A precise and accurate method for the quantitative determination of carbonate minerals by X-ray diffraction using a spiking technique

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SUMMARY. A precise and accurate X-ray diffraction method has been developed whereby the weight percentages of aragonite and low- and high-magnesium calcite are determined from the integrated peak areas of spiked and unspiked samples. The spike mixture was prepared from organisms extracted from the samples to be analysed. Use of a spiking method also avoided the preparation of working curves from artificial mixtures of carbonate minerals, which may not have the same diffraction behaviour as the unknowns. A test of the precision of the method indicates the following coefficients of variation: aragonite, 1·4 %; low-magnesium calcite, 1·5 %; high-magnesium calcite, 7·8 %. A test of the accuracy of the method indicates no significant bias in any of the carbonate results, except in samples where high-magnesium calcite values are below 10 %. Quartz may also be determined by this method (coefficient of variation 23·9 %; positive bias in values greater than 10 %).

THE present technique was developed during the study of temperate-water carbonate sediments from W. Ireland and stemmed from the method used by Till (1968) when investigating Bahamian carbonates. In any geochemical study of recent carbonates and their processes of diagenesis, both precise and accurate quantitative mineralogical data are required for aragonite, the calcites, and quartz, to relate to chemical and petrological data.

In the determination of carbonate minerals by X-ray diffraction procedures, most workers used calibration curves to determine the weight percentages of the different carbonate minerals. In these studies either peak-height intensities (Lowenstam, 1954; Turekian and Armstrong, 1960; Taft and Harbaugh, 1964) or peak-area intensities (Chave, 1962; Davies and Hooper, 1963; Billings and Ragland, 1968) were used. It is preferable to use peak areas in such studies since they are not affected so much by variations in crystallite size or orientation. In either case, the accuracy of the method depends to a large extent on the nature of the standards used to produce working curves.

Recently, infra-red spectroscopy has been applied by various workers (Adler and Kerr, 1962; Chester and Elderfield, 1967) for the determination of carbonate minerals. At present this technique is less precise and X-ray diffraction methods are more generally available to geologists.

In all these methods standards were used that were made from carbonate minerals from a variety of sources (both artificial and natural). Graf and Goldsmith (1963)

pointed out and Berner (1966) emphasized that standards for quantitative X-ray diffraction analysis must have the same diffracting efficiency and characteristics of preferred orientation, uniformity of crystallite size, and absorption effects as the unknown samples. Berner said that materials for standards should be handpicked from the actual unknown samples to produce realistic working curves. Since this can be very time consuming, it was not attempted by Berner, hence he only quoted peak area ratios.

In developing the present method, biogenic carbonates were being studied, and it was possible to isolate the pure phases from the samples by extracting the appropriate organisms. Working curves were not constructed, but each sample was spiked with a known mixture, thus allowing the percentages of constituent carbonate minerals to be calculated. Such a method should give accurate data, since it overcomes most of the problems raised by Graf and Goldsmith (1963) and Berner (1966).

Prior to the development of this method all samples had been run on a normal X-ray qualitative mineral identification run (4 to 44°2θ). Examination of these X-ray traces indicated that the ideal composition for the spike mixture was one containing 30 % low-magnesium calcite, 60 % aragonite, and 10 % quartz by weight. Such a mixture produced a marked and measurable change in peak areas of all the phases when combined in a 1 : 1 ratio with the original sample. In this study the main minerals under consideration were low-magnesium calcite (LMC), high-magnesium calcite (HMC), aragonite, and quartz. The LMC is defined here as that containing less than 4 mole % $MgCO_3$ (Chave, 1952).

Theory

In a multicomponent mixture, for a given X-ray diffraction peak: $I_a = K'_a w_a / \bar{\mu}^*$ (Brindley, 1961), where I_a is the reflected peak intensity for the mineral a, w_a is the weight percentage of a in the mixture, K'_a is a constant for the particular reflection of component a, and $\bar{\mu}^*$ is the average mass absorption coefficient of the mixture.

The value of $\bar{\mu}^*$ may change with the composition of the mixture, hence the relationship between I_a and w_a will not be linear in a mixture containing LMC, HMC, aragonite, and quartz.

From Brindley's equation it follows that if S_a and S_b are the percentages of a and b in the spike mixture, and the spike ratio is 1 : 1, then:

$$(I_a/I_b).(I'_b/I'_a) = \{w_a.(w_b+S_b)\}/\{w_b.(w_a+S_a)\},$$

where I_a and I_b refer to the unknowns and I'_a and I'_b to the spiked mixtures.

If one of the four minerals is omitted from the spike mixture (i.e. $S_b = 0$) the other minerals can be determined readily, using I_b and I'_b as reference peaks. In this study HMC was found to be the most suitable phase for omission from the spike mixture because of its variable composition (and hence variable K'). However, in samples containing little or no HMC it is necessary to choose another component for omission from the spike, preferably one that is a major constituent in the samples.

The method

Sample preparation. The bulk samples were thoroughly washed, air dried, and placed in an oven at 115 °C for two hours. A 100 g split of the bulk sample was then crushed in a pulverizing machine until a coarse sand size was obtained. An 8 g split of this was hand-ground in a mortar until all the material passed through a 250-mesh sieve. Aragonite inverts to its polymorph calcite on prolonged grinding and care must be taken during sample preparation.

Sample analysis. The powdered sample was back-packed into an aluminium sample-holder and analysed in a Philips X-ray diffractometer using: Ni filtered Cu-$K\alpha$ radiation, 40 kV, 20 mA, slit system 1°, 0·1°, 1°, scan rate $\frac{1}{8}$° per minute, rate meter 16, time constant 1, and scanning from 25·5°2θ to 32·0°2θ.

Spike preparation. A large number of carbonate-secreting organisms were hand picked from a wide variety of environments in the study area and their mineral composition was determined by X-ray analysis. The pure carbonate phases were thus isolated. Similarly a large number of quartz grains were hand picked from the samples.

The calcite, aragonite, and quartz were ground separately to 250 mesh, mixed in the determined proportions and homogenized in a mixing machine for 60 minutes. Enough spike mixture was prepared for the full number of analyses (0·5 g per sample). This detailed procedure was adopted to ensure that the spike mixture prepared was as similar as possible to the samples under analysis. Containing carbonate phases from the same sources, the spike mixture and the samples should be crystallographically identical (i.e. reflect X-rays with the same intensity and efficiency).

Spiked sample analysis. The previously analysed sample was mixed and homogenized for 30 minutes with the spike mixture in a 1:1 ratio. The spiked sample was analysed in the X-ray diffractometer under the same operating conditions as the unspiked sample. A 1:1 ratio of sample to spike was found to be most suitable in the present study, since it gave an appreciable change in all the peak areas measured. In other studies a change of the composition of the spike mixture or of the sample to spike ratio may be necessary.

Calculation of results. The following peak areas were measured on both spiked and unspiked sample diffraction traces, using a polar planimeter: 111 of aragonite at 26·22°2θ, $10\bar{1}1$ of quartz at 26·64°2θ, and $10\bar{1}4$ LMC plus HMC calcite peak at 29·4–30°2θ depending on magnesium content (Chave, 1952). The X-ray charts indicated that the skeletal calcites in the samples had a range of magnesium contents. At a very slow rate of scanning ($\frac{1}{8}$°/minute), the calcite peak showed two distinct modes, which can be attributed to LMC and HMC respectively. The difficulties encountered in partitioning the total curve into its LMC and HMC components have been pointed out by Chave (1962) and Weber (1968). In the present study, following Berner (1966), the total calcite peak area was calculated and the difference between

twice the half-area of the major mode and that of the total curve was considered to be HMC. This assumes the major mode to be bilaterally symmetrical. In other studies HMC may be the major mode, but the same partitioning procedure can be adopted. The first mode at or greater than $29.60°2\theta$ ($\pm 0.02°2\theta$) was taken to be HMC. The total curve partitioned in this way gave results whose accuracy was found to be satisfactory (table II).

After calculation of the peak areas the weight percentage of the different minerals were calculated by the above equation. However, the weight percentage of HMC cannot be determined from these equations. The total carbonate content of the samples was determined by digesting 1.5 g of the powdered sample in 3 % acetic acid and weighing the insoluble residue (essentially quartz plus clay minerals). The HMC was then found by difference. In this way, by combining a spiking procedure with determination of the insoluble residue the weight percentages of all carbonate minerals and quartz have been obtained. No working curves made from artificial standards have been employed and no assumptions about changes in the value of $\bar{\mu}*$, or about the value of the various K'_a have had to be made. A value for the non-quartz insoluble residue can also be obtained; generally this was found not to be very accurate, as explained below.

Precision and accuracy

To demonstrate the precision of the technique (expressed as the coefficient of variation of ten replicate analyses) results are presented in table I for a single test sample (C1122). This was separately prepared each time for loading into the sample-holder before diffraction analysis.

TABLE I. *Precision of ten replicate analyses of a single sample*

	LMC	Aragonite	Quartz	Insoluble residue	HMC
Mean	25.11 %	19.25 %	33.57 %	32.06 %	23.57 %
Standard deviation	0.37	0.26	8.03	0.18	1.85
Coefficient of variation	1.47	1.35	23.92	0.56	7.84

Instrumental precision was tested by making repeated measurements on the same prepared sample of spike mixture over a period of several days, without reloading the sample-holder. Preferred orientation and packing and preparation errors were tested by making repeated measurements on a specimen after reloading the sample-holder. No errors from these sources were found to be important.

The effect of crystallite size on quartz peak intensities was demonstrated by Gordon and Harris (1955, 1956) and by Brindley and Udagawa (1960). According to these authors the maximum reflected intensity of the quartz $10\bar{1}1$ peak is obtained over a size range of 5 to 20 μ and extinction effects decrease quartz peak intensities at crystallite sizes larger than 20 μ. Grinding down to finer sizes would have altered some aragonite to calcite in these samples. Therefore it was not possible to test crystallite

size effects on the peak intensities. Though this may be a source of error in the quartz determination it was assumed to be negligible in the case of the carbonate species.

To investigate the accuracy of the method five replicate analyses of each of five carefully prepared synthetic mixtures were made. The results are given in table II. Following Mandel (1964, pp. 123-6) a t-test was employed to see if the determined values showed any statistically significant bias from the real values at the 95 % level.

TABLE II. *Accuracy of five replicate analyses of each of five artificial mixtures*

Component	Real value (R)	Determined value (D)	Standard deviation (σ)	Bias factor (ϵ)	Significant bias ?*
HMC	5	3·6	0·36	0·42	Yes, —ve
LMC	50	51·8	0·67	0·83	Yes, +ve
Aragonite	35	34·3	0·65	0·80	No
Quartz	10	11·8	1·55	1·88	No
Insoluble residue		10·3			
HMC	10	9·5	0·87	1·10	No
LMC	40	40·2	1·22	1·50	No
Aragonite	20	20·4	1·10	1·35	No
Quartz	30	32·5	2·43	2·27	Yes, +ve
Insoluble residue		30·2			
HMC	20	20·4	1·65	2·03	No
LMC	40	40·0	1·45	1·67	No
Aragonite	15	15·1	1·44	1·64	No
Quartz	25	28·6	1·46	1·67	Yes, +ve
Insoluble residue		24·8			
HMC	40	38·7	1·55	1·90	No
LMC	25	25·5	0·92	1·11	No
Aragonite	5	5·7	0·82	1·02	No
Quartz	30	33·0	2·10	2·58	Yes, +ve
Insoluble residue		30·1			
HMC	50	50·9	1·33	1·64	No
LMC	5	5·3	0·74	0·91	No
Aragonite	40	39·3	1·06	1·30	No
Quartz	5	6·2	1·73	2·19	No
Insoluble residue		5·0			

* Bias significant at 95 % level if $|R-D| > \epsilon$; $\epsilon = (\sigma/\sqrt{n}).t$, where $n = 5$.

Discussion of results. Examination of table I indicates that the precision of LMC, HMC, and aragonite weight-percentage determinations is remarkably good. Co-efficients of variation are LMC (1·5 %), aragonite (1·4 %). The coefficient of variation for HMC (7·8 %) is higher than for the other carbonates because it is determined by difference rather than by direct calculation. The method also allows the presentation of a quartz value and 'clay content' (insoluble residue minus quartz value). The quartz determination shows a much broader range of variation (23·9 %) than the carbonate figures. This is to be expected because of the interference of mica, feldspar, and clay

mineral X-ray peaks lying very near to the main 10Ī1 quartz peak; this produces a composite peak whose exact limits are difficult to determine. For this same reason the quartz values tend to show a positive bias. This problem can be overcome by analysing the sample after heating to 950 °C (Till and Spears, 1969).

The results given in table II indicate that the accuracy of the method is very good. A significant bias in the carbonate mineral percentages is only seen when the HMC content is below 10 %. Since the HMC peak area is obtained by difference there is likely to be the same absolute error in its determination for all percentages of HMC. Consequently precision and accuracy of the HMC value would be expected to decline for small values of HMC. However, in such cases a different spike mixture should also be employed.

The majority of modern carbonate sediments contain more than 10 % HMC; consequently this method of obtaining precise and accurate quantitative figures for the carbonate minerals can be used with confidence in most studies.

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