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Geochemical aspects of the Santonian Chalk of Ramsgate, England, and the origin of the chert and clay minerals

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SUMMARY. The mineralogy and major-element geochemistry of thirty-seven samples from a borehole in the Upper Cretaceous Chalk (Santonian) of Kent has been determined. The mean carbonate content is 97 % and the carbonate is a low-Mg calcite (0.42 mol % $MgCO_3$). Most of the silica is deduced to be biogenic chert. The total clay content probably varies through the sequence due to changes in the rate of carbonate sedimentation. The clay composition remains relatively constant with smectite more abundant than illite. The smectite and K-feldspar could be formed from volcanic debris whereas illite and quartz are thought to be detrital.

THE Cretaceous Chalk in Britain is typically a very pure micritic limestone (Hancock, 1976). Most of the carbonate was produced by planktonic algae. Single, micron-sized plates are present and also circular, original groupings known as coccoliths. The carbonate is pelagic in origin, but was deposited in a shelf sea. The carbonate has suffered little recrystallization and thus the Chalk, particularly in southern England, is relatively soft. This lack of diagenetic alteration is attributed to an original low-Mg calcite composition (thermodynamically stable).

A comprehensive petrological account of the Chalk appears in the work of Hancock (1976). Also included are total analyses of fourteen representative Chalk samples. Nine samples were also analysed in the work of Pitman (1978). There are few other published analyses. Partial chemical analyses of the Chalk were used by Jeans (in press) in a study of diagenetic reactions in horizons of early lithification (hardgrounds) and the importance of reactions involving iron was recognized.

Acid-insoluble fractions of Chalk have been studied by a number of authors. In the Cenomanian Chalk in Britain, Jeans (1968) found that the clay minerals belonged to two main assemblages, one consisting of montmorillonite, illite, and quartz, with montmorillonite:illite ratios ≥ 0.7 and the other illite, kaolinite, chlorite, and vermiculite with montmorillonite:illite ratios < 0.2. The latter assemblage was thought to be detrital, whereas the montmorillonite and illite of the former assemblages were thought to have precipitated during diagenesis.

Stratigraphically higher Chalk samples were studied by Weir and Catt (1965). Acid-insoluble residues were size fractionated and the minerals identified. The clay fractions were also chemically analysed. The sand and silt fractions mainly consisted of flint and opaline silica, collophane, limonite, and quartz and the clay fractions montmorillonite, mica, quartz, and apatite. Subangular and angular grains of quartz were interpreted as detrital and so too were irregularly shaped clay-sized mica grains. Euhedral grains of apatite, quartz, baryte, and K feldspar were thought to be authigenic. The unusual but unvarying morphology of the montmorillonite and the rarity of kaolinite was possibly thought to be due to the action of the chalk sea environment on incoming detritus of variable composition. The non-carbonate fractions in samples from four boreholes were examined by Morgan-Jones (1977). The samples cover the stratigraphic range studied by Weir and Catt (1965) and Jeans (1968) and general confirmation of their clay mineral distributions were obtained. A regional variation was noted in the abundance of the non-carbonate fraction and changes attributed to groundwater circulation were observed. In the Chalk of the Paris Basin clinoptilolite occurs in association with smectite (montmorillonite) and 'cristobalite' (Pomerol and Aubry, 1977). This association is known in deep sea sediments where a volcanic origin is accepted by many authors, and thus Pomerol and Aubry suggest the same origin for these minerals in the Chalk. They relate the volcanic activity to opening of the North Atlantic and supporting stratigraphic evidence is presented including volcanic material in deep sea sediments of Cretaceous age.

Flints (cherts) are conspicuous in Chalk exposures and have attracted much interest. In more recent years the study of oceanic sediments has added considerably to the understanding of silica in sediments (Calvert, 1974; Wise and Weaver, 1974; Von Rad and Rosch, 1974). Nevertheless, it is not always clear if the silica is biogenic resulting from the mobilization of siliceous planktonic debris or is derived from the alteration of volcanic debris. Wise and Weaver (1974) adopt the view that the vast majority of oceanic cherts deposited since the Mid-Palaeozoic are biogenic. On the other hand, Pomerol and Aubry (1977) suggest that a biogenic origin for the silica in the Cretaceous Chalk of the Paris Basin has never been demonstrated.

In this paper major-element analyses are presented for Chalk samples analysed during an investigation of porewater reactions in the unsaturated zone of the Chalk.

Samples and analytical methods

Chalk samples were obtained from a borehole at Sprattling Court Farm (Grid. Ref. TR 351652) 3 km NW of Ramsgate in Kent. The borehole was drilled in the Upper Chalk within what is thought to be the upper part of *M. coranguinum* zone. A total of thirty-seven samples were analysed covering the depth range 7–42 m. Samples of about 0.5 kg in weight from which the porewater had been removed by centrifuging were air dried and crushed in a Tema disc mill. Several large flints were excluded. Major-element concentrations were determined by X-ray spectroscopy using samples prepared as fusion discs (Norrish and Hutton, 1969). Na however, was determined by atomic absorption spectrometry on a solution prepared by HF–$HClO_4$ digestion.

Insoluble residues from several representative samples were prepared using *N*/10 HCl and also NaOAc at pH 5. The residues were examined under the microscope and by X-ray diffraction.

Results and interpretation

The chemical variation found for the thirty-seven samples is not great and therefore the results are summarized in Table I. The mean carbonate content is 96.98% after correcting for CaO in apatite, based on the P_2O_5%, and allowing for MgO in the clay minerals. The carbonate composition is 99.58 mol% $CaCO_3$ and only 0.42 mol% $MgCO_3$. These Chalk samples do indeed consist of a low-Mg calcite and the non-carbonate contribution to the sediment is very small.

TABLE I. *Composition of Upper Chalk, Sprattling Court Farm, Kent*

	Number of samples = thirty-seven			
	Mean	Standard deviation	Maximum	Minimum
SiO_2	1.206	1.77	11.01	0.46
Al_2O_3	0.199	0.049	0.313	0.104
TiO_2	0.010	0.007	0.022	0.000
Fe_2O_3	0.098	0.059	0.341	0.041
MgO	0.218	0.012	0.252	0.200
CaO	54.305	1.13	55.38	49.26
Na_2O	0.113	0.204	0.96	0.01
K_2O	0.041	0.010	0.067	0.028
MnO	0.028	0.016	0.065	0.000
P_2O_5	0.142	0.022	0.182	0.092
SO_3	0.112	0.026	0.166	0.082
Ignition loss	43.31	0.81	45.01	40.24

Origin of the flints. The greatest variation is shown by SiO_2 (Table I). This is due to the inclusion of some flints in the samples. Silicates are not responsible for the silica variation because Al_2O_3 does not show a comparable variation to that of silica. The SiO_2 and Al_2O_3 concentrations are shown plotted on fig. 1. Two associations of silica are demonstrated, one with Al_2O_3, due to silicates, and the other, independent of Al_2O_3, due to flints. Wise and Weaver stressed (1974, p. 304) that volcanogenic chert should be associated with bentonite and that the amount of bentonite could possibly be considerable. The present data enable a quantitative approach to be adopted.

A maximum volcanic SiO_2 concentration can be postulated if it is assumed that all the Al_2O_3 in the sequence is volcanic in origin. The mean concentrations in Table I give a SiO_2/Al_2O_3 ratio for the Chalk of 6.06, whereas even in acid igneous rocks the ratio is lower, 4.75 (Krauskopf, 1967). The mean SiO_2 concentration in the Chalk should be not greater than 0.95% whereas the value for the samples analysed is 1.21%. However, the latter figure must be a minimum value for the sequence as a whole because large flints were excluded in the sampling. In order to obtain a more realistic value for the mean SiO_2 value for the borehole the core was resampled taking 3-kg samples. The acid-insoluble residue was determined using *N*/10 HCl, after rejection of the < 53 μm fraction. Visual examination confirmed that the residue consisted solely of flints and the weight percentage was therefore equated with the SiO_2%. A value of 6.02% was obtained, which is considerably in excess of the maximum volcanic level and therefore the flints in the sequence formed from biogenic silica. Based on these figures the maximum volcanic contribution to the total SiO_2 in the sediment is not greater than 15% and this assumes that the clay minerals are volcanic, which may not be so.

Abundance of the non-carbonate silt and clay fraction. Samples containing more than 1% total SiO_2 lie outside the normal population and if these samples are excluded, the remaining samples show a highly significant positive relationship with Al_2O_3 (fig. 1). The positive relationship is attributed to dilution of the non-carbonate silt and clay fraction by the carbonate, due to changes in the relative rates of deposition of the two fractions.

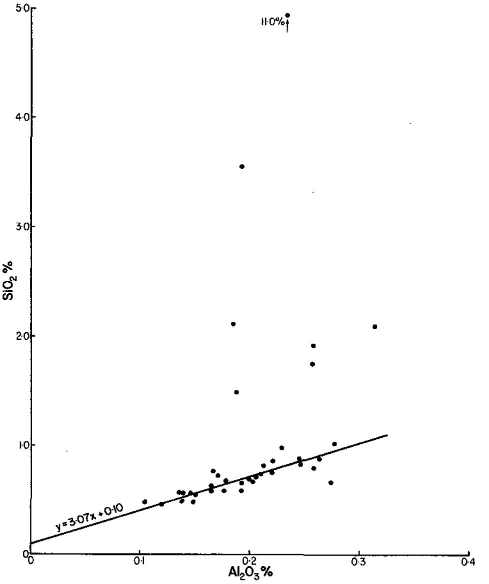

FIG. 1. Relationship between SiO_2 and Al_2O_3 concentrations, whole-rock Chalk samples. Reduced major axis regression equation shown.

Marl bands in Chalk represent an increase in the clay mineral content and Hancock (1976, p. 508) suggests they go with a break in the supply of calcite with the clay supply continuing and probably not at a faster rate. According to Jeans (1968) the clay mineralogy of the marl bands and the adjacent Chalk are closely comparable, which adds support to Hancock's interpretation. There is thus an argument in favour of major changes in the rate of carbonate sedimentation and it could be that much smaller changes are responsible for the positive relationship noted in this work between Al_2O_3 and SiO_2 concentrations.

The Al_2O_3 variation through the borehole is shown in fig. 2. Ascending the borehole the Al_2O_3 concentrations fluctuate but generally decrease to low values at a depth of about 20 m. There is a peak in the Al_2O_3 concentrations from 17–12 m and this is followed by lower values in the interval 12–6 m. The Al_2O_3 values vary in a systematic manner through the sequence but the sedimentological implications of this are unknown. This variation in the clay abundance can also be detected in the γ-ray log of the borehole run by the Water Research Centre.

Also shown on fig. 2 is the variation in total iron, expressed as Fe_2O_3, through the sequence. The iron might be anticipated to be clay-associated and indeed the Fe_2O_3 and Al_2O_3 profiles are similar in the upper part of the sequence, but at the base of the sequence, whereas Al_2O_3 increases, Fe_2O_3 decreases. The iron–clay proportions change, which could be original or secondary. It is possible that weathering reactions are responsible for the higher Fe_2O_3 content nearer to the surface, and that the iron has been deposited from infiltrating pore-water. Two samples have higher Fe_2O_3 concentrations, which could be original, possibly representing a diagenetic concentration, or secondary, perhaps associated with fissure flow in the unsaturated zone.

The Al_2O_3 and K_2O concentrations are plotted on fig. 3. The relationship is similar to that between SiO_2 and Al_2O_3 and the same explanation of dilution of the silicate fraction by carbonate is applicable. K_2O is present in the illite and to a lesser extent in K-feldspar. The X-ray diffraction traces of insoluble residues all showed that smectite was more abundant than illite, which is in agreement with the findings of Weir and Catt (1965). Quartz is also present in the X-ray diffraction traces and under the microscope angular silt-sized monocrystalline grains were identified that would appear to be detrital in origin. Based on average analyses of smectite and illite from Weaver and Pollard (1973) the average clay composition from the analyses of Table I was calculated at 0.44% smectite and 0.31% illite. The K feldspar content was estimated at 0.11% from the chemical analyses. The similarity between the K_2O *v.* Al_2O_3 and SiO_2 *v.* Al_2O_3 relationships suggests that the silicate fraction is relatively constant in composition although the amount varies due to carbonate dilution. The clay fractions analysed by Weir and Catt (1965, Table 5) likewise show a relatively constant K_2O/Al_2O_3 ratio. Their mean value was 0.216 with a standard deviation of only 0.018. In the present samples the mean value of the ratio is 0.206, which could be higher because the present samples are whole rock samples and K feldspar is more important in the sand and silt sizes.

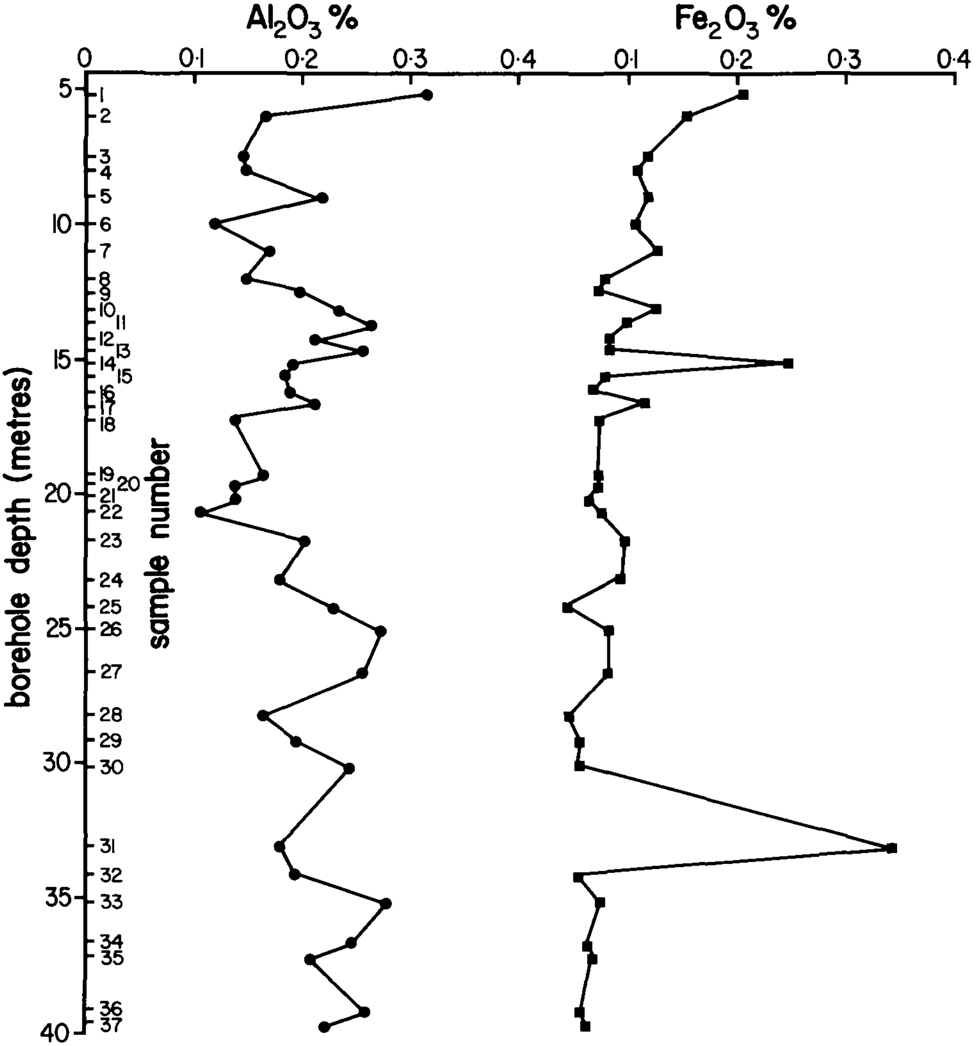

FIG. 2. Variation in Al_2O_3 and Fe_2O_3 concentrations with borehole depth, whole-rock Chalk samples.

Origin of the non-carbonate silt and clay fraction. Feldspars in the Chalk have been described by a number of authors (see Weir and Catt, 1965, and Jeans, 1968), and the occurrence of euhedral grains with well-developed crystal faces has suggested an authigenic origin. Weir and Catt (op. cit.) note in addition that the grains are untwinned and unaltered. Additional support for such an authigenic origin was obtained in the present work from the X-ray diffraction traces, which showed the K feldspar to be monoclinic rather that the usual triclinic feldspar in detrital sediments (Fellows and Spears, 1978). The most recent information on reactions in the system K_2O-Al_2O_3-SiO_2 H_2O indicates that the stability field of K feldspar will be readily attained in the porewaters of marine sediments, particularly if the system is saturated with respect to amorphous silica (Stablein and Dapples, 1977). The latter would certainly apply to the Chalk. It is perhaps more difficult to provide a source of ions enabling K feldspar to precipitate. In the sandstones examined by Stablein and Dapples the source was believed to be detrital feldspar. They also noted that illite was present with the K feldspar and apparently had not reacted. Clay minerals are an unlikely source of ions because firstly they generally show very little structural modification during halmyrolysis, and secondly during dia-

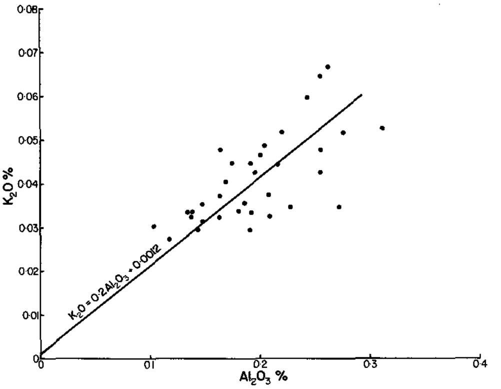

FIG. 3. Relationship between K_2O and Al_2O_3 concentrations, whole-rock Chalk samples. Reduced major axis regression equation shown.

genesis the most likely change is the conversion of montmorillonite to a mixed-layer mica-montmorillonite (Burst, 1959; Weaver, 1959; Dunoyer de Segonzac *et al.*, 1968; Perry and Hower, 1970), but in the Chalk montmorillonite survives, thus demonstrating that the required diagenetic level was not achieved. Gibbsite, which is out of its stability field in the porewater environment (Curtis and Spears, 1971), could alter to feldspar rather than to kaolinite provided that a sufficiently high activity of K^+ was maintained. However, detrital gibbsite would be accompanied by detrital kaolinite as in modern oceanic sediments (Biscaye, 1965; Griffin *et al.*, 1968) and kaolinite is far from conspicuous in the Upper Cretaceous Chalks. There remains an obvious possibility for the source of the K feldspar and that is volcanic materials, which are very unstable at the earth's surface, especially glass, and react rapidly. To quote Blatt *et al.* (1972), 'volcanic materials have no peer among naturally occurring particles as ready sources of Na, K, Al and Si'.

Volcanic materials in the marine environment react to form a range of minerals including zeolites and clay minerals, particularly smectites. This volcanic association has been cited by Pomerol and Aubrey (1977) for the clinoptilolite–smectite–'cristobalite' assemblage in the Chalks of the Paris Basin. These authors also draw attention to the occurrence of volcanic debris in the Cretaceous sediments in the Atlantic. Zeolites are very reactive in the diagenetic environment and clinoptilolite readily reacts to K feldspars as Sheppard and Gude (1969) so convincingly demonstrated. If clinoptilolite is not present now in the Chalks of southern England it could be that it reacted to form some of the K feldspar.

Smectite may also form during normal weathering processes and therefore its presence is not proof of a volcanic origin. On the other hand, if smectite is dominant in pelagic sediments, as in the Upper Cretaceous Chalk, then by analogy with modern sediments a volcanic origin can be postulated. In the Atlantic smectite forms from volcanic materials derived from the ridge system, but in the North Atlantic there is greater dilution by detrital clays, particularly illite, than in the South Atlantic. The composition of the land-derived clay minerals is related to latitude and at 40 °N more than 70% of the clay fraction consists of illite. This was the latitude of southern England during the Santonian (Smith and Briden, 1977) and therefore a high illite content in the detrital fraction would be predicted. Thus the illite in the Upper Cretaceous Chalk is thought to be detrital. This conclusion was also reached by Weir and Catt (1965) on the evidence of irregular-shaped mica grains. The shape of the quartz grains, namely angular to sub-angular, is also good evidence of a detrital origin.

It is uncertain how much land remained at the time of the maximum marine transgression during the Late Cretaceous (Hancock, 1976). However, the Chalks in this study pre-date the maximum transgression and the old mountains of Scotland and Wales may well have been exposed. These source rocks have a composition that would produce a significant proportion of illite in the detrital fraction unless weathering was extreme under tropical conditions, but this would give a kaolinite–gibbsite assemblage. During the Late Carboniferous the same source areas were exposed and illite is significant in the derived clay minerals.

The insoluble residue in these Upper Cretaceous Chalks is therefore thought to consist of a volcanic component represented by smectite and K feldspar (plus clinoptilolite elsewhere) and a detrital component consisting of quartz and illite. Other detrital clay minerals could be below detection limits due to the swamping action of the smectite. Earlier in the paper it was noted that the composition of the clay fraction remained relatively constant as the total amount varied due to dilution by the calcite. It can now be suggested that this is due to changes in the rate of carbonate production because to change the rate of clay sedimentation and maintain approximately the same proportions of volcanic and detrital material requires the rate of supply of both these components to change in a comparable manner, an unlikely coincidence. The apparent lack of fluctuations in the supply of volcanic material eliminates intermittent air-borne ashfalls and perhaps suggests instead erosion of an active ridge system by oceanic currents. The material eroded could include volcanics in all stages of alteration.

Thus the smectite could have been subjected to some transportation.

Finally it was argued earlier in the paper that if all the Al_2O_3 were volcanic, a maximum volcanic SiO_2 content could be determined. This SiO_2 content did not account for the SiO_2 present in the flints and therefore a biogenic origin was accepted. The actual volcanic SiO_2 content is much lower if the illite is detrital. Also if volcanics are derived from a ridge system then a lower SiO_2/Al_2O_3 ratio corresponding to basic rocks, rather than acid rocks, should be chosen. The figure for the maximum volcanic SiO_2 contribution to the sediment can therefore be reduced, which increases the discrepancy with the total SiO_2 present, thus strengthening the biogenic origin of the flints. The volcanic SiO_2 can in fact be accounted for by the smectite.

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