THE SYSTEM, WATER—SODIUM DISILICATE

G. W. MOREY AND EARL INGERSON.

ABSTRACT.

An apparatus has been constructed for studying the lowering of melting point of silicates when heated in steam at high pressures, and the results of a study of the system, water—sodium disilicate, are presented.

Water is an essential constituent of rock magmas, in which it exerts a profound effect both on physical characteristics such as viscosity and especially on the crystallization phenomena, which it affects not only by lowering the temperature of separation of crystalline minerals but also by determining the composition of the minerals which separate. In addition, the concentration of water in the crystallizing magma affords a source of internal pressure[1] which increases as cooling and consequent crystallization progress, up to the region of maximum pressure.

The study of the effect of water on mineral formation, the hydrothermal synthesis of minerals, owes its beginning largely to the French investigators Daubrée, St. Claire Deville, and Friedel and Sarasin. The voluminous literature of the subject has recently been critically summarized by Morey and Ingerson,[2] who point out that almost all the published work deals with the synthesis of silicate minerals by heating their components in closed vessels under conditions frequently not given and never either resembling the conditions found in nature or approximating to the equilibrium conditions in the systems under investigation. Clearly such studies are of little more than passing interest. There is need for the development of systematic information leading to a knowledge of the part played by water in silicate equilibria; of the phase equilibrium relationships in systems containing both water and silicates. Only on such information can be based a competent theory of the chemistry of the processes of magmatic differentiation, of mineral formation, and ore deposition.

The simplest systems that are pertinent to the problem are those binary and ternary systems containing water and silicates of the alkali metals. A beginning of such a study was made

[1] Morey, G. W.: J. Wash. Acad. Sci., 12, 219, 1922; J. Geol., 32, 291, 1924.
[2] Morey, G. W., and Ingerson, Earl: Econ. Geol., 32, 607, 1937.

by Morey and Fenner[3] with the system, water—potassium metasilicate—silica, which was made possible by the fortunate circumstance that over a wide range of composition the solutions formed could be quenched and the equilibria frozen by chilling the steel bomb used as a container. Such a method is not generally applicable, and a more powerful one had to be devised.

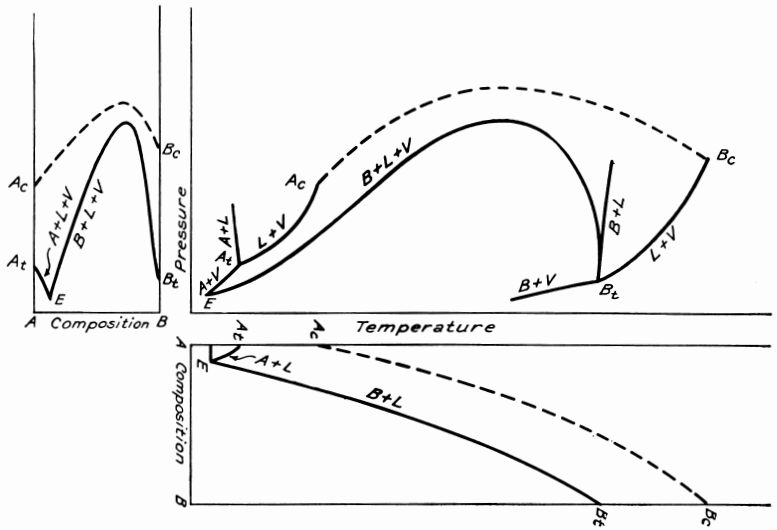

Fig. 1. Projections on the temperature-concentration, temperature-pressure, and pressure-concentration planes of a solid model which gives a diagrammatic representation of the phase equilibrium relationships in a binary system with components of widely different volatility, in which the critical or plait point curve is not intersected by the solubility curve. A_t and A_c, and B_t and B_c, represent the triple and critical points for the two components, respectively. E is the binary eutectic.

The new method, and its application to a simple binary system, are described below.

The theory of systems containing volatile components such as water together with non-volatile components such as silicates has been discussed by several authors, including Morey and Ingerson, who give references to other papers on the subject. In general the solubility or fusion curve is continuous from the eutectic or cryohydrate temperature to the melting point of the non-volatile component, although there are complications when

[3] Morey, G. W., and Fenner, C. N.: J. Am. Chem. Soc., 39, 1173, 1917.

critical end-points are met with or if the components become immiscible. For our present purpose these complications may be ignored, and discussion confined to the simple case illustrated diagrammatically in Fig. 1, in which are shown the projections of the solid P—T—X model on the temperature-concentration (T—X), pressure-temperature (P—T), and pressure-concentration (P—X) planes. In the T—X diagram, the temperature falls along the three-phase curve, B + L, which gives the simultaneous values of temperature and composition in the univariant system, solid + liquid +vapor. The freezing point of B is lowered on addition of the component of greater volatility until the eutectic E is reached. In the corresponding P—T projection are shown values of the vapor pressure of the solutions of composition given in the T—X diagram. It will be observed that the vapor pressure of these solutions first rises to a maximum as temperature is lowered, then falls to the eutectic at E. In the P—X projection are shown corresponding values of composition and vapor pressure. The steep rise of the curve is a usual characteristic of such systems.

We are especially interested in the upper part of the solubility curve, that is, in the lowering of freezing point of silicates on addition of water, and the relation between this lowering of freezing point and pressure. In order to investigate this we have constructed an apparatus which makes it possible to apply to meltings made in an atmosphere of steam at high pressures the "quenching method" so extensively used in the Geophysical Laboratory. By making a series of quenches under a constant pressure of steam, the freezing point of the solution at that temperature can be determined, and from a series of such measurements at constant pressure the P—T curve can be determined. Analysis of the quenches just at the liquidus gives the composition of the solution, and thus enables the determination of the three variables, pressure, temperature, and composition. It should be emphasized that in these experiments we are interested only in the saturation surface representing coexistence of solid, liquid, and vapor, not in the effect of pressure on melting point in the absence of vapor. The apparatus and method are evidently capable of solving many problems in this unexplored field. Our present study is confined to the system, H_2O—Na_2O—SiO_2, and in this paper the results will be restricted to the P—T curve of the binary system, H_2O—$Na_2O.SiO_2$.

The construction of the apparatus is illustrated by the dia-

TABLE I.

$Na_2O.2SiO_2$ in Steam up to 2000 lb./sq. in.

Run	Pressure lb.	Temp. ° C.	Time	Result
1	200	828.2	20 min.	Slightly sintered; crystalline.
2	200	843.3	20 min.	Glassy rim; crystals in center; not enough time.
3	200	843.3	30 min.	Top frothed; bottom glassy with crystals; not enough time.
4	200	835.1	2 hrs.	Glassy.
5	200	831.6	2½ hrs.	Glassy rim; crystals in center.
6	200	829.6	18 hrs.	Glassy rim; crystals in center.
1	500	784.9	6 hrs.	Sintered; crystalline.
2	500	807.7	4 hrs.	Sintered; crystalline.
3	500	819.1	16 hrs.	Glassy; frothed.
4	500	813.4	16 hrs.	Glassy; frothed.
5	500	810.9	16 hrs.	Sintered: crystalline.
6	500	812.4	12 hrs.	Glassy; center frothed.
7	500	811.9	20 hrs.	Glassy; frothed.
1	1000	805.4	16 hrs.	Glassy; top frothed.
2	1000	793.8	18 hrs.	No quench; frothed; probably above liquidus.
3	1000	789.3	14 hrs.	Glassy; top frothed.
4	1000	757.5	6 hrs.	Sintered; crystalline.
5	1000	773.1	20 hrs.	Sintered; crystalline.
6	1000	781.5	14 hrs.	Glassy; ran out of foil.
7	1000	777.4	6 hrs.	Sintered; crystalline.
8	1000	779.3	14 hrs.	Glassy.
1	2000	746.6	16 hrs.	Glassy.
2	2000	718.4	1½ hrs.	Not sintered.
3	2000	727.3	14 hrs.	Top part frothy, but crystalline.
4	2000	732.3	1½ hrs.	Glassy.
5	2000	729.2	16 hrs.	Top frothed; center crystalline; bottom some clear glass.
6	2000	730.4	18 hrs.	Glassy; top frothed.
7	2000	730.4	14 hrs.	Glassy; frothed.
8	2000	730.4	14 hrs.	Glassy; frothed, except center.

grammatic sketch shown in Fig. 2 and a photograph of the assembly is shown in Fig. 3. The central part of the quenching furnace, F, is much like the quenching furnaces used for the study of anhydrous systems. A refractory tube, one-half inch in internal diameter and eleven-sixteenths inch external diameter, is wound with 14.5 meters of 0.6 mm. platinum—10 per cent rhodium wire, giving a resistance of 10 ohms at room temperature.

The furnace is enclosed in a gas-tight bomb of stainless steel (Carpenter No. 2), six inches in external diameter, closed at

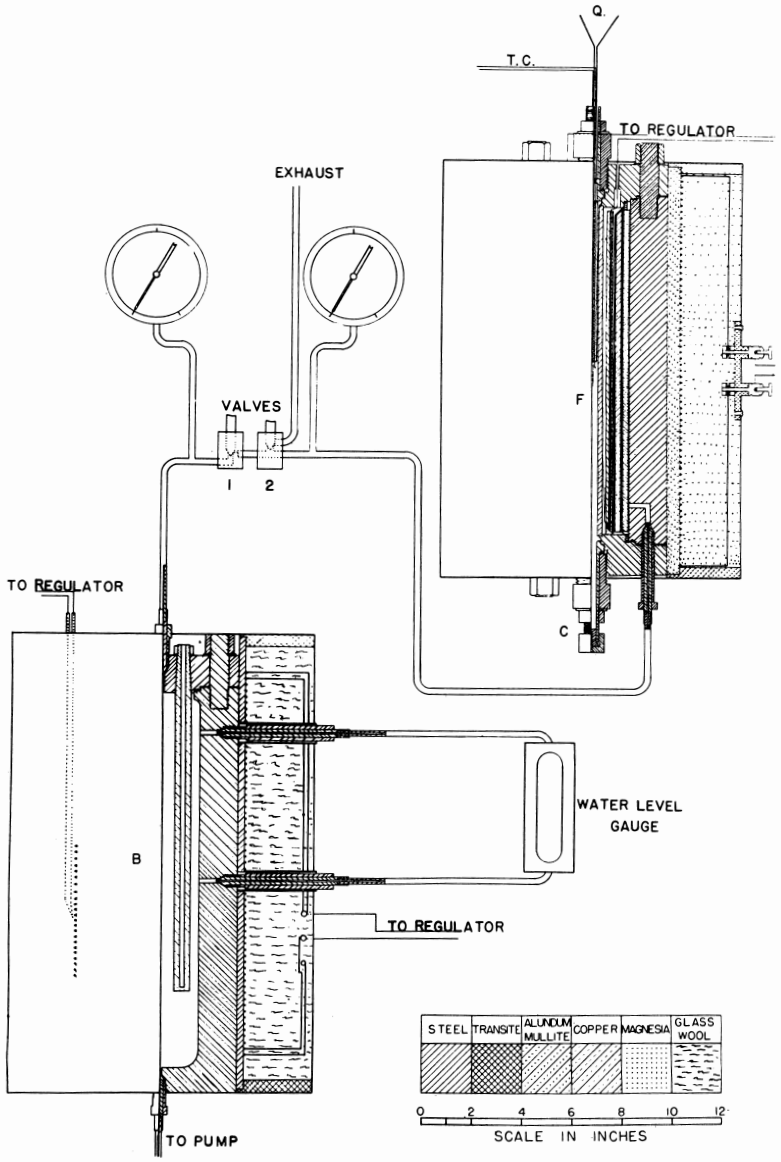

Fig. 2. Diagrammatic representation of an apparatus for quenching in steam at high pressure.

top and bottom by stainless steel covers, bolted down, and the joint made tight with a gold washer, the closure being of the

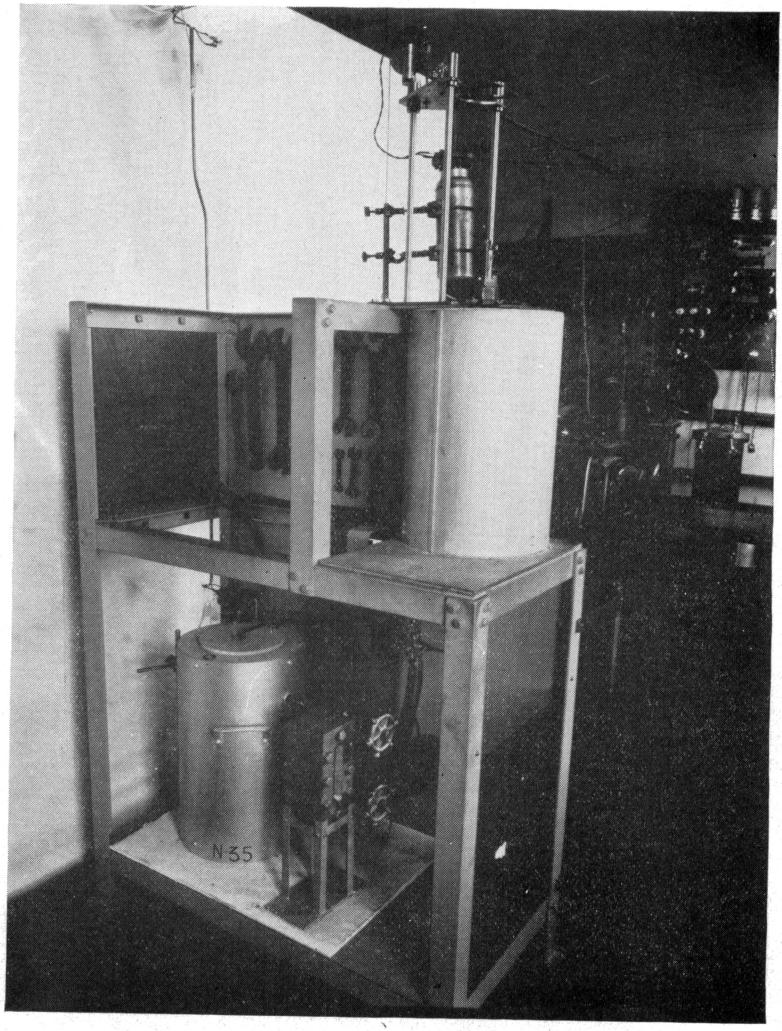

Fig. 3. Assembly of an apparatus for quenching in steam at high pressure.

type customarily used in this Laboratory. The bomb is provided with an inlet tube for the steam, and the necessary fittings for introducing the furnace leads, quenching leads and thermo-

couple wires, and for introducing and removing the charge. Between the furnace and the bomb are two cylindrical platinum baffles, one tight at the top, the other tight at the bottom, separated from each other, the bomb, and the furnace by three thick "sillimanite" tubes. This system of baffles prevents convection currents and ensures that the steam is heated to temperature before it comes in contact with the charge. Surrounding the stainless steel bomb is a furnace which serves to maintain the entire bomb at a temperature of about 500°, or lower if desired.

The charge, wrapped in platinum foil, is held in the hot spot of the high-temperature furnace by a porcelain ring suspended by a fine platinum wire from the quenching leads, Q. The quenching leads and thermocouple wires pass through limestone and talc packings in a plug fitted to the upper cover of the bomb, and made tight by a copper washer and the usual type of closure.

The temperature of the inner furnace is held constant by a Roberts wheatstone-bridge type furnace regulator, developed for that purpose at this Laboratory. The temperature of the outer furnace is controlled by a series rheostat, and requires no regulation.

Steam is generated in the boiler, B. The construction is similar to that of the bomb, except that simple cone-type high-pressure connections are used instead of the plugs necessary on the bomb. The metal is Carpenter's stainless steel No. 3. Insulation is with glass wool. A water-level gauge and a high-pressure pump make it possible to fill the boiler when it is in operation. Regulation is by means of a thermocouple placed almost against the heating coil, used in connection with a Leeds and Northrup Micromax regulator. A chromel-alumel thermocouple gives very good regulation below 270°, and above that two platinum—platinum rhodium couples in series are used.

The steam is led through a double valve and enters the bomb through the side. It thus is constrained to pass up and down through the baffle system before it enters the inner furnace tube at the bottom and comes into the hot spot of the furnace. The system of baffles has proved perfectly satisfactory in preventing fluctuations of temperature and minimizes drift of the hot spot when the pressure is changed.

The valve block contains two valves, one of which (1) separates the boiler and bomb, and the other (2) enables the bomb to be exhausted. Pressure gauges on each side of the valve

are used for general control. They are calibrated regularly against each other and against a dead-weight gauge, and during each run by measuring the temperature of the water in the boiler and comparing with steam tables.

The details of a run with this apparatus are as follows. A charge of about 20 milligrams of anhydrous material, wrapped in platinum foil, is suspended from the quenching leads. It makes little difference whether the initial material is crystalline or glassy. The plugs are tightened, and the temperature and pressure are brought to the desired values and maintained long enough for equilibrium to be reached. A heavy current is then passed through the quenching leads, Q, melting the fine wire supporting the charge, which drops into the quenching cup, C. The temperature of this cup is kept slightly above that of the boiler by means of a small supplementary heater, not shown.

The steam is then blown off by opening the exhaust valve after closing the intermediate valve. The screw cap is removed from the cup, and the charge taken out and examined with the petrographic microscope, to ascertain if it is all glassy and hence was above the liquidus. If the charge is found to contain some crystals, these are identified by determining their optical properties.

By a series of such quenches at constant pressure, with initial anhydrous material of the same composition, the liquidus at that pressure can be obtained; and by repeating at a series of pressures and a series of compositions of anhydrous materials, the entire system within the range of the apparatus can be worked out with certainty and precision comparable to those obtained in anhydrous quenchings. Below the critical point of water the boiler used affords the most convenient source of water pressure, and the precision with which the vapor pressure curve of water is known gives an exact knowledge of the pressure. At higher pressures dependence must be placed on gauges.

We have investigated in the manner described above a part of the system, H_2O—Na_2O—SiO_2. Anhydrous melts of several compositions have been prepared and the liquidus temperatures determined at one or more pressures. In only one case, sodium disilicate, $Na_2O.2SiO_2$, has a series of experiments at various steam pressures been completed. These are summarized in Table I. Fig. 4 shows the P—T diagram for the part of the binary system, H_2O—$Na_2O.2SiO_2$, which has been studied

The pressure increases more rapidly as the temperature falls, a circumstance to be expected from thermodynamic considerations in systems in which the volatile component is far above its critical temperature and is only slightly soluble. The maximum pressure has not been reached. It will be recalled that in the system, H_2O—$K_2O.2SiO_2$, the maximum was at about 75 atmospheres pressure, 600°, and 4 per cent H_2O by weight.

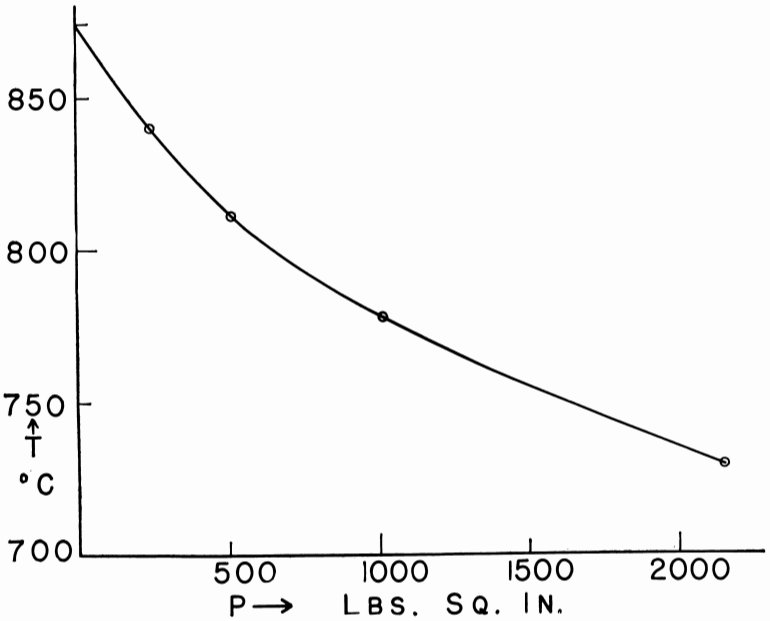

Fig. 4. Pressure-temperature diagram for solid-liquid-vapor equilibrium in the system, H_2O—$Na_2O.2SiO_2$.

The possibility of an appreciable volatilization of sodium oxide with steam at high pressure was of interest, and experiments were made with sodium metasilicate, $Na_2O.SiO_2$, to find if there was any change in composition under rather extreme conditions. No change could be detected.

This study, which is part of a comprehensive research program concerning water in alkali silicate melts, has been aided by means of special funds made available to the Carnegie Institution of Washington by the Carnegie Corporation of New York.