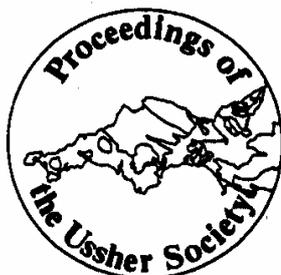


Clay mineral assemblages of Namurian shales in Devon and Cornwall

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The clay mineral assemblages of Namurian shales in Devon and Cornwall have been determined by X-ray diffraction analysis and compared to their stratigraphical and structural settings. Illite crystallinities indicate low grade metamorphic effects along the southern margin of the outcrop, accompanied by chlorite development. Away from this metamorphic influence, wide variations in the clay mineral assemblages are shown to be locally stratigraphically controlled, indicating a varied detrital mineralogy modified by diagenetic changes.

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Introduction

A preliminary study of the clay minerals present in the Crackington Formation (Namurian) shales just to the west of Exeter, revealed wide variations in the relative proportions of the common groups, illite, chlorite and kaolinite, (Grainger and George 1978). Within a few kilometres, the assemblage of clay minerals varies from illite alone, through illite with kaolinite, to illite and chlorite. Mixed layer clay, probably illite-smectite, was also detected. The areal distribution of the assemblages, simply divided into chloritic and non-chloritic, closely follows the east-west structural trend in the area. Structural mapping suggested a stratigraphical control on the clay minerals present. The investigation of weathering effects in that area showed no significant clay mineralogical alteration.

The assemblage of clay minerals in a marine shale of this age and deformational history is a function of its original detrital mineralogy, shallow and deep diagenetic effects, and possibly low grade metamorphism. As chlorite development is one of the first signs of regional metamorphism, chlorite distribution within a suite of shales like these, could simply indicate variations in late diagenetic and early metamorphic grade. However, any stratigraphical correlation suggests that the chlorite abundances observed are reflecting variations in the original detrital sediment mineralogy. In order to explore the relative importance of stratigraphy, diagenesis and metamorphism, sampling and X-ray diffraction analysis have been extended throughout much of the Namurian outcrop in Devon and Cornwall (Fig. 1). The main aim of this sampling was to collect from dated goniatites localities and places of diverse deformational history.

The seven areas indicated on Fig.1 are:

- A : the coastal section from Boscastle to Millook Haven
- B : the Launceston area
- C : the Okehampton area
- D : the Exeter area
- E: the Ashburton area
- F : the Bampton area
- G : the coastal section at Westward Ho! and Fremington

X-ray diffraction results

All samples for X-ray diffraction analysis were prepared by sedimentation on to glass slides, to provide orientation of the clay particles as described by Grainger and George (1978). The intention was always to view the results in a qualitative or semi-quantitative fashion, and so a consistent and efficient preparation and scanning procedure was adopted. Realistic clay mineral abundances can only be calculated from X-ray diffraction data if the variations of reflection intensities with grain size are assessed. Even then comparability between samples of markedly different crystallinities and minerals of different chemical composition is not possible without extremely detailed work. The only definitive basal, 001 diffraction peaks observed in the normal clay mineral range, were at d-spacings of 14Å (chlorite), 10Å (illite and mixed layer illite/smectite), and 7Å (kaolinite, and second order chlorite). The areas of these three peaks were measured, and form the basis of differentiation between assemblages. These uncorrected areas and the ratios between them, give indications about the presence and absence of the clay minerals and their

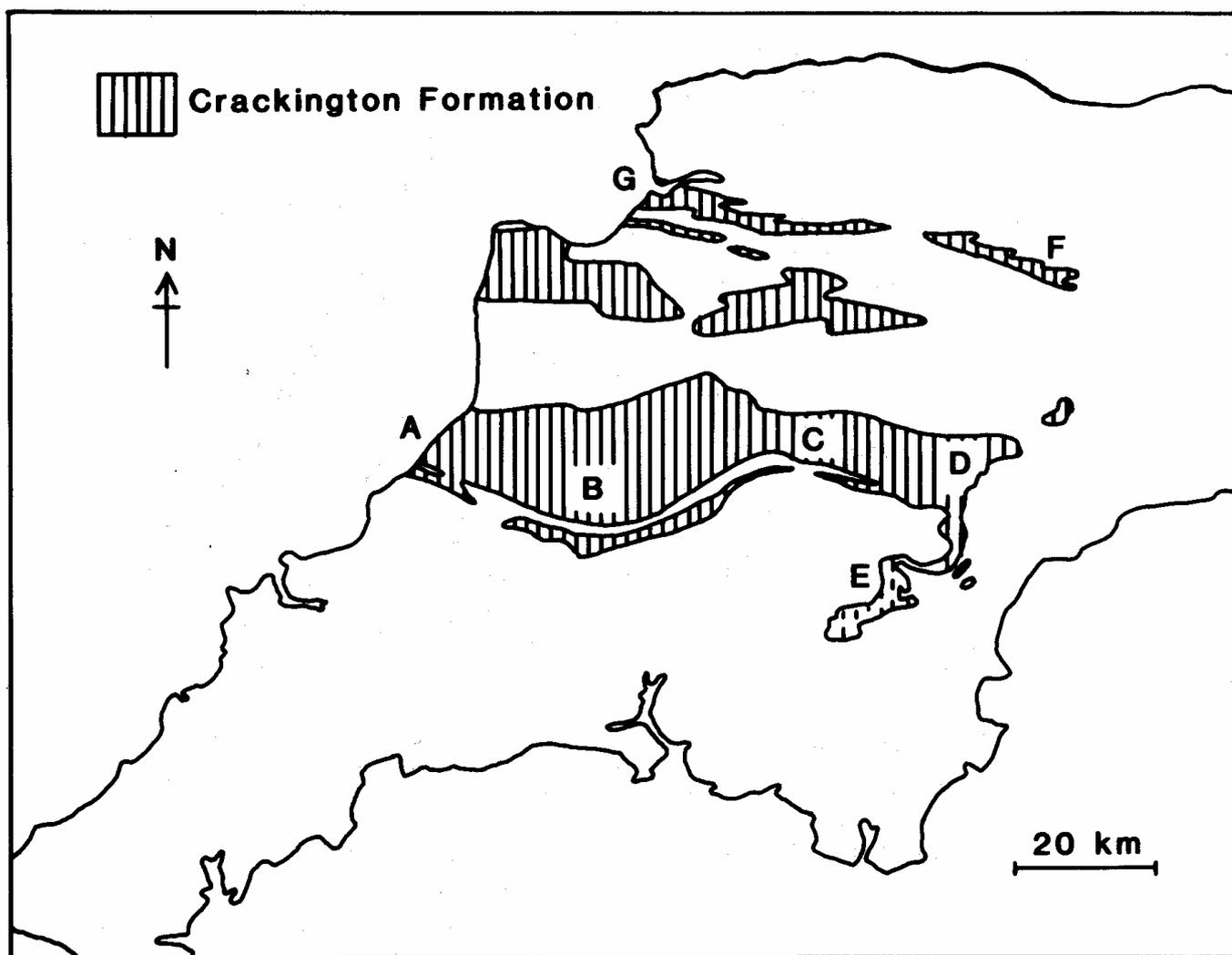


Figure 1. Map showing the approximate extent of the Crackington Formation, which includes all of the Namurian shales in Devon and Cornwall. A -G are the areas sampled. (Additional outcrops may occur in the Tavistock area, at present being mapped).

relative amounts, but they are not the same as absolute mineral abundances. In some cases glycolation, heat and acid treatments were carried out, and observations of other diagnostic peaks made, to confirm mineral identities, and to estimate the relative proportions of chlorite and kaolinite more closely.

In order to summarise the overall diversity of clay mineral assemblages found, the relative peak areas of the three main diffraction peaks have been plotted on a triangular diagram, for all samples collected (Fig. 2). These results have been grouped into four categories based on their position on the diagram, backed up by the additional identification procedures. The 10\AA peak area includes any illite-smectite mixed layer material present, as its presence or absence has not been separately determined in this diagram.

Group 1 consists of 13 results that cluster at the 100% 10\AA apex. These shales contain illite but no discernible quantities of either kaolinite or chlorite.

Group 2 includes all 32 results that plot along the axis of no 14\AA peak, indicating illite with varying amounts of kaolinite. Observations of higher order peaks that distinguish chlorite from kaolinite, and hydrochloric acid and heat treatments, confirm that the chlorite content in this group is of the order of 0-5%. For poorly crystalline kaolinite and illite, as those minerals appear to be, the relative abundances may be approximately equal to the relative peak areas (Schultz 1964). There is a complete range of kaolinite abundances relative to illite, up to almost 50:50, in this group.

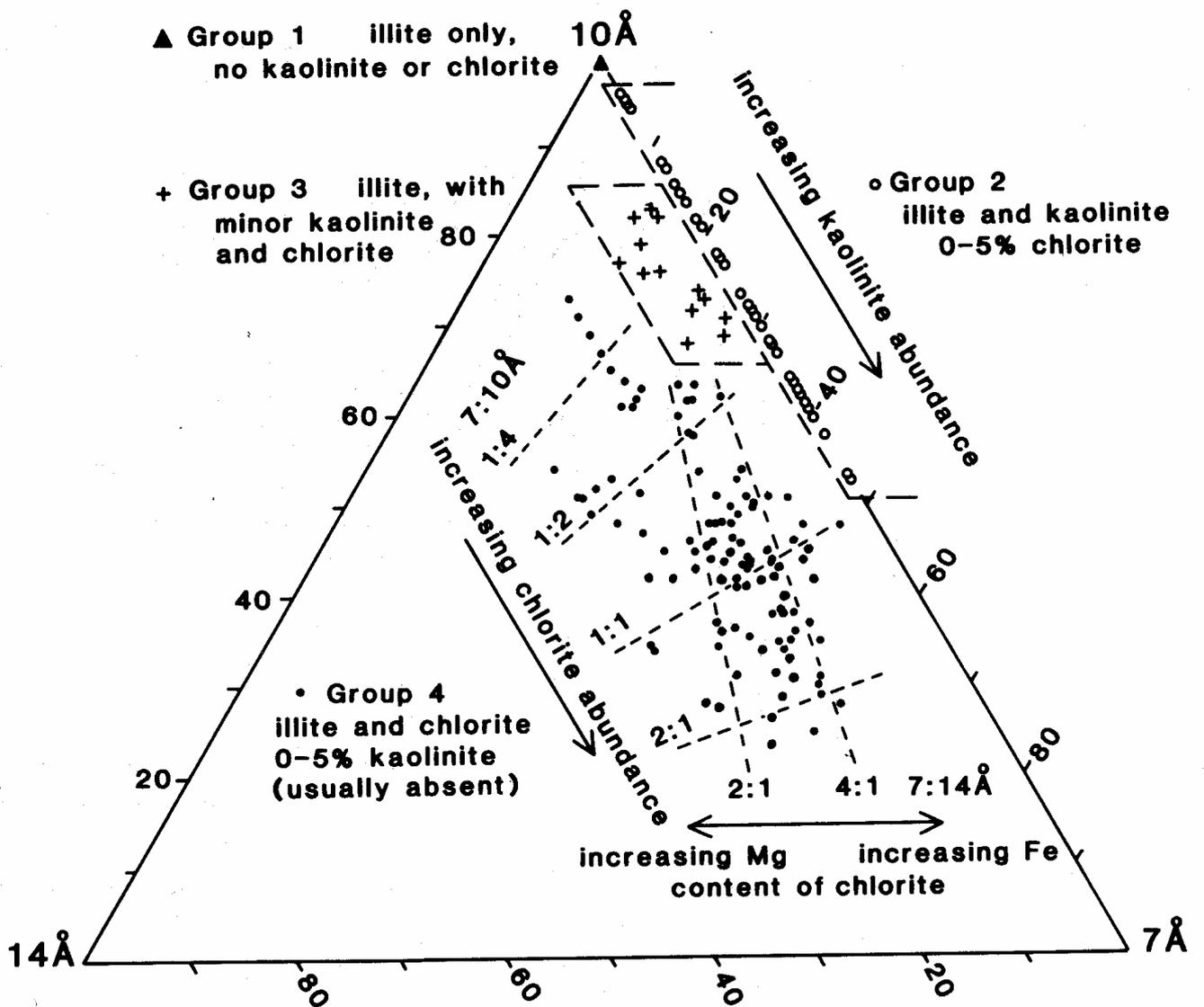


Figure 2. Relative proportions of the X-ray diffraction peak areas at approximately 7, 10 and 14 Å, for all of the samples analysed, showing the high diversity of clay mineral assemblages.

Group 3 is a less well defined set of 13 results in which the illite peak is dominant (>65% of the total three-peak area), and the 14Å peak small but measurable (<10%). These are illite-dominated assemblages with minor amounts of both chlorite and kaolinite present together. The ratio of chlorite to kaolinite, as determined by comparing the 004 chlorite peak and the 002 kaolinite peak, ranges very approximately between 1:3 and 3:1.

Group 4 represents the illite - chlorite - rich shales, in which kaolinite was determined to be absent or very minor. Although chlorite is forming both the 7Å and 14Å peaks in the absence of kaolinite, plotting this group on this type of diagram enables the spread of both the abundance and iron/magnesium content of the chlorite to be visualised. The lateral spread of the 7Å:14Å area ratio indicates that most of the chlorites are magnesium-rich, with those on the right of the diagram (Fig. 2) containing some iron also. This wide range of chlorite composition was confirmed by measuring the exact positions of the 14Å peaks, which varied from 13.9Å to 14.5Å. Further work is in progress on the chlorite geochemistry.

The 10Å illite peak, present for all the samples analysed, was further quantified by measuring its width at half the peak height. This is the extensively used crystallinity index following Kübler (1964, 1967, 1968). The measurements have been converted into degrees 2θ for CuKα radiation, to conform with other authors (Brazier and others 1979) and to allow comparisons to be made. This peak width parameter decreases with diagenetic and metamorphic temperature increase, as illite-smectite mixed layering converts to illite, and as the illite crystallinity improves. It has been used by many workers as an indicator of late diagenetic and early metamorphic zones (Frey 1970; Dunoyer de Segonzac 1970; Brazier and others 1979). Others have preferred the "Sharpness Ratio" devised by Weaver 1960; for example, Gill and others (1977). The nature and content of the mixed layer component (Reynolds and Hower 1970) can be assessed independently by glycolation of X-ray diffraction mounts. Srodon (1979) devised three parameters to quantify the mixed layer clay, which he considered to be sensitive diagenetic indicators, particularly in the middle diagenetic range. These are grain size dependent, however, and could not be measured with certainty from the present data. A comparison with the diffraction traces that Srodon (1979) shows, suggests that all of this Namurian mixed layer material is of the illite/smectite disordered type IS II of Reynolds and Hower (1970), in which the smectite layers constitute less than 15%.

Glycolation of a selection of samples from each group in Fig. 2 indicates that some expansive mixed layer clay occurs in each group in very variable amounts. This is an area that could be usefully researched in more detail. Fig. 3 shows typical 10Å peaks of different crystallinity indices, with the effects of glycolation indicated.

Accepting that the Kübler index is at least a qualitative indicator of diagenetic and metamorphic temperature, it has been plotted in Fig. 4 against the ratio of 7Å:10Å peak areas. For the illite-chlorite assemblages (group 4), this figure demonstrates quite clearly an overall increase in chlorite content with increasing illite crystallinity from 10Å peak widths of about 0.5° down to 0.2°, the lower limit observed. The large spread of chlorite contents, shown by the 7Å:10Å ratios, within the metamorphic zone is taken to be a consequence of varied initial mineralogy. The inclined upper boundary to the group 4 points, within the diagenetic zone, shows that where detrital chlorite is present, chlorite enhancement begins at lower temperatures.

The other three groups, 1-3, of mineral assemblages from Fig. 2 are also plotted on Fig. 4. These have chlorite as only a minor constituent occurring with kaolinite, or absent altogether. None of these samples have illite crystallinities of less than 0.3° peak width which corresponds to Kübler's (1968) division between the diagenetic zone and anchizone of metamorphism. They range from this limit to about 0.6° in a fairly random distribution. The group 2 assemblages of illite-kaolinite show a rapid decline in kaolinite content from 0.4° to 0.3°, which therefore seems to represent the temperature limit on kaolinite existence in this succession. It also seems to be the temperature above which metamorphic chlorite develops in shales containing no detrital chlorite.

Mixed layer illite - smectite has been found in samples from all four groups, at illite crystallinities down to about 0.35° peak width, which thus represents its diagenetic limit. If the peak widths had been measured on glycolated samples, to remove the illite - smectite influence, some of those points to the right of 0.35° would have been shifted by up to 0.1° to the left. However, the general pattern of results would not be significantly altered.

The conclusion from Fig. 4 is that this whole suite of samples started off with a diverse range of clay mineral assemblages, and that although relative abundances and crystallinities changed throughout diagenesis it is only at the threshold of metamorphism that major mineralogical substitution began. If the variety of assemblages below this threshold, in the diagenetic range, was simply a progression due to diagenesis, one would expect a more consistent trend with illite crystallinity to be apparent. There should also be a regular trend with stratigraphical level and hence depth of burial. The evidence from each area studied points more towards localised stratigraphical control, but not in a regular progression with age and depth. This supports the hypothesis that the influence of detrital clay mineralogy has been preserved, except where low metamorphic grade has been reached.

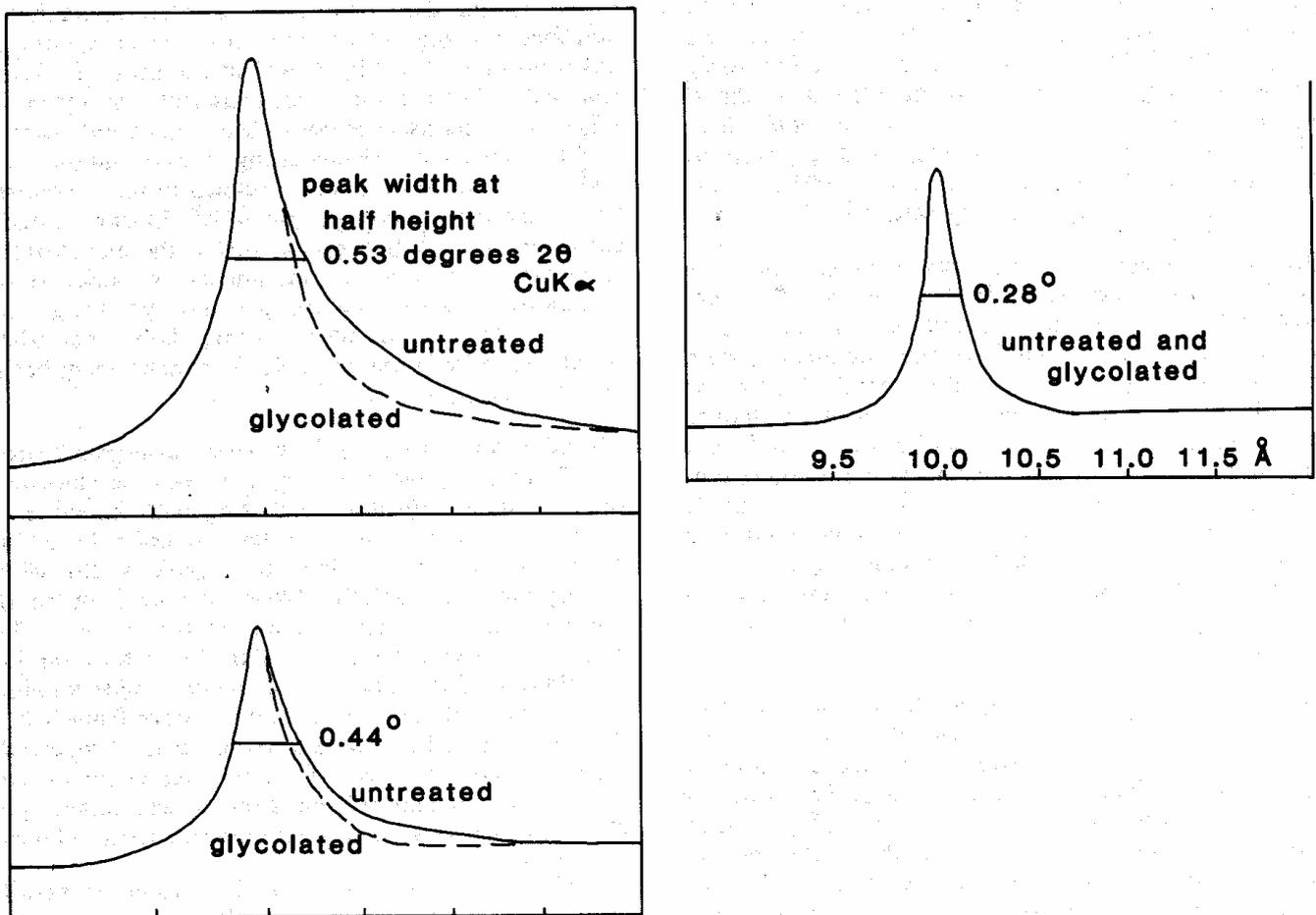


Figure 3. Typical X-ray diffraction traces of the illite plus illite-smectite 10Å peak

Boscastle to Millook Haven (A)

The section of coastline in North Cornwall exposing Namurian strata, from Boscastle to Millook Haven and beyond to Wanson Mouth (Fig. 5) has been studied extensively in terms of its structures, goniatices and sedimentology (Ashwin 1958; Mackintosh 1965; Dearman and others 1970; Freshney and others 1972). South of the important Rusey Fault the highly deformed black slates of Ashwin's (1958) Boscastle Measures, are quoted as being of a higher metamorphic grade and more chloritic than equivalent rocks to the north. From just south of the major fault at Rusey, the goniatices show a progressive younging of the strata northwards, from zone E2c up to the top of the Namurian at Wanson Mouth. Mackintosh (1964) also recognizes a progressive increase in the sandstone content upwards through the sequence, together with changes in turbidity current directions.

Twenty samples taken from south of the Rusey Fault, and twenty five from the north (mainly from goniatices localities), show some clear distinctions. In Fig. 6, the 10Å peak widths have been plotted against the relative sampling positions, measured directly north-south for convenience. All samples south of Rusey have a peak width less than 0.3° and are highly chloritic. Observation of these slates under the scanning electron microscope reveals angular, well formed crystals of 10-20 lam size, confirming a degree of recrystallization. From adjacent to the fault zone northwards, the 10Å peak widths are around 0.4°, ranging up to greater than 0.5°, and are randomly distributed. As predicted by earlier workers, the Rusey Fault represents a boundary between rocks of significantly different temperature grade; diagenetic to the north and low grade metamorphic zone to the south. Brazier and others (1979) in a regional study, obtained similar results in this area.

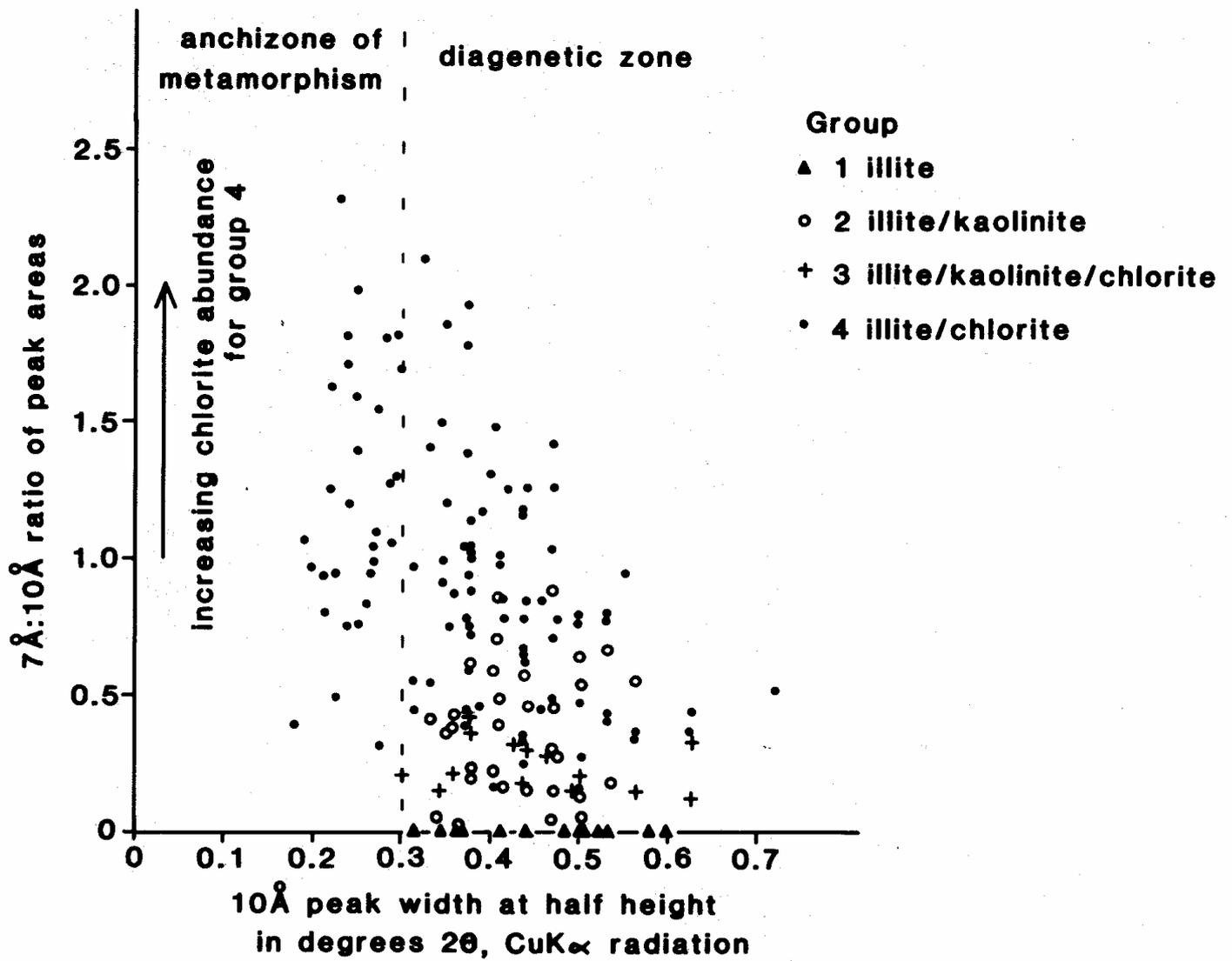


Figure 4. A comparison of clay mineral composition with illite crystallinity, showing the development of chlorite and the exclusion of kaolinite, and illite alone, as the 10Å peak width decreases.

One further comparison was made between the chlorites north and south of Rusey. The ratios of $14\text{\AA}:7\text{\AA}$ peak areas were calculated and found to be lower for the samples to the north, indicating less magnesium-rich chlorite than the metamorphic chlorites to the south. The 14\AA peak positions however, showed no significant trend.

Comparing those samples north of Rusey, which contain chlorite, to their respective stratigraphical positions, it is apparent that they all fall in the H1a to H2a range. A more detailed comparison of clay mineralogy and stratigraphy enables a tentative correlation to be made (Fig. 7, column A). The lower black shales of Rusey (E2) are dominantly illitic. The succeeding H1a and H1b zones show illite with high chlorite contents, the chlorite then decreasing in importance up through H1b and H2a zones. From H2b, at Crackington Haven, and all R1 and R2 localities from there northwards, no chlorite is found, but variable amounts of kaolinite are indicated by 7\AA peaks. Observation of these shales and slates by scanning electron microscopy shows a degree of microfabric orientation compatible with their field fissility. Clay particles are very thin and ragged in outline, but coalesced into aggregate sheets parallel to the fissility. Comparing chloritic and non-chloritic shales north of Rusey, there is no particular difference in microfabric.

Launceston Area (B)

Dated sample localities from this area range in age from E2 to R1a (McKeown and others 1973). Black slates and shales of E2 age contain predominantly illite with little or no kaolinite, and no chlorite. From zones H1a and H1b the assemblage is an illite-chlorite one (Fig. 7), and this chloritic assemblage may extend higher in the succession. The majority of the dated samples are confined to an area north of Launceston (and the "Rusey Line") where the shales have only been subject to diagenetic alteration (10\AA peak width around 0.4°). The Namurian slates immediately surrounding and to the south of Launceston exhibit low grade metamorphism in some localities, indicated by illite peak widths down to 0.25° and the occasional presence of paragonite.

Recent mapping in this area by one of us (G.W.), has delineated a thrust sheet of apparently overturned Namurian slates. The stratigraphical top of the sheet is chlorite-free material of high diagenetic grade, but going up through the sheet reveals an increasing illite crystallinity from 0.35° to 0.27° peak width, and chlorite contents approaching those of the Boscastle slates. Thus the metamorphic gradation appears inverted too within this thrust sheet.

Okehampton Area (C)

Eleven samples were collected from localities of goniatite zones H1a? to R2b, as quoted by Edmonds and others (1968). A clear correlation between conclusively dated sites and clay mineral composition is apparent, (Fig. 7, column C). A decrease and then an absence of chlorite occurs near the top of the succession. The H1 part of the succession is not certainly dated, but appears to be chloritic also.

Exeter Area (D)

Earlier mapping and X-ray diffraction analysis in the Alphin Brook area, west of Exeter, showed an east-west zone of non-chloritic shales along the Alphin Brook, flanked by chloritic shales to the north and south (Grainger and George 1978). A few goniatites found by one of us (P.G.) and Mr K. Page of Tedburn St Mary, in the A30 road excavations within the non-chloritic shales, at three localities, have been identified as belonging to zone H1a (Ramsbottom, personal communication). One further goniatite locality discovered by Mr Page in chloritic shales near Pocombe Bridge, Exeter, is of zone R1 (Ramsbottom, personal communication). These dates help to confirm the anticlinal structure suggested for the Alphin Brook area by Grainger and George (1978). A continuation of this non-chloritic exposure, becoming narrower eastwards and offset by faulting, has been mapped as far as the Exe Valley, at Exwick. On the eastern side of the Exe, in Exeter, samples from the definitively dated parts of the Bonhay Road section (zones H1b, H2a, H2b and R1a) all have some chlorite present. In the Teign Valley, samples collected from the Ashton member of the Crackington Formation, dated as E2c (Chesher 1969), are non-chloritic. This extends the correlation downwards from that near Exeter as shown in Fig. 7, column D.

As with the coastal section (A), scanning electron microscope observations confirm a microfabric compatible with the macroscopic sample description. The illite - kaolinite shale microfabric is generally less well aligned and coalesced in this area, accounting for its weakness and easier disintegration during weathering (Grainger and George 1978).

Ashburton Area (E)

Farther south, undated samples collected during recent mapping of Upper Carboniferous strata around Ashburton by Drs Selwood and Thomas, display compositions and crystallinities across the whole range of those found elsewhere. These suggest that a variety of stratigraphical and metamorphic levels are represented, brought into juxtaposition by thrusting. Further work could be done in this area.

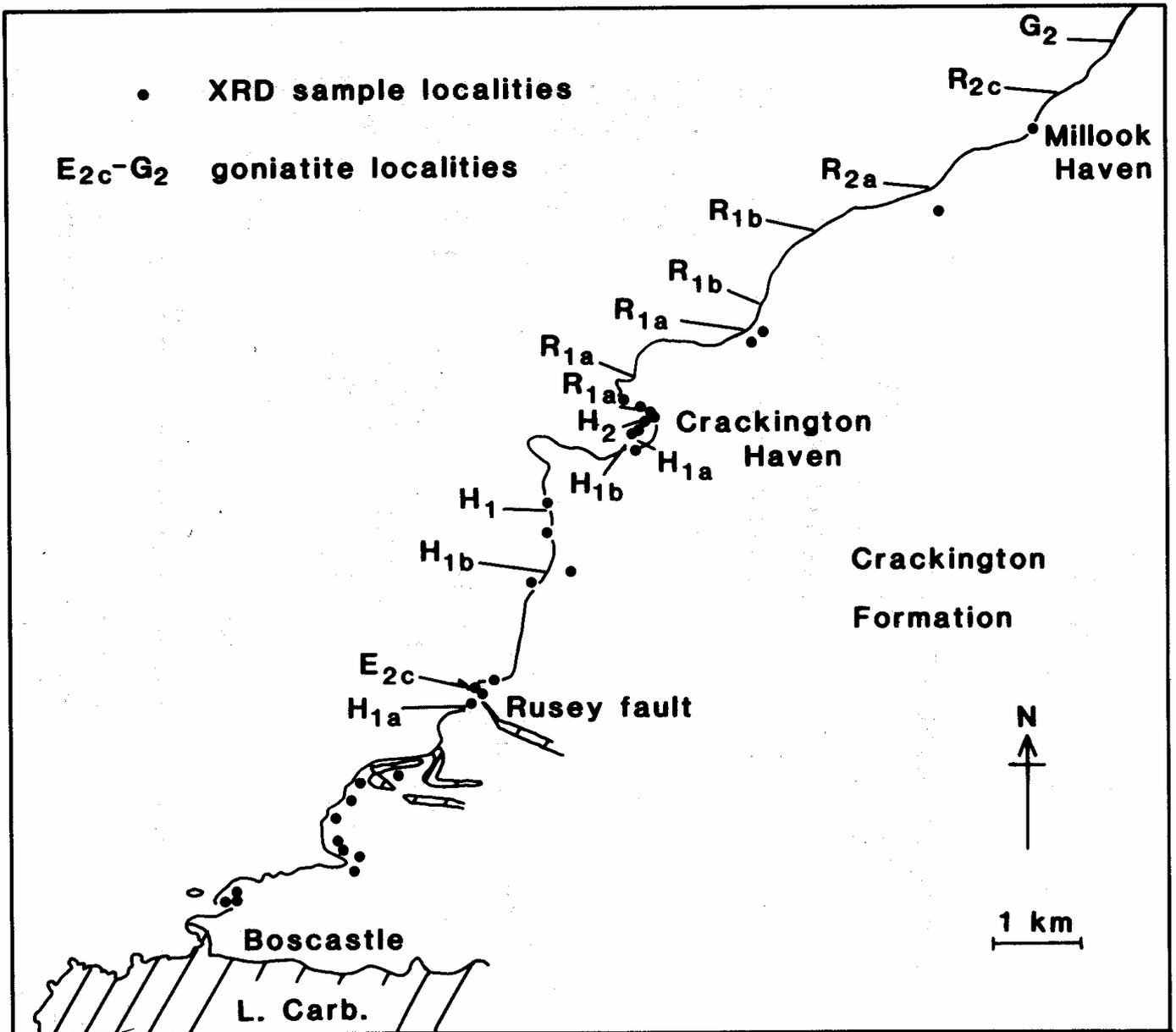


Figure 5. Sketch map of the north coast of Cornwall showing sample positions and goniomite localities

Bampton Area (F)

In north Devon the lower part of the Namurian succession is very thin compared to that in the south (Fig. 1). From the Dowhills Beds of E2 age, up through R1 (Webby and Thomas 1965), no samples contain chlorite, but kaolinite is present in some cases. From zones R2a up to G1, chlorite is found as an important component of the clay mineral assemblage, corresponding to the influx of frequent turbidite sandstones (Fig. 7, column F, G).

Westward Ho! and Fremington (G)

The Limekiln Beds of Prentice (1960) at Fremington yielded goniatites of R1 age and are largely illite-rich shales. By contrast, all of the uppermost Namurian, and Lower Westphalian rocks on the coast at Westward Ho! contain abundant chlorite, again accompanying frequent sandstone units. This matches the variations observed in the Bampton area.

Conclusions

Those parts of the Namurian strata, along the southern margin of the outcrop, that have been affected by major thrusting and low grade regional metamorphism are mainly slates, with crystalline chlorite developed which partially obliterates the earlier clay mineralogy. However, the crystallinity of the illite shows that chlorite contents vary widely at any one metamorphic temperature, indicating derivation from different clay mineral assemblages.

To the north of this metamorphic influence, variations in clay mineral assemblages can be observed in shales whose stratigraphy is known from their goniatites (Fig. 7). Within areas up to ten or twenty kilometres across, accepting the limited number of firm dates available, consistent stratigraphical variations have been recognised. These correlations vary from one area to the next and many more analyses are necessary to

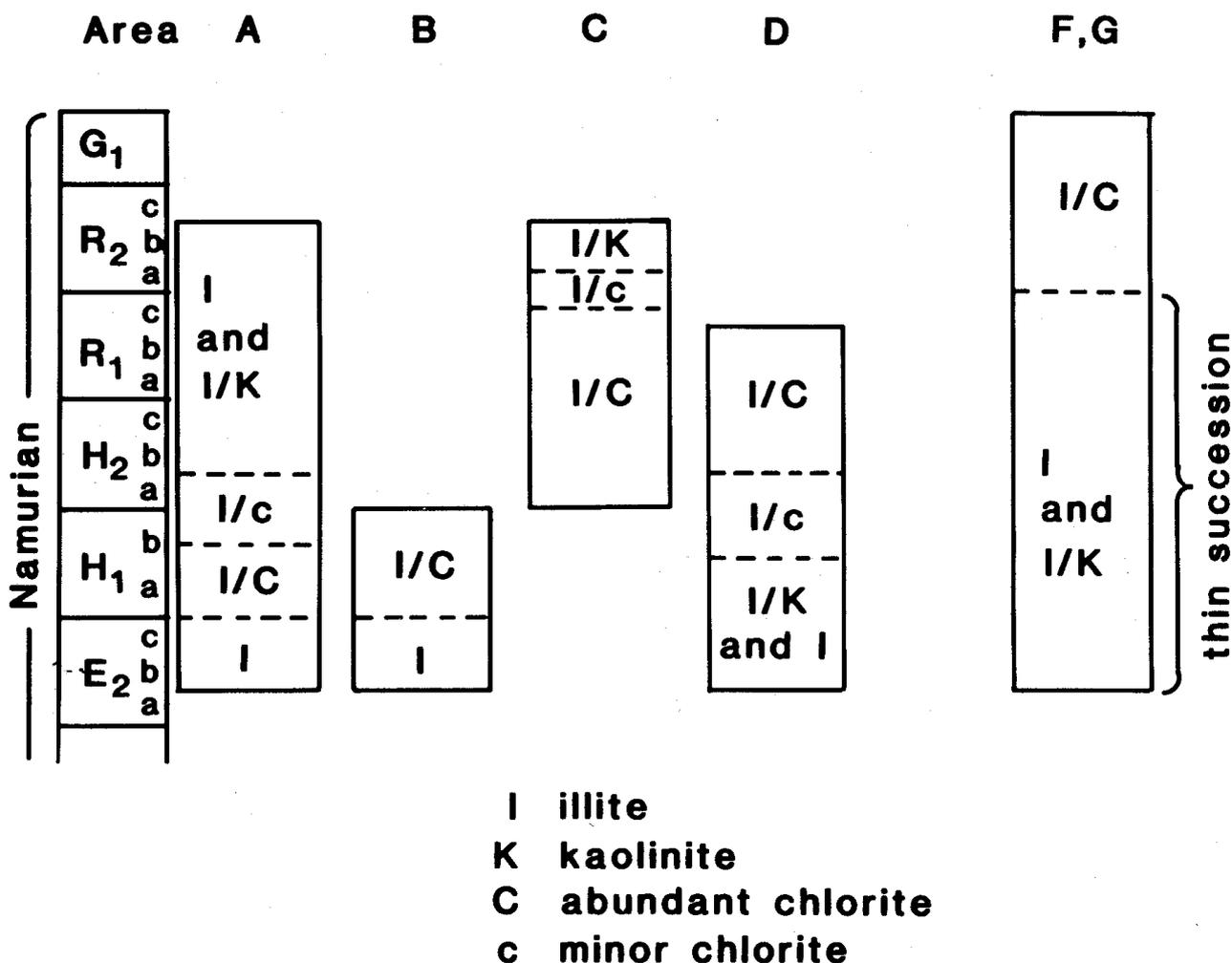


Figure 7. Tentative stratigraphical correlations between clay mineral assemblages and goniatitic zones, in each area sampled.

demonstrate more accurately the diachronous nature of the changes. With the evidence to date, it can be seen that everywhere the lowermost black shale sequences of E2 age are free of chlorite. This illite and illite-kaolinite assemblage may persist through H1a in the south-eastern part of the region, and in North Devon right through the H and R1 zones. The top of the succession also becomes free of chlorite in the southern outcrop, around H2b on the coast, and later further east.

Axial and lateral current directions of the turbidites are known to vary from area to area (Mackintosh 1965; Edmonds and others 1968) and with stratigraphical level. Changes in detrital clay, mineral assemblage are likely to be strongly influenced by changes in source area, and perhaps by tectonic activity in those areas. In the Okehampton area, for example, a change of current direction is documented (Edmonds and others 1968), from one predominantly from the east, to one from the north, near the top of the succession, which corresponds to a change to non-chloritic shales.

Much work remains to be done on the Crackington Formation to determine the origin of its sediments, and its diagenetic history in relation to its structures. This paper illustrates that there is a great potential in further study of the clay minerals.

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