The determination of the calcite : aragonite ratio in mollusc shells by X-ray diffraction

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Summary. By measuring the integrated line intensity on a Philips' X-ray diffractometer in place of the peak intensity and by paying due regard to the ease with which aragonite converts to calcite during cleaning and grinding operations, the proportion of calcite and aragonite in a pure calcium carbonate shell can be determined to within 1 % of the total in less than 30 minutes.

A STUDY of the effect of environment, particularly temperature and salinity, on the polymorphic composition of pure calcium carbonate shells requires an accurate method for determining the percentage concentration of calcite and aragonite.

Recent work in the United States (Lowenstam, 1954; Turekian and Armstrong, 1960; Chave, 1962) has shown that quantitative results can be obtained by X-ray diffraction techniques. Lowenstam (1954) and Turekian and Armstrong (1960) measured the peak heights of the calcite and aragonite lines and the former quotes an accuracy of ± 10 %. Chave (1962), in a paper published after the greater part of the present study was completed, measured the integrated line intensity and claims an accuracy of ± 5 %.

Method. Sample preparation is extremely important because of the ease with which aragonite converts to calcite. Both the drying of the shells in an oven set at $110°$ C and a prolonged period of grinding in a ball mill can cause a marked change in the aragonite line. This can be illustrated by subjecting a pure aragonite shell to various temperatures and periods of grinding. In fig. 1 the peak height of the aragonite line has been halved and the breadth of the line increased, while a comparatively small quantity of calcite has been produced. Because of the line broadening caused in this manner and the different degrees of inherent line broadening in different shell samples due to different crystallite size, the integrated line intensity should always be measured in preference to the peak height.

The powder is passed through a 200-mesh sieve and loaded in the standard aluminium holder, with the powder supported on the lower
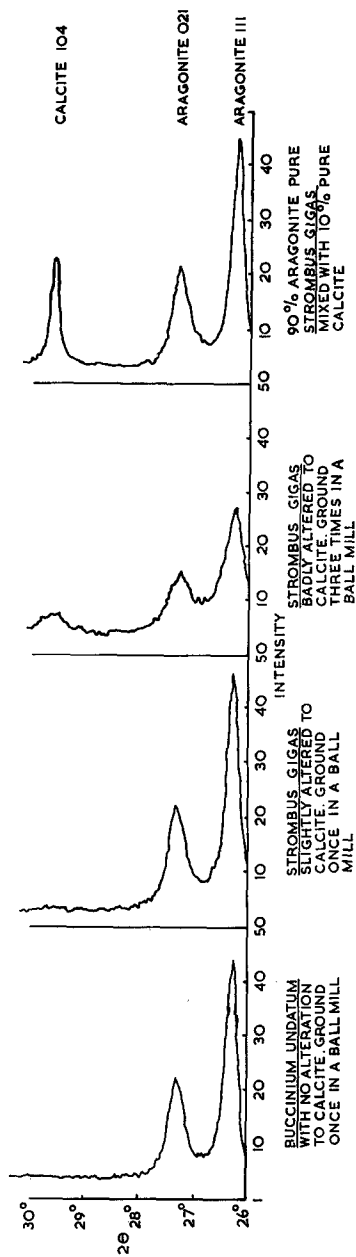
CALCITE AND ARAGONITE LINE PROFILES

FIG. 1. Effect of grinding on the profiles of the aragonite lines, showing decrease of peak height, increase of breadth, and formation of some calcite.

side by a glass plate. It is compacted as little as possible, consistent with adequately filling the holder and producing a flat surface. This method, described by McCreery (1949), reduces any possible preferred orientation.

The lines used for the analysis are the $10\bar{1}4$ calcite line and the 111 and 021 aragonite lines combined (fig. 1). The double aragonite line is used
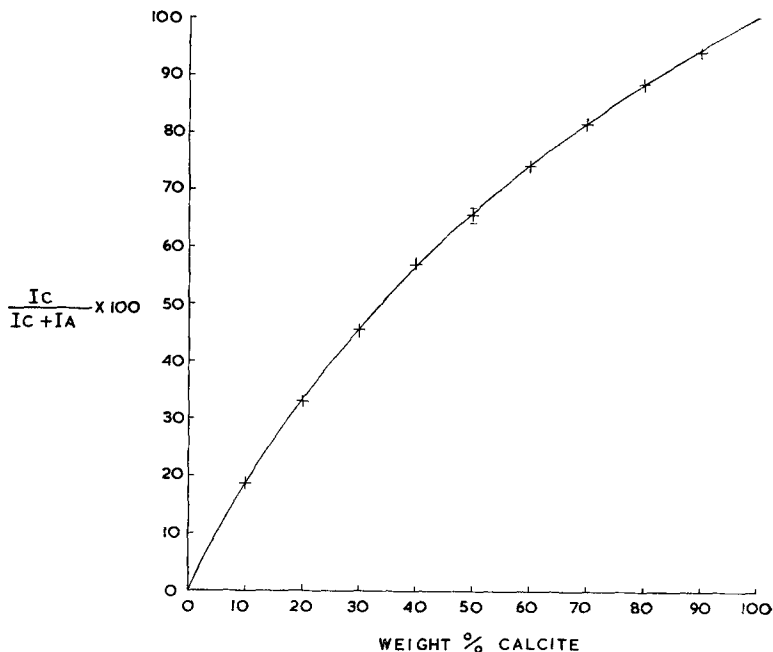

$$\frac{I_C}{I_C + I_A} \times 100$$

FIG. 2. Calcite: aragonite calibration curve.

because complete separation is impossible and measurements of a single line are affected by line broadening. Also, the aragonite pair gives a total count more similar to the single and much stronger calcite line.

The radiation from a copper target with a nickel filter is reflected from the specimen, collected by a scintillation counter in conjunction with a pulse height analyser, and recorded electronically. This combination gives a higher count:background ratio than a geiger counter, and 'dead time', which is difficult to calculate when measuring an integrated line intensity, can be ignored. The count is made by scanning the peak once in each direction from background to background over a precisely

determined period of time. The background is measured, subtracted from the total count, and the ratio $Ic/(Ic+Ia)$ calculated.

The calibration curve is constructed by mixing pure calcite and pure aragonite shells in different proportions, measuring the $Ic/(Ic+Ia)$ ratio and plotting these values against weight percent calcite (fig. 2).

TABLE I. Tests of the precision of the proposed method. In each pair of columns, values of 100 $I_c/(I_c+I_a)$ and of the deviations of these individual values from their mean are given, together with the mean and the mean deviation; the maximum deviation of a set is italicized. (I_c, intensity of the $10\bar{1}4$ calcite line; I_a of the unresolved 111, 021 aragonite line)

A	δA	B	δB	C	δC	D	δD
66·31	0·22	65·11	0·51	65·62	0·27	27·14	*1·13*
66·34	0·25	66·02	0·40	65·81	0·46	26·61	0·60
65·75	*0·34*	65·55	0·07	66·09	0·74	26·51	0·50
66·07	0·02	65·13	0·49	66·83	0·48	25·05	0·96
66·01	0·08	66·27	*0·65*	64·11	*1·24*	25·50	0·51
				64·63	0·82	25·77	0·24
				64·35	1·00	25·85	0·16
						25·58	0·43

Means:

66·09	0·18	65·62	0·42	65·35	0·72	26·01	0·57

A. Repeated measurements on the same sample of *Buccinium undatum* 50 % and *Ostrea edulis* 50 % without reloading, as a test of instrumental precision.

B. Repeated measurements on the same sample of *Strombus gigas* 50 % and *Ostrea edulis* 50 %, reloading the sample each time, as a test of sample preparation and instrumental precision.

C. Measurements of different shells or different portions of shells of *S. gigas* and *B. undatum*, in 1:1 proportion with *O. edulis*, as a test of the precision of the calibration curve.

D. Repeated measurements on an unknown sample of *Modiolus modiolus*, made on separate samples from one large shell.

Errors. The error involved in the measurement of an unknown sample will depend on the error in the positioning of the calibration curve and on the reproducibility of the measured intensity ratio.

Both will depend on the precision of the instrument; on the errors involved in packing the sample in the holder, in particular the presence of preferred orientation; and on the errors involved in the initial preparation of the sample, in particular the conversion of some aragonite to calcite.

The precision of the instrument is demonstrated in table I, columns A and δA, and the expected error from this source is 0·18 % calcite. The precision of the instrument and the errors involved in the packing of the sample are demonstrated in columns B and δB; the expected error

from both these sources is 0·42 % calcite. From this it can be concluded that preferred orientation is of little significance. Columns C and δC demonstrate the error involved in the position of any one calibration curve constructed from a single sample of pure calcite mixed in 1:1 proportions with various samples of pure aragonite. The extreme values are plotted in fig. 2 and the mean value lies close to the calibration curve. The error in the position of a calibration curve drawn through a series of points, each determined by averaging six or more different samples using different pure aragonite shells, will be insignificant. Finally, columns D and δD demonstrate the reproducibility of measurements made on samples from the same large shell which was broken into small chips by a hammer, carefully separated into eight equal samples and each ball-milled individually. The expected error from the mean in any one of these samples is 0·40 % calcite.

Given that the error in the position of the calibration curve is insignificant, as demonstrated above, the reproducibility of the unknown sample will be a measure of the total error of the method. That is, there is a 97 % probability that any one measurement on the unknown sample will give a calcite:aragonite ratio within 1 % of the true value. Owing to the slope of the calibration curve, this error will increase slightly towards the calcite end. At 50 % calcite concentration there will be an 87 % probability and at 75 % calcite concentration a 77 % probability, that any one measurement will be within 1 % of the true calcite: aragonite ratio.

Having constructed the calibration curve, unknown samples can be measured at the rate of two per hour.

References

CHAVE (K. E.), 1962. Limnology and oceanography, vol. 7, no. 2, pp. 218–23.
LOWENSTAM (H. A.), 1954. Journ. Geol., vol. 62, p. 284.
McCREERY (G. L.), 1949. Journ. Amer. Ceram. Soc., vol. 32, p. 141.
TUREKIAN (K. K.) and ARMSTRONG (R. L.), 1960. Journ. Marine Research, vol. 18, p. 133.