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VATERITE STABILITY

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ABSTRACT

Experiments involving electrical conductivity measurements of aqueous $CaCO_3$ solutions containing an excess of one or more of the polymorphic phases vaterite, aragonite, and calcite, indicate that in the unary $CaCO_3$ system a field of stability for vaterite exists at low temperatures. At one atmosphere pressure the maximum probable temperature for the vaterite-calcite equilibrium boundary and the vaterite-aragonite metastable equilibrium boundary is 10°C and 15°C, respectively. This information enables the probable low temperature phase relationships for the $CaCO_3$ system to be constructed.

With the exception of its occurrence in the Pesyanoe meterorite, each of the reported geologic occurrences of vaterite represents instances in which vaterite crystallized under *p-T* conditions outside its field of stability.

INTRODUCTION

Taken collectively, the many investigations of phase stability undertaken in the unary $CaCO_3$ system cannot be considered complete without definition of the stability field for the polymorphic phase vaterite. The presence of vaterite as a precipitate in laboratory preparations of $CaCO_3$ has been detected by numerous observers.[1] In contrast, the geologic occurrences of vaterite are apparently rare having been only infrequently documeted (Bentor *et al.*, 1963; Dufresne, 1962; McConnel, 1960). In each recorded instance vaterite is known to be metastable with respect to calcite and aragonite (Deer, Howie, and Zussman, 1962), yet its field boundaries for (meta)stability to this date remain to be determined. This paper reports the results of conductivity studies of $CaCO_3$ saturated aqueous solutions conducted at one atmosphere pressure which serve to delineate the equilibrium phase boundaries vaterite-calcite and vaterite-aragonite, thereby defining the field for vaterite stability.

Jamieson (1953) has demonstrated that equilibrium phase stability studies with the $CaCO_3$ system can be conducted at elevated pressures and temperatures through the indirect approach of measuring the electrical resistance of aqueous solutions of each polymorph. In aqueous solution the transition from a metastable phase to the stable phase proceeds extremely slowly; therefore, a metastable phase can closely approach equilibrium with its solution. In addition, since the ions released by each phase in solution are identical, the solubility of a me-

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[1] Fyfe and Bishoff (1968) and Bischoff (1968) contain extensive listings of references concerning laboratory preparations of metastable $CaCO_3$ phases.

tastable phase is independent of the presence of other less soluble, although more stable, phases. Experimental confirmation of the latter statement exists in that neither permutation of the order of insertion of phases into solution nor variations in the quanity of aragonite or calcite affects the steady state conductivity of vaterite solutions. This relationship also holds true for the steady state conductivity of aragonite solutions containing calcite. As a result of the above, the solubilities of each phase in aqueous solution are equal, and hence the conductivities of the respective solutions are equal, at a particular pressure and temperature corresponding to a point lying on either a two phase stable or a metastable equilibrium boundary.

EXPERIMENTAL

Resistance measurements over the range 26° to 96°C were carried out using a Freas conductivity cell immersed in an oil bath in conjunction with a Brown Electro-Measurements Impedence Bridge, Model 250-C, and General Radio Corporation Null Detector, Type 123B. The bridge was isolated from the 1000 cps generator by a General Radio Corporation transformer, Type 578B. Capacitance was balanced out by use of decade capacitors in shunt. The temperature of the cell-bath system was maintained to ± 0.2°C. De-ionized distilled water having a conductivity of less than 1.5×10^{-6}mho cm^{-1} was used for each determination and consequently, the CO_2 dissolved in solution never exceeded approximately 8 ppm (1.8×10^{-4}molal). Water corrections were not necessitated as such a correction never accounted for more than 1 percent of the measured conductivity.

Conductivity data was obtained for aqueous solutions prepared within the Freas cell. Powdered spectroscopic grade calcite, ground naturally occurring aragonite, and vaterite, prepared following the method of Favre (1946), were introduced into solutions in that order. Diffractometer analysis indicated that the aragonite was phase pure and that the vaterite contained traces of calcite. Subsequent to the insertion of each polymorph, the Freas cell was sealed and measurements taken until the resistance of the solution became constant in time. Apparent steady state conditions were usually observed after four to five days.

Since the equilibrium of a polymorph with its aqueous solution can be approached from both undersaturation and supersaturation by using appropriate procedures, one can interpret the steady state conductivity values that were observed in each instance as closely approximating those for a saturated $CaCO_3$ aqueous solution equilibrium determination if those values are equivalent. At constant temperature equilibrium is approached from undersaturation subsequent to the initial introduction of a polymorph into solution or, alternately, by rapidly reducing the temperature of a saturated solution, equilibrium can be approached from undersaturation at any desired lower temperature. Equilibrium can be approached from supersaturation by rapidly increasing the temperature of an already saturated solution to the temperature at which an equilibrium determination is desired. A close correspondence between values obtained by each procedure was observed with the temperature range 50° to 65°C. At lower temperatures the time requisite for steady state determinations arrived at from supersaturation was prohibitively long, and as a consequence only conductivity values reached from undersaturation were recorded.

RESULTS AND DISCUSSION

Figure 1 displays the difference between the conductivity of aqueous solutions of each polymorph as a function of temperature and contains

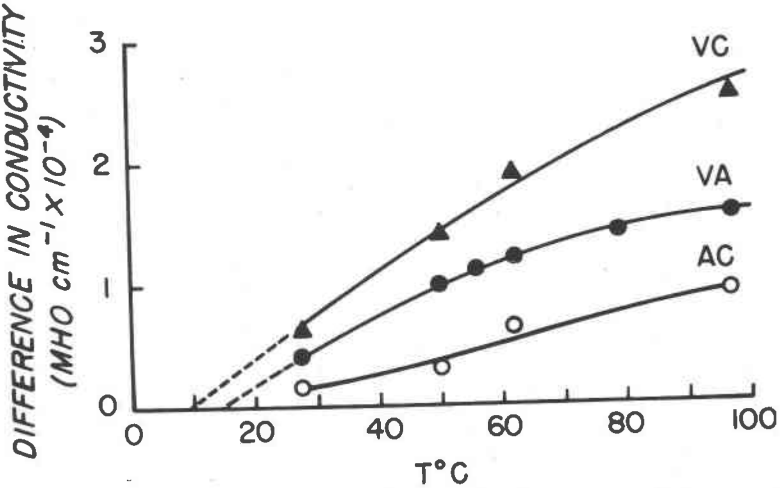

FIG. 1. Plot of difference in conductivity of saturated $CaCO_3$ aqueous solutions containing an excess of one or more of the polymorphic phases vaterite, aragonite, or calcite vs temperature. AC, results for solutions of aragonite and calcite; VA, results for solutions of vaterite and aragonite; VC, results for solutions of vaterite and calcite. Dashed lines represent extrapolations.

essential information relevant to vaterite stability. The difference in conductivity between vaterite and calcite solutions, curve VC, extrapolates to zero, marking the univarient boundary vaterite-calcite, in the neighborhood of 10°C. Extrapolation to zero difference of curve VA indicates that the vaterite-aragonite metastable equilibrium boundary at one atmosphere lies in the neighborhood of 15°C. Although such extrapolations are approximate, with the temperature indicated being the maximum probable upper limit, both a low temperature field of stability for vaterite and the relative stability of vaterite and aragonite within the calcite field are clearly indicated.

The relative densities of calcite, aragonite, and vaterite necessitate that the vaterite-calcite and vaterite-aragonite equilibirum boundaries have negative slopes. Each boundary must meet at the triple point calcite-aragonite-vaterite, at a *p-T* condition which remains unspecified by this study, as must also the calcite-aragonite equilibrium boundary. The latter, at present, is well defined only above 300°K (Goldsmith and Newton, 1970). These relationships are shown in Figure 2 which displays probable low temperature phase relationships for the $CaCO_3$ system. The calcite-aragonite boundary at lower temperatures is based on studies of Jamieson (1953). Relative stability of calcite, aragonite, and vaterite in low temperature fields is indicated within brackets, decreasing vertically.

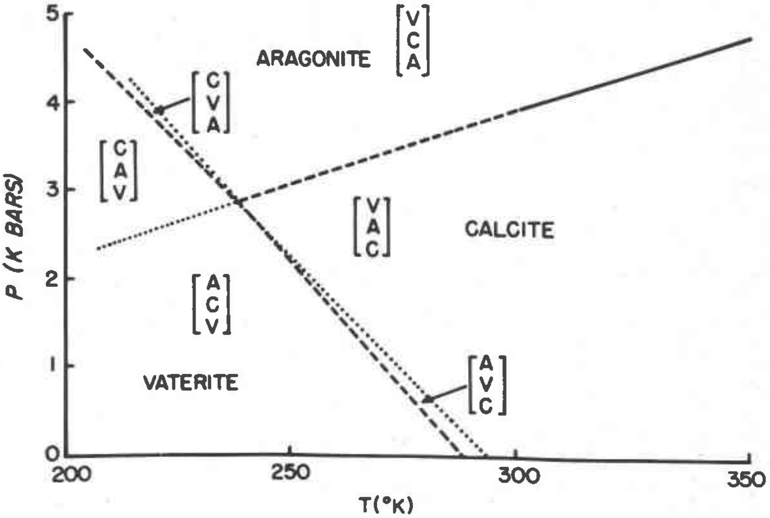

FIG. 2. Proposed low temperature phase relationships in the $CaCO_3$ system based on extrapolated data. - - - - stable equilibrium boundaries; · · · · · metastable equilibrium boundaries; —calcite-aragonite boundary from Jamieson (1953). The *p-T* coordinates of the triple point calcite-aragonite-vaterite remain undetermined.

VATERITE OCCURRENCES IN NATURE

Although rarely found in nature, the occurrence of vaterite has been recorded by a number of investigators. DuFresne *et al.* (1961) have reported the occurrence of vaterite exclusive of calcite, aragonite, and hydrous minerals in the Pesyanoe meteorite. These investigators have shown that the metorite once having cooled from temperatures of the order of 1100°C subsequently underwent several complex heating and cooling cycles. If one takes into account the temperatures to which the bulk material of the meteorite has been exposed, then it follows that the vaterite now present must necessarily have existed in the calcite modification at some point in its history. The subsequent transformation of calcite to vaterite, which evidently did take place, is allowable only within the vaterite stability field or a limited portion of the aragonite stability field. In either case the transformation is confined to low temperatures-the low temperature cycle.

Occurrences of vaterite essentially hydrothermal in origin have been reported by McConnel (1955) and Bentor *et al.* (1963). Probable temperatures prevailing at the time of vaterite crystallization prohibit the possibility that vaterite is an inversion product of calcite or aragonite, but rather imply its mode of formation to be metastable precipitation from aqueous solution within the calcite stability field. In these occurrences, subsequent to its formation, the vaterite has remained unsubected to either temperatures sufficient to overcome the kinetic barrier of its transformation to calcite, or, as noted by Northward *et al.* (1969), significant shearing forces.

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REFERENCES

BENTOR, Y. K., S. GROSS, AND L. HELLER (1963) Some unusual minerals from the "mottled zone" complex, Israel. *Amer. Mineral.* **48,** 924–930.

BISCHOFF, J. L., AND W. S. FYFE (1968) Catalysis, inhibition, and the calcite-aragonite problem, I, the aragonite-calcite transformation. *Amer. J. Sci.* **266,** 65–79.

——— (1968) Catalysis, inhibition, and the calcite-aragonite problem, II, the vaterite-aragonite transformation. *Amer. J. Sci.* **266,** 80–90.

DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock-forming minerals-Vol.* **5,** *Non-silicates.* London, Longmans, Green and Co. Ltd., 372 p.

DUFRESNE, E. R., AND E. ANDERS (1962) On the retention of primordial nobel gases in the Pesyanoe meteorite. *Geochim. Cosmochem. Acta,* **26,** 251–262.

FAIVRE, R. (1946) The physiochemical conditions for the precipitation of the three crystalline forms of calcium carbonate prepared by the double displacement of calcium. *C. R. Acad. Sci. Paris.* **222,** 140–141.

GOLDSMITH, J. R., AND R. C. NEWTON (1970) P-T-X relations in the system $CaCO_3$-$MgCO_3$ at high temperatures and pressures. *Amer. J. Sci.* **267-A,** 160.

JAMIESON, J. C. (1953) Phase equilibrium in the system calcite aragonite. *J. Chem. Phys.* **21,** 1385–1390.

MCCONNEL, J. D. C. (1960) Vaterite from Ballycraigy, Larne, Northern Ireland. *Mineral Mag.* **32,** 534–544.

NORTHWOOD, D. O., AND D. LEWIS (1969) Transformation of vaterite to calcite during grinding. *Amer. Mineral.* **53,** 2089–2092.

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