Perrierite in siliceous lavas from Mt Amiata, central Italy

PERRIERITE and chevkinite are rare *REE*-Ti silicates reported from granitic and syenitic pegmatites and igneous rocks, volcanic ash beds, ignimbrites, and anorthosite (e.g. Jaffe *et al.*, 1956; Young and Powers, 1960; Mitchell, 1966; Izett and Wilcox, 1968; Raade, 1970; Brooks and Rucklidge, 1976; Segalstad and Larsen, 1978; McDowell, 1979; Harding *et al.*, 1982). The minerals are easily confused because of their close chemical and structural relationships, which have been discussed by Bonatti and Gottardi (1954, 1966), Bonatti (1959), Gottardi (1960), Lima de Faria (1962), and Calvo and Faggiani (1974). Experimental studies revealed that perrierite and chevkinite exhibit thermal polymorphism within certain compositional ranges (Ito, 1967; Ito and Arem, 1971). The type locality of perrierite is Nettuno, Rome (Italy), where Bonatti and Gottardi (1950) found it as a new mineral in shore sands derived from pyroclastics. This communication describes an occurrence in siliceous lavas and, to the best of my knowledge, records the second discovery in Italy.

Routine energy-dispersive microprobe work on the lavas of Mt Amiata, a Pleistocene volcanic complex in southern Tuscany, which consists of lava and domes with both calcalkaline and potassic-alkaline affinities, revealed the presence of a *REE*-Ti silicate with a strong yellowish brown-reddish brown-opaque pleochroism. The mineral was found in studied specimens of the so-called early rhyodacites, which are K-rich lavas containing some 66 wt. % SiO₂. These mineralogically uniform rocks carry phenocrysts of plagioclase, sanidine, pyroxene (both ortho- and clino-), and biotite, in addition to about 61 % perlitic glass. Minor and accessory minerals are ilmenite, apatite, zircon, iron sulphide, and embayed quartz. Chemical and mineralogical details about these volcanics are to be found in Mazzuoli and Pratesi (1963) and Van Bergen *et al.* (1983). Mazzuoli and Pratesi (1963) reported the ubiquitous presence of very rare crystals of non-metamict allanite with a strong brown-opaque pleochroism. In the thin sections available for microprobe analysis, all grains that conform to this description proved to have the composition of perrierite or chevkinite, whereas allanite was not found. As these minerals are difficult to distinguish optically, this suggests that the *REE*-Ti silicate is a common accessory phase in all the siliceous lavas of Mt Amiata. Abundances do not exceed a few tiny grains per thin section, however.

The perrierite typically occurs as stubby rounded crystals of less than 200 μm. Some are included in orthopyroxenes, but most occur along orthopyroxene rims or as discrete grains. Elongate crystals also occur but are extremely rare. Texturally the mineral occupies a position in the crystallization sequence comparable to that of ilmenite, and was probably among the early forming minerals. Young and Powers (1960) reached a similar conclusion for chevkinites in a number of siliceous volcanic ashes from the United States, whereas McDowell (1979) suggested that the chevkinite in the Little Chief Granite, California appeared late in the period of phenocryst crystallization.

Several X-ray diffraction patterns of very small, unheated grains were made in a Gandolfi camera fitted with a two-axes rotating sample-holder. As pointed out by Bonatti and Gottardi (1954), Lima de Faria (1962), and Mitchell (1966), X-ray powder data should be sufficiently diagnostic to distinguish between natural perrierite, chevkinite, and allanite. The results correspond well to perrierite, although occasional reflections were found that could also be attributed to chevkinite. The determination as perrierite is based on the consistent presence of two characteristic strong reflections at *d*-values between 2.94 and 3.00 Å.

TABLE I. *Analyses and CIPW-norms of perrierite-bearing lavas*

	1	2		1	2
SiO₂	65.37	65.53	qz	19.54	19.89
TiO₂	0.62	0.60	or	31.02	30.73
Al₂O₃	15.64	15.60	ab	21.24	21.66
Fe₂O₃	0.76	0.66	an	15.90	15.72
FeO	2.76	2.77	di	0.72	0.19
MnO	0.06	0.06	hy	7.31	7.48
MgO	1.66	1.57	mt	1.10	0.96
CaO	3.58	3.40	il	1.18	1.14
Na₂O	2.51	2.56	ap	0.35	0.33
K₂O	5.25	5.20			
P₂O₅	0.15	0.14			
LOI	1.64	1.92			

1. Sample MA1.
2. Sample MA19.

Two samples were selected for quantitative analysis. Whole-rock major element compositions and CIPW norms are given in Table I. Perrierite analyses were performed with an automated TPD microprobe using wavelength-dispersive techniques and a Tracor–Northern correction program. Operating conditions were 15 kV acceleration voltage, c. 40 nA sample current and counting times between 20 and 100 seconds. Standards for Y and the rare-earth elements (*REE*) were the artificial glasses prepared by Drake and Weill (1972) which were moved under the beam during data collection. There are few recent (microprobe) analyses of perrierites and chevkinites (e.g. Brooks and Rucklidge, 1976; Segalstad and Larsen, 1978; McDowell, 1979; Harding et al., 1982). Older (wet chemical) data are summarized in Jaffe et al. (1956) and semiquantitative results for perrierite from occurrences in Virginia are reported in Mitchell (1966). In general, both minerals have variable but fairly similar compositions, except for some Sr, Th, or Nb-rich varieties (see Haggerty and Mariano, 1983). However, taking into account that certain 'chevkinites' have been re-identified as perrierites (Bonatti, 1959; Lima de Faria, 1962; Mitchell, 1966) the available analyses suggest that perrierites tend

to be slightly poorer in Fe_{tot} and richer in Al_2O_3 and CaO, within limited ranges for other elements. This observation is qualitatively consistent with experimental results which suggest that the transition of chevkinite to perrierite is influenced by the variation in ionic size in the distinct structural sites, and may be accompanied by the coupled substitution of (1) Ce by Ca, and Fe^{2+} by Al, (2) Fe^{2+} by Al, and Ti^{4+} by Al, and (3) Fe^{2+} by Al, and Si^{4+} by Al (Ito, 1967), although it should be noted that the situation in the natural minerals is still a matter of discussion (see Segalstad and Larsen, 1978; McDowell, 1979; Haggerty and Mariano, 1983).

The analysed grains from Mt Amiata show little variation and agree with this tendency in the chemical characteristics of perrierite, as they are poor in Fe_{tot} and fairly rich in Al_2O_3 and CaO, as well as in ThO_2 (Table II). Cation proportions are in agreement with the general formula REE_4^{3+} $M^{2+}(Ti^{4+}M^{2+})(TiO_4)_2(SiO_2O_7)_2$ given by Gottardi (1960). As appears from the partial *REE* pattern of chondrite-normalized abundances (fig. 1), the perrierite is extremely enriched in the light *REE* relative to the heavy *REE*, with a $(Ce/Y)_{ch}$ ratio of 135. This fractionation of the *REE* compares well with that found in a mineral referred to as *REE*-rich sphene from the Skye Tertiary granites (Exley, 1980). As tentatively suggested in Harding et al. (1982), this mineral may actually be chevkinite in view of their corresponding compositions. Other

TABLE II. *Electron microprobe analyses of perrierite from Mt Amiata*

Oxides			Cations†		
	1	2		1	2
SiO_2	19.93	19.74	Si	8.045	8.000
TiO_2	18.89	18.68	Ti	5.737	5.692
Al_2O_3	3.36	3.44	Al	1.600	1.647
FeO*	5.42	5.45	Fe	1.832	1.848
MgO	0.66	0.84	Mg	0.399	0.509
CaO	4.71	4.70	Ca	2.038	2.043
La_2O_3	9.91	9.28	La	1.477	1.387
Ce_2O_3	20.13	20.03	Ce	2.975	2.971
Pr_2O_3	2.14	2.18	Pr	0.315	0.323
Nd_2O_3	6.74	7.08	Nd	0.972	1.024
Sm_2O_3	0.74	0.72	Sm	0.103	0.102
Gd_2O_3	0.45	0.44	Gd	0.061	0.060
Y_2O_3	0.36	0.39	Y	0.078	0.086
ZrO_2	0.80	0.71	Zr	0.158	0.141
ThO_2	2.60	2.90	Th	0.239	0.268
Total	96.84	96.58	Σ	26.029	26.101

* Total iron listed as FeO.
† Cation proportions based on 44 oxygens.
1. Sample MA1 mean of 6 spots in 2 grains.
2. Sample MA19 mean of 9 spots in 3 grains.
Mn, P, and Nb were looked for but not detected. The presence of a few tenths of a percent Sc_2O_3 was semiquantitatively demonstrated for the perrierite in MA19.
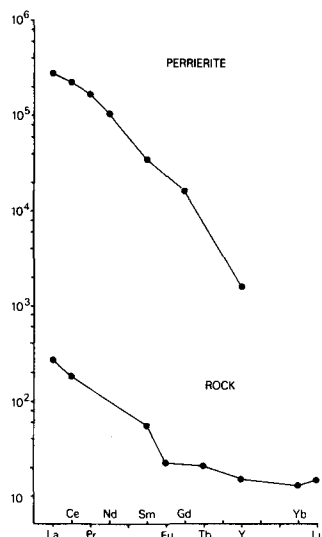

FIG. 1. Average chondrite-normalized abundances of *REE* and Y in the perrierite and in perrierite-bearing lavas (INAA data; van Bergen, in prep.). Note that Y is plotted in the place of Ho, and that the microprobe analyses of the mineral did not include Eu.

analyses of perrierite and chevkinite in the literature also indicate a strong preference for the light REE. Possible anomalies of Eu are not apparent because of difficulties in the determination of this element by the methods used.

Several chemical characteristics of the perrierite reflect those of the Mt Amiata lavas. Whole-rock trace element abundances (e.g. Ferrara et al., 1975 and 1976; Van Bergen et al., 1983; Van Bergen, in prep.) indicate very high contents of Th (37–45 ppm) and strong enrichment in the light REE, although the $(Ce/Y)_{ch}$ ratio of 12 is considerably lower than that of the perrierite. La, Ce, and Zr abundances in the glasses (c. 73 wt. % SiO_2) were reported by Ferrara et al. (1976) which allows calculation of perrierite–glass partition coefficients for these elements. Because only averaged compositions obtained from different samples can be used, these coefficients (Table III) are tentative, but

TABLE III. *Abundances of La, Ce, and Zr in perrierite and co-existing glass, and calculated partition coefficients*

	Perrierite* (%)	Glass† (ppm)	Partition coefficient
La	8.18	93	880
Ce	17.13	162	1057
Zr	0.56	149	38

* Mean values of MA1 and MA19.

† Mean values of four XRF-analyses of glasses separated from samples taken from the same lavas as MA1 and MA19 (Ferrara et al., 1976).

the chemical uniformity of the early rhyodacites should give a good approximation. The expected high coefficients emphasize the importance of perrierite in controlling the distribution of many trace elements in the lavas of Mt Amiata. This is also illustrated by the large proportions of total whole-rock abundances that the mineral contains, taking an assumed modal amount of only 0.05%: La—49%, Ce—59%, Sm—30%, Th—28%. Nevertheless, the REE pattern of perrierite is unlike that of the rhyodacite, even disregarding the significant negative Eu anomaly in the latter (fig. 1). This implies that other phases substantially contribute to the REE characteristics of the rock. Apatite and zircon are the most likely candidates in addition to the glass, but due to the relatively low levels of REE in these minerals this could only be qualitatively confirmed in the case of apatite.

Several authors have drawn attention to the role that accessory minerals such as apatite, allanite, zircon, sphene, and monazite may play in the evolution of felsic igneous rocks (e.g. Gromet and Silver, 1983), indicating the necessity to include these minerals in petrogenetic models, particularly those involving fractionation of the REE. Because perrierite and chevkinite have been recorded from various types of such rocks, and given the fact that trace amounts can be easily overlooked or misidentified, these minerals may be more common and thus petrologically more important than is generally realized. It is possible, for example, that perrierite and/or chevkinite may be present in other occurrences of the Tuscan Magmatic Province.

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Vening Meinesz Laboratory, Dept. of Geochemistry,
Institute of Earth Sciences, State University of Utrecht,
Budapestlaan 4, 3584 CD Utrecht, The Netherlands

MANFRED J. VAN BERGEN

A low-zinc chalcophanite from Norseman, Western Australia

DURING a recent investigation of Australian specimens of manganese oxide desert varnish the writer noted a specimen of chalcophanite which was deficient in zinc when compared with other specimens previously analysed. This note briefly describes the specimen and discusses its significance.

The specimen consisted of a black encrustation on lateritic clay coating a weathered basic rock, from the gold mining centre of Norseman, Western Australia. An examination of the crust by scanning electron microscopy revealed a mass of randomly arranged hexagonal crystallites, not unlike those of well-crystallized kaolinite. X-ray energy dispersive
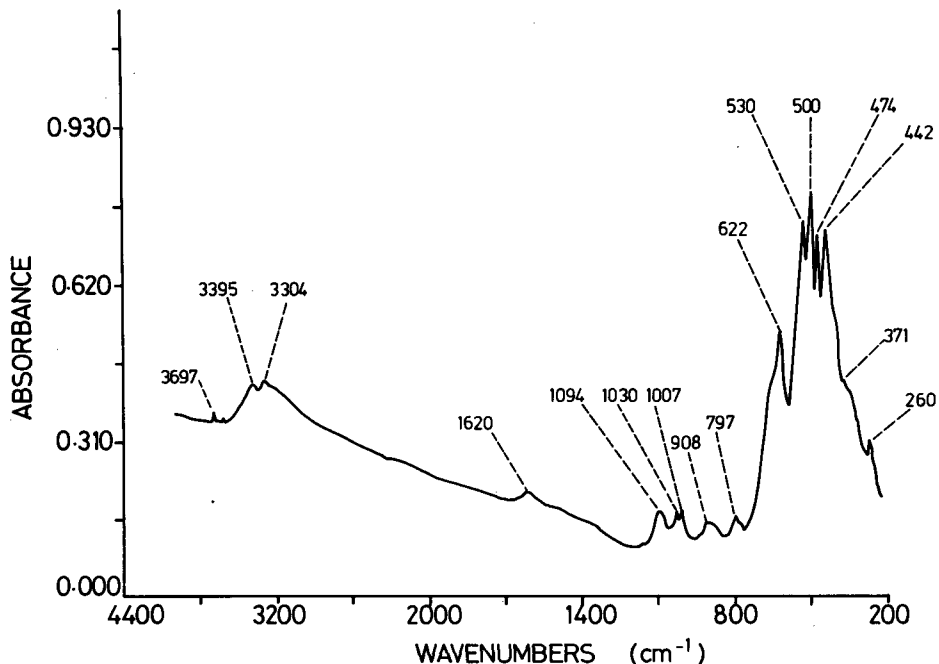

FIG. 1. Infra-red spectrum of chalcophanite and kaolinite from Norseman, Western Australia.