

# Zr-rich non metamict perrierite-(Ce) from holocrystalline ejecta in the Sabatini volcanic complex (Latium, Italy)

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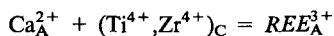
## Abstract

This paper reports the first *in-situ* finding of perrierite-(Ce) in Latium. The mineral occurs as brownish-red, transparent, well-developed, euhedral, prismatic crystals inside the miarolitic cavities of a holocrystalline ejectum from La Mola, Monti dell'Anguillara district, Sabatini volcanic complex.

The cell parameters (from Gandolfi film) are (in Å):  $a = 13.629(9)$ ,  $b = 5.727(1)$ ,  $c = 11.715(6)$ ,  $\beta(^{\circ}) = 113.74(2)$ ,  $V(\text{Å}^3) = 835.5(9)$ . The crystal-chemical formula, based on microprobe analysis of one grain, is:

$(\text{Ca}_{1.882}\text{Th}_{0.124}\text{REE}_{2.021}\text{Y}_{0.024})(\text{Fe}_{0.928}^{2+}\text{Mg}_{0.072})(\text{Ti}_{0.735}\text{Al}_{0.632}\text{Zr}_{0.484}\text{Nb}_{0.019}\text{Mn}_{0.033}\text{Mg}_{0.045})\text{Ti}_2(\text{Si}_{3.911}\text{Al}_{0.089})\text{O}_{22}$ .

This perrierite is the most Zr-rich described so far. The entry of Zr in the C site of the structure is related to the substitution of large amounts of Ca in the A site, according to the charge balancing relationship:



The genesis of perrierite-(Ce) from La Mola is linked to late pneumatolitic-pegmatitic hypabyssal stages of the regional volcanic activity.

**KEYWORDS:** Perrierite-(Ce), Sabatini, Latium, Italy, Ti-REE-silicate, zirconium, crystal-chemistry, cell parameters.

## Introduction

PERRIERITE is a rare REE-Ti-bearing silicate, which shows close similarities with chevkinite and with epidote group minerals such as allanite (Bonatti and Gottardi, 1954, 1966; Bonatti, 1959; Calvo and Faggiani, 1974). It is characteristically found in acid to intermediate igneous rocks (e.g. Jaffe *et al.*, 1956; Segalstad and Larsen, 1978; McDowell, 1979; van Bergen, 1984).

Perrierite-(Ce) was firstly reported from shore sands of the Tyrrhenian Sea in Latium, near

Nettuno, south of Rome (Bonatti and Gottardi, 1950). The perrierite-bearing sands were undoubtedly derived from disaggregated pyroclastic rocks belonging to the Alban Hills volcanic complex in the Roman Comagmatic Region (Washington, 1906), but until now the mineral has never been observed in any primary occurrence in that area, despite efforts of mineral researchers and hunters. Since then, perrierite-(Ce) has been reported only once *in-situ* from the Monte Amiata volcanics in the Tuscan Province (van Bergen, 1984). It occurs there as an accessory

phase together with ilmenite, apatite, zircon and iron sulphides in a rhyodacitic lava associated with early stages of the volcanic activity (Mazzuoli and Pratesi, 1963).

Here we describe a new occurrence from Latium, the first one *in-situ* within the Roman perpotassic province, from a holocrystalline ejectum enclosed in the pyroclastic units of the Sabatini volcanic group, north of Rome. To the best of our knowledge this is the most Zr-rich sample so far reported of this mineral.

### Occurrence

The ejectum containing the perrierite-(Ce) was collected at La Mola locality, Monti dell'Anguillara district, community of Anguillara, north of Rome, by F.S. Stoppani and D. Di Domenico. Perrierite-(Ce) occurs as brownish-red, transparent, euhedral prisms with pinacoidal end faces, implanted on the walls of miarolitic cavities, associated with titanite, zircon and baddeleyite. The host rock is mainly composed of sanidine, 'augitic' clinopyroxene, biotite and Fe-oxides. The perrierite-(Ce) crystals characteristically grow on top of the early-formed sanidine crystals. The mineral was initially identified on the basis of a Gandolfi film and qualitative microprobe analyses. The X-ray powder-pattern, recorded under Cu-K $\alpha$ , Ni-filtered radiation, was indexed in the space group  $P2_1/a$ . The unit-cell parameters, computed by a least-square refinement of the indexed reflections are (in Å):  $a = 13.629(9)$ ,  $b = 5.727(1)$ ,  $c = 11.715(6)$ ,  $\beta(^{\circ}) = 113.74(2)$ ,  $V(\text{Å}^3) = 835.5(9)$ .

### Chemistry

Quantitative analyses were done on a fully-automated CAMECA SX-50 microprobe operating in the wavelength-dispersive mode, at the University of British Columbia. Analytical conditions were: 15 kV excitation voltage, 30 nA beam current, peak count times 20 s for Mg, Al, Si, Ca, Ti, Mn, Fe, and 40 s for Y, Zr, Nb, Th, REE; background count times one-half of peak count-times; beam diameter 2  $\mu\text{m}$ . No elements other than those listed above were detected in wavelength-dispersive scans. The following standards were used: diopside (Si, Mg, Ca), grossular (Al), fayalite (Fe), spessartine (Mn), rutile (Ti), zircon (Zr), microlite (Nb), synthetic CeF<sub>2</sub> (Ce), thorium metal (Th), Drake and Weill's (1972) glasses (Y, La, Pr, Nd, Sm). Data reduction was done with the PAP  $\phi(\rho Z)$  method (Pouchou and Pichoir, 1984).

Two grains, R1 and R2, from the same ejectum were analysed. Table 1 gives the averages of three

spots in different parts of each grain, together with the calculated crystal-chemical formulae, in comparison with the data of other perrierite samples from several localities. Our microprobe analyses show that the two samples from La Mola are homogeneous and have the same composition within the error limits of the method.

When compared with analyses of other perrierites (Table 1), the main differences are in the Al, REE, Ca and Zr values. In particular, the perrierite-(Ce) described here is enriched in ZrO<sub>2</sub> and is comparable only with the Sr-perrierite from Baikol (Portnov, 1964).

### Crystal-chemistry

The idealized crystal chemical formula of perrierite and chevkinite minerals may be represented as  $A_4^{3+}B_2^{2+}C_2^{3+}Ti_2^{4+}O_8(Si_2O_7)_2$ , where  $A = REE$ ;  $B =$  divalent cations such as Fe<sup>2+</sup>, Mg;  $C =$  trivalent cations such as Fe<sup>3+</sup>, Al<sup>3+</sup>. Several substitutions are possible: the trivalent  $C$  cations may be partially replaced by divalent (notably Fe<sup>2+</sup>) as well as tetravalent (Ti and Zr) cations, the charge balance being restored by coupled substitutions of divalent (Ca), tetravalent (e.g. Th) and monovalent (notably Na) cations.

Following Gottardi (1960), the analyses were recalculated on the basis of 13 cations. These were assigned to the structural sites as follows: (1) all Si, together with sufficient Al to total 4.0, is assigned to the  $Z$  site; (2) two Ti atoms are assigned to the  $D$  site, the remainder being allotted to the  $C$  site; (3) all Fe is then assigned to the  $B$  site as Fe<sup>2+</sup>, and the site is filled up to 1.0 with Mg; (4) excess Mg, Al and Ti together with Zr, Nb and Mn are assigned to the  $C$  site. Finally (5) Ca, Th and REE are assigned to the  $A$  site. The total positive charges obtained are in the range 43.30–43.40, which is close to the ideal value 44, and suggests that the amount of Fe<sup>3+</sup> (and possibly Mn<sup>3+</sup>) that may be present is negligible. Because the tetrahedral site  $Z$  is filled almost completely with Si, the majority of Al enters the  $C$  site where it contributes > 30% of this site occupancy.

As already discussed by McDowell (1979), the structure refinements of Gottardi (1960) and Calvo and Faggiani (1974) indicate that Ca should not enter the  $B$  site because of its large size. The Sabatini perrierite-(Ce) described here is consistent with these structure refinements, but recalculation of some perrierite analyses from the literature (i.e. those from Norway and from Nettuno listed in Table 1) requires the assignment of significant amounts of Ca to the  $B$  site, because

of high *REE* and Na contents which completely fill the *A* site.

### Discussion

Perrierite and chevkinite both have two sets of infinite chains of octahedra centered by  $M^{3+}$  and Ti atoms running along *b*. The axes of the chains are rotated by  $90^\circ$  with respect to each other, and shifted by  $b/4$ . The chains are connected to form infinite octahedral sheets parallel to (001). These sheets are interleaved with  $Si_2O_7$  groups and  $B^{2+}$  octahedra, which are arranged in such a way as to form a composite layer. The *REE* ions lie between the disilicate groups and the octahedral sheets. Perrierite differs from chevkinite in the distribution of the *C* and Ti cations among the octahedral chains (Calvo and Faggiani, 1974).

The substitution of Ca for *REE* in highly coordinated polyhedra is observed in many *REE*-bearing silicates. This substitution holds also for perrierites and chevkinites, and can be seen in Fig.

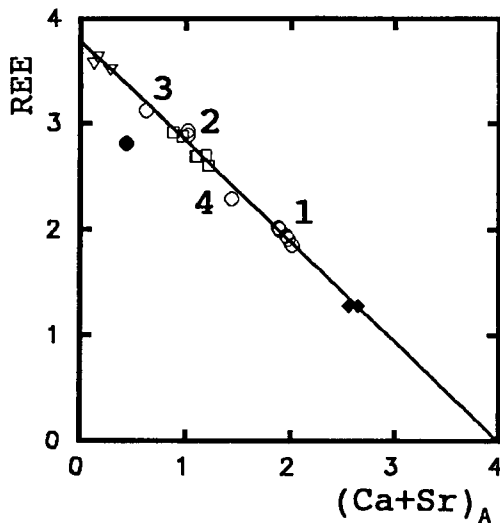
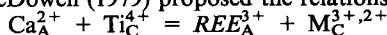


FIG. 1. Relationship between the (Ca + Sr) content and the *REE* content in the *A* site for perrierites and chevkinites. Regression line drawn across the perrierite samples only. Equation of  $Y = 3.78 - 0.95X$  ( $R_{\text{corr}} = 0.99$ ). Open circles: perrierites (1 = this work; 2 = perrierites from Mt. Amiata, van Bergen, 1984; 3 = perrierite from Norway, Segalstad and Larsen, 1978; 4 = Sr-perrierite from Baikal, Portnov, 1964); filled dot: perrierite from Nettuno (Bonatti and Gottardi, 1954); open squares: chevkinites from California (McDowell, 1979); open triangles: chevkinites from Norway (Segalstad and Larsen, 1978); filled diamonds, chevkinites from Parana (Haggerty and Mariano, 1983).

1 where  $(Ca + Sr)_A$  is plotted against total *REE*. A good correlation is seen with the exception of the holotype perrierite-(Ce) from Nettuno which shows a significant departure from the trend because of the large amount of Na assigned to the *A* site (Table 1).

McDowell (1979) proposed the relationship:



as the general balancing substitution occurring in Ca-*REE* minerals. This is effective also for perrierite and chevkinite, Fig. 2.

The location in the structure of the relatively large amounts of Zr in perrierite from La Mola deserves some comment. In principle, due to its size and charge, zirconium may replace silicon in the tetrahedral *Z* position, as it does in many silicates. Here, however, the tetrahedral sites are almost completely filled by Si (Table 1). Examination of all the available chemical data for perrierites and chevkinites reveals that perrierite from La Mola has 50% of the *A*-site filled by Ca, compared with less than 25% in almost all previously analysed perrierite and chevkinites, except for the Sr-rich examples. The remainder of the *A* site is occupied by *REE*; consequently, perrierite from La Mola has the lowest *REE* content (see Fig. 1 and Table 1). Given the Ca:*REE* ratio = 1:1, it is also likely that there may be some degree of ordering between Ca and *REE* in the *A* site. According to Gottardi

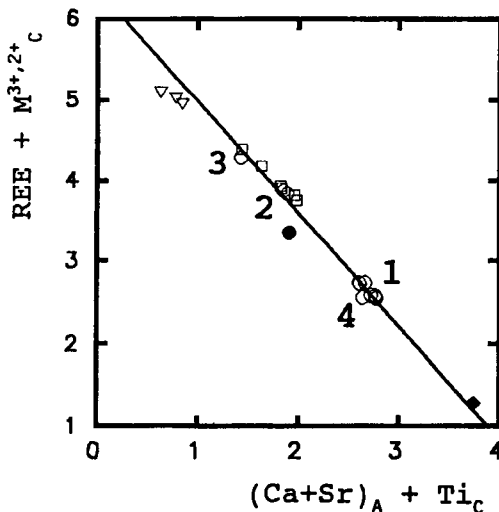


FIG. 2. Relationship between the (Ca + Sr) content on the *A* site + the Ti content on the *C* site as a function of the *REE* content at the *A* site + the  $M^{3+,2+}$  content on the *C* site for perrierites and chevkinites. Regression line drawn across perrierites only. Same symbols as in Fig. 1.

TABLE 1. Average analyses and crystal-chemical formulae for perrierites from La Mola (samples R1 and R2) in comparison with data for perrierites from several localities

	1	2	3	4	5	6
SiO <sub>2</sub>	20.91	21.25	19.93	19.31	20.64	20.30
TiO <sub>2</sub>	19.43	19.93	18.89	23.24	19.15	22.09
ZrO <sub>2</sub>	5.34	5.63	0.80	—	—	4.85
ThO <sub>2</sub>	2.95	2.09	2.60	4.05	0.68	0.54
Al <sub>2</sub> O <sub>3</sub>	3.24	3.27	3.36	0.67	0.38	0.48
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	1.26	—	1.65
Fe*	5.80	5.76	5.42	4.05	8.17	4.65
MgO	0.43	0.42	0.66	0.81	0.40	0.11
MnO	0.21	0.20	—	—	1.70	0.93
CaO	9.54	9.89	4.71	4.11	3.94	3.06
SrO	—	—	—	—	1.28	7.73
Na <sub>2</sub> O	—	—	—	1.05	0.47	0.72
K <sub>2</sub> O	—	—	—	—	—	0.14
La <sub>2</sub> O <sub>3</sub>	10.42	9.95	9.91	6.83	21.01	—
Ce <sub>2</sub> O <sub>3</sub>	14.39	14.26	20.13	31.80	18.24	32.14**
Pr <sub>2</sub> O <sub>3</sub>	1.10	1.03	2.14	—	2.16	—
Nd <sub>2</sub> O <sub>3</sub>	3.00	3.00	6.74	—	2.25	—
Sm <sub>2</sub> O <sub>3</sub>	0.11	0.16	0.74	—	nd	—
Gd <sub>2</sub> O <sub>3</sub>	—	—	0.45	—	nd	—
Y <sub>2</sub> O <sub>3</sub>	0.26	0.20	0.36	1.51	0.40	—
Nb <sub>2</sub> O <sub>5</sub>	0.24	0.26	—	—	—	—
Total	97.37	97.30	96.84	98.69	100.87	99.39
Total REE	29.02	28.40	40.11	38.63	43.66	32.14
Formulae on the basis of 13 cations						
(A)						
Ca	1.915	1.964	1.006	0.440	0.479	0.570
Sr	—	—	—	—	0.145	0.867
Th	0.126	0.088	0.118	0.183	0.030	0.024
La	0.720	0.680	0.729	0.500	1.512	—
Ce	0.987	0.968	1.469	2.313	1.303	2.292
Pr	0.075	0.070	0.155	—	0.154	—
Nd	0.201	0.199	0.480	—	0.157	—
Sm	0.007	0.010	0.051	—	—	—
Gd	—	—	0.031	—	—	—
Y	0.026	0.020	0.038	0.160	0.042	—
Na	—	—	—	0.404	0.178	0.270
K	—	—	—	—	—	0.035
ΣA	4.057	3.999	4.077	4.000	4.000	4.058
(B)						
Fe <sup>2+</sup>	0.909	0.893	0.904	0.565	0.655	0.752
Mg	0.091	0.107	0.096	—	—	0.032
Ca	—	—	—	0.435	0.345	0.064
Mn	—	—	—	—	—	0.152
ΣB	1.000	1.000	1.000	1.000	1.000	1.000

(1960), Galli (1965) and Calvo and Faggiani (1974), there are two distinct *A*-sites in perrierite, with irregular and slightly different coordination: *A*1, eight- to nine-fold coordinated, and *A*2 nine-

fold coordinated (Calvo and Faggiani, 1974). It is anticipated that a structural refinement which is underway will help to resolve this aspect of the crystal-chemistry.

TABLE 1. (contd.)

(C)						
Ti	0.738	0.778	0.982	1.472	0.810	1.212
Al	0.634	0.653	0.762	—	0.087	0.034
Fe <sup>3+</sup>	—	—	—	0.188	—	0.240
Zr	0.488	0.509	0.078	—	—	0.457
Nb	0.020	0.022	—	—	—	—
Fe <sup>2+</sup>	—	—	—	0.108	0.678	—
Mn	0.033	0.031	—	—	0.281	—
Mg	0.029	0.009	0.100	0.240	0.116	—
$\Sigma C$	1.942	2.002	1.922	2.008	1.972	1.943
(D)						
Ti	2.000	2.000	2.000	2.000	2.000	2.000
(Z)						
Si	3.918	3.939	3.973	3.836	4.022	3.925
Al	0.082	0.061	0.027	0.157	—	0.075
Charge	43.33	43.35	44.05	43.89	42.81	43.57

\* For microprobe analyses total Fe as FeO; \*\* given as total REE;  
nd = not determined.

- 1) Sample R1, this work, MPA, average of 3 spots over one grain.
- 2) Sample R2, this work, MPA, average of 3 spots over one grain.
- 3) Sample MA1 from M. Amiata (van Bergen, 1986), MPA, average of 6 spots over two grains. Mn, P and Nb looked for but not detected.
- 4) Holotype from Nettuno (Bonatti e Gottardi, 1954).
- 5) Perrierite from Bjørkedalen, Norway, MPA (Segalstad and Larsen, 1978). Includes 0.16 Tb<sub>2</sub>O<sub>3</sub> and 0.06 Yb<sub>2</sub>O<sub>3</sub> (oxide % by wt).
- 6) Sr-perrierite from Baikal (Portnov, 1964, as given in Haggerty and Mariano, 1983). Includes 0.08 H<sub>2</sub>O.

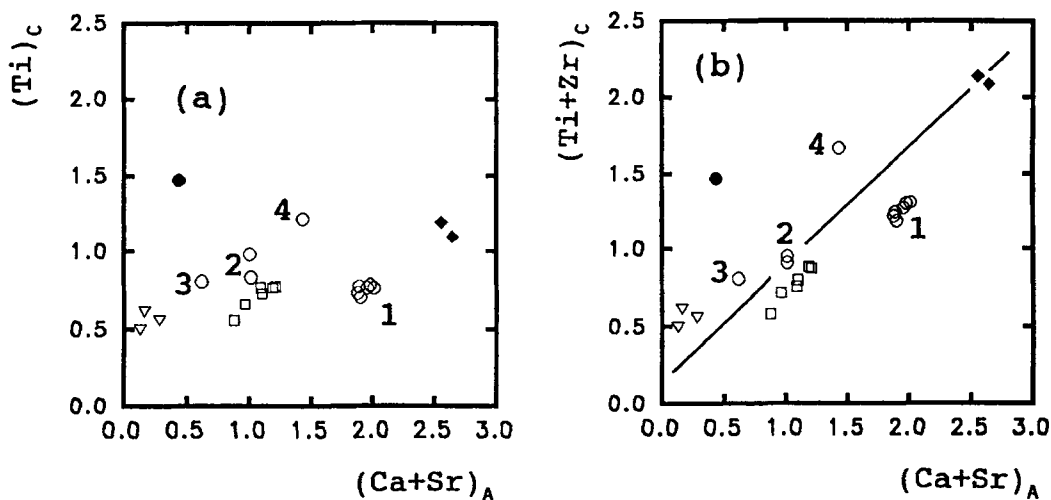
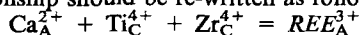


FIG. 3. Relationship between the (Ca + Sr) content on the A site against (a) the Ti content at the C site and (b) the (Ti + Zr) content on the C site for perrierites and chevkinites. Same symbols as in Fig. 1.

McDowell (1979) observed a linear trend relating  $Ti_C$  against  $Ca_A$  in chevkinites. However, in a plot of the  $Ca+Sr$  content in the  $A$  site against the  $Ti$  content in the  $C$  site for both perrierites and chevkinites, there is a clear scatter (Fig. 3a); only if  $(Ca+Sr)$  in  $A$  is plotted against  $Ti+Zr$  in  $C$ , there is now a relatively good linear correlation (Fig. 3b). The only exception is the Nettuno perrierite, where the large departure from the general trend is due to the very large amount of  $Ti$  assigned to the  $C$  site. Therefore, the  $Ca$  for  $REE$  substitution appears to be balanced mainly by the coupled substitution of tetravalent cations,  $Zr+Ti$  into the  $C$  site. Consequently, McDowell's relationship should be re-written as follows:



This is shown in Fig. 4 where it is apparent that the trend is now linear for all points, with an equation of  $Y = 3.92 - 0.59X$  ( $R^2 = 0.99$ ).

#### Genetical considerations

The stability of perrierite and its relationship to chevkinite are not well known. In synthetic systems (Ito and Arem, 1971), perrierite and chevkinite exhibit thermal polymorphism within a restricted compositional range, with chevkinite being stabilized, relative to perrierite, by higher temperatures, by  $A$  ions with smaller radii, and by  $B+C$  ions of larger radii. However, in natural systems the situation is not clear. For example, Young and Powers (1960) reported early crystal-

lization of chevkinite in several siliceous volcanic ashes, while McDowell (1979) described the appearance of chevkinite in the Little Chief Granite as late in the period of phenocryst crystallization. In the Bjorkedalen deposit, the only locality where both perrierite and chevkinite occur in the same rock, the two minerals do not coexist: they are restricted to different positions in the pegmatite, suggesting that the formation of one phase relative to the other is primarily controlled by bulk composition, rather than by the physical conditions (Segalstad and Larsen, 1978). For the Mt. Amiata perrierite, textural relationships indicate an early crystallization (van Bergen, 1984). At La Mola, perrierite-(Ce) is probably related to a late pegmatitic-pneumatolitic stage, comparable to that which produced most or all rare minerals occurring in the vugs of the sanidinitic ejecta of Latium (Della Ventura *et al.*, 1991, 1993).

Finally, as already pointed out by van Bergen (1984), one point ought to be stressed; perrierite (and possibly chevkinite) are probably much more common minerals within the Tuscan and Roman volcanic provinces than previously believed.

#### Conclusions

This paper reports the occurrence of non-metamict perrierite-(Ce) from the tephra of La Mola in the Roman comagmatic region (Latium, Italy). The mineral is significantly enriched in  $Zr$  relative to previously reported perrierites, and comparison are made with  $Zr$ -rich chevkinites. The substitution of  $Zr^{4+} + Ti^{4+}$  in the octahedral  $C$  site of the structure has been shown to balance the coupled substitution of large amounts of  $Ca$  for  $REE$  in the  $A$  site.

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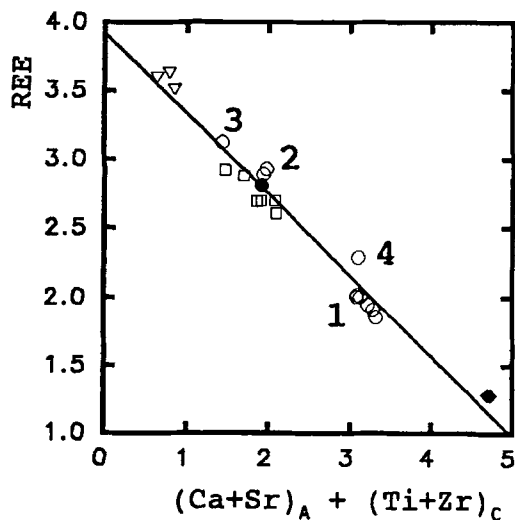


FIG. 4. Relationship between the  $(Ca+Sr)$  content at the  $A$  site plus the  $(Ti+Zr)$  content at the  $C$  site as a function of the  $REE$  content at the  $A$  site for perrierites and chevkinites. Same symbols as in Fig. 1.

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