EXPERIMENTAL DOLOMITIZATION AND ARAGONITIZATION AT LOW TEMPERATURES AND PRESSURES

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ABSTRACT

EXPERIMENTAL DOLOMITIZATION AND ARAGONITIZATION AT LOW TEMPERATURES AND PRESSURES

By

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Fine-grained, natural dolomite incongruently dissolves to form aragonite in artificial sea water solutions, the amount of aragonite produced being a function of the concentration of the sea water. While some aragonite was produced in dilute solutions, maximum yields occurred in solutions ranging from normal salinity to about 2½ times normal salinity. In solutions with still higher salinities the yield decreased. Reaction time is relatively short, with detectable aragonite produced in less than a day. This aragonite is very fine-grained, and since it is newly crystallized it has no strain from the grinding process which might exist in aragonite ground to such a fine size fraction. By using this aragonite, a study of the dolomitization reaction could be made. Solutions in contact with aragonitized dolomite were allowed to slowly evaporate to near dryness for 7 weeks. At the end of this time the solids

were filtered, dried, and analyzed. The amount of dolomite increased with respect to aragonite, with a slight shift of the dolomite 104 peak to a smaller cell size. It is postulated from evidence from the microprobe, X-ray diffraction, and staining techniques that the aragonite was converted to ordered dolomite.

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By

Patricia Lynne Orr

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INTRODUCTION

Although dolomites are very abundant in the geologic record, reasonable models of dolomite genesis have been proposed only since 1960. These models have been derived from field observations of ancient strata and from modern environments. However, laboratory experiments designed to clarify the nature of the reactions inferred from field observation has not been very successful. Indeed the first step--laboratory synthesis of dolomite under conditions consistent with field observation--has not been heretofore reported. Synthesis of dolomite analogous to recently formed natural dolomite was the object of this research.

Field Observations

In December, 1960, Adams and Rhodes from observation of West Texas Permian carbonates proposed the mechanism of "seepage refluxion." This involves production of a hypersaline brine near shore and movement of that brine through carbonate sediment, with the brine dolomitizing the carbonate as it migrated. Shortly after this, field occurrences of brines in contact with carbonates were documented at Bonaire, Netherlands Antilles, by Deffeyes et al. (1965), and the presence

of recently formed dolomite was affirmed. Subsequent work including that described below raise the possibility that seepage refluxion may not be the major dolomitization process as believed at the time of the Bonaire paper. It appeared from work by Hsu and Siegenthaler (1969) that the brine did not necessarily reflux through the carbonate in all cases, but the brine-carbonate reaction occurred wherever the two were in contact with each other.

Chave (1954) noted that in fine grained Pleistocene carbonates from California the amount of dolomite in the fine grained fraction varied inversely with the proportion of aragonite. Clayton et al. (1968), by isotopic methods, determined that dolomite forming in the Coorong of South Australia is not derived from preexisting calcite, but has a distinct origin of its own. Furthermore, dolomite has been observed forming in the natural environment today by Butler (1969) on the Trucial Coast, von der Borch (1965), Alderman (1965), and Skinner (1963) in South Australia, Clayton et al. (1968) in Deep Springs Lake, California, Deffeyes et al. (1965) and Murray (1969) on South Bonaire, Shinn et al. (1965) on Andros Island, Shinn (1968) and Atwood et al. (1970) in the Florida Keys, Graf et al. (1969) in Lake Bonneville, Utah, Thrailkill (1968) in Carlsbad Caverns, Friedman (1966) in a recent salt flat in West Texas, and by several others.

Since 1960, the frequency of discovery of new sites of dolomitization has increased greatly. Generally these dolomites occur in the fine grained fraction of carbonate beaches or briny lakes. Although these dolomites are correct in stoichiometric proportions, they do not generally exhibit all of the characteristic diffraction pattern for dolomite. That is, a continuum exists from a pattern showing all characteristic peaks, to patterns where only major peaks can be determined and low order reflection peaks are either absent or lost in a high noise level. Dolomites with these latter patterns are commonly present in recent dolomite, and commonly exhibit a relatively larger cell size. Graf (1956) characterized these dolomites as "protodolomites" and on the basis of the larger cell and the absence of the 221, $10\bar{1}$, and $11\bar{1}$ ordering peaks, suggested that the Ca and Mg atoms in such minerals were not mutually segregated in alternating planes separated by planes of carbonate groups, but were essentially randomly distributed within planes. The presence of superstructure reflections mentioned above are considered distinguishing characteristics of ordered dolomite (Berner, 1971). However, these peaks have very low intensities and may be obliterated by low signal to noise ratios. Secondary criteria for relatively high degrees of order include distinct and sharp diffraction peaks in more ordered dolomite compared to more diffuse

peaks in more disordered dolomite, and secondarily a relatively larger cell size in the more disordered structure.

Laboratory Research

Successful synthesis of dolomite has been achieved, but with either pH, P_{CO_2} (Baron, 1960), nature of reactants (Siegel, 1961; Glover and Sippel, 1967), temperature ranges (Graf and Goldsmith, 1956), or other experimental parameters being unrealistic when compared with the sedimentary environment. Solutions representing concentrated sea water under realistic environmental conditions have never spontaneously yielded dolomite or protodolomite in the laboratory (Berner, 1971). However, from the field observations it appears that the objective of precipitating dolomite directly from solution may be unrealistic with respect to the manner in which most geological dolomites have formed.

From the field observations described above it is evident that dolomitization involving reaction of fine grained aragonite with concentrated brines is of major geochemical interest. However, as will be discussed, experiments investigating the reaction brine plus fine grained aragonite yielding dolomite contain a wealth of hidden complexity.

First, natural dolomite is seldom simple calcium-magnesium-carbonate but contains a host of other cations--especially iron. These "impurities" probably play an important role in the kinetics of dolomitization and in the stability of the product. Thus the solute system is complex--especially in brines where ionic interaction is always a significant factor.

Second, suitable fine grained aragonite starting material cannot be simply obtained. Size reduction of coarser material by crushing or grinding produces lattice distortions and defects which increases effective free energy--an unwanted complication. Precipitation of aragonite from solution generally yields aragonite which within days spontaneously converts to calcite.

Third, the use of natural fine grained aragonitic mud was rejected because of the complex chemistry of the bulk sample--involving other minerals, organic substance and perhaps micro-organisms.

This research was designed to circumvent these difficulties. An aqueous system involving aragonitization of natural dolomite served to insure availability of minor elements and produced a stable fine grained aragonite. Although the initial grinding of the parent dolomite may have induced strain into that material this in no way could affect the main experimental system.

Preliminary Experimental Work

The plan of this experiment was to obtain a fine grained aragonite from reaction of aqueous solution with ground dolomite in a like manner as Garrels et al. (1960) and allow a sea water solution in contact with this aragonite to evaporate in hopes of converting the aragonite to stable calcium-magnesium-carbonate with stoichiometry of dolomite and, hopefully, ordering peaks characteristic of ordered dolomite.

MATERIALS, APPARATUS AND PROCEDURE

The sea water analogs used were composed of reagent grade chemicals weighed in a double-pan balance and dissolved in water which was distilled in a Barnstead still. The sea water formula used was Subows, taken from the Handbook of Oceanographic Tables. More concentrated solutions were attained by simply doubling, trebling, etc. the normal sea water formula.

Dolomite crystals from a vug in a core of the Dundee limestone were first powdered by hand in an agate mortar, and then ground in a mechanical grinder with alumina mortar and pestel for 12 hours. This was the initial carbonate material. The fine powder had a natural tendency to form small globules a few mm in diameter. These globules retained their individual integrity throughout the experiment, and reactions between solution and solid could be monitored on both the level of the micron-size particles and by the formation of reaction products in the globules from their boundaries inward.

In the aragonitization experiment, for the samples equilibrating one week or less the reaction vessels were disposable plastic cups with saran wrap

covers to retard evaporation. In the longer time runs capped plastic bottles were used to prevent evaporation of the solutions with consequent changes in composition of the supernatant reacting fluid. All systems at the end of reaction time were filtered in glass funnels using #2 filter paper. For the dolomitization reaction, the samples were put in covered plastic beakers for 8 days to yield aragonite, and then the covers were removed to allow evaporation and the consequent formation of brines to react with the aragonite to form dolomite.

ANALYTICAL TECHNIQUES

Staining

The powders resulting from the above experiments were filtered, dried, and then mounted in epoxy on glass slides. These mounts were ground down to yield a cross-section through the powder aggregates and the larger individual grains. The slides were immersed in 10 ml of an Alizarin Red S (ARS) solution of 200 ml .2% HCL + .100g ARS powder [modified from Friedman (1959) and Warne (1962]. The slides were then rinsed by dipping in distilled water, and allowed to air dry. Inspection of the stained slides was by the binocular petrographic microscope.

X-ray Diffraction

X-ray diffraction patterns were obtained from a General Electric XRD-6 diffractometer-goniometer with attached automatic recording unit. The samples were mounted on glass slides with a thin film of petroleum jelly and analyzed using CuK_{α} radiation. Aragonite proportions were calculated by determining the areas under the aragonite-111 and dolomite-112 peaks, and calculating the per cent aragonite of total carbonate present. This can be done fairly simply as the peak

height varies directly and in an almost linear fashion with respect to the proportional amount of carbonates present.

Microprobe

An electron microprobe was used for compositional determinations. Determination of Ca and Mg were made on all grains studied, as well as Fe, Na, Cl, and S being run on several representative samples.

RESULTS

Aragonitization

Dolomite ground for 12 hours in a mechanical mortar was immersed in sea water analogs ranging from distilled water, to 10 times normal sea water concentration. At the end of determined periods of time, the solid phases were removed from the system by filtration and identified by X-ray diffraction. Conditions of the experiment were room temperature and contact with the atmosphere. In most cases detectable aragonite was produced in a matter of hours (Figure 1). It should be noted that no aragonite thus formed inverted to calcite--even samples that remained in contact with solution for 5 weeks.

For distilled water and salinities up to about 7 times normal sea water, maximum yields were approached within the first 12 hours, although the solutions did show an increasing yield for about one week (Figure 2). As can be seen from the figures, the greatest yields were obtained from samples taken from solutions ranging from normal to slightly hypersaline concentrations. The distilled water 6½ times and 10 times normal sea water samples all gave much lower aragonite yields than the

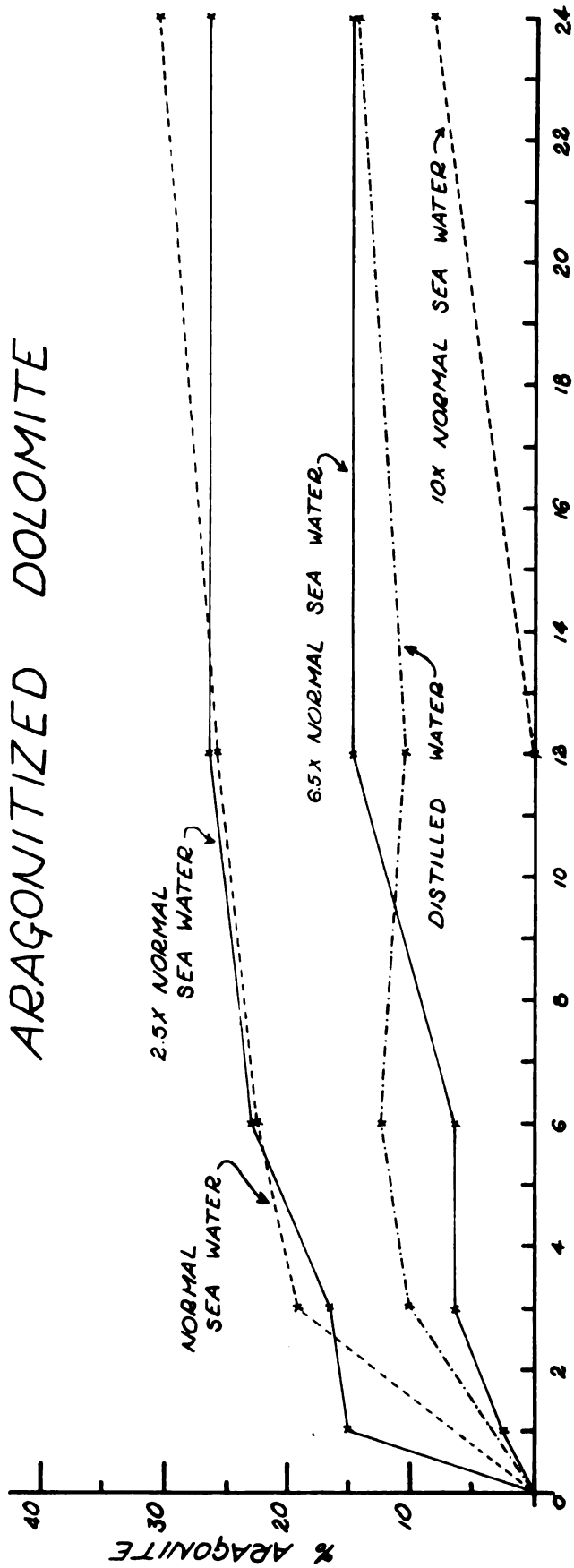

Figure 1.--Yield of aragonite with time from ground dolomite in contact with sea water analogs (0-24 hours).

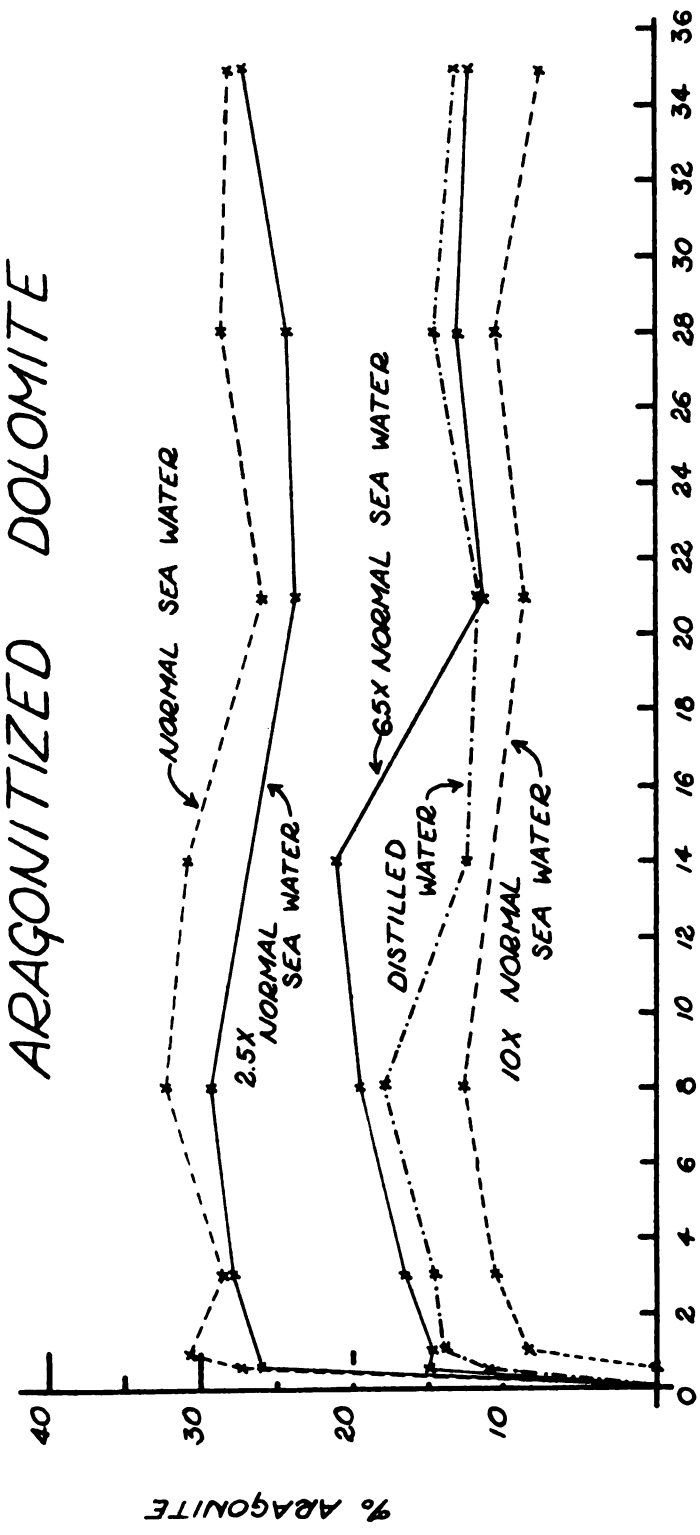

Figure 2.--Yield of aragonite with time from ground dolomite in contact with sea water analogs (0-35 days).

normal and 2½ times normal sea water solutions. It was predicted that the concentrated solutions would not produce as much aragonite, but the low amounts of aragonite in the distilled water runs implies that more factors than Mg-Ca ion concentrations affect the process. A complex or series of complexes between Ca, Mg, and the anions present in sea water may influence the reaction. It should be noted that the solutions 6½ and 10 times normal salinity contain non-carbonate solid phases, principally halite and gypsum, and that the relative proportion of solute species are no longer those present in the more dilute solutions.

The globules formed during the grinding process retained their individual integrity during the course of the reaction. Observation of a cross-sectional view of one of these globules indicates an aragonitic rim around a dolomite core. Figure 3a shows one such globule embedded in epoxy and stained with Alizarin Red S. Figures 3b and 3c are compositional traverses across one such globule. Both analytical techniques display clearly the aragonitic rim. The maximum amount of aragonite obtained was approximately 30% of the entire carbonate phase.

Figure 3a.--Globule of aragonitized dolomite embedded in epoxy and stained with ARS. Note aragonite rim (red) and core of original dolomite (purple).

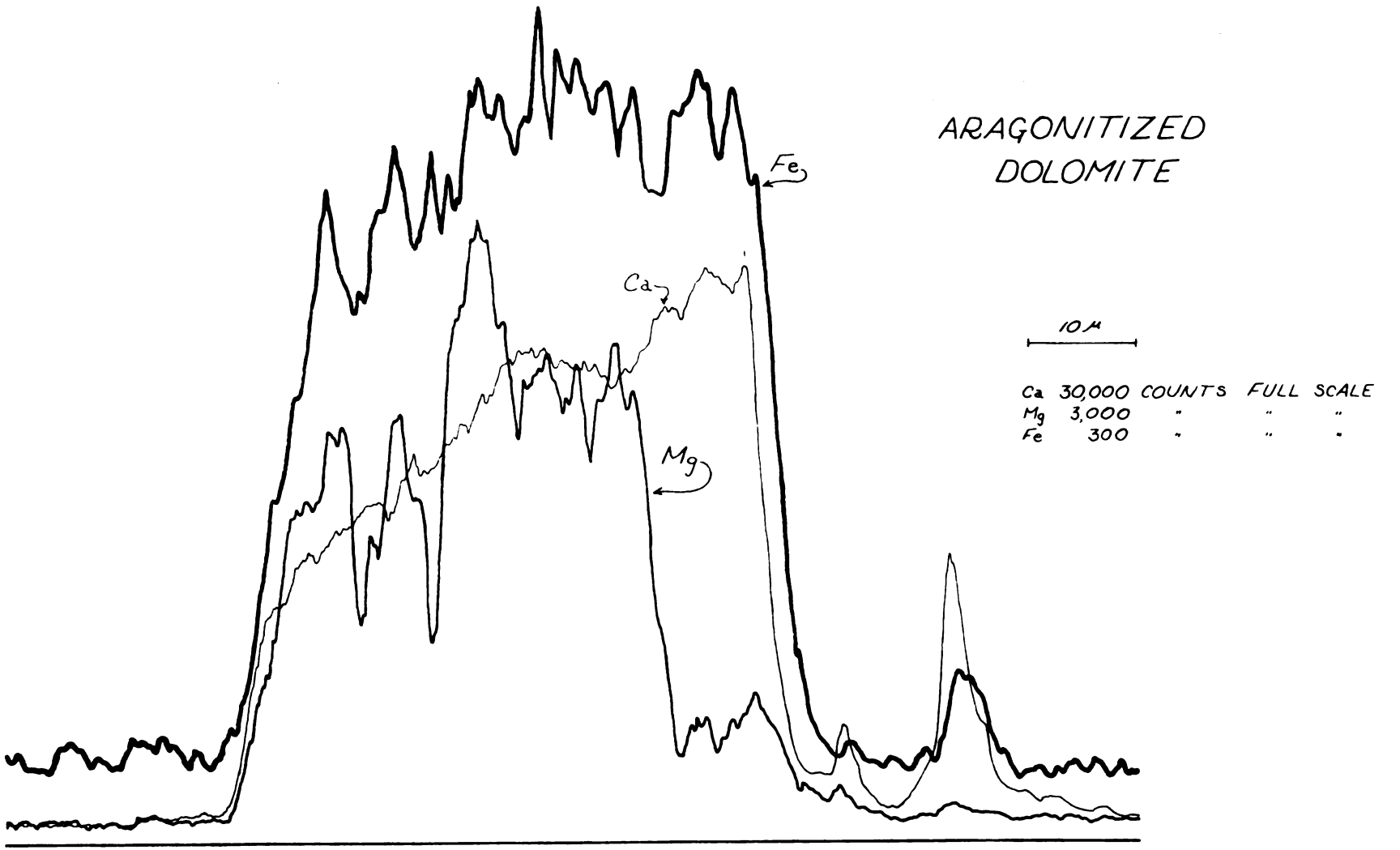

Figure 3b.--Variation in Ca, Mg, and Fe across aragonitized globule. Note each element was run at a different number of counts full scale.

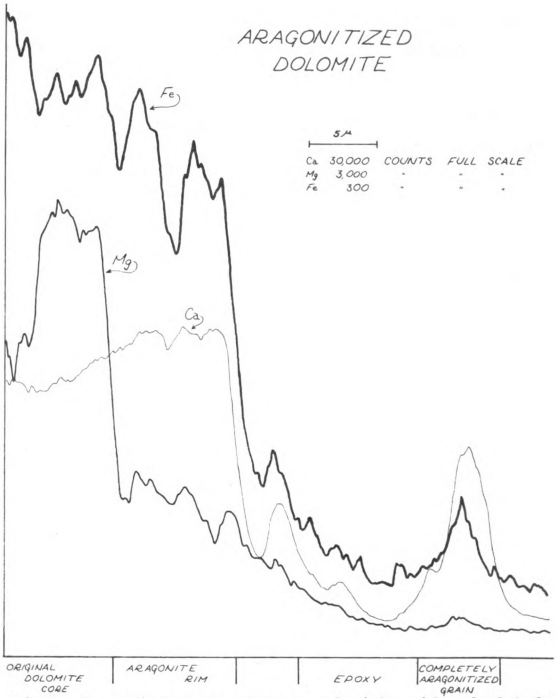

Figure 3c.--Microprobe traverse of right side of globule analyzed in 3b at higher magnification, illustrating the regions present within the globule.

Dolomitization

The attempt to synthesize dolomite herein presented takes advantage of three factors resulting from the aforementioned results. First, the ease with which stable aragonite is formed under natural conditions in the lab. Second, the natural adjustment of solute ratios by the presence of precipitated non-carbonate phases, and third, from preliminary experimental results, knowing that in a region more concentrated than approximately 200 g/l Cl dolomite can exist as a stable phase.

Four aragonite bearing samples were produced by reaction of powdered dolomite with solutions of 2½ times normal salinity. After 8 days one of the samples was filtered, dried, and analyzed by X-ray diffraction and the microprobe, and the presence of aragonite was confirmed. The remaining three beakers were uncovered and allowed to evaporate to near dryness at room conditions for approximately 7 weeks. At the end of this time the solids were filtered, dried, and analyzed. Comparison of diffraction peak areas indicated that the amount of dolomite increased with respect to aragonite. With respect to the original dolomite, a slight shift of .064 2θ (corresponding to a .0058 Å change in cell size) was also detected. Figure 4a is a photomicrograph of an epoxy mounted, original, unreacted dolomite aggregate stained with ARS. A microprobe traverse of such an

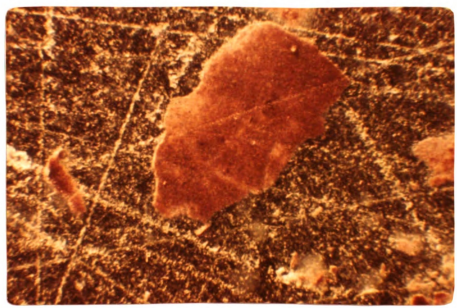

Figure 4a.--Photograph of epoxy-mounted original dolomite globule stained with ARS.

aggregate (4b) exhibits a characteristic Mg, Fe, and Ca composition of unaltered dolomite. Differential effects on this illustration are due to running the Fe and Mg on a much smaller full scale than the Ca. Figures 3a, 3b, and 3c depict a similar globule after aragonitization. The aragonite rim clearly is visible, both on the stained slide and in the microprobe results. Figure 5 compares the X-ray diffraction patterns of the original dolomite, aragonitized dolomite, and the new dolomite. Note that on the aragonitized dolomite the intensity 100 peak labeled D-112 is much lower in amplitude, but displays sharpness and symmetry of ordered dolomite. The greater signal to noise ratio resulted in the loss of the intensity 10 and less ordering peaks, although on some runs they were visible above the background. The uppermost graph of the new dolomite shows a sharp 112 peak but with relatively low amplitude. As with the graphs of the aragonitized dolomite, the ordering peaks can not be identified on this graph. Even at the expanded scale of 200 cps, no aragonite peaks could be identified with any confidence. Additional evidence that we are looking at new rather than old dolomite can be obtained from microprobe results. The two photographs in Figure 6a are reverse sample current images of an aggregate believed to have been dolomitized. The rectangular central inclusion is probably a fragment of original dolomite, with

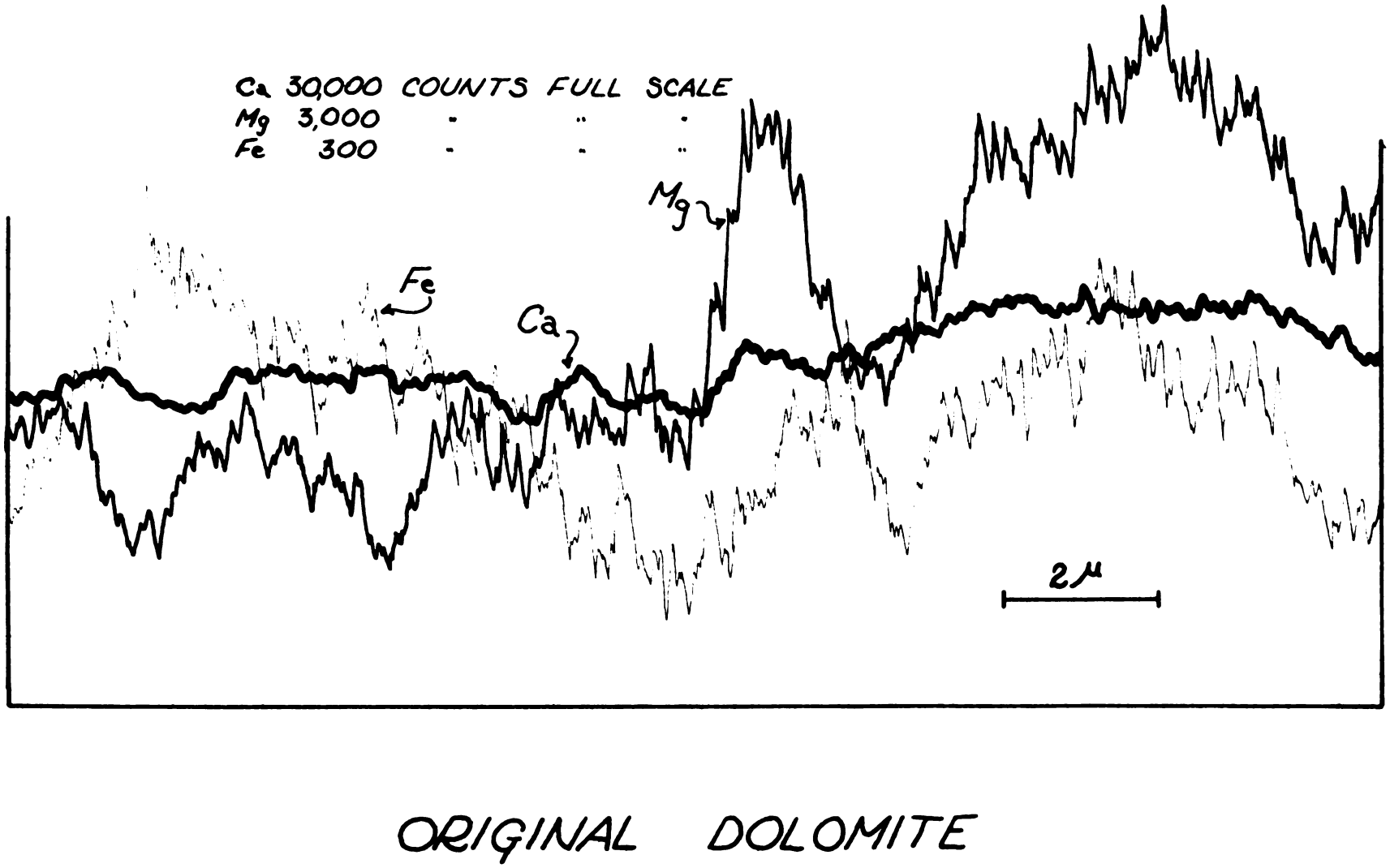

Figure 4b.--Microprobe traverse across original dolomite globule prior to aragonitization, indicating original amounts of Ca, Mg, and Fe present.

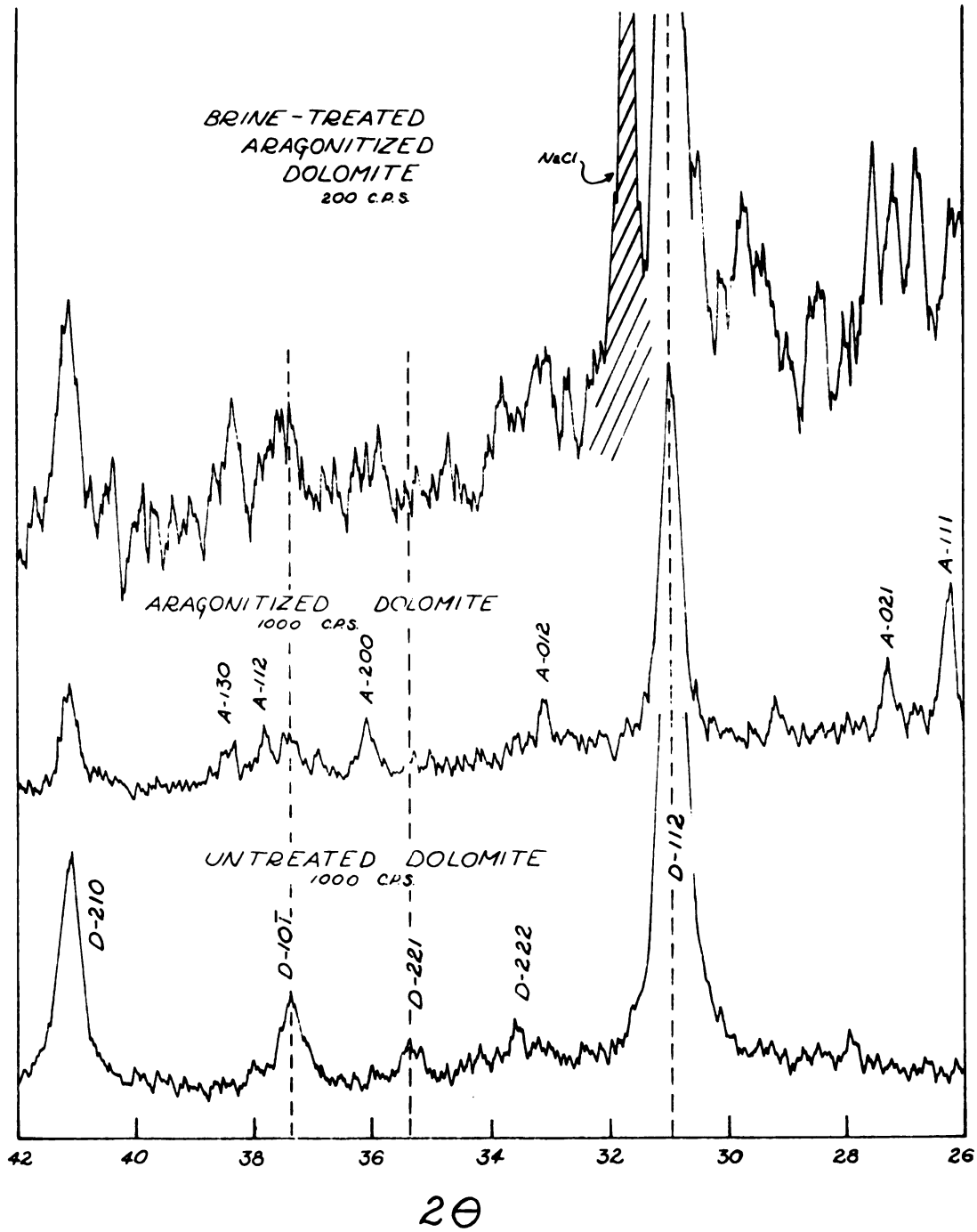

Figure 5.--X-ray diffraction patterns of original dolomite, aragonitized dolomite, and new dolomite (CuK_{α} radiation).

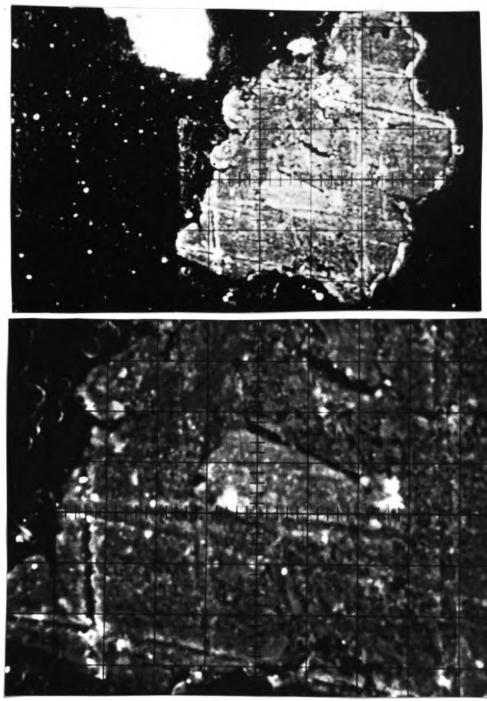

Figure 6a.--Microprobe reverse sample current photographs of dolomitized aragonite globule. Rectangular central inclusion is an original dolomite fragment.

the outer material being newly formed dolomite. Between the two is a residual rim of aragonite. The microprobe trace (Figure 6b) runs vertically down the center of the lower photograph, top being on the left. The first third on the left represents the outer, new dolomite, the central portion the original dolomite, then an aragonite rim characterized by the relative increase of Ca with respect to Mg, and the right-hand side being more new dolomite. Under higher magnification, the residual aragonite rim can be resolved on both sides of the original dolomite (6c).

Order versus Disorder

The smaller cell volume of the dolomite produced from aragonite coupled with the quality of the intensity 100 peak of dolomite inclines us to suspect that this new dolomite is probably ordered. Further evidence to support this view is provided by Figure 7. In a given dolomite, the ratio of areas under different peaks has a certain value, depending on the degree of ordering, orientation of the grains on the slide, and a few minor influences. This X-ray diffraction pattern is of new dolomite which has been separated from most of the non-carbonate phases it was associated with during formation. As can be seen, the major ordering peaks are visible. The ratio of their areas to the area of the dolomite $10\bar{1}$

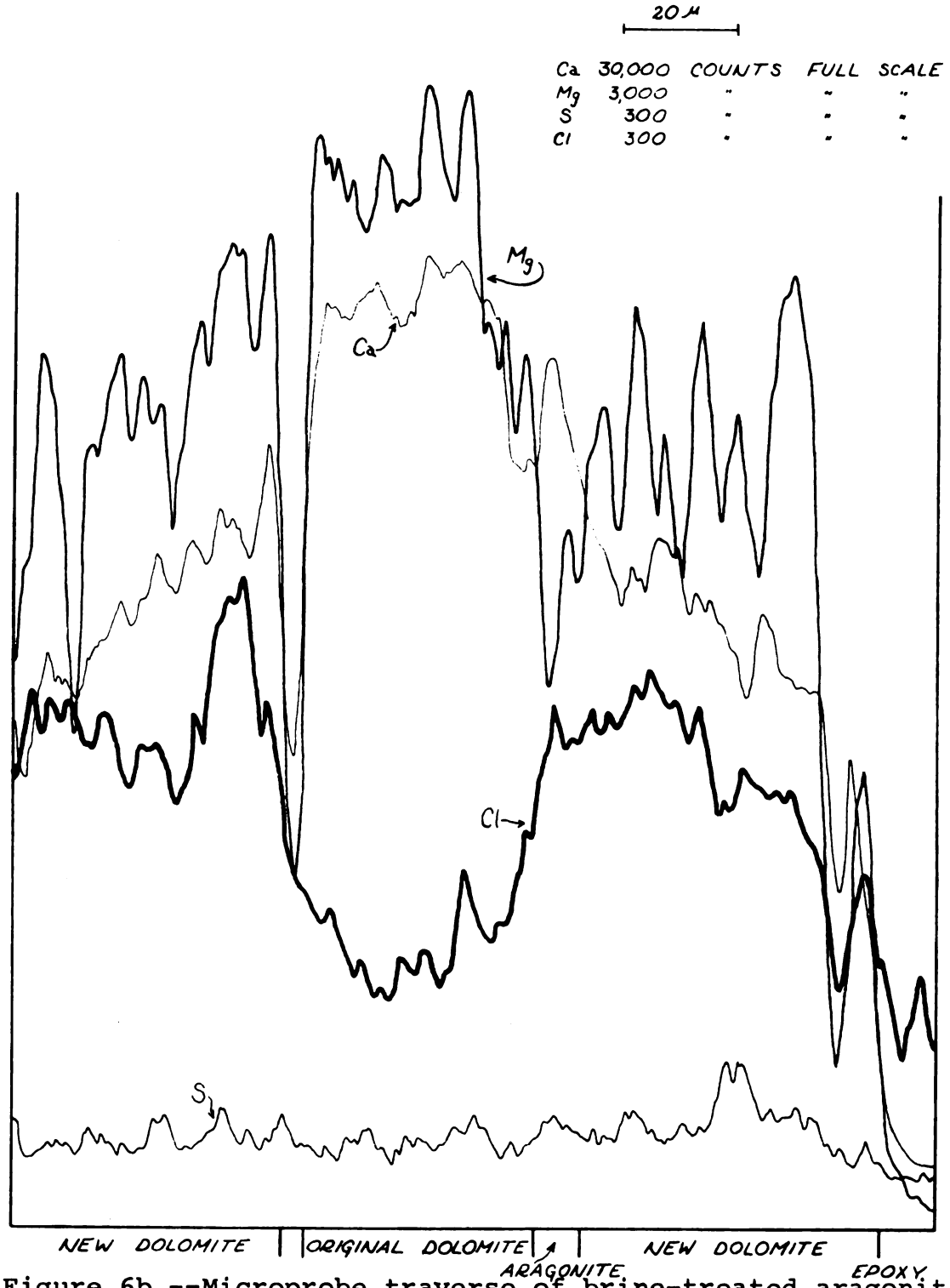

Figure 6b.--Microprobe traverse of brine-treated aragonitized dolomite globule showing new dolomite, original dolomite, and residual aragonite zone between the two.

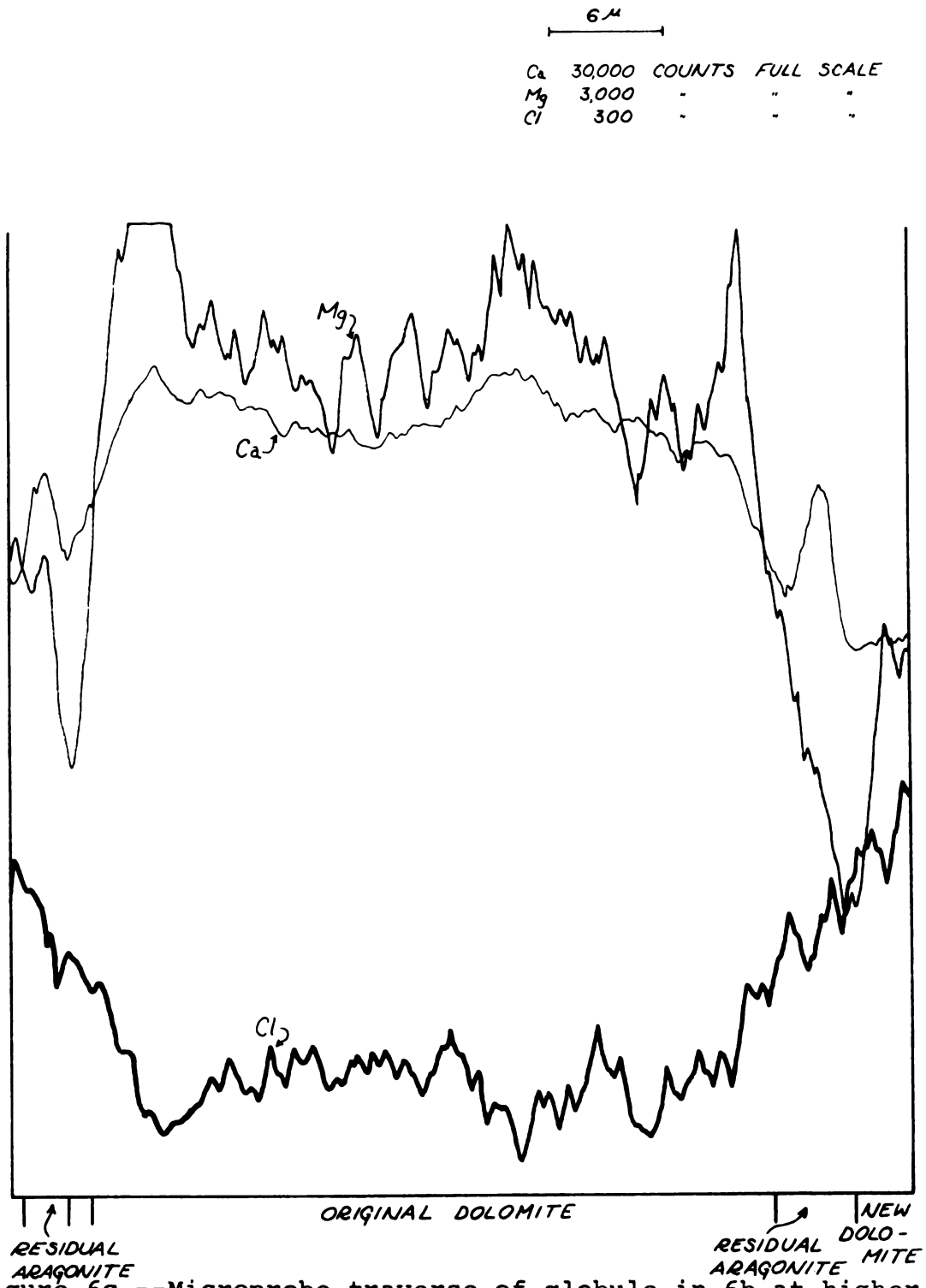

Figure 6c.--Microprobe traverse of globule in 6b at higher magnification, illustrating residual aragonite zone between new and original dolomite.

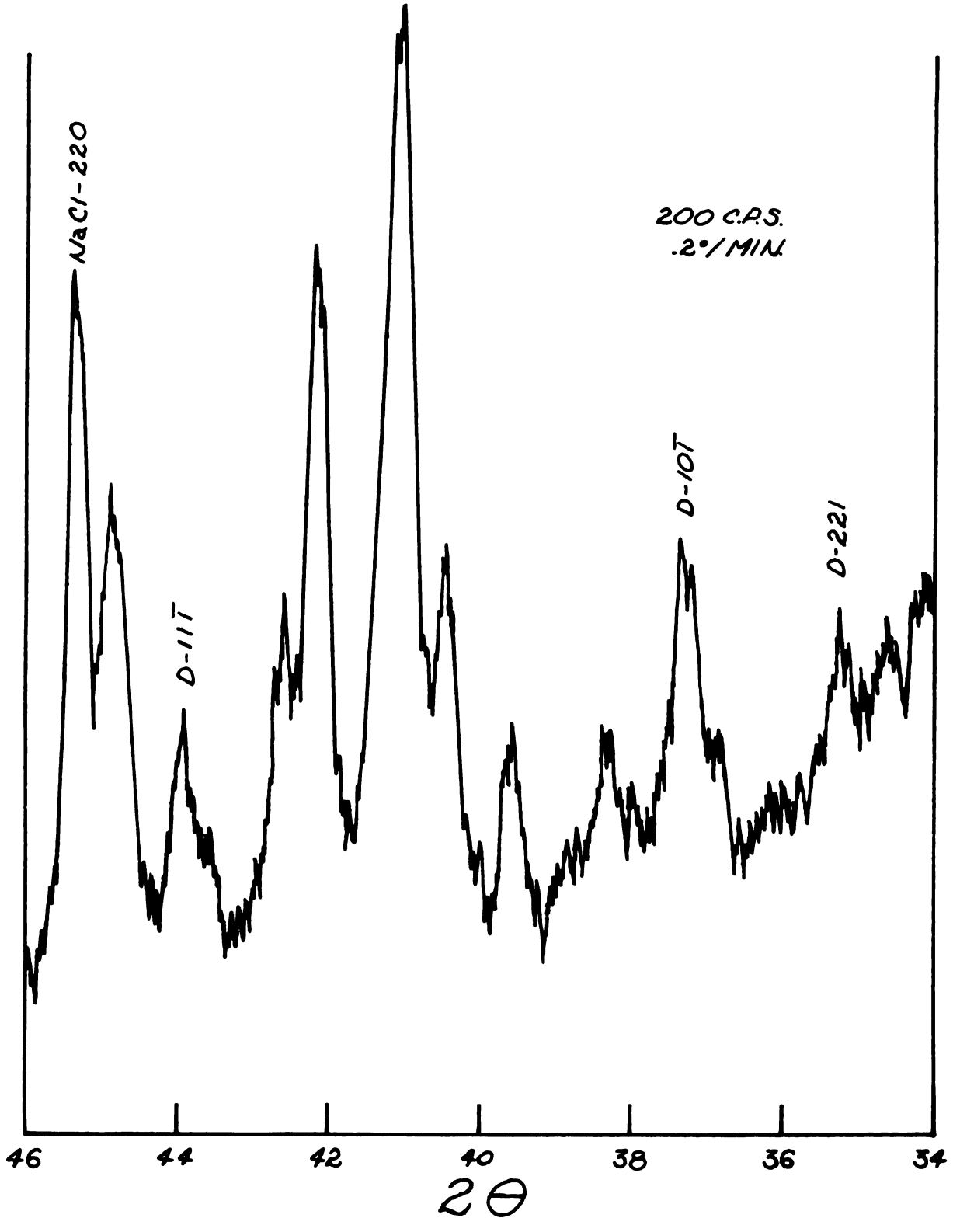

Figure 7.--X-ray diffraction pattern of brine-treated aragonitized dolomite (new dolomite) showing ordering peaks.

peak at 37.35° 2θ varies, but in no run was the ratio less than in the original dolomite, and in most cases it was more. This means that the new dolomite is probably contributing to all peaks, and that the ordering peaks are not just reflections from the remnant original dolomite. Also, the original remnant dolomite showed no ordering peaks in most of the aragonitized dolomite patterns, thus it would not be reasonable to suspect that they could be detected in the new dolomite unless more substance was present to yield a stronger reflection.

CONCLUSIONS

In summary, natural dolomite ground for 12 hours in a mechanical mortar, when in contact with sea water analogs of certain strengths, dissolves incongruently to yield aragonite. This aragonite, which is micron-size, can be reconverted to dolomite (probably ordered) in the lab by placing it in contact with sea water analogs which slowly evaporate to dryness during a period of about 7 weeks. The CO_2 pressure was that of atmospheric CO_2, e.g., $10^{-3.5}$ atm., and the temperature of the reacting solution was room temperature, e.g., 25°C.

From the above results, the relationships between compositional-crystallographic variations of dolomite and the variation of environmental parameters can be determined. Such research has shed great light on the natural genesis of single carbonates such as calcite, aragonite, and magnesite. The present worker has every reason to believe similar investigations of double carbonates will yield information of comparable values about the geochemical history of modern and ancient dolomites.

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