A NOTE ON THE HYDROTHERMAL SYNTHESIS OF SINGLE CRYSTALS OF SILICATES AND OTHER ROCK-FORMING MINERALS*

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Abstract

Single crystals of eucryptite as well as of numerous other minerals have been recently synthesized. The general technique involves placing the various components of a desired phase in separate compartments in a bomb and heating them under moderate to high pressures of water vapor. The materials diffuse together and solid phases nucleate and grow. The rate of availability of various metal components to a growing phase is very markedly a function of the *pH* of the solution.

During the last several years the writer has synthesized a considerable number of crystals of various silicates and other rock-forming minerals in crystals of sufficient size for goniometric and single crystal *x*-ray work. Among these have been various beryllium silicates, end members of feldspars, some micas, and a series of lithium-aluminum silicates, one of which is to be described in a forthcoming paper by M. Mrose. This note on the general method involved is presented with the thought that it may be of interest to mineralogists concerned with working out the properties of imperfectly crystallized naturally occurring minerals, and who are dissatisfied with the material nature sometimes provides.

The basic method is that of high pressure-high temperature hydrothermal synthesis, although the equipment involved is relatively simple. A bomb, the preferred design of which is shown in Fig. 2, is connected by means of a length of stainless steel capillary tubing to a pressure gage. Pressures may be obtained by partially filling the bomb with water before heating, or by connection to a pump. The bomb is heated in a thermostated furnace of convenient dimensions. The details of this bomb and its construction have been presented elsewhere (Kennedy, G. C., 1950). Bombs of this design, if made of appropriate materials, may be safely operated to temperatures of 800° C. and pressures of 2000 atmospheres.

The first step is that of the selection of the proper pressure temperature interval in which to carry out the synthesis. In general, rates of recrystallization of most minerals, exclusive of the sulfides, are extremely slow at temperatures below 400° C. Temperatures in the range of 500° to 700° C. may be satisfactorily used for most pegmatite minerals and vein

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minerals, providing the mineral under investigation does not have pressure sensitive polymorphs and does not contain a volatile. In general, also, the highest possible water pressure produces the most rapid recrystallization and the best growth, as the solvent power of superheated steam is essentially in proportion to its density.

Special problems are encountered in the synthesis of minerals which have pressure sensitive polymorphs. Well known examples of these are the transitions involving graphite-diamond, kyanite-andalusite, andalusite-sillimanite, kyanite-sillimanite, quartz-tridymite, albite plus nepheline-jadeite, and many others. Most of these are transitions of the *A*-*B* type shown in Fig. 1, where the boundary line between the stability fields of *A* and *B* is essentially a straight line extending to higher pressures at higher temperatures, although examples of transitions with negative slopes are known. The slope of this line is equal to $\Delta H/T\Delta V$ where ΔH is the heat of the transition, T is the temperature and ΔV is the volume change of the transition. The boundary curve between two minerals showing this type of transition will be *absolutely* straight only if the heat capacities and the compressibilities of the two phases remain unchanged with changes in pressure and temperature, or in case the changes, as they affect the terms ΔH and ΔV, exactly cancel each other out. Neither of these conditions exactly hold, but, over the range of possible laboratory experimental operations, hold as close first approximations. It is obvious that in order to bring about transition of phase *B* to phase *A*, combination of either high temperatures and high pressures or low temperatures and low pressures is required. Many difficulties are

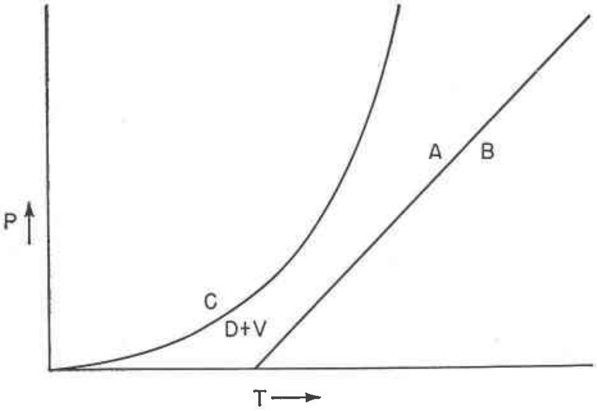

FIG. 1. Types of stability fields in a pressure versus temperature plot.

encountered in successfully bringing about these transitions. In many cases the rate of the transition is so slow at low temperatures as to make the transition impractical. Apparently the transition rate of graphite to diamond, phase *A* on our diagram, approaches zero at room temperature, even though the appropriate pressure be applied to graphite to bring it into the diamond stability field. Correspondingly, at the high temperatures where the reaction rate is appreciable, the pressure required to be in the stability field of phase *A* may be beyond that readily obtainable in the laboratory at the high temperatures. By contrast, however, transitions in the reverse direction, from *A* to *B*, are readily brought about in most cases by heat alone or heat in conjunction with some fluxing agent such as water.

Minerals which contain a volatile generally have stability fields of a somewhat different shape and have field boundary curves as shown in Fig. 1 of the *C-D* plus volatile type. In reactions of this class, the pressure axis of the graph shown in Fig. 1 is not the pressure on the mineral, but rather the partial pressure of the volatile involved at a transition temperature. High confining pressure on the mineral, in addition to the pressure of the volatile on the mineral, generally pivots the boundary curve in a lower temperature direction. The volatile involved in such a reaction may be CO_2, as in the case of quartz plus calcite→wollastonite plus carbon dioxide. CO_2 is involved in similar reactions for all the carbonate minerals.

Analogous reactions are found in most of the minerals which contain water. Among these reactions are such common ones as pyrophyllite →sillimanite plus water, paragonite→albite plus water, muscovite→orthoclase plus sillimanite plus water, etc., as well as a host of much more complex reactions such as those involved in the transition of amphiboles to pyroxenes. Boundary curves of this shape also delineate the stability fields of such simple reactions as those in which a mineral goes from one state of hydration to another, as in the case of nickel sulfate heptahydrate→nickel sulfate hexahydrate.

Similarly shaped boundary curves separate the stability field of the various sulfide minerals. At a given temperature most sulfide minerals are stable over only a very limited range of sulfur vapor pressures. At a higher sulfur vapor pressure the mineral reacts to form a mineral or minerals of higher sulfur content. At a lower sulfur vapor pressure, the mineral reacts to form a phase or phases of lower sulfur content. This may be done experimentally in the laboratory and characteristic "replacement" textures result. In this regard it is interesting to note that the usual paragenetic sequence observed in the sulfide minerals is the same sequence as is obtained by arranging the minerals in order of descending sulfur vapor pressure at a given temperature.

The equation of the field boundary curve of the *C-D* plus volatile type is again the Clapeyron equation of the form $dP/dT=\Delta H/T\Delta V$. Over the low volatile pressure range of the boundary curve, the equation of state for the ideal gas, $PV=RT$, may be substituted in the ΔV term neglecting the volume of the solid phase, thus the equation simplifies to the form $ln\ P=\Delta H/RT+C$, where C is the integration constant. At higher pressures much more complex formulations result, as the gases, such as water, depart sharply from ideality and the volume of the solid cannot be conveniently neglected. Existing gas data are sufficient, however, so that for most purposes only a single point on the curve need be determined experimentally and the position of the remainder of the curve may be computed with adequate accuracy.

The fact that hydration-dehydration reactions in the silicates must show a boundary curve of the *C-D* type is not fully appreciated by some of the present workers in the field of hydrothermal experimentation. An example of this is in recent work on the system alumina silica-water. This writer, in collaboration with G. J. F. MacDonald, has determined the transition pressure of the pyrophyllite-mullite reaction. The experimentally determined points are reasonably close to calculated values and theory and experiment are in accord. However, a recent paper, shows this as a reaction taking place at a temperature of 575° C. at all water pressures, ranging from 2000 p.s.i. (130 bars) to 28,000 p.s.i. (1900 bars). Such results could only approximately obtain if the volume of water vapor involved in the reaction were independent of pressure; whereas actually volume changes several fold in magnitude take place over this pressure interval.

It is significant to note that the vapor pressure, with which a crystal containing a volatile is stable, only becomes zero at a temperature of zero on the absolute scale, though the reaction rate may be negligible at temperatures as high as 600° absolute. Were there no carbon dioxide in the air, for example, and if the reaction rate was sufficiently rapid, calcite with quartz would be metastable and would break down to form wollastonite at room temperature.

The problems, therefore, in synthesizing crystals of these substances are obvious. At temperatures of 500° C. to 600° C. where rates of crystal growth are rapid, very large water pressures or pressures of some other gas may be required to reach the stability field of some of the volatile containing silicates. Conversely, difficulty is encountered in synthesizing some of the anhydrous silicates by hydrothermal means. If the vapor pressure of water is maintained high enough to promote rapid recrystallization, the hydrated phase may be obtained. This indeed is the problem in kyanite synthesis. Water vapor pressures of more than a few atmospheres, at temperatures where kyanite is presumed to be stable, will produce the hydrated phase pyrophyllite. For such cases, a solvent other than water must be found.

The techniques of producing single crystals of a mm. or more in dimensions are relatively simple for most minerals once the stability field of the mineral has been found, providing that temperatures of 400° to 700° C. may be employed and water pressures of 1000 to 2000 atmospheres are usable. A stoichiometric mixture of the finely powdered oxides is generally first prepared and held at temperature and pressure in the bomb for a few days. At the end of this time the bomb product is examined either microscopically or by *x*-ray techniques. If the reaction runs in the right direction, the product is generally made up of exceedingly fine crystals, for maximal nucleation is present under such conditions. Occasionally crystals of a millimeter or more result, but more usually the powder emerges from the bomb as a cake of crystallites.

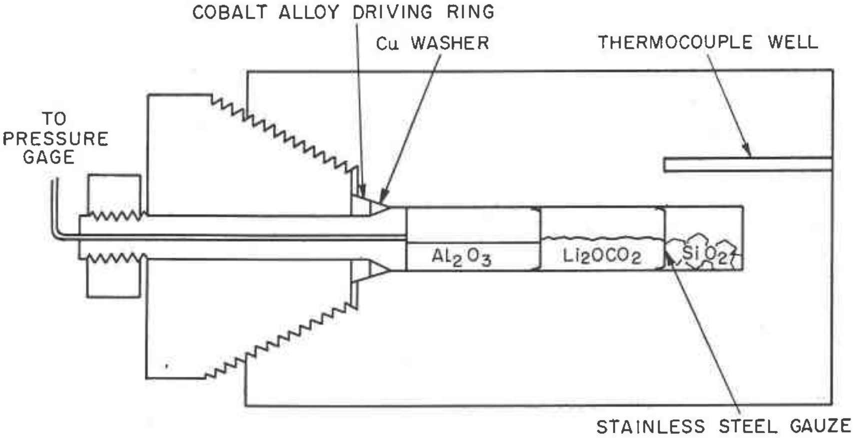

FIG. 2. Bomb showing arrangement of ingredients in eucryptite synthesis.

The bomb is next compartmented by the use of platinum or stainless steel gauze, as is illustrated in Fig. 2 for the case of the eucryptite synthesis. The various ingredients are placed in the separate compartments. The object of this arrangement is to force the various oxides to migrate by solution and diffusion in the dense hot water vapor to a common center or centers, where the appropriate phase will form and nucleate out. Such an arrangement greatly cuts down the number of crystal nucleii formed. A small number of larger crystals are formed instead of a large number of small crystals. Ingerson and Tuttle (1947) have described an arrangement, different in detail but similar in principal, used in the synthesis of single crystals of willemite. Though a single phase may form when a stoichiometric mixture is used, the common result is that a large number of different phases will form under the conditions as described above. In the case illustrated, a series of phases, rich in lithium to poor in lithium, including eucryptite, were found extending from the lithium end of the bomb to the aluminum end of the bomb. At least two of these phases yielded optical and *x*-ray data unlike those of any compounds for which the writer could find data in the literature. These may well have been metastably formed compounds.

In many syntheses it is desirable to speed up or slow down the rate at which certain ions are available to the growing crystal. Rate at which silica is made available to the growing crystal, for instance, may be readily controlled by varying the grain size of the silica at its source in the bomb. The silica supply may range from amorphous powdered silica to a single lump of crystalline quartz. If alkali is tolerable in the system, NaOH or KOH will greatly step up the rate at which silica is available.

The rate at which the metals ions is made available can be controlled by varying the *pH* of the solution used in the bomb. A few drops of HCl will permit volatile metal chlorides to form which readily move by diffusion in the dense vapor. This does not seem always desirable in the case of some of the aluminum silicates, where, under slightly acid conditions, the supply of aluminum may be so great that spontaneous nucleation is extremely rapid near the silica source, and large numbers of small crystallites are formed. It is to be remembered that aluminum is amphoteric, and under such conditions a neutral or weakly acid solution appears to give the best results. The use of acid solutions, particularly at high temperatures and low pressures, present many problems. Under these conditions, a chemically inert liner, generally platinum, must be used to protect the bomb walls from excessive corrosion and the sample from contamination. With such an arrangement, crystals of various metal oxides may be grown readily, but here silicates are exceedingly difficult to grow, for silica appears to be of very slight solubility in low pressure acid gases.

It is thus possible in most cases, by careful attention to *pH* and to the state of subdivision of the starting ingredients, to obtain an arrangement whereby the desired single crystals will grow at an appreciable rate and spontaneous nucleation may be held to a minimum. In the case of the eucryptite synthesis, coarse lumps of quartz were used for the silica supply, aluminum hydroxide was used for the aluminum supply, and lithium carbonate for the lithium supply. The dry bomb was first brought to temperature, 600° C., with the pressure line open. This served to permit dissociation of some of the lithium carbonate to lithium oxide plus carbon dioxide. Before the dissociation had gone to completion, however, the pressure line was connected to the bomb and the pressure brought to 2000 atmospheres by pumping in water. The resulting solution was weakly acid as some CO_2 continued to be evolved by the lithium carbonate. The bomb was held at temperature and pressure for one week. The run contained several of the lithium aluminum silicates, all well crystallized. Among the phases present was eucryptite in crystals 1 to 2 mm. length.

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