*The Canadian Mineralogist*
Vol. 41, pp. 1255-1270 (2003)

# THE MELILITE ($Gh_{50}$) SKARNS OF ORAVIŢA, BANAT, ROMANIA: TRANSITION TO GEHLENITE ($Gh_{85}$) AND TO VESUVIANITE

Ildiko KATONA

*Laboratoire de Pétrologie, Modélisation des Matériaux et Processus, Université Pierre et Marie Curie,*
*4, Place Jussieu, F-75252 Paris, Cedex 05, France*

Marie-Lola PASCAL[§]

*CNRS–ISTO* (*Institut des Sciences de la Terre d'Orléans*), *1A, rue de la Férollerie, F-45071 Orléans, Cedex 02, France*

Michel FONTEILLES

*Laboratoire de Pétrologie, Modélisation des Matériaux et Processus, Université Pierre et Marie Curie,*
*4, Place Jussieu, F-75252 Paris, Cedex 05, France*

Jean VERKAEREN

*Unité de Géologie, Université Catholique de Louvain-la-Neuve, Bâtiment Mercator,*
*3, Place Louis Pasteur, Louvain-la-Neuve, Belgium*

## ABSTRACT

Almost monomineralic Mg-rich gehlenite (~$Gh_{50}Ak_{46}Na\text{-}mel_4$) skarns occur in a very restricted area along the contact of a diorite intrusion at Oraviţa, Banat, in Romania, elsewhere characterized by more typical vesuvianite–garnet skarns. In the vein-like body of apparently unaltered gehlenite, the textural relations of the associated minerals (interstitial granditic garnet and, locally, monticellite, rare cases of exsolution of magnetite in the core zone of melilite grains) suggest that the original composition of the gehlenite may have been different, richer in Si, Mg, Fe (and perhaps Na), in accordance with the fact that skarns are the only terrestrial type of occurrence of gehlenite-dominant melilite. The same minerals, monticellite and a granditic garnet, appear in the retrograde evolution of the Mg-rich gehlenite toward compositions richer in Al, the successive stages of which are clearly displayed, along with the final transformation to vesuvianite. These changes include (1) the local development of small rounded patches with Al-rich compositions ($Gh_{60}$ to $Gh_{85}$), accompanied by monticellite, spurrite (or tilleyite, afwillite, kilchoanite) and, at a later stage, a granditic garnet, and (2) the complete transformation of gehlenite to vesuvianite, associated with minor clintonite (+ monticellite and probably ellestadite), usually along a sharp front typically rimmed by a 0.5-mm-wide zone of Al-rich gehlenite ($Gh_{85}$). The gehlenite rim, as well as the gehlenite in the local modifications, show a remarkable correlation between the åkermanite and Na-melilite contents, probably of crystal-chemical origin. The local modifications (1) are interpreted as nearly closed-system (except for Na and Fe) retrograde reactions at moderate temperature (500–600°C), controlled by the localized presence of small amounts of fluid at low pressure, mainly involving the transformation of the åkermanite component to monticellite. The silica released by this transformation resulted in the formation of spurrite (among others) and of the Na-melilite component at first, and garnet later. The subsequent transformation (2) of gehlenite to vesuvianite and clintonite, which involved silica metasomatism, may result from the more pervasive infiltration of the same fluid, at higher pressure, probably related to the development of the garnet–vesuvianite skarns elsewhere along the intrusive contacts.

*Keywords*: skarns, melilite, gehlenite, monticellite, clintonite, Oraviţa, Romania.

## SOMMAIRE

Les skarns développés au contact de l'intrusion dioritique d'Oraviţa, Banat, en Roumanie, sont en majeure partie constitués de vésuvianite et grenat, sauf sur une portion très limitée du contact, où ils sont formés de gehlenite massive, de composition ~$Gh_{50}Ak_{46}Na\text{-}mel_4$. Les autres minéraux, très subordonnés, ont avec la gehlenite des relations texturales qui suggèrent un développement secondaire: grenat calcique et, localement, monticellite interstitiels, exceptionnellement magnétite en lamelles d'exsolution dans le coeur de cristaux de gehlenite. En accord avec le fait que les skarns sont le seul type d'occurrence terrestre

---

[§] *E-mail address*: mlpascal@cnrs-orlreans.fr

de ce minéral, la gehlenite observée pourrait dériver d'une mélilite de composition différente, plus riche en Fe, Mg, Si (et probablement Na). Monticellite et grenat sont aussi les principaux minéraux produits par l'évolution rétrograde de la gehlenite magnésienne vers des compositions proches du pôle alumineux, dont les étapes (ainsi que la transformation finale de la gehlenite en vésuvianite) sont clairement exprimées. Elles comportent (1) le développement local de taches de composition $Gh_{60}$ à $Gh_{85}$ dans lesquelles apparaissent la monticellite et la spurrite (ou kilchoanite, tilleyite, afwillite) et, à un stade ultérieur, le grenat calcique. (2) La transformation complète de la gehlenite en vésuvianite associée à de la clintonite, le long d'un front métasomatique bordé par une frange de 0.5 mm de gehlenite $Gh_{85}$ accompagnée de monticellite et probablement ellestadite. La gehlenite alumineuse, dans les modifications locales comme dans la frange bordant la vésuvianite métasomatique, présente une remarquable corrélation entre les teneurs en åkermanite et Na-mélilite, probablement d'origine cristallochimique. Les modifications locales (1) sont interprétées comme une évolution rétrograde à température modérée (500–600°C) ne mobilisant que Na et Fe, sous l'effet de la présence localisée de fluides sous faible pression, dans laquelle le constituant åkermanite se décompose en monticellite, tandis que la silice produite par cette transformation apparaît sous forme de spurrite (ou tilleyite, *etc.*) et de composant Na-mélilite d'abord, de grenat ensuite. La transformation (2) implique un apport de silice et une pression fluide plus élevée que dans les modifications locales, et peut s'interpréter par une infiltration plus généralisée des mêmes fluides, probablement responsables du développement des skarns à vésuvianite–grenat ailleurs le long des contacts intrusifs.

*Mots-clés*: skarns, mélilite, gehlenite, monticellite, clintonite, Oraviţa, Roumanie.

## INTRODUCTION

Gehlenitic melilite is a rare mineral in terrestrial rocks; the gehlenite component [Gh, $Ca_2Al(AlSi)O_7$] only exceptionally exceeds 80 mol.% (Sabine *et al.* 1982). It is only found in high-temperature skarns and calcareous rocks affected by high-grade contact metamorphism (Nicholls 1971, Reverdatto *et al.* 1979), which also may contain melilite rich in the åkermanite end-member [Ak, $Ca_2MgSi_2O_7$] (Jamtveit *et al.* 1997, Owens 2000). According to the analytical data available, melilite from these types of occurrence is typically Na-poor, in contrast with the compositional range of magmatic melilite (Deer *et al.* 1986).

In the classic occurrence at Crestmore, California, where gehlenite belongs to complex mineral associations, Burnham (1959) and Wiechmann (1995) emphasized its metasomatic origin. A metasomatic origin is still clearer in the case of skarns developped at the expense of Mg- and Al-free limestones, and mainly consisting of Ca–Si minerals (wollastonite, spurrite, tilleyite, larnite), such as Scawt Hill (Tilley 1929, Tilley & Harwood 1931) and Carneal, Ireland (Sabine 1975, Sabine *et al.* 1982), Kushiro, Japan (Numano 1978, 1979), and Magureaua Vatei, Romania (Stefan *et al.* 1978, Pascal *et al.* 2001). In the latter occurrence, gehlenitic melilite forms massive, almost monomineralic bodies in exoskarns, in contact with or very close to typical endoskarns. Owing to their vein-like relations to their chemically contrasting host-rock, Al-free exoskarn, such Al-rich and Si-poor rocks are unlikely to have replaced calcite, and a genetic process by direct precipitation from the exoskarn-forming fluid seems most unlikely. Rather, they may be considered to result from the metasomatic modification of a protolith other than calcite marble. Among possible protoliths, it is reasonable to consider the magmatic rock closest to the gehlenite-bearing skarns where it can be observed, *i.e.,* where it has not been subsequently modified (changed to endoskarns). One such case is that of dolerite contacts at Scawt Hill, where a melilite also occurs, with a different, Na- and Fe-rich composition, in direct contact with the exoskarns, as the main constituent mineral of rocks interpreted to be the ultimate product of limestone assimilation by the silicate melt (Tilley & Harwood 1931). It seems reasonable to ask whether the gehlenite at Scawt Hill could be metasomatically derived from such melilite rocks of igneous origin.

Such a hypothesis may be investigated by observations of compositional changes in gehlenite, in response to retrograde reactions, from a comparatively Mg-rich composition ($Gh_{50}$) to nearly pure gehlenite ($Gh_{85–90}$), in the high-temperature skarns of the Romanian Carpathians. In fact, a few small relict crystals of Na- and Mg-rich melilite, in the compositional range of magmatic melilite, have been found recently in one of these occurrences (Pascal *et al.*, in prep.).

These retrograde reactions were briefly described in the two occurrences of the Apuseni Mountains (Pascal *et al.* 2001). The focus of the present study is a third occurrence of gehlenite, located at Oraviţa (Banat). Gehlenite was first found at Oraviţa in 1874 by Janovsky as "rolled pebbles enclosing grains of vesuvianite" (Dana 1915, who quoted results of two chemical analyses corresponding to a composition ~$Gh_{60}$). Constantinescu *et al.* (1988) reported the discovery of gehlenite in the Crisenilor ravine at Oraviţa, but provided only a very cursory description of the rock, and no new compositional data. The interest of this occurrence, compared to those of the Apuseni Mountains, lies in differences in the composition and texture of the apparently untransformed Mg-rich gehlenite and in the products of its retrograde reaction, which include (i) a larger grain-size of the minerals, allowing for more accurate analytical results and a much more detailed discussion of their chemical evolution, and (ii) a clearer (and different) process of transformation of gehlenite into vesuvianite and clintonite. If these retrograde reactions involved bulk chemical changes, they may provide an indication of earlier metasomatic processes suspected to have produced the Mg-rich gehlenite.

## GEOLOGICAL SETTING

The skarns of Oraviţa are developed at the expense of Cretaceous limestones and marls of the Crivina Formation, folded in a system of N–S-trending anticlines and synclines, belonging to the Resita anticlinorium in the Getic nappe. In the area of Oraviţa and Ciclova, this series is intruded by a small elongate (2 × 7 km) body of Miocene diorite, with some variations toward quartz diorite and monzonite. Large parts of its roof are still preserved. Some minor bodies of pegmatite, metric to decametric in scale, occur at a few places at the contacts. On the Oraviţa 1/50 000 geological map (Institutul de Geologie si Geofizica 1975), the gehlenite location, on the western side of Crisenilor gully, a few meters from the bottom, is simply labeled "hornfelses and marbles". The Crivina Formation near the intrusion includes one sequence of fine-grained marls interbedded in a series of limestones with thin argillaceous intercalations. In the metamorphic halo, the mineralogy of the former marls on the eastern flank of the Crisenilor gully consists of a fine-grained association of calcic plagioclase and clinopyroxene, with minor titanite, and typically without remaining calcite. Almost no skarn was found in these units, in agreement with the fact that their mineralogy is not essentially different from that of the diorite. At the contact with one pegmatite, fine-grained granditic garnet appears in these plagioclase–clinopyroxene hornfelses, leading up to the complete replacement of the plagioclase, but the texture remains that of a hornfels, never changing to that of a coarse-grained skarn.

West of a rather clear limit (Fig. 1), no calcic hornfels was observed, and the calc-silicate rocks are coarse-grained skarns, composed in most places of vesuvianite ± granditic garnet, more rarely of gehlenite, which may contain some wollastonite and, more commonly, calcite. Where the protolith can be observed in contact with such skarns, as on the footpath at the west and on the top of the exposures of melilite rock, it is calcite marble with minor Si- and Al-rich beds. The gehlenite skarns are known only in a 22 × 11 m area, limited to the north and south by other types of skarns. To the west, they disappear by erosion, and to the east, they are covered by overlying inner endoskarns or the igneous rock. Within this area, the gehlenite skarns typically occur together with igneous rocks and vesuvianite–garnet skarns, which suggests that they are not thick but outcrop along a structural surface (Fig. 1), owing to their resistance to weathering, as observed in occurrences in the Apuseni Mountains.

In Figure 1, the intrusive mass in the Crisenilor gully is not connected at the outcrop level with the larger mass located to the west, in agreement with the map by Ilinca *et al.* (1993). The gehlenite rocks occur within a band of rocks, ~70 m wide, that includes alternating skarns (mainly endoskarns) and igneous rocks of different kinds (including various types of pegmatites), which extends in the direction N50E. This band differs from the other more homogeneous parts of the intrusion. Brecciation of the skarns has been observed in the samples collected along part of the road from Mare Lake to the Rândunicii ravine, suggesting the existence of a fracture along this road. Among possible interpretations, our suggestion is that the intrusive rocks along the N50E heterogeneous band could represent a different stage of the intrusion, with the gehlenite skarns possibly developed as roof pendants, as in the case described by Jamtveit *et al.* (1997).

## MINERALOGY AND PETROLOGY OF THE GEHLENITE-BEARING ROCKS

For simplicity, in the forthcoming descriptions, the unaltered Mg-rich melilite-group mineral will be called melilite, and the name gehlenite will be restricted to the modified compositions richer in Al. Mineral compositions (about 400 analyses of melilite-group minerals, 100 of other minerals) were determined using Cameca Camebax and SX50 electron microprobes. As standards, we used well-characterized natural minerals (diopside, andradite, orthoclase, albite, fluorite) and synthetic oxides ($MnTiO_3$, $Cr_2O_3$, NiO, ZnS). Operating conditions were: 15 kV acceleration voltage and a beam current of 40 nA for garnet, pyroxene and monticellite. For light-element-bearing minerals (melilite, vesuvianite and micas), we used a beam current of 10 nA.

### *Unaltered melilite skarns*

*Zonation and textures.* In the zoned skarns of the Apuseni Mountains, the melilite-bearing area is comparatively narrow (~15 cm at Cornet Hill and ~ 1 m in the Upper Cerboaia Valley), and apparently continuous, at least in the restricted regions where the contacts could be observed. The area contains two melilite-bearing zones. One, a probable vein in the exoskarn very close to the former intrusive contact, consists of massive coarse-grained melilite (with quite variable grain-size), with a strong tendency to idiomorphism. The exoskarn in contact with the vein is composed of large crystals of wollastonite that leave interstitial spaces typically occupied by aggregates of melilite crystals; spurrite or tilleyite may occur instead of, or associated with, this wollastonite. The second zone, on the endoskarn side, is essentially made of a medium- to fine-grained association of melilite and wollastonite, interpreted as endoskarn because wollastonite displays the same typical texture in parallel fibers, although somewhat coarser-grained, as in the adjacent grossular–wollastonite endoskarns.

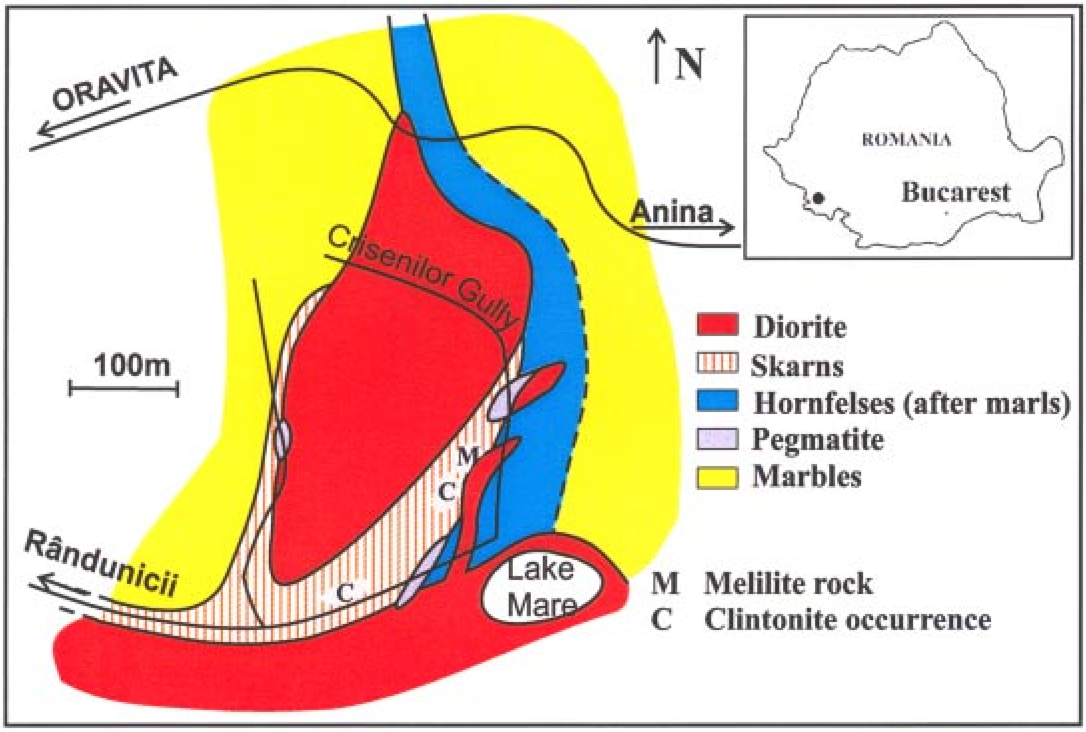
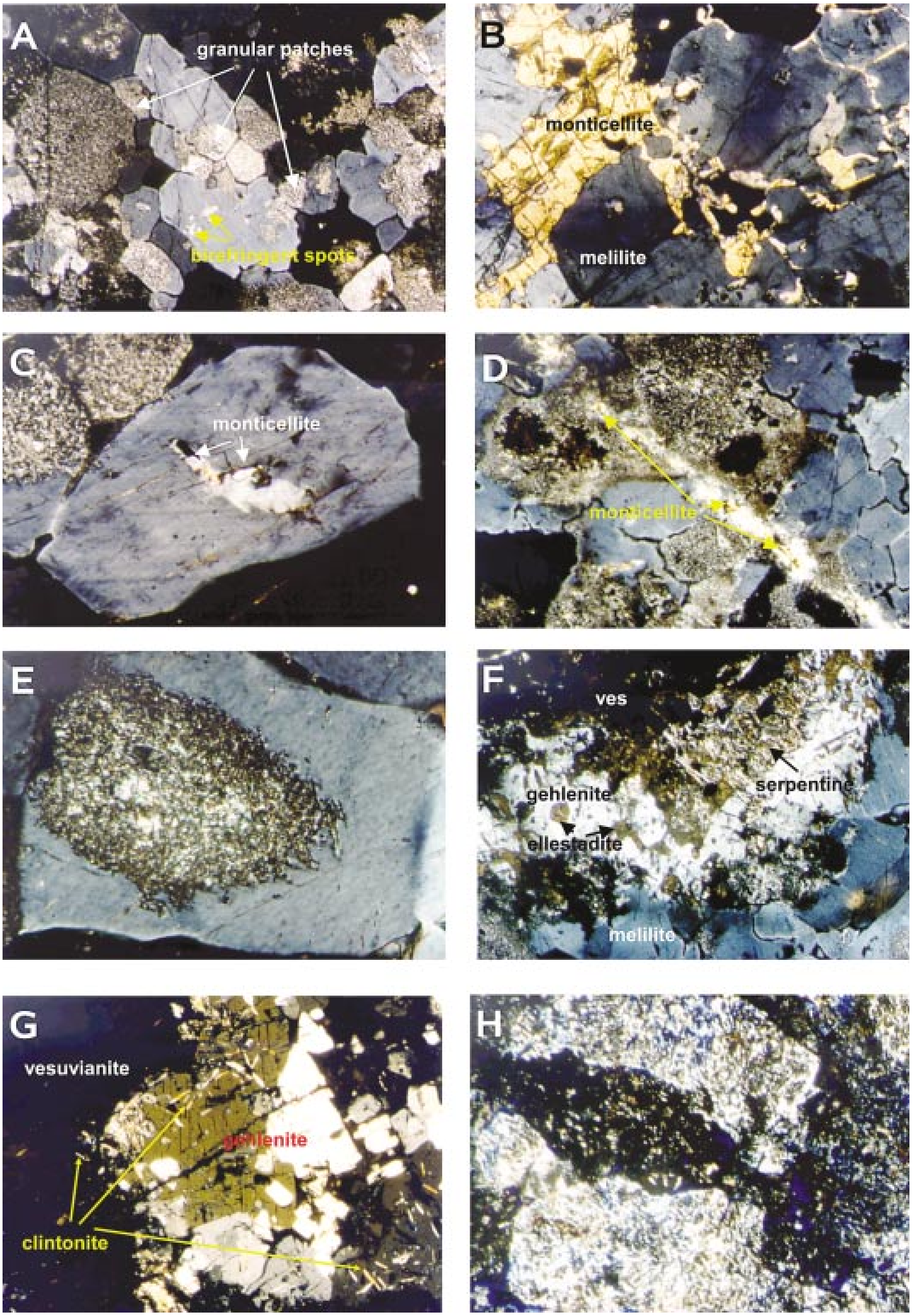


FIG. 1. Geological relationships in the skarn area at Oraviţa, Romania.

In contrast, at Oraviţa, no analogue of such melilite – fibrous wollastonite endoskarn has yet been found, and only slight zonation has been observed in the melilite skarns and related rocks (as may be expected if, as suggested above, the exposure is a structural surface). We found (i) a fibrous wollastonite – grossular endoskarn zone, and probably a vesuvianite zone, between the diorite and the melilite rock, (ii) on the other side of the melilite skarns, coarse-grained aggregates of wollastonite crystals included in the massive coarse-grained melilite, but also containing fine-grained cross-cutting veinlets of (earlier stage?) idiomorphic melilite, a texture typical of the exoskarn side of the melilite veins in the Apuseni Mountains. In one sample (OC 44), an appreciable amount of interstitial wollastonite occurs in very large elongate poikilitic patches, much resembling recrystallized wollastonite observed at the contact between the two melilite zones in the Upper Cerboaia Valley (Fig. 8A in Pascal *et al.* 2001). The melilite vein is characterized by a uniform grain-size, the grains being 0.5 mm on average and ranging from 0.2 to 2 mm (Fig. 2A). The grains show a moderate tendency to idiomorphism, and, where zoned, the zoning defines an idiomorphic outline without any sharp boundary between zones.

FIG. 2. Photomicrographs (crossed nicols). A. Typical melilite-bearing rock with local modifications of melilite, expressed by birefringent spots and granular patches. B. Monticellite interstitial between unaltered melilite crystals. C**.** Monticellite-bearing birefringent spot in melilite. D. Monticellite developed along a fracture, surrounded by gehlenite. Three brown patches of vesuvianite appear in the large granular patch, near the fracture. E. Granular patch: monticellite (bright), gehlenite (light grey) and granditic garnet. F. Gehlenite rim ($Gh_{85}$) between vesuvianite (top) and unaltered melilite (bottom). The mineral labeled "ellestadite" is altered to thaumasite. G. Front between vesuvianite (right) and gehlenite (left). Note the lamellae of clintonite included mainly in the gehlenite crystals. H. Melilite crystals affected by the granular modification (monticellite is yellow, gehlenite is white), and partly transformed to blue, strongly dispersive low-birefringence vesuvianite. The common extinction of gehlenite and 'homoaxial' vesuvianite is visible in the central crystal, which is similar to the crystals above and below but in extinct orientation. The bright spots in this crystal are monticellite granules. Width of field of view is 2.7 mm in A, B, D, F, G and H, and 0.72 mm in C and E.


A
granular patches
birefringent spots
B
monticellite
melilite
C
monticellite
D
monticellite
E
F
ves
serpentine
gehlenite
ellestadite
melilite
G
vesuvianite
gehlenite
clintonite
H

*Mineralogy of the melilite vein. Magnetite* occurs at a few places in the melilite veins in the Apuseni Mountains, as regularly distributed "exsolution-induced" lamellae in the cores of the melilite crystals, not accompanied by a visible modification of the host melilite (Pascal *et al.* 2001). Such lamellae are commonly replaced by small rectangular inclusions of *granditic garnet* with the same pattern. In the Oraviţa occurrence, similar inclusions of granditic garnet in melilite also exist, but magnetite has only been observed in one sample, as sparse, very small crystals. Granditic garnet also occurs at every place as spines, *i.e.,* thin interstitial veinlets between the melilite crystals. Both textural types of garnet are preserved without any visible change through the subsequent modifications of the melilite described below.

Two samples (OC 103 and OC 106) contain large skeletal crystals (up to 2 mm) of ferroan *monticellite*, and some associated *ellestadite* developed along the grain boundaries between the fresh melilite crystals (Fig. 2B). Where monticellite is absent, garnet spines appear in the same position.

The only opaque mineral general present, in addition to magnetite, albeit in small quantities, is *pyrrhotite* (exceptionally containing a little Ni). It occurs as small euhedral crystals, occasionally enclosed in melilite. They are not accompanied by any alteration of the primary silicates of the skarn. Pyrrhotite is known at Cornet Hill in the same situation, but is comparatively scanty.

*Perovskite*, which occurs in the melilite veins of the Apuseni Mountains, has never been observed in the melilite skarns at Oraviţa. Moreover, no Ti mineral was observed at Oraviţa in the endoskarns at the boundary with the diorite, whereas titanite within a few mm of the contact in the Apuseni Mountains is typically transformed into pseudomorphic aggregates of perovskite crystals.

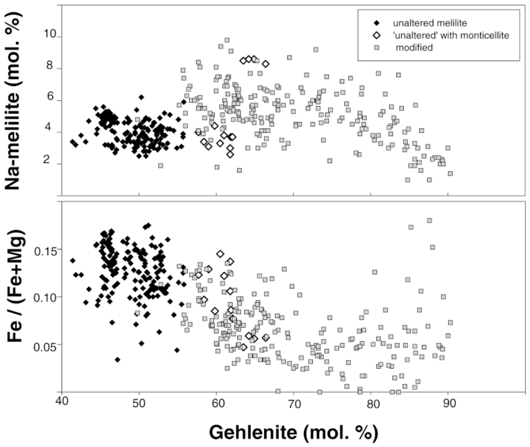


FIG. 3. Compositions of "unaltered" and modified melilite in skarns from Oraviţa.

The compositions of melilite are expressed here using the molar percentage of the gehlenite (Gh) and Na-melilite (Na-mel) end-members, and the atomic ratio Fe/(Fe + Mg) (Fig 3). The unaltered melilite at Oraviţa is in the range $Gh_{40–56}Na\text{-}mel_{2.5–5.8}$, except for grains in the skeletal monticellite-bearing samples, which have a compositional range ($Gh_{58–62}Na\text{-}mel_{2.6–4.2}$) in sample OC106 and ($Gh_{64–66}Na\text{-}mel_{8.1–8.6}$) in sample OC103, closer to that of the Apuseni melilite ($Gh_{55–70}Na\text{-}mel_{2.5–8}$). The Fe/(Fe + Mg) value in all crystals of unaltered melilite (Oraviţa and Apuseni Mountains) is in the range 0.05–0.18 (0.12 on average), with few values below 0.07.

### *Local modifications of melilite*

In many samples, coarse-grained melilite underwent local modifications of variable extent, which typically appear unrelated to original shapes of grains. These local modifications, preserving the texture of the original melilite rock as a whole (Fig. 2A), are observed almost everywhere (although rarely at Cornet Hill). We recognize two morphological types of modifications, the birefringent spots and the granular patches.

The *birefringent spots* consist of small patches, about 100 μm in diameter, of higher birefringence in the melilite grains. The compositions of melilite in such spots (Figs. 4, 5) show a sharp change to higher Gh contents (from ~50 to 60–70) and Na-mel contents (from 3–4 to 6–8), with differences from one sample to the other. Where the plane of the section is favorable, small grains of monticellite are observed in the spot (Fig. 2C , Table 1). In some cases, the spots as well as the monticellite grains are conspicuously distributed along a loose network of thin fractures (Fig. 2D). In a few spots, tiny crystals of either spurrite, kilchoanite (no structural data are available, but the polymorph rankinite is only stable at high temperature) or cuspidine (Cornet Hill) are observed, as well as idiomorphic pyrrhotite.

The *granular patches* are larger round patches characterized by a granular texture under the microscope (Figs. 2A, E). In many cases, these patches appear to cut across the earlier birefringent spots. In a few samples, they occur locally distributed along narrow fractures. Again, the dominant mineral in these patches is gehlenite, in crystallographic continuity with the enclosing melilite grain and showing a sharp increase in Gh content (up to 85%) and a strong decrease in the Fe/(Fe + Mg) value (Table 1, Fig. 5). For Gh contents of up to 75–80%, the Na-mel content is scattered but distinctly above the Na content of the original melilite, and slightly above that of the birefringent spots of similar Gh content.

The gehlenite has a spongy texture and includes more or less regularly distributed small grains of *monticellite*, *granditic garnet* (with a somewhat variable composition, commonly *ca.* $Grs_{50}$, Table 1) and, at least in some cases, other various calcium silicates (with Ca:Si > 1), commonly containing volatile constituents ($H_2O$, F or $CO_2$). *Spurrite*, alone or accompanied by *afwillite*, is common at Oraviţa, typically as single grains. These grains are larger than those of monticellite, invariably located near the center of the patch, roundish and occasionally ragged in outline. *Tilleyite* occurs in the same way, also accompanied by afwillite. Granditic garnet and, to a lesser degree, monticellite tend to be concentrated in larger patches or veinlets in the center of the granular patches.

In one sample (OC44), coarse-grained granular regions also contain *vesuvianite* as grains or small patches (Table 1). Vesuvianite has the same grain-size as the other minerals of the patches (gehlenite, monticellite and granditic garnet), and the textural relations between these minerals suggest equilibrium. This sample also includes the large crystals of sponge-like wollastonite noted above, with a distribution completely independent of the development of the granular patches, indicating that the wollastonite is inherited from a former stage. Neither wollastonite nor any Ca–Si–OH mineral was observed inside the patches, and the gehlenite is more Gh-rich (up to 90%) than in other samples.

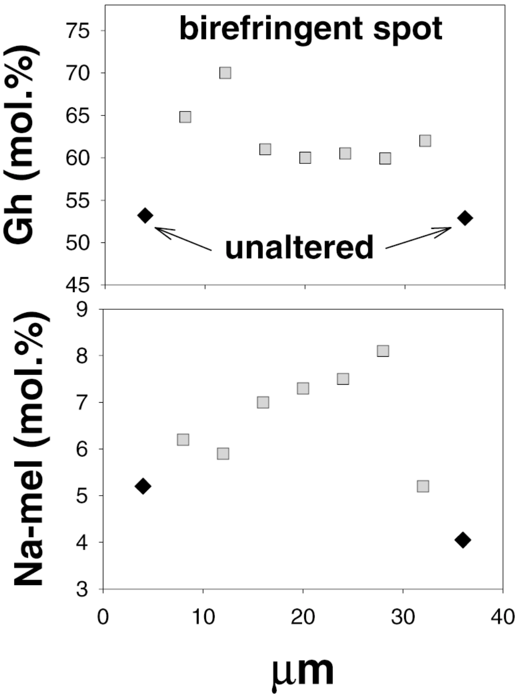


FIG. 4. Compositional profile of a birefringent spot (sample OC86), showing the enrichment in Na-mel and Gh components in the spot.

## *Breakdown of melilite*

In some samples other than OC44, vesuvianite appears in granular patches as irregular crystals (Fig. 2D). (In addition, unidentified phyllosilicates and hydroxides appear everywhere in the vesuvianite patches and along their boundaries, a phenomenon also observed in sample OC44). Therefore, the local modifications just described may correspond to the incipient stage of a process in which melilite is metasomatically replaced by vesuvianite.

*Metasomatic development of vesuvianite* (*or granditic garnet*). The changes from melilite to vesuvianite usually occur across sharp fronts. In the absence of local modifications, vesuvianite is separated from unaltered melilite by a rim of highly birefringent gehlenite in crystallographic continuity with the surrounding crystals of melilite (Fig. 2F). Two compositional profiles through such a rim of gehlenite around vesuvianite were obtained (Fig. 6). They show the sharp boundary between the unaltered melilite $Gh_{51}$ and the gehlenite rim, of more variable composition, $Gh_{72–87}$, in contact with vesuvianite. Near the rim, the apparently unaltered melilite shows over 60 µm a progressive increase in Na-mel content, from 5 to 7.5%.

The gehlenite zone locally contains radiating slender idiomorphic crystals of *ellestadite*, irregularly dispersed, but occurring mainly near the boundary with the

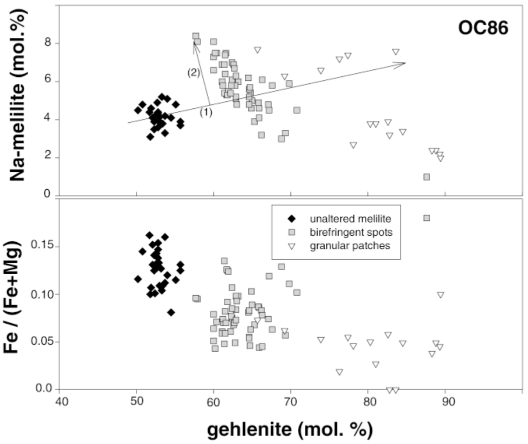


FIG. 5. Composition of gehlenite in the birefringent spots and granular patches in sample OC86. A. The increase in Na-mel and Gh contents in the birefringent spots cannot be explained only by the crystallization of monticellite, which would displace the composition of melilite along arrow (1) (constant Na:Mg ratio). A correlative transformation of part of the Gh component to Na-mel [arrow (2)] accounts for the negative correlations between Gh and Na-mel contents. B. Decrease in Fe/(Fe + Mg) in modified gehlenite up to $Gh_{85}$, then increase for $Gh_{>85}$.

TABLE 1. SELECTED MINERAL COMPOSITIONS FROM SKARNS OF ORAVIŢA, ROMANIA

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ wt.% | 33.76 | 30.82 | 31.38 | 25.00 | 24.37 | 24.77 | 37.33 | 27.44 | 37.80 | 36.23 | 35.55 | 15.69 |
| $TiO_2$ | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 | 0.00 | 0.01 | 0.00 | 0.06 | 0.00 | 0.14 | 0.00 |
| $Al_2O_3$ | 17.69 | 22.05 | 24.84 | 31.72 | 32.15 | 31.19 | 0.01 | 0.00 | 10.36 | 16.60 | 14.60 | 46.13 |
| $Cr_2O_3$ | | | | | | | 0.09 | | 0.07 | 0.00 | 0.00 | 0.00 |
| FeO | 1.88 | 0.89 | 0.19 | 0.02 | 0.59 | 0.24 | 4.01 | 0.02 | 15.41 | 3.71 | 5.87 | 1.06 |
| MnO | 0.04 | 0.04 | | 0.00 | 0.00 | 0.00 | 0.43 | 0.00 | 0.14 | 0.10 | 0.08 | 0.00 |
| MgO | 6.46 | 4.90 | 4.11 | 1.72 | 1.57 | 1.94 | 21.88 | 0.00 | 0.22 | 3.13 | 3.16 | 19.00 |
| CaO | 40.41 | 39.88 | 39.53 | 40.21 | 40.53 | 40.84 | 35.42 | 62.43 | 35.16 | 35.79 | 35.32 | 13.21 |
| $Na_2O$ | 0.36 | 0.43 | 1.12 | 0.26 | 0.21 | 0.20 | 0.00 | 0.08 | | 0.02 | 0.03 | 0.02 |
| $K_2O$ | 0.00 | 0.04 | | 0.00 | 0.02 | 0.00 | 0.00 | | | 0.02 | 0.00 | 0.00 |
| F | | | | | | | | | | 0.07 | 0.00 | 0.21 |
| Cl | | | | | | | | | | 0.02 | 0.02 | 0.00 |
| $H_2O$ calc. | | | | | | | | | | 1.75 | 1.80 | 4.16 |
| Total | 100.60 | 99.05 | 101.18 | 99.00 | 99.44 | 99.18 | 99.18 | 89.97 | 99.22 | 97.40 | 96.56 | 99.39 |
| Si *apfu* | 1.52 | 1.42 | 1.41 | 1.15 | 1.12 | 1.14 | 1.67 | 2.03 | 2.99 | 17.74 | 17.68 | 1.10 |
| Ti | | | | 0.00 | | | | | 0.00 | | 0.05 | |
| Al | 0.97 | 1.20 | 1.31 | 1.72 | 1.74 | 1.69 | 0.00 | | 0.97 | 9.57 | 8.56 | 3.82 |
| Cr | | | | | | | 0.00 | | 0.00 | 0.00 | 0.00 | 0.00 |
| Fe | 0.07 | 0.03 | 0.01 | 0.00 | 0.02 | 0.01 | 0.15 | 0.00 | 1.02 | 1.52 | 2.44 | 0.06 |
| Mn | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | | 0.01 | 0.04 | 0.03 | 0.00 |
| Mg | 0.43 | 0.34 | 0.28 | 0.12 | 0.11 | 0.13 | 1.47 | | 0.03 | 2.31 | 2.36 | 2.01 |
| Ca | 1.97 | 1.97 | 1.90 | 1.99 | 1.99 | 2.01 | 1.70 | 4.96 | 2.98 | 18.80 | 18.85 | 1.00 |
| Na | 0.03 | 0.04 | 0.10 | 0.02 | 0.02 | 0.02 | 0.00 | 0.01 | | 0.01 | 0.03 | 0.00 |
| K | | 0.00 | | | 0.00 | | | | | 0.01 | | |
| F | | | | | | | | | | 0.10 | | 0.05 |
| Cl | | | | | | | | | | 0.02 | 0.02 | |
| OH | | | | | | | | | | 5.73 | 5.99 | 1.95 |

The electron-microprobe data pertain to the following samples. (1) Unaltered melilite. The structural formula is calculated on the basis of five cations, and cation proportions are expressed in atoms per formula unit, *apfu* (OC48, #27/33). (2) Gehlenite in birefringent spot (OC44, #28/55). (3) Sodian gehlenite in granular patch (OC104, #35/40). (4) Fe-poor gehlenite in granular patch (OC50, #30/18). (5) Fe-rich gehlenite in granular patch (OC104, #6/18). (6) Gehlenite rim on vesuvianite (OC50, #30-39). (7) Monticellite, structural formula calculated for three cations (OC104, #6/25). (8) Spurrite, structural formula calculated for seven cations (OC86, #35/114). (9) Granditic garnet in granular patch. Structural formula calculated for eight cations (OC50, #29/17). (10) Vesuvianite in veins. Structural formula calculated for 50 cations and 78 (O,OH,F,Cl) (OC104, #8/36). (11) Vesuvianite homoaxial on gehlenite (OC104, #8/7). (12) Clintonite, structural formula calculated for eight cations (OC104, #8/57).

unmodified melilite, and almost wholly replaced by *thaumasite*. Rare *scawtite* also occurs in a similar fashion at the vesuvianite–gehlenite front. This mineral is also typical of the vesuvianite stage in the Apuseni Mountains, where it appears as the product of a low-temperature transformation of tilleyite. The gehlenite zone also contains *monticellite* grains, in many cases replaced by a serpentine-group mineral; larger crystals of monticellite are preserved, even in the vesuvianite zone.

*Clintonite* occurs as thin (typically <3 μm) grains oriented across and perpendicular to the vesuvianite–gehlenite contact. They also occur in the gehlenite close to the contact, and in the vesuvianite (Figs. 2G).

In the melilite ahead of the large-scale vesuvianite front, smaller (~5 mm) similar zoned systems occur in probable relation with small fractures. Still further from the front, such small zoned systems may contain granditic garnet instead of vesuvianite, with the same relations to accompanying minerals.

*Epitactic-like replacement of gehlenite by "homoaxial" vesuvianite.* In sample OC104, melilite is almost entirely affected by the granular modification, with the usual association of minerals, but the gehlenite compositions are richer in Na than in other samples (up to $Na\text{-}mel_{10}$, Fig. 7, Table 1). Veinlets of idiomorphic crystals of vesuvianite occur as axes of low-birefringence patches consisting of fine-grained serpentine, chlorite, thomsonite and hydrogrossular [$\sim Ca_3Al_2Si_{1.2}O_{4.8}(OH)_{7.2}$]. The spongy gehlenite adjacent to these veinlets is mostly transformed to vesuvianite without a definite front (Fig. 2H). Interestingly, the vesuvianite replaces the gehlenite with perfect pseudomorphism, which must reflect homoaxial replacement. The homoaxial vesuvianite has a lower birefringence than the vesuvianite in the veins, probably a reflection of its higher Fe and lower Al contents (Table 1). Its extinction and elongation appear to be the same as those of the adjacent gehlenite belonging to the same former original crystal of melilite. Owing to similarities in the unit-cell parameter ($2a_{\mathrm{mel}} \approx a_{\mathrm{ves}}$), an epitaxy along the plane (001) might *a priori* be expected. However, this plane does not play a special role in the mode of association observed in sample OC104.

This type of replacement seems similar to textures described from the Christmas Mountains in the Big Bend region of Texas (Joesten 1974) and is apparently quite rare in other skarns of the world. Among all our specimens of melilite skarns of Romania studied so far, it has been observed only in this sample and may be related to the peculiar Na-rich composition of gehlenite.

### *Interpretation of the retrograde reactions*

In summary, the original melilite underwent successive processes of modification that produced, at first, monticellite accompanied by spurrite or kilchoanite, then a granditic garnet in addition to monticellite and calcium silicates (spurrite, tilleyite, afwillite, or cuspidine at Cornet Hill), then vesuvianite. At each step, the recrystallized melilite shows an increase in the gehlenite content (Fig. 5). Whereas the complete replacement of melilite by vesuvianite has a clear metasomatic character, the question arises whether the local modifications resulted from isochemical retrograde reactions, locally favored by the presence of small amounts of fluid.

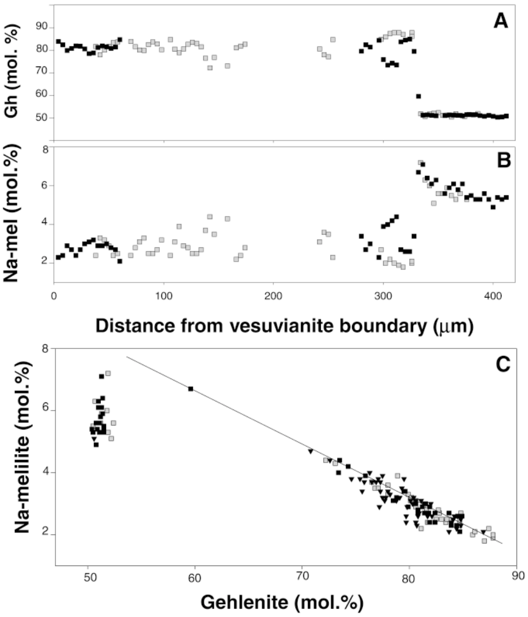


FIG. 6. A, B. Compositional profiles through a gehlenite rim around vesuvianite. The three series of data points have been chosen on slightly different portions of the cross section, in order to avoid altered areas. Note the Na-enrichment in the unaltered melilite, of uniform Gh content, near the gehlenite rim, and the small-scale compositional irregularities in the gehlenite rim. C. Negative correlation between the Gh and Na-mel contents in the gehlenite rim displayed in A and B (squares), and in another one (triangles).

### *The chemical evolution of melilite in the local modifications*

The compositional change of melilite in the *birefringent spots* corresponds to the transformation of part of the initial åkermanite component to monticellite, consistent with the reaction (1):

$$\underset{\text{åkermanite}}{Ca_2MgSi_2O_7} = \underset{\text{monticellite}}{CaMgSiO_4} + \underset{\text{wollastonite}}{CaSiO_3} \qquad (1)$$

experimentally observed to take place at 700°C under low pressure (Harker & Tuttle 1956). If the modification were isochemical, one would expect to find wollastonite in the birefringent spots around monticellite grains. Instead, Ca–Si minerals with Ca:Si > 1 were found in a few places, never wollastonite.

The crystallization of the Al- and Na-free monticellite should result in an increase in the Na-mel and Gh contents of melilite in a constant ratio (arrow 1 in Fig. 5). Instead, there is a clear negative correlation between the Na-mel (8 to 4%) and Gh (60 to 70%) contents of gehlenite in spots (Fig. 4A), which suggests that reaction (1) is not the only one involved in the formation of the spots. As the negative correlation is observed in individual spots (Fig. 4), it is not related to compositional differences in the original melilite, but reflects a reaction between the Na-mel and Gh components such as (2):

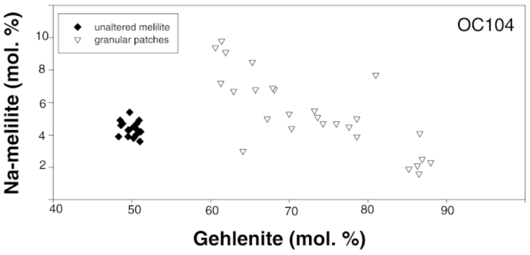


FIG. 7. Composition of gehlenite in granular patches in sample OC 104. The absence or scarcity of a graniditic garnet in this sample is probably related to the higher content in Na-mel, compared to other samples (Figs. 3 and 5).

$$\begin{array}{ll} \mathrm{CaSiO_3} + \tfrac{1}{3}\,\mathrm{Ca_2Al_2SiO_7} + \tfrac{1}{3}\,\mathrm{Na_2O} & \\ \text{wollastonite}\quad \text{gehlenite} & \\ = \tfrac{2}{3}\,\mathrm{CaNaAlSi_2O_7} + \mathrm{CaO} & (2) \\ \qquad \text{“Na-melilite”} & \end{array}$$

The trend in Figure 5 can be accounted for by a combination of reactions (1) and (2), with locally variable coefficients (arrows 1 and 2, respectively).

The significance of reaction (2) emerges on considering the general character of the negative correlation between Na-mel and Gh contents in all types of gehlenite studied here, including the spots, the granular patches and the rims around metasomatic vesuvianite (Fig. 6). The very regular correlation shown in Figure 6 is unlikely to be fluid-controlled, because the gehlenite rim shows compositional variations at a very small scale, hardly consistent with fluid–mineral equilibrium. The same observation applies to the birefringent spot shown in Figure 4. The probable cause for the correlation is a crystal-chemical control, a high content of Na-mel allowing for a higher åkermanite content than that stable under the same conditions in Na-free melilite. A similar correlation, although less regular and involving lower Na contents, has been noticed in melilite crystals from refractory inclusions of meteorites, formed or reworked under quite different conditions (MacPherson & Davis 1993).

From a mass-balance point of view, if reaction (2) in the birefringent spots were only a redistribution of the Na-mel and Gh components within the spots, without accompanying changes to the bulk composition, the average Na-mel:Gh ratio in the spots should be equal to that in the unaltered melilite. The analytical data (Fig. 5) suggest, but do not demonstrate, that the Na-mel:Gh ratio is slightly higher in the spots (0.092 ± 0.020) than in unaltered melilite (0.078 ± 0.010). We favor the idea that Na was introduced in small amounts through reaction (2), because combining reaction (1) with reaction (2) accounts for the Ca:Si > 1 character of the calcium silicates observed in the spots. For instance, considering the case of a kilchoanite-bearing spot, the combination [(1) + ⅓ (2)] is:

$$\begin{array}{ll} \mathrm{Ca_2MgSi_2O_7} + 1/9\,\mathrm{Ca_2Al_2SiO_7} + 1/9\,\mathrm{Na_2O} & \\ \text{åkermanite}\qquad\qquad \text{gehlenite} & \\ = \mathrm{CaMgSiO_4} + \mathrm{Ca_3Si_2O_7} + 2/9\,\mathrm{CaNaAlSi_2O_7} & (3) \\ \text{monticellite}\quad \text{kilchoanite}\qquad \text{“Na-melilite”} & \end{array}$$

The most important reaction involved in the first step of development of the *granular patches* is the same as in the birefringent spots, *i.e.,* a transformation of the åkermanite component to monticellite, the difference being the larger proportion of the åkermanite component consumed. The other feature of the melilite compositional trend in the granular patches is a strong decrease in the Fe/(Fe + Mg) value, compared to the primary melilite and also to the birefringent spots (Fig. 5). Because the Fe/(Fe + Mg) value of monticellite at Oraviţa is in the range 0.10–0.18, the same as the unaltered melilite, the production of monticellite alone should not affect this ratio greatly in the residual gehlenite. Assuming that the granular modification occurred under (almost) closed-system conditions, the observed change probably reflects the crystallization of a Fe-bearing mineral, *i.e.,* the granditic garnet, observed in the granular patches.

According to the assumption of an isochemical retrograde reaction, the decomposition of melilite in the system Al–Ca–Si–Mg–Fe can be written:

$$\begin{array}{ll} x\,\mathrm{Ca_2(Mg,Fe)Si_2O_7} + \mathrm{Ca_2Al_2SiO_7} & \\ \quad \text{åkermanite}\qquad\qquad \text{gehlenite} & \\ = x\,\mathrm{Ca(Mg,Fe)SiO_4} + \mathrm{Ca_3Al_2Si_3O_{12}} & \\ \quad \text{monticellite}\qquad \text{grossular} & \\ + \mathrm{Ca_{x-1}Si_{x-2}O_{3x-5}} & (4) \\ \quad \text{Ca–Si mineral} & \end{array}$$

which highlights the essential Ca:Si > 1 character of the calcium silicate produced in the granular patches, in response to the comparatively high silica content of the garnet. This conclusion does not depend on the actual composition of the granditic garnet produced, as the relation (5) involving the components andradite, kirschsteinite and the Fe-analogue of åkermanite (“Fe-Ak”) does not involve either Ca or Si:

$$\begin{array}{ll} \mathrm{Ca_2FeSi_2O_7} \;+\; \mathrm{CaFeSiO_4} + \tfrac{1}{2}\,\mathrm{O_2} & \\ \text{“Fe-akermanite”}\quad \text{kirschteinite} & \\ = \mathrm{Ca_3Fe_2Si_3O_{12}} & (5) \\ \quad \text{granditic garnet} & \end{array}$$

The silica necessary to crystallize garnet may be provided not only by the decomposition of Ak and Fe-Ak, but also by the decomposition of the other Si-rich melilite component, Na-mel. The corresponding decrease in the Na-mel content appears in Figure 5, where it corresponds to the region $\mathrm{Gh}_{>75}$. Because no Na-bearing mineral was formed as a result of this reaction, we assume that Na was carried away by the fluid.

The question whether, except for Na and volatile constituents, the granular patches formed under isochemical conditions has been investigated by mass-balance calculations. The reaction forming the granular patches (6) is written using the measured compositions of minerals in sample OC86:

$$\begin{array}{ll} \mathrm{Ca_{1.96}Na_{0.04}Mg_{0.37}Fe_{0.06}Al_{1.10}Si_{1.47}O_7} + u\,\mathrm{O_2} & \\ \qquad \text{unaltered melilite} & \\ = v\,\mathrm{Ca_{1.97}Na_{0.03}Mg_{0.12}Al_{1.73}Si_{1.15}O_7} & \\ \qquad\qquad \text{gehlenite} & \\ + w\,\mathrm{CaMg_{0.89}Fe_{0.11}SiO_4} & \\ \qquad \text{monticellite} & \\ + x\,\mathrm{Ca_3AlFeSi_3O_{12}} + y\,\mathrm{Ca_3Si_2O_7} + z\,\mathrm{Na_2O} & (6) \\ \qquad \text{garnet}\qquad\qquad \text{kilchoanite} & \end{array}$$

No set of values for the four coefficients *v, w, x, y* confirms, even approximately, the five mass-balance relations (Si, Ca, Al, Fe, Mg) implied by this reaction, indicating that at least one of these constituents was mobilized.

If we maintain the assumption of an inert behavior for Mg, Al and Fe, and assume that Ca or Si were mobilized, the coefficients *v, w, x* can be determined, and the reaction is:

$$\begin{aligned}&\text{unaltered melilite} + 0.005\ O_2 = 0.62\ \text{gehlenite}\\&+ 0.33\ \text{monticellite} + 0.02\ \text{granditic garnet}\\&+ 0.35\ CaO + 0.37\ SiO_2 + 0.02\ Na_2O \qquad \text{(6a)}\end{aligned}$$

A very small amount of garnet is produced from this reaction, in contrast with petrographic observations in most cases. Furthermore, large amounts of Ca and Si are released, with a Si:Ca ratio greater than 1, which is not consistent with the mineralogical composition of the granular patches.

A more realistic assumption is that Fe was introduced, according to:

$$\begin{aligned}&\text{unaltered melilite} + 0.12\ FeO + 0.04\ O_2\\&= 0.55\ \text{gehlenite} + 0.34\ \text{monticellite}\\&+ 0.14\ \text{garnet} + 0.04\ \text{kilchoanite} + 0.02\ Na_2O \qquad \text{(6b)}\end{aligned}$$

In most cases, the estimated proportion of minerals in the granular patches is in reasonable agreement with the coefficients of reaction (6b), and we conclude that the crystallization of a granditic garnet involved a fluid-based introduction of Fe.

A few cases of garnet-free or garnet-poor granular patches are found in sample OC104, the chemical features of which show the negative correlation of Na-mel and Gh components over an appreciably larger range than in other samples, extending to $Gh_{60}$Na-$mel_{10}$ (Fig. 7). This part of the trend resembles that corresponding to the birefringent spots in other samples, with a more important addition of Na. In accordance, the absence or scarcity of garnet is probably due to the uptake of Si, released by the transformation of åkermanite to monticellite, by "Na-melilite" instead of the granditic garnet, as in the birefringent spots.

*Vesuvianite* in sample OC44 also appears to be a product of an almost closed-system transformation, as in the granular patches. In this association again, four major phases are present in apparent equilibrium, the differences from the usual granular patches being the presence of vesuvianite and the absence of a Ca–Si mineral. As the Al:Mg ratio of vesuvianite is smaller than that of the gehlenite, its crystallization is expected to push the composition of the gehlenite still more in the direction of the Gh end-member, in accordance with the fact that the compositions of gehlenite in OC44 are the richest of all in the gehlenite component (90%). In this respect, the appearance of vesuvianite as a product of alteration of melilite seems the ultimate stage of the general process responsible for the evolution of melilite toward nearly pure gehlenite.

This evolution has not been observed going any farther than $Gh_{90}$, and the Al content of this early (relatively high-temperature) vesuvianite in melilite rocks is only in the range 16–17 wt.% $Al_2O_3$, below the maximum encountered for this mineral (18–19 wt% $Al_2O_3$). This may be related to the ubiquitous presence of Mg-dominant minerals, like monticellite (and probably later-formed serpentine), which prevent extreme depletion of Mg in the associated gehlenite and vesuvianite.

## *Metasomatic zonation associated with vesuvianite*

The metasomatism-induced features include the formation of zones with a reduced number of coexisting phases (no more than three), and the development of bulk-chemical changes from one zone to the other. One important compositional change from melilite to vesuvianite is the enrichment in Fe, also recorded by an increase in Fe/(Fe + Mg) value of the Gh-rich melilite, especially for $Gh_{>85}$ (Fig. 3). This increase is especially pronounced in sample OC104, where part of the vesuvianite (the homoaxial type) is richer in iron than the vesuvianite usually encountered in these skarns. Compared to the granular modification, which also involves Fe-enrichment, this enrichment has a different mineralogical expression. Also, the change of melilite to almost monomineralic vesuvianite involves Si-enrichment (Fig. 8), suggesting that introduction of Si from the fluid might be responsible for the appearance of these zoned systems.

The appearance of clintonite in the zoned systems is at first sight not in favor of an input of silica, as clintonite is a Si-poor mineral. The systematic occurrence of this mineral next to vesuvianite suggests that it represents the excess Al released by the transformation of the melilite into vesuvianite, which is poorer in Al. The overall chemical reaction (7) illustrates the inferred input of silica:

$$\begin{aligned}&10.7\ \underset{\text{melilite}}{Ca_{1.95}Na_{0.05}Mg_{0.40}Fe_{0.04}Al_{1.07}Si_{1.49}O_7}\\&+ 5.22\ H_2O + 1.35\ FeO + 3.97\ SiO_2\\&= 0.27\ Na_2O + \underset{\text{vesuvianite}}{Ca_{19}Fe_{1.6}Mg_2Al_{9.4}Si_{18}O_{68}(OH)_{9.4}}\\&+ 1.32\ \underset{\text{monticellite}}{CaMg_{0.89}Fe_{0.11}SiO_4}\\&+ 0.54\ \underset{\text{clintonite}}{CaMg_{2.03}Fe_{0.07}Al_{3.8}Si_{1.1}O_{10}(OH)_2} \qquad (7)\end{aligned}$$

The more extensive transformation observed in OC104, compared to the other samples, is perhaps related to the Na enrichment of the gehlenite, as already discussed. According to the laws of chromatography (Korzhinskii 1970), the rate of propagation of a metasomatic front is inversely proportional to the amount of the component that is added (or subtracted) to produce the reaction observed at this front. Assuming that this component is silica, the comparatively high content of silica in the Na-rich gehlenite could favor its transformation into vesuvianite.

## CONDITIONS OF STABILITY OF THE MINERAL ASSOCIATIONS

The sole thermochemical database that includes vesuvianite and such Ca–Si minerals as found in the granular modifications is Thermocalc (Holland & Powell 1998), which contains data for tilleyite and spurrite and closely reproduces the existing experimental equilibria in the system $CaO–MgO–SiO_2–CO_2–H_2O$ (Harker & Tuttle 1956, Walter 1963, Yoder 1968). Garnet on the join grossular–andradite and melilite on the join gehlenite–åkermanite have been considered to be ideal, respectively two-site and one-site solid solutions (Perchuk & Aranovich 1979, Charlu *et al.* 1981). The composition of garnet was taken as $Grs_{50}$ in accordance with that observed. The mole fraction of $CO_2$ in the fluid was set to a value (0.02) consistent with the presence of either spurrite or tilleyite in the granular patches.

Owing to the probable influence of the Na content of melilite on its field of stability, the most Na-poor compositions of gehlenite have been chosen to represent the spots ($Gh_{70}$) and the granular patches ($Gh_{80–85}$). In both cases, the field of stability of gehlenite is limited by the curves (b) and (c) (Fig. 9, Table 2).

The compositional change from the unaltered melilite ($Gh_{50}$) to the gehlenite of the spots obviously reflects a temperature lower than that of formation of the unaltered melilite. The change from the gehlenite of the spots to that of the granular patches may reflect a decrease in temperature or an increase in fluid pressure. The textural and chemical features indicate that the influence of the fluid was very restricted in the birefringent spots and more important in the granular patches, in accordance with the idea of an increasing pressure of fluid. The temperature and fluid pressure of formation of the granular patches are inferred from the first appearance of vesuvianite, where the gehlenite reaches the composition $Gh_{85}$, *i.e.*, 554°C, 150 bars (point vesuvianite – monticellite – granditic garnet – tilleyite – gehlenite $Gh_{85}$). Owing to the uncertainties associated with the calculation [the observed vesuvianite is somewhat different from that of the database, $Ca_{19}Mg_4Al_9Si_{18}O_{68}(OH)_9$], we conclude that the fluid pressure was low, and the temperature was in the range 500–600°C.

The reactions involved in the modifications of melilite, in the case of an isothermal evolution, are dis-

TABLE 2. REACTIONS IN FIGURES 9 AND 10, RELEVANT TO THE SKARNS OF ORAVIŢA, ROMANIA

| | |
|---|---|
| (a) | Spu + $CO_2$ = Til |
| (b) | 8 Ak + 3 Gh + 2 $CO_2$ = Til + 3 Grs + 8 Mtc |
| (c) | 8 Ak + 3 Gh + $CO_2$ = Spu + 3 Grs + 8 Mtc |
| (d) | 27 Ak + 11 Gh + 6 $CO_2$ + 9 $H_2O$ = 2 Ves + 23 Mtc + 3 Til |
| (e) | 3 Ak + 2 Gh + 9 Grs + Mtc + 9 $H_2O$ = 2 Ves |
| (f) | 5 Mtc + Til + 3 $SiO_2$ = 5 Ak + 2 $CO_2$ |
| (g) | Gh + Ak + $SiO_2$ = Grs + Mtc |
| (h) | 5 Gh + Spu + 8 $SiO_2$ = 5 Grs + $CO_2$ |
| (i) | 11 Gh + 12 Ak + 9 $SiO_2$ + 9 $H_2O$ = 2 Ves + 8 Mtc |

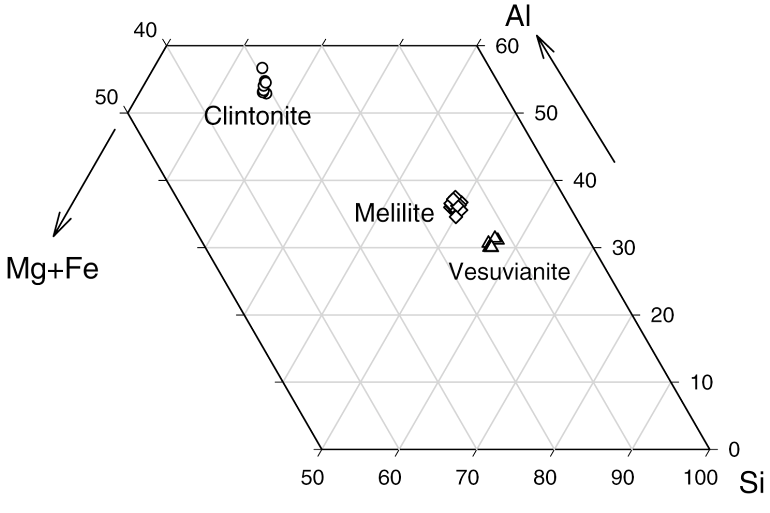


FIG. 8. Projection of melilite, vesuvianite and clintonite compositions (sample OC50) on the Al – Si – (Mg + Fe) plane (molar fractions).

played in Figure 10. The case of the normal granular patches (original rock composed only of melilite ± granditic garnet) is represented by an evolution along the curve melilite – granditic garnet – spurrite or tilleyite – monticellite. The activities of silica constrained by monticellite and gehlenite are much below that necessary for the stabilization of wollastonite, in agreement with the absence of this mineral. The case of OC44 (originally melilite + wollastonite) is represented by an evolution at higher activities of silica than the former case, owing to the presence of excess silica, and resulting in the absence of Ca–Si minerals and in the appearance of vesuvianite in equilibrium with a melilite more Gh-rich than in the former case, as observed.

Therefore, the birefringent spots, then the granular patches, including those of sample OC44, are very likely to result from the circulation of small (and increasing) amounts of fluids, chemically buffered by the surrounding melilite-bearing rock, except for Fe, Na and oxygen.

According to Figure 10, the metasomatic development of vesuvianite under increasing activity of silica implies a further increase in fluid pressure, which is consistent with the more pervasive infiltration and more important fluid-induced chemical changes involved in

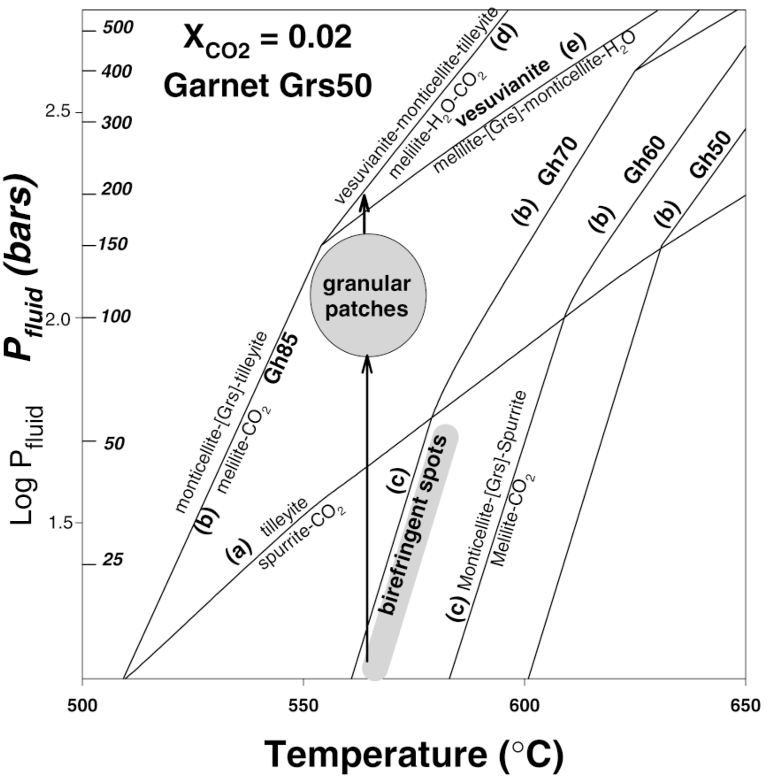


FIG. 9. Calculated *fluid pressure versus temperature* conditions of stability of gehlenite-bearing associations. The mole fraction of $CO_2$ was set to a value allowing for the successive appearance of spurrite, then tilleyite in the local modifications. Reaction stoichiometries in Table 2. Either temperature decrease or fluid pressure increase (arrow) drive the composition of gehlenite toward the Gh end-member. The smaller, earlier birefringent spots have compositions consistent with a lower fluid pressure than the later-formed, larger granular patches. The probable temperature is inferred from the appearance of vesuvianite together with gehlenite $Gh_{85}$ in most granular patches. Final replacement of gehlenite by vesuvianite occurs under further increase in fluid pressure (and associated metasomatism). Calculation from Thermocalc database and software. Symbols: Ak: åkermanite, Gh: gehlenite, Grs: grossular, Mtc: monticellite, Spu: spurrite; Til: tilleyite; Ves: vesuvianite. Square brackets indicate end-member in a solid-solution series.

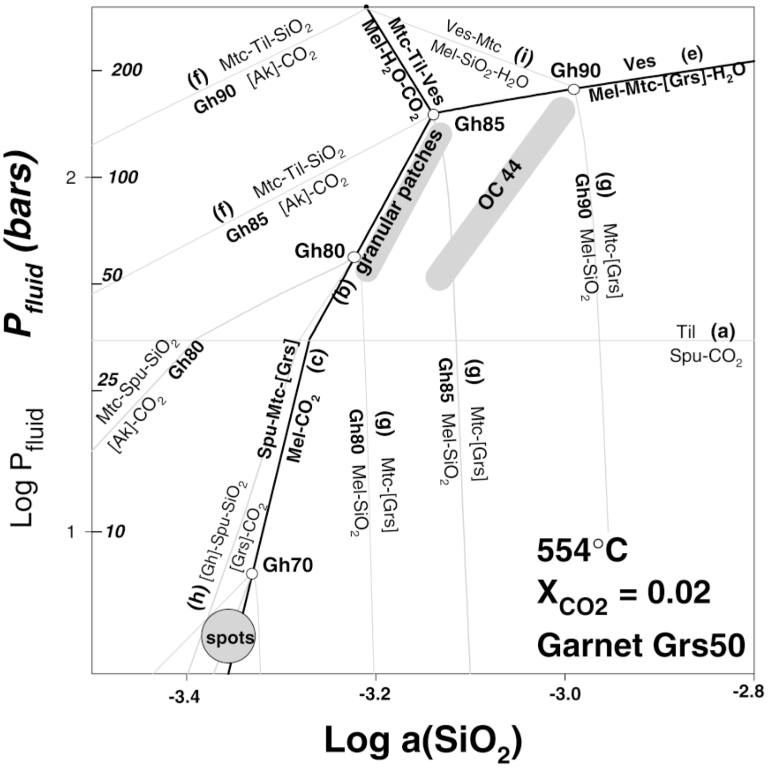


FIG. 10. Selected reactions in the plane *fluid pressure, activity of $SiO_2$* (with reference to quartz), at the temperature of the invariant point gehlenite ($Gh_{85}$) – vesuvianite – monticellite – granditic garnet – tilleyite. The compositional evolution of melilite in the local modifications followed the curves *b* then *c*, producing monticellite, spurrite or tilleyite and granditic garnet, until the $H_2O$ pressure was high enough for vesuvianite to become stable. In the sample OC44, which originally contained wollastonite, the evolution took place at higher activity of silica, which resulted in the absence of spurrite or tilleyite and the appearance of vesuvianite together with gehlenite more Al-rich ($Gh_{90}$) than in other samples.

the replacement of melilite by vesuvianite + clintonite, compared to the local modifications. Such increased pressure of fluid is probably also the reason why the OH-bearing clintonite is found in this transformation. An input of silica under lower pressure of fluid (but still higher than in the local modifications) would favor garnet instead of vesuvianite, which may correspond to the granditic-garnet-bearing type of zoned systems observed ahead of the vesuvianite front.

## DISCUSSION AND CONCLUSIONS

The transformation of melilite to vesuvianite occurred upon the fluid-based addition of silica and iron in the case of massive transformation along a metasomatic front, the aluminum released in the transformation remaining in place and being expressed as clintonite. All the clintonite observed at Oraviţa occurs close to the area of the melilite skarns (Fig. 1). This specific mode of occurrence appears to be typical of the transition between the realm of the melilite skarns and that of the vesuvianite–garnet skarns (to which most of the occurrences around the Oraviţa intrusion belong). The extensive development of vesuvianite–garnet skarns along the diorite contacts, compared to the restricted occurrence of melilite skarns, is strong evidence that vesuvianite, as the product of transformation of melilite or not, is the most general product of the late- to post-magmatic hydrothermal processes, at temperatures probably not higher than 600°C, postdating the development of the melilite skarns.

Small amounts of the same fluid, circulating along very thin fractures, probably induced the localized low-temperature partial decomposition of melilite, described as the local modifications and interpreted as being isochemical except for Na and Fe. The decomposition produced mainly gehlenite and monticellite, silica-deficient calcium silicates and a granditic garnet. Large variations in gehlenite compositions resulted from variations in fluid pressure, increasing from the earlier spots to the later-formed granular patches, perhaps from variations in temperature, but also at constant temperature and fluid pressure from the mobility of Na, through what appears as a coupling between the substitutions $(AlAl)(MgSi)_{-1}$ (Gh–Ak) and $(NaAl)(CaMg)_{-1}$ (Na-mel–Ak), not yet documented in the literature.

This process is obviously distinct from the earlier process that formed melilite ($Gh_{50}$). However, the "untransformed" melilite shares some similarities with the local modifications. (i) The comparatively Gh-rich composition of the "unaltered" melilite in the skeletal monticellite-bearing areas, although rather homogeneous within a given sample, is similar to that in the spots and may also be derived by a similar transformation of the same type, albeit more pervasive and with a wider scale of Mg mobility. The same conclusion may apply to the compositionally similar melilite of the Apuseni Mountains occurrences, where a still more diffuse expression of such early changes is reflected by a network of monticellite veinlets observed in one sample at Cornet Hill (Pascal *et al.* 2001). (ii) The garnet spines observed at any place along the grain boundaries of melilite, and in the same position as monticellite in the skeletal monticellite-bearing samples, recalls the appearance of the granditic garnet in the local modifications as an alternative to the increase in the Na-mel content of gehlenite.

Such analogies are consistent with the idea that the melilite in the vein-like bodies may derive from an earlier composition that was richer in Mg in the occurrences of the Apuseni Mountains (the most Mg-rich composition encountered at Oraviţa is $Gh_{41}$), and richer in Na in almost all cases, the Si and Al contents of the former Na-mel component being now expressed as the ubiquitous interstitial grranditic spines. The unusually high Na content noticed in localized parts of the sample OC104 (in the gehlenite and in the later-formed thomsonite) may result from the low-temperature breakdown of a better-preserved original Na-rich melilite. The presence of exsolution-induced lamellae of magnetite in the core of some melilite crystals also suggests that the presently observed melilite recrystallized from a precursor richer in Fe.

The pervasive character of such transformations and the associated wider scale of mobility of Na, Fe (and Mg), compared to that involved in the local modifications, imply a higher pressure of fluid and also a higher temperature, in agreement with the temperature range (750–800°C) commonly estimated for the formation of gehlenite-bearing skarns (Nicholls 1971, Reverdatto *et al.* 1979, Wiechmann 1995, Pascal *et al.* 2001). As the original melilite, whatever its composition, was thermally stable in this temperature range, we believe that the suspected modifications resulted from metasomatism as the last step in a series of still not entirely understood processes of formation of the melilite veins.

## ACKNOWLEDGEMENTS

Thanks are due to S. Baudesson, G. Badin and G. Drouet for preparing the thin sections, and to the electron-microprobe team at Camparis. Helpful discussions with T. Berza and S. Marincea are appreciated. We gratefully acknowledge the help of our colleagues, D. Velde for letting us share her knowledge of the literature on melilite, and J. Moutte for translations from Japanese. This paper has benefitted greatly from insightful comments and suggestions made by G.M. Dipple, B.E. Owens and R.F. Martin.

## REFERENCES

BURNHAM, C.W. (1959): Contact metamorphism of magnesian limestones at Crestmore, California. *Geol. Soc. Am., Bull.* **57**, 879-928.

CHARLU, T.V., NEWTON, R.C. & KLEPPA, O.J. (1981): Thermochemistry of synthetic $Ca_2Al_2SiO_7$ (gehlenite) – $Ca_2Mg Si_2O_7$ (åkermanite) melilites. *Geochim. Cosmochim. Acta* **45**, 1609-1617.

CONSTANTINESCU, E., ILINCA, G. & ILINCA, A. (1988): Contributions to the study of the Oraviţa–Ciclova skarn occurence, southwestern Banat. *D.S. Inst. Geol. Geofiz.* **72–73/2**, 27-45.

DANA, E.S. (1915): *Descriptive Mineralogy* (6th ed.). John Wiley & Sons, New York, N.Y.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1986): *Rock-Forming Minerals. Disilicates and Ring Silicates* (2nd ed.). Longman, Harlow, U.K.

HARKER, R.I. & TUTTLE, O.F. (1956): The lower limit of stability of åkermanite ($Ca_2MgSi_2O_7$). *Am. J. Sci.* **254**, 468-478.

HOLLAND, T.J.B. & POWELL, R. (1998): An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations : the system $K_2O$–$Na_2O$–$CaO$–$MgO$–$MnO$–$FeO$–$Fe_2O_3$–$Al_2O_3$–$TiO_2$–$SiO_2$–C–$H_2O$–$O_2$. *J. Metamorphic Geol.* **8**, 89-124.

ILINCA, G., MARINCEA, S., IANCU, V., RUSSO-SANDULESCU, D. & SEGHEDI, I. (1993): Mineral occurrences in southwestern Banat. *Rom. J. Mineral.* **74**, 1-39.

INSTITUTUL DE GEOLOGIE SI GEOFIZICA (1975): Geologic Map of Romania, scale 1/50000, sheet Oraviţa.

JAMTVEIT, B., DAHLGREN, S. & AUSTRHEIM, H. (1997): High-grade contact metamorphism of calcareous rocks from the Oslo rift, Southern Norway. *Am. Mineral.* **82**,1241-1254.

JOESTEN, R. (1974): Pseudomorphic replacement of melilite by idocrase in a zoned calc-silicate skarn, Christmas Mountains, Big Bend region, Texas. *Am. Mineral.* **59**, 694-699.

KORZHINSKII, D.H. (1970): *Theory of Metasomatic Zoning*. Clarendon, Oxford, U.K.

MACPHERSON, G.J. & DAVIS, A.M. (1993): A petrologic and ion microprobe study of a Vigarano Type B refractory inclusion: evolution by multiple stages of alteration and melting. *Geochim. Cosmochim. Acta* **57**, 231-243.

NICHOLLS, I.A. (1971): Calcareous inclusions in lavas and agglomerates of Santorini volcano. *Contrib. Mineral. Petrol.* **30**, 261-276.

NUMANO, T. (1978): Geological and geochemical studies on gehlenite–spurrite skarns at Kushiro, the town of Tojo, Hiroshima Prefecture. I. Geology and petrochemistry of the skarn region. *Bull. School Educ., Okayama Univ.* **49**, 25-47 (in Japanese).

________ (1979): Geological and geochemical studies on gehlenite–spurrite skarns at Kushiro, the town of Tojo, Hiroshima Prefecture. II. Occurrences of gehlenite skarns at the Hirata outcrop. *Bull. School Educ., Okayama Univ.* **50**, 257-282 (in Japanese).

OWENS, B.E. (2000): High-temperature contact metamorphism of calc-silicate xenoliths in the Kigaplait Intrusion, Labrador. *Am. Mineral.* **85**, 1595-1605.

PASCAL, M.-L., FONTEILLES, M., VERKAEREN, J., PIRET, R. & MARINCEA, S. (2001): The melilite-bearing high-temperature skarns of the Apuseni mountains, Carpathians, Romania. *Can. Mineral.* **39**, 1405-1434.

PERCHUK, L.L. & ARANOVICH, L.Y. (1979): Thermodynamics of minerals of variable composition: andradite–grossularite and pistacite–clinozoisite solid solutions. *Phys. Chem. Minerals* **5**, 1-14.

REVERDATTO, V.V., PERTSEV, N.N. & KOROLYUK, V.N. (1979): $P_{CO2}$ – T-evolution of zoning in melilite during the regressive stages of contact metamorphism in carbonate-bearing rocks. *Contrib. Mineral. Petrol.* **70**, 203-208.

SABINE, P.A. (1975): Metamorphic processes at high temperature and low pressure: the petrogenesis of the metasomatized and assimilated rocks of carneal, Co. Antrim. *Phil. Trans. R. Soc.* **A 280**, 225-269.

________, STYLES, M.T. & YOUNG, B.R. (1982): Gehlenite, an exomorphic mineral from Carneal, Co. Antrim, Northern Ireland. *Rep. Inst. Geol. Sci.* **82**, 61-63.

STEFAN, A., ISTRATE, G. & MEDESAN, A. (1978): Gehlenite in calc-skarns from Magureaua Vatei–Cerboaia (Apuseni Mountains – Romania). *Rev. Roum. Géol., Géophys. et Géogr., Géol.* **22**, 155-160.

TILLEY, C.E. (1929): On larnite, (calcium orthosilicate, a new mineral) and its associated minerals from the limestone contact-zone of Scawt Hill, Co. Antrim. *Mineral. Mag.* **22**, 77-86.

________ & HARWOOD, H.F. (1931): The dolerite – chalk contact of Scawt Hill, Co Antrim. The production of basic alkali rocks by assimilation of limestone by basaltic magma. *Mineral. Mag.* **22**, 439-468.

WALTER, L.S. (1963): Experimental studies of Bowen's decarbonation series. 1. P–T univariant equilibria of the "monticellite" and "åkermanite" reactions. *Am. J. Sci.* **261**, 488-500.

WIECHMANN, M.J. (1995): *Contact Metamorphism and Skarn Formation at Crestmore, California.* Ph.D. thesis, Johns Hopkins Univ., Baltimore, Maryland.

YODER, H.S., JR. (1968): Akermanite and related melilite-bearing assemblages. *Carnegie Inst. Wash., Year Book* **66**, 471-477.

*Received July 14, 2002, revised manuscript accepted July 26, 2003.*