

## **Recommended Method for Semi-quantitative Measurement of Aragonite – Calcite – Dolomite Mixtures by Powder X-ray Diffraction**

### **Summary**

For a very well-ground sample that consists of calcite with either aragonite or dolomite, or both, powder X-ray diffraction data should be measured in the range 28 to 38°2θ for Co *K*α radiation.

For a binary mixture of calcite and aragonite, the heights of the calcite  $d_{104}$  and aragonite  $d_{111}$  and  $d_{021}$  peaks can be taken from the IDE file produced by JADE 9. The ratio of the calcite peak height to the sum of the calcite and aragonite peak heights –  $I_c/(I_c+I_a)$  – yields the x-variable. The polynomial:  $y = 56.2982x^3 - 1.1170x^2 + 45.2572x$  gives the weight percent calcite of the mixture. The proportion of aragonite can be calculated by difference from 100%.

For a binary mixture of calcite and dolomite, the heights of the calcite  $d_{104}$  and dolomite  $d_{104}$  peaks can be taken from the IDE file produced by JADE 9. The ratio of the calcite peak height to the sum of the calcite and dolomite peak heights –  $I_c/(I_c+I_d)$  – yields the x-variable. The polynomial:  $y = 9.1926x^2 + 90.8447x$  gives the weight percent calcite of the mixture. The proportion of dolomite can be calculated by difference from 100%.

In the case of a ternary mixture of calcite, aragonite, and dolomite, peak height data can be taken from the IDE files generated automatically by JADE 9. The relative weight proportions of calcite and aragonite, and of calcite and dolomite, are determined using the above two polynomial expressions. Using the relative weight fraction of calcite as a common denominator, the final weight fractions of all three carbonate minerals are then determined.

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## **Introduction**

Semi-quantitative phase proportions can be simply determined for mixtures of carbonate minerals by powder X-ray diffraction, as outlined by Davies and Hooper (1962) for calcite and aragonite, and by Royse et al. (1971) for calcite and dolomite. These methods rely on measurement of a few closely spaced X-ray diffraction peaks, and are thus easy to calibrate and implement. The precision and accuracy of the phase proportions determined by these particular peak-height methods are similar to those of whole-pattern fitting methods (i.e., Rietveld refinement: Young 1993; Madsen and Scarlett 2008).

## **Diffraction Peaks**

The diffraction peaks of interest follow, expressed both in angstroms, and in angular position for Co and Cu X-ray tubes. Note that different settings can be used for the various space groups.

Aragonite,  $\text{CaCO}_3$ , space group  $Pm\bar{c}n$  (no. 62, alternative setting of  $Pnma$ ), diffraction peaks:

- $d_{111} = 3.396 \text{ \AA}$ :  $30.57^\circ 2\theta$  for Co  $K\alpha$ ,  $26.24^\circ 2\theta$  for Cu  $K\alpha$ ,
- $d_{021} = 3.273 \text{ \AA}$ :  $31.74^\circ 2\theta$  for Co  $K\alpha$ ,  $27.25^\circ 2\theta$  for Cu  $K\alpha$ .

Calcite,  $\text{CaCO}_3$ , space group  $R\bar{3}c$  (no. 167), diffraction peak:

- hexagonal setting  $d_{104} = 3.036 \text{ \AA}$ :  $34.30^\circ 2\theta$  for Co  $K\alpha$ ,  $29.42^\circ 2\theta$  for Cu  $K\alpha$ ,
- rhombohedral setting  $d_{112} = 3.036 \text{ \AA}$ :  $34.30^\circ 2\theta$  for Co  $K\alpha$ ,  $29.42^\circ 2\theta$  for Cu  $K\alpha$ .

Dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , space group  $R\bar{3}$  (no. 148), diffraction peak:

- hexagonal setting  $d_{104} = 2.885 \text{ \AA}$ :  $36.16^\circ 2\theta$  for Co  $K\alpha$ ,  $31.00^\circ 2\theta$  for Cu  $K\alpha$ ,
- rhombohedral setting  $d_{112} = 2.885 \text{ \AA}$ :  $36.16^\circ 2\theta$  for Co  $K\alpha$ ,  $31.00^\circ 2\theta$  for Cu  $K\alpha$ .

Quartz,  $\text{SiO}_2$ , space group  $P3221$  (no. 154), diffraction peak:

- $d_{011} = 3.343 \text{ \AA}$ :  $31.06^\circ 2\theta$  for Co  $K\alpha$ ,  $26.66^\circ 2\theta$  for Cu  $K\alpha$ .

Note that in the hexagonal setting Miller index 104 is equivalent to Miller-Bravais index 10-14.

Quartz may be used to calibrate the angular position of the diffraction pattern.

## **Calibration of Method**

### **Carbonate Materials**

Aragonite: twinned crystals (trillings) from Minglanilla, Spain.

Calcite: optical quality (Iceland spar) from an unspecified locality, possibly Mexico.

Dolomite: optical quality from the Mount Brussilof mine, British Columbia, Canada.

## **Experimental Methods**

The carbonate materials were crushed separately, wrapped in plastic, with a hand sledgehammer. Between 10 to 20 g of each crushed material was pulverized in a steel ring-and-puck mill for 0.5 min (Spex Shatterbox). Mixtures of carbonate powders were prepared by weight (to the nearest milligram). Each 1.000 g weighed mixture was dry-mixed by shaking in a Spex Mixer/Mill for 5 min. The mixtures were then individually wet-ground for 2.2 minutes in a McCrone Micronizing Mill using a miniaturized tungsten carbide grinding assembly, with 2.5-3.0 mL of ethanol. The resultant powders were dried under a heat lamp.

Each micronized mixture was top-loaded onto a silicon zero-background mount, and the powder X-ray diffraction patterns were obtained as follows: continuous mode,  $0.02^\circ 2\theta$  per step,  $8^\circ 2\theta$  per minute,  $5\text{-}90^\circ 2\theta$ , with a D/teX Ultra silicon strip detector (about 11 minutes acquisition time), 0.5 Hz sample rotation, and Rigaku Ultima IV diffractometer: Bragg-Brentano geometry, 38 kV, 38 mA, Co  $K\alpha$  radiation (6.925425 keV), Fe  $K\beta$  filter, divergent slit  $\frac{2}{3}^\circ$ , height slit 10 mm, open scatter slit, receiving slit 8 mm.

The range  $5\text{-}90^\circ 2\theta$  was measured to enable Rietveld refinement of the phase proportions, for comparative purposes. For peak-fitting purposes, the range  $28\text{-}38^\circ 2\theta$  (assuming Co  $K\alpha$  radiation) is sufficient.

## **Results**

The XRD-based methods of Davies and Hooper (1962) and Royse et al. (1971) rely on measurement of the heights of characteristic peaks in the diffraction patterns. For comparison, the peak heights were determined by two methods in the software program JADE 9 (from MDI):

1. by using the peak heights generated automatically in the \*.IDE file by the JADE 9 software in conjunction with the appropriate mineral entries from the ICDD-PDF,
2. by fitting pseudo-Voigt distributions consisting of  $K\alpha_1$  and  $K\alpha_2$  doublets to each peak.

Tables 1 and 2 list the sample information and peak-height data determined for the calcite-aragonite mixtures from the IDE files and the pseudo-Voigt fitting, respectively. The method of Davies and Hooper (1962) involves the ratio of the main calcite peak to the sum of the two aragonite peaks.

Table 1. Peak heights from IDE files for calcite-aragonite mixtures.

| File   | Sample | aragonite<br>(wt%) | calcite<br>(wt%) | I(111)a | I(021)a | I(104)c | Ic/(Ic+Ia) | Ia/(Ic+Ia) |
|--------|--------|--------------------|------------------|---------|---------|---------|------------|------------|
| X03616 | A3     | 3                  | 97               | 141     | 87      | 11368   | 0.980      | 0.020      |
| X03617 | A5     | 5                  | 95               | 215     | 134     | 13356   | 0.975      | 0.025      |
| X03618 | A10    | 10                 | 90               | 256     | 161     | 8137    | 0.951      | 0.049      |
| X03620 | A50    | 50                 | 50               | 1442    | 735     | 5048    | 0.699      | 0.301      |
| X03621 | A80    | 80                 | 20               | 2204    | 1198    | 1961    | 0.366      | 0.634      |
| X03622 | A90    | 90                 | 10               | 2708    | 1427    | 1139    | 0.216      | 0.784      |
| X03663 | A90    | 90                 | 10               | 1890    | 954     | 751     | 0.209      | 0.791      |
| X03666 | A90    | 90                 | 10               | 3172    | 1651    | 1294    | 0.212      | 0.788      |
| X03623 | A95    | 95                 | 5                | 3041    | 1546    | 625     | 0.120      | 0.880      |
| X03624 | A97    | 97                 | 3                | 2397    | 1270    | 294     | 0.074      | 0.926      |

Table 2. Peak heights from pseudo-Voigt fits for calcite-aragonite mixtures.

| File   | Sample | aragonite<br>(wt%) | calcite<br>(wt%) | I(111)a | I(021)a | I(104)c | Ic/(Ic+Ia) | Ia/(Ic+Ia) |
|--------|--------|--------------------|------------------|---------|---------|---------|------------|------------|
| X03616 | A3     | 3                  | 97               | 113     | 62      | 8402    | 0.980      | 0.020      |
| X03617 | A5     | 5                  | 95               | 178     | 81      | 10270   | 0.975      | 0.025      |
| X03618 | A10    | 10                 | 90               | 196     | 90      | 5738    | 0.953      | 0.047      |
| X03620 | A50    | 50                 | 50               | 1158    | 631     | 3656    | 0.671      | 0.329      |
| X03621 | A80    | 80                 | 20               | 1732    | 849     | 1431    | 0.357      | 0.643      |
| X03622 | A90    | 90                 | 10               | 2079    | 1108    | 776     | 0.196      | 0.804      |
| X03663 | A90    | 90                 | 10               | 1410    | 733     | 525     | 0.197      | 0.803      |
| X03666 | A90    | 90                 | 10               | 2436    | 1295    | 916     | 0.197      | 0.803      |
| X03623 | A95    | 95                 | 5                | 2275    | 1189    | 443     | 0.113      | 0.887      |
| X03624 | A97    | 97                 | 3                | 1792    | 937     | 204     | 0.070      | 0.930      |

I = peak intensity, a = aragonite, c = calcite.

Tables 3 and 4 list the sample information and peak-height data determined for the calcite-dolomite mixtures from the IDE files and the pseudo-Voigt fitting, respectively. The method of Royse et al. (1971) involves the intensity (height) ratio of the main calcite peak to the main dolomite peak.

Table 3. Peak heights from IDE files for calcite-dolomite mixtures.

| File   | Sample | dolomite<br>(wt%) | calcite<br>(wt%) | I(104)d | I(104)c | Ic/(Ic+Id) | Id/(Ic+Id) |
|--------|--------|-------------------|------------------|---------|---------|------------|------------|
| X03626 | D5     | 5                 | 95               | 649     | 13713   | 0.955      | 0.045      |
| X03627 | D10    | 10                | 90               | 1009    | 9767    | 0.906      | 0.094      |
| X03628 | D20    | 20                | 80               | 1857    | 8057    | 0.813      | 0.187      |
| X03629 | D50    | 50                | 50               | 6844    | 7552    | 0.525      | 0.475      |
| X03630 | D80    | 80                | 20               | 10048   | 2739    | 0.214      | 0.786      |
| X03662 | D80    | 80                | 20               | 9731    | 2650    | 0.214      | 0.786      |
| X03665 | D80    | 80                | 20               | 10807   | 3019    | 0.218      | 0.782      |
| X03631 | D90    | 90                | 10               | 11958   | 1354    | 0.102      | 0.898      |
| X03632 | D95    | 95                | 5                | 14368   | 805     | 0.053      | 0.947      |
| X03633 | D97    | 97                | 3                | 17513   | 647     | 0.036      | 0.964      |
| X03664 | D97    | 97                | 3                | 18089   | 709     | 0.038      | 0.962      |
| X03667 | D97    | 97                | 3                | 17823   | 682     | 0.037      | 0.963      |

Table 4. Peak heights from pseudo-Voigt fits for calcite-dolomite mixtures.

| File   | Sample | dolomite<br>(wt%) | calcite<br>(wt%) | I(104)d | I(104)c | Ic/(Ic+Id) | Id/(Ic+Id) |
|--------|--------|-------------------|------------------|---------|---------|------------|------------|
| X03626 | D5     | 5                 | 95               | 497     | 10320   | 0.954      | 0.046      |
| X03627 | D10    | 10                | 90               | 707     | 6874    | 0.907      | 0.093      |
| X03619 | D20    | 20                | 80               | 2536    | 10689   | 0.808      | 0.192      |
| X03628 | D20    | 20                | 80               | 1338    | 5837    | 0.814      | 0.186      |
| X03629 | D50    | 50                | 50               | 5199    | 5645    | 0.521      | 0.479      |
| X03630 | D80    | 80                | 20               | 7254    | 2009    | 0.217      | 0.783      |
| X03662 | D80    | 80                | 20               | 6911    | 1929    | 0.218      | 0.782      |
| X03665 | D80    | 80                | 20               | 7760    | 2139    | 0.216      | 0.784      |
| X03631 | D90    | 90                | 10               | 8540    | 978     | 0.103      | 0.897      |
| X03632 | D95    | 95                | 5                | 10075   | 550     | 0.052      | 0.948      |
| X03633 | D97    | 97                | 3                | 12410   | 404     | 0.032      | 0.968      |
| X03664 | D97    | 97                | 3                | 13230   | 436     | 0.032      | 0.968      |
| X03667 | D97    | 97                | 3                | 12816   | 419     | 0.032      | 0.968      |

I = peak intensity, c = calcite, d = dolomite.

### Polynomial Relationships

For the calcite-aragonite mixtures, third-order polynomial expressions (constrained to pass through the origin) were derived to relate the proportion by weight of calcite or aragonite to the ratios of their principal diffraction peaks. The peak-height data from the IDE files and from the pseudo-Voigt fitting yielded separate polynomial expressions whose results differ by an absolute maximum of 1 wt%, and thus only the IDE expressions are presented here (Figures 1 and 2), as these are much faster to obtain. The analogous polynomial expressions based on pseudo-Voigt fitting are not presented in this report.

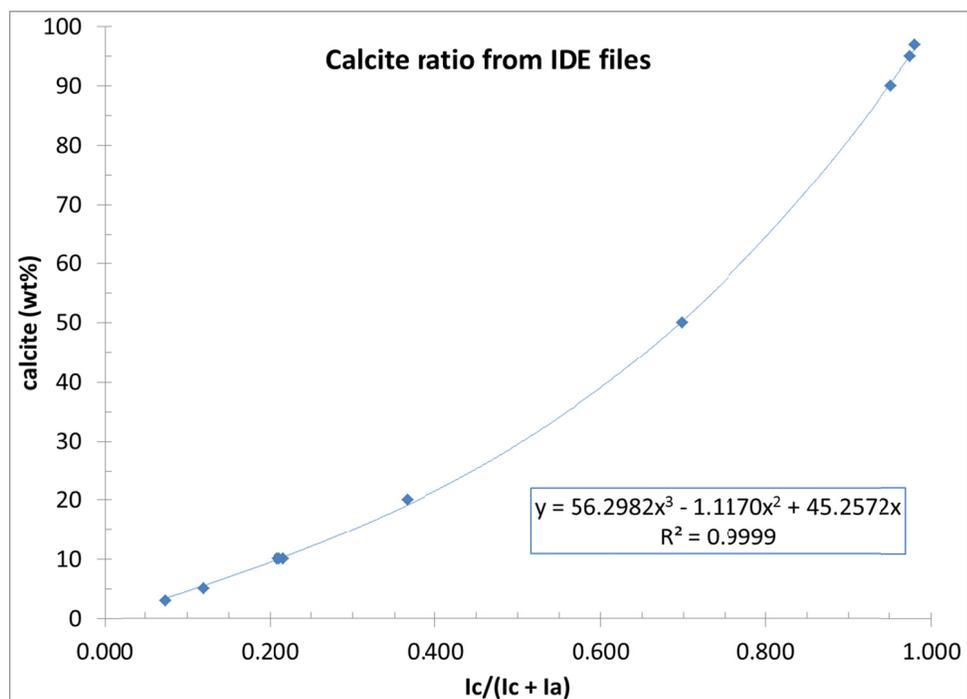


Figure 1. The relationship between the XRD peak intensity ratio ( $I_c/I_c+I_a$ ) to the weight fraction of calcite in the calcite-aragonite mixtures listed in Table 1.

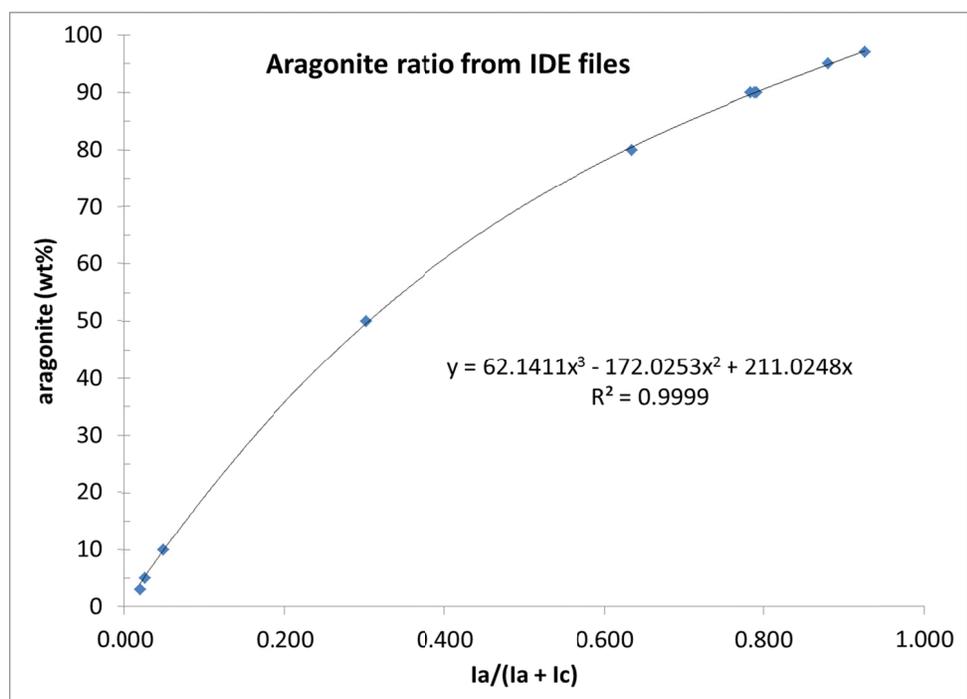


Figure 2. The relationship between the XRD peak intensity ratio ( $I_a/I_a+I_c$ ) to the weight fraction of aragonite in the calcite-aragonite mixtures listed in Table 1.

For the calcite-dolomite mixtures, second-order polynomial expressions (constrained to pass through the origin) were derived to relate the proportion by weight of calcite or dolomite to the ratios of their principal diffraction peaks. The peak-height data from the IDE files and from the pseudo-Voigt fitting yielded polynomial expressions whose results differ by an absolute maximum of 0.5 wt%, and thus the IDE expressions are presented here for simplicity (Figures 3 and 4). The analogous polynomial expressions based on pseudo-Voigt fitting are not presented in this report.

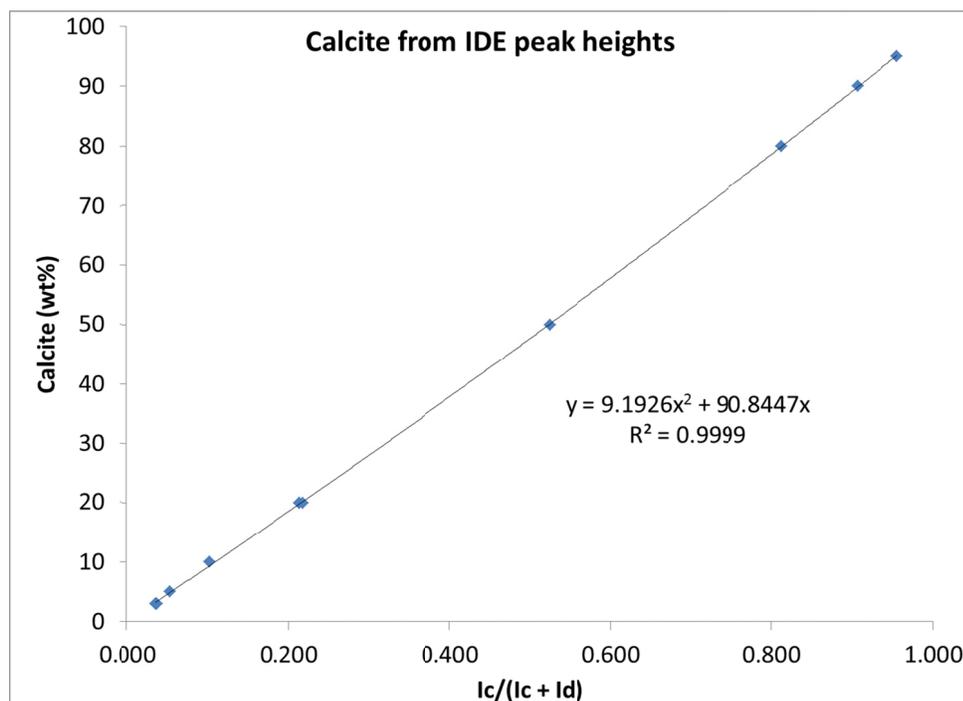


Figure 3. The relationship between the XRD peak intensity ratio ( $I_c/I_{c+Id}$ ) to the weight fraction of calcite in the calcite-dolomite mixtures listed in Table 3.

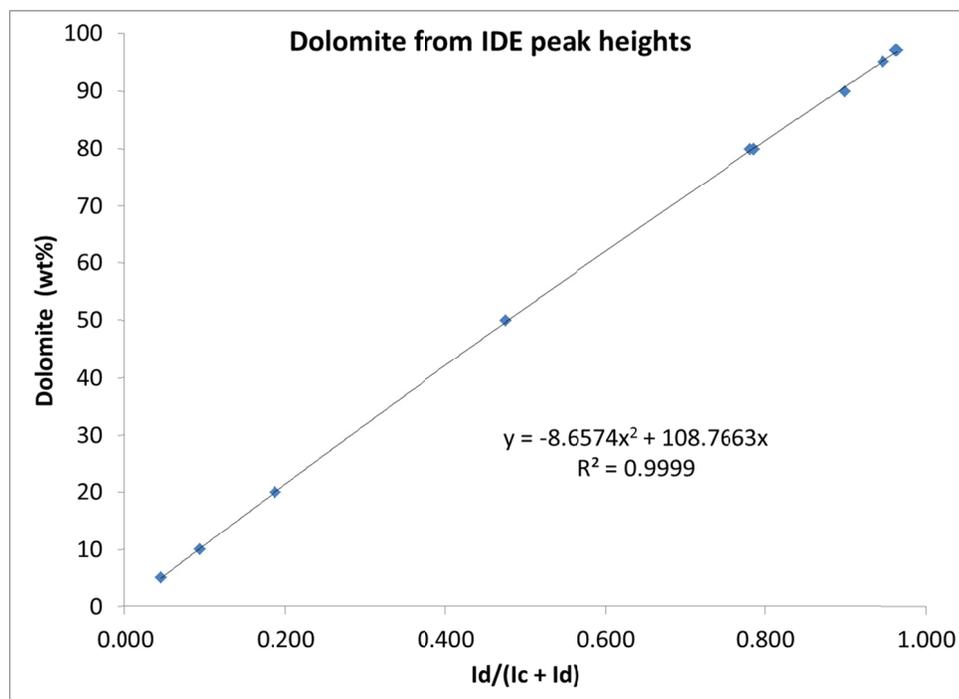


Figure 4. The relationship between the XRD peak intensity ratio ( $I_d/I_c+I_d$ ) to the weight fraction of dolomite in the calcite-dolomite mixtures listed in Table 3.

The polynomial expressions recommended for general use are those shown in Figures 1 and 3, which involve determination of the proportion of calcite in calcite-aragonite, and calcite-dolomite mixtures, respectively. In each case, the proportion of the other phase can be calculated by difference.

### Precision and Accuracy

Use of the IDE data and the pseudo-Voigt fitting for the same data files permits an estimate of uncertainty due to data processing. Such an estimate must be presented in the form of the uncertainty of the intensity ratio, as this is the quantity derived directly from the measurement. Each intensity ratio varies from 0 to 1. In the calcite-aragonite mixtures, the range in differences in the  $I_c/(I_c+I_a)$  ratios between the IDE data and the pseudo-Voigt fits is -0.002 to 0.028 with an average of 0.009 (Tables 1 and 2). In the calcite-dolomite mixtures, the range in differences in the  $I_c/(I_c+I_d)$  ratios between the IDE data and the pseudo-Voigt fits is -0.006 to 0.004 with an average of -0.001 (Tables 3 and 4).

In addition, triplicate samples permit an estimate of uncertainty due to sample measurement. For the IDE data obtained for the calcite-aragonite mixtures, the range of values in the  $I_c/(I_c+I_a)$  ratio for triplicate samples is 0.007, whereas for the pseudo-Voigt fits the corresponding range is 0.001 (Tables 1 and 2). For the IDE data obtained for the calcite-dolomite mixtures, the range of values in the  $I_c/(I_c+I_d)$  ratios of several sets of duplicate and triplicate samples is 0.000 to 0.006 with an average of 0.003. In contrast, the corresponding range for the pseudo-Voigt fits is 0.002 to 0.004 with an average of 0.003 (Tables 3 and 4). The ensuing portion of this report concentrates on the IDE results, as these are rapid and simple to obtain.

The polynomial expressions shown in Figures 1-4 based on the IDE data listed in Tables 1 and 3 can be used to calculate weight proportions of the carbonate minerals for each measured sample: Table 5. The differences between the original weighed proportions, and those calculated from the polynomial expressions can be taken as estimates of the inaccuracy of these expressions. The resultant estimate of inaccuracy shown by the differences in wt% data (Table 5) subsumes the imprecision in the intensity ratios (discussed above) that are due to data processing and sample measurement.

Table 5. Comparison of weighed and calculated carbonate contents.

| File   | Sample | weighed            | weighed          | IDE ratio       | IDE ratio         | aragonite  | calcite   |
|--------|--------|--------------------|------------------|-----------------|-------------------|--|---|
|        |        | aragonite<br>(wt%) | calcite<br>(wt%) | $I_a/(I_c+I_a)$ | $I_c/(I_c + I_a)$ | calculated (wt%)<br>$y = 62.1411x^3 - 172.0253x^2 + 211.0248x$ | calculated (wt%)<br>$y = 56.2982x^3 - 1.1170x^2 + 45.2572x$ |
| X03616 | A3     | 3                  | 97               | 0.020           | 0.980             | 4.1  | 96.3  |
| X03617 | A5     | 5                  | 95               | 0.025           | 0.975             | 5.3  | 95.1  |
| X03618 | A10    | 10                 | 90               | 0.049           | 0.951             | 9.9  | 90.5  |
| X03620 | A50    | 50                 | 50               | 0.301           | 0.699             | 49.7   | 50.3  |
| X03621 | A80    | 80                 | 20               | 0.634           | 0.366             | 80.5   | 19.2  |
| X03622 | A90    | 90                 | 10               | 0.784           | 0.216             | 89.7   | 10.3  |
| X03663 | A90    | 90                 | 10               | 0.791           | 0.209             | 90.0   | 9.9   |
| X03666 | A90    | 90                 | 10               | 0.788           | 0.212             | 89.9   | 10.1  |
| X03623 | A95    | 95                 | 5                | 0.880           | 0.120             | 94.8   | 5.5   |
| X03624 | A97    | 97                 | 3                | 0.926           | 0.074             | 97.2   | 3.4   |

| File   | Sample | weighed           | weighed          | IDE ratio    | IDE ratio    | dolomite   | calcite  |
|--------|--------|-------------------|------------------|--------------|--------------|--|--|
|        |        | dolomite<br>(wt%) | calcite<br>(wt%) | Id/(Ic + Id) | Ic/(Ic + Id) | calculated (wt%)<br>$y = -8.6574x^2 + 108.7663x$ | calculated (wt%)<br>$y = 9.1926x^2 + 90.8447x$ |
| X03626 | D5     | 5                 | 95               | 0.045        | 0.955        | 4.9  | 95.1   |
| X03627 | D10    | 10                | 90               | 0.094        | 0.906        | 10.1   | 89.9   |
| X03628 | D20    | 20                | 80               | 0.187        | 0.813        | 20.1   | 79.9   |
| X03629 | D50    | 50                | 50               | 0.475        | 0.525        | 49.8   | 50.2   |
| X03630 | D80    | 80                | 20               | 0.786        | 0.214        | 80.1   | 19.9   |
| X03662 | D80    | 80                | 20               | 0.786        | 0.214        | 80.1   | 19.9   |
| X03665 | D80    | 80                | 20               | 0.782        | 0.218        | 79.7   | 20.3   |
| X03631 | D90    | 90                | 10               | 0.898        | 0.102        | 90.7   | 9.3  |
| X03632 | D95    | 95                | 5                | 0.947        | 0.053        | 95.2   | 4.8  |
| X03633 | D97    | 97                | 3                | 0.964        | 0.036        | 96.8   | 3.2  |
| X03664 | D97    | 97                | 3                | 0.962        | 0.038        | 96.6   | 3.4  |
| X03667 | D97    | 97                | 3                | 0.963        | 0.037        | 96.7   | 3.4  |

For the calcite-aragonite mixtures, the range of differences between the weighed values and those calculated based on the IDE data (Figures 1 and 2) are -1.1 to 0.8 wt% with an average absolute difference of 0.35 wt% (the polynomials derived from the pseudo-Voigt fits give similar values, but are not presented here).

For the calcite-dolomite mixtures, the range of differences between the weighed values and those calculated based on the IDE data (Figures 3 and 4) are -0.7 to 0.7 wt% with an average absolute difference of 0.22 wt% (the polynomials derived from the pseudo-Voigt fits give similar values, but are not presented here).

Although the average absolute uncertainties are relatively small, the ranges are considerably larger. Therefore, it is recommended that the user be conservative in estimating the analytical precision and accuracy for results derived from the polynomial expressions given here, and use +/- 1 wt% for both.

### Comparison to Rietveld Refinement

Rietveld refinement of the powder X-ray diffraction patterns obtained for the samples listed in Tables 1-4 was undertaken with the use of the freeware program GSAS (Larson and Von Dreele 2000). For the calcite-aragonite mixtures, the differences between the weighed values and those determined by Rietveld refinement range from -1.8 to 1.8 wt% with an average absolute

difference of 1.4 wt%. For the calcite-dolomite mixtures, the differences between the weighed values and those determined by the mathematically demanding and time-consuming Rietveld refinements range from 0.4 to 3.5 wt% with an average absolute difference of 1.6 wt%. This level of agreement is typical of semi-quantitative phase analysis by Rietveld refinement of laboratory X-ray data (Madsen and Scarlett 2008), and is an order of magnitude larger than the statistical uncertainty reported by the Rietveld refinement program GSAS.

For simple binary mixtures of carbonate minerals, both the simple peak-ratio methods, and the computationally more sophisticated Rietveld method give results that are similar in their level of agreement with the weighed values.

### **Ternary Mixtures**

Davies and Hooper (1962), and Royse et al. (1971) proposed peak ratio methods to determine the proportions of binary carbonate mixtures from powder XRD data. For a ternary mixture of aragonite, calcite, and dolomite, it is possible to determine their relative weight fractions by combining the use of the polynomial expressions determined in Figures 1 and 3.

Table 6 lists three ternary mixtures of aragonite, calcite, and dolomite. Peak height data were taken from the IDE files automatically generated by the JADE 9 software. The relative weight proportions of calcite and aragonite were determined using the polynomial expression from Figure 1, and an aragonite/calcite ratio calculated from these wt% results. The relative weight proportions of calcite and dolomite were determined using the polynomial expression from Figure 3, and a dolomite/calcite ratio calculated from these wt% results.

For a given ternary mixture of calcite, aragonite, dolomite, the actual calcite content is a constant, and thus can be used as a common denominator, despite the use of different polynomial expressions. The relative weight proportions of each carbonate mineral are ratioed to that of calcite, and the three resulting ratios (aragonite/calcite, calcite/calcite = 1, and dolomite/calcite) are summed. The final weight proportions of each carbonate mineral are determined by dividing each ratio by that sum (Table 6).

For the ternary mixtures listed in Table 6, the differences between the weighed values and those determined from the combination of IDE polynomial expressions range from -0.9 to 1.4 wt%, with an average absolute difference of 0.7 wt%. In comparison, Rietveld refinements (using GSAS) of the same data have a range of differences from -2.5 to 1.8 wt%, with an absolute average difference of 1.5 wt%. The results from both techniques (simple peak-height relationships and numerically-intensive Rietveld refinements) are in good agreement.

Table 6. Data for ternary carbonate mixtures.

| Sample                          | M1     | M2     | M3     |
|---------------------------------|--------|--------|--------|
| File                            | X03634 | X03635 | X03636 |
| aragonite wt%                   | 40.0   | 16.0   | 21.0   |
| calcite wt%                     | 36.0   | 15.0   | 68.0   |
| dolomite wt%                    | 24.0   | 69.0   | 11.0   |
| IDE data                        |        |        |        |
| I(111)a                         | 1414   | 815    | 758    |
| I(021)a                         | 713    | 344    | 376    |
| I(104)c                         | 4337   | 2543   | 7556   |
| I(104)d                         | 2552   | 9896   | 1087   |
| Ic/(Ic + Ia)                    | 0.6709 | 0.6869 | 0.8695 |
| calcite wt% (Fig. 1 polynomial) | 46.9   | 48.8   | 75.5   |
| aragonite wt% (by difference)   | 53.1   | 51.2   | 24.5   |
| Ic/(Ic + Id)                    | 0.6296 | 0.2044 | 0.8742 |
| calcite wt% (Fig. 3 polynomial) | 60.8   | 19.0   | 86.4   |
| dolomite wt% (by difference)    | 39.2   | 81.0   | 13.6   |
| aragonite/calcite (wt%/wt%)     | 1.1337 | 1.0488 | 0.3242 |
| calcite/calcite (wt%/wt%)       | 1.0000 | 1.0000 | 1.0000 |
| dolomite/calcite (wt%/wt%)      | 0.6438 | 4.2753 | 0.1568 |
| sum of wt% ratios               | 2.7775 | 6.3241 | 1.4810 |
| final Aragonite (wt%)           | 40.8   | 16.6   | 21.9   |
| final Calcite (wt%)             | 36.0   | 15.8   | 67.5   |
| final Dolomite (wt%)            | 23.2   | 67.6   | 10.6   |
| GSAS Rietveld refinement data   |        |        |        |
| aragonite (wt%)                 | 38.2   | 14.7   | 21.7   |
| calcite (wt%)                   | 35.3   | 13.9   | 66.3   |
| dolomite (wt%)                  | 26.5   | 71.4   | 12.0   |

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## Addendum

### Calculations in the presence of two compositions of calcite.

The in-house report “Recommended Method for Semi-quantitative Measurement of Aragonite – Calcite – Dolomite Mixtures by Powder X-ray Diffraction” dating from February 8, 2012 does not consider the case in which two populations of calcite compositions are present.

The following discussion assumes solid solution of only Mg for Ca in the calcite structure. Substitution of Mg for Ca in calcite leads to changes in the volume of the unit cell and molar mass, with consequent changes in the  $d$ -spacing of an X-ray reflections (and therefore the Lorentz-polarization correction, and to a lesser extent the Debye-Waller factor), the structure factor of that reflection, and also the bulk density.

The combination of these factors leads to a reduction in intensity for the  $d_{104}$  reflection for Mg-bearing calcite in comparison to end-member calcite. For data from a powder diffractometer, intensity is proportional to the square of the structure factor amplitude, absorption, the Lorentz-polarization factor and the Debye-Waller factor (aka temperature factor), as follows:

$$I = |F|^2 P \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M} \quad \text{where } F \text{ is the structure factor: } F_{hkl} = \sum_1^J f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$

In the presence of 2 compositions of calcite, it may be possible to add their intensities together to treat them as a single variable. The intensity of the Mg-bearing calcite will have to be corrected prior to use. After determination of “total calcite”, the proportions of the two populations of calcite can be estimated by comparison of their *corrected* relative intensities.

Unit cell and compositional data were taken from the following references: Althoff (1977) – ICSD 10405; Effenberger et al., (1981); Paquette & Reeder (1990) – ICSD 40108 and 40109; Maslen et al., (1995) – ICSD 80869; and Falini et al., (1998) – ICSD 86161. The data of Althoff (1977) proved inconsistent with the other four references, and were not included in the regression analysis. Where necessary, calculations used  $\text{Co } K\alpha = 1.78899 \text{ \AA}$ .

The data for calcite and Mg-bearing calcite from these references were entered into the Windows program PowderCell v2.4 (Kraus & Nolze, 1996), and the position of the 104 *d*-spacing tabulated (hexagonal setting of the unit cell), along with its structure factor amplitude  $|F_{104}|$  and density. Figure 1 shows the variation of the  $d_{104}$  reflection as a function of Mg-content.

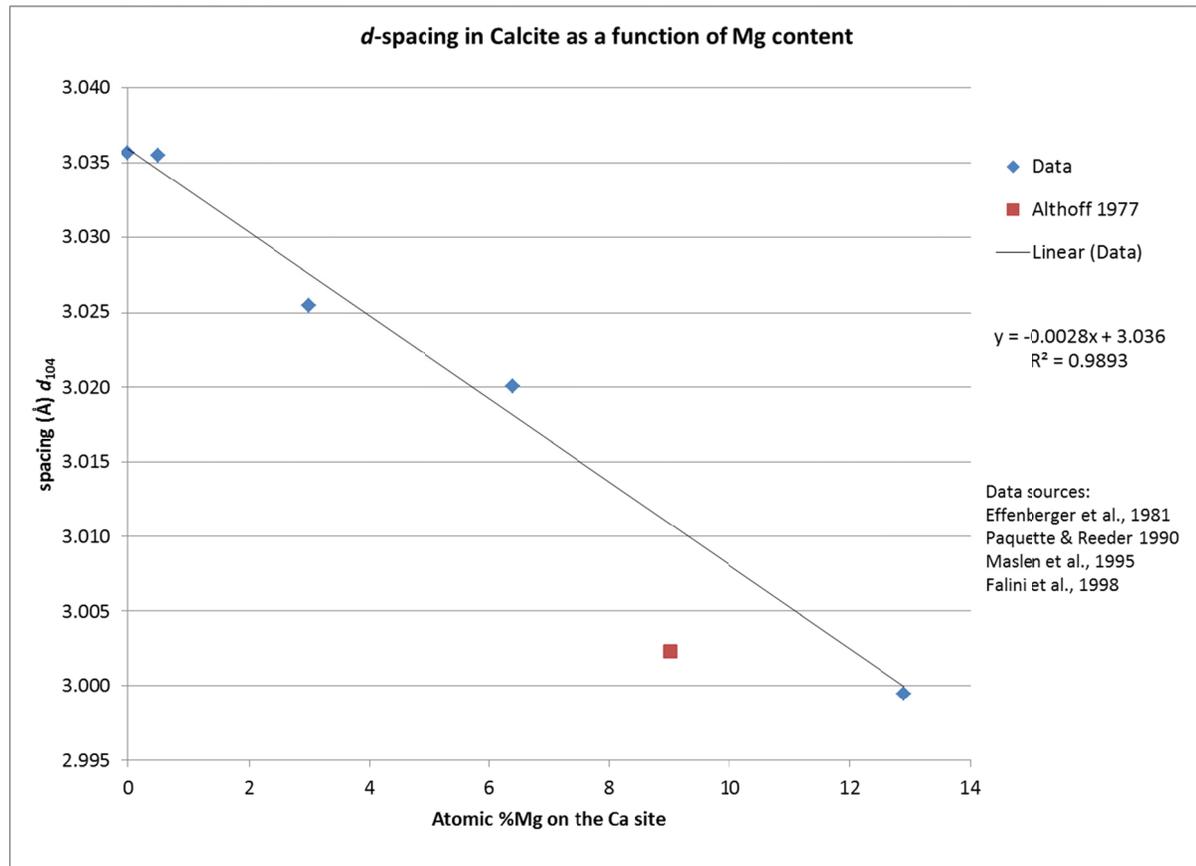


Figure 1. The relationship between composition and *d*-spacing for the 104 reflection of calcite.

Neglecting the data of Althoff (1977), the linear function  $y = -0.0028x + 3.036$  has a very high correlation coefficient ( $R^2 = 0.9893$ ); the implication is that the *d*-spacing is a simple linear function of the composition, and that the latter could be estimated from measurement of the former.

Similarly, the structure factor amplitudes calculated with PowderCell for data just from the four references shows a very linear correlation with composition (Figure 2):  $y = -0.4313x + 151.65$ ,  $R^2 = 0.999$ .

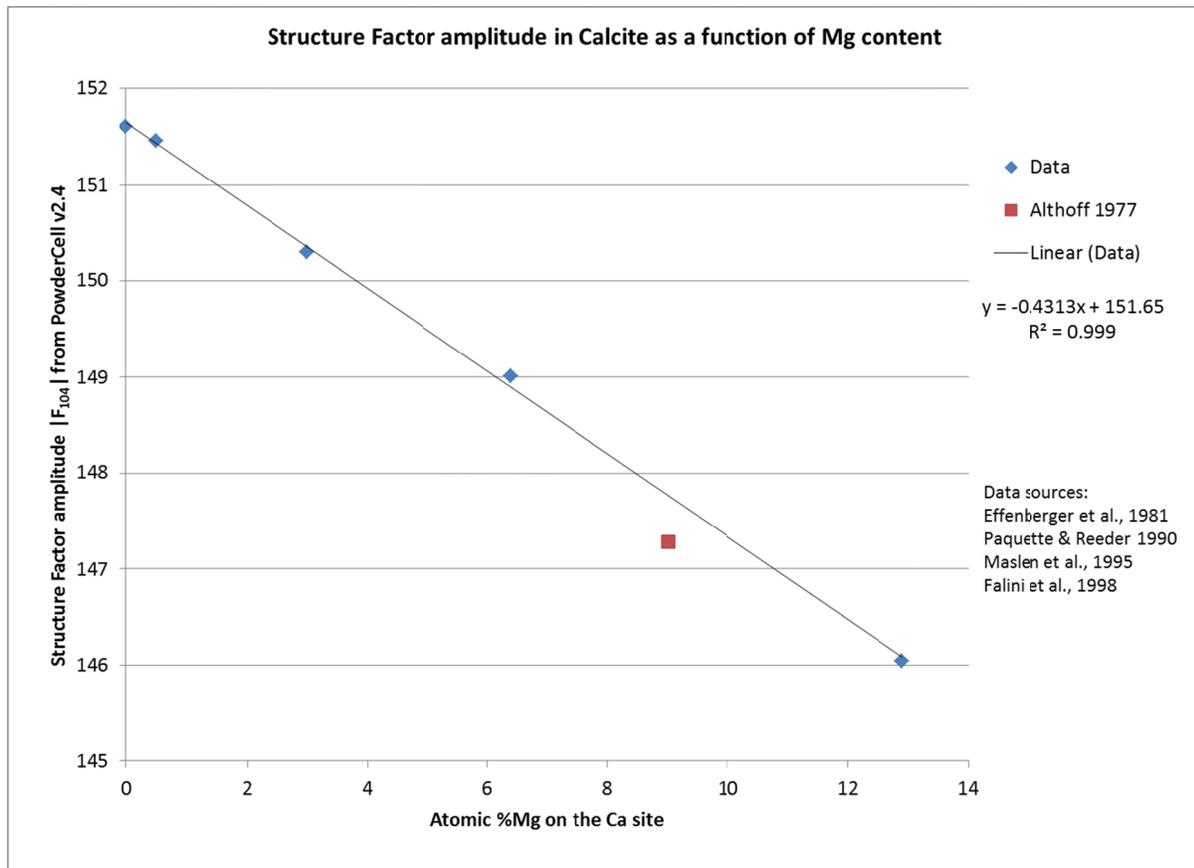


Figure 2. The relationship between composition and structure factor amplitude for the 104 reflection of calcite.

Of the various factors that affect diffracted intensity of a reflection in data derived from a flat-plate powder diffractometer, only multiplicity remains the same between calcite and magnesian calcite. Along with the structure factor data from PowderCell, corrections for Lorentz-polarization, change in absorption (based on change in density), and the Debye-Waller factor were calculated for the  $d_{104}$  reflection of the calcite compositions shown in Figures 1 & 2. The change in intensity of this reflection was tabulated relative to the end-member calcite of Maslen et al. (1995), and a correction factor calculated, as shown in Figure 3. The relationship between  $d$ -spacing ( $x$ ) and the intensity correction factor ( $y$ ) is modelled by a linear regression with  $y = -2.5687x + 8.7980$ , and  $R^2 = 0.9940$ .

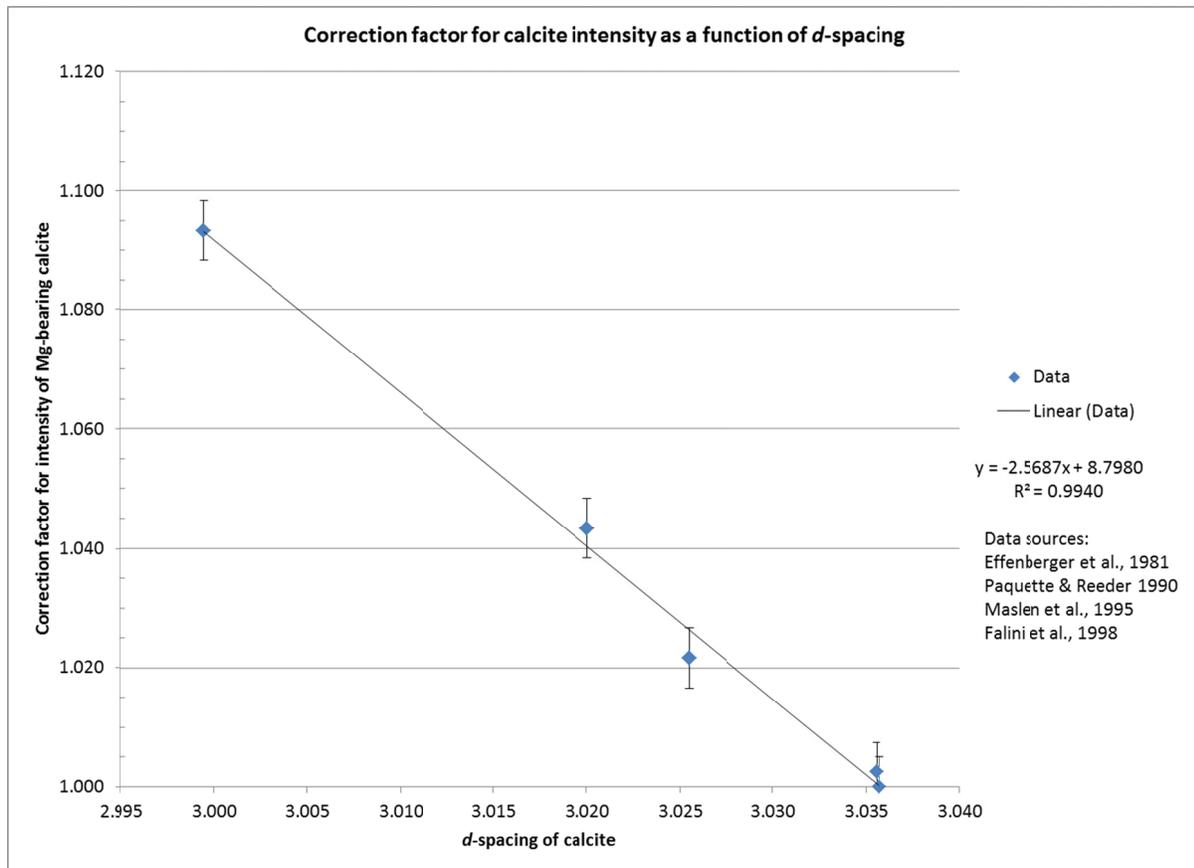


Figure 3. The relationship between the  $d_{104}$  reflection of calcite and the calculated correction factor for observed intensities. Error bars for intensity are estimated at 0.5%.

Example: X11685 consists of two populations of calcite along with aragonite and some halite. From the \*.IDE file generated by MDI-JADE software, the  $d_{104}$ -spacing of the 1<sup>st</sup> calcite is at 3.0293 Å with a height of 1796, the  $d_{104}$ -spacing of the 2<sup>nd</sup> calcite is at 2.9941 Å with a height of 7304. To compare these calcite measurements on a uniform basis, their intensities should both be corrected with respect to end-member calcite. Thus, the correction factor for the intensity of the 1<sup>st</sup> calcite is 1.0166, and its corrected intensity is 1826. The correction factor for the 2<sup>nd</sup> calcite is 1.10706, and its corrected intensity is 8086.

In file X11685, the heights of the aragonite  $d_{111}$  and  $d_{021}$  peaks are 6898 and 3757, respectively. The ratio of the total corrected intensity for calcite  $d_{104}$  peak height to the sum of the calcite and aragonite peak heights,  $I_c/(I_c+I_a)$  is:  $(1826+8086)/(1826+8086+6898+3757) = 0.4819$ . The polynomial:  $y = 56.2982x^3 - 1.1170x^2 + 45.2572x$  gives the weight percent calcite,

in the aragonite – calcite mixture. Thus, of the carbonates present, total calcite is 27.9 wt%, and aragonite is 72.1 wt%.

The calcite fraction can be split back into the 2 populations based on their relative corrected intensities. The 1<sup>st</sup> calcite has corrected intensity of 1826, and total corrected intensity for calcite is 9912 (from 1826+8086). The 1<sup>st</sup> calcite therefore makes up 18.4% of total calcite; this is 5.1 wt% of the total carbonate present. The 2<sup>nd</sup> calcite therefore makes up 22.8 wt% of the total carbonate present, and aragonite remains at 72.1 wt%. Although these abundances are presented here to the nearest 0.1 wt%, in the absence of independent tests, the uncertainties are estimated to be greater by at least an order of magnitude.

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