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## Chemical variation in a partially dolomitized Viséan limestone bed, Isle of Man

J. A. D. DICKSON AND C. BARBER

Department of Geology, University of Nottingham, England

**SUMMARY.** The analysis of an acid-soluble and acid-insoluble fraction of one systematically sampled, partially dolomitized limestone bed is reported. The original lime sediment, composed principally of skeletal remains, pellets, occasional intraclasts, detrital quartz, illite, and muscovite has been modified by the addition of calcite, dolomite, and dickite cements and has been patchily replaced by dolomite, quartz, and pyrite. Rapid chemical and mineralogical variations occur over short distances, i.e. within 10 m. Fe and Mn are both present in greater concentration in dolomite than in calcite. Dolomite itself varies in overall composition within the limestones and dolostones but is always Sr-deficient. The insoluble residue is dominated by quartz. Authigenic quartz occurs but its distribution is controlled by pre-existing detrital quartz so SiO<sub>2</sub> distribution corresponds to a detrital arrangement. TiO<sub>2</sub> and K<sub>2</sub>O follow the distribution of SiO<sub>2</sub> and are believed to be sited in detrital minerals, muscovite, and other unidentified minerals. Sulphur, present in pyrite, has a patchy distribution but is deficient in totally dolomitized areas suggesting removal of pyrite during dolomitization.

SYSTEMATIC sampling of limestones to determine variations in composition is usually carried out either at frequently spaced intervals throughout a stratigraphical sequence or over larger areas from a single horizon. Detailed sampling over short distances is rare. This paper reports on a detailed sampling programme carried out on a single stratum of the Lower Michelinia Beds of Viséan age (C<sub>2</sub>) from Lough Skillicore, the Isle of Man (fig. 1 and Lewis, 1930). The work was intended to determine the compositional variations of the carbonate and non-carbonate fractions, and the overall chemical and mineralogical variations within the limestone. The particular horizon chosen is displaced by minor faults but is exposed for 220 m along a low cliff (fig. 2) allowing easy sampling of fresh rock. The horizon has proved particularly interesting for it has a great variety of diagenetic minerals, which are heterogeneously distributed.

*Sampling and analysis.* Two limestone blocks (approx. 15 cm diameter) were collected from each of 44 stations (fig. 2). Each block was sliced vertically, one half being crushed for chemical and mineralogical analysis, whilst the second half was utilized for petrographic study. The chemical analysis was conducted on an acid-soluble fraction and an acid-insoluble fraction, details of which are given by Barber (1975). The calcite/dolomite ratio was determined by X.R.D. by reference to standard mixtures (Tennant and Berger, 1957). This method involves comparison of peak heights, which, although less accurate than using peak areas (Runnells, 1974; Gavish and Friedman, 1973; Milliman and Bornhold, 1973) is much quicker. The error introduced by this method and that due to compositional variations of the carbonates is, in terms of absolute dolomite percentage,  $\pm 5\%$ , which is unimportant for the purpose of this work.

The mineralogical and chemical data are displayed (figs. 3 and 4) using SYMAP (SYN-agraphic MAPPING, Laboratory of Computer Graphics, Harvard University, U.S.A.). The computer maps have been retraced from the original printout for clarity. It is possible that significant lithological variations exist between sampling stations.

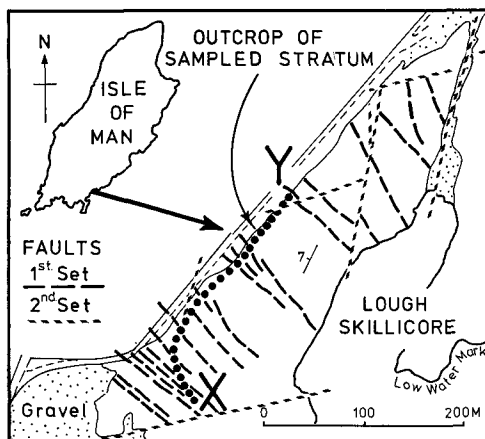


FIG. 1. Location of samples. Outcrop of Lower Michelinia Beds shaded; outcrop of analysed stratum shown by dotted line, marked X-Y. Two sets of faults shown as dashed lines.

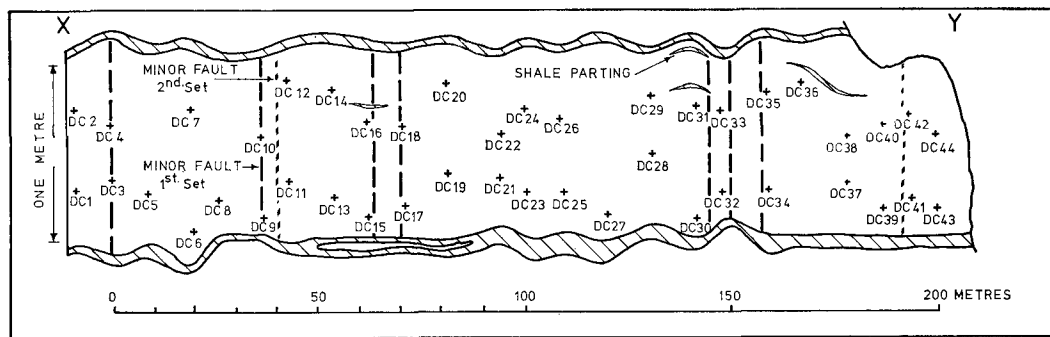


FIG. 2. Section of stratum showing sample stations located X-Y on fig. 1. Oblique ruling indicates shale; vertical dashed lines represent minor faults.

*Depositional components.* The original sediment was a lime sand with practically no mud-grade material except that trapped within chambered shells or piped down burrows. Primary sedimentary laminae, often dipping at  $5^\circ$  to  $15^\circ$  to the bedding, and signs of burrowing can be seen on deeply weathered surfaces. Lithologically the bed is a mixture of biosparites and pel-sparites (Folk, 1959) or alternatively grainstone (Dunham, 1962). The grains are dominantly skeletal. Pockets of bellerophontid gastropods and rugose corallites can be recognized in the field and are set in a dominantly crinoidal limestone. In thin section bivalve and gastropod casts, *Koninckopora*, brachiopods, foraminifera, ostracods, heterophyllid corals, and bryozoa are recognized. Scolecodonts dominate the phosphatic microfossils found in insoluble residues, although conodonts are also present. The dominant non-skeletal carbonate grains are pellets,

probably of faecal origin. Intraclasts of pelmicrite occur and are sometimes difficult to distinguish from micritized grains (Bathurst, 1966). Micritization particularly affects foraminifera and *Koninckopora*.

Detrital quartz appears to be common but its importance, volumetrically, is difficult to assess because of authigenic growth. No clear distinction exists between core and overgrowth. A detrital origin for some of the quartz is indicated by a mixture of undulose and non-undulose quartz, by monocrystalline and polycrystalline grains, by the quartz being arranged geopetally with other fine-grained sediment, and by primary lamination being visible on weathered outcrop by the distribution of quartz. The latter feature is particularly remarkable in dolomitized areas for most primary carbonate features have been destroyed by the dolomitization.

Detrital muscovite flakes occur in most sections but, volumetrically, are a minor constituent.

*Diagenetic components.* One of the earliest diagenetic events was the solution of bivalve and gastropod shells, presumably composed of aragonite. The pore spaces in the sediment have been filled with a succession of precipitates, the first of which is zoned calcite. A period of aragonite solution was complete before calcite cementation began, for the same number of calcite zones occur in the infilling of the shell moulds as in the intergranular areas. Calcite cementation is followed by zoned dolomite, dickite, and finally by another stage of calcite precipitation. In addition to the passive addition of these minerals in pore spaces, quartz and pyrite have grown by replacement. The most important replacive mineral, however, is dolomite, which unlike the pore-filling dolomite occurs in patches often replacing all pre-existing calcite.

Many minor faults affect the Skillicore outcrop and, although the throw of these faults is only a matter of a few decimeters, two distinct sets can be determined (fig. 1). The earliest set of faults, chiefly oriented NW-SE, have no associated veining or alteration, but the second set of faults, NNE-SSW and ENE-WSW, cut the first set and throw them laterally. The later set possesses dolomite veins along the fractures and the replacement dolomite occurs around these faults in a zone from 1 to 5 m wide on both sides of the fracture. Some of the dolomitized limestone beds adjacent to the second set of faults have developed vugs, which are centripetally lined with dolomite, chalcopyrite, calcite, and aragonite crystals. In the field the replacement dolomite weathers a striking brown colour. This brown coloration is probably due to localized dedolomitization of ferroan dolomite as reported by Al-Hashimi and Hemingway (1973).

The two generations of dolomite are petrographically distinctive. The dolomite cement occurs scattered throughout the entire bed as large crystals up to 3.5 mm diameter. The replacement dolomite is composed of smaller crystals up to 1 mm diameter, which occur in the areas of intense alteration. Both dolomites post-date calcite cementation and the larger cement crystals are often enclosed by the smaller replacement dolomite. This suggests that the latter post-dates the former but no unambiguous textural evidence is present. Both dolomites are zoned with inclusions and with respect to ferrous iron.

Pyrite occurs as framboids and in larger euhedral crystals. By analogy with other limestones higher in the sequence (Dickson and Barber, 1976), the framboidal pyrite is a very early diagenetic product whereas the larger euhedral crystals belong to a later diagenetic event.

Authigenic quartz occurs as overgrowths on detrital quartz, and dickite occurs in void infillings, post-dating calcite and dolomite cementation.

#### *Interpretation of analytical results*

*Carbonates.* The soluble fraction consists principally of Ca, Mg, and Fe with minor Mn, Sr, and Al, these varying considerably in both the analysed limestone and dolostone (Table D). The overall composition of carbonate minerals, and the variation in the distribution of calcite

TABLE I. Analysis of 27 limestones and 17 dolostone samples from a single stratum of the Lower Michelinia Beds

	Rocks						Insoluble Residue		
	Limestone		Dolomite		Total	Soluble	Insoluble	Limestone	Dolomite
	Total	Soluble	Insoluble	Soluble					
SiO <sub>2</sub>	8.78 2.63-20.49	-	8.78 2.63-20.49	-	10.05 3.28-20.00	10.05 3.28-20.00	87.12	81.87	
Al <sub>2</sub> O <sub>3</sub>	0.51 0.12-1.15	0.03 0.0-0.07	0.48 0.11-1.08	-	0.63 0.24-1.32	0.56 0.19-1.15	5.17	5.00	
TiO <sub>2</sub>	0.02 0.01-0.06	-	0.02 0.01-0.06	-	0.02 0.01-0.04	0.02 0.01-0.04	0.25	0.21	
Fe <sub>2</sub> O <sub>3</sub>	1.49 0.66-2.76	1.33 0.54-2.62	0.16 0.07-0.51	-	4.14 1.59-6.44	0.18 0.07-0.4	2.26	1.81	
MgO	2.79 1.08-6.51	2.74 1.05-6.44	0.05 0.01-0.14	-	16.08 9.37-19.04	0.19 0.0-0.67	0.69	1.90	
CaO	47.06 36.11-52.88	46.98 36.03-52.82	0.08 0.03-0.25	-	28.10 24.74-40.4	0.27 0.02-1.06	1.26	2.81	
Na <sub>2</sub> O	0.00 -	-	0.00 -	-	0.00 -	0.00 -	0.02	0.02	
K <sub>2</sub> O	0.05 0.01-0.19	-	0.05 0.01-0.19	-	0.06 0.02-0.12	0.06 0.02-0.12	0.57	0.54	
MnO	0.17 0.08-0.33	0.17 0.08-0.33	0.00 0.00	-	0.61 0.23-1.03	0.01 0.0-0.03	0.02	0.07	
S	0.08 0.02-0.34	-	0.08 0.02-0.34	-	0.04 0.01-0.09	0.04 0.01-0.09	1.22	0.42	
Sr	326 145-484	319 134-478	6.8 2-21	-	60 19-91	6.45 3.79-14	87	53	
I.R.	9.8	-	-	-	11.9	-	-	-	

Dolostones contained no detectable calcite, limestones contained from 10% to 43% dolomite. I.R. = insoluble residue. Arithmetic means and ranges are shown as wt % except for Sr which is in ppm.

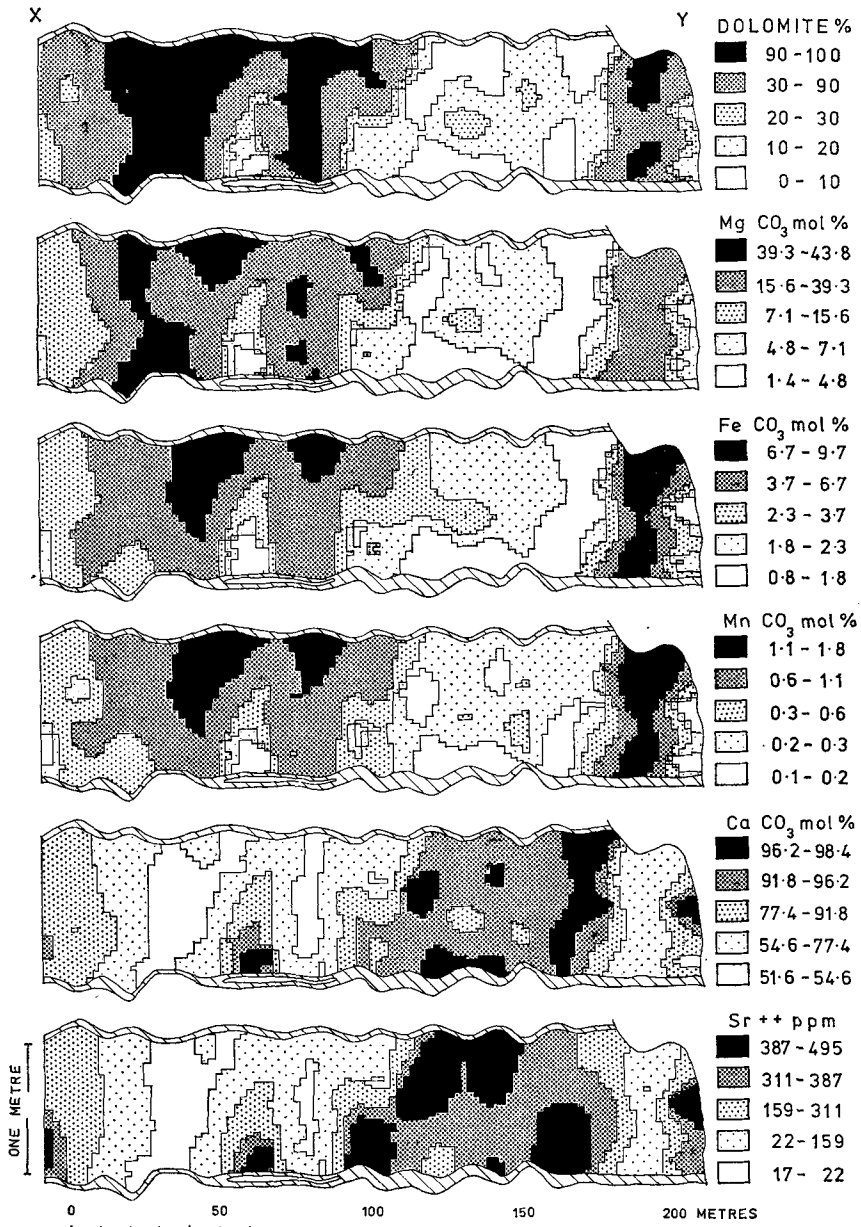


FIG. 3. SYMAP conformant diagram produced from 44 data points as shown on fig. 2. Dolomite map indicates dolomite/calcite composition. Positive correlation between mol % MgCO<sub>3</sub>, FeCO<sub>3</sub>, and MnCO<sub>3</sub> and dolomite may be contrasted with negatively correlated mol % CaCO<sub>3</sub> and Sr ppm.

and dolomite in the horizon, can be deduced from the acid-soluble determinations, which are shown in fig. 3 as SYMAP projections.

Fig. 3 shows a clear association of Fe and Mn with Mg and dolomite, while Sr and Ca are negatively correlated with dolomite, which indicates that dolomite contains significantly more Fe and Mn and less Sr than calcite (see also Table I).

Comparison of the X.R.D. patterns for the Skillicore samples indicates significant shifts of the  $10.4 \text{ \AA}$  dolomite reflection. Dolomites from the S.W. end of the section give values near the theoretical  $2\theta$  angle of  $30.98^\circ$  for pure dolomite (Graf, 1961), whilst dolomites from the N.E. end of the section show reflections centred at  $30.80^\circ$ , all angles being measured relative to a quartz internal standard. The peak shifts can be explained by variations in composition of the dolomites (Graf, 1961). The overall dolomite composition is non-stoichiometric, varying from 51.58 to 60.87 mol %  $\text{CaCO}_3$  whilst the Mg/Fe ratio of the dolomites varies between 10.89 and 2.24. Clear compositional differences exist between the totally dolomitized areas shown in fig. 3. The dolomites to the N.E. (DE39 to DC42), near Y, have an average composition  $\text{Ca}_{56.96}\text{Mg}_{33.06}\text{Mn}_{1.48}\text{Fe}_{8.50}(\text{CO}_3)_{100}$ ; the dolomites near the centre of the outcrop (DC17 to DC20+DC24) have an average composition  $\text{Ca}_{53.16}\text{Mg}_{39.82}\text{Mn}_{1.04}\text{Fe}_{5.98}(\text{CO}_3)_{100}$  and the dolomites in the S.W., near X, (DC6 to DC12+DC14) have an average composition  $\text{Ca}_{53.60}\text{Mg}_{39.94}\text{Mn}_{0.91}\text{Fe}_{5.55}(\text{CO}_3)_{100}$ .

A relationship between the chemical variation and the two petrographic dolomite types, if any exists, has not been established by the present methods of study.

The Skillicore dolomites are particularly rich in Mn and deficient in Sr. Land *et al.* (1975) and Till (1971) report much lower Mn concentration in ancient dolostones and recent carbonate sediments. They both conclude that Mn distribution is controlled by clays or organic matter in the carbonate rock and sediments and is not sited in carbonate minerals, which is clearly not the case in this study (Table I). Sr, however, is apparently not unusually low in the Manx dolomite. Behrens and Land (1972) suggest that marine dolomites should contain 600 to 700 ppm Sr but the Skillicore dolomite contains 18 to 84 ppm Sr, a value that corresponds with figures recorded by Weber (1964) and Land *et al.* (1975) for ancient dolomites. Land *et al.* deduce that such a low concentration of Sr is due to equilibration with fresh water during diagenesis.

*Acid-insoluble fraction.* The dominance of quartz in the insoluble residue is clearly shown in Table I and fig. 4. Quartz is of mixed detrital/authigenic origin but its distribution is related primarily to its detrital arrangement as shown on deeply weathered surfaces where cross-lamination is displayed by weathered-out quartz grains. The authigenic quartz has simply enlarged the detrital grains. The distribution of  $\text{K}_2\text{O}$ , which reflects the variation in amount of illite and muscovite in the rocks, is correlated with  $\text{TiO}_2$  (fig. 5). The combined distribution  $\text{TiO}_2 + \text{K}_2\text{O}$  is similar to that of  $\text{SiO}_2$  (fig. 4), suggesting that these reflect the overall distribution of detrital phases. The similar Ti/K ratio in the samples suggests that these elements are part of a detrital fraction of reasonably uniform composition along the horizon. The amount of Ti, however, is too large for all of it to be sited in illite or muscovite, which indicates the presence of an unidentified Ti-bearing mineral.

The  $\text{K}_2\text{O}$  distribution is less correlated with that of  $\text{Al}_2\text{O}_3$  (figs. 4 and 5), indicating little correspondence between the occurrence of detrital illite and muscovite and that of authigenic dickite. It is therefore doubtful whether the dickite is the product of a detrital precursor, which is supported by petrographic evidence.

The expected relationship between Fe and S (both occur in pyrite), is poor (fig. 4). This is due to Fe-rich dolomite remaining undissolved after acid digestion, which will also affect the Mg and Ca figures for the insoluble fraction. The distribution of S is patchy (fig. 4), the lowest concentration being confined to totally dolomitized areas, which suggests that pyrite may well have been unstable in the dolomitizing pore fluids. If this were so, the breakdown of pyrite could supply at least part of the iron incorporated in the dolomite. However, unless considerably more pyrite were present in the original undolomitized rock than is present now (based on the amounts of acid-soluble Fe in the limestones and dolostones; 0.8 to 9.3% pyrite would

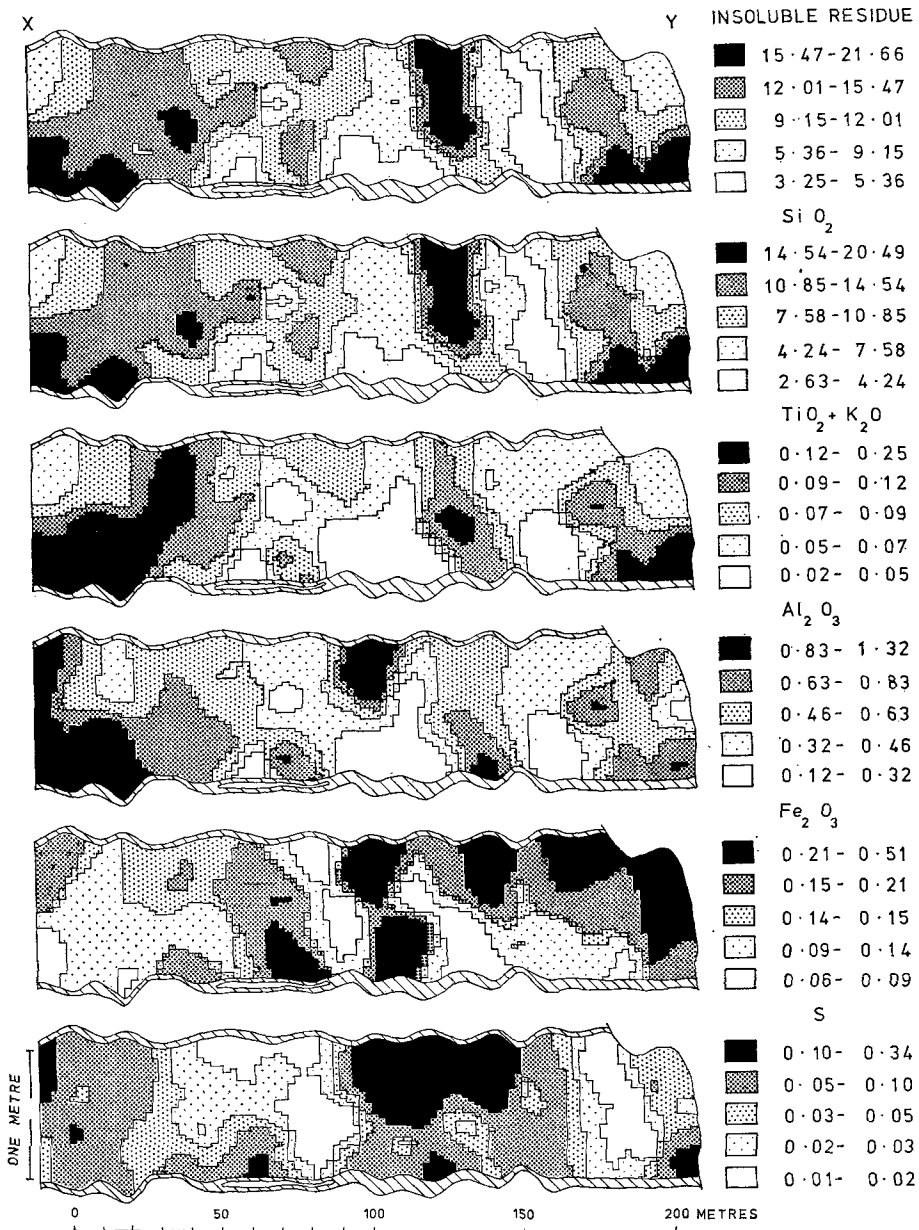


FIG. 4. SYMAP conformant diagram produced from 44 data points as shown on fig. 2. Good correlation between SiO<sub>2</sub> and combined TiO<sub>2</sub> + K<sub>2</sub>O with the insoluble residue is evident. Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and S are poorly correlated; for further details see text.

have been required in the pre-dolomitized limestone compared with less than 0.1% now present in the limestones), an additional source of Fe would be required to account for the iron of the ferroan dolomites.

The overall distributions of acid-insoluble components in the limestones and dolostones are variable. In the cases of SiO<sub>2</sub>, TiO<sub>2</sub>, and K<sub>2</sub>O they appear to be related to a patchy

distribution of detrital quartz, clay, mica, and possibly heavy minerals. The poor correspondence between the distribution of  $\text{Al}_2\text{O}_3$  and particularly Fe and S, and those of  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{K}_2\text{O}$  is due to the authigenic growth of dickite and pyrite, whose spatial distributions are not related to that of the detrital minerals.

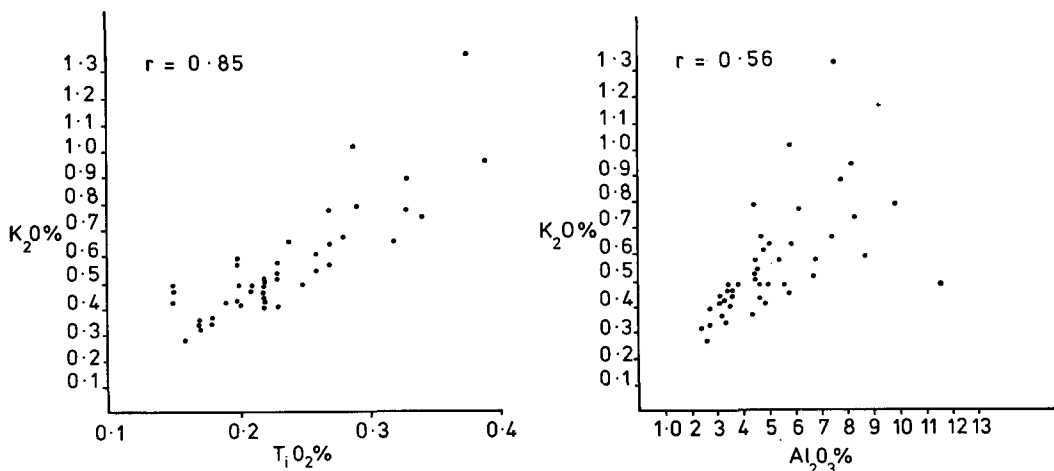


FIG. 5. Scatter diagram from 44 data points of  $\text{K}_2\text{O}$  against  $\text{TiO}_2$  and  $\text{K}_2\text{O}$  against  $\text{Al}_2\text{O}_3$ . Pearson correlation coefficient shown for each oxide pair.

### Conclusions

The programme of sampling and analysis has found considerable variation in the chemical and mineralogical composition of a coarse-grained dolomitized limestone. The variations are related to patchy, incomplete dolomitization of the limestone, to the variation in composition of the dolomite, to the patchy distribution of detrital quartz, clay, and mica and to a further complex distribution of authigenic non-carbonates dickite and pyrite. The variation in the distribution of the carbonate minerals was not as expected from a previous, limited investigation, and could only have been established by systematic, detailed sampling of the horizon. The large variations in the analyses here suggest that no one sample can be regarded as representative of a limestone bed. Similar variations, albeit of lower magnitude, were determined in the carbonate and non-carbonate fractions of fine-grained concretionary limestones from the same area (Dickson and Barber, 1976).

The methods of analysis described in the paper, which involve the separation of acid-soluble and insoluble fractions of the limestones and dolostones, have determined the distribution of both carbonate and non-carbonate minerals, and indicate variations in the compositions of dolomite. It must be remembered however, that the separations are not absolute with respect to any one mineral. It is not possible to use this data for the study of any individual mineral species, for most minerals have more than one generation and many are zoned. However, the technique described provides an overview of the chemical variations in a particular stratum and gives a basis for more detailed investigation.

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