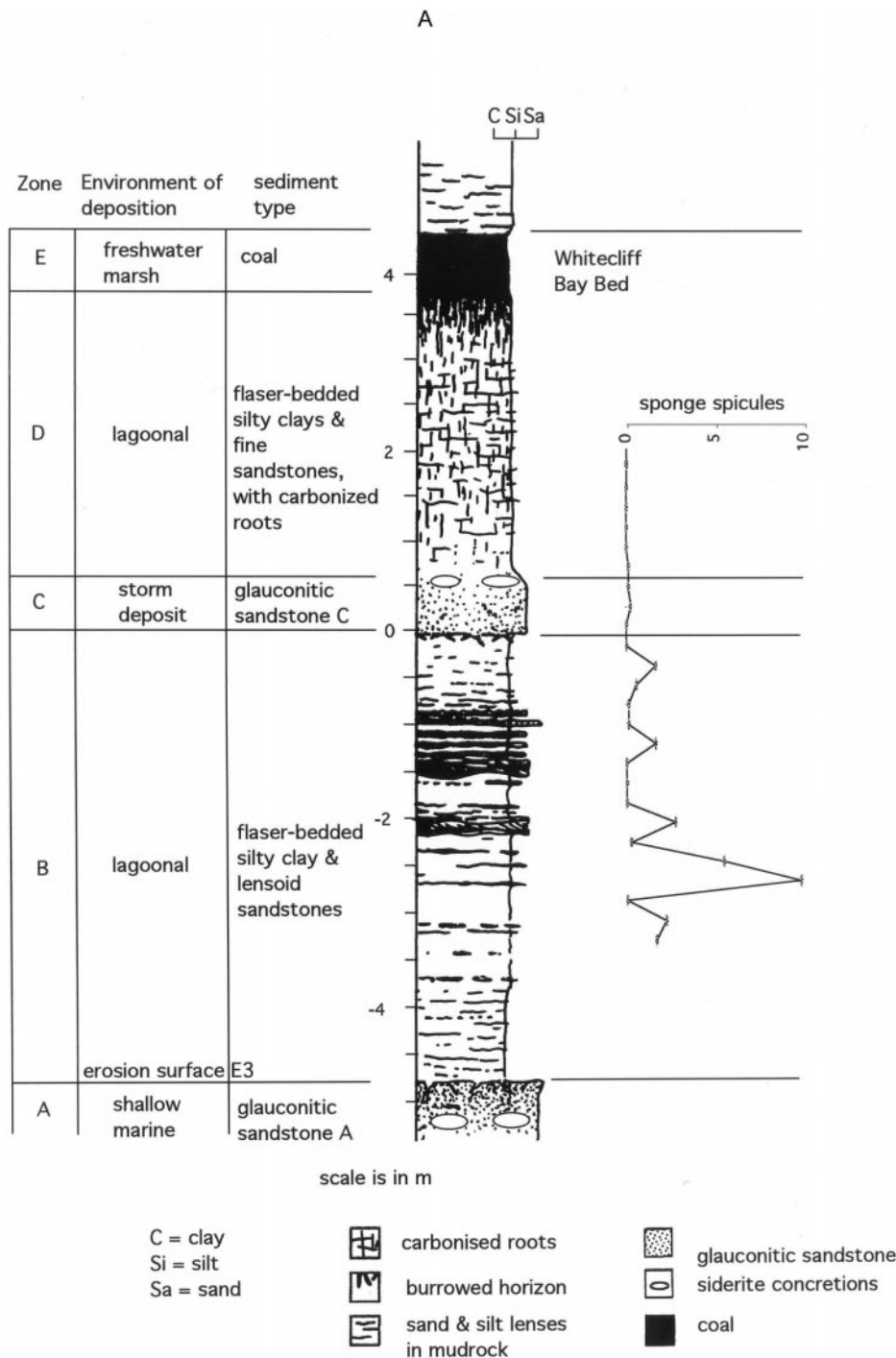


FIG. 2.—A) Lithological section with sedimentological description and zonation, environments of deposition, and point-counted abundances of sponge spicule (including spicule solution cavities and pyritized spicules) indicated. B) Lithological section with semiquantitative XRD determined abundances of opal-CT, clinoptilolite, and smectite in the $< 4 \mu\text{m}$ fraction for all samples.

DISCUSSION

ton groups, but the other two preservation modes are not found. Preservation of spicules as opal-CT external molds has been described from the Eocene of Messel in Germany (Finks et al. 2003) and pyritized spicules are well known from the Paleozoic of North America (e.g., Hall and Clark 1899).

The siliceous spicules belong to either hexactinellid or demosponge taxa (Finks et al. 2003) but are insufficiently well preserved to determine their taxonomic affinity more precisely. Both groups have spicules consisting mainly of opal A, and thus can occupy both freshwater and marine environments. Inasmuch as the present records are from likely brackish paleoenvironments, either possibility exists.

The unique occurrence in the Bracklesham Group of opal-CT and clinoptilolite cements, and the absence of feldspar grains, in an 8.5 m thick unit containing sponge spicules, suggests that their origins are linked. SEM observations suggest that the origins of the two minerals are related because they are intergrown and both are clearly authigenic. The open-textured smectite seen in opal-CT-cemented and clinoptilolite-cemented beds may also be authigenic. Clinoptilolite has a calculated precipitation temperature of $30\text{--}60^\circ\text{C}$ (Ijima 1978), which is consistent with it having precipitated at or around the same time as the opal-CT. For the Wittering Formation this

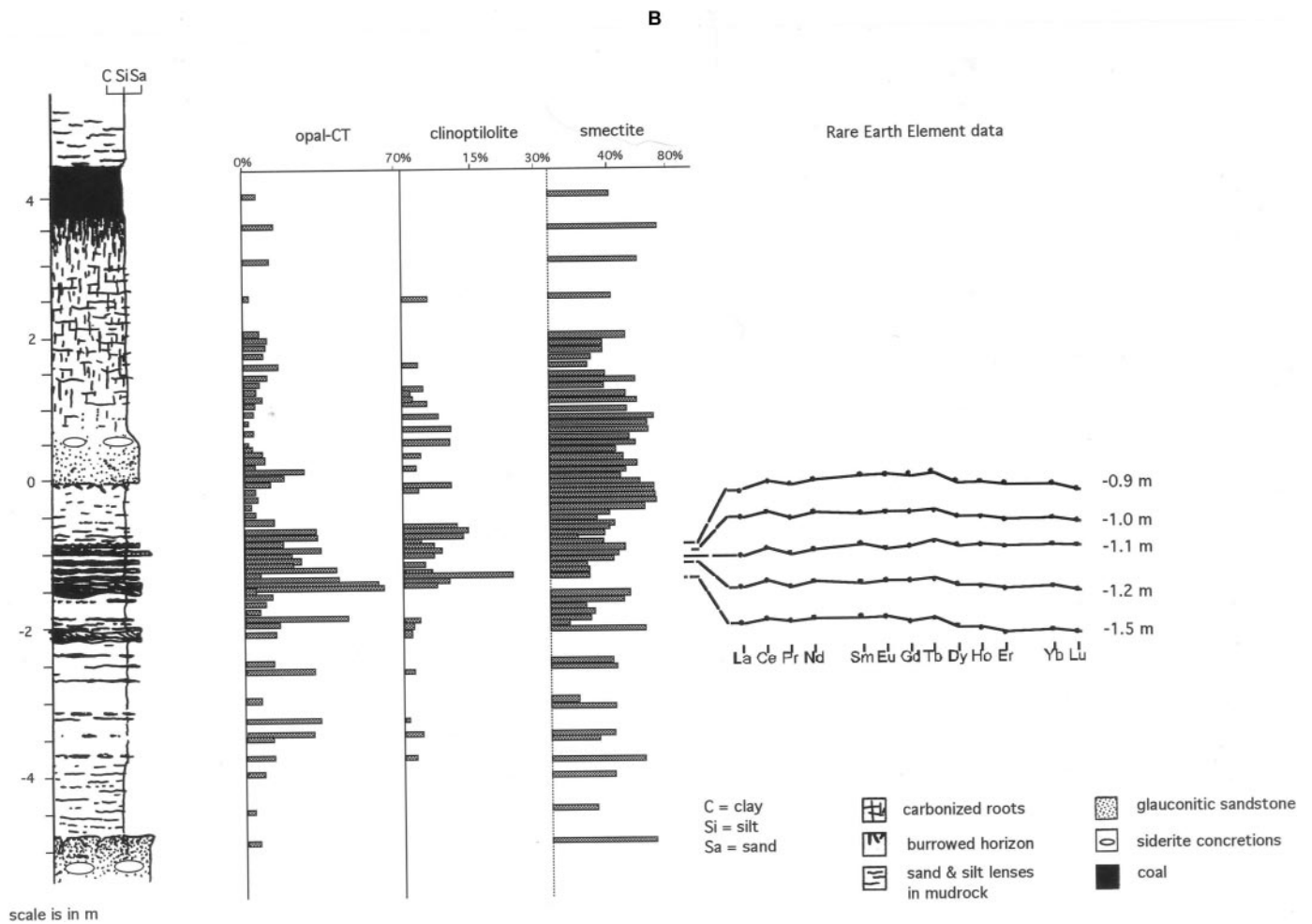


FIG. 2.—Continued.

TABLE 1.—Quantitative whole-rock XRD analyses. Numbers are percentages. Note that some pyrite has been altered to gypsum via recent weathering.

Depth (m)	Lithology	Illite & Glauconite		Quartz	K Feldspar	Gypsum	Opal-CT	Clinoptilolite	Pyrite
		Smectite	Glauconite						
6.5	mudstone	41	30	26	2	0	0	0	1
3.5	mudstone	30	58	11	0	0	0	0	0
3.0	mudstone	36	40	22	0	1	0	2	0
1.9	mudstone	27	50	21	0	2	0	0	0
1.6	mudstone	31	50	18	0	1	0	0	0
1.5	mudstone	32	43	24	0	1	0	0	0
1.1	mudstone	49	28	23	0	0	0	0	0
1.0	mudstone	34	46	20	0	0	0	0	0
0.3	sandstone B	35	18	44	0	1	0	2	0
0.1	mudstone	36	39	22	0	0	0	2	0
-0.2	mudstone	35	39	25	0	1	0	0	0
-0.5	mudstone	31	46	23	0	0	0	0	0
-0.7	sandstone/mudstone	19	15	50	0	2	7	7	0
-1.4	sandstone	18	21	40	0	5	10	4	2
-1.5	mudstone	34	53	14	0	0	0	0	0
-2.0	sandstone	5	26	37	0	5	25	2	0
-2.5	mudstone	40	36	22	0	1	1	0	0
-3.0	mudstone	28	58	14	0	0	1	0	0
-3.5	mudstone	29	43	25	0	1	3	0	0
-5.0	sandstone A	3	25	64	8	0	0	0	0
-6.0	sandstone A	6	21	60	13	0	0	0	0

implies precipitation of opal-CT and clinoptilolite soon after burial, and is consistent with these sediments having a maximum burial depth of around 200 m (Gale et al. 1999). The dissolved-silica concentration and the pH of unmodified seawater are too low for zeolite formation, while the formation of both zeolite and smectite requires a variety of other ions, of which Al³⁺ is most problematic, having a very low solubility in water. These factors are discussed below.

Comment on Precipitation of Zeolite and Opal-CT

Formation of clinoptilolite requires silica and alumina plus alkali and alkaline earth metal cations. Activity diagrams for the system Ca–Na–K–Al–Si plus H₂O calculated by Bowers and Burns (1990) indicate that the formation of clinoptilolite is favored by a temperature of ~ 25°C and SiO₂ activities higher than allowed by the presence of quartz. The latter is achieved when clinoptilolite coexists with opal. The temperature control has been observed both in natural systems (Hay and Sheppard 1977) and in hydrothermal experiments (Boles 1971; Hawkins et al. 1978; Knauss et al. 1985). Clinoptilolite has a maximum stability field where Al activity is intermediate, which can be achieved in natural systems by the assemblage amorphous silica plus smectite (Bowers and Burns 1990). In the following, we discuss how the geochemical environment of the Wittering Formation zones B–D may have developed a pore fluid that lay within the range predicted by thermodynamic calculations.

The presence of sponge spicules with moldic porosity cemented by opal-

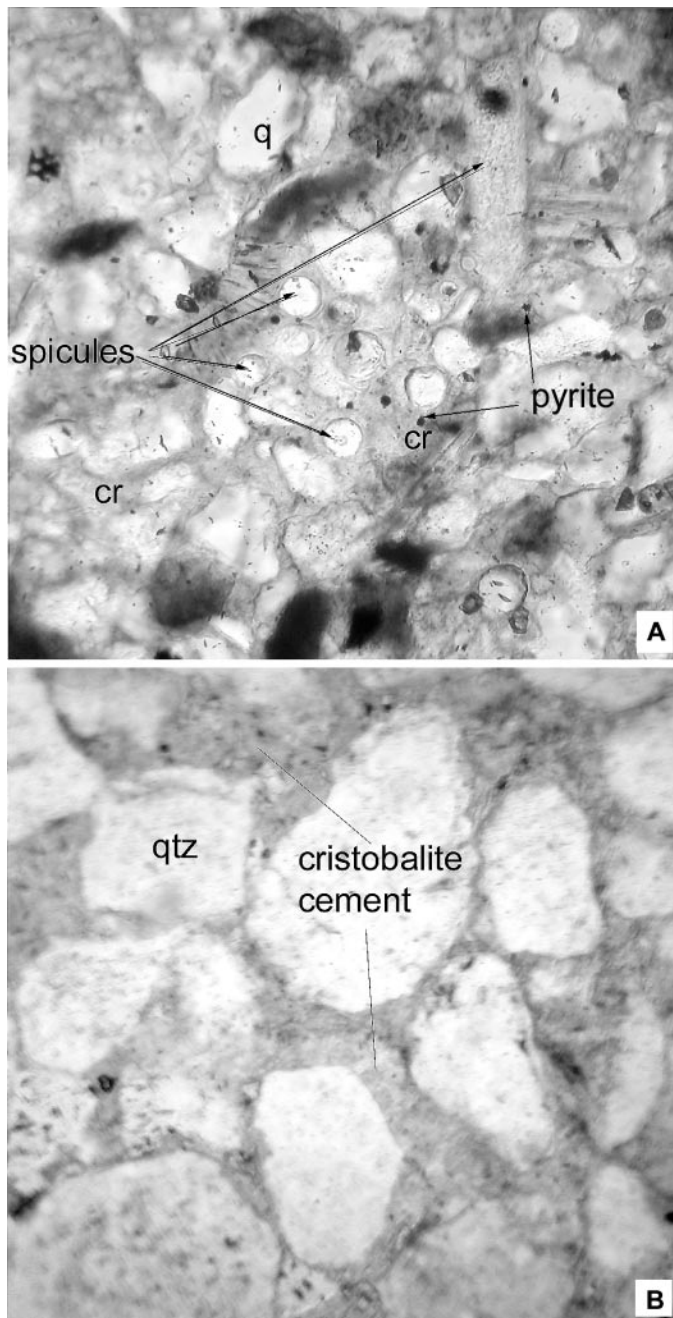


FIG. 3.—**A**) Thin-section optical micrograph of sandstone from -2.65 m, showing sponge spicules in cristobalite-cemented sandstone; cr = cristobalite, q = quartz grain. Field of view = $400 \mu\text{m}$. **B**) Thin section optical micrograph of sandstone from -0.95 m, showing cristobalite cemented sandstones; qtz = quartz grain. Field of view = $400 \mu\text{m}$.

CT strongly suggests that the spicules were the source of the opal-CT. Sponge spicules are opal-A, which undergoes transformation to opal-CT during diagenesis. The rate-determining steps in the opal-A to opal-CT transition are alkalinity, concentration of dissolved magnesium, and temperature (Kastner et al. 1977). The transition typically takes place over the temperature range $20\text{--}50^\circ\text{C}$ (Hesse 1990; Knauth 1994). The presence of spicule cavities (Fig. 4B) implies that this is a dissolution-precipitation reaction. Bennett et al. (1991) found that silica concentration in porewater can be enhanced by up to a factor of two where silica-organic-acid com-

plexes form in sediment beneath peat bogs. Many (probably all) plant roots secrete low-molecular-weight organic acids that are important in mineral dissolution (Deng and Dixon 2002). These root exudates are “food” for microbial communities, which subsequently become more abundant and active in the rhizosphere. These microbial communities enhance dissolution through the production of their own organic acids. We suggest that roots from the overlying histosol released organic acids that were able to form such complexes with dissolving sponge spicules. During subsequent burial, increased alkalinity resulting from microbially mediated organic-matter diagenesis may have been the trigger for breakdown of silica-organic-acid complexes resulting in opal-CT precipitation.

Previously it has been suggested that the source of cations required for clinoptilolite precipitation is dissolution of volcanic ash (Read and Eisbacher 1974; Tsolis-Katagas and Katagas 1990; Pablo-Galan and Chavez-Garcia 1996; Noh and Boles 1993; De Ros et al. 1997; Jeans et al. 1997; Noh 1998; Ogihara 2000) or clay minerals (Michalopoulos et al. 2000). Dissolution of feldspar (the latter now absent from the zeolite and opal-CT cemented interval of the Wittering but not from the rest of the formation) suggests that this mineral could be the main source of alumina and cations for zeolite and smectite formation. Dissolution of feldspar rather than clay is known to occur in sediment beneath peat bogs at the present day (Bennett et al. 1991). Evaporative concentration of seawater, though rare, is known to create conditions favorable for clinoptilolite formation (Rouchy et al. 1995). This is a further possible mechanism for clinoptilolite formation in the intertidal sediments of the Wittering Formation.

Precipitation of zeolites is also favored by alkaline pH. Alkalinity can be increased during early diagenesis through degradation of discrete organic matter by iron-reducing bacteria (Curtis 1977, 1987), and may be further increased in the zone of sulfate reduction if H^+ ions are removed as H_2S gas (Coleman 1985). In the Wittering Formation the intertidal mudstones are fairly organic-rich (typically 4–6% organic matter) and may have been an important source of alkalinity. The presence of early diagenetic siderite concretions in the glauconitic sandstones at $+0.5$ m and -3.25 m is also consistent with enhanced alkalinity through microbial diagenesis (Huggett et al. 2000). As described above for opal CT precipitation, we propose that in the Wittering Formation increased alkalinity may have been the trigger for breakdown of silica-organic-acid complexes and consequent clinoptilolite formation. We note that in recent pelagic sediment clinoptilolite precipitation is concentrated at 7–12 m burial depth, which is consistent with this occurring within the zone of microbially mediated diagenesis.

Role of Volcanic Ash

The pH of the seawater, the aSiO_2 , and the $(\text{Na} + \text{K})/\text{H}^+$ may all be increased by alteration of volcanic glass to smectite (Tsolis-Katagas and Katagas 1990), which makes volcanic ash an obvious potential precursor to both zeolites and opal-CT (Nielsen and Heilmann-Clausen 1988; Shepard 1989; Ogihara and Ijima 1989). We observed no direct evidence, such as volcanic shards or pseudomorphs of volcanic shards, in the Wittering Formation. The sandstones with erosional bases with which the clinoptilolite concentrations are associated may have cut down through an ash band, with the result that ash became incorporated into the sediment. This would require that either the ash horizon has been entirely reworked, or that it is restricted to the subsurface and has not yet been identified from boreholes; in our opinion both of these are unlikely. The Faroe-Greenland volcanic province is also an unlikely source of ash in the Wittering Formation for the following reasons. Firstly, ash deposits in the Rosnæs Clay Formation and the base of the Lillebælt Clay Formation are sparse compared with those in the earliest Eocene Balder Formation (Nielsen and Heilmann-Clausen 1988), which is stratigraphically equivalent to division A of the London Clay Formation, an interval that includes no zeolites in the Isle of Wight (Huggett and Gale 1998). Secondly, given that the paleogeography was similar to that which now exists, it is likely that the prevailing wind direc-

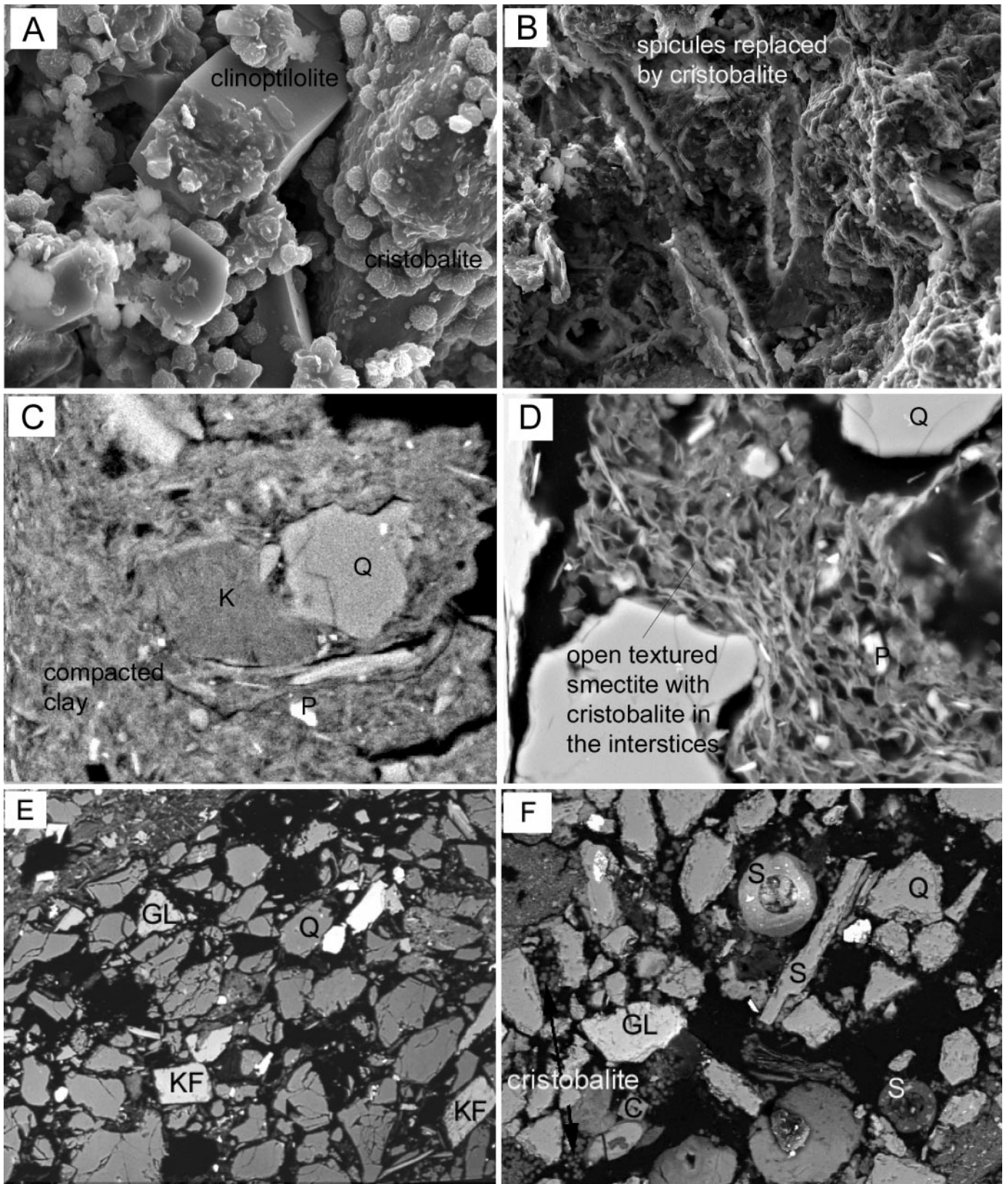


FIG. 4.—A) Fracture-surface SEM of clinoptilolite in sandstone marginally overgrown by grain-coating cristobalite spheres. Field of view = 360 μm . B) Fractured surface SEM of sponge spicules with moldic porosity cemented by spherulitic cristobalite (clayey sandstone). Field of view = 250 μm . C) Back-scattered SEM of compacted detrital smectite in mudstone. Q = quartz with overgrowths, possibly inherited, K = kaolinite after mica, P = pyrite. Field of view = 60 μm . D) Mudstone back-scattered SEM of open-textured smectite with cristobalite in the interstices. Q = quartz, P = pyrite. Field of view = 60 μm . E) Backscattered SEM of glauconitic sandstone A; this sandstone has feldspar unlike those above it with cristobalite and clinoptilolite; Q = quartz grain, KF = K feldspar grain, GL = glauconite pellet. Field of view = 360 μm . F) Sponge-spicule-rich sandstone from -0.7 m; S = sponge spicule, Q = quartz grain, GL = glauconite pellet. Field of view = 360 μm .

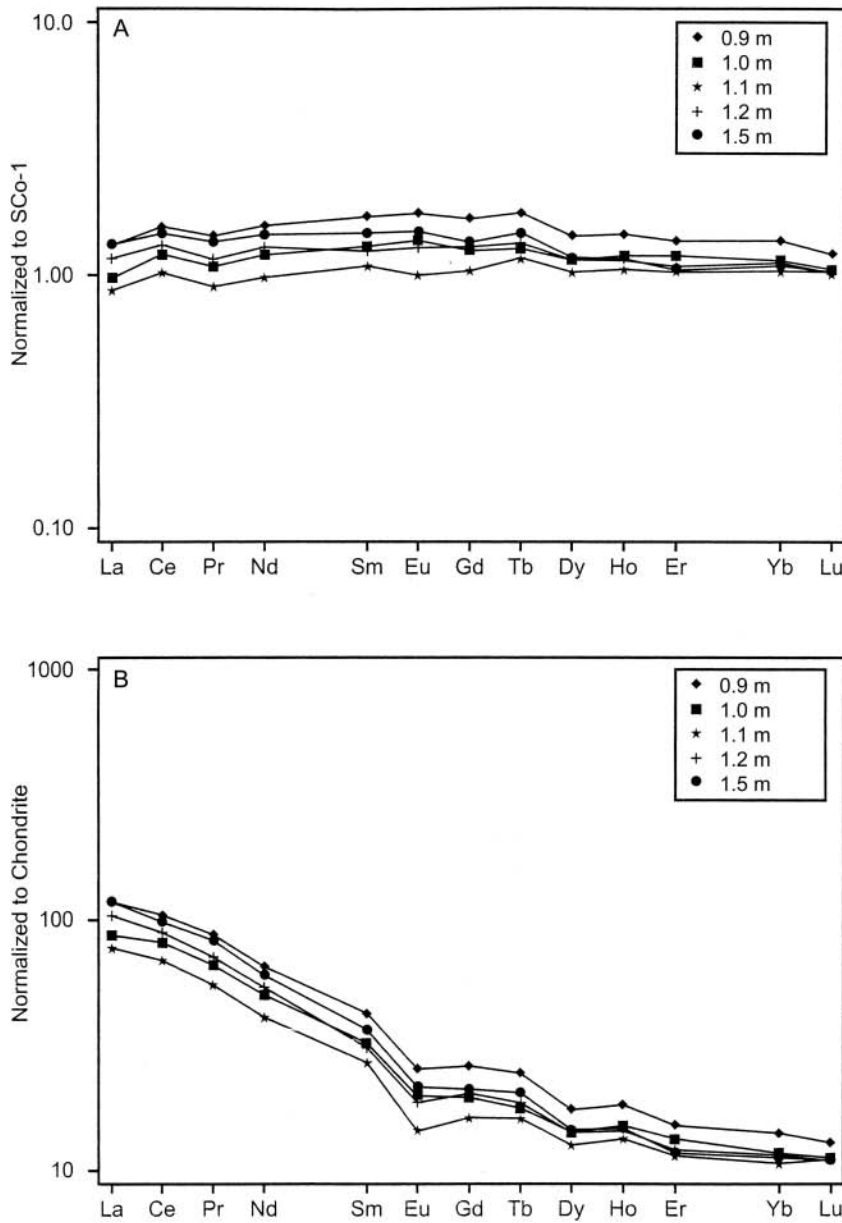


FIG. 5.—A) Chondrite and B) Cody Shale normalized REE data for samples from—0.9 m,—1 m,—1.1 m,—1.2 m, and—1.5 m.

TABLE 2.—Strongest X-ray diffraction reflections and their relative intensities for clinoptilolite, heulandite, and the Wittering zeolite. The clinoptilolite and heulandite data are from Mumpton (1960).

Reflection	Clinoptilolite from Hector, California		Heulandite from New Jersey		Wittering Formation Zeolite		
	d	I/I	d	I/I	d	I/I	I/I after heating
0 2 0	9.00	10	8.90	10	8.97	10	10
2 0 0	7.94	4	7.94	2	7.93	2	2
2 0 -1	6.77	3	6.80	1	not detected		
0 0 1	6.64	2	6.63	1	not detected		
3 1 -1	5.24	3	5.24	1	5.25	0.5	0.5
0 0 4	3.96	10	3.97	2	3.97	8	8
2 4 0	3.90	8	3.89	3	3.90	6	6
2 2 -2	3.42	6	3.40	2	not detected*		
1 5 1	2.97	5	2.97	4	2.97	3	2

* Too close to the quartz 101 reflection.

tion was, as now, from the southwest. This would make it unlikely that ash produced over 2500 km to the north would be deposited in the Hampshire Basin. Tertiary rhyolites (precise age unknown but probably older than the Wittering Formation) are known from Antrim in northeastern Ireland (Old 1975). These are a more likely ash source than the Faroe-Greenland province, because the source is situated northwest of the Isle of Wight, which is closer to the prevailing wind direction than is north, and it is approximately 1000 km nearer, though still no less than 700 km from Hampshire. In conclusion, the case for a volcanic source is not a strong one.

However inasmuch as volcanic ash can be associated with zeolite deposits we decided to investigate the REE chemistry of a selection of samples with low and high clinoptilolite contents. REE analysis has proved to be particularly effective in the recognition of bentonites and volcanic ash in sediments (e.g., Wray 1999; Jeans et al. 2000). If alteration occurs within a fully open marine system the resultant REE profile commonly contains a marked negative cerium anomaly, reflecting the seawater influence (Vitali

TABLE 3.—Means and standard deviations for 5 EDS analyses of zeolite crystals. Fe is presumed to be Fe₂O₃, Fe(II) was not analyzed.

	Mean of 5 Analyses
SiO ₂	68.1 ± 3.2
Al ₂ O ₃	12.7 ± 1.0
Fe ₂ O ₃ *	0.5 ± 0.3
MgO	0.8 ± 0.2
CaO	2.2 ± 0.4
K ₂ O	1.2 ± 0.7
Na ₂ O	0.8 ± 0.4
N ₂ O	14.2 ± 2.6
Total	100

et al. 2000). In contrast, the REE distribution in detrital shales is remarkably consistent and predictable, and is normally unaffected by diagenetic processes (Haskin et al. 1966; Fleet 1984; McLennan 1989). Acidic to intermediate volcanic rocks, such as those found in Tertiary successions in the British Isles and surrounding seas (Knox and Morton 1983; Bell and Emeleus 1988; Knox and Morton 1988; Nielsen and Heilmann-Clausen 1988) have significantly higher REE contents than that found in shales and typically display a marked negative europium anomaly. Hence normalization of sample data to shale values enables a distinction to be made between detrital and volcanically derived clays and, if beds are volcanogenically derived, may also provide information as to the timing of the alteration of volcanic ash to clay and zeolite.

The shale-normalized REE plots derived from this study are broadly horizontal and have values comparable to those commonly found in detrital shale. Furthermore, the plots do not display evidence of a cerium anomaly, implying negligible alteration in the presence of seawater. We therefore conclude that there is no evidence from REE profiles for a significant volcanic component in the sediment at the time of deposition. Support for this conclusion is also provided by TiO₂/Al₂O₃ data for the beds, which have a mean ratio of 0.06. Previous workers (e.g., Spears and Kanaris-Sotiriou 1979; Teale and Spears 1986) have noted that bentonites and tonsteins tend to have somewhat lower TiO₂/Al₂O₃ values (commonly below 0.02) whilst the values derived from the beds examined in this study fall into the range of values typical of detrital beds. Overall, we conclude that the beds are predominantly of detrital origin and that there is no geochemical evidence to support a volcanic contribution to these units.

CONCLUSIONS

An unusual set of circumstances may have existed during burial of the estuarine sediments in the Wittering Formation, resulting in precipitation of zeolite in estuarine biogenic silica-rich sediment, rather than in the more usual deep-water setting. This investigation demonstrates a novel route by which the pore-fluid chemistry required for zeolite formation can be achieved. The unusual circumstances were the presence of locally abundant sponge spicules and enhanced organic acid activity due to the presence of roots from the overlying buried histosol. Sponge spicules (opal A) have been dissolved and/or replaced by opal CT, indicating that the spicules were a source of the opal-CT. The dissolution of biogenic opal and formation of silica-organic-acid complexes may have sufficiently enhanced pore water aSiO₂ for clinoptilolite to precipitate. The pH of unmodified seawater is too low for zeolite formation, but increased alkalinity resulting from organic-matter degradation and enhanced availability of Al, Fe, Ca, Mg, K, and Na through dissolution of feldspar, and possibly clay, by rhizosphere organic acids may have triggered precipitation of clinoptilolite and opal-CT. Although zeolite precipitation has in many instances been linked to volcanic-ash dissolution, ash need not be a prerequisite for the reaction and we conclude from the REE element data that it is not.

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The data described in this paper have been archived, and are available in digital form, at the SEPM data archive, URL: <http://www.sepm.org/archive/index.html>; e-mail: kfarnsworth@sepm.org.

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APPENDIX I

Depth in m	% Sponge Molds	% Pyritized Spicules	% Sponge Spicules	% Other Pyrite	% Glauconite Pellets	% Clay-rich Matrix	% Macro Porosity	% Organic Matter	% Quartz
-3.45	1.00	0.00	1.50	5.00	0.00	40.00	0.00	0.50	52.00
-3.00	0.00	0.00	2.00	1.00	1.00	68.20	0.00	1.00	26.80
-2.50	0.00	0.00	0.00	3.00	2.00	85.00	0.00	5.50	4.50
-2.65	2.50	2.00	7.00	1.00	10.00	40.00	0.00	0.00	37.50
-1.99	2.50	1.00	4.00	1.00	10.00	10.00	0.00	0.50	71.00
-1.50	0.00	0.00	0.20	3.50	0.50	83.50	0.00	1.50	10.80
-1.40	0.50	0.50	2.00	6.00	15.00	10.00	0.00	2.00	64.00
-1.20	0.00	0.00	0.00	3.00	1.00	90.00	0.00	1.00	5.00
-1.15	0.00	0.00	0.00	3.00	1.00	45.00	5.00	0.00	46.00
-0.95	0.00	0.00	0.00	0.00	1.00	30.00	10.00	0.10	58.90
-0.90	0.00	0.00	1.50	5.00	2.00	5.00	10.00	0.00	76.50
-0.70	0.10	0.00	0.10	5.00	0.50	40.00	0.00	5.00	49.30
-0.60	0.01	0.00	0.10	0.40	0.30	50.00	1.00	1.00	47.19
-0.50	0.00	0.00	0.50	7.00	1.00	80.00	0.00	4.00	7.50
0.00	1.00	0.00	1.50	3.00	1.00	12.00	23.50	1.50	56.50
-0.05	0.00	0.00	0.00	3.00	0.20	60.00	0.00	2.00	34.80
0.10	0.00	0.00	0.00	1.50	2.00	40.00	0.00	0.00	56.50
0.20	0.10	0.00	0.20	0.50	2.00	42.00	0.00	0.10	55.10
0.40	0.00	0.00	0.10	0.50	3.00	42.00	0.00	0.00	54.40
1.00	0.00	0.10	0.00	3.40	0.50	94.00	0.00	0.50	1.50
1.50	0.00	0.00	0.00	6.50	1.50	86.50	0.00	1.50	4.00
1.90	0.00	0.00	0.00	3.00	1.00	91.50	0.00	4.00	0.50
3.00	0.00	0.00	0.00	7.50	0.50	88.00	0.00	3.00	1.00
4.00	0.00	0.00	0.00	0.50	0.10	98.00	0.00	1.40	0.00

APPENDIX II

	NASC	0.9 m	1 m	1.1 m	1.2 m	1.5 m
SiO ₂	64.80	62.21	67.68	67.53	61.62	59.03
Al ₂ O ₃	16.90	15.80	13.00	9.79	15.22	15.40
Fe ₂ O ₃ (t)	6.33	6.35	5.56	4.28	5.75	6.49
MnO	0.06	0.021	0.024	0.016	0.022	0.029
MgO	2.85	1.83	1.61	1.14	1.82	1.91
CaO	3.56	0.106	0.170	0.208	0.220	0.564
Na ₂ O	1.15	0.280	0.366	0.364	0.340	0.274
K ₂ O	3.99	2.62	2.29	1.83	2.53	2.53
TiO ₂	0.78	0.905	0.769	0.707	0.845	0.804
P ₂ O ₅	0.11	0.029	0.023	0.019	0.030	0.034
Ba	636.0	261.4	232.9	212.6	254.2	263.3
Be		2.4	2.2	1.5	2.3	2.5
V		125.5	96.9	63.3	112.4	114.0
Cr	124.5	131.3	102.2	86.0	120.1	120.5
Co	25.7	30.9	22.4	14.5	23.7	25.8
Ga		20.7	16.1	11.8	18.8	18.9
Rb	125.0	143.3	119.2	89.1	141.7	139.3
Nb		13.9	12.2	10.4	13.9	13.2
Ni	58.0	57.9	46.5	31.9	45.1	53.1
Cs	5.2	11.0	8.9	6.2	10.3	10.4
Hf	6.3	4.9	4.8	5.7	4.9	4.2
Sc	14.9	18.7	13.9	10.8	16.9	16.7
Sr	142.0	71.5	71.8	66.5	73.0	86.4
Ta	1.1	1.1	1.0	0.9	1.0	0.9
Th	12.3	15.0	9.7	8.1	10.9	11.6
U	2.7	2.8	2.0	2.0	2.3	2.5
Y		33.9	28.1	25.5	28.3	27.1
Zr	200.0	161.6	167.3	203.9	160.2	146.7
SCo-1						
La	29.5	38.7	28.8	25.7	34.3	39.1
Ce	58.5	90.6	70.5	59.9	76.9	85.3
Pr	6.88	9.86	7.43	6.19	7.97	9.32
Nd	26.4	41.3	31.7	25.7	34.0	38.1
Sm	5.08	8.63	6.57	5.51	6.31	7.44
Eu	1.13	1.98	1.55	1.12	1.45	1.67
Gd	4.35	7.25	5.43	4.50	5.63	5.86
Tb	0.66	1.16	0.84	0.77	0.88	0.97
Dy	4.26	6.07	4.89	4.37	4.92	5.01
Ho	0.89	1.29	1.06	0.94	1.02	1.04
Er	2.52	3.44	3.01	2.59	2.73	2.65
Yb	2.28	3.12	2.60	2.36	2.54	2.48
Lu	0.36	0.44	0.38	0.38	0.37	0.38

SCo-1 = USGS reference material Coby Shale. Major elements are in oxide weight percent, minor elements are in $\mu\text{g/g}$.