CONDITIONS FOR THE FORMATION OF PARAGONITE

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Abstracts

It is possible to synthesize paragonite hydrothermally in acid solutions. X-ray powder photographs confirm these results. Reasons for the scarcity of paragonite are advanced.

There has been considerable discussion, especially lately,[1] with regard to the validity of paragonite as a species. A number of analyses are now available that seem to leave little doubt that soda micas actually exist. On the other hand, there have been no x-ray structure data on paragonite.

It occurred to the writer to synthesize the mineral by the same method he had used to obtain muscovite.[2] The gold-lined bomb used for these experiments has been described a number of times. The bomb has a volume of 50 cc. In each of the two experiments it was filled with 20 cc. of N/0.103 HCl solution. The air above the solution was displaced by CO_2 at atmospheric pressure and room temperature. The other constituents of the bomb were:

> 318 mg. $Al(OH)_3$ = artificial bayerite containing 37% H_2O.
> 270 mg. "Silicic acid." It contains 10.36% H_2O = approx. $SiO_2 \cdot \frac{1}{2}H_2O$.
> 2000 mg. NaCl, analytical grade.

The ratio of $Al(OH)_3 : SiO_2 \cdot \frac{1}{2}H_2O$ was equivalent to $Al_2O_3 : SiO_2$ in paragonite. The amounts theoretically were sufficient to produce 500 mg. of paragonite. The temperature was $400° \pm 5°$ C. and the length of the experiment was 7 days.

The product was carefully boiled with distilled water several times after removal from the bomb, dried on a steam radiator and x-rayed. Unfiltered Fe radiation was used. The camera had a radius of 57.3 mm. Very good negatives were obtained. These resemble natural and synthetic muscovite, but there are distinct differences in spacings. The planar-spacings together with those of synthetic muscovite are listed in Table 1. The intensities of the natural and synthetic products are quite different for the basal plane reflections due to the preferred orientation of the cleavage particles of natural muscovite. The particles of synthetic micas are so small that such preferred alignment does not occur in mounting the powders. The theoretical intensities of the basal reflections were com-

[1] McCormick, R. B., Paragonite from Pizzo Forno, Ticino, Switzerland: *Am. Mineral.*, **19**, 431–432 (1934).

Schaller, W. T., and Stevens, R. E., The validity of paragonite as a mineral species: *Am. Mineral.*, **26**, 541–545 (1941).

[2] Gruner, J. W., Formation and stability of muscovite in acid solutions at elevated temperatures: *Am. Mineral.*, **24**, 524–528 (1939).

puted for paragonite and compared with the observed ones. The agreement is as good as can be expected in powder photographs.

TABLE 1. PLANAR SPACINGS AND RELATIVE INTENSITIES OF SYNTHETIC
PARAGONITE AND SYNTHETIC MUSCOVITE
Unfiltered Fe K radiation. Camera radius 57.3 mm.

PARAGONITE			MUSCOVITE		
Spacing	Intensity	Indices	Spacing	Intensity	Indices
9.79	5	002	10.09	6	002
4.81	2	020β	4.86	2	020β
4.42	8	020	4.44	7	020
4.24	0.5		3.898	1	
3.515	3	006β	3.649	2	006β
3.352	0.5				
3.204	8	006	3.339	6	006
3.052	2		3.118	1	
2.798	3	β	2.822	2	β
2.677	1		2.708	1	
2.533	8		2.560	6	
2.417	3	008	2.471	2	008
			2.370	2	
2.215	0.5		2.239	2	
2.168	1				
2.092	2		2.138	2	
2.043	0.5				
1.934	2	0010	2.016	1	0010
			1.974	1	
1.855	2		1.872	1	
1.776	0.5				
1.676	1		1.703	1	
1.643	2	060β	1.653	2	
1.605	1				
1.559	0.5				
1.488	7	060	1.501	5	060

Mention must be made that some boehmite AlO(OH) had also been produced in the experiments. Its two strongest lines, which do not coincide with any of paragonite, could easily be observed. These occur at 6.04 Å and 2.34 Å. Boehmite is a frequent product in the writer's hydrothermal experiments, but it is also the most abundant aluminum hydroxide in some bauxites. It may be pointed out at this place that x-ray powder diffraction lines of boehmite as recorded recently[3] by Mehmel,

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[3] Mehmel, Martin, Datensammlung zum Mineralbestimmen mit Röntgenstrahlen: *Fortsch. Min., Krist.* und *Petr.*, **23**, 103 (1939).

and supposed to be used for identification of minerals, are not the lines of boehmite but of some substance unknown to the writer.

Why boehmite should have formed with the paragonite in the experiments mentioned is a question not readily answered, unless boehmite is an intermediate product and would disappear after equilibrium was reached. There is one other possibility. Considerable amounts of the silica present might be prevented from forming paragonite by the large excess of sodium in the solution. The aluminum hydroxide remaining might form boehmite. About 0.1 g. of the sample was analyzed for Na_2O by Dr. R. B. Ellestad. The percentage was 5.4 as compared with 8.11 for theoretically pure paragonite. At least a part of this deficiency can be ascribed to the admixture of boehmite. If this is done this synthetic material probably contains at least as much Na_2O as some natural paragonites reported by Schaller and Stevens.[4]

One wonders why paragonite is relatively uncommon in nature. Perhaps this scarcity is only apparent since paragonite cannot be distinguished from muscovite by its optical properties. There certainly seems to be no lack of sodium in many places where muscovite has formed. Among the numerous analyses of mica one would expect more soda mica, if the scarcity of paragonite were not real.

Then the question naturally arises, why are potassium micas so much more abundant. There seem to exist about three to four times as many species of silicates containing sodium as silicates with potassium. This preponderance may be caused by the small size of the sodium ion (0.96 Å) compared with the potassium ion (1.33 Å). A large cation, potassium, needs a much larger space and for this reason must surround itself with more oxygen ions to form a stable structure. In other words, it will have a coordination of 10 to 12. Such positions in natural silicates are uncommon except in a few "open" structures as in mica, feldspar and leucite. On the other hand, the smaller sodium cation usually has only 6 to 8 coordinates, or bonds, and fits into a more compact structure of SiO_4 or AlO_4 tetrahedra. This coordination permits a far greater variety of stable structures. Also sodium, due to its similar size, does replace calcium, and more rarely, magnesium in a number of silicates.

For this very reason, however, sodium ions enter potassium positions in the mica structure only under very special conditions, for here they must occupy positions which are evidently too large and possess, therefore, too weak and too many bonds. In the iron and magnesium micas, sodium ions in potassium positions are even more scarce on account of the still larger spacings in the structure. Lithium being much smaller than

[4] *Op. cit.*, p. 544.

sodium occupies aluminum positions, the potassium positions being barred to it. One of the special conditions under which paragonite can form is that of the experiments described. In neutral or basic solutions of similar experiments the author did not produce paragonite, but nepheline or unidentified products.

CONCLUSIONS

Paragonite mica was produced synthetically in N/.10 HCl solutions at 400° C. X-ray powder photographs show that the spacing of the unit cell normal to (001) is 19.33 ± 0.02 Å, compared with 20.0 Å in muscovite. The width (b_0) of paragonite is $8.90 \pm .02$ Å and of muscovite $9.00 \pm .02$ Å. It is thought that paragonite is uncommon because sodium ions are so small that they will not fit readily into the potassium positions of the micas. They prefer positions with 6 to 8 bonds to the potassium positions which have twelve, unless no other positions are available. In HCl solutions the aluminum micas seem to be the only alkali-bearing silicates which are comparatively stable, and for this reason sodium mica can form. It must not be concluded, however, that paragonite could form only in acid solutions.