Subsolidus solubility between $R_2^{..}SiO_4$ and $LiR^{..}PO_4$: a hydrothermal investigation

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Summary. The subsolidus phase equilibrium of the lithiophilite–tephroite system was studied in the temperature range 500 to 900° C. The solubility of tephroite in lithiophilite is limited and increases with temperature. The reaction is very sluggish and has peculiar kinetic properties. No reverse solubility was observed. Similar asymmetry was found in the $LiMgPO_4$–forsterite system of which a preliminary study was made. Apparent absences of silicate phosphate olivine solid solutions in nature are related to our experimental findings and to geological factors.

THE replacement of Si by Al to give derivative isotypic structures has been recognized since 1864 (Tschermak). The replacement of Si by P to give isotypes has been less well studied and promises greatly to extend the range of silicate chemistry. Not all isotypic structures, however, are miscible, even if their lattice dimensions are very similar (as is the case with the SiO_2–$AlPO_4$ system, Robinson and McCartney, 1964).

Concerning the mineralogical evidence for Si–P interchange, Koritnig (1964) pointed out that it appears to become more difficult as the degree of direct linking by O–Si–O bonds between SiO_4 tetrahedra increases, i.e. in the order neso-, soro-, ino-, phyllo-, and tecto-silicates. The only known mixed tecto-silicate appears to be viséite (McConnell, 1952). Among the neso-structures there is at least limited solubility in the zircon–xenotime system (Kimura and Hironaka, 1936; Hata, 1938; Dennen and Shields, 1956; Jefford, 1962). Since it was first suggested by Wylie (1948), it is generally accepted that monazite can also incorporate Si. Apatite has two substitution series; in one of them replacement of P by Si is balanced by equal replacement of P by S, giving the mineral wilkeite or ellestadite depending on the degree of substitution (McConnell, 1937). In the other series, abukumalite,

increasing amounts of Si are balanced by trivalent cations, especially Ce (Hägele and Machatschki, 1939; Machatschki, 1942). Mixed 'silicate-pyromorphite' of composition $Pb_5(PO_4)_2SiO_4$ was prepared by Merker and Wondratschek (1960). Mason and Berggren (1941) reported about 10 % replacement of Si in spessartine; Nicolas and Rosen (1963) reported about 30 % replacement of P in gorceixite. Hey (1962) refers to several other rare phosphate-silicates, some of which are of known structure, and to the synthetic intermediate compounds and solid solutions of the Ca_2SiO_4–$Ca_3(PO_4)_2$ system, as well as to other slag minerals.

In spite of the abundance of silicate olivines in nature and the occurrence of the isotypic phosphate-olivines of composition $M^{\cdot}M^{\cdot\cdot}PO_4$, no mixed phosphate–silicate olivines have as yet been reported, although on the basis of the above references mutual solubility is very likely. We have investigated the lithiophilite–tephroite system; the corresponding system with Fe in place of Mn is also of geological interest, but is more difficult experimentally, because of easy oxidation. The use of the hydrothermal method is necessary both to reach equilibrium and to reproduce the condition of formation of pegmatites in which the lithiophilite crystallizes.

Experimental

A.R. reagents were used for the preparation of all materials. Lithiophilite was prepared from lithium carbonate and manganese ammonium phosphate according to the method of Thilo (1941). After heating and cooling, the mixture was reground and reheated, repetition giving a light grey product. In order to make tephroite, pure $MnC_2O_4.2H_2O$, prepared according to Robin (1953), and dry, precipitated amorphous silica, weighed in the correct proportions, were mixed for an hour under benzene and for an hour under ether. After removal of solvent, the mixture was transferred to a 5-mm diameter gold tube, together with about 10 % water, and the tube was sealed. The gold tube was heated in a cold-seal Tuttle pressure vessel (Tuttle, 1949) at 800° C and 1000 atm for one day, and then contained a white or light-grey product. If the conditions are not optimum, $MnCO_3$ may also be formed, and this can be avoided by the high temperature chosen and by the long period of heating. Lithiophilite and tephroite samples prepared as described above were found by chemical analysis to contain up to 4 mole % $Mn^{\cdots}$. Lithium magnesium phosphate was also made according to the method of Thilo (1941) from lithium carbonate and magnesium ammonium phosphate. Forsterite was prepared by the hydrothermal treatment of an appropriate mixture of MgO and SiO_2, following Bowen and Tuttle (1949).

In order to measure the mutual solubility, the two weighed components were mixed under ether for an hour, the solvent was removed and the mixture was transferred to a gold tube of 1 mm diameter together with water mineralizer. No reaction was observed in the

absence of water. At first only about 10 % water (by weight on the wet material) was added, giving a mixture which behaved like a powder; then it was realized that the reaction proceeds further if at least 20 % water (calculated as above) was used, so that the mixture was a slurry. The tube was then sealed and was treated in the apparatus described above by either of two methods, (A) or (B). In the former the temperature was raised directly to the required value, taking care not to overshoot because the exsolution process on cooling from overshooting proceeds by a different type of phase change from that on heating. After at least two days, the material was examined by means of X-rays and then returned for identical hydrothermal treatment for another few days, examined again and so on until there was no change in composition, i.e. until we reached what we describe as the final stationary concentration. In method (B), the hydrothermal treatment was maintained for a few days at a higher temperature, so that a solution supersaturated at the lower temperature of interest was prepared. Then at this latter temperature, the supersaturated starting material was treated in the same way as described in method (A).

A Philips diffractometer was used for the X-ray examination. We then used a counting rate computer to establish the precise peak positions, using Cu-$K\alpha$ radiation for the 211 and 131 reflections and Cu-$K\alpha_1$ for the 222 reflection. The errors in 2θ values listed in table I are those due to variation in counting rate; in solubility experiments they were sometimes greater, especially for the 222 peaks. The error due to geometrical factors is usually eliminated by the addition of an internal standard, but such addition would have prevented us from returning the samples for further hydrothermal treatment. Using pure quartz powder for calibration, we found that in our diffractometer an internal standard is not necessary, provided that the sample on the glass slide is very thin, so that it is practically in the same plane as the surface of the silicon slab that is used to set the goniometer. However, most samples used for solubility work contained a phase of pure tephroite, because this does not dissolve any lithiophilite as far as can be determined from peak positions. In these samples the tephroite could be used as an internal standard for a slight adjustment to 2θ values of the solid solutions.

In order to establish the relation between the three peak positions and the composition of the solid solution, correlation curves (fig. 1 and table I) were constructed by subjecting mixtures of weighed components to hydrothermal treatment for some days at temperatures up to 950° C and pressures up to 1500 atm in order to reach the homogeneous region of the phase diagram (fig. 3). The solid solutions are formed by the gradual dissolution of tephroite in lithiophilite, and this process is very slow if only a little free tephroite is left. For a few samples we were not able, therefore, to bring all the tephroite into solution and

in calculating the concentration it was necessary to allow for the presence of free tephroite in the following way.

The ratio (r') of the 222 peak area of the solid solution phase to that of the tephroite phase was determined. If the mole ratio of the two phases is $r = kr'$ it can be shown that X, the mole fraction of tephroite in the solid solution is given by

$$X = \tau - \lambda/kr',$$

where λ is the mole fraction of lithiophilite in the whole mixture and τ is that of tephroite. The value of k was found by separate experiments on unreacted mixtures of tephroite and lithiophilite and on unreacted mixtures of tephroite and solid solutions, the values of r being known for these mixtures from the quantities weighed out and the values of r' being found from X-ray diffraction. From these experiments k was found to vary between 1·2 and 1·7 and a mean value of 1·35 was used. As seen from the equation for X above, the correction term is small for large values of r', for which this method was used. In table I, the values of r' and τ are given as footnotes for those experiments where the dissolution of tephroite was incomplete.

Results

X-ray data as a function of concentration. From the experiments in which peak positions were determined as a function of composition of the solid solution, the dimensions of the unit cells were calculated. Results are given in table I and fig. 2. Within experimental error our values for the unit-cell dimensions of lithiophilite agree with those of Geller and Durand (1960) and our tephroite values with those of O'Daniel and Tscheischwili (1944). It will be seen from plotting the data given in the table that Vegard's law is best obeyed by the c dimension. As indicated by Zen (1956), this law is best discussed in terms of molar volumes, since perfect solutions would give an additive volume relation, and strictly speaking the lattice dimensions of perfect solutions would not be additive, although the changes are usually so small that additive volume usually implies effectively additive lattice dimensions. It will be seen from fig. 2 that for tephroite in lithiophilite there is a positive departure from additivity of volume, as would be expected from the separation into two phases, which implies imperfection in solution. It is interesting that many compounds with olivine-type structure appear to form perfect solutions in the liquid and the solid phase (Bradley, 1962).

Solubility measurements. From the study of peak positions for all experiments it is evident that tephroite dissolves at most 1 to 2 % lithiophilite. Results for the solubilities of tephroite in lithiophilite are
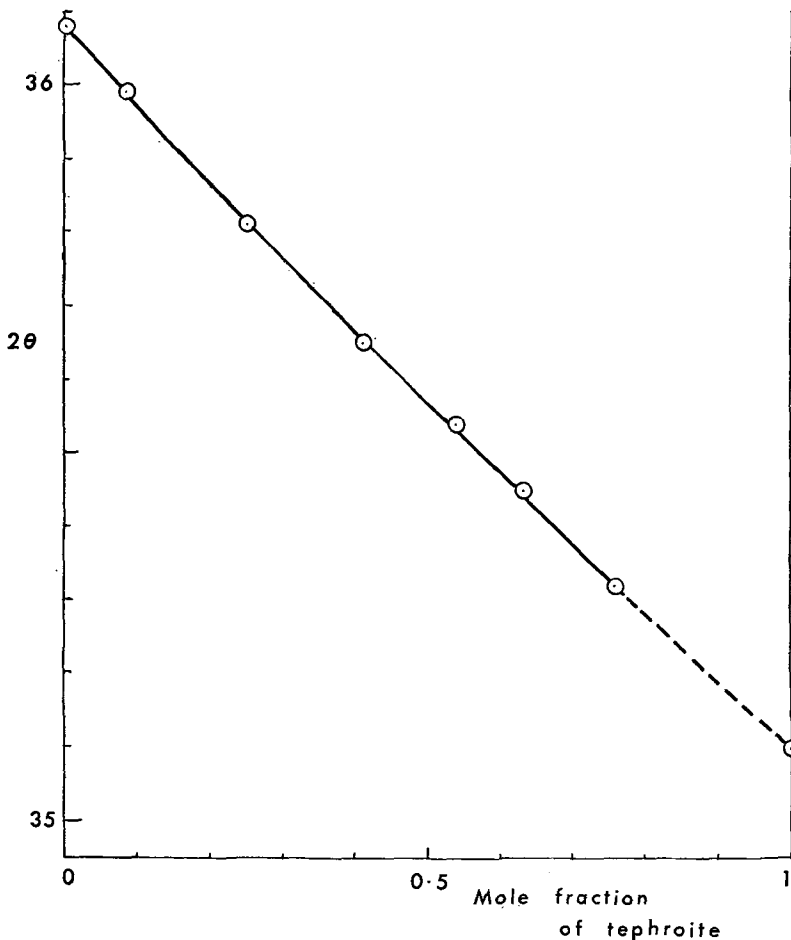

Fig. 1. Variation with composition of lithiophilite–tephroite solid solutions of 2θ values for 211 reflections.

given in table II in the form of the final stationary concentrations X (not necessarily true solubilities); data obtained at intermediate times are given for two representative experiments later. Solubility data given in table II were obtained mainly from the 211 peak positions

when available; the 222 peak positions are less sharp and the 131 peaks less separated. There was good agreement between concentration data obtained from the three peaks. Starting concentrations X_0 were zero unless otherwise stated. The mixtures, after hydrothermal treatment, were found to contain up to 1 mol % Mn$^{\cdots}$.

In method (A) there are always two phases present in the product, one being pure tephroite, the other a solid solution, the tephroite concentration of which increases with time, approaching a limit X. The rate of dissolution of tephroite increases with temperature and pressure,

TABLE I. Change of unit-cell dimensions with composition. X = mole fraction of tephroite in solid solution; v = volume of unit cell

				Lattice dimensions			
X	d_{222}	d_{211}	d_{131}	a	b	c	v
0	1·7605 Å	2·4893 Å	2·5467 Å	6·096 Å	10·431 Å	4·7369 Å	301·2 Å³
0·0819	—	2·4953	2·5544	—	—	—	—
0·250	1·7748	2·5075	2·5674	6·136	10·516	4·7794	308·4
0·413*	1·7846	2·5184	2·5794	6·156	10·555	4·8151	312·9
0·538	1·7098	2·5259	2·5859	6·171	10·571	4·8368	315·5
0·632†	1·7947	2·5322	2·5895	6·188	10·577	4·8471	317·2
0·756	1·8013	2·5411	2·5960	6·209	10·590	4·8683	320·1
1	1·8111	2·5565	2·6033	6·250	10·590	4·8968	324·1
σ	±0·0004	±0·0008	±0·0009	±0·003	±0·005	±0·0002	±0·3

* τ 0·437, r' 16·57.   † τ 0·6445, r' 23.

and with the amount of free tephroite present (hence final r' values are given in table II). The higher final concentrations are therefore probably nearer the true equilibrium results than the lower ones; compare experiments 8 and 3, 10 and 7; in each pair, higher initial mole fractions of tephroite lead to higher values of X in the product, and to lower values of r'. Experiments 2 and 5 show the reproducibility (± 4 %). The apparent solubility increases with pressure (compare experiments 6, 2, 5, and 4 at 795° C and experiments 7 and 9 at 845° C): this effect is in the opposite sense to that expected from the volume changes shown in fig. 2. It is probable that below 795° C the final stationary concentrations are much below equilibrium solubilities.

With method (B) there is either no change at all, or a third phase of lower concentration X' is formed additionally to the pure tephroite phase and to the parent solid solution of higher tephroite concentration. A progressive decrease in concentration of tephroite in the parent solid solution was not observed, i.e. the changes observed in method (B) are not the reverse of those observed in method (A). According to the Phase Rule the solid solution of higher tephroite concentration must disappear completely with time if equilibrium is reached, and this was
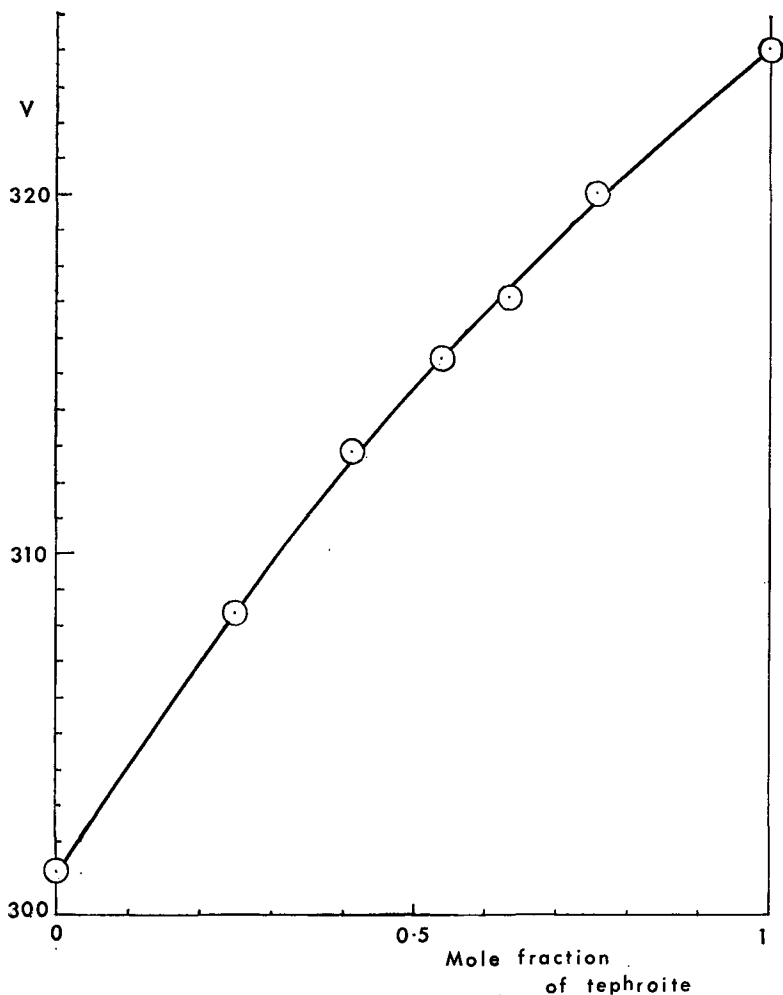
FIG. 2. Variation with composition of lithiophilite–tephroite solid solutions of unit cell volume (in Å³).

observed with some of the experiments (see later). The reaction is very slow unless there is sufficient supercooling; in experiments 15 and 16, temperatures 570° and 510° C respectively, the third phase gradually disappeared, and hence equilibrium may be supposed to have been reached in a few days, but at 612° C (experiment 17) three phases remained and at 660° C (experiment 18) only a trace of the low

concentration phase had been formed, even after the long time indicated. If this trend is extrapolated to the higher temperatures of experiments 22 and 23, it is not surprising that there was no change, in spite of the initial concentrations, which, according to fig. 3, are most probably supersaturated at the temperatures of the measurements.

TABLE II. Solubility measurements for tephroite in lithiophilite. The pressure was 1000 atmospheres except for experiments 6A, 10A, 7A, 8A, and 3A, for which it was 500 atmospheres. The end-product contained two phases except for experiments 17B and 18B, where it contained three; three phases were present at the end of the first day in experiments 16B and 15B, but only two finally. The starting material for experiment 12A was the product from experiment 11A

Expt. no.	Temp.	Time, days	X_0	τ	r'	X	X'
Experiments by method A:							
13A	695° C	20	—	0·5383	0·44	0·02	—
11A	745	26	—	0·6445	0·52	0·20	—
12A	745	15	0·20	0·6445	0·51	0·23	—
6A	795	29	—	0·6445	1·93	0·47	—
2A	795	14	—	0·6445	3·18	0·51	—
5A	795	13	—	0·6445	2·88	0·55	—
4A	795	12	—	0·6445	7·86	0·61	—
10A	845	18	—	0·7565	2·09	0·63	—
7A	845	19	—	0·6445	8·9	0·62	—
9A	845	12	—	0·7565	2·5	0·67	—
8A	895	8	—	0·8000	1 to 2	0·76	—
3A	895	8	—	0·7565	7·04	0·72	—
Experiments by method B:							
16B	510	5·6	0·45	0·6445	—	—	0·09*
15B	570	5	0·45	0·6445	—	—	0·12*
17B	612	83	0·48	0·6445	—	0·75	0·22†
18B	660	43	0·49	0·6445	—	0·53	0·18†
23B	715	35	0·61	0·6445	—	0·62	— ‡
22B	795	2·7	0·72	0·7565	—	0·73	— ‡

* Three phases at end of first day.   † No equilibrium.   ‡ No change.

Fig. 3 serves three purposes: To establish the solubility curve, using only those experiments that, following the explanations above, are likely to be nearest to true equilibrium. To present striking examples of non-equilibrium stationary states among experiments (A) (experiments 13, 11, 12). And to illustrate the tendency for supersaturation during cooling by plotting the unchanging concentrations of experiments 22 and 23.

The sluggishness of a reaction is not unusual in hydrothermal work. With our system, however, stationary concentrations are reached that

in certain instances are certainly not equilibrium values; similar phenomena were observed in hydrothermal work by Kennedy (1959). In experiments (A) the somewhat poor reproducibility of the stationary concentrations and their increase with pressure (although there is an
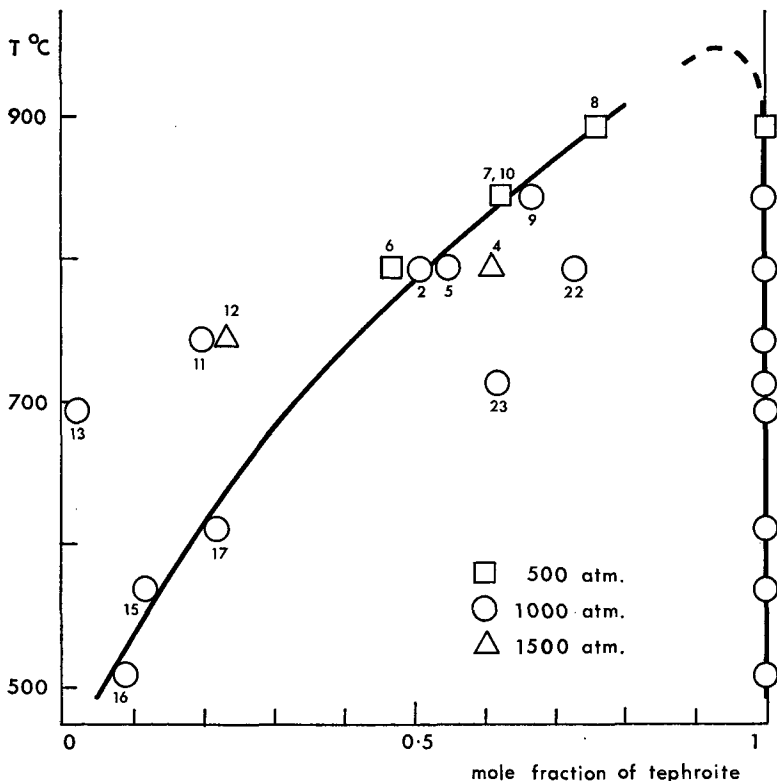

FIG. 3. Solubility diagram for the system lithiophilite–tephroite. Points are numbered to correspond with table II. The tendency to exhibit non-equilibrium stationary states is illustrated by points 11, 12, 13. Supersaturation during cooling is shown by points 22, 23. The remaining points approximate to conditions of equilibrium solubility.

increase of volume during mixing) suggest that the stationary states fall short of the equilibrium solubility values, even if this is not always as striking as in experiments 13, 11, 12. In conclusion, concerning the final stationary concentrations, we can state that we found a temperature-dependent limited solubility of tephroite in lithiophilite, but the position of the solvus is not quite certain.

We present the time dependence of two typical experiments in order to emphasize the peculiarities.

Experiment No. 2 (method A)

Time (days)	2	4	6	8	10	14
X	0·40	0·460	0·485	0·48	0·52	0·51

We see the progressive increase in concentration (in this experiment we changed from 10 % to 20 % water after 8 days). If two compounds of comparable solubilities reacted in the liquid phase and the product formed by nucleation, the simultaneous presence of three phases would be expected and it would be difficult to explain the above process by a liquid-state reaction, although hydrothermal reactions dependent on such nucleation mechanisms certainly exist (Fyfe, Turner, and Verhoogen, 1958). On the other hand the mechanism observed by Wyart and Sabatier (1958), which involves solid-state diffusion facilitated by defects caused by water, would probably make our solid solutions at intermediate times inhomogeneous, and this also was not observed. The progressive change in concentration, where observed, must have been noticed in the formation of other solid solutions, but has been reported by Rosenberg (1963) only.

Experiment No. 17 (method B) with third phase

Time (days)	0	6	36	83
X'	—	0·11	0·20	0·22
X	0·48	0·52	0·68	0·69

The progressive increase of tephroite concentration in the original solution phase is of course understandable if the second solution phase of lower tephroite concentration separates out of it. Similar trends in the second solution phase (X') may be due to its being in contact with the original solution phase, the tephroite concentration of which increases with time. There seems to exist a one-sided barrier preventing the separation out of tephroite from solid solution in a back-reaction that would be the exact reverse of the forward dissolution reaction, and therefore the back-reaction must proceed via the formation of a third, tephroite-poor phase. We are not in a position to explain this barrier and also we are unable to choose between a liquid- and a solid-phase reaction mechanism.

Forsterite—LiMgPO₄ system. LiMgPO₄ has an olivine structure (Thilo, 1941); we find cell-dimensions: a 5·901±0·002, b 10·13±0·001, c 4·687±0·0002 Å.

Preliminary studies have been made on the formation of solid solutions between forsterite and $LiMgPO_4$ by mixing the components in equal molar quantities and subjecting them to the hydrothermal treatment at 800° C and 1000 atm for 2 days, or 950° C and 200 atm for 2 days. The positions of the peaks of the pure compounds were compared with their positions after hydrothermal treatment of the mixture, using thin samples for X-ray work, without an added internal standard. We have assumed that to a first approximation the curves of 2θ against composition are linear. Results are given in table III.

TABLE III. Miscibility of Mg_2SiO_4—$LiMgPO_4$

Indices		Mg_2SiO_4 2θ	$LiMgPO_4$ 2θ	Mole fraction of solute in Mg_2SiO_4	in $LiMgPO_4$
222	pure	52·33	53·04	0·02	0·11
	in s.s.	52·35	52·97		
223	pure	69·60	70·64	0·01	0·10
	in s.s.	69·61	70·54		

It will be seen that in this system the concentration of silicate reached in the phosphate phase is considerably less than in the previous system, but that the solvus has a similar asymmetry.

Discussion. The asymmetry of the solvus is somewhat surprising in view of the similarity between the structures of the phosphates and silicates chosen. They both belong to the *Pmnb* spacegroup. There are of course other examples of asymmetry, even in the liquid state (e.g. fluorocarbon–hydrocarbon systems). With solid solutions, the system $CaCO_3$–$MgCO_3$ provides a somewhat similar example, although it is complicated by the appearance of the compound, dolomite. (Harker and Tuttle, 1955; Goldsmith and Heard, 1961). Asymmetry has also been reported by Alberman *et al.* (1951) for the UO_2–CaO system and by Miller *et al.* (1963) for the GeO_2–SiO_2 system, where, however, the components do not have the same structure.

The structural factors that must contribute to the lattice energy and to the energy of solution are:

	Si	P	O	Mg	Mn	Li
Atomic radii (Slater, 1964)	1·10	1·00	0·60	1·50	1·40	1·45 Å
	Si^{4+}	P^{5+}	O^{2-}	Mg^{2+}	Mn^{2+}	Li^+
Ionic radii (Pauling)	0·41	0·34	1·40	0·65	0·80	0·60 Å
Electronegativity (Allred-Rochow)	1·74	2·06	3·50	1·23	1·60	0·97

When in our system PO$_4$ is replaced by SiO$_4$ and simultaneously Li by Mn (or Mg), it would be expected on simple electrostatic grounds that the lattice energy of tephroite would be greater than that of lithiophilite, and that the lattice energy of the solid solution would be intermediate. The consequent picture of a regular solution can explain phase separation but not asymmetry unless the molar volumes of the components are appreciably different and volume fractions are used instead of mole fractions; however our molar volumes differ only by about 8 %. A theoretical approach might depend on the variation of covalent character with composition. In lithiophilite even the Mn–O bond is partly covalent as shown by the magnetic studies of Mays (1963), which indicated a super-exchange through the chain Mn–O–P–O–Mn and the same may apply to silicate-olivines. Another possible approach is via crystal-field theory. There is no crystal-field stabilization energy for Mn·· in a perfect octahedral field, but the octahedra in lithiophilite are distorted (Geller and Durand, 1960) and the same is possible in tephroite. The solid solution will contain additional local distortions, because the volumes of the constituents are not equal.

Miller et al. (1963) attribute the asymmetry of their GeO$_2$–SiO$_2$ system to kinetic factors preventing the establishment of equilibrium in one of the phases. This is less likely in our system because the tephroite remained pure in both forward and back-reaction.

Mineralogical discussion. Having established that there is a limited temperature-dependent solubility of tephroite in lithiophilite and some sort of solubility of forsterite in LiMgPO$_4$, it is very likely that the more common rock forming olivines, if present, could dissolve in lithiophilite, triphylite, and natrophilite, which occur in pegmatites. Absence of such observation[1] is presumably due to the high water content and high silica content of pegmatites, which do not favour the formation of silicate-olivines, although in a few cases fayalite was found in pegmatites (Fersman, 1931; King, 1961). Moreover, lithiophilite crystallizes at the pneumatolytic stage of pegmatites, i.e. in the temperature range 400° to 600° C (Fersman, 1931; Turner and Verhoogen, 1951), where, according to our results, the solubility of silicates is likely to be small and would decrease further if hydrothermal conditions were maintained during cooling to lower temperature. If pegmatite intruded into olivine-

[1] The Editor has suggested that the absence of a report on SiO$_2$ does not necessarily mean that SiO$_2$ is absent, since many phosphate analyses are made without specific search for SiO$_2$, which if found is sometimes regarded as an impurity and not listed. Further experimental work on this point is desirable.

bearing rock, silicate–phosphate reaction at the interphase must be considered. However, the effect of water in decomposing silicate-olivines would compete with this interphase reaction, which according to our relevant experiments (A) is slow in the temperature range of the pneumatolytic stage.

References

ALBERMAN (K. B.), BLAKEY (R. C.), and ANDERSON (J. S.), 1951. Journ. Chem. Soc., p. 1352 [M.A. **11**–433].

BOWEN (N. L.) and TUTTLE (O. F.), 1949. Bull. Geol. Soc. Amer., vol. 60, p. 439 [M.A. **11**–93].

BRADLEY (R. S.), 1962. Amer. Journ. Sci., vol. 260, p. 550 [M.A. **15**–522].

DENNEN (W. H.) and SHIELDS (R.), 1956. Amer. Min. vol. 41, p. 655 [M.A. **13** 375].

FERSMAN (A. E.), 1931. Les pegmatites, Acad. Sci. URSS, pp. 55, 414, and 402.

FYFE (W. S.), TURNER (F. J.), and VERHOOGEN (J.), 1958. Metamorphic Reactions and Metamorphic Facies, Geol. Soc. Amer., Memoir 73, p. 80 [M.A. **14**–88].

GELLER (S.) and DURAND (J. L.), 1960. Acta Cryst. vol. 13, p. 325.

GOLDSMITH (J. R.) and HEARD (H. C.), 1961. Journ. Geol., Chicago, vol. 69, p. 45 [M.A. **15**–275].

HÄGELE (G.) and MACHATSCHKI (F.), 1939. Naturwiss., vol. 27, p. 132 [M.A. **7**–395].

HARKER (R. I.) and TUTTLE (O. F.), 1955. Amer. Journ. Sci., vol. 253, p. 274 [M.A. **13**–176].

HATA (S.), 1938. [Sci. Papers Inst. Phys. Chem. Research Tokyo, vol. 34, p. 619]; abstr. M.A. **7**–264.

HEY (M. H.), 1962. Chemical Index of Minerals, British Museum (Natural History), p. 214.

JEFFORD (G.), 1962. Amer. Min., vol. 47, p. 1469.

KENNEDY (G. C.), 1959. Amer. Journ. Sci., vol. 257, p. 567 [M.A. **14**–335].

KIMURA (K.) and HIRONAKA (Y.), 1936. [Journ. Chem. Soc. Japan, vol. 57, p. 1195]; abstr. M.A. **7**–263.

KING (E. A., Jr.), 1961. Amer. Min., vol. 46, p. 747 [M.A. **15**–395].

KORITNIG (S.), 1964. Naturwiss. vol. 51, p. 633.

McCONNELL (D.), 1937. Amer. Min., vol. 22, p. 977 [M.A. **7**–14].

—— 1952. Ibid., vol. 37, p. 609 [M.A. **12**–169].

MACHATSCHKI (F.), 1942. Zentr. Min. Geol. Paleont., Abt. A, p. 1 [M.A. **8**–303].

MASON (B.) and BERGGREN (T.), 1941. [Geol. För. Förh., vol. 63, p. 413]; abstr. M.A. **8**–338.

MAYS (J. M.), 1963. Physical Reviews, vol. 131, p. 38.

MERKER (L.) and WONDRATSCHEK (H.), 1960. Zeit. Krist. vol. 113, p. 475.

MILLER (W. S.), DACHILLE (F.), SHAFER (E. C.), and ROY (R.), 1963. Amer. Min., vol. 48, p. 1024 [M.A. **16**–527].

NICOLAS (J.) and ROSEN (A.), 1963. Bull. Soc. franç. Min. Crist., vol. 86, p. 383.

O'DANIEL (H.) and TSCHEISCHWILI (L.), 1944. Structure Reports, vol. 9, p. 261 [M.A. **9**–231].

ROBIN (J.), 1953. Bull. Soc. Chim. France, Mémoires, p. 1078.

ROBINSON (P.) and McCARTNEY (E. R.), 1964. Journ. Amer. Ceram. Soc., vol. 47, p. 587.

ROSENBERG (P. E.), 1963. Amer. Min. vol. 48, p. 1397 [M.A. **16**–623].

SLATER (J. C.), 1964. Journ. Chem. Physics, vol. 41, p. 3199.

THILO (E.), 1941. Naturwiss., vol. 29, p. 239 [M.A. 8–220].

TSCHERMAK (G.), 1864. [Sitzungsber. Akad. Wiss. Wien, vol. 50, p. 566]; abstr. in Eitel (W.), 1958, Geol. Soc. Amer., Special Paper 66, p. 53 [M.A. 14–89].

TURNER (F. J.) and VERHOOGEN (J.), 1951. Igneous and Metamorphic Petrology, p. 332, McGraw-Hill, New York.

TUTTLE (O. F.), 1949. Bull. Geol. Soc. Amer., vol. 60, p. 1727.

WYART (J.) and SABATIER (G.), 1958. Bull. Soc. franç. Min. Crist., vol. 81, p. 223 [M.A. 14–332].

WYLIE (A. W.), 1948. Nature, vol. 161, p. 97 [M.A. 10–538].

ZEN (E–An), 1956. Amer. Min., vol. 41, p. 523 [M.A. 13–198].