

dimension, equal to 17.82 Å compared to a  $b_0$  dimension of 20.49 Å in mordenite. Comparison of the  $bc$  crystallographic planes of heulandite and brewsterite Perrotta and Smith (1964), Figures 3 and 4 show similar arrangements of the 8-, 6-, and 4-member rings. This similarity is also seen by the nearly equal cell dimensions of heulandite ( $b = 17.82$ ,  $c = 7.43$  Å) and brewsterite ( $b = 17.51$ ,  $c = 7.74$  Å) in this crystallographic plane.

Full matrix least squares refinement of the structure is presently underway. A more detailed description, interpretation, and listing of data of the refined version of this structure is planned for publication at a later date in this journal.

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#### GROWTH OF SYNTHETIC CALCITE SINGLE CRYSTALS

J. F. NESTER AND J. B. SCHROEDER, *The Perkin-Elmer Corporation, Research Department, Norwalk, Connecticut.*

Calcite is an important optical material because of its high birefringence and availability as large, good quality, natural crystals. While sizeable quantities of natural calcite crystals are found in the earth's crust, at present all important sources of high quality crystals are foreign, and since the availability of these crystals at reasonable prices cannot be assured, we have undertaken a program to explore the possibility of producing large, high quality calcite crystals in the laboratory.

Growth from a stoichiometric melt is rendered very difficult by virtue of the high partial pressure of  $CO_2$  over  $CaCO_3$  at high temperatures (Smythe and Adams, 1923). Published data (Jamieson, 1960) indicates that the application of pressure tends to stabilize the aragonite structure of  $CaCO_3$ . On the other hand, most natural calcite is formed hydrothermally and small, synthetic crystals of unspecified quality have been prepared by this technique (Ikornikova, 1961). The low solubility of  $CaCO_3$

in water even in the presence of additives makes the growth of large crystals from aqueous solution impractical at ordinary pressures. Because of these apparent difficulties associated with other growth techniques, the flux method was chosen for the growth of calcite crystals under this program.

Since the published data (Smythe and Adams, 1923) indicated that decomposition of  $\text{CaCO}_3$  occurs rapidly above about  $800^\circ\text{C}$ , initial efforts were directed toward finding a solvent in which appreciable quantities of  $\text{CaCO}_3$  could be dissolved at temperatures below  $800^\circ\text{C}$  in air. The following molten solvents were tried unsuccessfully under these condi-

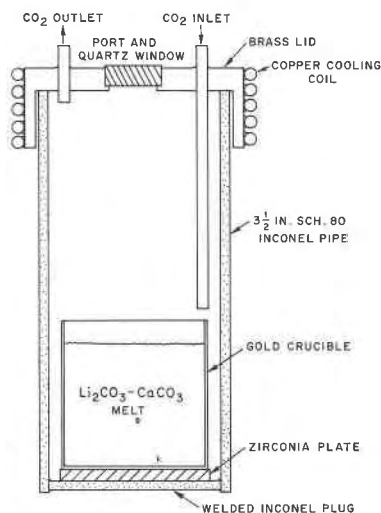


FIG. 1. Schematic representation of the crystal growing chamber.

tions:  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{NaNO}_3$ ,  $\text{LiNO}_3$ ,  $\text{CaCl}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{LiCl}$  and  $\text{KCl}$ . In each of these, the  $\text{CaCO}_3$  was either insoluble or only sparingly soluble or was decomposed by the solvent.

We also investigated the use of  $\text{Ca}(\text{NO}_3)_2$  as a solvent for calcite. The calcite is stable and sufficiently soluble to be grown. However, the rapid decomposition of the nitrate above  $500^\circ\text{C}$  in air is a serious drawback to this scheme.

Phase equilibria data (Levin, *et al.* 1964) indicated that  $\text{CaCO}_3$  was soluble in  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , but that in the latter two systems double salts such as  $\text{K}_2\text{CO}_3 \cdot 2\text{CaCO}_3$  were formed. Thus,  $\text{Li}_2\text{CO}_3$  was selected as a solvent and found satisfactory for precipitating calcite from solution upon cooling.

The procedure used to prepare calcite crystals was as follows: reagent

grade  $\text{CaCO}_3$  and  $\text{Li}_2\text{CO}_3$  were mixed in a 1:1 mole ratio and charged into a 7.5-cm diameter  $\times$  7.5-cm height gold crucible. The crucible and contents were placed in a globar furnace, heated to ca  $800^\circ\text{C}$  and then cooled at 0.5 to  $1.0^\circ\text{C/hr.}$  to about  $650^\circ\text{C}$ , then furnace cooled to room temperature. Because  $\text{Li}_2\text{CO}_3$  reportedly (Janz and Lorenz, 1961) has a decomposition pressure of over 100 mm of Hg at  $800^\circ\text{C}$ , the entire process was carried out in an inconel chamber under a flowing  $\text{CO}_2$  atmosphere to prevent decomposition, shown schematically in Figure 1.

The crystals formed as platelets by spontaneous nucleation at the melt surface. They were identified as calcite by X-ray diffraction, and their single-crystal nature was established with the use of the polarizing microscope. Figure 2 shows typical results obtained from this process. The platelets were bound by  $\{00.1\}$  planes. Microscopic examination and

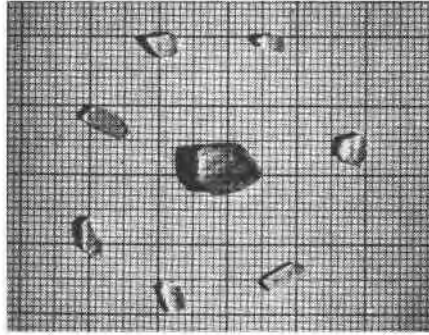


FIG. 2. Synthetic calcite crystals, grid in millimeters.

X-ray rocking angle curves indicated that the crystals were of good quality. The absorption spectra of the synthetic material was identical with that of good natural calcite over the entire transparent region of the spectrum. Crystals up to  $1\text{ cm} \times 1\text{ cm} \times 0.1\text{ cm}$  free from inclusions are occasionally obtained, although normally platelets several millimeters on an edge result. The growth of larger crystals is aided by the addition of 1 mole percent  $\text{Na}_2\text{CO}_3$  to the melt which apparently acts as a growth inhibitor in a manner analogous to that observed in the case of  $\text{Li}_2\text{O}_3$  with  $\text{Al}_2\text{O}_3$  (Chase, 1964). No modification of the growth morphology was effected by the  $\text{Na}_2\text{CO}_3$  addition. Efforts to obtain similar results by the addition of small quantities of  $\text{B}_2\text{O}_3$  or  $\text{SiO}_2$  were unsuccessful.

It should be possible to change the growth morphology by additions to the melt, because hydrothermal crystals are bounded by  $\{10.49\}$  faces (Ikornikova, 1961) indicating that the growth anisotropy is probably due to a surface phenomenon.

Separation of the crystals from the solvent presented serious problems which have not been satisfactorily resolved. The close chemical similarity between  $\text{Li}_2\text{CO}_3$  and  $\text{CaCO}_3$  makes separation by conventional methods (*i.e.* preferential leaching of the solvent) difficult. Published data (Handbook of Chemistry and Physics, 1960) suggests that  $\text{Li}_2\text{CO}_3$  is sufficiently soluble in  $\text{H}_2\text{O}$  to permit leaching of this flux material by flowing water. Such attempts were made, but our empirical results indicate that the solubilities of  $\text{Li}_2\text{CO}_3$  and  $\text{CaCO}_3$  in water are quite similar, *i.e.* rather low. Some success resulted from efforts to preferentially dissolve the  $\text{Li}_2\text{CO}_3$  in a saturated solution of  $(\text{NH}_4)_2\text{SO}_4$  at room temperature. However, the calcite was also slightly attacked by the solution and leaching periods of up to four weeks with constant agitation were required to obtain reasonable separation. Some platelets could be separated simply by mechanical means although their size was limited due to fracture during removal. The most suitable separation scheme devised consisted of draining off the flux after completion of the growth cycle by puncturing the bottom of the gold crucible with a graphite probe. Even then some flux adhered to the crystals and was difficult to remove. Melt pour-off techniques were tried but resulted in loss of the crystals due to thermal shock.

The melt drain-off scheme allowed us to observe that once the surface of the melt had been covered with a layer of calcite crystals, rapid growth took place beneath this layer as revealed by multiply intergrown and randomly oriented crystals that had trapped flux. On the assumption that this effect was the result of shielding of the melt from the  $\text{CO}_2$  atmosphere by the crystalline layer, the furnace was arranged so that the coolest temperatures were at the bottom of the crucible. No apparent improvement was observed, and separation of the crystals was made more difficult since they were at the bottom of the crucible. Efforts to obtain more orderly growth by seeding also met with very limited success using both natural calcite crystals and second-generation flux-grown crystals. It is possible that the random growth effect is due to a lowered thermal gradient once the melt surface is covered. In that event, a flux-pulling technique such as that described by Linares (Linares, 1964) using a cooled seed to induce a steep thermal gradient might solve the problem.

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SODIUM, POTASSIUM, AND FERROUS IRON CONTENTS OF SOME  
SECONDARILY HYDRATED NATURAL SILICIC GLASSES<sup>1</sup>

DONALD C. NOBLE, *U. S. Geological Survey, Denver, Colorado.*<sup>2</sup>

INTRODUCTION

A few workers (e.g., Bowen, 1938, p. 26-27) recognized many years ago that certain natural silicic glasses have unusual sodium and potassium contents. Robert L. Smith of the U. S. Geological Survey strongly suspected that natural glasses which have undergone secondary hydration (Ross and Smith, 1955; Friedman and Smith, 1958), although fresh appearing, may have lost or gained significant amounts of certain constituents in addition to water, and warned colleagues against basing petrogenetic interpretations on chemical analyses of rocks containing hydrated glass. Lipman (1965), using data from the literature and unpublished data from the files of the U. S. Geological Survey, showed that many rocks containing large amounts of secondarily hydrated glass contained significantly lower amounts of sodium and silica than did primarily crystallized (Lipman, 1965, p. D2) rocks from the same units. As discussed by Lipman, these changes are almost certainly the result of leaching of the glass and by ion exchange with ground water.

MATERIAL STUDIED

During the study of several volcanic centers in southern Nevada over the past several years, the writer has collected nonhydrated glasses for chemical analysis wherever possible. Nonhydrated glasses are completely unaltered and exactly represent the composition of the magmatic liquids on solidification. Such glasses are preferable to crystallized material for

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<sup>2</sup> Present address: Department of Geological Sciences, Harvard Univ., Cambridge, Mass. 02138.