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MEASUREMENT OF SMALL CHANGES IN LATTICE SPACING APPLIED TO CALCITES OF A PENNSYLVANIAN AGE LIMESTONE

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ABSTRACT

The shift in position of an *x*-ray diffraction peak is measured by changes in the ratio of the integrated intensities of portions of the peak on each side of its center for standardized angular intervals. The observed ratios can be converted into changes in lattice spacing. An example is given where these changes in spacing have been used for determination of the amount of Mg^{2+} substitution in calcites of a Pennsylvanian Age limestone.

INTRODUCTION

The position of the (211) reflection from calcite has been observed to change due to the presence of Mg^{2+} and other substitutions in the lattice, particularly Fe^{2+} and Mn^{2+} (Chave, 1952; Goldsmith, *et al.*, 1955, 1958). The Mg^{2+} in place of Ca^{2+} in the calcite lattice makes the unit cell smaller, this change in size producing a shift in position of the diffraction maximum or peak. Since the amount of substitution observed in most natural calcites is small (Chave, 1954), the magnitude of the shift of the calcite peak is very small. The technique described in this paper allows rapid measurement of small changes in the position of a diffraction peak. The observed shifts in the diffraction peak from the position for pure calcite may be used to determine the amount of Mg^{2+} (or corresponding amount where Fe^{2+} and Mn^{2+} are present) substituted for Ca^{2+} in the calcite lattice from data published by Chave (1952) and by Goldsmith, *et al.* (1955, 1958). Other Mg^{2+}-bearing minerals such as dolomite and magnesite do not interfere with this determination. Application has been made to the calcites of a group of Pennsylvanian age core samples.

TECHNIQUE

The position of the calcite (211) reflection with respect to (111) reflection from CdO added as a standard was determined from diffracted intensities integrated over each 0.2° (2θ) angle at a scanning rate of 0.2° in 40 seconds and recorded in the angular region from 24° to 36° (2θ). Small shifts in the position of the calcite peak must be measured relative to some standard peak because experimental factors, such as the position of the sample surface with respect to the *x*-ray beam, are practically impossible to keep constant to a hundredth of a degree. The starting position of the spectrometer can be chosen such that the integrating intervals incorporating the standard peak would appear as shown in Fig. 1 in which A, B, and C represent the integrated intensity recorded for each of these 0.2° (2θ) intervals minus the average background intensity for a corresponding angular and time interval. Experimentally, peaks such as these from well crystallized materials have a breadth of 0.2° (2θ) at half maximum intensity when a 0.2° scanning slit is used for the counter. Although these peaks are composed of the unresolved reflections from Cu $K\alpha_1$ and $K\alpha_2$ *x*-rays, the peak from the (211) reflection of calcite has little asymmetry and the same shape as the peak from the (111) CdO reflection and is separated from it by about 3.6° (2θ). The position of the center of either one of these peaks can be expressed in terms of the ratio of A to B. The position of the (111) CdO standard reflection is related to $R_1 = A_{111}/B_{111}$ and the position of the (211) calcite reflection is related to $R_2 = A_{211}/B_{211}$. The position of the (211) calcite reflection relative to the (111) CdO reflection is then a function of R_2 and R_1. As anticipated, the ratios R_1 and R_2 are sensitive to small changes in the relative position of the peaks. Choosing the starting position as shown so that A = B for the standard peak, $R_1 = 1.00$, the values of R_2 show the changes in position of the (211) calcite reflection. In the special case where $R_2 = 1.00$, the two peaks are separated by an integral multiple of 0.2° (2θ). In practice, it was impossible to keep $R_1 = 1.00$, so the observed values of R_1 and R_2 were used to determine the ratio R_2/R_1. This ratio was shown to be as valid a measure of the changes in the (211) calcite reflection as R_2 in the following manner.

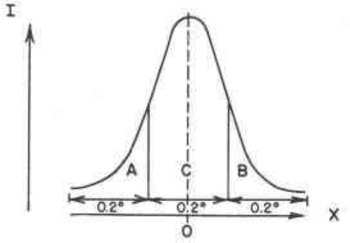

FIG. 1. Integrating intervals chosen for (111) CdO standard peak.

The intensity distribution of an *x*-ray reflection can be expressed in the form of a Gaussian error curve, the intensity at any position x being $n_0(x) = A_0 e^{-\sigma_0^2 x^2}$. From observed line profiles, that is, experimental diffracted intensity curves, σ_0 was found to have a constant value of 8.0 for the part of the intensity curve represented by A and B. With the aid of a digital computer, numerical integrations of the portions of the Gaussian curve represented by A and B in the figure above were made to correct observed values of R_1 to 1.00 and give corresponding corrected values for R_2. The values of $R_2/R_1 = R_2$ obtained from the corrected data showed only small deviations in the fourth figure from the observed

R_2/R_1 ratios for more than a hundred cases. Since the data are given to only three significant figures, the observed values of R_1 and R_2 may be used to determine R_2/R_1. The agreement of observed and corrected ratios also shows that the effect of any asymmetry of the diffraction peaks is negligible.

At the same time the R_2/R_1 values were computed, the angular difference between the center of the (211) calcite reflection and the (111) CdO reflection was calculated by the computer. These data were used to obtain the curve (Fig. 2) showing the relation between R_2/R_1 and the change in the d_{211} spacing of the calcite in each sample from $d_{211} = 3.036$ Å spacing for pure calcite. The amount of Mg^{2+} substitution for Ca^{2+} represented by these changes in spacing was determined from the published data of Goldsmith *et al.* (1955).

APPLICATION

An example of the kind of analysis that can be made using this technique is given below. Samples of a Pennsylvanian age limestone mass were taken from two experimental Core Holes, I and II, Wise County, Texas. The cores of Core Hole I were sampled at 4-foot intervals over 228 feet and the limestone portion of the cores of Core Hole II was sampled at 2-foot intervals over 263 feet. Each sample was crushed and then ground to pass a 400-mesh sieve. Then ten per cent CdO standard was added to each sample. These components were placed in a 2-ml vial with two 5-mm glass beads, mixed for one minute by a Wig-L-Bug, then emptied. The composite sample was placed in the vial without the glass beads and mixed another minute by the Wig-L-Bug. Each sample was then loaded into a rotating sample holder (Waite, 1963) for the GE XRD-3D Spectrogoniometer and irradiated with CuKα *x*-rays. The integrated intensities were measured by means of a Berkeley Type 2200-2 Scaler and recorded using their Model 1452 Digital Recorder. The total integrated intensities of the principal *x*-ray diffraction peaks of calcite, dolomite, quartz and other minerals present referred to those of the standard CdO peaks were used to obtain a quantitative measure of the amount of these minerals present in the sample.

The results of these analyses are illustrated by Figs. 3 and 4. The largest amount of Mg^{2+} substituted for Ca^{2+} in the calcite lattice is represented by the smallest R_2/R_1 ratio. The maximum amount of Mg^{2+} (and/or Fe^{2+} and Mn^{2+}) in these calcites expressed as $MgCO_3$ is 2 mol per cent as determined from the smallest R_2/R_1 ratio, the curve of Fig. 2 and data from Table 5, p. 93, of Goldsmith and Graf (1958). This amount of Mg^{2+} is within the limits found by Chave (1954), who gives the amount of $MgCO_3$ in the calcites of all pre-Tertiary sediments as less than 4 mol per cent.

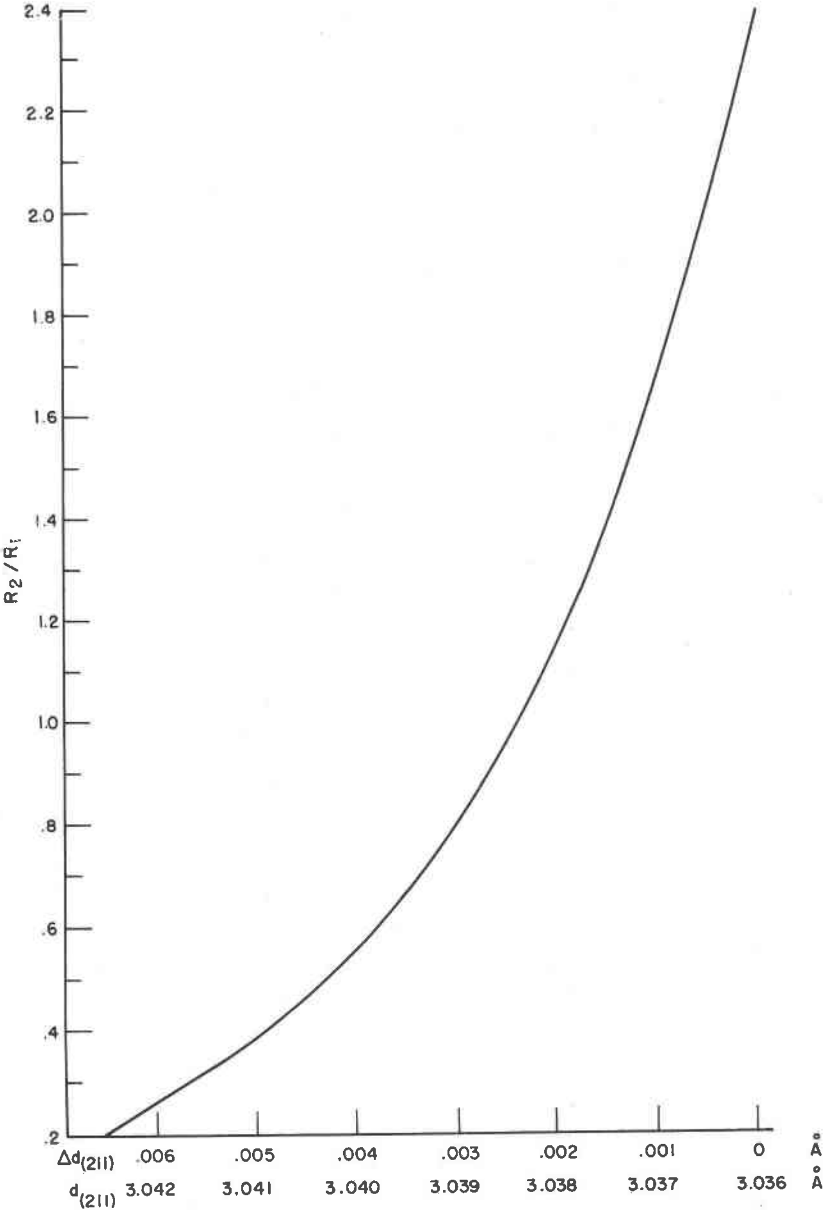

FIG. 2. R_2/R_1 from measured integrated intensities versus change of d_{211} calcite spacing.

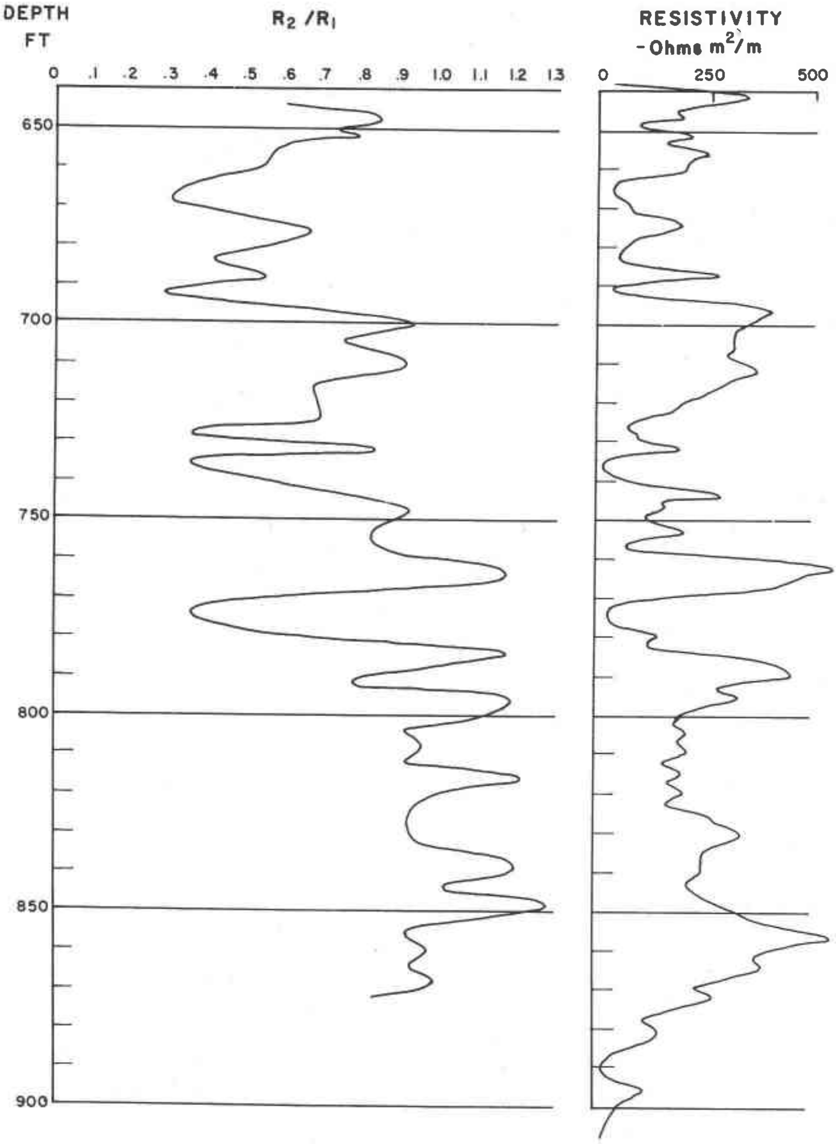

Fig. 3. R_2/R_1 log compared with short normal resistivities of Core Hole I limestone.

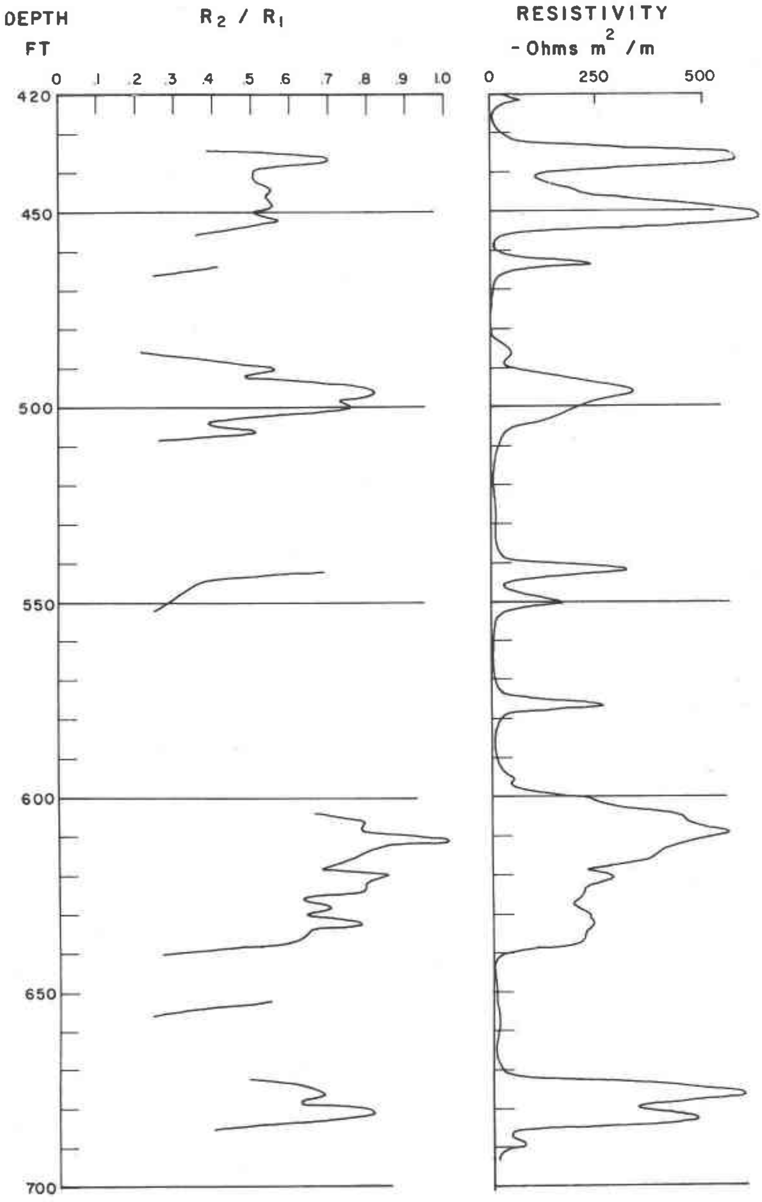

FIG. 4. R_2/R_1 log compared with short normal resistivities of Core Hole II limestone.

The electric logs shown in the right hand portions of Figs. 3 and 4 measure, in place, the electrical resistivity of these two core holes. The shape of the logs shows a considerable degree of correlation with the corresponding depth plots of R_2/R_1. The low resistivity regions, indicating shale stringers in the limestone, correspond in general to the low ratios of R_2/R_1, which indicate a larger amount of Mg^{2+} (and/or Fe^{2+} and Mn^{2+}) substitution in the calcite lattice. It appears that the degree of substitution is related to the occurrence of shale, with the shale possibly having served as a source of the substituted ions.

The average deviation in the ratio R_2/R_1 for each sample is between ±1 and ±5 per cent, which is the precision to be expected from the number of counts recorded for the A and B portions of the (211) calcite and (111) CdO reflections. The maximum deviation for 75 per cent of the samples is less than ±15 per cent, most of the deviations larger than this result from low count rates encountered in measurement of the larger peak shifts for which $R_2/R_1 < 0.4$. For these larger peak shifts, the error can be minimized by careful selection of the starting position of the detector. Of course, the range of peak shift measured can be extended by the similar use of intensities from other integrating intervals.

CONCLUSION

This method provides a rapid and accurate means of measuring small changes in the position of the principal x-ray diffraction peak. It can be used in the presence of large amounts of most other minerals because the (211) calcite reflection and the (111) CdO reflection are relatively free from interferring lines of other minerals. Thus other Mg-bearing minerals do not influence this measure of Mg^{2+} substitution in calcite.

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