

GEHLENITE FROM THREE OCCURRENCES OF HIGH-TEMPERATURE SKARNS, ROMANIA: NEW MINERALOGICAL DATA

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ABSTRACT

Gehlenite is a common mineral in three high-temperature calcic skarns in Romania: Măgureaua Vaței and Cornet Hill in Apuseni Mountains and Oravița in Banat. In all three occurrences, a gehlenite zone occurs within the contact between dioritic or monzodioritic bodies of Upper Cretaceous age and carbonaceous sequences of Mesozoic age. The melilite solid-solutions vary from Ak_{34.1} to Ak_{51.2} (mean Ak_{41.2}) at Oravița, from Ak_{30.4} to Ak_{42.9} (mean Ak_{38.3}) at Măgureaua Vaței, and from Ak_{24.3} to Ak_{41.7} (mean Ak_{32.9}) at Cornet Hill, respectively. The content of “Na-melilite” is low, from up to 1.96 mol.% at Cornet Hill to up to 3.60 mol.% at Oravița. The cell parameter *a* ranges from 7.679(3) to 7.734(3) Å at Oravița, from 7.683(4) to 7.735(1) Å at Măgureaua Vaței, and from 7.684(3) to 7.733(1) Å at Cornet Hill, whereas *c* varies from 5.043(3) to 5.065(3) Å at Oravița, from 5.040(1) to 5.070(3) Å at Măgureaua Vaței, and from 5.044(1) to 5.067(4) Å at Cornet Hill. It is not possible to quantify the variations in the crystallographic parameters by considering only the åkermanitic substitution because the “Na-melilite” and “Fe-åkermanite” substitutions also play an important role. The cell parameter *a* remains practically constant within experimental errors, in spite of the increasing åkermanite-for-gehlenite substitution, due to the opposite influence of the “Na-melilite” component. The åkermanite substitution prevails over the opposite influence of “Na-melilite” in increasing the cell volume, and is additive to the influence of “Na-melilite” in decreasing the cell parameter *c*. The record in the infrared-absorption spectra of bands located at ~855 cm⁻¹ and ~670 cm⁻¹, respectively, which may be tentatively assigned to Al–O–Al stretching, is indicative of the presence of gehlenite-rich members of the melilite group in all the three occurrences.

Keywords: gehlenite, physical properties, crystal chemistry, unit-cell parameters, infrared absorption data, high-temperature skarn, Romania.

SOMMAIRE

La gehlénite est un minéral commun dans trois occurrences de skarn calcique de haute température en Roumanie: Măgureaua Vaței et Cornet Hill dans les monts Apuseni, et Oravița en Banat. Aux trois endroits, une zone à gehlénite apparaît dans la zone du contact entre des corps dioritiques ou monzodioritiques d'âge Crétacé supérieur et des séquences carbonatées d'âge Mésozoïque. Les solutions solides du groupe de la mélilite vont de Ak_{34.1} à Ak_{51.2} (en moyenne Ak_{41.2}) à Oravița, de Ak_{30.4} à Ak_{42.9} (en moyenne Ak_{38.3}) à Măgureaua Vaței, et de Ak_{24.3} à Ak_{41.7} (en moyenne Ak_{32.9}) à Cornet Hill. Les teneurs du pôle “Na-mélilite” sont faibles, allant de 1.96% (base molaire) à Cornet Hill jusqu'à 3.60% à Oravița. Les paramètres de la maille sont très variables: le paramètre *a* varie entre 7.679(3) et 7.734(3) Å à Oravița, entre 7.683(4) et 7.735(1) Å à Măgureaua Vaței, et entre 7.684(3) et 7.733(1) Å à Cornet Hill, tandis que *c* varie de 5.043(3) à 5.065(3) Å à Oravița, de 5.040(1) à 5.070(3) Å à Măgureaua Vaței, et de 5.044(1) à 5.067(4) Å à Cornet Hill dans les échantillons analysés. Il est impossible de quantifier la variation des paramètres cristallographiques en tenant compte de la seule substitution åkermanitique, car les substitutions impliquant les composantes “Na-mélilite” et “Fe-åkermanite” jouent également un rôle important. Le paramètre de maille *a* reste pratiquement constant dans les limites des erreurs expérimentales, en dépit de la progression de la substitution åkermanitique à cause de l'influence compensatoire de la substitution de la composante “Na-mélilite”. L'influence de la substitution åkermanitique dans l'augmentation du volume de la maille unitaire est plus forte que l'influence opposée de la substitution impliquant le pôle “Na-mélilite”, les deux types de substitution jouant ensemble un rôle important dans la diminution du paramètre *c* de la maille réticulaire. La présence, dans les spectres d'absorption infrarouge, des deux bandes localisées à ~855 cm⁻¹ et ~670 cm⁻¹, qui peuvent être attribuées aux vibrations des liaisons Al–O–Al, témoigne de la présence des compositions gehlénitiques du groupe de la mélilite aux trois endroits.

Mots-clés: gehlénite, propriétés physiques, cristalochimie, paramètres réticulaires, données d'absorption infrarouge, skarn de haute température, Roumanie.

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INTRODUCTION

Gehlenite, ideally $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$, is a rather rare mineral within the melilite group; its terrestrial occurrences are restricted to high-grade contact-metamorphosed impure limestones, *in situ* self-combusted carbonaceous formations, and calcium-rich ultramafic volcanic rocks (Deer *et al.* 1992). Worldwide, over forty occurrences of gehlenite have been reported in high-temperature calcic skarns (Reverdatto 1970, Deer *et al.* 1986, Piret 1997, and references therein). Three occurrences of this mineral species are known so far in Romania: Măgureaua Vaței – Cerboia Valley (Ștefan *et al.* 1978, Pascal *et al.* 2001), Cornet Hill (Istrate *et al.* 1978, Pascal *et al.* 2001, Marincea *et al.* 2001) and Oravița – Ogașul Crișenilor (Constantinescu *et al.* 1988, Katona *et al.* 2003). A fourth occurrence of gehlenite, recently identified at Ciclova, is under study.

Information on gehlenite from Romania is rather meager, dispersed in papers describing individual occurrences and, in most cases, incomplete. The available data on gehlenite from Oravița was for example restricted to a mere identification and to sparse optical data until the study of Katona *et al.* (2003), who gave more accurate petrographic and chemical data. Data on chemical composition are commonly not accompanied by structural characteristics (*e.g.*, by crystallographic parameters), infrared behavior or physical parameters. In the present paper, we intend to supplement the available information on the mineral chemistry with comprehensive analytical data concerning the physical properties, the unit-cell parameters and the infrared behavior.

GEOLOGICAL SETTING

The occurrences of gehlenite described herein are related to the occurrences at Măgureaua Vaței and Cornet Hill in Apuseni Mountains and Oravița in Banat (Fig. 1). All of them are related to Upper Cretaceous intrusions that could be correlated with the “banatic” magmatic event, using the term as first defined by von Cotta (1864). In all three occurrences, an extensive metasomatism affected calcium-rich protoliths, *i.e.*, marbles on developed Callovian – Aptian limestones and marls from the Reșița – Moldova Nouă synclorium at Oravița (Ilinca *et al.* 1993), and Tithonic – Kimmeridgian reef limestones of the Căpâlnaș–Tchereu unit (Lupu *et al.* 1993) at Măgureaua Vaței and Cornet Hill. The magmatic intrusions at the contact are mainly dioritic at Oravița (Dupont *et al.* 2002) and monzodioritic to quartz monzodioritic at Măgureaua Vaței and Cornet Hill (Ștefan *et al.* 1988). Absolute ages are known only for the intrusion from Oravița, where Soroiu *et al.* (1986) reported K–Ar ages on biotite of 79 ± 3 to 77 ± 3 Ma.

The skarns are barren, typically zoned, and quite similar in their internal structure. A gehlenite zone

occurs near the contact between a dioritic or monzodioritic body and carbonaceous sequences of Mesozoic age. Gehlenite could also occur in association with spurrite and tilleyite in the outer skarn zones, at Cornet Hill (Marincea *et al.* 2001). Table 1 gives additional information concerning the mineral assemblages in the gehlenite-bearing skarns.

In the localities examined, gehlenite mainly occurs in the inner skarn zones, being the main mineral in the outer endoskarn or inner exoskarn. The mineral assemblages in these zones strongly suggest that gehlenite was mainly formed through reactions involving pre-existing plagioclase and calcite. Two of the reactions evaluated by Hoschek (1974) in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ are especially pertinent: (1) $2 \text{ anorthite} + 3 \text{ calcite} = \text{ gehlenite} + \text{ grossular} + 3 \text{ CO}_2$ and (2) $\text{ anorthite} + 2 \text{ calcite} = \text{ gehlenite} + \text{ wollastonite} + \text{ CO}_2$. Both of them imply high temperatures of reaction, in the range quoted by Pascal *et al.* (2001) for Măgureaua Vaței and Cornet Hill (about 750°C) and low pressures, up to 1 kbar, for $0.1 < X(\text{CO}_2) < 1$. These temperatures are high enough to produce âkermanite-rich compositions similar to those described by Katona *et al.* (2003) in the

TABLE 1. MINERAL ASSEMBLAGES IN THE GEHLENITE-BEARING SKARNS OF ROMANIA

| Mineral species | Oravița | Măgureaua Vaței | Cornet Hill |
|--------------------|---------|-----------------|-------------|
| gehlenite | ■ | ■ | ■ |
| spurrite | ◆ | ■ | ■ |
| diopside | ◆ | ■ | ■ |
| tilleyite | ◆ | □ | ■ |
| awillite | ■ | ◆ | □ |
| grossular | ● | ● | ● |
| titanian andradite | □ | ● | ◆ |
| andradite | ◆ | ● | □ |
| spinel | □ | ◆ | □ |
| magnetite | ◆ | ◆ | ◆ |
| monticellite | ● | ■ | ◆ |
| wollastonite | ◆ | ■ | ● |
| perovskite | ◆ | ■ | ◆ |
| vesuvianite | ■ | ● | ● |
| clintonite | ■ | □ | □ |
| phlogopite | □ | ◆ | □ |
| ellestadite-(OH) | ■ | ◆ | ■ |
| calcite | ■ | ■ | ■ |
| aragonite | ■ | □ | ◆ |
| pyrrhotite | ◆ | ◆ | ◆ |
| djerfisherite | □ | □ | ? |
| cuspidine | ? | □ | ? |
| scawtite | □ | □ | ● |
| thaumasite | ◆ | ◆ | ◆ |
| clinochlore | ◆ | ◆ | ◆ |
| chrysotile | ◆ | ◆ | ◆ |
| hibschite | ● | ● | ● |
| kamaishillite | □ | ? | □ |
| bichschillite | □ | ? | ? |
| xonotlite | ◆ | ● | ◆ |
| thomsonite | ● | ● | ● |
| gismondine | □ | □ | ● |
| mountainite | □ | □ | ? |
| foshagite | □ | □ | ? |
| plombierite | ◆ | ■ | ◆ |
| tobermorite | ◆ | ◆ | ◆ |
| riversideite | □ | □ | ■ |
| portlandite | □ | □ | □ |
| allophane | ● | ● | ● |

Symbols: ■ major; ● common; ◆ minor; ■ rare; ◇ very rare; ? doubtful identification; □ not found.

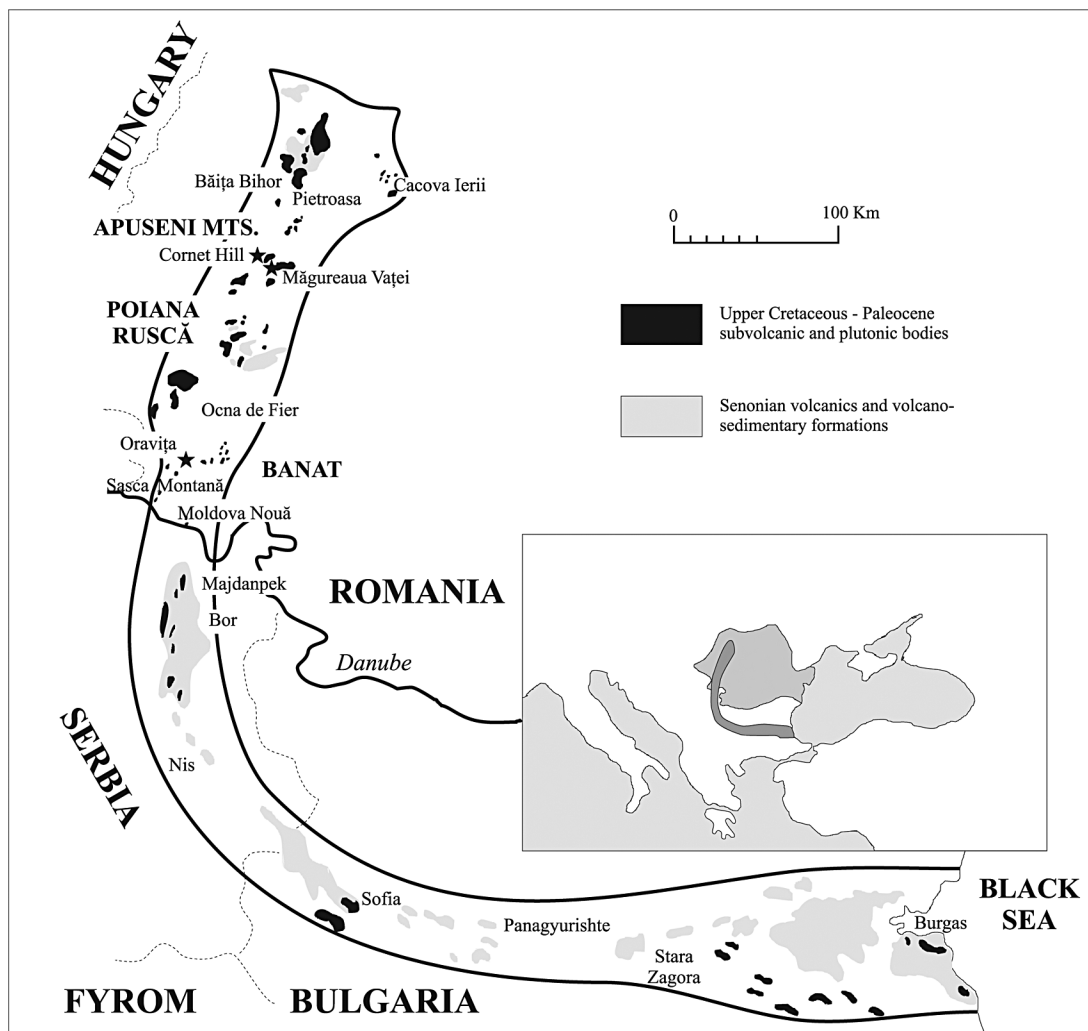


FIG. 1. Map showing the extension of the Banatitic petrographic province within the Carpatho-Balkan area. Redrawn from Cioflica & Vlad (1973). The occurrences analyzed in this paper are marked with stars.

“spots” from Oravița, where the inclusions of monticellite in the primary gehlenite indicate its somewhat earlier crystallization. A second generation of gehlenite, poorer in Mg, may be clearly distinguished at Oravița, where Katona *et al.* (2003) described both Mg-rich primary gehlenite (referred to as melilite) and secondary gehlenite, issued from the retrograde evolution of the Mg-rich gehlenite toward compositions richer in Al, by reactions that also produce monticellite, spurrite and garnet of the grossular-andradite solid-solution series. A retrograde alteration, similar with that described by Reverdatto *et al.* (1980) at the exocontact of the Anakite dolerite massif, may be also distinguished at Măgureaua

Vaței and Cornet Hill, where some gehlenite grains show a Mg-poor core and a more åkermanitic rim.

The specimens analyzed during this study pertain to all generations of gehlenite, our efforts being directed toward the selection of the most homogeneous samples, free of other mineral inclusions and unaffected by the early metasomatic processes, which produced replacements of gehlenite by vesuvianite and hibschite.

MODE OF OCCURRENCE

The mineral was found in the following contexts and parageneses: (1) blocky gehlenite associated mainly

with wollastonite, perovskite, ellestadite and garnet (Măgureaua Vaței, Cornet Hill), with monticellite, grossular-andradite garnet, wollastonite and ellestadite (Oravița) or with wollastonite, perovskite and ellestadite (Cornet Hill) in the inner skarn zone; (2) veins or clusters of gehlenite surrounded by spurrite and associated with perovskite and garnet in the median skarn zone, or with wollastonite and tilleyite in the outer skarn zone (Cornet Hill).

Late-stage, metasomatic, topotactic replacements of gehlenite by "homoaxial" vesuvianite, as described by Joesten (1974) and Katona *et al.* (2003), were found in all the three occurrences, but are most common at Oravița and Măgureaua Vaței. Local modifications that internally affect the original crystals, described as "birefringent spots" and "granular patches" by Katona *et al.* (2003), are frequent at Oravița and scarce at Măgureaua Vaței and Cornet Hill. As much as possible, the samples selected for this study have not undergone such modifications. Late-hydrothermal replacement of gehlenite by hibschite, thomsonite, and 11 Å tobermorite is common. Weathering crusts, identified as containing hydrogrossular (hibschite) and allophane, were identified on the exposed surfaces at Măgureaua Vaței.

Textural aspects and reciprocal relations with other minerals at the scale of the thin sections were extensively illustrated by Marincea *et al.* (2001), Pascal *et al.* (2001) and Katona *et al.* (2003). In the Romanian occurrences, gehlenite is typically coarse-grained; it normally forms euhedral, rarely subhedral, grains, 0.3 mm to nearly 1 cm across. Pegmatite-like developments, leading to crystals of up to 8 cm across, are typical at Măgureaua Vaței (Fig. 2). All crystals show a well-defined morphology, with a short prismatic to tabular habit; they consist of tetragonal prisms {100} simply terminated with {001} pinacoids.

ANALYTICAL PROCEDURES

Electron-microprobe analyses (EMPA) were carried out using a fully automated CAMECA SX-50 electron microprobe operated in the wavelength-dispersive mode at Université Pierre-et-Marie-Curie (Paris VI). The instrument was operated at an accelerating voltage of 15 kV, with a beam current of 10 nA measured on brass. The beam diameter was fixed at 7 μm . The standards and operating conditions were the same as those described by Marincea *et al.* (2001). Data reduction was done using the PAP correction procedure (Pouchou & Pichoir 1985). The estimated accuracy of the analytical data is $\pm 1\%$ of the amount present.

X-ray powder-diffraction (XRD) analysis was performed on a Siemens D-5000 Kristalloflex automated diffractometer equipped with a graphite diffracted-beam monochromator (CuK α radiation, $\lambda = 1.54056 \text{ \AA}$). The operating conditions were the same as described by Marincea *et al.* (2001). Synthetic silicon (NBS 640b) was used as an external standard in order to verify the

accuracy of the measurements. The unit-cell parameters were calculated by least-squares refinement of the XRD data, using the computer program of Appleman & Evans (1973) modified by Benoit (1987).

Part of the infrared absorption spectra was obtained using a SPECORD M-80 spectrometer, in the frequency range between 250 and 4000 cm^{-1} . The spectral resolution was 0.4 cm^{-1} . The spectra were obtained using a standard pressed-disk technique, after embedding 1 mg of mechanically ground mineral powder in 200 mg of dry KBr and compacting under 2500 N/cm² pressure. Another part of the spectra was recorded using a Fourier-transform Thermo Nicolet Nexus spectrometer, in the frequency range between 400 and 4000 cm^{-1} , using KBr pellets, with a spectral resolution of 1 cm^{-1} . Two mg of gehlenite powder were embedded in this case in 148 mg of KBr. Previous to the IR or FTIR analysis, the material was carefully hand-picked, and the final purity was checked by X-ray powder diffractometry.

The indices of refraction were determined using a conventional JENAPOL-U petrographic microscope with a spindle stage and calibrated immersion liquids (Cargille or temperature-calibrated oils), with a 589-nm interference filter.

CHEMICAL DATA

In addition to the only available result of a bulk wet-chemical analysis of a sample from Măgureaua Vaței (Ștefan *et al.* 1978), there are several EMP analyses (Pascal *et al.* 2001, Marincea *et al.* 2001, Katona *et al.* 2003). Several new EMP analyses were done in order to offer an accurate assessment of the chemical variations at each occurrence. In all but few cases, the back-scattered electron (BSE) imagery reveals that the mineral is compositionally homogeneous. Several spots on the same grain were analyzed first, however, to check the homogeneity of the mineral thoroughly, and several grains were analyzed in the same thin section. Two deviations from the total homogeneity were observed:

(1) Gehlenite from Oravița is nearly homogeneous in (BSE) images, but moderate patchy variations were observed in some samples in the contents of Na *versus* Mg; these variations seem to correspond to the "birefringent spots" observed by Katona *et al.* (2003).

(2) Gehlenite from Cornet Hill and Măgureaua Vaței shows, within individual samples (at the scale of the same thin section), compositional variation that rarely exceeds 5 mol.% of individual end-members and largely stems from compositional zoning. Slight core-to-rim compositional variations may be observed in most of the grains, which generally show an outward increase in the åkermanite component.

Although a significant range of gehlenite compositions is observed at each of the three occurrences, compositional variations within individual samples are much more restricted. The composition of the Cornet



FIG. 2. Photographs of a specimen of blocky gehlenite from Măgureaua Vaței: general image (top) and detail (bottom). The forms recognizable are tetragonal prisms $\{100\}$ terminated with $\{001\}$ pinacoids.

Hill gehlenite was given by Marincea *et al.* (2001); Tables 2 and 3 only give the data for samples from Oravița and Măgureaua Vaței, respectively. The structural formulae, calculated on the basis of 14 oxygen atoms per formula unit (*apfu*), generally display an incomplete tetrahedral occupancy and a slight excess of cations in the octahedral *O* sites, suggesting that some

Ca may be present at the tetrahedral *T* sites (notations after Louisnathan 1971). The compositions in terms of end members were calculated assuming that all of the Mg, Mn and Fe^{2+} is included in åkermanite and all the Na and K is included in sodium melilite. In all cases, the analyzed samples are mostly gehlenite – åkermanite solid solutions, with a limited range of “Na-melilite”

TABLE 2. REPRESENTATIVE COMPOSITIONS OF GEHLENITE FROM ORAVIȚA

| Sample N ⁽¹⁾ | 2289 11 | 2290 9 | 2291 12 | 2307 11 | 2308 11 | 2311 7 | 2312 4 | 2313 6 | 2314 8 | 2333 6 | 2337 13 | 2338 5 |
|--------------------------------|------------|-----------|------------|------------|------------|-----------|-----------|-----------|-----------|-----------|------------|-----------|
| SiO ₂ wt.% | 31.71 | 31.44 | 32.37 | 29.82 | 31.28 | 31.27 | 31.54 | 31.30 | 29.66 | 32.55 | 33.37 | 30.83 |
| TiO ₂ | 0.08 | 0.03 | 0.08 | 0.07 | 0.01 | 0.05 | 0.02 | 0.06 | 0.01 | 0.02 | 0.01 | 0.00 |
| Al ₂ O ₃ | 20.11 | 20.45 | 18.76 | 23.32 | 20.39 | 20.66 | 19.45 | 21.61 | 21.97 | 17.89 | 16.73 | 21.92 |
| FeO ⁽²⁾ | 0.91 | 0.99 | 1.43 | 1.31 | 1.06 | 1.40 | 1.25 | 0.98 | 1.47 | 1.56 | 1.66 | 0.72 |
| MgO | 5.57 | 5.78 | 6.20 | 4.31 | 5.37 | 5.04 | 5.63 | 4.62 | 4.82 | 5.91 | 6.56 | 4.80 |
| MnO | 0.06 | 0.07 | 0.12 | 0.04 | 0.06 | 0.06 | 0.07 | 0.04 | 0.08 | 0.11 | 0.09 | 0.09 |
| CaO | 39.89 | 39.74 | 40.36 | 40.14 | 39.41 | 40.55 | 40.06 | 38.98 | 41.13 | 40.24 | 40.16 | 39.45 |
| Na ₂ O | 0.45 | 0.52 | 0.33 | 0.30 | 0.50 | 0.57 | 0.41 | 0.55 | 0.35 | 0.39 | 0.38 | 0.62 |
| K ₂ O | 0.02 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.03 | 0.03 | 0.01 |
| Total | 98.80 | 99.03 | 99.66 | 99.33 | 98.09 | 99.61 | 98.44 | 98.15 | 99.51 | 98.70 | 98.99 | 98.44 |
| Si <i>apfu</i> | 2.932 | 2.902 | 2.979 | 2.750 | 2.914 | 2.882 | 2.938 | 2.903 | 2.749 | 3.028 | 3.094 | 2.856 |
| Al | 1.068 | 1.098 | 1.021 | 1.250 | 1.086 | 1.118 | 1.062 | 1.097 | 1.251 | 0.972 | 0.906 | 1.144 |
| T sites | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 |
| Ti | 0.006 | 0.002 | 0.006 | 0.005 | 0.001 | 0.003 | 0.001 | 0.004 | 0.001 | 0.001 | 0.001 | 0.000 |
| Al | 1.124 | 1.127 | 1.014 | 1.284 | 1.153 | 1.126 | 1.073 | 1.265 | 1.148 | 0.990 | 0.922 | 1.249 |
| Fe ²⁺ | 0.070 | 0.076 | 0.110 | 0.101 | 0.083 | 0.108 | 0.097 | 0.076 | 0.114 | 0.121 | 0.129 | 0.056 |
| Mg | 0.768 | 0.795 | 0.851 | 0.592 | 0.746 | 0.693 | 0.782 | 0.639 | 0.666 | 0.820 | 0.907 | 0.663 |
| Mn | 0.005 | 0.005 | 0.009 | 0.003 | 0.005 | 0.005 | 0.006 | 0.003 | 0.006 | 0.009 | 0.007 | 0.007 |
| T' sites | 1.973 | 2.005 | 1.990 | 1.985 | 1.988 | 1.935 | 1.959 | 1.987 | 1.935 | 1.941 | 1.966 | 1.975 |
| Ca | 3.952 | 3.930 | 3.979 | 3.965 | 3.934 | 4.005 | 3.997 | 3.874 | 4.084 | 4.011 | 3.990 | 3.916 |
| Na | 0.081 | 0.093 | 0.059 | 0.054 | 0.090 | 0.102 | 0.074 | 0.099 | 0.063 | 0.070 | 0.068 | 0.111 |
| K | 0.002 | 0.001 | 0.001 | 0.002 | 0.001 | 0.001 | 0.001 | 0.001 | 0.002 | 0.004 | 0.004 | 0.001 |
| O sites | 4.035 | 4.024 | 4.039 | 4.021 | 4.025 | 4.108 | 4.072 | 3.974 | 4.149 | 4.085 | 4.062 | 4.028 |
| Σ cations | 10.008 | 10.031 | 10.028 | 10.007 | 10.012 | 10.043 | 10.031 | 9.962 | 10.084 | 10.026 | 10.027 | 10.003 |
| Na-mel % | 2.41 | 2.71 | 1.55 | 1.83 | 2.69 | 2.95 | 2.04 | 3.32 | 1.84 | 1.88 | 1.70 | 3.60 |
| Geh | 56.59 | 55.56 | 51.13 | 64.07 | 57.19 | 57.50 | 54.44 | 62.27 | 58.86 | 50.98 | 47.12 | 61.61 |
| Åk | 37.60 | 38.11 | 41.95 | 29.15 | 36.12 | 34.25 | 38.74 | 30.76 | 33.60 | 41.14 | 44.85 | 32.10 |
| Fe-Åk | 3.40 | 3.62 | 5.37 | 4.95 | 3.99 | 5.30 | 4.77 | 3.64 | 5.70 | 6.00 | 6.33 | 2.68 |

These results were acquired with an electron microprobe. Oxides are first presented in wt.%, then converted to cation numbers on the basis of fourteen atoms of oxygen per formula unit (*apfu*). The compositions are then expressed in terms of end-members (mol.%). (1) Number of point analyses; (2) total iron is expressed as FeO. Note that the symbols Geh and Åk stand for the end-members gehlenite and åkermanite, Ca₂Al(AlSi)O₇ and Ca₂MgSi₂O₇, respectively. These are names of mineral species. The symbols Na-mel and Fe-Åk represent the end-members "Na-melilite" and "Fe-åkermanite", NaCaAlSi₂O₇ and Ca₂FeSi₂O₇, respectively, which are not known as minerals. For this reason, they are used in quotation marks in the text.

and "Fe-åkermanite" (terms as defined compositionally by Nurse & Midgley 1953). Figure 3 summarizes the compositional variation of the mineral in the system CaNaAlSi₂O₇ ("Na-melilite") – Ca₂Al₂SiO₇ (gehlenite) – Ca₂MgSi₂O₇ + Ca₂FeSi₂O₇ (åkermanite + "Fe-åkermanite").

A few remarks must be drawn on the basis of the results in Tables 2 and 3, corroborated with data given by Marincea *et al.* (2001) and the projections in Figure 3: (1) Al at the tetrahedral T' sites (notation after Louisnathan 1971) was found to occur in amounts significantly greater than Mg, which implies that the melilitic samples described herein may all be referred to as gehlenite, which is confirmed by the compositions recast as end members in all but one cases (sample 2337 in Table 2). (2) All the projections in Figure 3 are, more or less, situated along the join gehlenite – åkermanite

+ "Fe-åkermanite", not far from the projections of the melilite from the Ca-rich "type-A" inclusions in the Allende meteorite, given by Grossman (1975) and Deer *et al.* (1986). (3) For the analyzed samples, the solid solutions toward åkermanite + "Fe-åkermanite" vary from Åk_{34.1} to Åk_{51.2} (mean Åk_{41.2}) at Oravița, from Åk_{30.4} to Åk_{42.9} (mean Åk_{38.3}) at Măgureaua Vaței, and from Åk_{24.3} to Åk_{41.7} (mean Åk_{32.9}) at Cornet Hill, respectively. Gehlenite from Oravița exhibits a wider range in composition than gehlenite from other two occurrences (Table 2). Individual crystals from this occurrence exhibit no obvious zoning, but display more significant intergranular ranges in composition, mainly in terms of their Na, Mg and Fe contents. (4) The "Na-melilite" substitution is minor, averaging 2.38 mol.% CaNaAlSi₂O₇ at Oravița, 2.85 mol.% at Măgureaua Vaței, and only 0.70 mol.% at Cornet

Hill. Gehlenite from Cornet Hill has characteristically lower contents in "Na-melilite" than gehlenite from the other two occurrences (Fig. 3). (5) The percentages of "Fe-åkermanite" also is low, ranging from 2.68 to 6.33 mol.% at Oravița (average 4.65 mol.%), from 2.21 to 8.61 mol.% at Măgureaua Vaței (average 5.24 mol.%), and from 1.36 to 4.82 mol.% at Cornet Hill (average 3.44 mol.%). The lowest contents of this end member were recorded in the samples from Cornet Hill, which are generally the closest to the gehlenite end-member.

X-RAY POWDER DATA

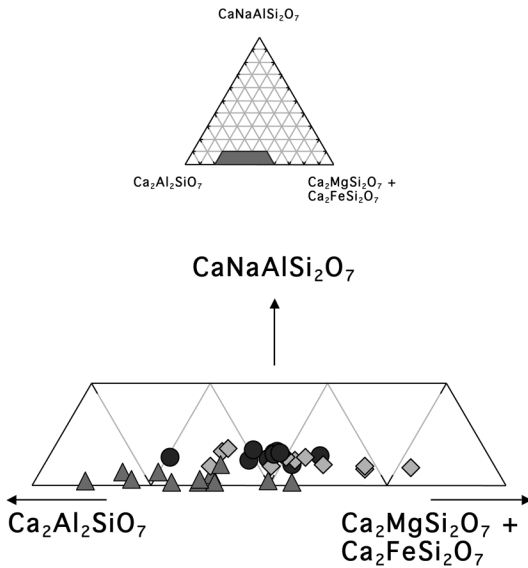
X-ray powder-diffraction patterns of about 50 samples of gehlenite were recorded in order to select the best to be used to calculate the cell parameters. The primary patterns are available upon request from the first author. The cell parameters were successfully

refined on the basis of a tetragonal $P2_1m$ cell, after indexing the patterns in analogy with PDF 74-1607 and 79-2422. Sets of 37 to 53 reflections in the 2θ range between 10° and 80° ($\text{CuK}\alpha$, $\lambda = 1.54056 \text{ \AA}$) for which unambiguous indexing was possible were used to refine the cell dimensions of 27 representative samples; results are summarized in Table 4. The values obtained are highly variable, which may reflect both the differences in chemical composition between the analyzed samples and an anomalous behavior of the cell parameters, characteristic of gehlenite (Gemmi *et al.* 2007). In fact, as observed by Louisnathan (1971), the differences in ($d_{\text{obs.}} - d_{\text{calc.}}$) values and the errors in the refined unit-cell dimensions were, for many samples, too large, and could not be assigned to the variability in chemical composition. This behavior can be correlated with an excess of Si and a deficiency of Al with respect to the Mg content, which implies a defective, non-

TABLE 3. REPRESENTATIVE COMPOSITIONS OF GEHLENITE FROM MĂGUREAUA VAȚEI

| Sample | P 4 | P 48 | 1509 | 1519 | 2125 | 2128 | 2234 | 2317 | 2318 | 2349 |
|--------------------------------|--------|--------|--------|-------|--------|-------|--------|--------|--------|--------|
| N ⁽¹⁾ | 8 | 8 | 4 | 3 | 3 | 3 | 10 | 4 | 3 | 4 |
| SiO ₂ wt. % | 31.26 | 31.21 | 29.46 | 31.64 | 31.75 | 31.73 | 30.03 | 30.71 | 31.25 | 31.14 |
| TiO ₂ | 0.01 | 0.02 | 0.00 | 0.04 | 0.00 | 0.04 | 0.05 | 0.01 | 0.02 | 0.03 |
| Al ₂ O ₃ | 20.84 | 20.66 | 23.96 | 20.65 | 19.56 | 20.62 | 20.69 | 21.74 | 20.86 | 20.73 |
| FeO ⁽²⁾ | 1.63 | 1.36 | 0.83 | 0.60 | 1.16 | 1.39 | 2.20 | 1.83 | 1.58 | 1.27 |
| MgO | 4.86 | 5.06 | 3.99 | 5.84 | 5.79 | 4.61 | 4.14 | 4.51 | 4.88 | 5.07 |
| MnO | 0.07 | 0.04 | 0.03 | 0.01 | 0.07 | 0.08 | 0.31 | 0.04 | 0.05 | 0.06 |
| CaO | 40.31 | 40.41 | 40.29 | 39.69 | 39.51 | 39.66 | 39.68 | 40.38 | 40.39 | 40.33 |
| Na ₂ O | 0.54 | 0.57 | 0.44 | 0.38 | 0.56 | 0.41 | 0.39 | 0.62 | 0.57 | 0.59 |
| K ₂ O | 0.04 | 0.06 | 0.01 | 0.00 | 0.01 | 0.02 | 0.13 | 0.03 | 0.05 | 0.06 |
| Total | 99.56 | 99.39 | 99.01 | 98.85 | 98.41 | 98.56 | 97.62 | 99.87 | 99.65 | 99.28 |
| Si <i>apfu</i> | 2.883 | 2.882 | 2.722 | 2.915 | 2.951 | 2.942 | 2.842 | 2.828 | 2.880 | 2.878 |
| Al | 1.117 | 1.118 | 1.278 | 1.085 | 1.049 | 1.058 | 1.158 | 1.172 | 1.120 | 1.122 |
| T sites | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 |
| Ti | 0.001 | 0.001 | 0.000 | 0.003 | 0.000 | 0.003 | 0.003 | 0.001 | 0.001 | 0.002 |
| Al | 1.148 | 1.131 | 1.331 | 1.157 | 1.094 | 1.195 | 1.150 | 1.187 | 1.146 | 1.136 |
| Fe ²⁺ | 0.125 | 0.105 | 0.064 | 0.046 | 0.090 | 0.108 | 0.174 | 0.141 | 0.122 | 0.098 |
| Mg | 0.667 | 0.697 | 0.549 | 0.802 | 0.802 | 0.637 | 0.583 | 0.619 | 0.670 | 0.699 |
| Mn | 0.005 | 0.003 | 0.002 | 0.001 | 0.006 | 0.006 | 0.024 | 0.003 | 0.004 | 0.005 |
| T' sites | 1.948 | 1.939 | 1.946 | 2.009 | 1.992 | 1.949 | 1.934 | 1.950 | 1.943 | 1.940 |
| Ca | 3.982 | 3.998 | 3.988 | 3.918 | 3.935 | 3.940 | 4.023 | 3.984 | 3.988 | 3.994 |
| Na | 0.097 | 0.102 | 0.079 | 0.068 | 0.101 | 0.074 | 0.071 | 0.111 | 0.102 | 0.106 |
| K | 0.004 | 0.007 | 0.001 | 0.000 | 0.001 | 0.002 | 0.016 | 0.004 | 0.006 | 0.007 |
| O sites | 4.083 | 4.107 | 4.068 | 3.986 | 4.037 | 4.016 | 4.110 | 4.099 | 4.096 | 4.107 |
| Σ cations | 10.031 | 10.046 | 10.014 | 9.995 | 10.029 | 9.965 | 10.044 | 10.049 | 10.039 | 10.047 |
| Na-mel % | 2.96 | 3.14 | 2.69 | 2.02 | 2.86 | 2.37 | 2.53 | 3.46 | 3.15 | 3.27 |
| Geh | 58.10 | 57.52 | 66.95 | 57.10 | 54.26 | 60.54 | 58.83 | 59.61 | 58.04 | 57.67 |
| Åk | 32.83 | 34.21 | 27.20 | 38.66 | 38.59 | 31.75 | 30.03 | 30.11 | 32.86 | 34.29 |
| Fe-Åk | 6.11 | 5.13 | 3.16 | 2.21 | 4.30 | 5.33 | 8.61 | 6.82 | 5.95 | 4.77 |

These results were acquired with an electron microprobe. Oxides are first presented in wt.%, then converted to cation numbers on the basis of fourteen atoms of oxygen per formula unit (*apfu*). The compositions are then expressed in terms of end-members (mol.%). (1) Number of point analyses; (2) total iron is expressed as FeO. Note that the symbols Geh and Åk stand for the end-members gehlenite and åkermanite, Ca₂Al(AlSi)O₇ and Ca₂MgSi₂O₇, respectively. These are names of mineral species. The symbols Na-mel and Fe-Åk represent the end-members "Na-melilite" and "Fe-åkermanite", NaCaAlSi₂O₇ and Ca₂FeSi₂O₇, respectively, which are not known as minerals. For this reason, they are used in quotation marks in the text.



stoichiometric structure with Ca vacancies, as observed by Gemmi *et al.* (2007).

It seems clear, however, that there is a certain degree of correlation between chemical attributes and cell parameters. Studies of synthetic material reported by Ervin & Osborn (1949), Christie (1962), Edgar (1965) and Henmi (1976) show that from gehlenite to åkermanite, the *a* parameter increase and the *c* parameter decreases. On the other hand, the increasing contents of “Na-melilite” decrease both the *a* and *c* cell parameters, the decrease in *a* being more evident (Edgar 1965). The unit-cell volume increases from gehlenite

FIG. 3. Triangular diagram showing the compositional range of gehlenite from the Romanian occurrences in terms of the “Na-melilite” – gehlenite – åkermanite + “Fe-åkermanite” solid-solution series. Samples from Oravița (diamonds), Măgureaua Vaței (dots) and Cornet Hill (triangles).

TABLE 4. CRYSTALLOGRAPHIC VERSUS CHEMICAL PARAMETERS IN ROMANIAN GEHLENITE

| Sample | <i>a</i> (Å) | <i>c</i> (Å) | <i>V</i> (Å ³) | Fe-Åk | Åk | Na-mel | <i>k</i> | N ⁽¹⁾ |
|------------------------|--------------|--------------|----------------------------|-------|-------|--------|----------|------------------|
| Oravița | | | | | | | | |
| 2290 | 7.734(3) | 5.045(2) | 301.8(2) | 3.62 | 38.11 | 2.71 | 0.255 | 48 |
| 2291 | 7.722(3) | 5.051(3) | 301.2(2) | 5.37 | 41.95 | 1.55 | 0.299 | 48 |
| 2307 | 7.679(3) | 5.065(3) | 298.7(2) | 4.95 | 29.15 | 1.83 | 0.211 | 48 |
| 2308 | 7.722(3) | 5.054(3) | 301.3(3) | 3.99 | 36.12 | 2.69 | 0.245 | 42 |
| 2311 | 7.702(2) | 5.043(2) | 299.1(2) | 5.30 | 34.25 | 2.95 | 0.240 | 37 |
| 2312 | 7.691(1) | 5.056(1) | 299.1(1) | 4.77 | 38.74 | 2.04 | 0.271 | 40 |
| 2313 | 7.697(1) | 5.049(1) | 299.1(1) | 3.64 | 30.76 | 3.32 | 0.204 | 40 |
| 2329 | 7.712(3) | 5.044(2) | 300.0(2) | - | - | - | - | 39 |
| 2332 | 7.714(1) | 5.050(1) | 300.5(6) | - | - | - | - | 44 |
| 2333 | 7.705(1) | 5.050(1) | 299.8(7) | 6.00 | 41.14 | 1.88 | 0.296 | 40 |
| Măgureaua Vaței | | | | | | | | |
| P 4 | 7.718(3) | 5.049(2) | 300.7(1) | 6.11 | 32.83 | 2.96 | 0.236 | 40 |
| P 27 | 7.683(4) | 5.063(3) | 298.8(3) | - | - | - | - | 40 |
| P 48 | 7.690(3) | 5.060(2) | 299.2(2) | 5.13 | 34.21 | 3.14 | 0.238 | 41 |
| 1509 | 7.713(2) | 5.043(1) | 300.0(1) | 3.16 | 27.20 | 2.69 | 0.182 | 44 |
| 1519 | 7.693(3) | 5.070(3) | 300.0(2) | 2.21 | 38.66 | 2.02 | 0.254 | 49 |
| 2125 | 7.735(1) | 5.040(1) | 301.5(1) | 4.30 | 38.59 | 2.86 | 0.262 | 48 |
| 2128 | 7.717(2) | 5.045(1) | 300.4(1) | 5.33 | 31.75 | 2.37 | 0.228 | 53 |
| 2234 | 7.687(3) | 5.063(3) | 299.2(1) | 8.61 | 30.03 | 2.53 | 0.237 | 40 |
| 2317 | 7.727(2) | 5.040(1) | 300.9(1) | 6.82 | 30.11 | 3.46 | 0.220 | 48 |
| 2318 | 7.712(2) | 5.045(1) | 300.1(1) | 5.95 | 32.86 | 3.15 | 0.234 | 38 |
| Cornet Hill | | | | | | | | |
| P 57 | 7.733(1) | 5.050(1) | 302.0(4) | 1.36 | 33.64 | 1.96 | 0.216 | 43 |
| 2160 | 7.684(3) | 5.061(2) | 298.8(4) | - | - | - | - | 42 |
| 2167 | 7.687(4) | 5.067(4) | 299.4(2) | 2.06 | 24.88 | 1.31 | 0.168 | 39 |
| 2264 | 7.708(2) | 5.054(2) | 300.3(2) | - | - | - | - | 51 |
| 2300 | 7.730(1) | 5.044(1) | 301.4(1) | 4.57 | 30.71 | 0.21 | 0.229 | 51 |
| 2301 | 7.728(1) | 5.044(1) | 301.2(5) | - | - | - | - | 50 |
| 2315 | 7.696(3) | 5.058(2) | 299.5(2) | 3.86 | 37.87 | 0.30 | 0.270 | 48 |

(1): number of lines used for refinements.

to åkermanite (Ervin & Osborn 1949, Charlu *et al.* 1981) and decreases with the content of “Na-melilite” (Edgar 1965).

It appears that the influence of the chemical composition of gehlenite on its cell parameters may be better described by using four mean ionic radii calculated as averages of the ionic radius of the specific cations entering the structural sites in each end-member. These specific radii could be expressed as:

$$r_{\text{Na-mel}} = (r^{\text{VIII}}\text{Na} + r^{\text{IV}}\text{Al} + r^{\text{IV}}\text{Si})/3 = 0.61 \text{ \AA};$$

$$r_{\text{Geh}} = (r^{\text{VIII}}\text{Ca} + 2 r^{\text{IV}}\text{Al})/3 = 0.633 \text{ \AA};$$

$$r_{\text{Åk}} = (r^{\text{VIII}}\text{Ca} + r^{\text{IV}}\text{Mg} + r^{\text{IV}}\text{Si})/3 = 0.65 \text{ \AA};$$

$$r_{\text{Fe-Åk}} = (r^{\text{VIII}}\text{Ca} + r^{\text{IV}}\text{Fe}^{2+} + r^{\text{IV}}\text{Si})/3 = 0.67 \text{ \AA}.$$

The calculations were carried out using the ionic radii given by Shannon (1976) for the cations involved ($r^{\text{VIII}}\text{Na} = 1.18 \text{ \AA}$, $r^{\text{IV}}\text{Al} = 0.39 \text{ \AA}$, $r^{\text{IV}}\text{Si} = 0.26 \text{ \AA}$, $r^{\text{VIII}}\text{Ca} = 1.12 \text{ \AA}$, $r^{\text{IV}}\text{Mg} = 0.57 \text{ \AA}$ and $r^{\text{IV}}\text{Fe}^{2+} = 0.63 \text{ \AA}$). The differences between the mean specific radius of the gehlenite end-member and that of “Na-melilite” on the one hand and “Fe-åkermanite” on the other are the largest, suggesting that the maximal influence in changing the reticular parameters increases with the “Na-melilite” and “Fe-åkermanite” substitutions.

Using the mean specific radii and the percentages in the end-members, we could calculate the comprehensive factor k as an expression of the difference in the steric hindrance between the cations defining the åkermanite-type substitution and the cations determining the “Na-melilite”-type substitution in gehlenite. The value of k can be calculated as:

$$k = [(\text{mol.}\% \text{ “Fe-åkermanite”}) \cdot r_{\text{Fe-Åk}} + (\text{mol.}\% \text{ åkermanite}) \cdot r_{\text{Åk}} - (\text{mol.}\% \text{ “Na-melilite”}) \cdot r_{\text{Na-mel}}]/100 (\%)$$

Values of k for all but six samples considered here are given in Table 4, together with their cell parameters. Imagining sets of binary diagrams $a-k$, $c-k$ and $V-k$, respectively, a few conclusions may be drawn on the basis of the data in the table.

The cell parameter a decreases very slightly with k , the correlation coefficient being -0.04 . In fact, a remains practically constant within experimental errors. For the three populations of samples in Table 4, the trend is clearly decreasing for the samples from Oravița and Măgureaua Vaței and apparently increasing for the samples from Cornet Hill, where the number of projections is significantly low. In conclusion, the influence of the åkermanite substitution in the decrease of a is practically equivalent to the opposite influence of “Na-melilite”.

The decrease in c with increasing k is more evident (correlation coefficient -0.06), but is also practically

obscured if the experimental errors are taken into consideration. The data seem also contradictory since the c versus k trend is decreasing for the samples from Oravița and Cornet Hill and apparently increasing from the samples from Măgureaua Vaței, which also changes into a negative correlation if the outliers are removed. The influence of “Na-melilite” in the decrease of c thus is to be added to the influence of åkermanite, but their combined influence is not important.

There is a clear positive correlation between V and k , which is better depicted in Figure 4. The correlation coefficient is $+0.18$, implying that the influence of the åkermanite content in the solid solution on the increasing of the cell volume prevails over the opposite influence of “Na-melilite”.

Strong deviations from the ideal regression line may be observed in all cases. An explanation for this behavior is that the defective structure with Ca vacancies of the gehlenite samples analyzed by us considerably influences the refinement of their cell parameters.

OPTICAL AND PHYSICAL PROPERTIES

In all three occurrences, gehlenite shows a macroscopic color that varies from dark gray to bluish gray. The mineral is colorless to pale yellow in thin section, the color being most intense in the samples from Oravița. Anomalous interference-colors, in tints of bluish grey and Berlin blue, were very rarely observed in samples from Măgureaua Vaței and Oravița. The mineral is uniaxial negative, even in the åkermanite-rich samples from Oravița. The measured indices of refraction of representative samples approaching the

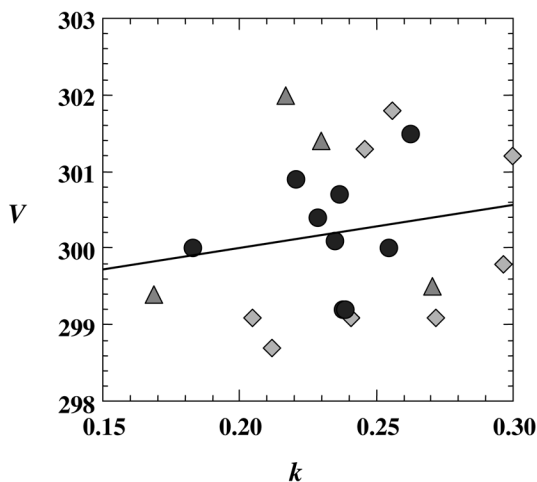


FIG. 4. Diagram showing the correlation between the cell volume V and the chemical-structural factor k . Symbols as in Figure 3.

mean composition are given in Table 5. They were used to calculate the mean indices of refraction to be used in the Gladstone–Dale computations [$\bar{n} = (2\omega + \varepsilon)/3$] (Table 5). The measured indices of refraction are relatively close to those given for the stoichiometric gehlenite [$\omega = 1.669$ and $\varepsilon = 1.658$: Nurse & Midgley (1953), Kolesova & Ismatov (1971) and Deer *et al.* (1986)] and suggest a composite influence of substitutions of $2 \text{ Al} \leftrightarrow \text{Mg} + \text{Si}$ and $\text{Ca} + \text{Al} \leftrightarrow \text{Na} + \text{Si}$ type (resulting in decreasing indices of refraction) and 2 Al

$\leftrightarrow \text{Fe}^{2+}(\text{Mn}^{2+}) + \text{Si}$ (resulting in increasing indices of refraction, as established by Nurse & Midgley 1953).

The densities of representative samples of gehlenite were measured on fine-grained micromounts, using a Berman balance and toluene as displacement fluid (Table 5). The calculated densities (D_x) of another 21 samples were obtained on the basis of chemical data (Marincea *et al.* 2001, Tables 2 and 3) and of unit-cell volumes (Table 6), for $Z = 2$ formula units per cell (Deer *et al.* 1986). The measured densities are in good agreement with the calculated values. The densities of samples are very similar with the values reported by Kolesova & Ismatov (1971) and Deer *et al.* (1986) for natural gehlenite: $3.02 < D < 3.07 \text{ g/cm}^3$.

Calculations using the Gladstone–Dale relationship and the constants of Mandarino (1981), result in excellent compatibility-indices for the samples from Măgureaua Vaței and only good compatibility-indices for the samples from Cornet Hill, whereas the samples from Oravița have, in all but two cases (which are excellent), superior compatibility-indices on the scale of Mandarino (1981), recorded in Table 6. The use of

TABLE 5. PHYSICAL PARAMETERS OF GEHLENITE

| Occurrence | Oravița | Măgureaua Vaței | Cornet Hill |
|----------------------------|----------|-----------------|-------------|
| Sample | 2290 | 2234 | 2167 |
| ω | 1.644(1) | 1.655(1) | 1.660(2) |
| ε | 1.640(1) | 1.651(1) | 1.655(1) |
| D_m (g/cm ³) | 3.020(5) | 3.064(2) | 3.065(2) |
| \bar{n} | 1.643 | 1.654 | 1.658 |

TABLE 6. CALCULATED PHYSICAL PARAMETERS OF SELECTED SAMPLES OF GEHLENITE FROM ROMANIA

| Sample | $M^{(1)}$ | $V^{(2)}$ | D_x | K_C | D'_x (3) | \bar{n}_x (4) | K_p (5) | $1-(K_p/K_C)$ |
|------------------------|-----------|-----------|-------|--------|------------|-----------------|-----------|---------------|
| Oravița | | | | | | | | |
| 2290 | 549.158 | 301.8 | 3.021 | 0.2079 | 3.093 | 1.628 | 0.2129 | -0.024 |
| 2291 | 551.048 | 301.2 | 3.037 | 0.2079 | 3.093 | 1.631 | 0.2117 | -0.018 |
| 2307 | 550.268 | 298.7 | 3.058 | 0.2080 | 3.091 | 1.636 | 0.2103 | -0.011 |
| 2308 | 549.117 | 301.3 | 3.025 | 0.2079 | 3.093 | 1.629 | 0.2125 | -0.022 |
| 2311 | 551.678 | 299.1 | 3.062 | 0.2079 | 3.093 | 1.637 | 0.2100 | -0.010 |
| 2312 | 550.854 | 299.1 | 3.057 | 0.2079 | 3.093 | 1.636 | 0.2103 | -0.012 |
| 2313 | 546.971 | 299.1 | 3.036 | 0.2080 | 3.091 | 1.631 | 0.2118 | -0.018 |
| 2333 | 551.729 | 299.8 | 3.055 | 0.2078 | 3.094 | 1.635 | 0.2105 | -0.013 |
| Măgureaua Vaței | | | | | | | | |
| P 4 | 551.575 | 300.7 | 3.045 | 0.2078 | 3.147 | 1.633 | 0.2148 | -0.034 |
| P 48 | 551.491 | 299.2 | 3.060 | 0.2078 | 3.147 | 1.636 | 0.2137 | -0.029 |
| 1509 | 549.557 | 300.0 | 3.041 | 0.2080 | 3.144 | 1.633 | 0.2151 | -0.034 |
| 1519 | 547.210 | 300.0 | 3.028 | 0.2080 | 3.144 | 1.630 | 0.2160 | -0.038 |
| 2125 | 549.618 | 301.5 | 3.026 | 0.2078 | 3.147 | 1.629 | 0.2161 | -0.040 |
| 2128 | 549.090 | 300.4 | 3.034 | 0.2079 | 3.146 | 1.631 | 0.2155 | -0.037 |
| 2234 | 554.933 | 299.2 | 3.079 | 0.2078 | 3.147 | 1.640 | 0.2124 | -0.022 |
| 2317 | 552.586 | 300.9 | 3.048 | 0.2078 | 3.147 | 1.633 | 0.2145 | -0.032 |
| 2318 | 551.802 | 300.1 | 3.052 | 0.2078 | 3.147 | 1.634 | 0.2143 | -0.031 |
| Cornet Hill | | | | | | | | |
| P 57 | 547.973 | 302.0 | 3.012 | 0.2080 | 3.163 | 1.627 | 0.2185 | -0.050 |
| 2167 | 543.543 | 299.4 | 3.014 | 0.2082 | 3.160 | 1.627 | 0.2183 | -0.049 |
| 2300 | 549.327 | 301.4 | 3.025 | 0.2079 | 3.165 | 1.629 | 0.2175 | -0.046 |
| 2315 | 550.621 | 299.5 | 3.052 | 0.2079 | 3.165 | 1.634 | 0.2156 | -0.037 |

(1) molecular mass, as calculated on the basis of electron-microprobe analyses, (2) unit-cell volume (in Å³), as deduced from least-squares refinement of X-ray powder data, (3) calculated according to Gladstone–Dale law, using the mean index of refraction (Table 5) and the chemical molar refractivity (K_C), (4) $\bar{n}_x = D_x \cdot K_C + 1$; (5) $K_p = (\bar{n} - 1)/D_x$.

a single value for the mean index of refraction, as well as the optical anomalies recorded in the melilite group (Deer *et al.* 1986), clearly result in systematic errors when applying the Gladstone–Dale approach. The anomalous behavior of the cell volume of compositions close to the gehlenite end-member (Deer *et al.* 1986) could result in appreciable errors in applying the Gladstone–Dale relation.

INFRARED ABSORPTION DATA

Figure 5 displays the FTIR absorption spectra obtained for three representative samples of gehlenite from Oravița, Măgureaua Vaței and Cornet Hill, respectively, whereas Table 7 gives the wavenumbers, characters and intensities of the infrared absorption bands recorded for many samples, as well as attempts

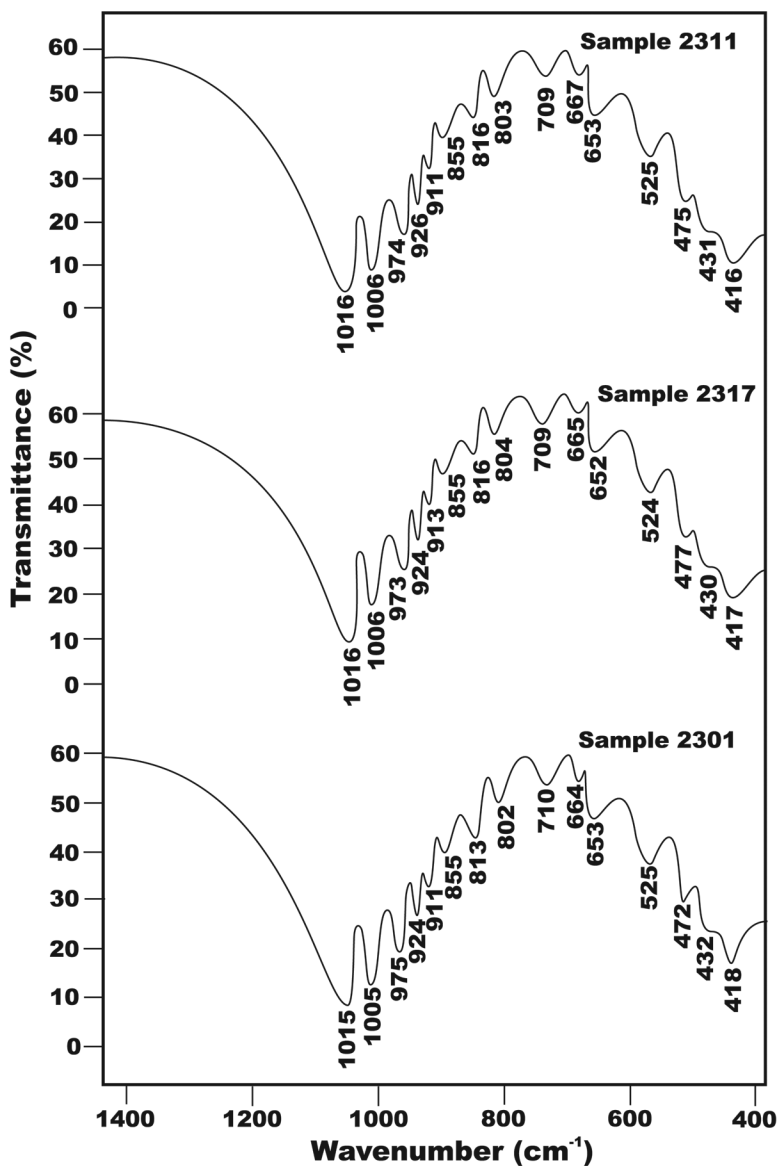


FIG. 5. FTIR spectra of three representative samples of gehlenite from high-temperature skarns in Romania. Samples from Oravița (top), Măgureaua Vaței (middle) and Cornet Hill (bottom).

to assign the bands. The primary records are available upon request from the first author.

Factor-group analysis shows that the D_{2d} crystal symmetry of gehlenite, which implies (3N-3) optic modes, must generate 34 infrared- and 43 Raman-active modes, as follows (Sharma *et al.* 1983):

$$\Gamma = 10A_1 (R) + 6A_2 (IR) + 7B_1 (R) + 10B_2 (R, IR) + 18E (R, IR)$$

If we accept the lowering of the crystal symmetry from D_{2d} to S_4 due to the disorder occupancy at one of the C_s sites, which statistically accommodates either a Si or an Al ion, as mentioned by Burshein *et al.* (1993), we could theoretically expect no less than 35 infrared- and 51 Raman-active modes.

Only up to 17 of the 34 or 35 expected infrared-active modes were detected, however, in the infrared absorption spectra recorded between 400 and 1600 or 4000 cm^{-1} by various authors (*e.g.*, Moenke 1966, Sahama & Lehtinen 1967, Kolesova & Ismatov 1971, Ștefan *et al.* 1978, Burshein *et al.* 1993, Chihara *et al.* 2007). The infrared absorption spectra recorded by

us between 250 and 4000 cm^{-1} contain 23 absorption bands, whose tentative assignments are given in Table 7 and generally agree with those given by Burshein *et al.* (1993). The absences, which may be due to accidental degeneracies of some modes, their weak intensities, or both, were also observed on our FTIR spectra. Overlaps of some bands owing to the nonstoichiometry of the natural samples are not excluded. Regarding the spectra, a few remarks are considered to be important.

Although both the mineral powder and the KBr were previously stored in a desiccator, many of the IR and FTIR spectra show absorption bands due to molecular water (Table 7). This may be due to the adsorbed water, whose occurrence is quite normal in the very fine-grained samples analyzed by us, with large specific surfaces, or to the presence of molecular H_2O in their structure. In fact, small amounts of gehlenite hydrate could easily form at room temperature by reactions involving the alteration products of gehlenite (Kuzel 1976, and references therein) and can be admixed with our material. Note that Moenke (1966) also recorded the presence of a band attributable to the fundamental H-O-H stretching of molecular water, at $\sim 3430\text{ cm}^{-1}$,

TABLE 7. POSITIONS AND TENTATIVE ASSIGNMENTS OF THE INFRARED ABSORPTION BANDS RECORDED FOR SELECTED SAMPLES OF GEHLENITE FROM THE THREE ROMANIAN OCCURRENCES VERSUS SIMILAR DATA IN LITERATURE*

| Oravița | | Măgureaua Vaței | | Cornet Hill | | Moenke K & I (1966) I (1971) | | Vibrational mode | Structural group | Ch | I |
|-------------------|---------------------|-------------------|---------------------|-------------------|---------------------|------------------------------|------------------|----------------------------------|-------------------------------------|----|----|
| IR ⁽¹⁾ | FTIR ⁽²⁾ | IR ⁽³⁾ | FTIR ⁽⁴⁾ | IR ⁽⁵⁾ | FTIR ⁽⁶⁾ | | | | | | |
| - | 3447(5) | 3440 | 3427(19) | 3440 | 3416(17) | 3430 | — ⁽⁷⁾ | vH-OH | H ₂ O ⁽⁹⁾ | vb | m |
| - | 1622(9) | 1568 | 1627(7) | 1620 | 1633(7) | - | — ⁽⁷⁾ | δH-OH | H ₂ O ⁽⁹⁾ | vb | m |
| 1020 | 1016(1) | 1020 | 1016(1) | 1025 | 1015(1) | 1020 | 1023 | ν_{as} Si-O-Si | (Si,Al) ₂ O ₇ | sh | vs |
| 1010 | 1006(1) | 1000 | 1006(1) | 1008 | 1005(1) | - | - | ν_{as} Si-O-Al | (Si,Al) ₂ O ₇ | sh | vs |
| 975 | 974(1) | 970 | 973(1) | 975 | 975(1) | 980 | 976 | ν_{as} (Si,Al)O ₃ | (Si,Al) ₂ O ₇ | sh | vs |
| 916 | 926(1) | 940 | 924(1) | 925 | 924(1) | 922 | 921 | ν_{as} (Si,Al)O ₃ | (Si,Al) ₂ O ₇ | sh | vs |
| 905 | 911(1) | 912 | 913(2) | 910 | 911(3) | 880 | 890 | ν_s (Si,Al)O ₃ | (Si,Al)O ₇ | b | vs |
| 854 | 855(1) | 856 | 855(1) | 855 | 855(2) | 860 | 863 | ν_{as} Al-O-Al | AlO ₄ (?) | sh | vs |
| 820 | 816(1) | 815 | 815(1) | 815 | 813(1) | 815 | - | ν_s (Si,Al)O ₃ | (Si,Al) ₂ O ₇ | sh | vs |
| 808 | 803(2) | 802 | 804(1) | 800 | 802(2) | - | 803 | ν_s (Si,Al)O ₃ | (Si,Al) ₂ O ₇ | sh | vs |
| 712 | 709(2) | 715 | 709(2) | 712 | 710(2) | 715 | 714 | ν_s Si-O-Al | (Si,Al) ₂ O ₇ | b | w |
| 670 | 667(6) | 670 | 665(1) | 670 | 664(1) | 675 | 685 | ν_s Al-O-Al | AlO ₄ (?) | sh | w |
| 660 | 653(4) | 662 | 652(4) | 655 | 653(1) | - | 647 | ν_s Si-O-Si | (Si,Al) ₂ O ₇ | sh | m |
| 525 | 525(1) | 527 | 524(1) | 525 | 525(2) | 527 | 530 | δ_s Si-O-Al(?) | (Si,Al) ₂ O ₇ | sh | m |
| 478 | 475(2) | 478 | 476(3) | 478 | 472(4) | 485 | 480 | — ⁽¹⁰⁾ | | b | vs |
| 434 | 431(1) | 435 | 431(1) | 430 | 432(1) | 435 | 432 | — ⁽¹⁰⁾ | | i | vs |
| 416 | 416(1) | 418 | 417(1) | 415 | 418(1) | 420 | 415 | δ_s Si-O-Al(?) | (Si,Al) ₂ O ₇ | b | vs |
| 390 | — ⁽⁸⁾ | 388 | — ⁽⁸⁾ | 390 | — ⁽⁸⁾ | — ⁽⁸⁾ | — ⁽⁸⁾ | Ca(?)O | CaO ₈ (?) | sh | s |
| 378 | - | - | - | 372 | - | - | - | — ⁽¹⁰⁾ | | sh | w |
| 340 | - | 340 | - | 340 | - | - | - | — ⁽¹⁰⁾ | | b | m |
| 307 | - | 310 | - | 303 | - | - | - | Ca(?)O | CaO ₈ (?) | sh | w |
| 290 | - | 284 | - | 290 | - | - | - | — ⁽¹⁰⁾ | | sh | m |
| 272 | - | 272 | - | 270 | - | - | - | — ⁽¹⁰⁾ | | sh | m |

* Wavenumbers in cm^{-1} . Abbreviations represent: vb: very broad, b: broad, sh: sharp, i: inflexion, vs: very strong, s: strong, m: medium, w: weak, ν_s : symmetric stretching, ν_{as} : antisymmetric stretching, δ_s : in-plane bending, δ_{as} : out-of-plane bending. Moenke: Moenke (1966), K & I: Kolesova & Ismatov (1971), Ch: character, I: intensity.

(1) sample 2311; (2) analyzed samples: 2290, 2307, 2311, 2312; (3) sample 2234; (4) analyzed samples: 1509, 1519, 2125, 2128, 2317; (5) sample 2301; (6) analyzed samples: 2264, 2300, 2301, 2315; (7) not recorded before 1200 cm^{-1} ; (8) not recorded below 400 cm^{-1} ; (9) molecular water; (10) composite, mainly lattice vibrations.

but the equivalent bending (at $\sim 1600\text{ cm}^{-1}$) was not reported.

The very intense complex of bands between 800 and 1050 cm^{-1} groups, mainly $T\text{--}O\text{--}T$ stretching (where T is a four-fold coordinated Si or Al) involves the bridging oxygen of the pyrosilicate anions or the "lateral" (Si,Al) O_3 groups. The band at $\sim 855\text{ cm}^{-1}$, considered by Sahama & Lehtinen (1967) as characteristic of the gehlenite-rich members of the melilite solid-solutions, could reasonably be attributed to the Al–O–Al antisymmetric stretching. Another band, at $\sim 670\text{ cm}^{-1}$, may be assigned to the Al–O–Al symmetric stretching, as the (AlO $_4$) tetrahedra with point symmetry $\bar{4}$ are present in the structure of gehlenite (Louisnathan 1971).

The splitting of the complex of absorption bands centered at about 950 cm^{-1} , considered as very sensitive to chemical substitutions by Chihara *et al.* (2007), does not afford any distinction between the åkermanite-rich compositions from Oravița and the samples from the other two occurrences.

The absorption bands between 400 and 550 cm^{-1} could not be unequivocally assigned owing to the superposition of lattice modes and Si–O–Al bend, but at least two of the bands in the region must be due to vibrations involving four-fold coordinated Al. The same uncertainty concerns the assumption of the bands due to Ca–O vibrations involving the CaO $_8$ polyhedra in the structure, but at least two of the bands in the spectral region between 200 and 400 cm^{-1} are due to such vibrations.

ACKNOWLEDGEMENTS

This work was financed by the National Authority for Scientific Research in Romania through the projects 31–030/2007, 31–063/2007, 91–017/2007 and 58/2008. The research was also supported by the cooperative MECI – CGRI research program between the Romanian and the Walloon governments, under the Project 2.11/2007 and by a TEMPRA grant awarded to the senior author by the Rhône-Alpes Region in 1999–2000. Fruitful discussions on the field with Jean Verkaeren, Marie-Lola Pascal, Essaïd Bilal and Régis Piret are highly appreciated. Thanks are due to Messrs. Hubert Rémy, Michel Fialin and to Mrs. Claudine Richard (CNRS, Université Paris VI) for advice on the use of the electron microprobe, to Mr. Jean Naud (Université Catholique de Louvain) for part of the X-ray powder-diffraction work, and to Miss Gabriela Stelea (GIR, Bucharest) for part of the infrared work. Mr. Régis Piret (Université Catholique de Louvain) kindly communicated some of the XRD and EMP analyses used for this study. The quality of this contribution was improved after reviews by Drs. Marie-Lola Pascal and Mehmet Taner. Associate Editor Tassos Grammatikopoulos is gratefully acknowledged for handling the manuscript.

REFERENCES

- APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv., Comput. Contrib.* **20** (NTIS Doc. **PB-216188**).
- BENOIT, P.H. (1987): Adaptation to microcomputer of the Appleman–Evans program for indexing and least-squares refinement of powder-diffraction data for unit-cell dimensions. *Am. Mineral.* **72**, 1018–1019.
- BURSHAIN, Z., SHIMONY, Y., MORGAN, S., HENDERSON, D.O., MU, R. & SILBERMAN, E. (1993): Symmetry lowering due to the site-occupation disorder in vibrational spectra of gehlenite, Ca $_2$ (Al,Si)AlO $_7$. *J. Phys. Chem. Solids* **54**, 1043–1049.
- CHARLU, T.V., NEWTON, R.C. & KLEPPA, O.J. (1981): Thermochemistry of synthetic Ca $_2$ Al $_2$ SiO $_7$ (gehlenite) – Ca $_2$ MgSi $_2$ O $_7$ (åkermanite) melilites. *Geochim. Cosmochim. Acta* **45**, 1609–1617.
- CHIHARA, H., KOIKE, C. & TSUCHIYAMA, A. (2007): Compositional dependence of infrared absorption spectra of crystalline silicates. III. Melilite solid solution. *Astronomy & Astrophys.* **464**, 229–234.
- CHRISTIE, O.H.J. (1962): On sub-solidus relations of silicates. III. A contribution to the chemistry of melilites. *Norsk Geol. Tidsskr.* **42**, 1–29.
- CIOFLICA, G. & VLAD, Ș. (1973): The correlation of the Laramian metallogenic events belonging to the Carpatho-Balkan area. *Rev. Roum. Géol., Géophys., Géogr., sér. Géol.* **17**, 217–224.
- CONSTANTINESCU, E., ILINCA, G. & ILINCA, A. (1988): Contributions to the study of the Oravița–Ciclova skarn occurrence, southwestern Banat. *D.S. Inst. Geol. Geofiz.* **72-73/2**, 27–45.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1986): *Rock-Forming Minerals. 1B. Disilicates and Ring Silicates* (second ed.). Longman, London, U.K. (285–334).
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1992): *An Introduction to the Rock-Forming Minerals* (second ed.). Longman, Hong Kong.
- DUPONT, A., VANDER AUWERA, J., PIN, C., MARINCEA, Ș. & BERZA, T. (2002): Trace element and isotope (Sr, Nd) geochemistry of porphyry- and skarn-mineralising Late Cretaceous intrusions from Banat, western South Carpathians, Romania. *Mineral. Deposita* **37**, 568–586.
- EDGAR, A.D. (1965): Lattice parameters of melilite solid solutions and a reconnaissance of phase relations in the system Ca $_2$ Al $_2$ SiO $_7$ (gehlenite) – Ca $_2$ MgSi $_2$ O $_7$ (åkermanite) – NaCaAlSi $_2$ O $_7$ (soda melilite) at 1000 kg/cm 2 water vapor pressure. *Can. J. Earth. Sci.* **2**, 596–621.
- ERVIN, G., JR. & OSBORN, E.F. (1949): X-ray data on synthetic melilites. *Am. Mineral.* **34**, 717–722.

- GEMMI, M., MERLINI, M., CRUCIANI, G. & ARTIOLI, G. (2007): Non-ideality and defectivity of the åkermanite–gehlenite solid solution: an X-ray diffraction and TEM study. *Am. Mineral.* **92**, 1685–1694.
- GROSSMAN, L. (1975): Petrography and mineral chemistry of Ca-rich inclusions in the Allende meteorite. *Geochim. Cosmochim. Acta* **39**, 433–454.
- HENMI, C. (1976): Synthesis of bicchulite from gehlenite solid solution. *Mineral. J.* **8**, 171–183.
- HOSCHEK, G. (1974): Gehlenite stability in the system CaO–Al₂O₃–SiO₂–H₂O–CO₂. *Contrib. Mineral. Petrol.* **47**, 245–254.
- ILINCA, G., MARINCEA, Ș., RUSSO-SĂNDULESCU, D., IANCU, V. & SEGHEDI, I. (1993): Mineral occurrences in southwestern Banat, Romania. *Rom. J. Mineral.* **76**, Suppl. 2, 1–39.
- ISTRATE, G., ȘTEFAN, A. & MEDEȘAN, A. (1978): Spurrite and tilleyite in the Cornet Hill, Apuseni Mountains, Romania. *Rev. Roum. Géol., Géoph., Géogr., sér. Géol.* **22**, 143–153.
- 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.
- KATONA, I., PASCAL, M.-L., FONTEILLES, M. & VERKAEREN, J. (2003): The melilite (Gh₅₀) skarns at Oravița, Banat, Romania: transition to gehlenite (Gh₈₅) and to vesuvianite. *Can. Mineral.* **41**, 1255–1270.
- KOLESOVA, V.A. & ISMATOV, A.A. (1971): Study of the melilite-type compounds of Ca_xY_{2–x}Be_yAl_{2–y}SiO₇ composition. *Neorgan. Mater.* **7**, 1279–1281 (in Russian).
- KUZEL, H.-J. (1976): Crystallographic data and thermal decomposition of synthetic gehlenite hydrate 2CaO•Al₂O₃•SiO₂•8H₂O. *Neues Jahrb. Mineral., Monatsh.*, 319–325.
- LOUISNATHAN, S.J. (1971): Refinement of the crystal structure of a natural gehlenite, Ca₂Al(Al,Si)₂O₇. *Can. Mineral.* **10**, 822–837.
- LUPU, M., AVRAM, E., ANTONESCU, E., DUMITRĂCĂ, P., LUPU, D. & NICOLAE, I. (1993): The Neojurassic and the Cretaceous of the Drocea Mts.: the stratigraphy and the structure of an ensialic marginal basin. *Rom. J. Tectonics Reg. Geol.* **75**, 53–66.
- MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441–450.
- MARINCEA, Ș., BILAL, E., VERKAEREN, J., PASCAL, M.-L. & FONTEILLES, M. (2001): Superposed parageneses in the spurrite-, tilleyite-, and gehlenite-bearing skarns from Cornet Hill, Apuseni Mountains, Romania. *Can. Mineral.* **39**, 1435–1453.
- MOENKE, H. (1966): *Mineralspektren*. Academie Verlag, Berlin, Germany.
- NURSE, R.W. & MIDGLEY, H.G. (1953): Studies on the melilite solid solution. *J. Iron and Steel Inst.* **174**, 121–131.
- PASCAL, M.-L., FONTEILLES, M., VERKAEREN, J., PIRET, R. & MARINCEA, Ș. (2001): The melilite-bearing high-temperature skarns of the Apuseni Mountains, Carpathians, Romania. *Can. Mineral.* **39**, 1405–1434.
- PIRET, R. (1997): *Minéralogie et géochimie des skarns de haute température des régions de Măgureaua Vaței et de Cornet Hill (Monts Apuseni)*. M.Sc. thesis, Université Catholique de Louvain, Belgium.
- POUCHOU, J.L. & PICOIR, F. (1985): PAP φ(ρZ) procedure for improved quantitative microanalysis. In *Microbeam Analysis* (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California (104–106).
- REVERDATTO, V.V. (1970): Pyrometamorphism of limestones and the temperature of basaltic magmas. *Lithos* **3**, 135–143.
- REVERDATTO, V.V., PERTSEV, N.N. & KOROLYUK, V.N. (1980): Zoning of melilite grains as an indicator of regressive evolution of metamorphic process in carbonate-bearing rocks. In *Inhomogeneity of Minerals and Crystal Growth*. Proc. Eleventh Gen. Meeting, Int. Mineral. Assoc. (Novosibirsk), 59–65 (in Russian).
- SAHAMA, T.G. & LEHTINEN, M. (1967): Infrared absorption of melilite. *C.R. Soc. Géol. Finlande* **39**, 29–40.
- SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. A* **32**, 751–767.
- SHARMA, S.K., SIMONS, B., YODER, H.S., JR. (1983): Raman study of anorthite, calcium Tschermak's pyroxene, and gehlenite in crystalline and glassy states. *Am. Mineral.* **68**, 1113–1125.
- SOROIU, M., CATILINA, R. & STRUTINSKI, C. (1986): K–Ar ages on some igneous rocks from the southwestern end of the South Carpathians (Banat Hills). *Rev. Roum. Phys.* **31**, 849–854.
- ȘTEFAN, A., ISTRATE, G. & MEDEȘAN, A. (1978): Gehlenite in calc-skarns from the Măgureaua Vaței – Cerboia (Apuseni Mountains – Romania). *Rev. Roum. Géol., Géophys., Géogr., Sér. Géol.* **22**, 155–160.
- ȘTEFAN, A., LAZĂR, C., BERBELEAC, I. & UDUBAȘA, G. (1988): Evolution of the banatic magmatism in the Apuseni Mountains and the associated metallogenesis. *D. S. Inst. Geol. Geofiz.* **72–73**(2), 195–213.
- VON COTTA, B. (1864): *Erzlagerstätten im Banat und in Serbien*. W. Braumüller, Vienna, Austria.

Received May 19, 2010, revised manuscript accepted July 22, 2011.