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CHEVKINITE AND PERRIERITE: SYNTHESIS, CRYSTAL GROWTH AND POLYMORPHISM[1]

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ABSTRACT

Synthetic chevkinite and perrierite, $Ln^{3+}{}_4M^{2+}(Ti^{4+}M^{2+})_2(Ti^{4+}O_4)_2\cdot(Si_2O_7)_2$; $M^{2+}=Fe^{2+}$, Co, Ni and Mg; $Ln^{3+}=$La, Ce, Pr, Nd and Sm, demonstrate polymorphism (1 st order transition) within certain chemical compositions. $Mg_2Pr_4Ti_3Si_4O_{22}$ and $Ni_2Pr_4Ti_3Si_4O_{22}$, crystallized from the gels as perrierites (low temperature form) at temperatures of approximately 990°C in air, transform to chevkinites (high-form) by elevating temperatures above 1070°C. The unit-cell dimensions for these two sets of perrierite-chevkinite polymorphs were obtained from computer refined X-ray powder diffractometer data.

Nearly all of the chevkinites and perrierites are primary phases. Single crystal growth was effected directly from melt either by slow cooling or pulling. The crystals of all the probable end members have been obtained up to maximum size 2mm.

Single crystal X-ray studies using the precession method indicate space group $P2_1/a$ for the synthetic Co-Pr and Mg-Nd chevkinite, and Mg-La perrierite. The space group originally reported for the natural specimens is $C2/m$.

Wet chemical analyses of the synthetic crystals for Mg-La perrierite and Mg-Nd chevkinite confirmed the existing structural formula for both minerals.

Infrared spectra of chevkinite and perrierite are very similar except very small changes in absorption frequencies accompanied with the polymorphic transitions.

Chevkinite and perrierite are structurally similar minerals bearing a superficial resemblance to members of the epidote group. It has been suggested (Gottardi, 1960; Bonatti and Gottardi, 1966; Pen and Pan, 1964) that they offer an example of layer polymorphism in sorosilicates involving a translation of half a cell period.

In a previous synthesis study (Ito, 1967) using gels that had been precipitated from a sodium-containing solution it was shown that under isothermal and isobaric conditions, the transition between perrierite and chevkinite is a function of ionic size in the A (rare earth), B (divalent metal) and C (trivalent metal) sites of the idealized formula:

$$A_4^{3+}(\mathrm{X})B^{2+}(\mathrm{VI})C_2^{3+}(\mathrm{VI})\mathrm{Ti}_2^{4+}\mathrm{O}_8(\mathrm{VI})(\mathrm{Si}_2^{4+}\mathrm{O}_7)_2 \qquad \mathrm{X,\ VI,\ IV} = \text{Coord. no.}$$

$$A = Ln^{3+}, \mathrm{Ca, Sr}; \qquad B = \mathrm{Fe^{2+}, Mg, Mn^{2+}}; \qquad C = \mathrm{Ti^{4+}, Fe^{2+}, Al^{3+}, Fe^{3+}, Mg}$$

The author (Ito) stated at that time that chevkinite and perrierite are strictly speaking not polymorphs.

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The results of new phase syntheses in air (980–1,300°C) and under water pressure (250–3,000 bar, 550–720°C) using alkali-free gels prepared by an ion exchange resin method (Ito and Johnson, 1968) reveal that chevkinite and perrierite exhibit thermal polymorphism only within certain compositional ranges.

Although numerous chemical analyses of naturally-occurring chevkinite and perrierite have been reported, and the structural formulas (given above) determined, some ambiguities remain because of the rather complex chemical composition of natural material. Chemical analysis of separated grains of the synthetic minerals may confirm that chevkinite and perrierite do have the same formula.

Structural analysis (Bonatti and Gottardi, 1966; Pen and Pan, 1964) suggested that chevkinite and perrierite are polymorphs but natural chevkinite and perrierite are often metamict, resulting in poor X-ray diffraction photographs. Heating experiments used to improve their crystallinity have been ineffective. While the structure determination reported to the literature may be basically correct, the superior crystallinity of synthetic chevkinite and perrierite has revealed additional structural information. Results are reported here of space group determinations for synthetic chevkinite and perrierite, as deducted from precession photographs.

SYNTHESIS

The starting materials were prepared by slow evaporation (in a teflon container) of stoichiometric mixtures of reagent grade $Mg(OH)_2$, $NiCO_3$ or $CoCo_3$, freshly prepared mixed hydroxides of titanium and rare earths (La, Pr, Nd, and Sm), and resin-prepared silicic acid solution (Ito and Johnson, 1968).

The phase synthesis experiments were carried out in air. Temperatures were regulated to within 5°C with a solid state or proportional controller, and calibrated periodically using a digital millivoltmeter with a Pt-Pt+Rh 10 percent thermocouple. The results are summarized in Figure 1, in terms of temperature, ionic radii of rare earths occupying *A* sites, and the divalent ions occupying *B* and *C* sites. Fe^{2+} and Ce^{3+} were excluded, because the experiments with these elements cannot be performed in air. Data shown in Figure 1 for Fe^{2+} and Ce^{3+} were therefore extrapolated using the results obtained with other ions.

Several experiments using cold seal bombs were carried out in order to study the chevkinite-perrierite transition under hydrothermal conditions.

The detailed results of the above experiments, including those of the reaction reversal, summarized in Tables I and II, have been deposited with the National Auxiliary Publication Service.[1]

SINGLE CRYSTAL GROWTH

We found that nearly all of the chevkinite and perrierite of the compositions studied crystallize as a primary phase. Single crystal growth

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[1] Order NAPS Document 01223 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences Inc., 22 West 34 Street, N. Y., N. Y. 10001; remit $1.00 for microfiche or $3.00 for photocopies, in advance to ASIS-NAPS.,

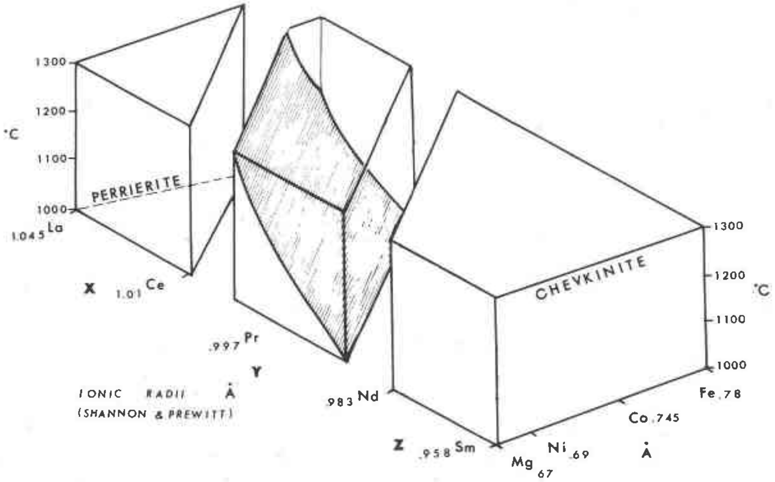

FIG. 1. Phase relation between chevkinite and perrierite. The diagram is drawn three dimensionally in terms of temperature, the ionic radii of rare-earth ions occupying *A* sites and the divalent ions occupying *B* sites and a half of *C* sites according to the crystal structure analysis. Block X = perrierite single phase region; Block Y = the compositional range where polymorphic transitions from perrierite to chevkinite occur; Block Z = chevkinite single phase region. Shaded curved plane in block Y shows an idealized transition temperatures. The values for Fe^{2+} and Ce^{3+} given are extrapolated.

experiments were carried out using oxides as starting materials by slow cooling, from 1,480°C to 1,000°C at a rate of 2–5° per hour of a clear melt having the composition[1] $M_2^{2+}Ln_4^{3+}Ti_3Si_4O_{22}$ (M^{2+} = Mg, Ni and Co; Ln^{3+} = La, Pr, Nd and Sm). The results are given in Table 1.

Attempts were made to grow a large single crystal of $Mg_2La_4Ti_3Si_4O_{22}$, perrierite, by pulling from melt at the temperatures above 1,480°C by W. S. Brower at the National Bureau of Standards. The boules of approximately 1.5 cm diameter consisting of greyish aggregates of perrierite crystals (maximum size 2 mm) have been obtained.

CHEMICAL ANALYSES

Chemical analyses of hand-picked samples (approx. 100 mg) were performed for pure Mg-Nd chevkinite and Mg-La perrierite. The results for Mg-Nd chevkinite are: $MgO = 6.6$ percent, $Nd_2O_3 = 53.6$ percent, $TiO_2 = 19.5$ percent, $SiO_2 = 19.0$ percent or, expressed as a formula: $Mg_{2.04}Nd_{3.98}Ti_{3.05}Si_{3.95}O_{22}$. The Mg-La perrierite gave: $MgO = 6.4$ percent, $La_2O_3 = 53.3$ percent, $TiO_2 = 19.7$ percent, $SiO_2 = 19.4$ percent

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[1] The structural formula has been given by Gottardi (1960) as $M^{2+}Ln_4^{3+}(Ti^{4+}M^{2+})(TiO_4)_2(Si_2O_7)_2$ but for simplification the chemical formula will be written hereafter $M_2^{2+}Ln_4^{3+}Ti_3Si_4O_{22}$.

Table 1. Single Crystals Obtained for Synthetic Chevkinite and Perrierite

Formulas	Temp (C°)	Soaking (hr)	Cooling rate (C°/h)	Color	Size (mm)	Other minor phases identified
Perrierite						
$Mg_2La_4Ti_3Si_4O_{22}$	1400–1200	10	4	Pale Pink	2	—
$Ni_2La_4Ti_3Si_4O_{22}$	1460–1200	10	4	Green	1	High-$La_2Si_2O_7$
$Co_2La_4Ti_3Si_4O_{22}$	1400–1050	20	2	Red-brown	1	High-$La_2Si_2O_7$ & unidentified Cryst.
Chevkinite						
$Mg_2Nd_4Ti_3Si_4O_{22}$	1460–1280	10	4	Purple	3	Apatite[a]
$Mg_2Pr_4Ti_3Si_4O_{22}$	1460-1280	10	4	Light green	1	Apatite[a]
$Mg_2Sm_4Ti_3Si_4O_{22}$	1460–1280	10	4	Light green	2	Apatite,[a] $Sm_2Ti_2O_7$
$Ni_2Nd_4Ti_3Si_4O_{22}$	1460–1280	10	4	Blue green	Massive	Apatite[a]
$Ni_2Pr_4Ti_3Si_4O_{22}$	1460–1280	10	4	Dark green	Massive	Apatite[a]
$Ni_2Sm_4Ti_3Si_4O_{22}$	1460–1100	10	4	Green	1	Apatite[a]
$Co_2Nd_4Ti_3Si_4O_{22}$	1400–1050	20	2	Red-brown	2	Apatite[a], High-$Nd_2Si_2O_7$
$Co_2Pr_4Ti_3Si_4O_{22}$	1400–1050	20	2	Red-brown	2	Apatite[a]
$Co_2Sm_4Ti_3Si_4O_{22}$	1400–1050	20	2	Red-brown	2	Apatite[a], $Sm_2Ti_2O_7$

[a] Oxy-silicate apatites (Ito, 1968).

resulting in the formula: $Mg_{1.9}La_{4.0}Ti_{3.01}Si_{4.0}O_{22}$. Both analyses confirmed the structural formula to be $M_2^{2+}Ln_4^{3+}Ti_3Si_4O_{22}$ (Gottardi, 1960; Pen and Pan, 1964).

X-Ray Data

Unit cell dimensions were measured for two sets of chevkinite-perrierite polymorphs:

$$Mg_2Pr_4Ti_3Si_4O_{22} \text{ perrierite} \xrightarrow{1070 \pm 10°C} \text{chevkinite}$$

$$Ni_2Pr_4Ti_3Si_4O_{22} \text{ perrierite} \xrightarrow{1060 \pm 10°C} \text{chevkinite}$$

Table 2. Unit-Cell Dimensions of Two Sets of Synthetic Polymorphs for Chevkinite and Perrierite

Formulas	a(Å)	b(Å)	c(Å)	β	$100 \wedge 10\bar{2}$	V(Å³)
$Mg_2Pr_4Ti_3Si_4O_{22}$						
Perrierite, *low*	13.57 (1)	5.643 (3)	11.66 (1)	113.1 (1)	101.2	822 (2)
Chevkinite, *high*	13.376 (2)	5.7074 (7)	11.016 (2)	100.71 (1)	112.70	826.3 (2)
(Transition at 1,070°C in air)						
$Ni_2Pr_4Ti_3Si_4O_{22}$						
Perrierite, *low*	13.57 (1)	5.655 (3)	11.70 (1)	113.34 (4)	101.30	825 (1)
Chevkinite, *high*	13.362 (3)	5.683 (1)	11.008 (3)	100.69 (3)	113.21	821.4 (4)
(Transition at 1,060°C in air)						
$Mg_2La_4Ti_3Si_4O_{22}$ (Perrierite)	13.786 (4)	5.6766 (9)	11.791 (3)	113.88 (2)	101.18	843.7 (4)

Indexing of powder diffractometer data was facilitated by the results of single-crystal precession studies. Cell dimensions in Table 2 were refined using the least-squares program of Burnham (1962). Powder data clearly revealed differences between chevkinite and perrierite, and the monoclinic angle, beta, is especially characteristic to variations in these minerals. Details of the refinement methods used are summarized in a previous paper (Ito and Arem, 1970). Unambiguously indexed powder data for two typical compounds: $Mg_2La_4Ti_3Si_4O_{22}$ (perrierite) and $Mg_2Pr_4Ti_3Si_4O_{22}$ (chevkinite) are given in Table 3.

Single crystal diffraction studies were carried out using precession techniques with Mo radiation. The photographs indicate space group

TABLE 3. X-RAY POWDER DATA FOR SYNTHETIC CHEVKINITE AND PERRIERITE

Cu radiation (Ni-filtered)

$Mg_2Pr_4Ti_3Si_4O_{22}$, Chevkinite $P2_1/a$, $a=13.376$ (2), $b=5.7074$ (7), $c=11.015$ (2)$\beta=100.71$ (1)				$Mg_2La_4Ti_3Si_4O_{22}$, Perrierite $P2_1/a$, $a=13.786$ (4), $b=5.6766$ (9), $c=11.791$ (3)$\beta=113.88$ (2)			
hkl	I/I_0	*d* (obs.)	*d* (calc.)	*hkl*	I/I_0	*d* (obs.)	*d* (calc.)
002	60	5.42	5.41	002	20	5.39	5.39
$\bar{1}11$	50	4.85	4.85	110	15	5.17	5.17
111	30	4.58	4.58	$\bar{1}11$	5	5.01	5.00
003	30	3.60	3.60	111	10	4.40	4.39
310	50	3.47	3.47	$\bar{1}12$	20	4.09	4.09
$\bar{3}11$	50	3.46	3.46	003	20	3.59	3.59
400	2	3.285	3.286	$\bar{3}11$	60	3.57	3.57
311	80	3.173	3.175	112	10	3.457	3.457
$\bar{3}12$	60	3.140	3.142	$\bar{1}13$, 021	5	3.211	3.212
$\bar{1}13$	10	3.081	3.079	400	5	3.155	3.151
$\bar{4}02$	40	3.076	3.073	$\bar{4}03$	10	3.064	3.062
401	59	2.992	2.993	$\bar{3}13$	40	2.991	2.995
113	20	2.872	2.873	311	100	2.962	2.960
020	60	2.854	2.854	020	60	2.831	2.838
021	10	2.759	2.759	113	40	2.746	2.746
312	70	2.744	2.746	004	80	2.695	2.695
004	100	2.708	2.706	$\bar{4}04$	3	2.645	2.644
$\bar{4}12$	10	2.705	2.706	$\bar{2}21$	2	2.618	2.617
$\bar{4}03$	20	2.690	2.691	220	3	2.585	2.588
402	10	2.602	2.602	$\bar{1}14$	10	2.571	2.572
022	20	2.525	2.524	312	10	2.513	2.517
221	10	2.499	2.502	022	10	2.509	2.511
114	15	2.336	2.334	$\bar{5}12$	3	2.476	2.475
$\bar{4}04$	10	2.309	2.310	402	5	2.337	2.339
023	10	2.238	2.238	$\bar{6}03$	5	2.253	2.254

TABLE 3. (*Continued*)

$Mg_2Pr_4Ti_3Si_4O_{22}$, Chevkinite $P2_1/a$, $a=13.376$ (2), $b=5.7074$ (7), $c=11.015$ (2)$\beta=100.71$ (1)				$Mg_2La_4Ti_3Si_4O_{22}$, Perrierite $P2_1/a$, $a=13.786$ (4), $b=5.6766$ (9), $c=11.791$ (3)$\beta=113.88$ (2)			
hkl	I/I_0	*d* (obs.)	*d* (calc.)	*hkl*	I/I_0	*d* (obs.)	*d* (calc.)
$\bar{6}01$	30	2.230	2.229	114	5	2.244	2.243
$\bar{6}02$	5	2.176	2.176	023	5	2.225	2.227
$\bar{4}21$	35	2.164	2.164	$\bar{4}21$	8	2.185	2.184
420	10	2.157	2.155	$\bar{4}22$	10	2.174	2.174
$\bar{4}22$	5	2.091	2.091	313	8	2.139	2.138
601	8	2.074	2.073	420	5	2.110	2.109
421	10	2.067	2.065	$\bar{6}04$	5	2.127	2.126
223	3	2.049	2.048	$\bar{4}23$	5	2.083	2.082
314	10	1.997	1.997	421	5	1.973	1.972
$\bar{3}15$	8	1.972	1.972	024	40	1.954	1.954
024	20	1.963	1.963	$\bar{1}31$	5	1.862	1.863
$\bar{4}23$	10	1.957	1.958	$\bar{3}16$, $\bar{7}12$	2	1.855	1.855
115	5	1.950	1.950	$\bar{7}13$	20	1.851	1.851
230	5	1.827	1.827	$\bar{2}25$	5	1.811	1.811
224	5	1.815	1.815	006, $\bar{7}14$	10	1.797	1.797
$\bar{7}12$	8	1.790	1.790	$\bar{6}22$	8	1.788	1.786
710	10	1.783	1.783	$\bar{6}16$	5	1.769	1.769
$\bar{2}32$	5	1.758	1.759	404	8	1.731	1.731
$\bar{2}25$	5	1.733	1.732	$\bar{6}24$, $\bar{1}33$, $\bar{7}15$	5	1.702	1.702
232	15	1.705	1.705	620	5	1.688	1.688
331	10	1.702	1.703	$\bar{4}07$	20	1.677	1.677
$\bar{3}33$	5	1.619	1.619	$\bar{3}33$	5	1.668	1.667
$\bar{8}03$	5	1.613	1.612	331	5	1.662	1.661
424	5	1.593	1.593	$\bar{3}17$	10	1.613	1.613
007	3	1.545	1.546	$\bar{6}25$	5	1.607	1.607
811	5	1.524	1.524	$\bar{4}26$	8	1.599	1.598
713	5	1.497	1.497	$\bar{6}07$, $\bar{7}16$	5	1.585	1.585
$\bar{4}26$	3	1.474	1.474	007	5	1.541	1.540
425	5	1.442	1.442	026	8	1.518	1.518
040	5	1.427	1.427	622	3	1.480	1.480
$\bar{3}35$	2	1.410	1.410	432, $\bar{3}35$	5	1.470	1.471
340	5	1.356	1.356	$\bar{2}27$	20	1.433	1.432
$\bar{7}32$	5	1.339	1.339	040	8	1.419	1.419
				140, $\bar{8}25$, $\bar{5}35$	5	1,410	1,410
				$\bar{2}07$	10	1.374	1.373
				623	10	1.365	1.367
				142	5	1.349	1.349

$K\alpha_1=1.54051$ Å. All *d* values calculated with computer program (IBM-7094) and are given in Ångstroms.

$P2_1/a$ for both chevkinite ($Mg_2Nd_4Ti_3Si_4O_{22}$ and also $Co_2Pr_4Ti_3Si_4O_{22}$) and for perrierite ($Mg_2La_4Ti_3Si_4O_{22}$). The space group previously reported for natural material is $C2/m$.

Many relatively weak reflections violating the *C*-centering extinction criteria in the space group $C2/m$ (class hkl, $h+k=2n$) were observed in photographs of the synthetic crystals. Diffraction maxima observed with the synthetic crystals obey the following restrictions: $0k0$, $k=2n$ and $h0l$, $h=2n$, indicating that both minerals possess a primitive, rather than a face-centered lattice, but an *a*-glide plane is present. This was, in fact, predicted by Bonatti (1959) for perrierite—"If stronger photographs should reveal more spots, perrierite would have a primitive cell." We do not conclude at this stage, however, that all naturally-occurring crystals of perrierite and chevkinite should have the same space group as the synthetic crystals, owing to the far greater complexity in chemical composition of the natural materials. Further crystal structure refinement work, using data from well crystallized synthetic crystals, will doubtless yield more information on the structure of both perrierite and chevkinite.

INFRARED SPECTRA

Infrared spectra of synthetic chevkinite and perrierite are very similar, and resemble closely to that of epidote (Figure 2). The spectra consist of a characteristic triplet (1110–990 cm^{-1}) which may be due to a TiO_4 group and a quadruplet (940–825 cm^{-1}) which is definitely due to a bent Si_2O_7 group[1]. This is expected from the structural similarity demonstrated by the X-ray studies. There are, however, distinguishable and consistent differences in the frequencies between the two types of structure (Table 4). One peak of the triplets at 1,100 cm^{-1} and less prominently one peak of the quadruplets at 840 cm^{-1} shift significantly toward the high frequency side with the structural change from perrierite to chevkinite. As might be expected, these shifts are more pronounced with the structural change which would affect the Si_2O_7 configuration than to effects of the replacement of the ions occupying *A* (lanthanides) and (*B* and *C*) (divalent ions) sites.

PHASE STUDIES

A polymorphic transition (in air) from perrierite (low temperatures) to chevkinite (high temperatures) occurs within a compositional range shown as block Y in Figure 1. Typical examples of this transition in air are as follows:

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[1] These interpretations were made by K. H. Butler, Sylvania Electric Products Inc., Danvers, Mass.

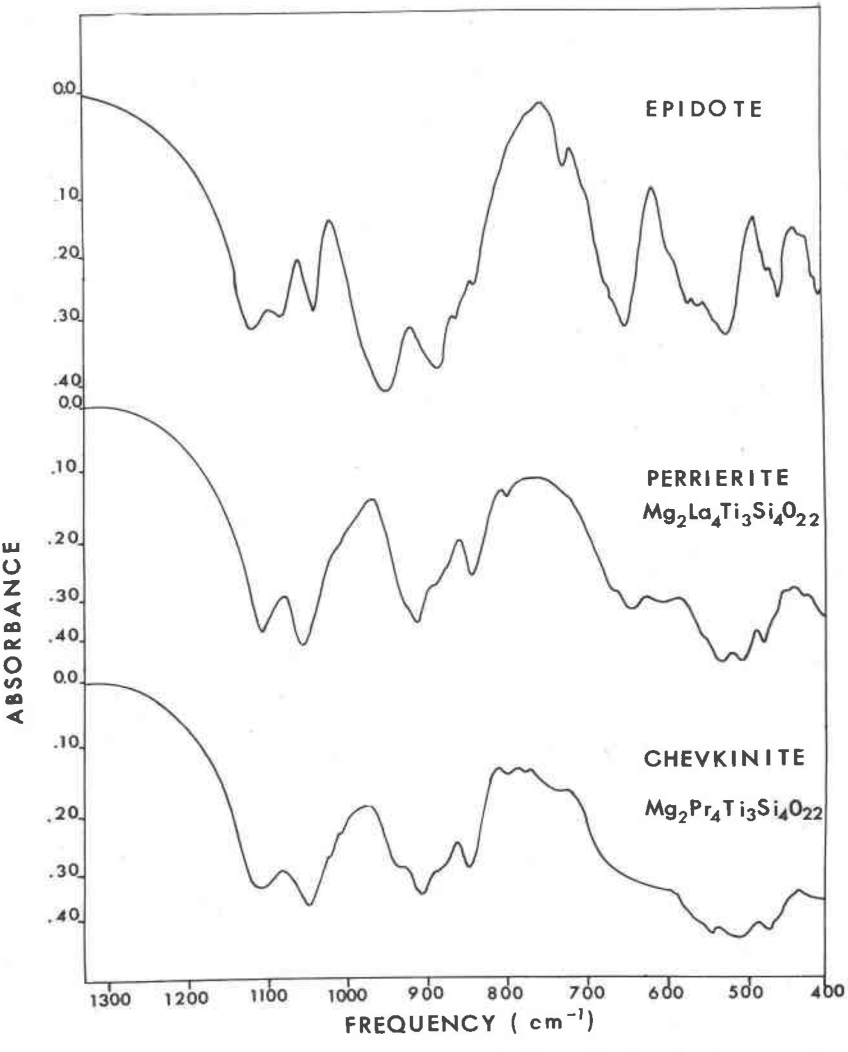

FIG. 2. Infrared absorption spectra of synthetic chevkinite, $Mg_2Pr_4Ti_3Si_4O_{22}$, perrierite $Mg_2La_4Ti_3Si_4O_{22}$ and epidote from Poison Creek, Plumas County, California. Sample (1 mg) in potassium bromide disks (99 mg).

$$\text{perrierite} \xrightarrow[1070 \pm 10°C]{Mg_2Pr_4Ti_3Si_4O_{22}} \text{chevkinite}$$

$$\text{perrierite} \xrightarrow[1060 \pm 10°C]{Ni_2Pr_4Ti_3Si_4O_{22}} \text{chevkinite}$$

TABLE 4. INFRARED SPECTRA OF SYNTHETIC CHEVKINITE AND PERRIERITE (RANGE 1200 cm^{-1} TO 700 cm^{-1})

S = Strong, M = Medium and W = Weak

	Composition	Frequencies (cm^{-1}) Triplet			Quadruplet			
		1	2	3	1	2	3	4
	Perrierite							
a	$Co_2La_4Ti_3Si_4O_{22}$	1101(m)	1047(s)	1005(w)	920(w)	900(s)	880(w)	834(m)
b	$Ni_2La_4Ti_3Si_4O_{22}$	1090(m)	1045(s)	1005(w)	924(w)	897(s)	868(w)	832(m)
c	$Mg_2La_4Ti_3Si_4O_{22}$	1097(m)	1046(s)		923(w)	904(s)	884(w)	835(m)
	Chevkinite							
d	$Co_2Pr_4Ti_3Si_4O_{22}$	1119(m)	1040(s)	1000(w)	936(w)	910(s)	887(w)	872(m)
e	$Co_2Nd_4Ti_3Si_4O_{22}$	1122(m)	1042(s)	1010(w)	935(w)	904(s)	878(w)	847(m)
f	$Co_2Sm_4Ti_3Si_4O_{22}$	1114(m)	1035(s)	1007(w)	928(w)	900(s)	870(w)	840(m)
g	$Ni_2Pr_4Ti_3Si_4O_{22}$	1126(s)	1049(s)		934(w)	907(s)	886(w)	850(m)
h	$Ni_2Nd_4Ti_3Si_4O_{22}$	1113(m)	1036(s)	1003(w)	923(w)	896(s)	870(w)	840(m)
i	$Ni_2Sm_4Ti_3Si_4O_{22}$	1120(m)	1046(m)	1000(w)	930(w)	904(m)	880(w)	848(m)
j	$Mg_2Pr_4Ti_3Si_4O_{22}$	1116(m)	1048(s)	1004(w)	933(w)	905(s)	880(w)	845(m)
k	$Mg_2Nd_4Ti_3Si_4O_{22}$	1122(m)	1046(s)	1000(w)	934(w)	903(m)	873(m)	841(m)
l	$Mg_2Sm_4Ti_3Si_4O_{22}$	1126(m)	1057(s)		940(w)	916(m)	871(w)	854(m)
	Perrierite-Chevkinite, isochemical polymorph							
m	$Ni_2Pr_4Ti_3Si_4O_{22}$ (perrierite, low)	1107(m)	1046(s)	1005(w)	922(w)	900(s)	872(w)	832(m)
g	$Ni_2Pr_4Ti_3Si_4O_{22}$ (chevkinite, high)	1126(m)	1049(s)		934(w)	907(s)	886(w)	850(m)
N	$Mg_2Pr_4Ti_3Si_4O_{22}$ (perrierite, low)	1107(m)	1052(s)	1001(w)	923(w)	906(m)	876(w)	832(m)
i	$Mg_2Pr_4Ti_3Si_4O_{22}$ (chevkinite, high)	1116(m)	1048(s)	1004(w)	933(w)	905(s)	880(w)	845(s)

A mechanism has been proposed (Bonatti and Gottardi, 1966) for the transition from perrierite to chevkinite, involving structural translation of a period of half a cell on octahedral layers parallel to (001). A result of this relationship is the equivalence of the direction [001] in perrierite and [$\bar{1}$02] in chevkinite. Therefore the β angle in chevkinite corresponds to the angle [100]$\wedge$[$\bar{1}$02] in perrierite, and vice versa. The apparent change in β in the polymorphic transition reflects the difference in axial orientation between chevkinite and perrierite. Significant variations were also observed (Table 2) in cell dimensions *a* and *c*, while *b* and the unit cell volume remained fairly constant.

It is also clear that the transition temperatures can be related to the ratio of the ionic radii of the ions occupying the *A* (rare earth) sites and the *B* and *C* sites (divalent ions).

The transition temperatures given as a curved plane in the diagram (Figure 1) are somewhat idealized. The actual plane of equilibrium temperatures in terms of ionic radii of these sites do not actually follow a smooth curve as given in the diagram. This may be due in part to the difficulty in assigning correct radius values to the divalent ions, especially Ni^{2+} which, in oxides, tends to cause octahedral distortion (Dunitz and Orgel, 1957).

Another likely explanation is that part of the low temperature region (Fig. 1) of the perrierite field may be metastable because the reaction reversal was not effected at that temperature. The perrierite in this region may be converted to chevkinite by longer heating. The curved transition plane might actually thus be a nearly flat section in the three-dimensional diagram (Fig. 1).

Attempts were made to reverse the reaction of perrierite to chevkinite for materials of three compositions: $Ni_2Pr_3LaTi_3Si_4O_{22}$, $Mg_2Pr_3LaTi_3Si_4O_{22}$ and $CoLa_3PrTi_3Si_4O_{22}$. Reversal was not achieved in a period of 10 days when precrystallized chevkinite was heated at 1,100°C much below the transition temperature (approximately 1,200°C). As shown in Figure 1, a distinct region should exist in which thermal polymorphism between chevkinite and perrierite occurs. Results of slow cooling (from 1,460 to 1,050°C) of the melts having the composition of $Mg_2(Pr_{80-70}La_{20-30})_4Ti_3Si_4O_{22}$ show (Table II) that the reaction is in fact reversible. Within this compositional range, for the composition where transition temperatures are above 1,250°C, the reverse reaction from chevkinite to perrierite seems complete, and only perrierite is found in the final cooled run products. For the composition where the transition occurs below 1,200°C, the reverse reaction is sluggish, and chevkinite does not totally transform to perrierite.

The results of the cooling experiments are consistent with the phase boundary predetermined by the gel syntheses. However, the cooling experiments always produced perrierites and chevkinites accompanied by a small amount of additional phases such as oxysilicate-apatites (Ito, 1968) or $Ln_2^{3+}Ti_2O_7$ (Ln = Lanthanides).

Despite the considerable structural similarity of the two minerals, the sluggishness of transformation and the persistent presence of a two-phase region suggests that this transition is of the first order, reconstructive type.

The results of hydrothermal experiments for the Mg-Pr analogs showed that under water pressure the chevkinite structure is more stable than that of perrierite of equivalent composition. Much higher P_{H_2O} at lower temperatures favors the formation of silicate hydroxy apatites, $Ln_2Si_2O_7$ (Felsche and Hirsiger, 1969) or cerite (Ito, 1968). Neither chevkinite nor perrierite was obtained at temperatures below 550°, regardless of water pressure.

Previously reported heating experiments of two metamict samples (Lima de Faria, 1962; Mitchell, 1966) did not succeed in converting perrierite to chevkinite, even hydrothermally (Ito, 1967). These facts are consistent with our experiments, which proved that there are large compositional ranges where perrierite is the only stable phase up to the melting point.

Our experimental results have not shown any indication that chevkinite can be converted to perrierite by elevating temperature or pressure. The range in which the reverse reaction from chevkinite to perrierite occurs is limited, and the reaction is rather sluggish. Therefore, an interpretation previously given (Ito, 1967) seems more likely. That is, the formation of perrierite from the natural chevkinite by heating in air is not a polymorphic transition, but rather the result of a process of decomposition, oxidation and recrystallization after the expulsion of CeO_2 and oxidation of FeO to Fe_2O_3.

The observation that most chevkinites remained unchanged by heating (Lima de Faria, 1962) up to 1,300°C is consistent with our experiments. These chevkinites will probably melt congruently with further elevation of temperature. It should be remembered, however, that the present experiments do not use a composition range including all the elements present in the naturally-occurring minerals. These other elements may also play a role in determining the stability of the chevkinite versus the perrierite structure.

NATURAL OCCURRENCES

Perrierite and chevkinite occur chiefly in pegmatites, but they have also been found in other igneous rocks as accessory minerals (Jaffe, Evans, and Chapman, 1956; Izett and Wilcox, 1968). Among all the known localities, only a Virginia pegmatite (Mitchell, 1966) and the Cenozoic ash beds of the Western United States (Izett and Wilcox, 1968) contain both minerals. Coexisting chevkinite and perrierite have not yet been reported.

The chemical and spectrographic analyses of these minerals found in adjacent localities do not reveal distinct differences in chemical composition. If these chevkinites and perrierites are indeed chemically similar, chevkinite is most likely to have crystallized at an earlier stage (higher temperature and presumably higher pressure) of magmatic differentiation or pegmatite formation than did perrierite. There is a possibility that previously-crystallized chevkinite could have been converted to perrierite, if a very slow cooling process were involved.

On the other hand, if these two minerals occur in localities where no great temperature-pressure changes occurred during the course of crystallization, the formation of chevkinite versus perrierite must be due to a considerable variation in composition. Such a change would be represented as a horizontal traverse across the idealized boundary in the three-dimensional diagram (Figure 1). This interpretation was already implied to some extent in the previous study (Ito, 1967), and seems valid for most of the natural occurrences.

It seems worth mentioning in passing that in the growth runs of chevkinite, good crystals of oxy-apatite (up to 2–3 mm with well-formed prisms, often terminated at one end) were formed, embedded in a large mass of chevkinite (Table 3). Chevkinite found in Cenezoic ash beds of the Western United States (Izett and Wilcox, 1968) contain needle-like inclusions of apatite. These inclusions could be one of the silicate apatites (Ito, 1968).

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