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NEW DATA ON KENTROLITE AND MELANOTEKITE: TERNARY PHASE RELATIONS IN THE SYSTEM PbO-Fe_2O_3-SiO_2

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ABSTRACT

A phase identical with melanotekite is readily prepared by heating the composition $2PbO \cdot Fe_2O_3 \cdot 2SiO_2$ in an air atmosphere at 650°–700°C. Results of heating experiments and crystallographic examination of naturally occurring melanotekite confirm this formula. Melanotekite is orthorhombic, space group P***, $a=6.97$, $b=11.0$, $c=9.83$ Å. Kentrolite, $2PbO \cdot Mn_2O_3 \cdot 2SiO_2$, is isostructural with melanotekite; $a=7.00$, $b=11.0$, $c=9.97$ Å. $Z=4$.

Laboratory studies to determine the subsolidus compatibility triangles show that at 650°C, melanotekite can coexist with the following minerals: alamosite ($PbSiO_3$), quartz, hematite, magnetoplumbite ($PbO \cdot 6Fe_2O_3$), and plumboferrite ($PbO \cdot 2Fe_2O_3$). In addition a new ternary phase, probably $12PbO \cdot Fe_2O_3 \cdot 2SiO_2$, has been encountered.

INTRODUCTION

Analyses of kentrolite by Damour and Von Rath (1880) and of melanotekite by Lindstrom (1880) indicated the approximate chemical composition $2PbO \cdot R_2O_3 \cdot 2SiO_2$ (R = Mn, Fe). Goniometric data indicated that kentrolite and melanotekite were members of an isomorphous series. At that time it was not certain that the manganese and iron were present in the tripositive oxidation state. Warren (1898) established that iron and manganese were tripositive. However, his analyses of single crystals of melanotekite indicated a molar ratio ($Fe_4^{3+}O_3$) $Pb_3(SiO_4)_3$ or $3PbO \cdot 2Fe_2O_3 \cdot 3SiO_2$. Gabrielson (1962) was apparently unaware of Warren's study and therefore used the Flink formula, $Pb_2(R^{3+})_2 Si_2O_9$; R = Mn, Fe. The density and unit-cell volume indicated that the unit cell contained four formula units. Gabrielson also determined the crystal structure of kentrolite ($R = Mn^{3+}$).

STUDIES OF NATURAL KENTOLITE AND MELANOTEKITE

Samples of kentrolite and melanotekite were obtained from the United States National Museum and were designated as follows: C3224, melanotekite, Långban, Sweden; R3889 kentrolite, Långban,* Sweden; C3223, kentrolite, Långban. The latter specimen contained kentrolite crystals in a matrix of other phases and a handpicked kentrolite concentrate was prepared from this specimen. The bulk densities of the massive specimens C3224, and R3889 were 6.040 and 5.961 ± 0.005 g/cc., respectively. The density of the kentrolite concentrated as determined from 3.5 gm.

* Designated Långbanshyttan in the U.S.N.M. collection; the longer name is not used in Sweden.

was 6.2 ± 0.1 g/cc. Densities were determined with a Beckman air comparison pyknometer.

Typical X-ray powder patterns of kentrolite and melanotekite are shown in Table 1. Single crystals of kentrolite were readily extracted from C3223. X-ray rotation and Weissenberg photographs gave a primitive orthorhombic cell with $a=7.00$ Å, $b=11.04$ Å, $c=9.97$ Å. The axial ratios derived from these cell dimensions (0.634, 1.00, 0.903) are in good agreement with those derived from goniometric study (orthorhombic; 0.633, 1.00, 0.899 respectively); Strunz (1957). Determination of the space group is handicapped by a large number of systematic weaknesses and it is difficult to distinguish the true absences from weaknesses. For

TABLE 1. INDEXED POWDER X-RAY DATA FOR KENTROLITE

(U.S.N.M. C3223)

dÅ	I	hkl	dÅ	I	hkl	dÅ	I	dÅ	I
5.56	ms	020	2.90	vs	113	2.28_8	w	1.943	mw
5.10	mw	111	2.86	vs	202, 211	2.22_8	vw	1.892	m
5.01	w	002	2.84	s	023, 221	2.20_6	vw	1.877	mw
3.71	s	022	2.73_5	vs	040, 212	2.17_1	vw	1.834	m
3.51	s	200	2.70_5	w	132	2.12_7	m	1.818	w
3.24	s	122, 130	2.60_7	vw	123	2.11_0	m	1.791	vw
3.17	vw	013, 211	2.55_0	w	140	2.09_4	w	1.751	w
3.11	w	131	2.48_3	w		2.03_1	vw	1.732	vw
3.04	mw	?	2.42_1	w		1.994	w	1.704	mw
2.96	m	032, 220	2.356	vw		1.973	w	1.652	mw
			2.23_3	vw					

Melanotekite (USNM C3224). The first 17 powder lines from $d=\infty$ to 2.5 Å, have the following d (Å) and relative intensities:

5.62, s; 5.05, s; 4.95, w; 3.78, s; 3.57, s; 3.32, s; 3.22, vw; 3.16, w; 3.01, w; 2.95, vs; 2.92, vs; 2.91, s; 2.89, m; 2.78, vs; 2.72, mw; 2.61, vw; 2.59_8 mw.

example, amongst the $h00$ reflections only reflections equal to $2n$ appeared to be present. It was first thought that of the $00l$ reflections only those equal to $2n$ appeared to be present but long exposures disclosed that $l=5$ was present, but weak. Kentrolite and melanotekite crystals gave identical patterns of systematic weaknesses. Therefore the space group could not be positively determined but the crystals definitely have a primitive diffraction aspect. Gabrielson gives a unit cell virtually identical with that obtained in the present study. However, he concluded that the crystals were centered, and produced a structure based on the space group $C222_1$ (No. 20). Consideration of the strong sets of reflections only leads to Gabrielson's space group: consideration of the systematically weak reflections, found in all the crystals examined in this study, leads to the primitive aspect. The weak reflections were most

readily apparent in Weissenberg photographs parallel to c; Gabrielson had no photographs in this direction. This, together with the limited range of F_{obs}, suggests that the weak reflections may well have been present, but overlooked, in Gabrielson's study. In general the 'R' factor for Gabrielson's data (calculated by the present writer as 32–34 percent in the hOl and Okl sections) suggest that the silicon and oxygen positions are not very well established. A new structure determination is now being made by L. S. Dent Glasser. In addition, several crystals gave a few weak, nonintegral reflections: these belong to some other crystalline phase. The other phase was not visible upon optical examination of the crystals and was not identified further.

TABLE 2. CHEMICAL ANALYSES OF MELANOTEKITE—KENTROLITE

	Melanotekite				Kentrolite		Atomic Ratios			
	Lindstrom		Warren		Damour	Flink	Lindstrom	Warren (average)	Damour	Flink
	I	II	I	II			II			
SiO_2	17.32	17.22	15.51	15.48	15.95	17.68	2.18	2.06	1.98	2.36
PbO	55.26	58.42	55.50	55.63	59.79	55.72	2.00	2.00	2.00	2.00
Fe_2O_3	23.18	22.81	27.49	27.52	—	5.58				
Mn_2O_3	0.76	0.63	—	—	22.26	21.18	1.10	1.37	1.00	1.27
H_2O	—	—	0.68	0.67	—	—				
CaO	—	—	—	—	—	0.91				
X*	3.59	0.84	—	—	—	—				
			Mole Fraction							
SiO_2	0.420	0.412	0.381		0.393	0.412				
PbO	0.363	0.378	0.367		0.398	0.351				
R_2O_3	0.217	0.210	0.252		0.209	0.237				

* X = CaO, M_gO, Na_2O, K_2O, BaO, CuO, FeO, P_2O_5 and Cl.

Melanotekite crystals from C3224 gave a primitive orthorhombic cell with $a = 6.97$ Å, $b = 11.0$ Å, $c = 9.93$ Å. The two crystals examined did not give any nonintegral reflections.

Dana (1898) gives 6.19 as the density of kentrolite. The unit-cell volume as determined in the present study is 760 Å^3. The Warren formula for this series ($3PbO \cdot 2M_2O_3 \cdot 3SiO_2$) gives a formula weight of 1165.5 for kentrolite. The number of formula units per cell, Z, is 2.4. If, however, the "rejected" formula is used, the formula weight becomes 724.3 and $Z = 3.91$. For $Z = 4.00$, the theoretical density would be 6.31. Thus the formula $2PbO \cdot M_2O_3 \cdot 2SiO_2$ provides a better fit to the crystallographic data. The analytical data are compared in Table 2.

The analytical data for both Mn and Fe-rich end members are included. Both members have the same symmetry and complete solid solution exists between them (Professor C. Frondel, oral communication).

Except for Warren's data, the analyses are compatible with the 2:1:2 ratio.

Samples of kentrolite (USNM C 3223) and melanotekite (USNM C 3224) were heated to 120°C and 700°C. Handpicked concentrates of both kentrolite (C 3223) and melanotekite (C 3224) lost some weight on heating to 120°C (0.04 and 0.02 wt. % resp.). On further heating to 700°C, neither lost more than an additional 0.02 weight percent, and the X-ray pattern remained unchanged. Differential thermal analysis of kentrolite did not reveal any thermal effects between 22°C–840°C. The sample was still unmelted at 840°C and gave an unchanged powder pattern after cooling to room temperature.

Studies on PbO-Fe_2O_3-SiO_2 and PbO-Mn_2O_3-SiO_2 compositions. A mixture of composition $2PbO \cdot Fe_2O_3 \cdot 2SiO_2$ heated to 700°C in air gave an apparently single-phase product. Guinier photographs showed that the powder pattern was identical with that obtained from natural melanotekite. However, the composition $3PbO \cdot 2Fe_2O_3 \cdot 3SiO_2$ reacted at 700°C, gave a powder pattern of a two phase mixture: melanotekite plus hematite. The hematite remained even after repeated crushing and resintering. Thus this composition lies at least approximately on the join melanotekite-hematite.

Oxide mixtures of the composition $2PbO \cdot Mn_2O_3 \cdot 2SiO_2$ sintered at 700°C in air yield an apparently single-phase preparation. The powder pattern matched that of kentrolite at the larger spacings. The over-all fit, especially for the weaker lines, became less perfect at spacings below approximately 2.5 Å. The differences between the two powder patterns may be due to slight differences in symmetry between natural and synthetic phases, but it is more likely that the appreciably large cell dimensions of the synthetic product, compared with those of kentrolite, are sufficient to cause the minor differences observed. No chemical analyses of the kentrolite were available, but kentrolite commonly contains a relatively high iron content (Table 2), and its unit-cell size is appreciably smaller than that of the synthetic Mn end-member. The sintered preparations did not yield single crystals suitable for X-ray diffraction study.

It was felt that a knowledge of the subsolidus compatibility triangles would be helpful in further confirming the formula of melanotekite. In addition to melanotekite, the PbO-Fe_2O_3-SiO_2 system contains six compositions which are represented by one or more naturally-occurring phases. The compositions and polymorphic forms relevant to the present study are: SiO_2: quartz, $PbSiO_3$: alamosite, PbO: litharge, massicot: $PbO \cdot 2Fe_2O_3$, plumboferrite: $PbO \cdot 6Fe_2O_3$, magnetoplumbite and Fe_2O_3:

hematite. In addition the phases $2PbO \cdot SiO_2$, $4PbO \cdot SiO_2$ (α, β and γ polymorphs) and $2PbO \cdot Fe_2O_3$ are known from phase equilibrium studies of the PbO-SiO_2 and PbO-Fe_2O_3 systems. In order to understand the ternary phase relationships, it was necessary to make a few additional experiments on the limiting one and two component systems.

The effect of SiO_2 and Fe_2O_3 on the polymorphism of PbO. PbO occurs in two well characterized polymorphs: the low temperature form is red PbO, or litharge: the high form is yellow PbO, or massicot. The high-low inversion at $\sim$ 450°C is sluggish, and yellow PbO is readily preserved to room temperature even during slow cooling. Appropriate mixtures of either yellow or red PbO and SiO_2 were heated to 650°C and subsequently cooled. Only yellow PbO and $\gamma 4PbO \cdot SiO_2$ were identified. However, appropriate PbO-Fe_2O_3 mixtures gave only red PbO under the same conditions. A few PbO-Fe_2O_3-SiO_2 compositions gave both red and yellow PbO phases, but several regrindings and refirings resulted in complete conversion of the PbO to litharge. Differential thermal analyses of several litharge-containing compositions did not reveal any heat effects which might be due to the partial or complete conversion of massicot→litharge during the cooling stage. It is probable that Fe_2O_3 has a stabilizing influence on red PbO. Powder patterns of this stabilized red PbO were identical in spacings and relative intensities with those reported for pure red PbO (Swanson and Fuyat, 1954) except that the 101, 200 and 202 reflections were diffuse; the others were sharp.

The lead silicates. Geller, Creamer and Bunting (1934) reported the existence of three polymorphs of $4PbO \cdot SiO_2$. The β phase was stable from 720°–140°C; at the lower temperature it underwent a rapid inversion to γ-$4PbO \cdot SiO_2$. This was also confirmed in the present study by D.T.A; a reversible heat effect was found to extend over a 5–10°C range, centered at 143° $\pm$ 2°C. The existence of the other reported polymorphic form, α-$4PbO \cdot SiO_2$, stable from 720°C to the incongruent melting point at 725°C, is less certain. It was found that runs quenched from 732°C or slightly over, yielded yellow PbO in glass. However at 727°C, the PbO was partially surrounded by a fibrous birefringent phase together with some glass. This birefringent phase gave a characteristic X-ray powder pattern and is presumably "α-$4PbO \cdot SiO_2$". It was also obtained at 720°C together with PbO and β-$4PbO \cdot SiO_2$, but not at lower temperatures. The texture of the birefringent phase in the 732°C run certainly suggests that the α phase arises from devitrification of part of the liquid during the quenching stage. It is thus uncertain if its composition is

$4PbO \cdot SiO_2$. Powder data are shown in Table 3. Powder data for the other lead silicates are in good agreement with those reported by Argyle and Hummel (1960).

The lead ferrites. Berger and Pawlek (1957) and Mountvala and Ravitz (1962) studied the lead ferrites. Three compounds were found: $2PbO \cdot Fe_2O_3$, $PbO \cdot 2Fe_2O_3$ and $PbO \cdot 6Fe_2O_3$. Mountvala and Ravitz were unable to synthesize these phases at temperatures below 650, 750, and 760°C, respectively and assumed that these temperatures corresponded to the lower limit of stability of the phases. In the present study, fine-grained PbO and Fe_2O_3 were observed to have reacted, forming $2PbO \cdot Fe_2O_3$ at 600°C, and $2PbO \cdot 2Fe_2O_3$ and $PbO \cdot 6Fe_2O_3$ at 650°C. Crystalline samples of each of the three phases showed no tendency to decompose in runs of 10 days' duration at 600° and 14 days at 550°C. Therefore, there is no positive evidence that these phases have the lower limit of stability shown by Mountvala and Ravitz. Likewise, no positive evidence for the variable composition reported for these phases was found. The natural occurrences of plumboferrite and magnetoplumbite do not suggest temperatures of formation above 750–760°C, nor do the limited number of analyses of natural minerals suggest the existence of a relatively wide band of compositions. Powder data for the $2PbO \cdot Fe_2O_3$ phase are reported in Table 3. The strong reflections can be indexed on the basis of a primitive cubic cell with $a \simeq 3.89$ Å. On account of the high pseudosymmetry it would by unwise to deduce a true cell from the remaining weaker powder reflections.

Ternary phase relations. Thirty-one PbO-Fe_2O_3-SiO_2 compositions were prepared. The phases present in the heated compositions were determined and these data used to construct the subsolidus compatibility triangles as shown in Figure 1. In addition to melanotekite, another ternary phase, designated as *X* in Figure. 1, was encountered. This phase gives the characteristic X-ray diffraction pattern shown in Table 3. Its exact composition is uncertain, but lies at or close to the molar ratio $12PbO \cdot Fe_2O_3 \cdot 2SiO_2$. An apparently single-phase preparation of this composition has a density of 8.1 g/cc: it is weakly ferromagnetic. The relatively low content of Fe_2O_3 and SiO_2, coupled with the high formula weight of lead makes it difficult to locate the composition to an accuracy better than ± 2 mole percent. The X-ray powder pattern of the *X* phase bears a striking resemblance to that of red PbO, except that the reflections of the *X* phase are shifted considerably to shorter spacings. The strongest lines can thus be indexed on the basis of a primitive tetragonal pseudocell having $a = 3.83$, $c = 4.82$ Å. This represents a substantial

TABLE 3. X-RAY POWDER DATA FOR SELECTED PbO-Fe_2O_3-SiO_2 PHASES

"α-$4PbO \cdot SiO_2$"[1]		$2PbO \cdot Fe_2O_3$[2]			Phase X, probably $12PbO \cdot Fe_2O_3 \cdot 2SiO_2$[2]		
*d*Å	*I*	*d*Å	*I*	*hkl*[3]	*d*Å	*I*	*hkl*[4]
6.60	w	4.52	w		6.80	m	
5.62	mw	4.00	vw		5.35	w	
5.43	mw	3.88	s	100	4.70	m	
5.40	vw	3.50	ms		3.75	w	
4.25	vw	3.12	ms		3.34	m	
4.19	vw	3.06	m		3.05	w	
4.00	mw[5]	2.75–7[6]	vvs	110	3.00	vs	101 (vvs)
3.77	ms	2.34	s	111	2.71	s	110 (vs)
3.49	mw	2.17	w		2.64	w	
3.41	mw	1.970	w		2.41	m	002 (m)
3.34	m	1.94[6]	vs	200	2.39	w	
3.29	ms	1.870	w		2.36	mw	
3.21	m	1.74[6]	w	210	2.30	w	
3.09	s[5]	1.59[6]	vs	211	2.19	w	102 (vw)
3.05	m	1.375	vs	220	2.17	w	
3.02	vs	1.230	s	310	2.04	w	
2.92	s[5]				1.922[6]	ms	200 (m)
2.84	s				1.918	ms	
2.82	m	*a*	3.90 Å		1.835	mw	
2.78	m				1.805	s	112 (s)
2.74	m[5]				1.710	w	
2.69	s				1.698	vw	
2.67	w				1.615	s	211 (s)
2.56	vw				1.580	vw	
2.49_5	ms				1.550	w	
2.42_0	m				1.502	m	202 (w)
2.30_5	s				1.484	m	103 (m)
2.29_5	w				1.460	w	113 (w)
2.24_0	m				1.435	vw	
2.23_0	w				1.356	ms	220 (s)
2.22_0	m						
2.170	m						
2.115	w						
1.998	s[5]						
1.880	m						
1.810	m						

[1] Sample prepared by heating $4PbO \cdot SiO_2$ composition 4 hrs. at 727°C.

[2] Guinier photograph.

[3] Pseudo cubic cell.

[4] Pseudo tetragonal cell with $a = 3.83$ Å, $c = 4.82$ Å. Intensities in parentheses after the (*hkl*) values are those for red PbO: Tetragonal, $a = 3.973$, $c = 5.019$ Å.

[5] Probably yellow PbO.

[6] Diffuse reflection.

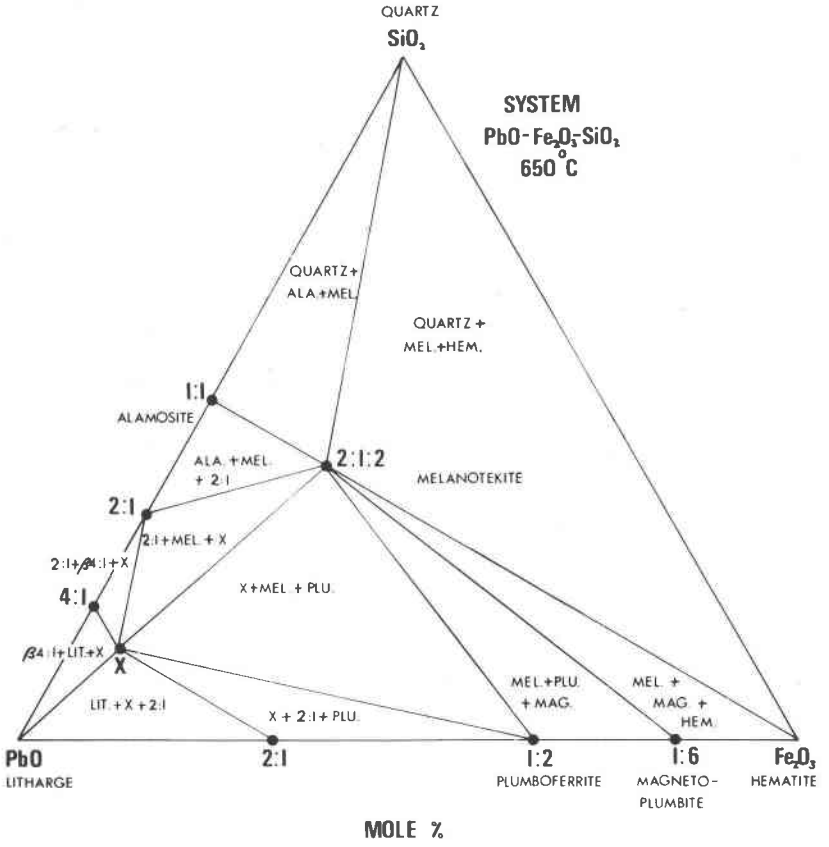

FIG. 1. Subsolidus compatibility relations. Phase X is probably $12PbO \cdot Fe_2O_3 \cdot 2SiO_2$: see text. Phases known to occur in nature have been designated with their mineralogical names; the first three letters of these names are used as abbreviations.

contraction in cell dimensions: litharge has $a = 3.97$, $c = 5.02$ Å. Mixtures on the PbO-X join were examined to see if the X phase might represent a solid solution based on litharge itself. However, the position and intensity of reflections in the powder patterns suggest that PbO and X occur as discrete phases and that the similarity in powder patterns is not caused by solid solution in the litharge phase. It is suggested that the arrangement of lead atoms in the X phase is basically similar to that found in red PbO. Differential thermal analysis of the X phase did not reveal any heat effects between 24° and 740°C. The X phase remained unmelted at 740°C. Weight change studies were made on the X-phase composition to see if it gained or lost oxygen upon heating in air. Previously dried

PbO, SiO_2 and Fe_2O_3 were used as starting materials. After heating the 12 $PbO \cdot Fe_2O_3 \cdot 2SiO$ composition in air for three days at 650°C, three days at 675, and three days at 700°C a 10-gram sample had a cumulative weight loss of 0.0012 gram. It is not therefore likely that the *X* phase contains lead or iron in some higher oxidation state *e.g.*, Pb^{4+}, Fe^{4+}, unless the rather unlikely assumption is made that the lead present in some higher oxidation state is gravimetrically balanced *e.g.*, by reduction of iron to Fe^{2+}.

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