

The optical orientation is  $\alpha \rightarrow a \beta \rightarrow b \gamma \rightarrow c$  in both cases, with the same crystallographic orientation (100)-cleavage,  $c$ -elongation. Deer, Howie and Zussman (1963) interchange  $a$  and  $b$ , so as to have a (010)-cleavage, but fail to interchange the same axes when giving the optical orientation.

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## SEPARATION OF DOLOMITE FROM FINE GRAINED RECENT SEDIMENTS

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## INTRODUCTION

Various methods are available for separating dolomite from ancient limestones. These include the use of acetic acid buffered with sodium acetate [Peterson, von der Borch and Bien (1966) and Goldsmith and Graf (1958)], the use of phosphoric acid [Degens and Epstein (1964) and Weber (1964)], and the use of dilute HCl [Deffeyes and Martin (1962)]. Unfortunately, these methods are not applicable to separation of dolomite from most Recent carbonate sediments. This is due to (1) the fine grained nature of such sediments, and, (2) the presence of Mg-rich calcites. These two factors result in a lack of differential solubility between carbonate phases in the reagents mentioned preventing use of these reagents in dolomite separations.

Recently a technique has been developed in this laboratory which enables separation of fine grained recent dolomites from coexisting calcite, high Mg-calcite, and aragonite using disodium ethylenediaminetetracetic acid (di-Na-EDTA). The technique makes use of information published by Hill and Runnels (1960) which points out that calcite and

dolomite have differential etching properties in EDTA and data published by Glover (1961) which shows that this differential is greatest at pH 6.3.

#### METHOD

Separation experiments were performed on Recent carbonate sediments. X-ray diffraction analysis of these samples showed that they contained dolomite as well as high Mg-calcite, calcite and aragonite. No dolomite rhombs were visible in any of the samples, the particle size of the dolomite being less than five microns. Attempts to separate dolomite from these samples using acetic acid-sodium acetate buffer and phosphoric acid failed due to the high rate of dissolution for the fine grained dolomite. Thus, a new separation technique was developed using di-Na-EDTA according to the following scheme.

*Step 1:* Aliquots of approximately 40 grams each are dried, ground and X-ray diffraction patterns run. The amount of each carbonate phase present is determined to  $\pm 10\%$  using X-ray peak heights and correcting their relative intensities by comparison to the intensities for pure component standards.

*Step 2:* The amount of di-Na-EDTA necessary to dissolve all the carbonates except dolomite is calculated and enough 0.27 M solution of di-Na-EDTA to give a 25% to 50% molar excess prepared. This solution is brought to a pH of 6.0 to 6.5 by adding pellets of NaOH and is then added to the sample.

*Step 3:* The resulting slurry is stirred for 15 minutes, the pH being monitored and kept constant by adding drops of dilute HCl when needed.

*Step 4:* After 15 minutes the reaction is quenched by centrifuging down the remaining sediment. A small portion of the sediment is taken with a pipette, dried on a glass slide, and the X-ray diffraction pattern run over the  $2\theta$  range of interest. If high Mg-calcite, calcite or aragonite are still present, step 3 is repeated. If after repeating step 3 three or four times the dolomite is still not pure, the di-Na-EDTA solution is removed and steps 2 and 3 repeated.

#### RESULTS

Figure 1 shows the effects of a single EDTA separation on a recent carbonate sample. The original sample contained large amounts of high Mg-calcite, calcite and aragonite as can be seen in the X-ray diffraction pattern labeled "before separation." After separation the X-ray pattern for the same  $2\theta$  interval showed only the same  $2\theta$   $d_{112}$  peak for dolomite, as shown in Figure 1. This type of result is generally achieved with one or two EDTA separations on samples where the dolomite present is not too Ca-rich (as indicated by the position of the  $d_{112}$  diffraction peak) and/or is present in appreciable amounts.

The more Ca-rich dolomites present a greater separation problem since they are quite similar in solubility to high Mg-calcite. In samples where exceptionally Ca-rich dolomites are present repeated separations

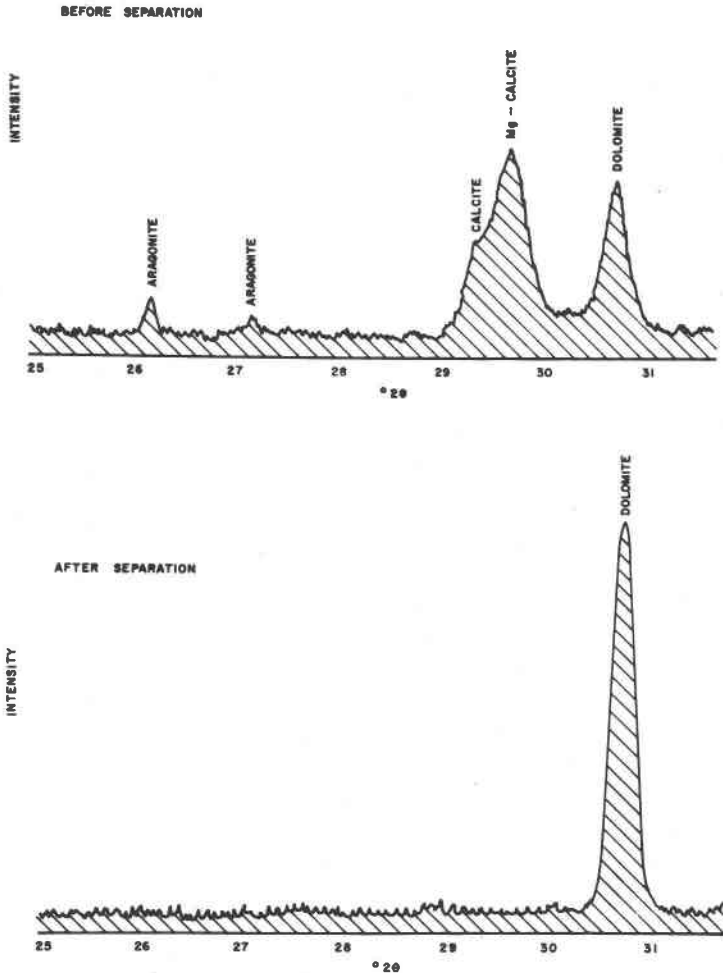


FIG. 1. X-Ray diffraction pattern for sample of recent carbonate sediment before and after EDTA separation ( $\text{CuK}\alpha$  radiation).

may be necessary with a distinct possibility that complete separation may not ever be attained.

Repeated separations present a problem in themselves due to preferential solubility of the more Ca-rich dolomites as compared to the more ideal dolomites. As noted by Peterson *et al.* (1966) Recent dolomites generally do not contain a single composition of dolomite but, rather a range of compositions. Since *some* of the dolomite always dissolves during beneficiation the preferred solubility of the Ca-rich varieties will cause

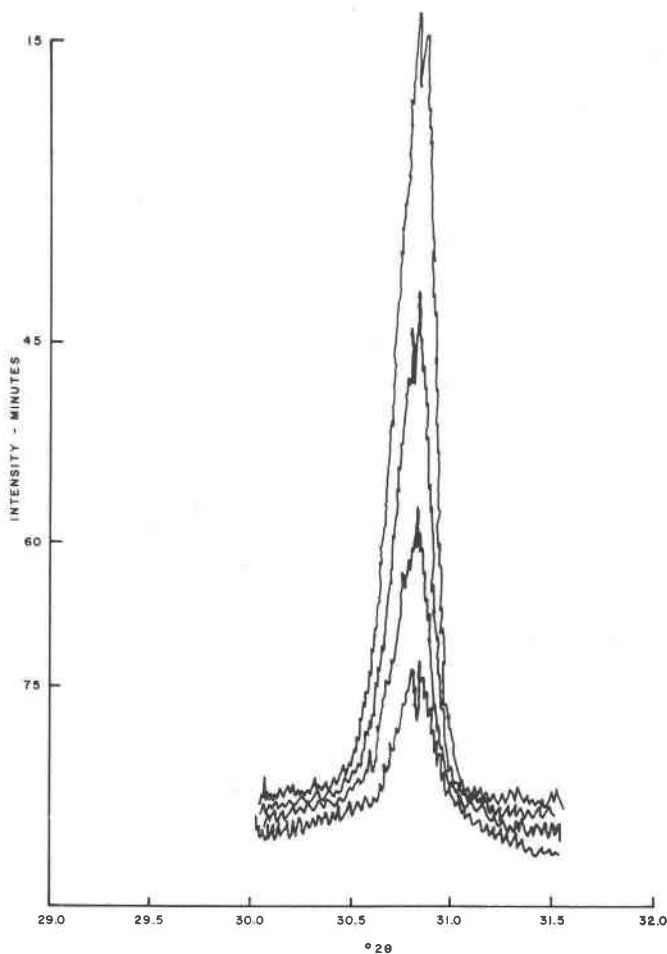


FIG. 2.  $d_{112}$  shift of dolomite with increasing reaction time.

some bias in the final sample. Figure 2 shows the effects of this bias when separation is carried to extreme and a large amount of the dolomite is dissolved. In the case shown, 75 minutes of reaction time with 0.27 M di-Na-EDTA shifted the dolomite  $d_{112}$  peak (the position of which is an indication of Ca-richness) approximately  $0.1^\circ 2\theta$  as compared to the same sample reacted for 15 minutes. Thus, experimenters should be aware that separated dolomite is not necessarily the same exact composition as the dolomite in the original sample. This is especially true when repeated separations must be performed on the same sample.

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## A TECHNIQUE FOR USING TWINS IN CRYSTAL STRUCTURE REFINEMENT

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If the crystal structure of a compound is known and a twin must be used for refinement of the structure, then the twinning relation can be used to interpret the observed intensity values. The problem becomes the task of calculating the crystal-volume ratio, which may be defined as the ratio  $K = V_{\beta}/V_{\alpha}$  of the volume  $V_{\beta}$  of the smaller crystal to the volume  $V_{\alpha}$  of the larger crystal,  $0 < K < 1$ . If the twin produces two sets of reflections, each set self-consistent within its own indexing, then the crystal-volume ratio can be calculated by direct comparison of equivalent reflections from each set. If the two twinned crystals produce reflections that are superimposed on each other, then a least-squares solution can be employed as described below. This method has been used successfully (Freed and Peacor, 1967) for a case which yielded the value  $K = 0.07$ .

Let  $v_1, v_2, \dots, v_n$  be the volume fractions of the  $n$  constituent crystals in the twin, so that  $\sum_{i=1}^n v_i = 1$ . For a given reflection  $hkl$  the intensities will be  $v_1I, v_2I, \dots, v_nI$ , where  $I$  stands for  $I(hkl)$ , the intensity contributed by a volume equal to the total volume  $\sum v_i$  of the twin. In a two crystal twin, the fractions will be  $v$  and  $(1-v)$ , and the crystal-volume ratio can be expressed  $K = (1-v)/v$ .

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