# A STUDY OF CHEVKINITE AND PERRIERITE[1]

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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, $Fe^3$, Ga or $(Me^{2+}Ti^{4+})$. 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 metamict 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 $(Si_2O_7)$ 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

$$A_4{}^{X3+}B^{VI2+}C_2{}^{VI3+}Ti_2{}^{VI4+}O_8(Si_2{}^{IV4+}O_7)_2$$
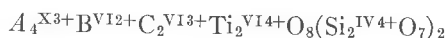
The type perrierite from Nettuno, Italy, used in the structural study shows a considerable range of substitution into the several sites, and the actual composition, as shown by the analysis reported by Bonatti and Gottardi (1954), is close to $(Ce_{2.31}La_{0.50}Y_{0.16}Th_{0.19}Ca_{0.53}Na_{0.31})$ $(Fe^2{}_{0.63}Ca_{0.34})$ $(Ti_{1.48}Fe^3{}_{0.19}Mg_{0.24}Fe^2{}_{0.05})$ $(TiO_4)_2$ $(Si_{1.92}Al_{0.08}O_7)_2$.

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 $Ga_2O_3$, $La_2O_3$, $Pr_3O_{11}$, $Nd_2O_3$, $Sm_2O_3$, $Gd_2O_3$, 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 hydroscopic 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 $Ce^{3+}$. 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 |
|---|---|---|---|---|
| $Ce_4Fe_1Al_2Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $Ce_4Fe_1(Al_1Fe_{.5}Ti_{.5})Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $Ce_4Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Chevkinite |
| $Ce_4Fe_1(Al_1Ti_1)Ti_2Si_3Al_1O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $(Ce_2Ca_2)Al_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Neither |
| $(Ce_{2.5}Ca_{1.5})Al_1(Al_{.5}Fe_{.5}Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite (weak) |
| $(Ce_{3.5}Ca_{.5})Fe_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perr. (7), Chev. (3) |
| $(Ce_{3.75}Ca_{.25})Fe_1(Fe_{.87}Al_{.13}Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Chev. (95), Perr. (5) |
| $La_4Ni_1Fe_2^{3+}Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $La_4Ni_1Fe_2^{3+}Ti_2Si_4O_{22}$ | 1100 | 1 | 20 | Perrierite |
| $La_4Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $La_4Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 40 | Perrierite |
| $(La_3Ca_1)Fe_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $La_4Fe_1Al_2Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite, plus? |
| $La_4Fe_1(Al_1Ti_1)Si_3AlO_{22}$ | 700 | 2000 | 40 | Neither |
| $Pr_4Co_1Fe_2^{3}Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Chev., plus? |
| $Pr_4Co_1Fe_2^{3}Ti_2Si_4O_{22}$ | 1100 | 1 | 20 | Chev. (weak) |
| $Pr_4Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Chevkinite |
| $Pr_4Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 40 | Chevkinite |
| $(Pr_3Ca_1)Fe_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $Pr_4Fe_1Al_2Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $Pr_4Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $Nd_4Fe_1Al_2Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perrierite |
| $(Nd_3Ca_1)Fe_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Perr. (6), Chev. (4) |
| $Sm_4Fe_1Al_2Ti_2Si_4O_{22}$ | 700 | 2000 | 40 | Chevkinite, poor |
| $(Sm_3Ca_1)Fe_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 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 |
|---|---|---|---|---|
| $Ce_4Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 20 | Chevkinite |
| $Ce_4Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 40 | Chev. (8), Perr. (2) |
| $Ce_4Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 40 | Perrierite, plus? |
| $(Ce_2La_2)Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 40 | Chevkinite |
| $(Ce_1La_3)Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 48 | Chev. (9), Perr. (1) |
| $(Ce_3Ca_1)Fe_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 650 | 2000 | 15 | Perrierite |
| $(Ce_3Sr_1)Fe_1(Al_1Ti_1)Ti_2Si_4O_{22}$ | 650 | 2000 | 24 | Perrierite; lessingite |
| $(Ce_3Sr_1)Fe_1(Ga_1Ti_1)Ti_2Si_4O_{22}$ | 700 | 2000 | 20 | Perrierite, plus? |
| $(Ce_3Ca_1)Fe_1(Ga_1Ti_1)Ti_2Si_4O_{22}$ | 600 | 2000 | 20 | Chevkinite, plus? |
| $(Ce_{3.4}Ca_{.6})Fe_1(Fe_{.5}Al_{.8}Ti_{.7})Ti_2Si_4O_{22}$ | 700 | 2000 | 24 | Chev. (4), Perr. (6) |
| $(Ce_{3.7}Ca_{.3})(Fe_1(Fe_{.75}Al_{.4}Ti_{.85})Ti_2Si_4O_{22}$ | 700 | 2000 | 24 | Chev. (6), Perr. (4) |
| $(Ce_{3.8}Ca_{.2})Fe_1(Fe_{.5}Al_{.3}Ti_{.9})Ti_2Si_4O_{22}$ | 700 | 2000 | 24 | Chevkinite |
| $La_4Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 48 | Chev. (9), Perr. (1) |
| $La_4Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1200 | 1 | 20 | Perrierite |
| $La_4Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1150 | 1 | 10 | Perrierite |
| $(La_2Nd_2)Ni_1(Ni_1Ti_1)_2Ti_2Si_4O_{22}$ | 1100 | 1 | 24 | Perr. (9), Chev. (1) |
| $(La_2Pr_2)Co_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 72 | Perr. (5), Chev. (5) |
| $(La_2Pr_2)Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1180 | 1 | 10 | Perrierite |
| $La_4Fe_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 48 | Chev. (7), Perr. (3) |
| $La_4Mg_1(Mg_1To_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 24 | Perrierite |
| $(La_{.6}Pr_{3.4})Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 24 | Perr. (5), Chev. (5) |
| $(La_3Pr_1)Ni_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 48 | Perrierite |
| $(La_{1.3}Pr_{2.7})Ni_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 24 | Chev. (8), Perr. (2) |
| $(La_3Pr_1)Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 72 | Perr. (9), Chev. (1) |

TABLE 1—(*continued*)

| Formula | Temp. (C°) | Pressure (bars) | Time (hours) | Phases |
|---|---|---|---|---|
| $(La_{3.4}Pr_{.6})Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 72 | Perr. (9), Chev. (1) |
| $(La_{2.6}Pr_{1.4})Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 48 | Chev. (9), Perr. (1) |
| $(La_1Pr_3)Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 72 | Perr. (6), Chev. (4) |
| $(La_2Pr_2)Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1150 | 1 | 10 | Chevkinite |
| $Pr_4Mg_1(Mg_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 24 | Perrierite |
| $Pr_4Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1200 | 1 | 12 | Chevkinite |
| $Pr_4Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1200 | 1 | 12 | Chevkinite |
| $Pr_4Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 20 | Chevkinite |
| $Nd_4Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 48 | Chevkinite |
| $Nd_4Fe_1(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 680 | 2000 | 15 | Chevkinite |
| $Nd_4Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1150 | 1 | 10 | Chevkinite |
| $Nd_4Mg_1(Mg_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 24 | Chevkinite |
| $(Sm_2Nd_2)Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 12 | Chevkinite |
| $(Sm_2Nd_2)Co_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 12 | Chevkinite |
| $(Sm_2Nd_2)Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 0100 | 1 | 12 | Chevkinite |
| $Sm_4Ni_1(Ni_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 12 | Chevkinite |
| $Sm_4Co_1(Co_1Ti_1)Ti_2Si_4O_{22}$ | 1100 | 1 | 12 | Chevkinite |
| $Sm_4Fe(Fe_1Ti_1)Ti_2Si_4O_{22}$ | 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) (31$\bar{2}$) (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 $\beta$ 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

| hkl | Pr₄Ni(NiTi)Ti₂Si₄O₂₂ 1200°C, 1 bar, 12 h | | | Sm₄Ni(NiTi)·Ti₂Si₄O₂₂ 1200°C, 1 bar, 12 h | | Nd₄Co(CoTi)·Ti₂Si₄O₂₂ 1100°C, 1 bar, 48 h | | Ce₄Fe(FeTi)·Ti₂Si₄O₂₂ 700°C, 2000 bars, 20 h | | Madagascar, Recryst. (HM 85151) 700°C, 2000 bars | | New Hampshire (heated) Jaffe (1956) | | Ural, Type Specimen Macharokin (1959) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $d_{obs.}$ | $d_{calc.}$ | I | $d_{obs.}$ | I | $d_{obs.}$ | I | $d_{obs.}$ | I | $d_{obs.}$ | I | $d_{obs.}$ | I | $d_{obs.}$ | I |
| 002 | 5.39 | 5.39 | 10 | 5.36 | 20 | 5.37 | 10 | 5.43 | 30 | 5.46 | 10 | 5.44 | 20 | — | — |
| 11$\bar{1}$ | 4.83 | 4.83 | 10 | 4.81 | 20 | 4.84 | 15 | 4.89 | 40 | 4.87 | 10 | 4.86 | 40 | — | — |
| 111 | 4.56 | 4.56 | 15 | 4.53 | 30 | 4.57 | 20 | 4.61 | 30 | 4.61 | 20 | 4.60 | 40 | — | — |
| 003 | 3.59 | 3.59 | 10 | 3.56 | 5 | 3.60 | 20 | 3.62 | 20 | 3.59 | 5 | 3.63 | 5 | — | — |
| 31$\bar{1}$ | 3.45 | 3.431 | 30 | 3.429 | 40 | 3.458 | 40 | 3.479 | 50 | 3.477 | 30 | 3.47 | 20 | 3.465 | 5 |
| 311 | 3.16 | 3.16 | 60 | 3.149 | 70 | 3.162 | 60 | 3.184 | 80 | 3.184 | 50 | 3.20 | 100 | — | — |
| 31$\bar{2}$ | 3.131 | 3.118 | 50 | 3.112 | 60 | 3.127 | 50 | 3.162 | 75 | 3.153 | 40 | 3.15 | 100 | 3.156 | 8 |
| 402 | 3.066 | 3.043 | 30 | 3.044 | 40 | 3.064 | 40 | 3.093 | 30 | 3.093 | 20 | 3.08 | 40 | — | — |
| 401 | 2.990 | 2.970 | 20 | 2.957 | 20 | 2.972 | 50 | 3.003 | 30 | 3.007 | 15 | 3.00 | 20 | 2.980 | 5 |
| 113 | 2.864 | 2.862 | 5 | — | — | — | — | 2.904 | 5 | — | — | — | — | — | — |
| 020 | 2.839 | 2.840 | 40 | 2.829 | 80 | 2.848 | 100 | 2.871 | 60 | 2.871 | 20 | 2.86 | 70 | 2.850 | 7 |
| 312 | 2.728 | 2.731 | 80 | 2.704 | 50 | 2.730 | 60 | 2.753 | 50 | 2.759 | 100 | 2.76 | 20 | — | — |
| 004 | 2.701 | 2.700 | 100 | 2.681 | 100 | 2.698 | 100 | 2.720 | 100 | 2.720 | 90 | 2.71 | 100 | 2.702 | 10 |
| 220 | 2.605 | 2.603 | 5 | 2.573 | 5 | 2.605 | 3 | 2.611 | 10 | 2.612 | 10 | 2.61 | 5 | 2.600 | 1.5 |
| 022 | 2.512 | 2.513 | 30 | 2.512 | 20 | 2.540 | 70 | 2.532 | 20 | 2.538 | 10 | 2.53 | 20 | 2.520 | 1 |
| 222 | 2.411 | 2.414 | 20 | 2.409 | 10 | 2.428 | 3 | 2.436 | 10 | — | — | 2.44 | 5 | — | — |
| 404 | 2.301 | 2.294 | 30 | 2.313 | 5 | 2.327 | 5 | 2.342 | 10 | 2.308 | 8 | 2.32 | 5 | — | — |
| 023 | 2.225 | 2.228 | 40 | 2.208 | 15 | 2.220 | 10 | 2.241 | 20 | 2.241 | 30 | 2.24 | 5 | 2.229 | 2 |
| 421 | 2.153 | 2.149 | 30 | 2.144 | 30 | 2.158 | 40 | 2.174 | 40 | 2.170 | 50 | 2.17 | 70 | 2.163 | 8 |
| 42$\bar{2}$ | 2.083 | 2.075 | 30 | 2.069 | 20 | 2.106 | 10 | 2.101 | 5 | 2.097 | 8 | 2.08 | 5 | — | — |
| 024 | 1.954 | 1.957 | 30 | 1.943 | 30 | 1.967 | 10 | 1.971 | 50 | 1.971 | 40 | 1.97 | 50 | 1.960 | 8 |
| 424 | 1.782 | 1.785 | 5 | 1.766 | 10 | 1.779 | 5 | 1.798 | 20 | 1.792 | 10 | 1.79 | 5 | 1.780 | 1.5 |
| 225 | 1.720 | 1.721 | 15 | 1.708 | 10 | 1.720 | 10 | 1.742 | 5 | 1.732 | 20 | 1.74 | 5 | 1.732 | 3 |
| 331 | 1.697 | 1.694 | 10 | 1.691 | 20 | 1.697 | 5 | 1.708 | 10 | 1.705 | 10 | 1.70 | 5 | — | — |

CuKα, Ni filter, diffractometer.

TABLE 3. X-RAY POWDER DATA FOR PERRIERITE

| hkl | $La_2Ni(NiTi)Ti_2Si_4O_{22}$ 1200°C, 1 bar, 8 h $d_{obs.}$ | $d_{calc.}$ | $I$ | $LaCo(CoTi)\cdot Ti_2Si_4O_{22}$ 1150°C, 1 bar, 10 h $d_{obs.}$ | $I$ | $(Ce_2Ca_1)Fe(AlTi)\cdot Ti_2Si_4O_{22}$ 650°C, 2000 bars, 15 h $d_{obs.}$ | $I$ | $(Ce_3Sr)Fe(AlTi)\cdot Ti_2Si_4O_{22}$ 650°C, 2000 bars, 24 h $d_{obs.}$ | $I$ | Ilmen, Urals. Recryst. (H.M. 96869) 700°C, 2000 bars $d_{obs.}$ | $I$ | Nettuno, Italy. Bonatti (1959) Unheated. $d_{obs.}$ | $I$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 002 | 5.40 | 5.39 | 20 | 5.41 | 5 | 5.35 | 10 | 5.37 | 20 | 5.34 | 15 | 5.34 | 65 |
| 110 | 5.16 | 5.15 | 10 | 5.18 | 8 | 5.14 | 8 | 5.13 | 20 | 5.15 | 10 | 5.13 | 25 |
| $11\bar{1}$ | 4.97 | 4.98 | 8 | 4.99 | 2 | 4.96 | 5 | 4.93 | 10 | 4.98 | 5 | 4.06 | 20 |
| 003 | 3.59 | 3.59 | 10 | 3.59 | 8 | 3.58 | 10 | 3.58 | 5 | 3.57 | 10 | 3.56 | 20 |
| $31\bar{1}$ | 3.561 | 3.556 | 50 | 3.570 | 30 | 3.523 | 30 | 3.545 | 40 | 3.537 | 40 | 3.53 | 15 |
| $40\bar{1}$ | 3.437 | 3.412 | 10 | 3.463 | 5 | 3.424 | 3 |  |  | 3.435 | 5 | 3.43 | 20 |
| 400 | 3.146 | 3.142 | 20 | 3.163 | 5 | 3.110 | 10 | 3.131 | 5 | 3.106 | 10 | 3.15 | 15 |
| $40\bar{3}$ | 3.060 | 3.061 | 10 | 3.060 | 15 | 3.011 | 30 | 3.027 | 5 | 3.021 | 15 | 3.03 | 20 |
| $31\bar{3}$ | 2.980 | 2.990 | 90 | 2.990 | 85 | 2.957 | 90 | 2.968 | 100 | 2.959 | 90 | 2.96 | 100 |
| 311 | 2.953 | 2.947 | 100 | 2.963 | 100 | 2.928 | 100 | 2.945 | 90 | 2.938 | 100 | 2.93 | 55 |
| 020 | 2.824 | 2.824 | 50 | 2.838 | 40 | 2.819 | 50 | 2.820 | 50 | 2.822 | 60 | 2.82 | 65 |
| 021 | 2.731 | 2.730 | 10 | 2.749 | 20 | 2.717 | 20 | 2.723 | 10 | 2.722 | 5 | 2.73 | 15 |
| 004 | 2.696 | 2.696 | 60 | 2.696 | 60 | 2.679 | 40 | 2.682 | 50 | 2.677 | 70 | 2.673 | 20 |
| $40\bar{4}$ | 2.638 | 2.645 | 5 | 2.635 | 2 | 2.600 | 5 | 2.614 | 5 | 2.612 | 5 | 2.550 | 15 |
| 022 | 2.498 | 2.500 | 30 | 2.515 | 10 | 2.494 | 20 | 2.529 | 10 | 2.495 | 15 | 2.488 | 15 |
| $60\bar{2}$ | 2.250 | 2.290 | 2 | 2.289 | 5 | 2.231 | 5 | 2.296 | 5 | 2.220 | 5 | 2.229 | 50 |
| $42\bar{1}$ | 2.176 | 2.174 | 20 | 2.181 | 5 | 2.159 | 10 |  |  | 2.169 | 20 | 2.166 | 25 |
| $42\bar{5}$ | 2.166 | 2.165 | 40 | 2.166 | 5 | 2.149 | 30 | 2.161 | 60 | 2.154 | 20 | 2.156 | 25 |
| $60\bar{4}$ | 2.139 | 2.122 | 5 | 2.123 | 3 | 2.087 | 10 | 2.096 | 5 | 2.097 | 5 | 2.095 | 15 |
| 600 | 2.089 | 2.093 | 30 | 2.105 | 20 | 2.060 | 5 | 2.071 | 10 | 2.056 | 5 | 2.081 | 15 |
| 024 | 1.950 | 1.949 | 40 | 1.954 | 5 | 1.940 | 30 | 1.949 | 60 | 1.949 | 20 | 1.941 | 50 |
| 031 | 1.847 | 1.853 | 20 | 1.850 | 5 | 1.823 | 3 | 1.848 | 5 | 1.821 | 3 |  |  |
| 230 | 1.804 | 1.802 | 3 | 1.804 | 5 | 1.796 | 2 |  |  |  |  |  |  |
| $11\bar{6}$ | 1.791 | 1.792 | 5 | 1.795 | 5 | 1.781 | 3 |  |  | 1.781 | 3 | 1.779 | 15 |
| $42\bar{5}$ | 1.763 | 1.763 | 10 | 1.758 | 10 | 1.738 | 5 | 1.748 | 5 | 1.735 | 5 |  |  |
| $22\bar{4}$ | 1.729 | 1.723 | 10 | 1.732 | 5 | 1.717 | 5 | 1.718 | 5 | 1.720 | 3 | 1.719 | 10 |
| $62\bar{4}$ | 1.693 | 1.696 | 10 | 1.691 | 2 | 1.682 | 5 |  |  | 1.679 | 5 |  |  |
| $51\bar{3}$ | 1.659 | 1.672 | 20 | 1.664 | 10 | 1.648 | 10 | 1.655 | 10 | 1.650 | 10 | 1.658 | 10 |
| 625 | 1.600 | 1.603 | 10 | 1.599 | 5 | 1.581 | 5 | 1.592 | 30 | 1.587 | 5 | 1.649 | 15 |
|  |  |  |  |  |  |  |  |  |  |  |  | 1.585 | 15 |

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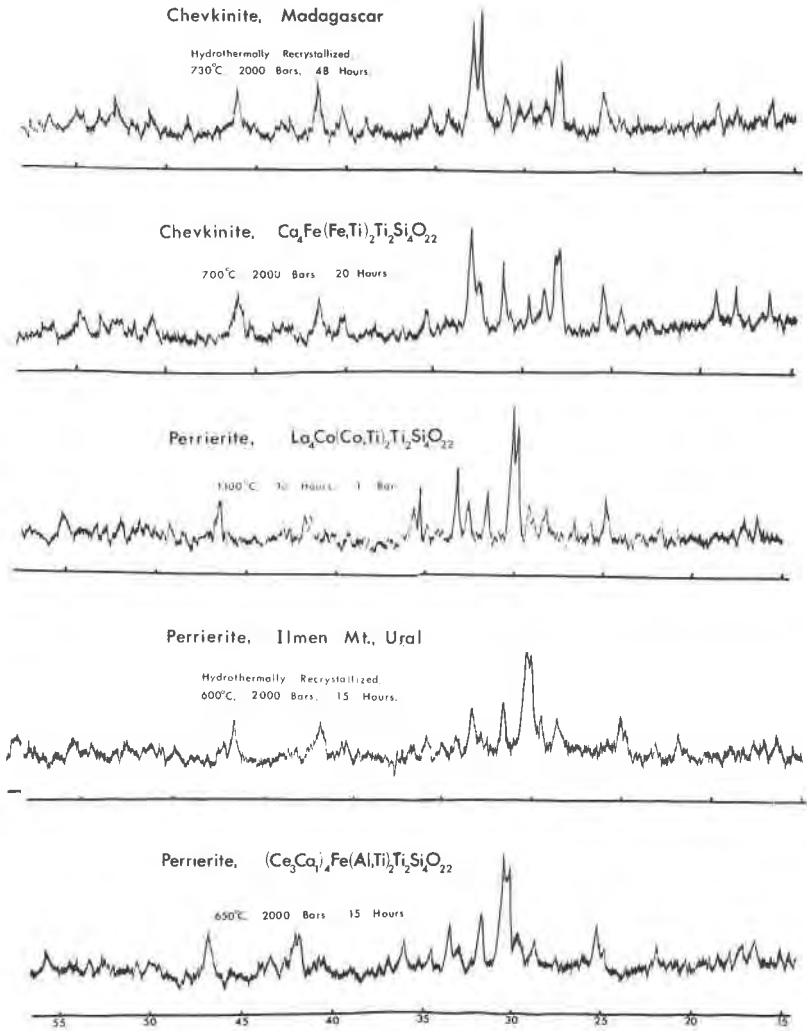
Fig. 1. X-ray diffractometer chart patterns of natural and synthetic analogues of perrierite and chevkinite. Cu radiation, Ni filter.

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

| | $a$ | $b$ | $c$ | $\beta$ |
|---|---|---|---|---|
| **Natural crystals** | | | | |
| Chevkinite, Stark, N. H., U. S. (Jaffe *et al*) | 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 $Ce_4Fe(FeTi)Ti_2Si_4O_{22}$ | 13.30 | 5.73 | 11.07 | 100.9 |
| Chevkinite $Pr_4Ni(NiTi)Ti_2Si_4O_{22}$ | 13.24 | 5.68 | 10.98 | 100.8 |
| Chevkinite $La_4Fe(FeTi)Ti_2Si_4O_{22}$ | 13.50 | 5.75 | 11.10 | 001.0 |
| Chevkinite $Pr_4Co(CoTi)Ti_2Si_4O_{22}$ | 13.28 | 5.72 | 11.05 | 100.8 |
| Chevkinite $Nd_4Fe(FeTi)Ti_2Si_4O_{22}$ | 13.18 | 5.71 | 11.03 | 100.8 |
| Chevkinite $Pr_4Fe(FeTi)Ti_2Si_4O_{22}$ | 13.24 | 5.73 | 11.05 | 100.6 |
| Chevkinite $(Ce_2La_2)Fe(FeTi)Ti_2Si_4O_{22}$ | 13.39 | 5.75 | 11.08 | 100.9 |
| Chevkinite $Nd_4Ni(NiTi)Ti_2Si_4O_{22}$ | 13.14 | 5.68 | 10.96 | 100.8 |
| Chevkinite $Nd_4Co(CoTi)Ti_2Si_4O_{22}$ | 13.15 | 5.70 | 10.97 | 100.7 |
| Chevkinite $Sm_4Co(CoTi)Ti_2Si_4O_{22}$ | 13.12 | 5.68 | 10.95 | 101.0 |
| Chevkinite $Sm_4Ni(NiTi)Ti_2Si_4O_{22}$ | 13.12 | 5.66 | 10.90 | 100.9 |
| Chevkinite $Nd_4Mg(MgTi)Ti_2Si_4O_{22}$ | 13.22 | 5.71 | 11.00 | 101.0 |
| | | | | |
| Perrierite $La_4Co(CoTi)Ti_2Si_4O_{22}$ | 13.77 | 5.68 | 11.80 | 113.8 |
| Perrierite $(La_2Nd_2)Ni(NiTi)Ti_2Si_4O_{22}$ | 13.59 | 5.64 | 11.73 | 113.5 |
| Perrierite $La_4Mg(MgTi)Ti_2Si_4O_{22}$ | 13.78 | 5.67 | 11.78 | 113.7 |
| Perrierite $Pr_4Mg(MgTi)Ti_2Si_4O_{22}$ | 13.77 | 5.66 | 11.78 | 113.6 |
| Perrierite $(La_2Pr_2)Ni(NiTi)Ti_2Si_4O_{22}$ | 13.66 | 5.66 | 11.68 | 113.7 |
| Perrierite $(La_3Pr_1)Ni(CoTi)Ti_2Si_4O_{22}$ | 13.74 | 5.67 | 11.72 | 113.7 |
| Perrierite $La_4Ni(NiTi)Ti_2Si_4O_{22}$ | 13.74 | 5.64 | 11.77 | 113.8 |
| Perrierite $(Ce_3Ca_1)Fe(AlTi)Ti_2Si_4O_{22}$ | 13.55 | 5.63 | 11.70 | 113.6 |
| Perrierite $(Ce_3Sr_1)Fe(Al_1Ti)Ti_2Si_4O_{22}$ | 13.58 | 5.64 | 11.73 | 113.6 |
| Perrierite $(La_3Sr_1)Fe(GaTi)Ti_2Si_4O_{22}$ | 13.82 | 5.68 | 11.84 | 113.9 |
| Perrierite $Pr_4FeAl_2Ti_2Si_4O_{22}$ | 13.48 | 5.61 | 11.57 | 113.5 |
| Perrierite $(La_3Ca_1)Fe(AlTi)Ti_2Si_4O_{22}$ | 13.72 | 5.65 | 11.74 | 113.8 |
| Perrierite $Pr_4Fe(AlTi)Ti_2Si_3AlO_{22}$ | 13.56 | 5.62 | 11.62 | 113.4 |
| Perrierite $(Pr_3Ca_1)Fe(AlTi)Ti_2Si_4O_{22}$ | 13.54 | 5.61 | 11.58 | 113.7 |
| Perrierite $Ce_4FeAl_2Ti_2Si_4O_{22}$ | 13.48 | 5.60 | 11.57 | 113.5 |
| Perrierite $Nd_4FeAl_2Ti_2Si_4O_{22}$ | 13.45 | 5.59 | 11.48 | 113.5 |
| Perrierite $Ce_4Fe(Fe_{.5}Al_1Ti_{.5})Ti_2Si_4O_{22}$ | 13.63 | 5.65 | 11.82 | 113.8 |
| Perrierite $Ce_4Fe(AlTi)Ti_2Si_3AlO_{22}$ | 13.72 | 5.65 | 11.68 | 113.9 |

turally like chevkinite; when $K < 0$, the phases are structurally like per-
rierite.

The transition of chevkinite to perrierite also was observed by the
coupled partial replacement of (1) Ce by Ca or Sr and of $Fe^{2+}$ by Al; (2)
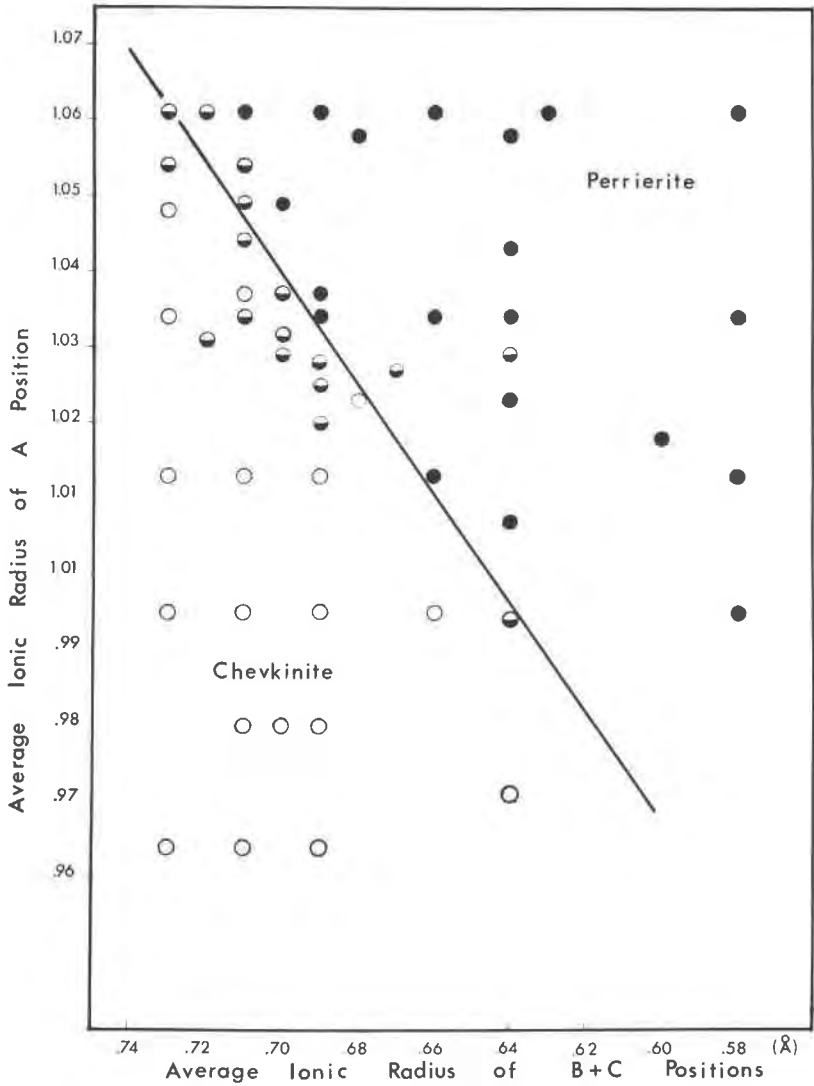
FIG. 2. Distribution of synthetic perrierite and chevkinite as a function of the average ionic radii of the A and the B+C positions. Half-circles indicate syntheses in which mixtures of chevkinite and perrierite were obtained.

$Fe^{2+}$ 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 $Pr_2O_{3+x}$. 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.

### REFERENCES

BONATTI, S. (1959) Chevkinite, perrierite and epidote, *Amer. Mineral.* **44**, 114–137.

BONATTI, S. AND G. GOTTARDI (1966) Un caso di polimorfismo a strati in sorosilicati: perrierite e chevkinite, *Period. Mineral.* **35**, 69–91.

GOTTARDI, G. (1960) Crystal structure of perrierite, *Amer. Mineral.* **45**, 1–14.

JAFFE, H. W., EVANS, H. T., JR. AND CHAPMAN, R. W. (1956) Occurrence and age of chevkinite from Devil's Slide fayalite-quartz syenite near Stark, New Hampshire, *Amer. Mineral.* **41**, p. 474–487.

KAUFFMAN, A. J. JR. AND H. W. JAFFE (1946) Chevkinite (tscheffkinite) from Arizona, *Amer. Mineral.* **31**, 582–588.

LIMA DE FARIA, J. (1962) Heat treatment of chevkinite and perrierite, *Mineral. Mag.* **45**, 1–14.

MACHAROKIN, B. A. (1955) Chevkinite from the Ilmen Mountains, *Zap. Vses. Mineral. Obshch. U.S.S.R.* **88**, 547–553.

MITCHELL, R. S. (1966) Virginia metamict minerals: perrierite and chevkinite, *Amer. Mineral* **51**, 1394–1405.

PAULING, L. (1948) *The Nature of the Chemical Bond*, 2nd ed. Cornell Univ. Press, Ithaca, New York, p. 346, 350.

TEMPLETON, D. H. AND DAUBEN, C. H. (1954) Lattice parameter of some rare earth compounds and a set of crystal radii, *J. Amer. Chem. Soc.* **76**, p. 5237.