

## THE ACTION OF HOT WATER ON SOME FELDSPARS

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### ABSTRACT

Hot water was passed over the feldspars contained in closed bombs, the total amount of solution weighed and analyzed, and the material remaining in the bomb studied with  $x$ -rays and the petrographic microscope. At 350° C., 5000 psi, the solution obtained from orthoclase and from albite contained over 90% of the dissolved material in the feldspar ratio. At lower temperatures and pressures, 200° C. and 2000 psi, and 100° and 40 psi, albite was decomposed in greater proportion. At 350° and 2000 psi a large amount of analcime was found in the albite experiment, but none at the lower temperatures.

There have been many studies of the reaction between water and feldspars. Some of these were in the earliest periods of hydrothermal experimentation, when pressures were not controlled and not known, and the emphasis was chiefly on the synthesis of the feldspars. Other experiments dealt with the decomposition of feldspars by acid, alkaline, or salt solutions. These experiments have been critically summarized by Morey and Ingerson (1937). Bowen and Tuttle (1950) studied the system  $H_2O-NaAlSi_3O_8-KAlSi_3O_8$  at pressures up to 2000 bars and temperatures up to 800° C. However, there have been few studies of the effect of water alone below its critical temperature—just hot water. Norton (1937) studied the alteration of orthoclase, anorthite, and albite by liquid water containing from 1 to 23% carbon dioxide at temperatures from 225° to 350° C. The experimental arrangement was such that the finely powdered feldspar was subjected to a continuous extraction by freshly condensed liquid for 10 to 33 days. Albite was but slightly altered, with possible formation of paragonite; orthoclase was converted to sericite.

The apparatus we used (Fig. 1) was similar to that used by Morey and Hesselgesser (1951) in their study of the solubility of some minerals in superheated steam. Distilled water is pumped into a pressure line, in which there are a pressure gauge, pressure cylinder, ballast cylinder, filter, and a bomb made from 303 stainless steel. The connecting high-pressure tubing also is of stainless steel. The pressure gauge is a calibrated Bourdon gauge; the pressure regulator a Baldwin fluid pressure cell, the sensitive elements of which are two Baldwin strain gauges used in conjunction with a special Brown electronic potentiometer. The ballast cylinder has a volume of 2240 ml., and the leads to it are so arranged that the flow may be in either direction. In the pressure line, just before the bomb, is a small cylinder which contains amberlite IR-120 (H) cation exchange resin followed by a porous stainless steel filter with a mean pore

opening of 20 microns. This is to remove any contaminant, especially iron oxide resulting from corrosion in the pump or pressure line. The water passes through the heated bomb, then through a zig-zag cooling coil, to the throttling valve, after which it is collected, weighed, and analyzed. The furnace has two windings, each of which is controlled by a Brown electronic controller, using chromel-alumel thermocouples inserted in wells as indicated. Temperature is measured by platinum-10%

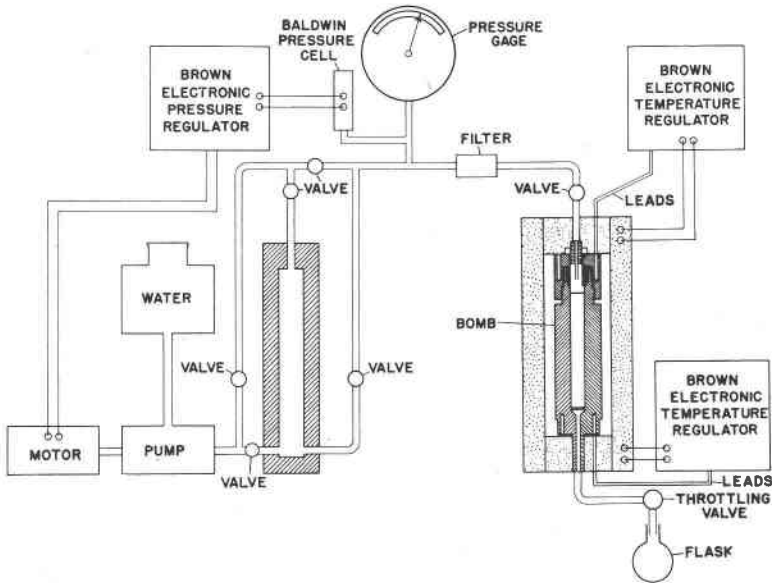


FIG. 1. Diagrammatic outline of pressure apparatus. Distilled water is pumped into the pressure line, which includes a reservoir, a reading gauge, and a regulator to maintain the pressure constant. The solid material is contained in the bomb and heated in the regulated electric furnace. The water is changed to steam, passes over the solid and out of the bomb, constant pressure being maintained on the cooled water until the throttling valve is reached. The condensed water is collected, weighed, and analyzed.

rhodium thermocouples similarly placed in wells in the bomb, and the two temperatures are maintained the same within  $\pm 2^\circ \text{C}$ .

The first series of runs were made at  $350^\circ \text{C}$ ., 5000 psi, using microcline from the Derry mine in Quebec, crushed to pass  $1/4''$  mesh, and held on a 20-mesh screen, and the fines were removed by washing. The feldspar rested on a porous stainless steel filter, having a mean pore opening of 20 microns, and was covered with a similar filter. The solution was caught in 3-liter flasks, acidified with HCl, and evaporated to dryness in large porcelain dishes. Analyses were made by standard methods (Hillebrand and Lundell, 1929). The  $\text{SiO}_2$  was filtered off after the usual treat-

ment with concentrated HCl, the filtrate again evaporated to dryness, and the precipitate digested overnight with dilute HCl. The combined  $\text{SiO}_2$  was ignited to constant weight, evaporated with HF and  $\text{H}_2\text{SO}_4$ , and the  $\text{SiO}_2$  determined by difference. The residue was  $\text{Al}_2\text{O}_3$ , which was added to the main portion.  $\text{Al}_2\text{O}_3$  was determined by double precipitation with  $\text{NH}_4\text{OH}$  and ignition to constant weight. The ammonium salts in the filtrate were removed by heating with concentrated  $\text{HNO}_3$ , the residue converted to sulfate, and weighed as  $\text{K}_2\text{SO}_4$ . It was difficult to be sure all the material was removed from the large porcelain dish, but the same dish was used repeatedly without further washing for each determination, so that the total error from this source was small.

This run lasted 103 days. The total weight of solution was 194,432 g., and the total weight of dissolved material 52.1564 g., which is 268 parts per million. This is not a true solubility. None of the results reported here represent a true solubility, but represent rates of reaction under the conditions of the experiment. The amounts of constituent oxides dissolved were:  $\text{K}_2\text{O}$ , 8.9268;  $\text{Al}_2\text{O}_3$ , 8.6760;  $\text{SiO}_2$ , 34.5536. These are in the weight ratio of 1.03:1:3.98, or in the mole ratio of 1.11:1:6.76. If all the  $\text{Al}_2\text{O}_3$  is calculated to orthoclase, it would give 47.3580 g., or 90.8%. Under the requisite conditions, this presumably could be transported and could crystallize out as orthoclase.

The remainder in solution, after subtracting  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  corresponding to the above amount of orthoclase, is an excess of  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ . The amounts are:  $\text{K}_2\text{O}$ , 0.9091 g.;  $\text{SiO}_2$ , 3.8893. These are in the molecular ratio of 1:6.71.

The residue remaining in the bomb was studied with both the petrographic microscope and  $x$ -rays. There was much orthoclase remaining, both as large fragments and as fine powder. The large fragments had a white coating, which proved to be muscovite and boehmite,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The greater part of the fine-grained material in the bomb was boehmite. If  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$  is decomposed and leaves a residue of either muscovite or boehmite, the solution should contain excess  $\text{K}_2\text{O}:\text{SiO}_2$  in the ratio of 1:6. The ratio found was 1:6.71. This could be due to analytical error or to formation of an amount of a clay mineral too small to detect with either the microscope or  $x$ -ray.

Three separate runs were made with albite. The first of these was at  $350^\circ \text{C}$ ., 5000 psi, and lasted 38 days. It was terminated by the exit tube being stopped up with analcime,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and there was some analcime on the filter disc above the albite. The total weight of solution obtained was 78,005 g. The amounts of constituent oxides dissolved were:  $\text{Na}_2\text{O}$ , 2.8358 g.;  $\text{Al}_2\text{O}_3$ , 4.4307 g.;  $\text{SiO}_2$ , 17.5250 g.; a total of 24.7915 g., corresponding to 318 parts per million dissolved material. The dis-

solved material has a weight ratio  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$  of 0.64:1:3.96, and a mole ratio of 1.05:1:6.71. The amount of albite corresponding to the amount of dissolved alumina is 22.79 g., or 91.9% of the total solution. The excess  $\text{Na}_2\text{O}$  is 0.1415 g. and excess  $\text{SiO}_2$ , 1.8624 g., a mole ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  or 1:13.6.

The material remaining in this bomb was in part a fine powder, in part original grains of albite covered by a thin white coating, and there was well-formed analcime between the upper filter plate and the top of the bomb. The white coating on the albite proved to be largely muscovite, with some paragonite. The Amelia County, Va., albite was from the same lot as that used by Day and Allen (1905), which contained 11.47%  $\text{Na}_2\text{O}$  and 0.20%  $\text{K}_2\text{O}$ . The amount of muscovite which would correspond to all the  $\text{K}_2\text{O}$  corresponding to the known amount of  $\text{Na}_2\text{O}$  which was found in the solution would be 0.41 g. Practically all the  $\text{K}_2\text{O}$  must have been held in the surface as muscovite. This reaction has interesting implications with regard to the common sericitic alteration of plagioclase. We are grateful to our colleague Dr. H. S. Yoder for making an intensive study of the muscovite, which proved to be exceptionally good crystals of a 1M muscovite. The fine powder in the bomb was chiefly boehmite,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , together with some analcime.

If the albite were completely dissolved as albite, or if it were completely decomposed leaving boehmite, the mole ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  in the solution should be 1:6. The ratio found was 1:13.6. This excess could be caused by the formation of analcime,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . The amount of analcime calculated from the 1.8629 g. of excess silica is 6.5 g., which probably is of the right order of magnitude.

A similar run was made with a powdered albite at 200° C. and 2000 psi. In this case the total weight of water collected was 279,438 g. The total amount of material dissolved was 14.6594 g., which is equivalent to 53 parts per million. The total of the analyses gives:  $\text{Na}_2\text{O}$ , 2.1127 g.;  $\text{Al}_2\text{O}_3$ , 2.0167 g.;  $\text{SiO}_2$ , 10.5300 g. This is a weight ratio of  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$  of 1.05:1:5.22, or a mole ratio of 1.72:1:8.86. If the alumina is calculated to albite, it gives 10.372 g. albite, or 70.7% of the total amount of dissolved material. The excess of  $\text{Na}_2\text{O}$  is 0.8873 g.; of  $\text{SiO}_2$ , 3.2626; which gives a mole ratio of 1:3.8. Examination of the residual material showed no analcime whatever, only residual albite, boehmite, and some kaolinite. The kaolinite lines were strong.

Another run was made with powdered albite at 100° C. and the city water pressure, about 40 pounds. The container in this case was a tube of Airdi steel, which unfortunately was strongly attacked, and the solution carried over a considerable amount of iron oxide. As the solution first came over it was clear and colorless, but on standing it gradually

precipitated red ferric oxide, and it is probable that the iron is originally in solution as ferrous oxide. The city water used in this run was passed through a Barnstead demineralizer cartridge. The weight of the alumina was corrected for the iron oxide content, as determined by fusion with pyrosulfate, solution of the melt, reduction in a Jones reductor, and titration with potassium permanganate. The total weight of water collected was 384,269 g. The total amount of material dissolved was 2.4411, which is equivalent to 6.4 parts per million. The total of the analyses gives:  $\text{Na}_2\text{O}$ , 0.3349 g.;  $\text{Al}_2\text{O}_3$ , 0.2333 g.;  $\text{SiO}_2$ , 1.8729 g. This is a weight ratio of  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$  of 1.44:1:8.03, or a mole ratio of 2.35:1:13.57. If all the alumina is calculated to albite it gives 1.2063 g., or 49.4% of the total dissolved material. The excess of  $\text{Na}_2\text{O}$  is 0.1923 g.; of  $\text{SiO}_2$ , 1.0437 g., which gives a mole ratio of 1:5.5. In this case also muscovite was found on the surface of the albite grains, and the altered residue consisted of boehmite and kaolinite.

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