

SYNTHESIS, STABILITY AND POLYTYPOISM OF NICKEL
AND GALLIUM PHLOGOPITE*CYRUS KLINGSBERG AND RUSTUM ROY, *The Pennsylvania State
University, University Park, Pennsylvania.*

ABSTRACT

Phlogopites have been synthesized with Ni^{2+} substituting for Mg^{2+} and Ga^{3+} for Al^{3+} . The Ni-phase was prepared only as the 3T polytype; the Ga-member could not be indexed on any simple basis. Their decomposition temperatures under hydrothermal conditions have been determined and compared to that for phlogopite. The nickel substitution hardly affects the stability, whereas replacement of aluminum by gallium lowers the equilibrium dissociation temperature by 100°C .

INTRODUCTION

The aim of this work is to provide data upon which generalizations relating ionic composition to properties may be based. Theoretical approaches to crystal chemistry are severely limited by both the absence of thermochemical data on all but the commonest phases, and by the complexity of the mathematical treatment of the crystal energetics approach to any but the simplest arrangements. The general problem at hand is to relate the composition of a mica with its equilibrium thermal stability. The effect of composition on polytypism has also been examined.

For this purpose we have compared the following phases:



The nickel phlogopite represents the substitution (only in the octahedral layer) of a more polarizable non-noble gas ion for the magnesium with hardly any change in size. The gallium on the other hand, presumably, enters only the tetrahedral layer, and again reflects the influence of increased polarizability, but also of slightly increased size.

EXPERIMENTAL

Mixtures of the desired compositions were prepared by the nitrate-organic silica method described by Roy (1956). The concentrated aqueous solution of the desired nitrates (of Mg, Ni, Al or Ga) are added to a solution of ethyl orthosilicate in absolute ethyl alcohol. A large excess of water is added and enough alcohol to give a clear solution. The mixture is heated not higher than 60°C . for several hours, and after a very loose gel-like structure is formed, the potassium hydroxide solution

* Contribution No. 56-47, College of Mineral Industries, The Pennsylvania State University; University Park, Pennsylvania.

is added and the whole stirred. The gel is allowed to set and is dehydrated and ignited at about 350° C.

These starting materials are amorphous to x -rays and are several orders of magnitude more reactive than a mechanical mixture of the oxides. They are placed in platinum envelopes and heated at the appropriate temperatures and pressures in test-tube-type stellite vessels. The experimental methods have been described by Roy, Roy and Osborn (1950).

RESULTS

The mixtures both yielded well-crystallized micas (as evidenced by their powder x -ray patterns) when heated at moderate temperatures and pressures ($\sim 700^\circ$ C., 15,000 psi). The crystals were very small and only rarely were small hexagonal flakes visible at the highest magnification of the polarizing microscope. The following table compares some properties of the micas:

TABLE 1

	Mg Phlog. (Yoder)	Ni Phlog.	Ga Phlog.
Basal spacing	10.15 Å	10.17 Å	10.26 Å
Refractive index (γ)	1.588	1.652	1.598

Forty-three runs were made to determine the two p - t curves for the decomposition of the nickel and gallium phase. The runs reported in Table 2 are in general somewhat more conclusive than those reported by Yoder and Eugster (1954) in the same pressure range for the Mg-phlogopite. Still they are not long enough to establish equilibrium unequivocally. While it would be very desirable to make longer runs than those reported, the temperatures and pressures are very near the limit for the vessels. In the absence of unequivocal data the results must be interpreted with considerable circumspection. For most of the cases each run was started with two starting materials: one, a pre-crystallized synthetic mica, and the other the "amorphous" gel. However, even under these conditions, during the few minutes (15-30 min.) required for the vessel to come to temperature the "amorphous" material undoubtedly had crystallized partly to a mica. It is not feasible to avoid this crystallization in this case by taking up the temperature first and then letting in the water pressure, since this causes the anhydrous phases including NiO to be formed before the run starts. These anhydrous phases persist metastably for very long periods. In the light of these facts certain non-rigorous criteria are necessary to decide where the univariant equi-

TABLE 2

Temp. (° C.)	Pressure (psi)	Time (hrs.)	Initial Condition	Results
Ni-Phlogopite				
900	2,000	71	xl.	Phlog.
900	2,000	71	gel	NiO and Leucite
910	3,300	72	xl.	Phlog.
910	3,300	72	gel	Phlog.
950	2,000	11½	xl.	Phlog.
950	2,000	11½	gel	NiO and Leucite
975	5,000	45	xl.	Phlog.
975	5,000	45	gel	Phlog.
1002	6,000	17½	xl.	Phlog. and Leucite
1002	6,000	17½	gel	Phlog. and Leucite
Ga-Phlogopite				
799	2,000	47	xl.	Phlog. and Forsterite
799	2,000	47	gel	Phlog. and Forsterite
850	5,000	240	gel	Phlog.
900	7,500	48	xl.	Phlog.
900	7,500	48	gel	Phlog.
900	11,000	117	xl.	Phlog.
900	11,000	117	gel	Phlog.
900	10,000	120	xl.	Phlog.
900	10,000	120	gel	Phlog.
920	13,000	48	xl.	Phlog.
920	13,000	48	gel	Phlog.
920	5,000	144	xl.	Forst.+Leucite
920	5,000	144	gel	Forst.+Leucite
950	6,000	138	xl.	Phlog.+Forst.
950	6,000	138	gel	Phlog.+Forst.
970	15,000	10	xl.	Phlog.
970	15,000	10	gel	Phlog.
985	15,000	9½	xl.	Phlog.
985	15,000	9½	gel	Phlog.+Forst.
990	15,000	13	xl.	Phlog.+Forst.
990	15,000	13	gel	Phlog.+Forst.
1014	10,000	5½	xl.	Phlog.+Forst.
1014	10,000	5½	gel	Phlog.+Forst.

Abbreviations: Phlog. = phlogopite; Forst. = forsterite; xl = crystal.

librium curve lies. Runs in which both starting materials yield the anhydrous phases—even in part only—are obviously points above the curve. Runs in which well-formed mica is obtained from both starting materials have to be repeated for longer and longer times to be sure that

it is not metastable persistence of the mica. Confirmation is sought by obtaining decomposition with very much shorter runs at about 10° C. above the long runs which gave only the mica.

The reaction involved in both cases is presumed to be analogous to the Mg-phlogopite decomposition, i.e.: $2 \text{ phlogopite} \rightleftharpoons 3 \text{ Mg}(\text{Ni})_2\text{SiO}_4 + \text{K-Al}(\text{Ga})\text{Si}_2\text{O}_6 + \text{KAl}(\text{Ga})\text{SiO}_4$. Evidence for the actual formation of the forsterite and leucite phases is ample in both cases, whereas even the detection of KAlSiO_4 is questionable in the hydrothermal decomposition products of both micas. Dry decomposition attempted at 1200° C. for 48 hours caused melting of the gallium composition and the formation of only NiO as a crystalline phase from the nickel member. Evidence that these are the equilibrium anhydrous phases is therefore not conclusive.*

From the curves of Fig. 1 it can be seen that where data have been obtained the Ni curve is almost identical with the Mg curve. It actually lies about 10–20° C. lower than the Mg-mica curve of Yoder and Eugster but this is well within the limits of error and correspondence across laboratories. The Ga-mica curve on the other hand is definitely (~100° C.) lower than the aluminum counterpart. DeVries and Roy (1955) have discussed elsewhere the significance of the influence of the ionic size and polarizability on stability of the layer lattice minerals. Crystal growth seemed to be quite unaffected by these ionic substitutions. There was no marked tendency for either of these micas to grow much faster or larger than the other.

POLYTIPIISM OF THE Ni AND Ga PHLOGOPITES

(By F. H. Gillery)

Specimens of the nickel and gallium phlogopites (respectively $\text{K}_2\text{Ni}_6(\text{Al}_2\text{Si}_6)\text{O}_{20}(\text{OH})_4$ and $\text{K}_2\text{Mg}_6(\text{Ga}_2\text{Si}_6)\text{O}_{20}(\text{OH})_4$), were examined by x -ray powder techniques to determine the polymorphic varieties. The former was found to have a one-layer monoclinic or a three-layer trigonal structure. A consideration of the stacking possibilities of mica layers showed that these two types of structure should be indistinguishable from powder photographs of trioctahedral micas. An indexed powder pattern is given in Table 3.

The gallium phlogopite proved to be a more difficult problem. It was impossible to index the x -ray diagram completely on either a 1M, 2M, 3T, or 6T basis. The pattern appears to be more complex than any of these types.

* A long, low-P, high-T run gave, in addition to leucite and forsterite, diffraction peaks which could very well represent Ga-kaliophillite.

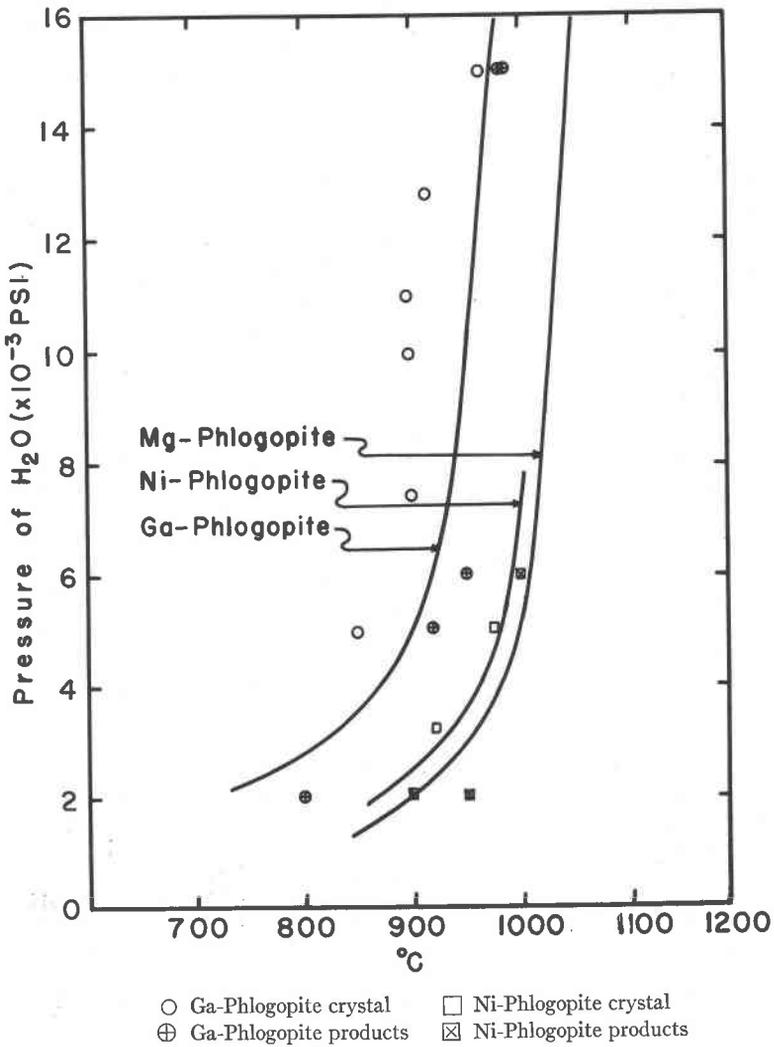


FIG. 1. Curves showing stability relationships.

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TABLE 3. INTERPLANAR SPACINGS AND INDICES OF NICKEL PHLOGOPITE (3T BASIS)

$d(\text{\AA}), \textit{obs.}$	Int., est.	hkl	$d(\text{\AA}), \textit{calc.}$
10.15	10	00.3	10.17
5.512	4	?	—
5.065	5	00.6	5.083
4.557	6	10.0; 10.1	—
3.927	5	10.4	3.932
3.672	6	10.5	3.668
3.389	10	00.9	3.389
3.164	6	10.7	3.160
2.928	6	10.8	2.932
2.720	4	10.9	2.726
2.612	10	11.2	2.611
2.542	6	00.12	2.542
2.501	4	11.4	2.503
2.430	10	11.5	2.431
2.359	2	?	—
2.291	3	20.0	2.295
2.264	5	11.7	2.264
2.176	9	11.8	2.176
2.089	8	20.6	2.092
1.997	7	11.10	2.000
Cell Parameters			
$a=5.300 \text{\AA}$		$c=30.51 \text{\AA}$	

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