

THE DECOMPOSITION OF MICROCLINE, ALBITE AND NEPHELINE IN HOT WATER*

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ABSTRACT

The decomposition of microcline, albite, and potassium-bearing nepheline was investigated by slowly pumping distilled water at 295° C and 2500 psi over each sample for 135 days. The liquids collected from the bombs were analyzed for Na₂O, K₂O, Al₂O₃, and SiO₂. Microcline was partially decomposed to muscovite. The total amount of material in solution averaged 167 ppm and the pH averaged 7.9. Albite partially altered to boehmite, paragonite, and an amorphous material. The total amount of material in solution averaged 243 ppm and the pH averaged 7.9. An alteration profile was found in the nepheline sample container. Mainly muscovite plus minor analcite were found at the exit end of the container while mainly boehmite was found at the entrance end. The total amount of material in solution averaged 440 ppm and the pH averaged 9.7 with a high of 10.2. The ratio of sodium to potassium in the solutions leached from each of the minerals was greater than the ratio of sodium to potassium in the starting material.

INTRODUCTION

Three long-term experiments have been carried out to investigate the behavior of microcline, albite, and nepheline when water at 295° C. and 2500 psi is pumped over each sample. Similar experiments using the same microcline and albite, but at different temperatures and pressures have been reported by Morey and Chen (1955). Khitarov (1958) also has conducted solution experiments on oligoclase using a continuous leaching technique. Hemley (1959) has measured the equilibrium quotients for the hydrolysis reactions of K-feldspar to mica+silica and of mica to kaolinite in the temperature range 200° to 500° C. at various high pressures. However, solubilities of all the components in the system were not measured by Hemley.

It is emphasized that all the solution results given in this paper represent rates of reaction under the conditions of the experiments, and not the equilibrium solution or equilibrium hydrolysis of the minerals under consideration.

APPARATUS

The apparatus is shown schematically in Fig. 1. The sample is contained within an 8-inch long, $\frac{1}{4}$ inch i.d. stainless steel tube fitted at one end with a porous stainless steel filter having a mean pore opening of 20 microns. The sample holder fits snugly into the middle of a two foot long steel bomb and is held in place by a stainless steel support tube. The encasing bomb has pressure fittings at each end. Water under pres-

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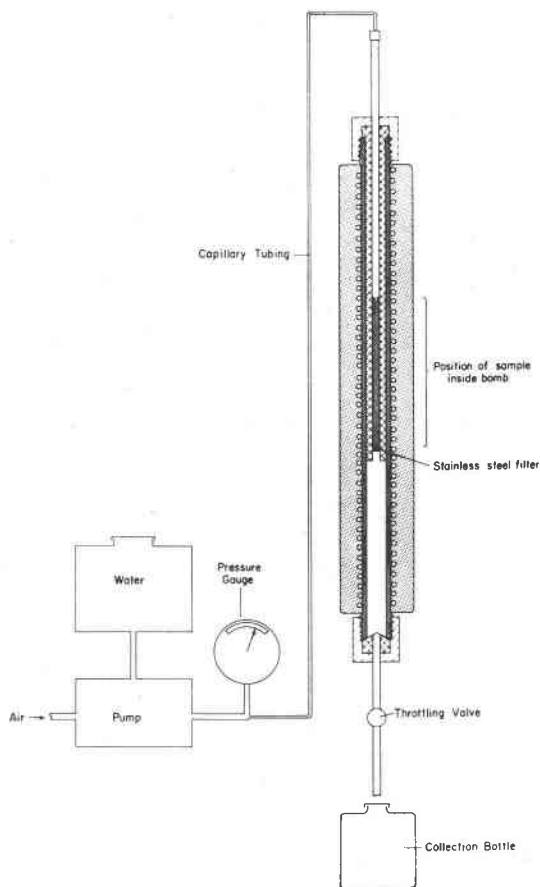


FIG. 1. Schematic diagram of pressure apparatus.

sure is introduced into the top of the bomb by means of an air-actuated diaphragm pump. The water passes down through the powdered samples and out of the bottom of the bomb where it is collected. The rate of flow of the fluid out of the bomb is controlled by a throttling valve. As liquid drips out of the bomb the resulting pressure drop in the high pressure system is sensed across the diaphragm in the pump. This actuates the pump automatically to send more water into the bomb to maintain the predetermined pressure. Friction in the pumping system may cause temporary pressure drops of 100 to 200 psi.

An electrical resistance furnace is wound directly around the outside of the bomb, sheet mica being used as an insulating material next to the bomb. Temperature control was by manual settings of a variac voltage regulator.

Temperature was measured by a platinum-10% rhodium thermocouple wrapped against the outside of the bomb adjacent to the middle of the sample container. Temperatures were continuously recorded on a multiple-record strip chart recorder. During the period when samples were collected the temperature did not vary more than $\pm 5^\circ$ C. from 295° C. There was no provision for measuring the temperature gradient along the length of the sample holder while liquid was being collected from the bomb. However, the temperature gradient was probably small as the furnace windings project six inches beyond each end of the sample holder. Also, in a similarly conducted experiment using a 10-inch long bomb and a furnace of different design, the authors found that an initial ten degree temperature gradient from the top to the bottom of the bomb

TABLE 1.—CHEMICAL ANALYSES OF STARTING MATERIALS
[Analyst, Paula M. Montalto]

	Microcline	Albite	Nepheline
	(weight per cent)	(weight per cent)	(weight per cent)
SiO ₂	65.06	68.06	42.34
Al ₂ O ₃	18.90	20.00	34.22
Fe ₂ O ₃	.06	.04	.06
CaO	.04	.15	.45
Na ₂ O	2.90	11.49	15.73
K ₂ O	13.30	.15	6.45
H ₂ O ⁺	.03	.01	.28
H ₂ O ⁻	.03	.01	.06
	100.32	99.91	99.59

was reduced to no temperature gradient within one minute after starting to drip liquid from the bomb.

STARTING MATERIALS

The minerals used as starting materials for the experiments reported here were 1) large crystals of perthitic microcline from the Derry mine in Quebec, 2) crystals of albite from Amelia County, Virginia, and 3) massive nepheline from Bancroft, Ontario. Chemical analyses of these minerals are tabulated in Table 1.

EXPERIMENTAL PROCEDURE

Each silicate was crushed to pass a 20-mesh screen and collected on an 80-mesh screen and the fines were removed by washing. Eight to nine grams of the dried sample were weighed into the sample holder. Each bomb was assembled and placed upright in a supporting rack. As

soon as the desired temperature was attained and stabilized, water was pumped into the bomb. Approximately 34 to 38 ml. of water at 295° C. and 2500 psi were maintained in the bombs at all times.* Each week day during an eight-hour period liquid was dripped at as uniform a rate as possible from the bombs into polyethylene bottles. The throttling valves were closed at night. During the first five days of liquid collection 50 to 100 ml. per day were obtained from each bomb. The average drip rate was 0.1 to 0.2 ml. per minute. Thereafter, generally 200 to 250 ml. per bomb per day were collected and the average drip rate was 0.8 to 1.0 ml. per minute. Most of the liquid was collected at the fairly slow uniform rates indicated by the average values. However, there were considerable variations in the rate of drip. There were extended periods when no liquid dripped from the bombs and other periods when the drip rate increased to as much as 4 ml. per minute.

The solutions were analyzed by colorimetric methods (Shapiro and Brannock, 1956) for K_2O , Na_2O , Al_2O_3 , and SiO_2 . We are grateful to Leonard Shapiro for his assistance in carrying out these analyses.

For the first five days of liquid collecting each of the liquid samples was individually analyzed. Then for four weeks each two day's collections were combined for analyses and for the last 14 weeks each week's collections were combined for one analysis.

No apparent precipitation of oxides from solutions occurred when the solutions were obtained from the bombs or upon standing at room temperature and pressure. At the end of 135 days no precipitate was found in the exit tubing of the bombs and no visible precipitate formed in the collection bottles. Samples of solutions from the two feldspars were analyzed for aluminum immediately after collection and again after 12 days. No change in the aluminum contents of the solutions were found. Both solutions had pH values of 7.9 and the concentrations of Al_2O_3 were 38 ppm for the albite solution and 27 ppm for the microcline solution. Similarly a nepheline solution of pH 9.5 gave identical results of 159 ppm Al_2O_3 in solution before and after eight months of storage.

At the termination of the experiments the alteration products left in the sample containers were examined optically and by x-ray.

RESULTS

Microcline

The data obtained from the microcline experiment are summarized in Table 2. The initial weight of the microcline sample was 8.810 g.

* An exception was at the end of 33 days when the bombs were cooled and taken apart to investigate the progress of the alteration of the samples. The bombs were re-assembled and the experiments continued using the same then partially altered material.

After 135 days 2.075 g. or 23.6% of the sample had been dissolved in 12,460 g. of solution. This is 167 ppm of solids put into solution.

The molecular ratio of $(K_2O + Na_2O) : Al_2O_3 : SiO_2$ should be 1:1:6 if the microcline dissolved stoichiometrically. The measured ratio in solution was 1.60:1:9.85. If all the K_2O in solution is calculated to orthoclase, the orthoclase amounts to 1.063 g., or 51%; if the remaining Al_2O_3 in solution is calculated to albite, the albite amounts to 0.329 g. or 16%.

TABLE 2. MICROCLINE EXPERIMENTAL DATA

	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Total
Average solubility in ppm for first 33 days and 22 collections	147	25	15	12	199
Average solubility in ppm for the last 102 days and 39 collections	108	19	14	10	151
Average solubility in ppm for the total of all runs*	121	21	14	11	167
Grams dissolved in the first 33 days	.578	.098	.058	.049	.783
Grams dissolved in the last 102 days	.924	.161	.122	.085	1.292
Total grams dissolved	1.502	.259	.180	.134	2.075
Mole ratios for the first 33 days	10.00:1 : .640: .823				
Mole ratios for the last 102 days	9:74:1 : .822: .867				
Mole ratios for the total	9.85:1 : .752: .850				
Temperature: 295° ± 5° C.	Initial weight of sample: 8.810 g.				
Pressure: 2500 ± 200 psi	Weight of liquid pumped over sample:				
Duration of experiment: 135 days	First 33 days— 3,941.5 g.				
	Last 102 days — 8,515.5 g.				
	Total —12,460.0 g.				

* Calculated by dividing the total grams dissolved by the total amount of liquid pumped over the sample.

The remainder, 0.683 g. or 33%, is Na_2O and SiO_2 in the molecular ratio of 1:6.4. There has evidently been much decomposition, with extraction of Na_2O and SiO_2 .

The dissolving liquid was distilled water having an initial pH of 5.8 caused by a small amount of dissolved atmospheric CO_2 . The pH of the solution collected from the bomb varied from 7.7 to 8.2 and averaged 7.9.

The solution of oxides, particularly SiO_2 , was greater during the first days of pumping water over the microcline than during the last. For the first five collections of liquid from the bomb, SiO_2 was found to be about 200 ppm and the total solids 270 ppm. The high values for silica

then tapered off and the values for the dissolved material were fairly constant for the remainder of the runs. Albite behaved in a similar manner.

This initial high solubility was probably due to strained surface conditions imparted to the feldspar grains as the original large single crystals were crushed. As soon as the molecular-sized "ragged areas" on the grain surfaces were dissolved away or hydrolyzed to mica, the

TABLE 3. ALBITE EXPERIMENTAL DATA

	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Total
Average solubility in ppm for first 33 days and 22 collections	178	38	0.7	32	249
Average solubility in ppm for the last 102 days and 39 collections	171	38	0.6	31	241
Average solubility in ppm for the total of all runs*	172	38	0.7	32	243
Grams dissolved in the first 33 days	.637	.137	.003	.114	.891
Grams dissolved in the last 102 days	1.620	.363	.006	.298	2.287
Total grams dissolved	2.257	.500	.009	.412	3.178
Mole ratios for the first 33 days	7.91:1:.02:1.37				
Mole ratios for the last 102 days	7.58:1:.02:1.35				
Mole ratios for the total	7.65:1:.02:1.36				
Temperature: 295° ± 5° C.	Initial weight of sample: 9.257 g.				
Pressure: 2500 ± 200 psi	Weight of liquid pumped over sample:				
Duration of experiment: 135 days	First 33 days — 3,570 g.				
	Last 102 days — 9,497 g.				
	Total — 13,067 g.				

* Calculated by dividing the total grams dissolved by the total amount of liquid pumped over the sample.

amount of dissolved silica in the solutions decreased. The comparatively large initial solution values may in part be due to slower rates of pumping liquid over the samples. However, similar slow rates of liquid collection were made at a later time without any increase in the amount of SiO₂ in solution.

No alteration products were apparent when the microcline was examined 33 days after the start of the experiment. After 135 days a large amount of unaltered feldspar still was present. Muscovite, partially coating most of the feldspar grains throughout the sample container, was the only alteration product found. If microcline is decomposed and leaves

only a residue of muscovite, the solution obtained from the bomb should contain excess $(K_2O + Na_2O) : SiO_2$ in the molecular ratio 1:6. As already pointed out, the ratio found was 1:6.4.

Delicate, skeleton like portions of the perthite were found where water first came in contact with the microcline. The sodium-rich layers had been dissolved out, leaving behind portions of the potassium-rich layers.

Morey and Chen (1955) found that microcline from the Derry mine altered to both boehmite and muscovite at 350° C. and 5000 psi.

Albite

The data obtained from the albite experiment are summarized in Table 3. The initial weight of the albite sample was 9.257 g. After 135 days 3.178 g. or 34% of the sample had been dissolved in 13,067 g. of solution. This is 243 ppm. The pH of the distilled water pumped into the bomb was 5.8 and the pH of the solution collected from the bomb varied from 7.7 to 8.0 and averaged 7.9.

The experimentally measured molecular ratio of $(Na_2O + K_2O) : Al_2O_3 : SiO_2$ was 1.38:1:7.65. Excesses of 0.115 g. Na_2O and 0.486 g. SiO_2 exist in solution over the amounts which could combine with all the Al_2O_3 in solution for form albite. The amount of albite which could precipitate is 2.025 g. corresponding to 81% of the dissolved material.

After 135 days boehmite and paragonite were found partially coating albite grains throughout the sample container. No other alteration product was found by x-ray diffraction. However, a microscopic examination of the alteration products revealed that low birefringent blades of paragonite and granular boehmite are set in a gelatinous matrix. If paragonite and boehmite were the only alteration products the molecular ratio of the excess $Na_2O : SiO_2$ in solution should have been 1:6. The molecular ratio was measured to be 1:4.3. Such a ratio would be expected if an allophane-like material were forming.

In similarly conducted experiments Morey and Chen (1955) found that the Amelia albite altered to boehmite, analcite, and dioctahedral micas at 350° C. and 5000 psi. The mole ratio of excess $Na_2O : SiO_2$ in solution was 1:13.6. At 200° C. and 2000 psi they found that albite altered to boehmite and kaolinite and the mole ratio of excess $Na_2O : SiO_2$ in solution was 1:3.8.

Nepheline

The data obtained from the nepheline experiment are summarized in Table 4. The initial weight of the nepheline sample was 8.453 g. After 135 days 12,796 g. of liquid had passed over the nepheline, dissolving

5.630 g. of material or 67% of the sample. This amounts to 440 ppm. It should be noted, however, that the average parts per million was 491 for the first 33 days and only 416 for the last 102 days.

The pH of the CO₂-bearing distilled water pumped into the bomb was 5.8 and the pH of the solution collected from the bomb varied from 9.2 to 10.2. During the first 48 days of pumping liquid over the nepheline the pH varied from 9.9 to 10.2 and averaged 10.0. Later, as the nepheline

TABLE 4. NEPHELINE EXPERIMENTAL DATA

	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Total
Average solubility in ppm for first 33 days and 22 collections	200	148	30	113	491
Average solubility in ppm for the last 102 days and 39 collections	188	118	24	86	416
Average solubility in ppm for the total of all runs*	192	127	26	95	440
Grams dissolved in the first 33 days	.793	0.587	0.121	0.450	1.951
Grams dissolved in the last 102 days	1.662	1.040	0.215	0.762	3.679
Total grams dissolved	2.455	1.627	0.336	1.212	5.630
Mole ratios for the first 33 days	2.29:1 : .22:1.26				
Mole ratios for the last 102 days	2.66:1 : .22:1.21				
Mole ratios for the total	2.57:1 : .22:1.25				
Temperature: 295° ± 5° C.	Initial weight of sample: 8.453 g.				
Pressure: 2500 ± 200 psi	Weight of liquid pumped over sample:				
Duration of experiment: 135 days	First 33 days— 3,969 g.				
	Last 102 days— 8,829 g.				
	Total —12,798 g.				

* Calculated by dividing the total grams dissolved by the total amount of liquid pumped over the sample.

grains became coated with alteration products the pH gradually decreased, reaching the lowest pH values toward the termination of the runs.

For the first 33 days the dissolved material had an average measured molecular ratio of (Na₂O + K₂O):Al₂O₃:SiO₂ of 1.48:1:2.29. From this solution 84% of the dissolved material or 1.637 g. could precipitate as nepheline. The remainder, after the subtraction of Na₂O, Al₂O₃, and SiO₂ for nepheline, is an excess of 0.138 g. Na₂O, 0.215 g. K₂O, and 0.412 g. SiO₂. The molecular ratio of excess (Na₂O + K₂O):SiO₂ is 1:0.61.

For the last 102 days the dissolved material had an average molecular

ratio of $(\text{Na}_2\text{O} + \text{K}_2\text{O}) : \text{Al}_2\text{O}_3 : \text{SiO}_2$ of 1.43:1:2.66. From this solution 79% of the dissolved material or 2.920 g. could precipitate as nepheline. This compares very closely with the 84% for the first 33 days. However, the molecular ratio of excess $(\text{Na}_2\text{O} + \text{K}_2\text{O}) : \text{SiO}_2$ in solution is almost reversed. Instead of 1:0.61, it is 1:1.53. After subtracting for nepheline there are excesses in solution of 0.132 g. Na_2O , 0.215 g. K_2O , and 0.412 g. SiO_2 .

After 33 days a mixture of boehmite and muscovite was found replacing all the nepheline at the very top of the sample container, where fresh water first came in contact with the sample. At the exit end (bottom) of the sample holder the nepheline was unaltered. No trace of paragonite or analcite was found at this time.

When the experiment was terminated, after 135 days, mainly muscovite and small amounts of analcite were at the exit end of the container along with a few small residual grains of nepheline ensheathed by mica. In the middle and upper part of the container dioctahedral mica and boehmite mixtures were present. At the top of the container, where fresh water came in contact with the sample, only boehmite and minor amounts of paragonite were found. It is possible that paragonite may have been present elsewhere in the sample container, its presence masked by muscovite.

DISCUSSION OF RESULTS

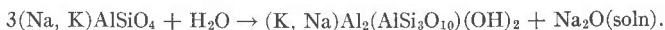
The dissolution and alteration of the minerals dealt with in this experimentation were carried out mainly in a dynamic open system. During the hours when samples were collected, the main movement of dissolved material was by a flushing action of liquid flowing in one direction into the top and out the bottom of the bomb. In such a system large concentration gradients of metal cations and of hydrogen ions (pH) result owing to the continued reaction of an increment of solution with solids as the solution moves through the bomb. Thus, the concentration and pH of the relatively dilute solution at the top of the sample holder may be appropriate for the formation there of one alteration product while at another point in the sample holder a different concentration and pH may be appropriate for the formation of a different alteration product.

In contrast, during the periods when no fluid was removed from the system, movement of material in solution was mainly by ionic diffusion and by convection of the liquid caused by temperature gradients. Both effects would tend toward equalizing the chemical potential of each ionic species throughout the sample holder. Thus, some alteration products which formed during the dynamic periods when liquid was ex-

tracted might become unstable in the presence of and react with quiescent liquids which remain in the bomb for relatively long periods. On the other hand, some alteration products would be expected to become stable over a much greater portion of the sample holder when there is opportunity for chemical potential gradients to be decreased.

Most of the alteration products probably formed during and shortly after the periods when water was dripped from the bombs. Only relatively small amounts of alteration products would be expected to form during "quiescent" periods for the following reasons. The starting materials are stable in the temperature-pressure environment of the experiments. Therefore, the starting materials will dissolve and alteration products will crystallize out of solution only until the chemical potential of each component is the same both in the solution and in each solid in which the component occurs. As soon as equilibrium is attained no further increase in the amounts of alteration products will take place as long as the temperature, pressure, and concentrations of ions in solution remain constant. During the periods when solution was dripped from the bombs the concentrations of ions in contact with solids at a given point within a bomb is constantly subject to change owing to liquid flow. In this case alteration products may continuously form in an attempt to reach equilibrium with each new portion of liquid passing by.

The alteration within the nepheline sample holder may be visualized as proceeding in the following manner: Decomposition of the nepheline was very rapid at the top of the container where fresh distilled water first came in contact with it. Muscovite was probably the first alteration product to form according to the hydrolysis reaction



This would account for the very high sodium content in the analyzed solutions during the first few days of the experiment. The first solution collected from the bomb contained 328 ppm Na_2O . Alteration proceeded from the top of the container downward. At a time when fresh nepheline still existed at the bottom, muscovite which had replaced nepheline in the top portion of the sample column began to decompose, leaving boehmite behind according to the reaction,



This reaction led to an increase in solution of SiO_2 in respect to Na_2O and accounts for the reversal in the mole ratios of excess $\text{Na}_2\text{O}:\text{SiO}_2$ after the initial days of sample collection. Boehmite probably accompanied muscovite from a very early stage in the experiment.

Analcite probably began to form at a stage when the decomposition of muscovite in the upper part of the bomb allowed relatively high

concentrations of dissolved SiO_2 to pass over yet unaltered nepheline below.

It is difficult to account for the position of paragonite in the upper part of the sample holder accompanying boehmite. One possibility is that muscovite and paragonite formed concurrently. This would imply that paragonite is more resistant to breakdown by leaching than is muscovite. The paragonite certainly did not form as a decomposition product of muscovite as the ratio Na/K would not be high enough in

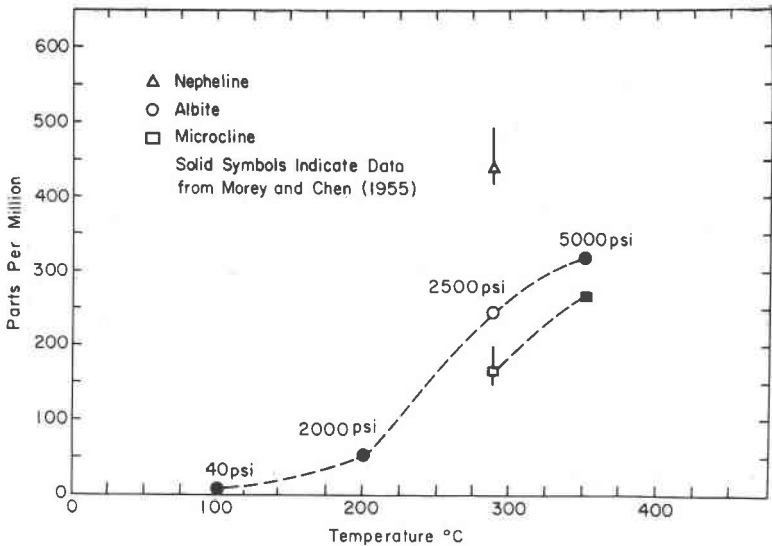


FIG. 2. Average total amounts of oxides in solution extracted from microcline from the Derry mine, albite from Amelia County, Va., and nepheline from Bancroft, Ontario. These are not equilibrium values, but rather chemical solution values obtained by decomposition of the samples under the conditions of the experiment.

solution. The paragonite might possibly form as a result of the decomposition of analcite. Another possibility is that the paragonite formed during quiescent periods when diffusion of sodium and silica back into the upper region of the sample holder may have allowed these components to react with boehmite. Potassium ions may not have migrated to the top of the container as rapidly as the sodium ions owing to their larger size and to rapid reactions forming muscovite lower in the container.

A comparison of the average total amounts of material in solution extracted from microcline from the Derry mine, albite from Amelia County, Va., and nepheline from Bancroft, Ontario, is shown in Figure 2.

The behavior of nepheline under the conditions of these experiments was markedly different from that of the two feldspars. Nepheline in the top of the container quickly reacted with fresh water coming in contact with it. Water at the top of the sample holder soon approached saturation with dissolved material and the rate of attack upon nepheline further down in the tube was slow. An alteration profile was thus set up with each successive increment of fresh solution attacking the nepheline a little further down in the sample holder. As the nepheline was used up and alteration products became more abundant, the chemical picture for the sample container as a whole gradually changed. This was reflected in a gradual change in quantities and proportions of dissolved materials in the solutions obtained from the bomb. A new chemical system gradually worked its way down in the sample holder as nepheline was successively used up at lower and lower levels.

The feldspars, on the other hand, were not rapidly decomposed when distilled water first came in contact with them at the top of the container. Concentration and pH gradients were never as large in the feldspar containers as in the nepheline container. Therefore, an alteration profile similar to that found in the nepheline container did not develop. An alteration profile formed only to the extent that there were more of the same kind or kinds of alteration products in the top of the sample container than in the bottom.

In all the experiments potassium tended to remain behind as muscovite and the solutions were enriched in sodium.

REFERENCES

- HEMLEY, J. J. (1959), Some mineralogical equilibria in the system $K_2O-Al_2O_3-SiO_2-H_2O$: *Am. Jour. Sci.*, **257**, 241-270.
- KHITAROV, N. I. (1958), On the reaction of oligoclase with water under conditions of high temperature and pressure: *Trudy Pyatogo Soveschchaniya Eksper. i Tekhn. Mineralog. i. Petrog.*, 208-213.
- MOREY, G. W., AND CHEN, W. T. (1955), The action of hot water on some feldspars: *Am. Mineral.*, **40**, 996-1000.
- SHAPIRO, L., AND BRANNOCK, W. W. (1956), Rapid analysis of silicate rocks: *U. S. Geol. Survey Bull.*, **1036-C**.

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