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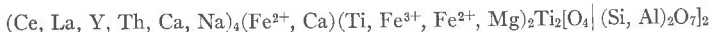
Nos. 1 and 2

THE CRYSTAL STRUCTURE OF PERRIERITE

GLAUCO GOTTARDI, *Istituto di Mineralogia dell'Università di Pisa, Italy*

ABSTRACT

The crystal structure of perrierite (space group $C2/m$) has been determined by x-rays. The following chemical formula has been attributed to the mineral:



The unit cell contains two formula units.

Perrierite is a sorosilicate, with a high number of O-atoms not bonded to silicon. In its structure there are two types of Ti-O octahedral chains along the b -axis; the chains are connected in order to give a sheet parallel to (001). Each Ce atom is surrounded by 10 oxygens; each Fe^{2+} by 6 oxygens. Interatomic distances are of the expected magnitude.

INTRODUCTION

Perrierite, a titanosilicate of rare earth and iron, was found as a new mineral in the shore sands at Nettuno, Roma, Italy, by Bonatti and Gottardi (1950), who gave the morphological crystallography and a chemical analysis. Later the same authors (1954) published the x-ray crystallography of the mineral and a new chemical analysis made on a purer sample, and pointed out that perrierite was a mineral distinct from chevkinite; the crystallographic similarity of the two minerals and epidote was illustrated. The relation between perrierite, chevkinite, and epidote was fully described on the basis of new data on chevkinite [Jaffe, Evans and Chapman (1956)] by Bonatti (1959). The chemical formulas of both chevkinite and perrierite were not known until now: a solution of the problem is offered by the knowledge of the structure and is presented in this paper.

X-RAY CRYSTALLOGRAPHY

The unit cell of perrierite, as determined by Bonatti and Gottardi (1954), has the following dimensions:

$$a = 13.59 \text{ kX} = 13.61 \text{ \AA}$$

$$b = 5.61 \text{ kX} = 5.62 \text{ \AA}$$

$$c = 11.61 \text{ kX} = 11.63 \text{ \AA}$$

$$\beta = 113^\circ 28'$$

Space group $C/2m$

The a axis of the unit cell corresponds to the c axis of the morphological interpretation. Such a change is advisable to obtain the conventional orientation of the centered monoclinic cell; moreover the original morphological interpretation emphasizes the similarities with epidote.

As to the number of atoms per unit cell, this is uncertain, but it is very probable that there are eight Ce atoms (more exactly rare earth-atoms).

For purposes of structure determination, Buerger precession photographs around [010] were taken with Zr-filtered Mo-radiation as follows: two equators, one with a precession angle $\mu = 25^\circ$ (exposure 18 hours), the other with $\mu = 30^\circ$ (exposure 50 hours); first layer with $\mu = 30^\circ$ (20 hours), second layer with $\mu = 20^\circ$ (20 hours). Intensities were measured by direct photometry of the negatives, since the Kodak Crystalex films used have a linear increase of density with the intensity of incident beam. Long exposures were needed in view of the small crystal size (about 100μ in length, 40μ in diameter). No absorption correction was applied. Intensities were put into an absolute scale only after having solved the structure; at the same time a temperature factor was calculated by comparison of F_o and F_c , and a value $B = 0.65 \text{ \AA}^2$ was adopted.

From these films the following constants were calculated:

$$a = 13.61 \pm 0.02 \text{ \AA}$$

$$c = 11.67 \pm 0.01 \text{ \AA}$$

$$\beta = 113^\circ 30'$$

Space group $C 2/m$ was found to be correct.

DETERMINATION OF THE STRUCTURE

In solving the structure of perrierite the following facts have been kept in mind:

- (1) Perrierite, like epidote, has a very short period along [010], $b = 5.62 \text{ \AA}$, a length which corresponds to twice the diameter of an oxygen anion: as in the space group $C 2/m$ there are mirror planes normal to [010] at distance $b/2$, oxygen anions can only have four values of the y -coordinate: $0, \frac{1}{4}, \frac{3}{4}, 1$. This limitation is practically valid for the other ions also.
- (2) In view of the morphological similarities of perrierite and epidote, it is very probable that the chains of Al-O octahedra stretched along the b axis [found by Ito (1950) in the structure of epidote] are to be found also in the structure of perrierite as Ti-O chains.
- (3) In the unit cell of perrierite there are eight Ce atoms, which are much heavier than the other atoms: this fact presents both advantages and disadvantages. The advantages are to be found in the interpretation of the Patterson synthesis (since the Ce-influenced maxima must be very easy to find) and in giving the signs to the F values. The disadvantages are present when interpreting Fourier syntheses, since the Ce maxima must be much stronger than the others, and especially much stronger in comparison with O maxima, whose localization may be very difficult.

On the basis of these facts, one can readily deduce the features of the (010) Patterson projection of perrierite. First, given a crystal belonging to space group $C 2/m$, its (010) projection has translations $a/2$, c , and a symmetry corresponding to plane group $p2$. In a (010) Fourier projection of perrierite one must see only four Ce maxima, and of these four maxima only two are independent. Let F_1 and F_2 represent the two independent Fourier maxima, and $F_{1'}$ and $F_{2'}$ those dependent upon the first two. Then in the Patterson projection one must find the following maxima:

- $P_{11'}$ joining the Fourier maxima $F_1F_{1'}$
- $P_{22'}$ joining the Fourier maxima $F_2F_{2'}$
- $P_{12+1'2'}$ joining the Fourier maxima F_1F_2 and $F_{1'}F_{2'}$
- $P_{12'+1'2}$ joining the Fourier maxima $F_1F_{2'}$ and $F_{1'}F_2$

Therefore in the Patterson projection the Ce atoms produce four independent peaks, two of which are twice as intense as the other two. Let us suppose, in order to simplify matters, that a Patterson peak were to have a value equal to the Z-number product of the interacting atoms; then a peak Ce-Ce is as great as $Z_{Ce}^2 = 3364$. In our Patterson projection one must find two independent maxima equal to 3364 and two equal to 6728.

As stated above, we have considered as probable the presence of Ti-O octahedra in chains running from the origin of the unit cell along the b -axis. Then in the (010) Fourier projection we have two superimposed Ti atoms at the origin. In the Patterson projection Ti-Ce maxima are not negligible in comparison with Ce-Ce maxima, although the atomic number of titanium is only 22: a Ti-Ce peak is equal to $Z_{Ti} \cdot Z_{Ce} = 1276$, but this value must be doubled for the superimposition of two Ti atoms in the projection and redoubled for the titanium being at the origin. Thus in Patterson projection a Ti-Ce peak may be as great as 5104. Let us observe that, since Ti atoms are placed at the origin, the Patterson Ti-Ce peaks are coincident with the Fourier Ce peaks.

Summarizing, if the hypotheses are correct, one must find in the Patterson (010) projection of perrierite: two independent peaks whose height is proportional to 6728, two independent peaks whose height is proportional to 5104, two independent peaks whose height is proportional to 3364. In this sense one must say "proportional to" rather than "equal to," because in calculating the synthesis only relative $|F|^2$ values were used.

The calculated Patterson synthesis is seen in Fig. 1. The projection is consistent with the predicted results. Since the positions of the Ce and Ti atoms in the Fourier projection are known, one has a sure method for

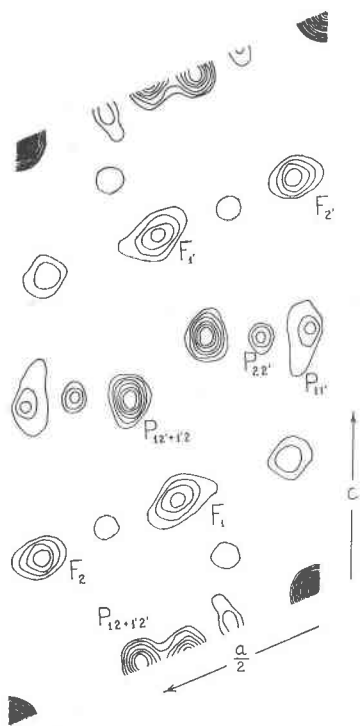


FIG. 1. Patterson (010) projection of perrierite. Contours at arbitrary intervals.

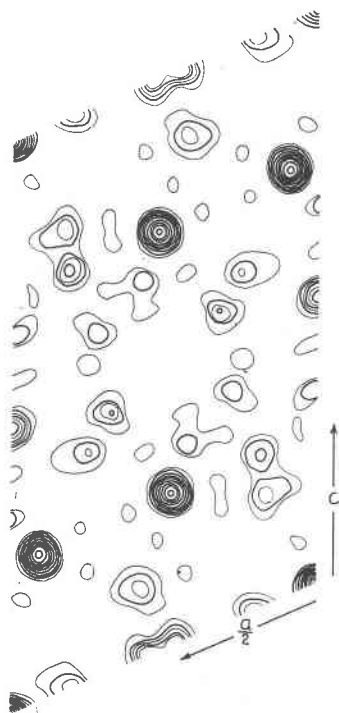


FIG. 2. Fourier (010) projection of perrierite. Heavy contours at 20 e. \AA^{-2} intervals, light contours at intermediate values, zero lines being omitted.

giving the signs to the F values. On this basis four Fourier syntheses were successively calculated, introducing more and more structure factors, as the positions of the different atoms were found. After the fourth synthesis, the positions of the O atoms not superimposed in projection ($\text{O}_6\text{O}_7\text{O}_8$) were not yet certain, since their maxima in the projection were no greater than many parasite maxima. It is necessary to point out that until the fourth synthesis, only F values with $\sin\theta < 0,422$ were used, these being the only ones present in the (010) equator photograph with the precession angle $\mu = 25^\circ$. After the fourth synthesis, an equator photograph was taken with a greater precession angle ($\mu = 30^\circ$). This introduced about forty new structure factors with $0,422 < \sin\theta < 0,500$. The fifth Fourier synthesis is represented in Fig. 2. In this projection parasite maxima are still present, especially around Ce peaks, but not so strong as in previous syntheses; in any case all peaks corresponding to atoms are distinguishable and stronger than parasite maxima.

The interpretation of this projection is as follows: the four major peaks are due to Ce atoms; and the peak at the origin is due to two superimposed Ti atoms. There are three other relevant maxima, obviously due to heavy atoms, of which two are interdependent and one independent. Finally there are 18 weaker maxima, of which 12 are twice as intense as the other 6: from the first 12, 8 were attributed to two superimposed oxygens, and 4 to silicon; the remaining 6 were attributed to single oxygens.

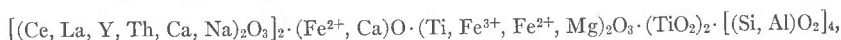
One can exclude the possibility that the above-mentioned three relevant maxima represent superimposed atoms, as these maxima are half as intense as the origin peak, and also because we know that these positions are occupied only by Ti and Fe atoms, i.e. by atoms as heavy as those at the origin. Hence the complete unit cell contains the following atoms:



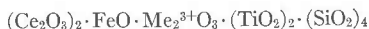
or as oxides



From the known chemical composition of perrierite [Bonatti and Gottardi (1954)] it is possible to write the exact formula as:



In the following, a simplified formula will be used:



This will be discussed in detail later on.

Regarding the interpretation of Fourier synthesis, there is yet an uncertainty, since it is not known whether there are Ti atoms or Me^{3+} atoms at the origin. But the problem is unsolvable with perrierite, because it has a chemical composition such that the Me^{3+} is represented almost entirely by Ti.

The above interpretation of the Fourier synthesis is seen in Fig. 3, in which one can read the height of each atom from the (010) plane as a fraction of the b length. The determination of the y parameters is obvious, as previously mentioned. For most cations the choice is even more limited, as only values such as 0 and $\frac{1}{2}$ are permitted by symmetry. The choice is uncertain only for Fe^{++} ($x=0$, $z=\frac{1}{2}$) and for Me^{3+} ($x=0$, $z=0$), for which either the parameter $y=0$ or $y=\frac{1}{2}$ is possible. To avoid these uncertainties comparisons were made of F_o and F_c values with indices $h1l$. Parameters so selected are given in Table 1.

F_o and F_c values are listed in Tables 2, 3 and 4. One observes that, of the values of the first and second layers, those corresponding to the "blind zone" are missing (the blind zone is always present in non-

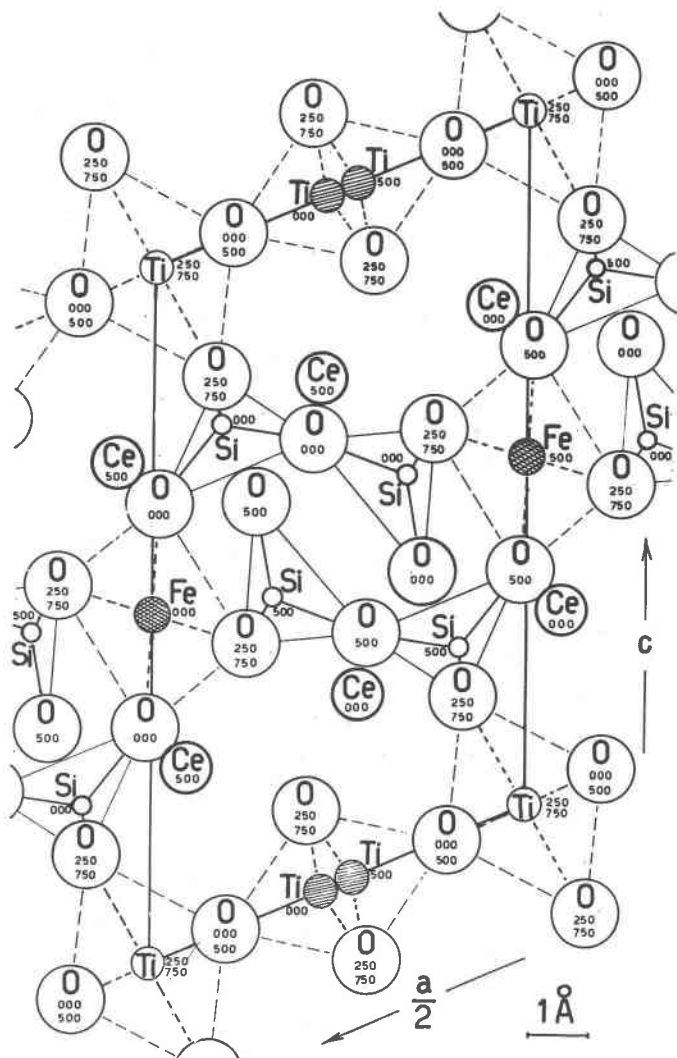


FIG. 3. The structure of perrierite projected on (010). The numbers give the y -parameters as permillage of the b -length. Coordination tetrahedra and octahedra are indicated.

equator photographs taken with the Buerger camera). This is no disadvantage, as these structure factors are of use only in a simple comparison of F_o and F_c .

As said previously, calculated structure factors have been corrected by a temperature factor with $B=0, 65 \text{ \AA}^2$.

TABLE 1. ATOMIC PARAMETERS OF PERRIERITE

Atom	Number of atoms in unit cell	Position	x/a	y/b	z/c
Si ₁	4	i	0.4085	0.000	0.734
Si ₂	4	i	0.1615	0.000	0.546
Ti	4	g	0.000	0.250	0.000
Me ⁺⁺⁺	4	i	0.270	0.000	0.000
Fe ⁺⁺	2	d	0.000	0.500	0.500
Ce ₁	4	i	0.238	0.000	0.266
Ce ₂	4	i	0.047	0.000	0.742
O ₁	8	j	0.085	0.250	0.194
O ₂	8	j	0.291	0.250	0.123
O ₃	8	j	0.3745	0.250	0.400
O ₄	4	i	0.103	0.000	0.997
O ₅	4	i	0.397	0.000	0.003
O ₆	4	i	0.492	0.000	0.660
O ₇	4	i	0.286	0.000	0.657
O ₈	4	i	0.1385	0.000	0.399

Reliability indexes of the structure are given in Table 5. The agreement between the observed and the calculated structure factors is satisfactory, bearing in mind the difficulty of getting strong reflections.

DESCRIPTION OF THE STRUCTURE

Perrierite is a sorosilicate because of the presence of Si₂O₇ groups in its structure. Its cationic charges are also balanced by oxygen ions not bounded to Si, there being 4 of these for each Si₂O₇ group.

But the more obvious structural groups in perrierite are the Ti-O chains parallel to the *b*-axis: every two octahedra have an edge in common (hence two vertices, that is, two oxygen ions). Actually there are two series of octahedral chains parallel to the *b*-axis, which together form a layer. The first series of chains starts at the origin of the lattice, as was apparent before beginning the solution of the structure. The other series is rotated 90° with respect to the first and is formed by oxygen with one cation which it is necessary to denote by Me⁺⁺⁺, even though, in the perrierite samples examined, about 75% of the lattice position is taken up by Ti⁴⁺ itself, while the rest is taken by Fe³⁺ and Mg²⁺. The lattice position of Me⁺⁺⁺ is such that the various cations of the chain form a zigzag structure parallel to *b*. This arrangement is obviously due to the strong repulsion between the near cations Me³⁺ and Ce³⁺. The resulting distortion in the Me³⁺ octahedron is very great, but probably is compensated by a similar pattern of the O₄ and O₅ oxygens, which should not

TABLE 2. F_o AND F_c VALUES FOR $h0l$ REFLECTIONS

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	146	-161	6	0	1	0	+43	-10	0	11	122	-121
0	0	3	177	+209	6	0	2	264	+242	-10	0	12	0	+13
0	0	4	335	+421	6	0	3	146	-149	-10	0	13	32	+61
0	0	5	67	+36	6	0	4	103	-118	-10	0	14	138	+102
0	0	6	110	-110	6	0	5	67	+82	-10	0	15	20	-52
0	0	7	240	+235	6	0	6	130	+85	12	0	0	32	+45
0	0	8	276	+318	6	0	7	162	-155	12	0	1	0	+29
0	0	9	43	-55	6	0	8	47	-53	12	0	2	32	+51
0	0	10	39	-42	6	0	9	177	+138	12	0	3	0	-18
0	0	11	181	+206	6	0	10	39	+30	12	0	4	55	+80
0	0	12	166	+168	6	0	11	130	-119	12	0	5	0	+18
0	0	13	111	-100	6	0	12	16	-14	12	0	6	35	+59
0	0	14	0	-20	-6	0	1	178	-178	12	0	7	0	-8
0	0	15	193	+197	-6	0	2	173	+187	-12	0	8	0	-18
2	0	0	0	+6	-6	0	3	0	-5	-12	0	2	67	+79
2	0	1	0	-62	-6	0	4	181	-187	-12	0	3	0	+18
2	0	2	32	-7	-6	0	5	79	-63	-12	0	4	87	+68
2	0	3	0	+25	-6	0	6	201	+208	-12	0	5	0	-5
2	0	4	87	+59	-6	0	7	0	-10	-12	0	6	110	+110
2	0	5	146	+107	-6	0	8	118	-76	-12	0	7	0	+47
2	0	6	0	-25	-6	0	9	0	+32	-12	0	8	95	-70
2	0	7	126	-112	-6	0	10	28	+63	-12	0	9	0	+16
2	0	8	0	+26	-6	0	11	75	-71	-12	0	10	95	+92
2	0	9	75	+51	-6	0	12	47	-58	-12	0	11	39	+73
2	0	10	39	+22	-6	0	13	39	+64	-12	0	12	0	-38
2	0	11	87	-59	-6	0	14	32	+71	-12	0	13	0	+6
2	0	12	79	+56	-6	0	15	0	-32	-12	0	14	122	+112
2	0	13	0	+36	8	0	0	79	+119	14	0	0	0	-19
2	0	14	0	-1	8	0	1	158	+207	14	0	1	146	-154
-2	0	2	32	+66	8	0	2	63	+41	14	0	2	87	+126
-2	0	3	87	-89	8	0	3	79	-78	14	0	3	162	+125
-2	0	4	118	+104	8	0	4	39	+83	14	0	4	75	-106
-2	0	5	59	-20	8	0	5	142	+192	14	0	5	59	-58
-2	0	6	103	+109	8	0	6	0	+3	-14	0	1	217	+193
-2	0	7	55	-35	8	0	7	0	-13	-14	0	2	79	+106
-2	0	8	0	+11	8	0	8	47	+100	-14	0	3	209	-181
-2	0	9	71	-62	8	0	9	51	+58	-14	0	4	0	-19
-2	0	10	39	+4	8	0	10	0	-8	-14	0	5	209	+167
-2	0	11	32	+50	-8	0	1	193	-205	-14	0	6	55	+86
-2	0	12	110	+82	-8	0	2	193	+172	-14	0	7	221	-201
-2	0	13	0	-11	-8	0	3	280	+330	-14	0	8	110	+84
-2	0	14	39	-28	-8	0	4	39	+65	-14	0	9	193	+165
-2	0	15	0	+2	-8	0	5	177	-142	-14	0	10	0	+3
4	0	0	225	+256	-8	0	6	162	+152	-14	0	11	154	-141
4	0	1	193	+198	-8	0	7	181	+166	-14	0	12	83	+80
4	0	2	181	-185	-8	0	8	0	+30	-14	0	13	142	+128
4	0	3	39	-64	-8	0	9	138	-119	-14	0	14	95	-77
4	0	4	272	+313	-8	0	10	233	+240	16	0	0	0	+18
4	0	5	47	+22	-8	0	11	138	+145	16	0	1	47	-27
4	0	6	0	-7	-8	0	12	47	-52	16	0	2	0	+17
4	0	7	39	-32	-8	0	13	0	-37	-16	0	1	0	+6
4	0	8	225	+235	-8	0	14	158	+168	-16	0	2	0	-6
4	0	9	87	+45	-8	0	15	95	+102	-16	0	3	0	+10
4	0	10	0	-76	10	0	0	87	-88	-16	0	4	0	+1
4	0	11	0	+11	10	0	1	0	+42	-16	0	5	0	+22
4	0	12	114	+149	10	0	2	248	+216	-16	0	6	0	+29
4	0	13	0	+3	10	0	3	0	+17	-16	0	7	0	+6
-4	0	1	0	-25	10	0	4	154	-122	-16	0	8	0	+18
-4	0	2	0	-20	10	0	5	0	+8	-16	0	9	0	-27
-4	0	3	244	+251	10	0	6	193	+211	-16	0	10	0	+45
-4	0	4	154	+178	10	0	7	0	-50	-16	0	11	51	-54
-4	0	5	256	-276	10	0	8	0	-50	-16	0	12	24	+40
-4	0	6	0	+26	10	0	9	0	+54	-18	0	3	87	-68
-4	0	7	237	+243	-10	0	1	87	+92	-18	0	4	110	+110
-4	0	8	154	+134	-10	0	2	185	+163	-18	0	5	118	+115
-4	0	9	143	-126	-10	0	3	0	-44	-18	0	6	32	-52
-4	0	10	0	+20	-10	0	4	91	-82	-18	0	7	32	-52
-4	0	11	197	+216	-10	0	5	142	+125	-18	0	8	146	+125
-4	0	12	87	+76	-10	0	6	197	+193	-18	0	9	150	+150
-4	0	13	158	-159	-10	0	7	51	-71	-18	0	10	79	-58
-4	0	14	79	+91	-10	0	8	0	-47					
-4	0	15	67	+100	-10	0	9	146	+167					
6	0	0	185	-158	-10	0	10	142	+129					

TABLE 3. F_o AND F_c VALUES FOR hkl REFLECTIONS

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	1	3	116	+107	5	1	3	44	-42	9	1	4	148	-116
1	1	4	32	+46	5	1	4	0	+58	9	1	5	0	-39
1	1	5	0	-42	5	1	5	0	-48	9	1	6	0	+8
1	1	6	148	-136	5	1	6	48	-67	-9	1	1	72	+86
1	1	7	136	+148	5	1	7	0	+5	-9	1	2	0	-57
1	1	8	0	-35	5	1	8	0	-3	-9	1	3	40	-71
1	1	9	0	-26	5	1	9	0	-24	-9	1	4	52	-71
1	1	10	0	-35	-5	1	1	0	-29	-9	1	5	0	+24
1	1	11	0	+56	-5	1	2	180	-139	-9	1	6	52	-61
-1	1	3	124	-98	-5	1	3	0	+8	-9	1	7	0	-48
-1	1	4	200	+150	-5	1	4	52	+53	-9	1	8	0	-16
-1	1	5	100	+71	-5	1	5	0	-32	-9	1	9	0	-36
-1	1	6	240	-200	-5	1	6	224	-231	-9	1	10	0	-27
-1	1	7	0	-19	-5	1	7	152	+138	-9	1	11	0	-31
-1	1	8	192	+153	-5	1	8	0	+10	-9	1	12	0	-34
-1	1	9	0	-17	-5	1	9	56	-83	11	1	0	180	-187
-1	1	10	188	-157	-5	1	10	132	-117	11	1	1	60	-125
-1	1	11	52	+55	-5	1	11	136	+104	11	1	2	208	+182
-1	1	12	64	+66	-5	1	12	0	+3	11	1	3	0	-58
3	1	0	0	-6	7	1	0	44	-60	11	1	4	64	-93
3	1	1	398	+420	7	1	1	272	+246	-11	1	1	0	+13
3	1	2	116	-141	7	1	2	124	+84	-11	1	2	208	+229
3	1	3	184	-223	7	1	3	128	-128	-11	1	3	0	+57
3	1	4	144	+134	7	1	4	0	-56	-11	1	4	180	-233
3	1	5	240	+267	7	1	5	196	+189	-11	1	5	80	+107
3	1	6	184	-171	7	1	6	0	-7	-11	1	6	160	+208
3	1	7	164	-123	7	1	7	64	-93	-11	1	7	0	+14
3	1	8	201	+171	7	1	8	0	+2	-11	1	8	160	-194
3	1	9	164	+133	-7	1	1	176	-183	-11	1	9	104	+146
3	1	10	144	-150	-7	1	2	224	+195	-11	1	10	140	+165
-3	1	2	96	-97	-7	1	3	220	+222	13	1	0	0	-36
-3	1	3	410	+398	-7	1	4	132	-138	13	1	1	112	-105
-3	1	4	32	-29	-7	1	5	38	-91	13	1	2	0	-23
-3	1	5	240	-246	-7	1	6	188	+186	-13	1	1	0	+51
-3	1	6	60	+74	-7	1	7	160	+162	-13	1	2	0	-31
-3	1	7	248	+248	-7	1	8	140	-156	-13	1	3	88	-124
-3	1	8	44	-71	-7	1	9	0	-32	-13	1	4	0	+22
-3	1	9	164	-152	-7	1	10	156	+163	-13	1	5	0	+42
-3	1	10	100	+103	-7	1	11	108	+101	-13	1	6	0	-76
-3	1	11	164	+144	-7	1	12	144	-153	-13	1	7	0	-62
-3	1	12	92	-87	9	1	0	168	-148	-13	1	8	0	-30
5	1	0	0	+5	9	1	1	56	-41	-13	1	9	0	+39
5	1	1	40	-31	9	1	2	0	-39					
5	1	2	140	-128	9	1	3	48	+48					

be exactly superimposed along b . But with the experimental data available, it is impossible to demonstrate such a zigzag pattern for these oxygens, for their Z value is too small in comparison with that of the other ions. The two series of chains, that of Ti^{4+} and that of Me^{3+} , form a layer parallel to (001) through the origin. The Si_2O_7 groups, which include all 6 oxygens coordinated by Fe^{++} , are arranged midway between two layers of octahedra.

The Ce^{+++} ions in coordination 10 lie between these layers of octahedra and the Si_2O_7 groups. Of the 10 oxygens which surround Ce , 6 are located at the vertices of a hexagon with a cation at the center, 3 above the hexagon, and one below.

TABLE 4. F_o AND F_c VALUES FOR $h2l$ REFLECTIONS

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	2	6	213	-172	-6	2	6	48	+36	-10	2	8	67	-104
0	2	7	124	+118	-6	2	7	137	-106	-10	2	9	0	-32
0	2	8	223	+206	-6	2	8	242	-253	-10	2	10	0	+51
0	2	9	105	-114	-6	2	9	0	-6	-10	2	11	102	-127
0	2	10	169	-162	-6	2	10	0	+50	-10	2	12	0	-20
0	2	11	143	+153	-6	2	11	73	-102	-12	2	10	0	-2
0	2	12	140	+129	-6	2	12	0	+23	12	2	1	54	-32
2	2	5	83	-101	8	2	0	0	+30	12	2	2	0	+23
2	2	6	70	-73	8	2	1	159	+158	12	2	3	0	+58
2	2	7	83	-88	8	2	2	0	-47	-12	2	1	0	-100
2	2	8	0	-43	8	2	3	146	-141	-12	2	2	0	+38
2	2	9	0	-12	8	2	4	0	+48	-12	2	3	0	-27
2	2	10	54	-68	8	2	5	0	+77	-12	2	4	0	-62
2	2	11	182	-139	8	2	6	0	-76	-12	2	5	48	-94
-2	2	7	217	-173	8	2	7	146	-36	-12	2	6	0	-2
-2	2	8	54	+48	-8	2	1	207	-193	-12	2	7	0	+23
-2	2	9	76	-83	-8	2	2	0	+17	-12	2	8	0	-64
-2	2	10	70	-51	-8	2	3	92	-95	-12	2	9	0	-44
-2	2	11	127	-84	-8	2	4	60	-46	-12	2	10	0	+32
-2	2	12	0	-38	-8	2	5	229	-242	-12	2	0	0	-103
4	2	4	134	+143	-8	2	6	175	+181	14	2	1	178	-178
4	2	5	0	-3	-8	2	7	124	+120	-14	2	1	0	+69
4	2	6	83	-108	-8	2	8	76	-60	-14	2	2	0	+46
4	2	7	115	-113	-8	2	9	185	-196	-14	2	3	188	-230
4	2	8	134	+124	-8	2	10	111	+108	-14	2	4	0	-18
4	2	9	0	-44	-8	2	11	73	-116	-14	2	5	105	+119
4	2	10	80	-80	-8	2	12	80	-116	-14	2	6	0	-3
-4	2	7	153	+127	10	2	0	175	-198	-14	2	7	172	-244
-4	2	8	0	+32	10	2	1	134	-121	-14	2	8	0	-2
-4	2	9	229	-221	10	2	2	162	+171	-14	2	9	96	+117
-4	2	10	0	-18	10	2	3	0	-38					
-4	2	11	89	+93	10	2	4	92	-136					
-4	2	12	0	+12	10	2	5	0	-30					
6	2	2	86	+42	10	2	6	111	+125					
6	2	3	255	-205	-10	2	1	60	+47					
6	2	4	191	-241	-10	2	2	102	-98					
6	2	5	76	+60	-10	2	3	0	-43					
6	2	6	108	+79	-10	2	4	169	-178					
6	2	7	210	-230	-10	2	5	0	-4					
6	2	8	108	-108	-10	2	6	130	+125					
6	2	9	0	+55	-10	2	7	150	-163					

TABLE 5. RELIABILITY INDEXES

	Number of reflections	Reliability indexes	
		including all reflections	including only observed reflections
(010) equator	218	0.244	0.165
(010) first layer	130	0.282	0.171
(010) second layer	112	0.332	0.156
All reflections	460	0.276	0.159

TABLE 6. INTERATOMIC DISTANCES IN PERRIERITE

Atom	Neighbour	Distance (Å)*	Atom	Neighbour	Distance (Å)*
Si ₁	O ₁ (2)	1.62	Ce ₁	O ₁ (2)	2.37
	O ₆	1.67		O ₂ (2)	2.48
	O ₇	1.53		O ₃ (2)	2.36
Si ₂	O ₃ (2)	1.68		O ₄	2.93
	O ₇	1.67		O ₇ (2)	3.02
	O ₈	1.61	O ₈	2.44	
Ti	O ₁ (2)	2.08	Ce ₂	O ₁ (2)	2.60
	O ₄ (2)	1.99		O ₂ (2)	2.55
	O ₅ (2)	1.99		O ₃ (2)	2.70
Me ⁺⁺⁺	O ₂ (4)	1.95		O ₄	2.76
	O ₄	2.21		O ₆ (2)	2.96
	O ₅	1.72	O ₈	2.40	
Fe ⁺⁺	O ₃ (4)	2.15			
	O ₆ (2)	1.91			

* The interionic distance error in the oxygen parameters is ± 0.05 Å, while that for the cation parameters is decidedly smaller.

Table 6 gives the interatomic distances between the various cations and the anions coordinated by them. There is a remarkable regularity, particularly in consideration of the difficulty in determining the position of light atoms, such as Si and O, close to heavy atoms, such as Ce.

Table 7 illustrates the balance between the oxygen anion charges and the cations surrounding them. Pauling's rule is normally fulfilled.

Finally it should be pointed out that the existence of the layer of octahedra parallel to (001), which morphologically is the plane (100), manifests itself in an outstanding manner: the (001) plane is not only always well developed in crystals, but it is frequently also a twin-plane. Thus it is evident that nucleation occurs precisely on that layer of octahedra, whose two faces are perfectly equivalent.

THE CHEMICAL FORMULA

In the preceding section the chemical formula of perrierite has been deduced from its crystal structure. By using (Si₂O₇) groups, we can write the formula as follows:

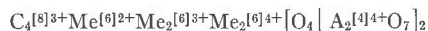
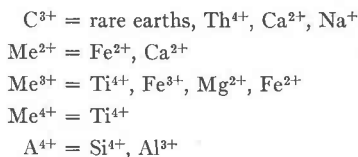


TABLE 7. BALANCE BETWEEN OXYGEN CHARGES AND SURROUNDING CATIONS

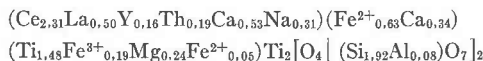
Anion	Balancing cations	Ratio of: charges of cation to coordination number	Total charges sur- rounding anion
O ₁	Ti	4/6	2.27
	Si	4/4	
	Ce	3/10	
	Ce	3/10	
O ₂	Me ⁺⁺⁺	3/6	1.60
	Me ⁺⁺⁺	3/6	
	Ce	3/10	
	Ce	3/10	
O ₃	Si	4/4	1.93
	Fe	2/6	
	Ce	3/10	
	Ce	3/10	
O ₄	Ti	4/6	2.43
	Ti	4/6	
	Me ⁺⁺⁺	3/6	
	Ce	3/10	
	Ce	3/10	
O ₅	Ti	4/6	1.83
	Ti	4/6	
	Me ⁺⁺⁺	3/6	
O ₆	Si	4/4	1.93
	Fe	2/6	
	Ce	3/10	
	Ce	3/10	
O ₇	Si	4/4	2.60
	Si	4/4	
	Ce	3/10	
	Ce	3/10	
O ₈	Si	4/4	1.60
	Ce	3/10	
	Ce	3/10	

where

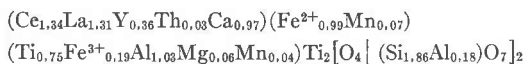


The isomorphic substitutions here listed have been found in perrierite from Nettuno, but obviously other substitutions are possible according to crystallochemical laws.

The exact formula, which is calculated from the chemical analysis of perrierite from Nettuno, is as follows:



A second occurrence of perrierite is known: the mineral of Kobe-Mura, Japan, studied by Takubo and Nishimura (1953) and named chevkinite, although it was demonstrated by Bonatti (1959) to be perrierite. From the chemical composition [analysis (2)] of the Kobe-Mura perrierite one can calculate the formula:



This formula does not seem applicable to the analyses of chevkinite; moreover chevkinite has a unit cell volume 7% greater than that of perrierite, and this leads one to suspect that there are more O atoms in the chevkinite unit cell than in the perrierite unit cell.

On the basis of this formula and of the unit cell dimensions, the theoretical specific gravity has been calculated, the result being $G = 4.77$; the experimental value [Bonatti and Gottardi (1954)] is $G = 4.45$. The theoretical value normally is greater than the experimental one; in this case the difference is large, but explainable considering that the measurement was made on a sample of very small crystals. The sample used for the determination of specific gravity was then destroyed during the chemical analysis. It did not seem useful to purify a new sample in order to make a new measurement of specific gravity, which would not contribute anything new to the information already secured.

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