

A STUDY OF CHEVKINITE AND PERRIERITE¹

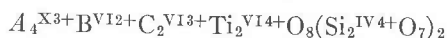
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ABSTRACT

Numerous analogues of chevkinite and perrierite, for which the idealized formula $A_4BC_2Ti_2Si_4O_{22}$ of Gottardi (1960) and Bonatti and Gottardi (1966) is accepted, have been synthesized hydrothermally and by solid state reaction. The compositions include material with A=rare-earths from La to Sm; B=Fe, Co, Ni, Mg; and C=Al, Fe³, Ga or (Me²⁺Ti⁴⁺). Coupled substitutions involving the partial entrance of Ca into A, Ti into C, and Al for Si also have been effected. Chevkinite and perrierite apparently have very similar but not identical compositions, while having the same formula-type, they are not polymorphs in the strict sense. They occupy regions of an extensive solid solution series, separated by a two-phase field, in which the structural transition apparently is controlled by the average size of the ions occupying the several structural sites. A tentative phase boundary is given. X-ray spacing data, unit-cell constants and thermal data are cited, as are observations on the recrystallization of metamictic natural material.

INTRODUCTION

The close geometrical relations of the rare-earth titanosilicates perrierite and chevkinite to each other and to allanite have been fully discussed by Bonatti (1959). The structural analysis of perrierite by Gottardi (1960) established this species as a sorosilicate containing (Si₂O₇) groups together with additional oxygen ions not bonded directly to Si. The idealized structural formula showing the coordination number and valence of the several structural sites may be written



The type perrierite from Nettuno, Italy, used in the structural study shows a considerable range of substitution into the several sites, and the actual composition, as shown by the analysis reported by Bonatti and Gottardi (1954), is close to (Ce_{2.31}La_{0.50}Y_{0.16}Th_{0.19}Ca_{0.53}Na_{0.31}) (Fe²⁺_{0.63}Ca_{0.34}) (Ti_{1.48}Fe³⁺_{0.19}Mg_{0.24}Fe²⁺_{0.05}) (TiO₄)₂ (Si_{1.92}Al_{0.08}O₇)₂.

The chemical composition of chevkinite, discussed by Bonatti (1959) and earlier by Jaffe, Evans and Chapman (1956) and others, has been problematic because of the wide variations shown by the numerous reported analyses. Recently, a structural model for chevkinite has been described by Bonatti and Gottardi (1966) which indicates that perrierite and chevkinite are polymorphs, related structurally by a type of layer translation. Both minerals hence can be referred to the same ideal-

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ized formula, as given first above. The available analyses of these minerals, however, although on the whole very similar, do not permit a clear recognition of the detailed compositional relations between them and of the bearing that this may have on the geometrical relations.

The present study reports the synthesis of 68 chemically different compounds that give the X-ray patterns of either perrierite or chevkinite. Accepting that these compounds all have the same general formula already indicated for perrierite and chevkinite, $A_4BC_2Ti_2Si_4O_{22}$, a matter on which no new evidence is presented here, the results indicate that these substances have very similar but not identical compositions and, strictly speaking, are not polymorphs.

METHODS OF SYNTHESIS

Both chevkinite and perrierite were synthesized by heating chemically prepared gels either hydrothermally or in air at 1 atm. The following reagents were used for the preparation of the gels: solutions of Na_2SiO_3 (0.2M), $TiCl_4$ (0.1M in 6N HCl), cerous sulfate (0.2M HCl 0.5N), cobalt nitrate (0.2M), nickelous nitrate (0.2M), aluminum nitrate (0.2M), nickelous nitrate (0.2M), aluminum nitrate (0.2M), strontium chloride (0.2M), calcium nitrate (0.2M) and thorium nitrate (0.2M); also crystalline ferrous ammonium sulfate and finely powdered Ga_2O_3 , La_2O_3 , Pr_2O_3 , Nd_2O_3 , Sm_2O_3 , Gd_2O_3 , MgO and $MnCO_3$. Appropriate amounts of the constituents desired in the final gel were placed into solution in approximately 100 ml of 0.05N HCl. The solution was brought to pH 12 by NaOH for compositions containing Ni, Co and Mg, and to pH 10 by NH_4OH for compositions containing Al, Ga and Ca. The resulting gelatinous precipitate was stirred magnetically. It was then centrifuged and washed three times passing 400 ml of cold distilled water. The washed gel was then dried at 120° in an evacuated oven. The dried gels are not hygroscopic and stay reactive over more than a year when kept in sealed vials.

The hydrothermal syntheses were made using cold-seal bombs of 10 ml and 25 ml capacities fitted with a silver liner. A small amount of ascorbic acid was added to the runs to maintain reducing conditions. About 50 mg of gel yielded approximately 20 mg of solid product. Dry syntheses were used for the Ni, Co and Mg analogues without Ce^{++} . The conditions of the hydrothermal and dry syntheses and the products are summarized in Table 1. The products in all instances were too fine grained for optical study but did afford good X-ray powder patterns. The Ni analogues of both chevkinite and perrierite were yellowish green in color and the Co analogues a much darker green. The hydrothermally synthesized analogues containing Fe were grayish black (chevkinites) or purple (perrierites).

It was found experimentally that phases of the perrierite and chevkinite types were formed over a considerable range of variation in the atomic ratios of the elements present in the gels. Foreign material was obviously present in some instances. Foreign material was also undoubtedly present in some other instances, because of the ratios employed, although it could not be recognized by optical or X-ray methods because it was poorly crystallized or was present in relatively small amounts. Apparently homogeneous material was obtained with syntheses having the ratios of Gottardi's formula, cited above, and relatively well crystallized material also was obtained with ratios extending to $A:(B+C):Ti:Si = 1:1:1:1$. Chemical analyses of the synthetic products could not be made because of uncertainty as to the presence of foreign or unreacted material and, in any case, because of the small size of the samples. The formulas cited for the products listed in Table 1 are arbitrarily given in terms of the idealized formula of Gottardi.

TABLE 1. EXPERIMENTAL RESULTS OF THE SYNTHESIS OF CHEVKINITE AND PERRIERITE

A. Gel composition same as formula given, Runs indicated as 1 bar made by solid state reaction in air, others hydrothermal. Approximate ratio of perrierite and chevkinite in two phase region is indicated.

Formula	Temp. (C°)	Pressure (bars)	Time (hours)	Phases
Ce ₄ Fe ₁ Al ₂ Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
Ce ₄ Fe ₁ (Al ₁ Fe ₅ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
Ce ₄ Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Chevkinite
Ce ₄ Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₃ Al ₁ O ₂₂	700	2000	40	Perrierite
(Ce ₂ Ca ₂)Al ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Neither
(Ce ₂ Ca ₁)Al ₁ (Al ₁ Fe ₅ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite (weak)
(Ce ₃ Ca ₁)Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perr. (7), Chev. (3)
(Ce ₃ Ca ₂)Fe ₁ (Fe ₁ Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Chev. (95), Perr. (5)
La ₄ Ni ₁ Fe ₂ ³⁺ Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
La ₄ Ni ₁ Fe ₂ ⁴⁺ Ti ₂ Si ₄ O ₂₂	1100	1	20	Perrierite
La ₄ Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
La ₄ Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	40	Perrierite
(La ₃ Ca ₁)Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
La ₄ Fe ₁ Al ₂ Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite, plus?
La ₄ Fe ₁ (Al ₁ Ti ₁)Si ₂ AlO ₂₂	700	2000	40	Neither
Pr ₄ Co ₁ Fe ₂ ³⁺ Ti ₂ Si ₄ O ₂₂	700	2000	40	Chev., plus?
Pr ₄ Co ₁ Fe ₂ ³⁺ Ti ₂ Si ₄ O ₂₂	1100	1	20	Chev. (weak)
Pr ₄ Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Chevkinite
Pr ₄ Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	40	Chevkinite
(Pr ₃ Ca ₁)Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
Pr ₄ Fe ₁ Al ₂ Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
Pr ₄ Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
Nd ₄ Fe ₁ Al ₂ Ti ₂ Si ₄ O ₂₂	700	2000	40	Perrierite
(Nd ₃ Ca ₁)Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Perr. (6), Chev. (4)
Sm ₄ Fe ₁ Al ₂ Ti ₂ Si ₄ O ₂₂	700	2000	40	Chevkinite, poor
(Sm ₃ Ca ₁)Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	40	Chevkinite, poor

B. Gel composition with ratio A: (B+C): Ti: Si = 1:1:1:1 and individual components as stated.

Formula	Temp. (C°)	Pressure (bars)	Time (hours)	Phases
Ce ₄ Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	20	Chevkinite
Ce ₄ Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	40	Chev. (8), Perr. (2)
Ce ₄ Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	40	Perrierite, plus?
(Ce ₂ La ₂)Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	40	Chevkinite
(Ce ₁ La ₃)Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	48	Chev. (9), Perr. (1)
(Ce ₃ Ca ₁)Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	650	2000	15	Perrierite
(Ce ₂ Sr ₁)Fe ₁ (Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	650	2000	24	Perrierite; lessingite
(Ce ₂ Sr ₁)Fe ₁ (Ga ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	20	Perrierite, plus?
(Ce ₃ Ca ₁)Fe ₁ (Ga ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	600	2000	20	Chevkinite, plus?
(Ce ₃ Ca ₁)Fe ₁ (Fe ₅ Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	24	Chev. (4), Perr. (6)
(Ce ₄ Ca ₁)Fe ₁ (Fe ₁ Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	24	Chev. (6), Perr. (4)
(Ce ₃ Ca ₂)Fe ₁ (Fe ₅ Al ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	700	2000	24	Chevkinite
La ₄ Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	48	Chev. (9), Perr. (1)
La ₄ Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1200	1	20	Perrierite
La ₄ Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1150	1	10	Perrierite
(La ₂ Nd ₂)Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	24	Perr. (9), Chev. (1)
(La ₂ Pr ₂)Co ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	72	Perr. (5), Chev. (5)
(La ₂ Pr ₂)Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1180	1	10	Perrierite
La ₄ Fe ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	48	Chev. (7), Perr. (3)
La ₄ Mg ₁ (Mg ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	24	Perrierite
(La ₃ Pr ₁)Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	24	Perr. (5), Chev. (5)
(La ₃ Pr ₁)Ni ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	48	Perrierite
(La ₁ Pr ₂)Ni ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	24	Chev. (8), Perr. (2)
(La ₃ Pr ₁)Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	72	Perr. (9), Chev. (1)

TABLE 1—(continued)

Formula	Temp. (C°)	Pressure (bars)	Time (hours)	Phases
(La _{3.4} Pr _{.6})Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	72	Perr. (9), Chev. (1)
(La _{2.6} Pr _{1.4})Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	48	Chev. (9), Perr. (1)
(La ₁ Pr ₃)Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	72	Perr. (6), Chev. (4)
(La ₂ Pr ₂)Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1150	1	10	Chevkinite
Pr ₄ Mg ₁ (Mg ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	24	Perrierite
Pr ₄ Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1200	1	12	Chevkinite
Pr ₄ Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1200	1	12	Chevkinite
Pr ₄ Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	20	Chevkinite
Nd ₄ Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	48	Chevkinite
Nd ₄ Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	15	Chevkinite
Nd ₄ Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1150	1	10	Chevkinite
Nd ₄ Mg ₁ (Mg ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	24	Chevkinite
(Sm ₂ Nd ₂)Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	12	Chevkinite
(Sm ₂ Nd ₂)Co ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	12	Chevkinite
(Sm ₂ Nd ₂)Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	0100	1	12	Chevkinite
Sm ₄ Ni ₁ (Ni ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	12	Chevkinite
Sm ₄ Co ₁ (Co ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	1100	1	12	Chevkinite
Sm ₄ Fe ₁ (Fe ₁ Ti ₁)Ti ₂ Si ₄ O ₂₂	680	2000	20	Chevkinite, plus?

X-RAY DATA

The synthetic products have been examined by the X-ray powder diffraction method, using a Philips diffractometer with Cu radiation, Ni filter, and a silicon internal standard. The patterns were identified by comparison with standard patterns of recrystallized natural chevkinite and perrierite. X-ray powder data cited in Tables 2 and 3 have been indexed according to the unit-cell constants given by Bonatti (1960) and by Jaffe, Evans and Chapman (1956). For the detailed indexing, synthetic La-Ni perrierite and Pr-Ni chevkinite were used because these analogues gave the best reflections. Typical X-ray powder diagrams of synthetic analogues of chevkinite and perrierite, including natural recrystallized chevkinite from Madagascar and perrierite from the Urals are given in Figure 1. After the indexing, the unit-cell constants of all analogues were calculated using the following reflections: chevkinite: (002) (11 $\bar{1}$) (111) (003) (311) (312) (402) (401) (020) (312) (004) (220) (022) (023) (024); perrierite: (002) (110) (003) (31 $\bar{1}$) (400) (311) (020) (004) (022) (600) (024). The unit cell dimensions a , b , c and β of selected specimens are listed in Table 4.

CRYSTAL CHEMISTRY AND PHASE RELATIONS

In interpreting the results of the syntheses, lacking direct analytical information, it was assumed that the perrierite-like and chevkinite-like phases identified in the runs conformed to the type of formula already stated. The several cations present in the initial gel were then assigned to the appropriate structural sites. On this basis, the results of the syntheses were plotted in Figure 2 in terms of the average ionic radii of the ions in the A and the (B + C) sites. The rare-earth radii used are those given by Templeton (1954) and those of the transition elements by Pauling (1948). The use of other sets of radii, such as those of Goldschmidt or Ahrens, do not significantly alter the data in a relative sense. The data clearly indicate that the transition from perrierite to chevkinite is influenced by the variation in ionic size in these sites, and that there is a

TABLE 2. X-RAY POWDER DATA FOR CHEVKINITE

<i>hkl</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i>	Sm ₂ Ni(NiTi) ·Ti ₂ Si ₂ O ₇ 1200°C, 1 bar, 12 h	Nd ₄ Co(CoTi) ·Ti ₂ Si ₂ O ₇ 1100°C, 1 bar, 48 h	CeFe(FeTi) ·Ti ₂ Si ₂ O ₇ 700°C, 2000 bars, 20 h	Madagascar, Recryst. (HM 85151) 700°C, 2000 bars	New Hampshire (heated) Jaffe (1956)	Ural, Type Specimen Macharokin (1959)
	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i>	<i>d</i> _{obs.}	<i>I</i>	<i>d</i> _{obs.}	<i>I</i>	<i>d</i> _{obs.}	<i>I</i>
002	5.39	5.39	10	5.37	10	5.43	30	5.46	10
111	4.83	4.83	10	4.84	15	4.89	40	4.86	40
111	4.56	4.56	15	4.57	20	4.61	30	4.60	40
003	3.59	3.59	10	3.60	20	3.62	20	3.63	5
311	3.45	3.431	30	3.429	40	3.479	50	3.47	20
311	3.16	3.16	60	3.162	60	3.184	80	3.20	100
312	3.131	3.118	50	3.127	50	3.162	75	3.15	100
402	3.066	3.043	30	3.044	40	3.093	30	3.08	40
401	2.990	2.970	20	2.957	20	3.003	30	3.00	20
113	2.864	2.862	5	—	—	2.904	5	—	—
020	2.839	2.840	40	2.829	80	2.871	60	2.86	70
312	2.728	2.731	80	2.704	50	2.753	50	2.76	20
004	2.701	2.700	100	2.698	100	2.720	100	2.72	100
220	2.605	2.603	5	2.573	5	2.611	10	2.61	5
022	2.512	2.513	30	2.512	20	2.532	20	2.53	20
222	2.411	2.414	20	2.409	10	2.436	10	2.44	5
404	2.301	2.294	30	2.313	5	2.342	10	2.32	5
023	2.225	2.228	40	2.208	15	2.241	20	2.24	5
421	2.153	2.149	30	2.144	30	2.174	40	2.17	70
422	2.083	2.075	30	2.069	20	2.101	5	2.08	5
024	1.954	1.957	30	1.943	30	1.967	10	1.97	50
424	1.782	1.785	5	1.766	10	1.798	20	1.79	8
225	1.720	1.721	15	1.720	10	1.742	5	1.74	5
331	1.697	1.694	10	1.697	5	1.708	10	1.70	5

CuK α , Ni filter, diffractometer.

TABLE 3. X-RAY POWDER DATA FOR PERRIERITE

<i>hkl</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i>	<i>L</i> a ₂ (CoTi) ·Ti ₂ Si ₄ O ₂₂ 1150°C, 1 bar, 10 h	(Ce,Ca)/Fe(AIT) ·Ti ₂ Si ₄ O ₂₂ 650°C, 2000 bars, 15 h	(Ce, Sr)Fe(AIT) ·Ti ₂ Si ₄ O ₂₂ 650°C, 2000 bars, 24 h	<i>d</i> _{obs.}	<i>I</i>	Ilmen, Urals. Recryst. (H.M. 96869) 700°C, 2000 bars	<i>d</i> _{obs.}	<i>I</i>	Nettuno, Italy. Bonatti (1959) Unheated.
002	5.40	5.39	20	5.41	5.35	5.37	5.34	15	5.34	5.34	65	5.34
110	5.16	5.15	10	5.18	5.14	5.13	5.13	20	5.15	5.13	25	5.13
111	4.97	4.98	8	4.99	4.96	4.93	4.98	5	4.98	4.96	20	4.96
003	3.59	3.59	10	3.59	3.58	3.58	3.57	10	3.57	3.56	20	3.56
311	3.561	3.556	30	3.570	3.523	3.535	3.537	40	3.537	3.56	15	3.56
401	3.437	3.412	5	3.463	3.424	—	3.435	5	3.435	3.43	20	3.43
140	3.146	3.142	20	3.163	3.110	3.131	3.106	10	3.106	3.15	15	3.15
403	3.060	3.061	15	3.060	3.011	3.027	3.021	5	3.021	3.03	20	3.03
313	2.980	2.990	90	2.990	2.957	2.968	2.959	90	2.959	2.96	100	2.96
315	2.953	2.947	100	2.963	2.928	2.945	2.938	100	2.938	2.93	55	2.93
020	2.824	2.824	50	2.838	2.819	2.820	2.822	60	2.822	2.82	65	2.82
021	2.731	2.730	10	2.749	2.717	2.723	2.722	5	2.722	2.73	15	2.73
004	2.696	2.696	60	2.696	2.679	2.682	2.677	70	2.677	2.673	20	2.673
404	2.638	2.645	5	2.635	2.600	2.614	2.612	5	2.612	2.610	15	2.610
022	2.498	2.500	30	2.515	2.494	2.529	2.495	15	2.495	2.488	15	2.488
602	2.250	2.290	2	2.289	2.231	2.296	2.220	5	2.220	2.229	50	2.229
421	2.176	2.174	20	2.181	2.159	—	2.169	20	2.169	2.166	25	2.166
422	2.166	2.165	40	2.166	2.149	2.161	2.154	20	2.154	2.156	25	2.156
604	2.139	2.122	3	2.123	2.087	2.096	2.097	5	2.097	2.095	15	2.095
600	2.089	2.093	30	2.105	2.060	2.071	2.056	5	2.056	2.081	15	2.081
024	1.950	1.949	40	1.954	1.940	1.949	1.949	20	1.949	1.941	50	1.941
031	1.847	1.853	20	1.850	1.823	1.848	1.821	3	1.821	—	—	—
230	1.804	1.802	3	1.804	1.796	—	—	—	—	—	—	—
110	1.791	1.792	5	1.795	1.781	—	1.781	3	1.781	1.779	15	1.779
425	1.763	1.763	10	1.758	1.738	1.748	1.735	5	1.735	—	—	—
224	1.729	1.723	10	1.731	1.717	1.718	1.720	3	1.720	1.719	10	1.719
624	1.693	1.696	10	1.691	1.682	—	1.679	5	1.679	—	—	—
513	1.659	1.672	20	1.664	1.648	1.655	1.650	10	1.650	1.658	10	1.658
625	1.600	1.603	10	1.599	1.581	1.592	1.587	5	1.587	1.649	15	1.649
										1.585	15	1.585

CuK α , Ni filter, diffractometer.

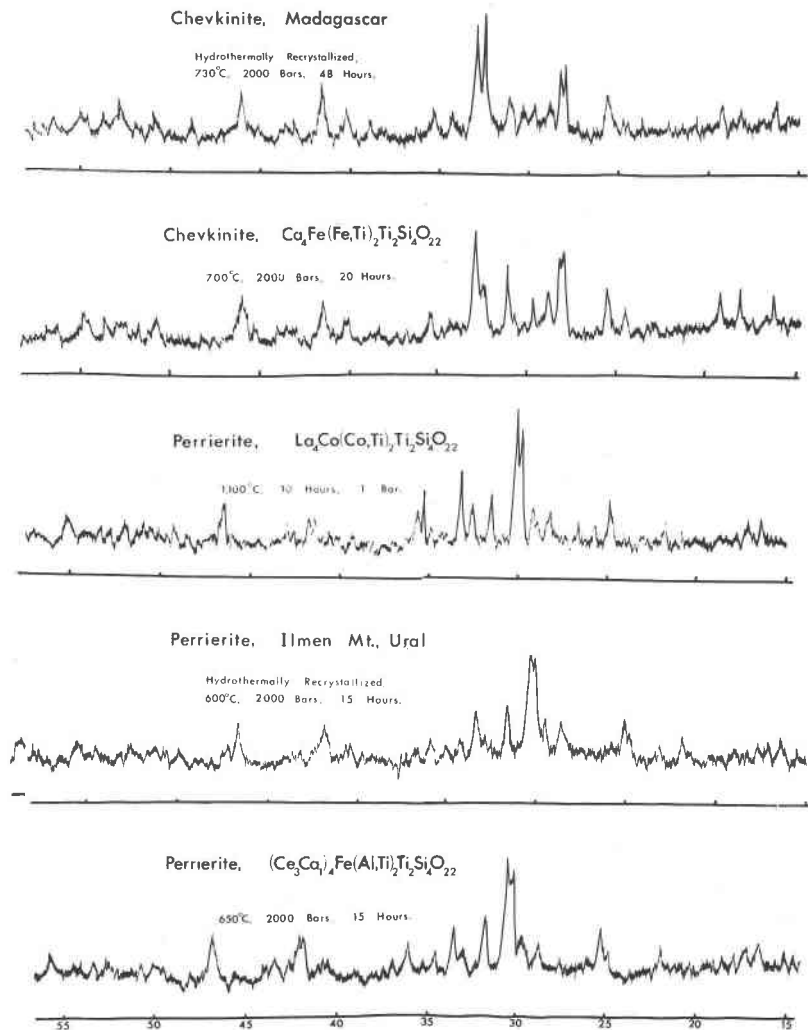


FIG. 1. X-ray diffractometer chart patterns of natural and synthetic analogues of perrierite and chevkinite. Cu radiation, Ni filter.

two-phase region between these phases. The phase boundary was determined and expressed mathematically as

$$K = (0.52 + 0.74 A) - X$$

where A is the average radius in the $(B + C)$ sites and X is the average radius of the ions in the A site. When $K > 0$, the phases formed are struc-

TABLE 4. UNIT-CELL CONSTANTS OF CHEVKINITE AND PERRIERITE

		<i>a</i>	<i>b</i>	<i>c</i>	β
Natural crystals					
Chevkinite,	Stark, N. H., U. S. (Jaffe <i>et al</i>)	13.44	5.72	11.10	100.20
Chevkinite,	Madagascar. (H.M. 85151, recryst.)	13.26	5.75	11.06	100.7
Pierrierite,	Nettuno, Italy (Bonatti)	13.59	5.61	11.61	113.28
Perrierite,	Ilmen, Urals (H.M. 96869, recryst.)	13.52	5.65	11.71	113.3
Synthetic crystals					
Chevkinite	Ce ₄ Fe(FeTi)Ti ₂ Si ₄ O ₂₂	13.30	5.73	11.07	100.9
Chevkinite	Pr ₄ Ni(NiTi)Ti ₂ Si ₄ O ₂₂	13.24	5.68	10.98	100.8
Chevkinite	La ₄ Fe(FeTi)Ti ₂ Si ₄ O ₂₂	13.50	5.75	11.10	001.0
Chevkinite	Pr ₄ Co(CoTi)Ti ₂ Si ₄ O ₂₂	13.28	5.72	11.05	100.8
Chevkinite	Nd ₄ Fe(FeTi)Ti ₂ Si ₄ O ₂₂	13.18	5.71	11.03	100.8
Chevkinite	Pr ₄ Fe(FeTi)Ti ₂ Si ₄ O ₂₂	13.24	5.73	11.05	100.6
Chevkinite	(Ce ₂ La ₂)Fe(FeTi)Ti ₂ Si ₄ O ₂₂	13.39	5.75	11.08	100.9
Chevkinite	Nd ₄ Ni(NiTi)Ti ₂ Si ₄ O ₂₂	13.14	5.68	10.96	100.8
Chevkinite	Nd ₄ Co(CoTi)Ti ₂ Si ₄ O ₂₂	13.15	5.70	10.97	100.7
Chevkinite	Sm ₄ Co(CoTi)Ti ₂ Si ₄ O ₂₂	13.12	5.68	10.95	101.0
Chevkinite	Sm ₄ Ni(NiTi)Ti ₂ Si ₄ O ₂₂	13.12	5.66	10.90	100.9
Chevkinite	Nd ₄ Mg(MgTi)Ti ₂ Si ₄ O ₂₂	13.22	5.71	11.00	101.0
Perrierite					
Perrierite	La ₄ Co(CoTi)Ti ₂ Si ₄ O ₂₂	13.77	5.68	11.80	113.8
Perrierite	(La ₂ Nd ₂)Ni(NiTi)Ti ₂ Si ₄ O ₂₂	13.59	5.64	11.73	113.5
Perrierite	La ₄ Mg(MgTi)Ti ₂ Si ₄ O ₂₂	13.78	5.67	11.78	113.7
Perrierite	Pr ₄ Mg(MgTi)Ti ₂ Si ₄ O ₂₂	13.77	5.66	11.78	113.6
Perrierite	(La ₂ Pr ₂)Ni(NiTi)Ti ₂ Si ₄ O ₂₂	13.66	5.66	11.68	113.7
Perrierite	(La ₂ Pr ₁)Ni(CoTi)Ti ₂ Si ₄ O ₂₂	13.74	5.67	11.72	113.7
Perrierite	La ₄ Ni(NiTi)Ti ₂ Si ₄ O ₂₂	13.74	5.64	11.77	113.8
Perrierite	(Ce ₃ Ca ₁)Fe(AlTi)Ti ₂ Si ₄ O ₂₂	13.55	5.63	11.70	113.6
Perrierite	(Ce ₃ Sr ₁)Fe(AlTi)Ti ₂ Si ₄ O ₂₂	13.58	5.64	11.73	113.6
Perrierite	(La ₃ Sr ₁)Fe(GaTi)Ti ₂ Si ₄ O ₂₂	13.82	5.68	11.84	113.9
Perrierite	Pr ₄ FeAl ₂ Ti ₂ Si ₄ O ₂₂	13.48	5.61	11.57	113.5
Perrierite	(La ₃ Ca ₁)Fe(AlTi)Ti ₂ Si ₄ O ₂₂	13.72	5.65	11.74	113.8
Perrierite	Pr ₄ Fe(AlTi)Ti ₂ Si ₃ AlO ₂₂	13.56	5.62	11.62	113.4
Perrierite	(Pr ₃ Ca ₁)Fe(AlTi)Ti ₂ Si ₄ O ₂₂	13.54	5.61	11.58	113.7
Perrierite	Ce ₄ FeAl ₂ Ti ₂ Si ₄ O ₂₂	13.48	5.60	11.57	113.5
Perrierite	Nd ₄ FeAl ₂ Ti ₂ Si ₄ O ₂₂	13.45	5.59	11.48	113.5
Perrierite	Ce ₄ Fe(Fe _{0.5} Al _{1.5})Ti ₂ Si ₄ O ₂₂	13.63	5.65	11.82	113.8
Perrierite	Ce ₄ Fe(AlTi)Ti ₂ Si ₃ AlO ₂₂	13.72	5.65	11.68	113.9

naturally like chevkinite; when $K < 0$, the phases are structurally like perrierite.

The transition of chevkinite to perrierite also was observed by the coupled partial replacement of (1) Ce by Ca or Sr and of Fe²⁺ by Al; (2)

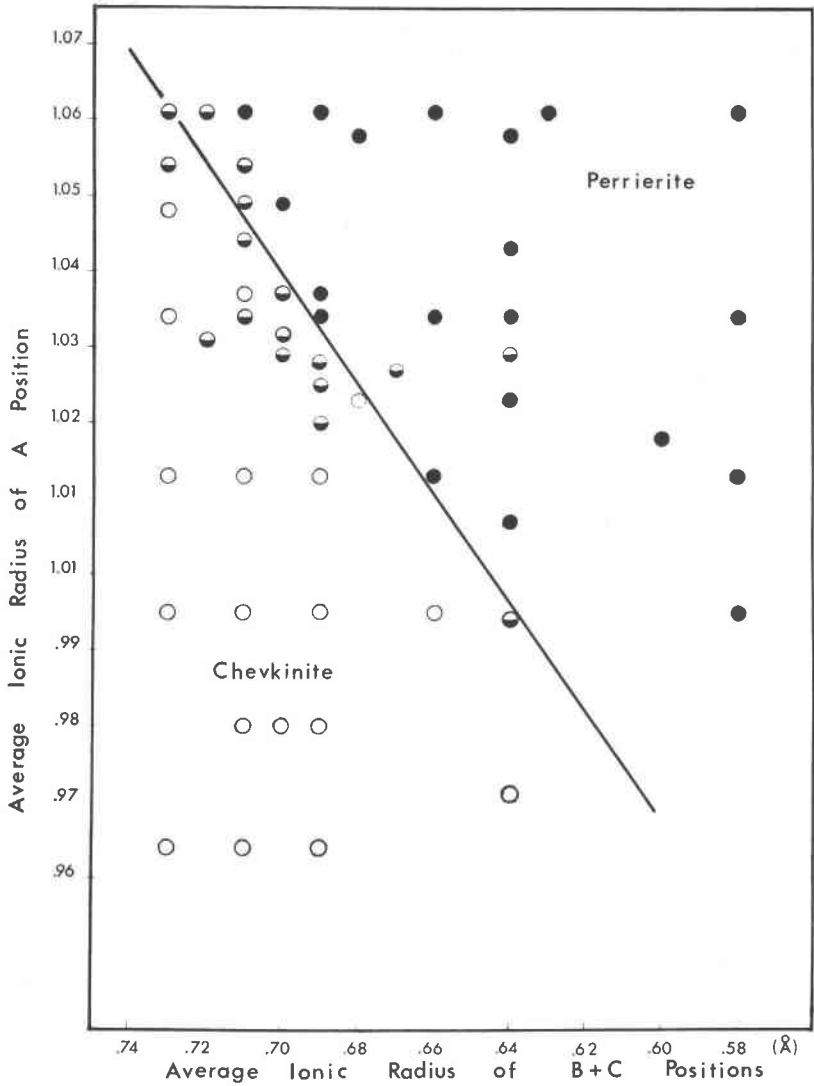


FIG. 2. Distribution of synthetic perrierite and chevkinite as a function of the average ionic radii of the A and the B+C positions. Half-circles indicate syntheses in which mixtures of chevkinite and perrierite were obtained.

Fe^{2+} by Al and of Ti^{4+} by Al; and (3) Fe^{2+} by Al and Si^{4+} by Al. The results of these experiments are included in Figure 2.

The situation in the natural minerals is more complex because of the wider range of substitution into the several sites and because of possible

uncertainty as to the structural role of certain ions. There is also uncertainty as to the accuracy of the analyses, since the wet chemical analysis of complex minerals such as perrierite and chevkinite is difficult, especially with regard to small amounts of Al, and there is the further possibility that the chemical composition has changed somewhat during the metamictization of these species. Nevertheless, most of the reported analyses of natural perrierite and chevkinite when recalculated into the formula stated fall into the appropriate regions in Figure 2.

It may be noted that the beta angles obtained from the X-ray data on these monoclinic species would vary systematically if they were drawn on Figure 2.

THERMAL BEHAVIOR

Under hydrothermal conditions, the synthetic analogues of chevkinite and perrierite begin to crystallize at an appreciable rate at 400°C, more rapidly at 600°–700°C, and remain stable up to at least 750°C at 2000 bars. When the gels are heated in air at 1 atm., the synthetic analogues of chevkinite are stable from at least 900° to 1300°C and of perrierite from 800° to 1300°C. The melting points are in the neighborhood of 1350°C. Lessingite, ilmenite and simple oxides have been identified as products of crystallization when the gels are heated at lower temperatures.

Lima de Faria (1962) has studied the behavior on heating, in air and in nitrogen, of metamict chevkinite and perrierite from many of the known localities. He observed that certain metamict chevkinite recrystallized as perrierite when heated in air, and suggested that perrierite was the oxidized equivalent of chevkinite, with Ce^{3+} converted to Ce^{4+} . A thermal study of chevkinite and perrierite from Virginia has been reported by Mitchell (1966) with results generally in agreement with those of Lima de Faria (1962). A study here of the thermal behavior of synthetic and natural chevkinites and perrierites has led to a different interpretation. When synthetic LaFe, CeFe, NdFe, PrFe and SmFe chevkinites are heated in air at approximately 1100°C for 1 hour it was found that the LaFe, NdFe and SmFe members remained unchanged, while the more readily oxidized Ce and Pr members decomposed and afforded CeO_2 and Pr_2O_{3+z} . It was also found that metamict perrierite from the Urals when heated hydrothermally in an inert or reducing atmosphere under 2000 bars completely recrystallized to perrierite when heated at 680°C for 3 hours, and was partly recrystallized at 500°C; no chevkinite was formed. Metamict Madagascar chevkinite recrystallized as chevkinite under the same treatment. These observations suggest that if metamict chevkinite is heated in air, some or all of the Ce and Pr ions present will be oxidized to a higher valency state and will be expelled from the structure. The re-

maining rare-earths and other ions may then recrystallize as perrierite or chevkinite depending on the new ratio of average ionic sizes in the several structural sites. The chevkinite from the Urals and Madagascar are close to the phase boundary, and may go from one to the other phase accompanying a small change in the ratio of ionic sizes. The chevkinite from New Hampshire (Jaffe *et al.*, 1956) and from Arizona (Kauffman and Jaffe, 1946) does not convert to perrierite on heating in air. The composition of this material is located well away from the phase boundary and hence is not as susceptible to a small change in radius ratio.

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