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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 Vaţei and Cornet Hill in Apuseni Mountains and Oraviţa 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 Oraviţa, from $Ak_{30.4}$ to $Ak_{42.9}$ (mean $Ak_{38.3}$) at Măgureaua Vaţei, 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 Oraviţa. The cell parameter *a* ranges from 7.679(3) to 7.734(3) Å at Oraviţa, from 7.683(4) to 7.735(1) Å at Măgureaua Vaţei, 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 Oraviţa, from 5.040(1) to 5.070(3) Å at Măgureaua Vaţei, 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 Vaţei et Cornet Hill dans les monts Apuseni, et Oraviţa 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 Oraviţa, de $Ak_{30.4}$ à $Ak_{42.9}$ (en moyenne $Ak_{38.3}$) à Măgureaua Vaţei, 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 Oraviţa. Les paramètres de la maille sont très variables: le paramètre *a* varie entre 7.679(3) et 7.734(3) Å à Oraviţa, entre 7.683(4) et 7.735(1) Å à Măgureaua Vaţei, 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 Oraviţa, de 5.040(1) à 5.070(3) Å à Măgureaua Vaţei, 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, cristallochimie, paramètres réticulaires, données d'absorption infrarouge, skarn de haute température, Roumanie.

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INTRODUCTION

Gehlenite, ideally $Ca_2Al(AlSi)O_7$, 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 Vaţei – Cerboaia Valley (Ştefan *et al.* 1978, Pascal *et al.* 2001), Cornet Hill (Istrate *et al.* 1978, Pascal *et al.* 2001, Marincea *et al.* 2001) and Oraviţa – Ogaşul Crişenilor (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 Oraviţa 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 Vaţei and Cornet Hill in Apuseni Mountains and Oraviţa in Banat (Fig. 1). All of them are related to Upper Cretaceous intrusions that could be correlated with the "banatitic" 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 Reşita – Moldova Nouă synclinorium at Oraviţa (Ilinca *et al.* 1993), and Tithonic – Kimmeridgian reef limestones of the Căpâlnaş–Techereu unit (Lupu *et al.* 1993) at Măgureaua Vaţei and Cornet Hill. The magmatic intrusions at the contact are mainly dioritic at Oraviţa (Dupont *et al.* 2002) and monzodioritic to quartz monzodioritic at Măgureaua Vaţei and Cornet Hill (Ştefan *et al.* 1988). Absolute ages are known only for the intrusion from Oraviţa, 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 $CaO–Al_2O_3–SiO_2–H_2O–CO_2$ are especially pertinent: (1) 2 anorthite + 3 calcite = gehlenite + grossular + 3 CO_2 and (2) anorthite + 2 calcite = gehlenite + wollastonite + CO_2. Both of them imply high temperatures of reaction, in the range quoted by Pascal *et al.* (2001) for Măgureaua Vaţei and Cornet Hill (about 750°C) and low pressures, up to 1 kbar, for $0.1 < X(CO_2) < 1$. These temperatures are high enough to produce åkermanite-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	Oraviţa	Măgureaua Vaţei	Cornet Hill
gehlenite	■	■	■
spurrite	♦	□	■
diopside	♦	◘	◘
tilleyite	◊	□	■
afwillite	◘	◊	□
grossular	●	●	●
titanian andradite	□	●	♦
andradite	♦	□	□
spinel	□	◊	□
magnetite	◊	◊	◊
monticellite	●	◘	◊
wollastonite	♦	■	●
perovskite	□	◘	♦
vesuvianite	■	●	●
clintonite	●	□	□
phlogopite	□	◊	□
ellestadite-(OH)	◘	◘	◘
calcite	■	■	■
aragonite	□	□	◊
pyrrhotite	◊	◊	◊
djerfisherite	□	□	?
cuspidine	?	□	?
scawtite	□	□	●
thaumasite	◊	◊	◊
clinochlore	♦	◊	◊
chrysotile	♦	◊	◊
hibschite	●	●	●
kamaishilite	□	?	□
bicchulite	□	?	?
xonotlite	◊	●	♦
thomsonite	●	●	●
gismondine	□	□	●
mountainite	□	□	?
foshagite	□	□	?
plombièrite	◊	◘	♦
tobermorite	◊	◊	♦
riversideite	□	□	◘
portlandite	□	□	◊
allophane	●	●	●

Symbols: ■ major; ● common; ♦ minor; ◘ rare; ◊ very rare; ? doubtful identification; □ not found.

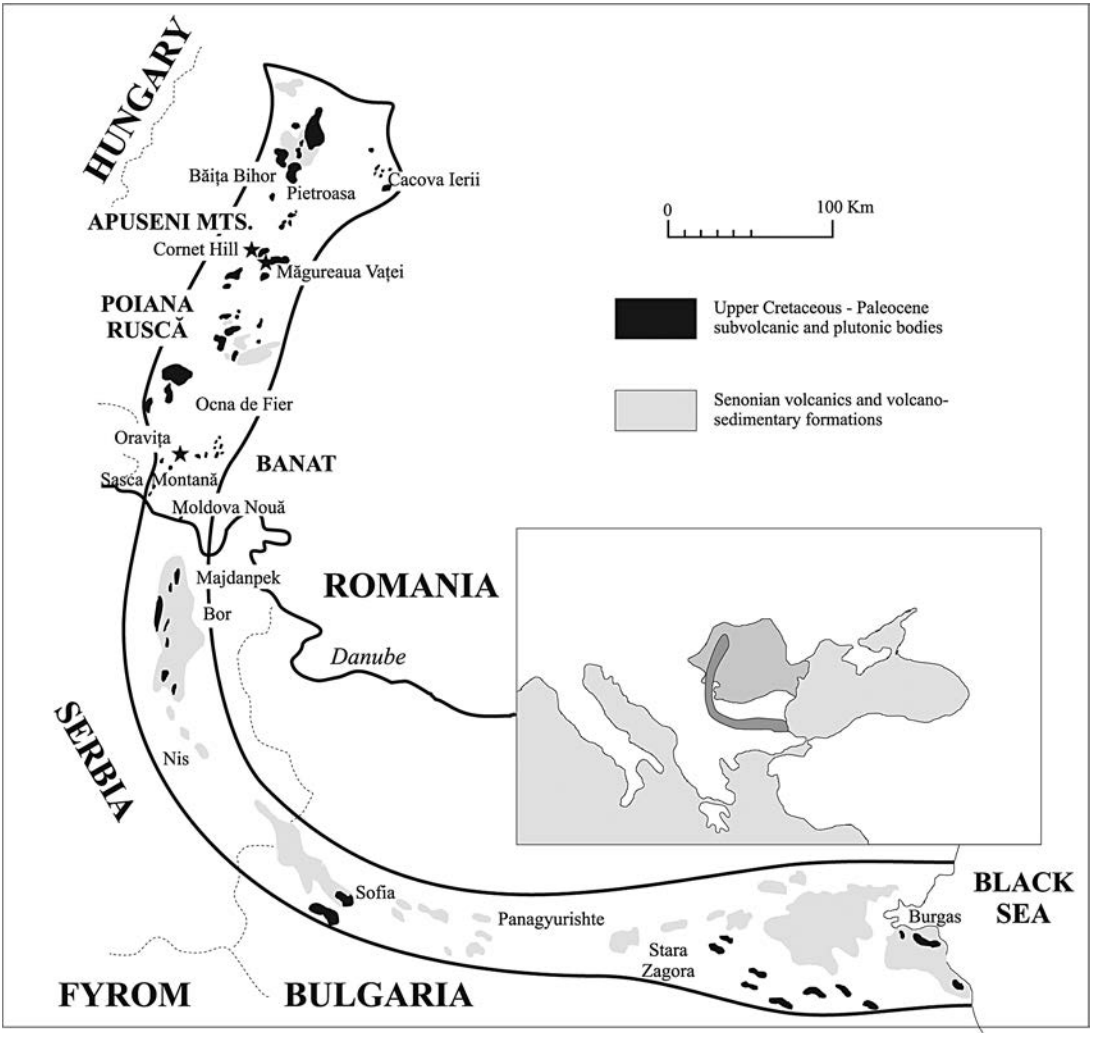

FIG. 1. Map showing the extension of the Banatitic petrographic province within the Carpatho-Balkan area. Redrawn from Cioflica & Vlad (1973). The occurrences analyzed in this paper are marked with stars.

"spots" from Oraviţa, 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 Oraviţa, 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 Vaţei 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 Vaţei, Cornet Hill), with monticellite, grossular–andradite garnet, wollastonite and ellestadite (Oraviţa) 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 Oraviţa and Măgureaua Vaţei. Local modifications that internally affect the original crystals, described as "birefringent spots" and "granular patches" by Katona *et al.* (2003), are frequent at Oraviţa and scarce at Măgureaua Vaţei 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 Vaţei.

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 Vaţei (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 ±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 (Cu$K\alpha$ radiation, $\lambda = 1.54056$ Å). 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/cm^2 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 Vaţei (Ştefan *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 Oraviţa 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 Vaţei 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 Vaţei: 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 Oraviţa and Măgureaua Vaţei, 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 ORAVIŢA

Sample	2289	2290	2291	2307	2308	2311	2312	2313	2314	2333	2337	2338
N(1)	11	9	12	11	11	7	4	6	8	6	13	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_2O_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_2O	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_2O	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 *apfu*	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, $Ca_2Al(AlSi)O_7$ and $Ca_2MgSi_2O_7$, respectively. These are names of mineral species. The symbols Na-mel and Fe-Åk represent the end-members "Na-melilite" and "Fe-åkermanite", $NaCaAlSi_2O_7$ and $Ca_2FeSi_2O_7$, 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 $CaNaAlSi_2O_7$ ("Na-melilite") – $Ca_2Al_2SiO_7$ (gehlenite) – $Ca_2MgSi_2O_7$ + $Ca_2FeSi_2O_7$ (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 $Ak_{34.1}$ to $Ak_{51.2}$ (mean $Ak_{41.2}$) at Oraviţa, from $Ak_{30.4}$ to $Ak_{42.9}$ (mean $Ak_{38.3}$) at Măgureaua Vaţei, and from $Ak_{24.3}$ to $Ak_{41.7}$ (mean $Ak_{32.9}$) at Cornet Hill, respectively. Gehlenite from Oraviţa 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.% $CaNaAlSi_2O_7$ at Oraviţa, 2.85 mol.% at Măgureaua Vaţei, 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 Oraviţa (average 4.65 mol.%), from 2.21 to 8.61 mol.% at Măgureaua Vaţei (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° (Cu$K\alpha$, λ = 1.54056 Å) 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 ($d_{\mathrm{obs.}} - d_{\mathrm{calc.}}$) 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 VAŢEI

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_2O_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_2O	0.54	0.57	0.44	0.38	0.56	0.41	0.39	0.62	0.57	0.59
K_2O	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 *apfu*	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, $Ca_2Al(AlSi)O_7$ and $Ca_2MgSi_2O_7$, respectively. These are names of mineral species. The symbols Na-mel and Fe-Åk represent the end-members “Na-melilite” and “Fe-åkermanite”, $NaCaAlSi_2O_7$ and $Ca_2FeSi_2O_7$, 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

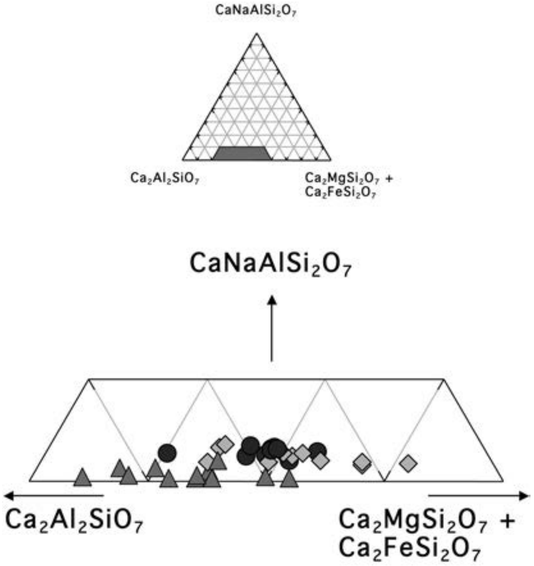

FIG. 3. Triangular diagram showing the compositional range of gehlenite from the Romanian occurrences in terms of the "Na-melilite" – gehlenite – åkermanite + "Fe-åkermanite" solid-solution series. Samples from Oraviţa (diamonds), Măgureaua Vaţei (dots) and Cornet Hill (triangles).

TABLE 4. CRYSTALLOGRAPHIC *VERSUS* CHEMICAL PARAMETERS IN ROMANIAN GEHLENITE

Sample	*a* (Å)	*c* (Å)	*V* ($Å^3$)	Fe-Åk	Åk	Na-mel	*k*	N$^{(1)}$
				Oraviţa				
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 Vaţei				
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:

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

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

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

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

The calculations were carried out using the ionic radii given by Shannon (1976) for the cations involved (r^{VIII}Na = 1.18 Å, r^{IV}Al = 0.39 Å, r^{IV}Si = 0.26 Å, r^{VIII}Ca = 1.12 Å, r^{IV}Mg = 0.57 Å and $r^{\text{IV}}\text{Fe}^{2+}$ = 0.63 Å). 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:

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

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 Oraviţa and Măgureaua Vaţei 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 Oraviţa and Cornet Hill and apparently increasing from the samples from Măgureaua Vaţei, 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 Oraviţa. Anomalous interference-colors, in tints of bluish grey and Berlin blue, were very rarely observed in samples from Măgureaua Vaţei and Oraviţa. The mineral is uniaxial negative, even in the åkermanite-rich samples from Oraviţa. The measured indices of refraction of representative samples approaching the

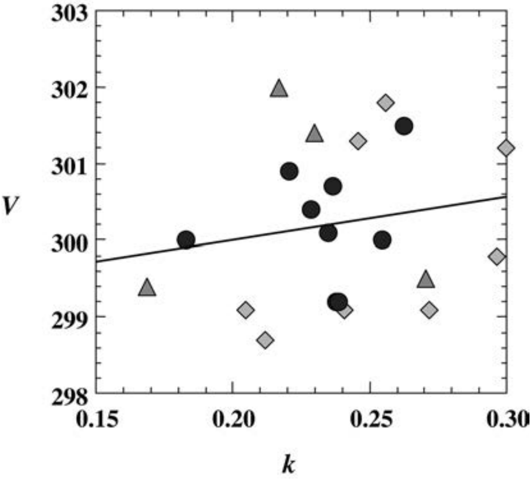

FIG. 4. Diagram showing the correlation between the cell volume *V* and the chemical-structural factor *k*. Symbols as in Figure 3.

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 Al ↔ Mg + Si and Ca + Al ↔ Na + Si type (resulting in decreasing indices of refraction) and 2 Al ↔ $Fe^{2+}(Mn^{2+})$ + Si (resulting in increasing indices of refraction, as established by Nurse & Midgley 1953).

TABLE 5. PHYSICAL PARAMETERS OF GEHLENITE

Occurrence	Oraviţa	Măgureaua Vaţei	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

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: $3.02 < D < 3.07$ 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 Vaţei and only good compatibility-indices for the samples from Cornet Hill, whereas the samples from Oraviţa 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 6. CALCULATED PHYSICAL PARAMETERS OF SELECTED SAMPLES OF GEHLENITE FROM ROMANIA

Sample	$M^{(1)}$	$V^{(2)}$	D_x	K_C	$D'_x{}^{(3)}$	$\bar{n}_x{}^{(4)}$	$K_P{}^{(5)}$	$1-(K_P/K_C)$
				Oraviţa				
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 Vaţei				
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 Å^3), 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 Oraviţa, Măgureaua Vaţei 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

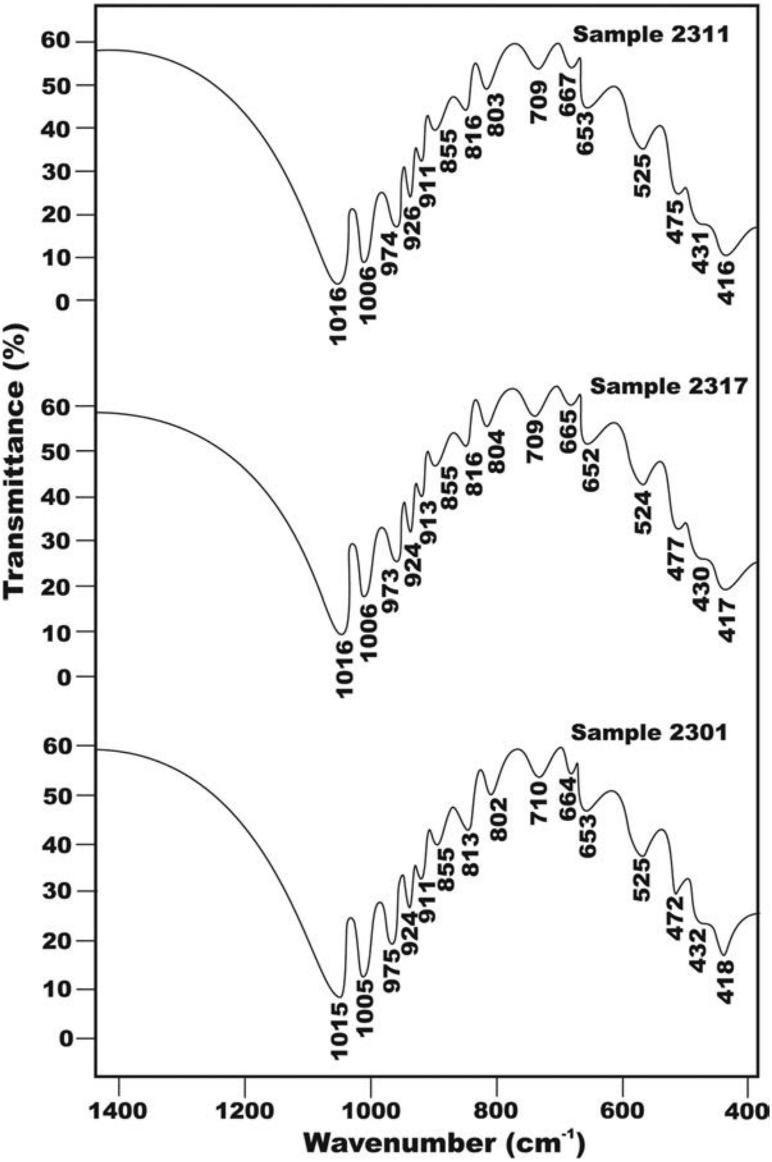

FIG. 5. FTIR spectra of three representative samples of gehlenite from high-temperature skarns in Romania. Samples from Oraviţa (top), Măgureaua Vaţei (middle) and Cornet Hill (bottom).

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):

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

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, Ştefan *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 ~3430 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 LITTERATURE*

Oraviţa		Măgureaua Vaţei		Cornet Hill		Moenke (1966)	K & 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	$H_2O^{(9)}$	vb	m
-	1622(9)	1568	1627(7)	1620	1633(7)	-	-$^{(7)}$	δH-OH	$H_2O^{(9)}$	vb	m
1020	1016(1)	1020	1016(1)	1025	1015(1)	1020	1023	v_{as}Si-O-Si	$(Si,Al)_2O_7$	sh	vs
1010	1006(1)	1000	1006(1)	1008	1005(1)	-	-	v_{as}Si-O-Al	$(Si,Al)_2O_7$	sh	vs
975	974(1)	970	973(1)	975	975(1)	980	976	$v_{as}(Si,Al)O_3$	$(Si,Al)_2O_7$	sh	vs
916	926(1)	940	924(1)	925	924(1)	922	921	$v'_{as}(Si,Al)O_3$	$(Si,Al)_2O_7$	sh	vs
905	911(1)	912	913(2)	910	911(3)	880	890	$v_s(Si,Al)O_3$	$(Si,Al)O_7$	b	vs
854	855(1)	856	855(1)	855	855(2)	860	863	v_{as}Al-O-Al	AlO_4(?)	sh	vs
820	816(1)	815	815(1)	815	813(1)	815	-	$v_s'(Si,Al)O_3$	$(Si,Al)_2O_7$	sh	vs
808	803(2)	802	804(1)	800	802(2)	-	803	$v_s'(Si,Al)O_3$	$(Si,Al)_2O_7$	sh	vs
712	709(2)	715	709(2)	712	710(2)	715	714	v_sSi-O-Al	$(Si,Al)_2O_7$	b	w
670	667(6)	670	665(1)	670	664(1)	675	685	v_sAl-O-Al	AlO_4(?)	sh	w
660	653(4)	662	652(4)	655	653(1)	-	647	v_sSi-O-Si	$(Si,Al)_2O_7$	sh	m
525	525(1)	527	524(1)	525	525(2)	527	530	δ_sSi-O-Al(?)	$(Si,Al)_2O_7$	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_{as}Si-O-Al(?)	$(Si,Al)_2O_7$	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, v_s: symmetric stretching, v_{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 ~ 1600 cm^{-1}) was not reported.

The very intense complex of bands between 800 and 1050 cm^{-1} groups, mainly *T*–O–*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 ~ 855 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 ~ 670 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 Oraviţa 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.

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