

NEW DATA ON MELIPHANITE, $\text{Ca}_4(\text{Na,Ca})_4\text{Be}_4\text{AlSi}_7\text{O}_{24}(\text{F,O})_4$

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ABSTRACT

We have made new chemical analyses of a large number of samples of meliphanite from Norway and of leucophanite from both Norway and Mont Saint-Hilaire, Quebec. Infrared spectra were collected on a sample of each mineral to confirm the lack of (OH) groups, inferred on the basis of absence of any absorption bands in the OH-stretch region. Four samples were chosen for crystal-structure analyses, two crystals of meliphanite from localities in Norway and two leucophanite samples (one *REE*-rich) from Mont Saint-Hilaire, Quebec. The anomalous biaxial character of tetragonal meliphanite is likely due to stress within the crystal structure as a result of twinning. The crystal structure of meliphanite from Arøy, Norway is presented in detail, as this represents material used in the early description of this mineral. It is tetragonal $\bar{I}4$, a 10.5257(3), c 9.8868(4) Å, V 1095.37(8) Å³ and $Z = 2$. The structure refined to $R = 0.025$ using 1578 observed ($>4\sigma F_o$) reflections. The crystal-structure analysis established the simplified formula $\text{Ca}_4(\text{Na,Ca})_4\text{Be}_4\text{AlSi}_7\text{O}_{24}(\text{F,O})_4$; the essential Al orders in the layer of tetrahedra, which differentiates it from leucophanite, $\text{Ca}_4\text{Na}_4\text{Be}_4\text{Si}_8\text{O}_{24}\text{F}_4$. Meliphanite is structurally related to the melilite group of minerals, in which the topology of the layer of tetrahedra defines a two-dimensional net $(5^3)(5^4)$. The expansion of this series of structures from melilite to leucophanite to meliphanite requires subtle modifications in this net to accommodate cation order, both among the larger cations and the small tetrahedrally coordinated cations. This ordering is dictated by local bond-valence requirements.

Keywords: meliphanite, Arøy, Norway, essential Al, structure, twinning, cation order, nets.

SOMMAIRE

Nous avons effectué de nouvelles analyses chimiques d'un grand nombre d'échantillons de méliphanite de Norvège et de leucophanite de Norvège et du Mont Saint-Hilaire, Québec. Chaque échantillon a été analysé par spectroscopie infrarouge afin de confirmer l'absence de bandes d'absorption dans la région de l'étirement des groupes OH. Nous avons choisi quatre échantillons pour une ébauche de la structure cristalline, deux de méliphanite de localités norvégiennes et deux de leucophanite (dont un enrichi en terres rares) du Mont Saint-Hilaire. Le caractère biaxe anormal de la méliphanite tétragonale serait dû aux contraintes à cause des macles. Nous décrivons en détail la structure de la méliphanite provenant d'Arøy, en Norvège, parce que c'est ce matériau qui a été utilisé dans les premières descriptions de cette espèce. Elle est tétragonale, $\bar{I}4$, a 10.5257(3), c 9.8868(4) Å, V 1095.37(8) Å³, avec $Z = 2$. La structure a été affinée jusqu'à un résidu R de 0.025 en utilisant 1578 réflexions observées ($>4\sigma F_o$). Nos résultats établissent la formule simplifiée de cette espèce: $\text{Ca}_4(\text{Na,Ca})_4\text{Be}_4\text{AlSi}_7\text{O}_{24}(\text{F,O})_4$; l'aluminium, essentiel, est ordonné dans la couche de tétraèdres, ce qui distingue la méliphanite de la leucophanite, $\text{Ca}_4\text{Na}_4\text{Be}_4\text{Si}_8\text{O}_{24}\text{F}_4$. La méliphanite est structurellement apparentée au groupe de la mélilite, dans lequel la topologie de la couche de tétraèdres définit un réseau bidimensionnel $(5^3)(5^4)$. L'expansion de cette série de structures, de la mélilite à la leucophanite et ensuite à la méliphanite, requiert des modifications subtiles du réseau afin d'accommoder la mise en ordre des cations, à la fois les plus gros et ceux qui possèdent une coordinence tétraédrique. Cette mise en ordre serait régie par les exigences locales des valences de liaison.

(Traduit par la Rédaction)

Mots-clés: méliphanite, Arøy, Norvège, Al essentiel, structure, maclage, mise en ordre des cations, réseaux.

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INTRODUCTION

Meliphanite was first described by Scheerer (1852) from Fredriksvårn (now Stavern), Norway. The original name, "melinophan", from Greek *meli*, honey, *phainomai*, to appear, alluded to its characteristic honey-yellow color. In the original description, Scheerer (1852) mentioned that the mineral also was found at Brevig (now Brevik) on the Langesundsfjord. Prior to this, Erdmann (1840) described in detail the mineral "leucophan" (now leucophanite) from Brevig. This name also alludes to the mineral's appearance, from the Greek, *leucos*, white.

The crystal structure of each mineral was described in 1967, leucophanite by Cannillo *et al.* (1967) and meliphanite by Dal Negro *et al.* (1967). Both structures were determined and refined using X-ray diffraction intensities measured by film techniques. The *R* indices were 0.094 for leucophanite and 0.104 for meliphanite. We refined the structure of leucophanite as part of another project (Grice & Hawthorne 1989), but the struc-

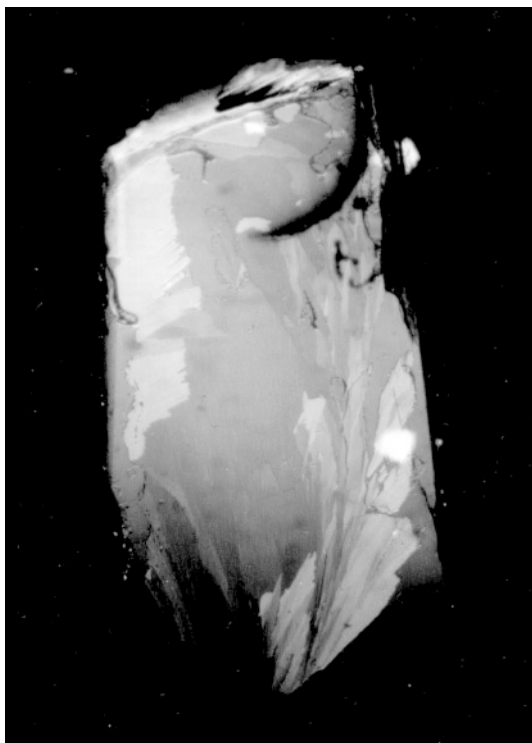


FIG. 1. A crystal fragment of meliphanite from Stokkøy, Norway (sample CMNMC 46861) oriented approximately on (001). In partially crossed nicols, the areas of uniaxial (dark shade) and biaxial character (lighter shade) can be readily seen. Width of field of view: 3 mm.

ture refinement of meliphanite would not refine to an acceptable level of confidence.

We have investigated about 50 specimens of leucophanite and meliphanite. Many of these were studied optically to check the indicatrix, and many were chemically analyzed with an electron microprobe. In total, four crystal-structure refinements were done: two on leucophanite (one reported in Grice & Hawthorne 1989) and two on meliphanite. Although good structure refinements were readily attained for leucophanite, initially those for meliphanite were unacceptable. The structure refinement of the sample from Stokkøy, Vestfold County, Norway (specimen CMNMC 46861), was our first indication of a problem. Several grains of this specimen were checked optically, and they are uniaxial. Further investigation of the sample showed areas in the crystal that are biaxial (Fig. 1).

Examination of the crystal-structure data of Dal Negro *et al.* (1967) revealed that the atom coordinates of meliphanite may be transformed into those of leucophanite using the relation $[x, y, z] \rightarrow [x - y + \frac{3}{4}, x + y, z + \frac{1}{4}]$. The relation between the two structures is discussed later. This relation suggested the possibility that meliphanite is merely twinned leucophanite and thus not a valid species. The accurate crystal-structure of meliphanite, criteria for its differentiation from leucophanite, and its geochemical significance have now been determined.

EXPERIMENTAL

Samples studied

Samples were selected from several collections: Canadian Museum of Nature (CMNMC), Ottawa, Canada; Geological Survey of Canada, Ottawa, Canada; Geological Museum (GM), Copenhagen, Denmark; Royal Ontario Museum, Toronto, Canada; Swedish Museum of Natural History (SMNH), Stockholm, Sweden and the Mineralogisk-Geologisk Museum (MGM), Oslo, Norway. We have not been successful in finding any of the meliphanite from the original description of Scheerer (1852). Initially, we believed that some of this "type material" was at Bergsakademie, Freiberg, but that is incorrect (A. Massanek, pers. commun.). The Swedish Museum of Natural History provided some of the material studied by Brögger (1890) and Bäckström (1890) for new chemical analyses and an investigation of optical properties. This is as close to "type" material as we could obtain, and it is the best standard for a definition of the species.

Optical properties

Although meliphanite is often cited in textbooks as having uniaxial optical properties, it has been known for some time that it can also display biaxial character (Vlasov 1966). In the samples we studied, we found both

uniaxial and biaxial meliphanite, but only biaxial leucophanite. Figure 1 shows a good example of meliphanite with both uniaxial and biaxial character (shades of grey indicate differing degrees of biaxial character).

Chemical analysis

To date, we have analyzed 34 samples of meliphanite and leucophanite with an electron microprobe. Table 1 gives average results of the chemical analyses of meliphanite from Norway (10 samples) and of leucophanite from both Norway (8 samples) and Mont Saint-Hilaire (16 samples, denoted MSH). Also in Table 1 are chemical data for specific samples used for crystal-structure analyses or X-ray powder diffraction. In all cases, we assumed Be to be present in stoichiometric amounts. Chemical analyses were done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine in XMAQNT (C. Davidson, CSIRO, pers. commun.). The

operating voltage of the electron probe was 15 kV, and the beam current was 20 nA, with a beam diameter of 40 μm . Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. A 100 s energy-dispersion scan indicated no elements with $Z > 8$ other than those reported here. The following standards were used in the electron-microprobe analyses: bytownite ($\text{SiK}\alpha$), tephroite ($\text{MnK}\alpha$), albite ($\text{NaK}\alpha$), diopside ($\text{CaK}\alpha$), phlogopite ($\text{FK}\alpha$), almandine ($\text{FeK}\alpha$), chrysoberyl ($\text{AlK}\alpha$), zincite ($\text{ZnL}\alpha$), synthetic yttrium iron garnet (YIG) ($\text{YK}\alpha$), and a set of synthetic REE phosphates ($\text{CeL}\alpha$, $\text{NdL}\alpha$, $\text{LaL}\alpha$, $\text{SmL}\alpha$, $\text{EuL}\alpha$, $\text{GdL}\alpha$, $\text{TbL}\alpha$, $\text{DyL}\beta$, $\text{HoL}\alpha$, $\text{ErL}\alpha$, $\text{TmL}\alpha$, $\text{YbL}\alpha$, $\text{LuL}\alpha$). Data for standards were collected for 50 s or 0.25% precision, whichever was attained first. The REE raw data were corrected for overlaps.

Infrared spectroscopy

The infrared-absorption spectra of meliphanite (Fig. 2a, sample SMNH 531225 from Arøy, Norway) and leucophanite (Fig. 2b, sample MGM 28481 from

TABLE 1. MELIPHANITE AND LEUCOPHANITE: CHEMICAL COMPOSITIONS (wt.%) AND UNIT FORMULA (*apfu*)

MELIPHANITE					LEUCOPHANITE						
	^{1,2} Arøy SMNH 531225	¹ Stokkøy CMNMC 46861	Av (10)	Range ¹	¹ MSH CMNMC 53455	¹ MSH CMNMC 36557	Av (16)	MSH Range	² Låven MGM 28560	Av (8)	Norway Range
Na ₂ O	8.14	8.12	8.30	7.50-9.01	12.80	13.13	12.77	12.58-13.13	12.65	12.52	12.39-12.69
CaO	29.85	29.10	29.08	27.79-30.3	20.70	16.65	19.76	16.19-22.37	21.81	22.12	21.57-22.92
MnO	0.00	0.00	0.03	0.00-0.19	0.21	0.15	0.07	0.00-0.23	0.12	0.15	0.07-0.19
FeO	0.16	0.17	0.19	0.14-0.22	0.00	0.00	0.00		0.00	0.00	
(BeO)	9.97	10.01	9.99	9.82-10.11	10.08	10.00	10.12		10.36	10.27	
Al ₂ O ₃	4.36	4.74	4.35	4.01-4.75	0.10	0.10	0.05	0.00-0.15	0.00	0.00	0.00-0.05
Y ₂ O ₃	0.00	0.00	0.02	0.00-0.22	0.19	1.00	0.44	0.00-1.11	0.21	0.06	0.00-0.21
La ₂ O ₃	0.00	0.00	0.00		0.34	0.95	0.25	0.00-0.97	0.10	0.10	0.00-0.18
Ce ₂ O ₃	0.00	0.15	0.11	0.15-0.26	1.14	2.73	1.05	0.14-3.34	0.38	0.33	0.00-0.54
Pr ₂ O ₃	0.00	0.00	0.00		0.00	0.40	0.11	0.00-0.41	0.00	0.00	
Nd ₂ O ₃	0.00	0.00	0.00		0.56	1.41	0.86	0.00-2.12	0.20	0.13	0.00-0.27
Sm ₂ O ₃	0.000	0.000	0.000		0.00	0.80	0.30	0.00-0.89	0.00	0.00	
Eu ₂ O ₃	0.000	0.000	0.000		0.00	0.00	0.01	0.00-0.85	0.00	0.00	
Gd ₂ O ₃	0.000	0.000	0.000		0.00	0.88	0.33	0.00-0.85	0.00	0.00	
Dy ₂ O ₃	0.000	0.000	0.000		0.00	0.00	0.05	0.00-0.45	0.00	0.00	
SiO ₂	42.84	43.27	43.29	42.00-44.21	48.96	48.18	49.01	47.35-50.61	50.21	50.19	49.81-50.41
F	6.50	6.39	6.47	5.81-7.01	7.05	7.71	7.40	6.29-8.32	8.01	7.12	6.21-8.01
O = F	-2.74	-2.69	-2.72	-2.45-2.95	-2.97	-3.25	-3.12		-3.37	-3.00	
TOTAL	99.08	99.26	99.11	97.91-100.17	99.26	100.84	99.46		100.68	99.99	
Na ⁺	1.318	1.309	1.341	1.233-1.452	2.050	2.120	2.043	1.961-2.155	1.971	1.969	1.942-2.003
Ca ²⁺	2.671	2.593	2.597	2.475-2.754	1.832	1.486	1.747	1.486-1.919	1.878	1.922	1.878-1.996
Mn ²⁺	0.000	0.000	0.002	0.000-0.014	0.015	0.011	0.005	0.00-0.17	0.008	0.010	0.005-0.017
Fe ²⁺	0.011	0.012	0.013	0.010-0.015					0.000		
Be ²⁺	2	2	2		2	2	2		2	2	
Al ³⁺	0.429	0.465	0.428	0.389-0.475	0.010	0.010	0.005	0.000-0.014	0.009	0.000	0.000-0.004
Y ³⁺	0.000	0.000	0.001	0.000-0.010	0.008	0.044	0.019	0.000-0.050	0.003	0.003	0.000-0.009
La ³⁺	0.000	0.000	0.000		0.010	0.029	0.008	0.000-0.031	0.011	0.003	0.000-0.005
Ce ³⁺	0.000	0.005	0.003	0.000-0.008	0.034	0.083	0.032	0.004-0.105	0.006	0.010	0.000-0.016
Pr ³⁺	0.000	0.000	0.000		0.000	0.012	0.003	0.000-0.013	0.000	0.000	
Nd ³⁺	0.000	0.000	0.000		0.017	0.042	0.025	0.000-0.064	0.000	0.004	0.000-0.008
Sm ³⁺	0.000	0.000	0.000		0.000	0.023	0.009	0.000-0.026	0.000	0.000	
Eu ³⁺	0.000	0.000	0.000		0.000	0.000	0.000	0.000	0.000	0.000	
Gd ³⁺	0.000	0.000	0.000		0.000	0.024	0.009	0.000-0.024	0.000	0.000	
Dy ³⁺	0.000	0.000	0.000		0.000	0.000	0.001	0.000-0.024	0.000	0.000	
Si ⁴⁺	3.578	3.598	3.608	3.562-3.648	4.044	4.013	4.044	4.010-4.076	4.034	4.070	4.030-4.085
F ⁻	1.717	1.681	1.706	1.559-1.825	1.842	2.031	1.931	1.713-2.114	2.035	1.826	1.617-2.035
O ²⁻	12.283	12.319	12.294		12.158	11.969	12.069		11.965	12.174	

¹ used in crystal-structure analysis; ² used in X-ray powder diffraction

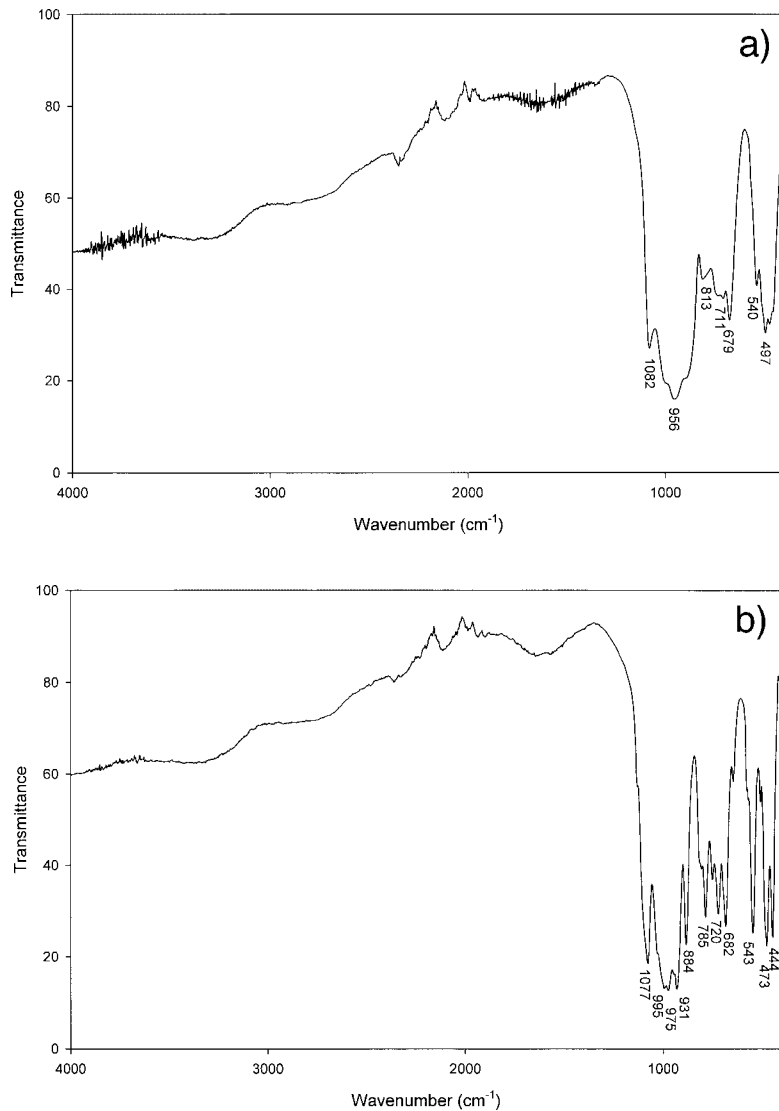


FIG. 2. Infrared-absorption spectra for (a) melphanite and (b) leucophanite.

Eikaholmen, Norway) were obtained using a Bomem Michelson MB-120 Fourier-transform infrared spectrometer. Of particular interest was the lack of any absorption bands in the 3000 cm^{-1} range indicative of presence of (OH). These two samples were chosen for their low F content; thus any substitution within this atomic site must be attributed to O^{2-} and not $(\text{OH})^-$. The absorption bands in the range 1200 to 700 cm^{-1} may be attributed to stretching modes of the tetrahedral groups. With melphanite having the greater number of distinct cation sites with tetrahedral coordination, one might

have expected the spectrum for melphanite to be more complicated (more splitting of bands) than that for leucophanite within this region, but the converse is observed.

X-ray powder diffraction

Powder X-ray-diffraction (XRPD) results were obtained using a Philips PW1729 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$) and a scan rate of 0.02° $2\theta/\text{s}$ for the 2θ range 10 to 120° 2θ (Table 2). Compari-

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR MELIPHANITE AND LEUCOPHANITE

Meliphanite (SMNH 531225) Arøy, Norway				Leucophanite (MGM 28560) Låven, Norway			
<i>l</i>	<i>d</i> obs	<i>d</i> calc	<i>hkl</i>	<i>l</i>	<i>d</i> obs	<i>d</i> calc	<i>hkl</i>
5	7.213	7.207	101	15	5.933	5.942	101
1	5.256	5.262	200				
10	4.950	4.944	002	35	4.978	4.983	002
				3	4.624	4.629	111
10	4.250	4.248	211	4	4.130	4.130	012
4	4.121	4.118	112	36	3.604	3.607	112
32	3.604	3.603	202	20	3.466	3.468	201
2	3.328	3.328	310	2	3.305	3.308	210
2	3.146	3.145	103	2	3.136	3.136	121
				19	3.029	3.031	103
38	2.9726	2.9731	222	54	2.9701	2.966	022
9	2.7999	2.7997	321				
100	2.7612	2.7610	312	100	2.7546	2.7560	212
4	2.6996	2.6998	213				
4	2.6315	2.6312	400	4	2.6121	2.6134	220
				1	2.5262	2.5279	221
3	2.4727	2.4720	004	5	2.4914	2.4915	004
1	2.4025	2.4022	303	1	2.4711	2.4693	023
				1	2.3890	2.3892	031
27	2.3458	2.3460	114	26	2.3611	2.3613	104
21	2.3226	2.3228	402	23	2.3408	2.3397	310
				15	2.3133	2.3144	222
9	2.2372	2.2374	204	4	2.2771	2.2777	311
22	2.2170	2.2173	332	6	2.2497	2.2490	114
1	2.1862	2.1853	323	29	2.2108	2.2108	302
3	2.1245	2.1250	422	5	2.1168	2.1178	312
1	2.0590	2.0588	501	2	2.0542	2.0540	223
1	2.0172	2.0182	413				
33	1.9845	1.9844	314	34	1.9902	1.9902	214
1	1.9184	1.9174	521				
2	1.9057	1.9048	512	3	1.8968	1.8966	322
6	1.8605	1.8606	400	25	1.8504	1.8501	400
2	1.8226	1.8232	215				
8	1.8056	1.8050	330	8	1.8043	1.8033	224
8	1.8017	1.8016	404	9	1.7946	2.7946	410
1	1.7730	1.7741	503	3	1.7696	1.7662	411
8	1.7541	1.7542	600	11	1.7547	1.7548	205
2	1.7409	1.7414	442	12	1.7434	1.7424	330
				7	1.7348	1.7344	402
32	1.7043	1.7045	424	38	1.7054	1.7066	134
7	1.6951	1.6956	532	6	1.6986	1.6885	412
5	1.6633	1.6642	620	8	1.6915	1.6610	006
4	1.6529	1.6532	602	11	1.6544	1.6540	420
3	1.6482	1.6480	006	4	1.6456	1.6446	332
1	1.6375	1.6373	325	1	1.6207	1.6207	106
3	1.5844	1.5844	514	15	1.5830	1.5835	324
4	1.5725	1.5727	206	2	1.5711	1.5700	422
2	1.5070	1.5068	226	6	1.5172	1.5173	315
16	1.4768	1.4769	316	14	1.4840	1.4849	126
2	1.4577	1.4578	534				
4	1.4000	1.3998	642	9	1.4023	1.4018	226
8	1.3967	1.3967	406	9	1.3986		
				4	1.3938		
3	1.3804	1.3805	624	6	1.3779		
3	1.3727	1.3726	336	5	1.3747		
3	1.3501	1.3499	426	8	1.3551		
7	1.3314	1.3310	732	8	1.3517		
3	1.3159	1.3156	800	8	1.3249		
2	1.2880	1.2879	516	10	1.3220		
1	1.2755	1.2752	554	8	1.3249		
2	1.2717	1.2715	327	10	1.3220		
4	1.2404			3	1.3085		
4	1.2360			4	1.3074		
5	1.2174			3	1.2725		
2	1.2064			3	1.2685		
2	1.2011			2	1.2465		
3	1.1343			2	1.2365		
3	1.1319			6	1.2341		
6	1.1090			3	1.2215		
6	1.1065			6	1.2193		
5	1.1049			6	1.2174		
2	1.0970			3	1.2154		
10	1.0943			5	1.2034		
10	1.0930			3	1.2006		
3	1.0104			2	1.1824		
				3	1.1723		
				3	1.1697		
				3	1.1253		
				3	1.1125		
				3	1.1105		
				2	1.1030		
				6	1.1003		
				8	1.0935		
				2	1.0591		
				2	1.0473		
				2	1.0460		
				2	1.0242		
				2	1.0233		
				2	1.0114		
				2	1.0095		

son of the XRPD spectra for meliphanite (sample SMNH 531225 from Arøy, Norway) and leucophanite (sample CMNMC 28560 from Låven, Norway) shows small but significant differences in *d*-values that distinguish the two species: for meliphanite 7.213, 4.250, 2.7999, 2.6996 Å, and for leucophanite, 5.933, 4.624, 3.466, 3.029 and 2.3611 Å.

Crystal-structure refinements

The crystal structure of two samples of meliphanite and two samples of leucophanite have been refined. The results of the crystal-structure analysis of leucophanite low in total REE (Table 1, sample CMNMC 53455) were provided by Grice & Hawthorne (1989). A second crystal of leucophanite with much higher concentrations of REE (Table 1, sample CMNMC 36557) was also refined, and brief mention is given to this experiment in the discussion below. For the intensity-data measurement, an equidimensional crystal of ~0.10 mm was used in all four cases. Intensity data were collected on a Siemens P3/P4 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated MoK α radiation. Diffraction data were collected to $2\theta = 60^\circ$ in $\theta:2\theta$ scan-mode, with scan speeds inversely proportional to intensity, varying from 1.5 to 29.3°/min. All calculations were done with the SHELXTL PC PLUS system of programs. For the ellipsoidal absorption correction, intense diffraction-maxima in the range 8 to $60^\circ 2\theta$ were chosen for Ψ diffraction-vector scans at 5° intervals of Ψ .

The two refinements of the meliphanite structure were done in the tetragonal space-group $\bar{I}4$ (#82). Care must be taken to correctly orient the direct cell with regard to the **a** and **b** vectors. These are not interchangeable in point group $\bar{4}$. If an incorrect orientation is adopted, we found that the refinement would not proceed beyond approximately $R = 0.10$; there is no easy way to determine this orientation uniquely prior to refinement. Both samples refined to a residual index of $R = 0.02$. The crystal from Arøy (sample SMNH 531225) is a single crystal with distinctly uniaxial optics. As this material is the sample closest to the type material available, we describe that structure in detail here. The crystal from Stokkøy (sample CMNMC 46861) is that shown in Figure 1, with biaxial optical character. It is likely that this biaxial optical character is caused by stress within the crystal structure due to twinning. A merohedral twin model with {100} as the twin plane had to be used to reduce the agreement factor below $R = 0.07$. At that level of refinement, there is very little distinction in ordering of cations within the Si, Al and Be tetrahedra; only after incorporating the twin model can this distinction be made. The crystal-structure analysis established the simplified formula as $\text{Ca}_4(\text{Na,Ca})_4\text{Be}_4\text{AlSi}_7\text{O}_{24}(\text{F,O})_4$; the essential Al orders in the layer of tetrahedra, differentiating it from leucophanite, $\text{Ca}_4\text{Na}_4\text{Be}_4\text{Si}_8\text{O}_{24}\text{F}_4$. Table 3 summarizes information

for this experiment (sample SMNH 531225), and Table 4 contains the final atom-coordinates, anisotropic-displacement parameters and bond-valence sums, and Table 5 contains selected interatomic distances and angles. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, K1A 0S2 Canada.

DISCUSSION OF MELIPHANITE AND RELATED STRUCTURES

Comparison of the atom coordinates for the meliphanite structure as determined by Dal Negro *et al.*

(1967) with our findings may be made directly, as our intensity data were reoriented. The Si(1) site of Dal Negro *et al.* (1967) is the Al site in the present refinement, and the Si sites are renumbered, keeping the same order. The crystal structure of meliphanite is layered on (001) (Fig. 3). The close relation of the meliphanite and leucophanite structures and the dominant twin-plane are shown in Figure 4. It should be noted that although one of the leucophanite crystals used in crystal-structure analysis is rich in REE (sample CMNMC 36557 in Table 1), the lowering of symmetry to triclinic reported by Cannillo *et al.* (1992) could not be confirmed. The statistics obtained in the authors' experiment would not allow an interpretation of ordering of REE within the

TABLE 3. MELIPHANITE: DATA COLLECTION AND
STRUCTURE-REFINEMENT INFORMATION

Locality: Arøy, Norway	Sample # SMNH 531225
Cell content: Ca ₄ (Na,Ca) ₄ Be ₄ AlSi ₇ O ₂₄ (F,O) ₄	Crystal size (mm) 0.15 x 0.15 x 0.10
Space Group: $\bar{I}4$ (No. 82)	Reflections collected 1870
<i>a</i> 10.5257(3) Å	Unique reflections 1613
<i>c</i> 9.8868(4) Å	Observed reflections (> 4σ <i>F_o</i>) 1578
<i>V</i> 1095.37(8) Å ³	Merged reflections 853
Radiation: MoKα	<i>R</i> (merge) = 0.0113
μ 1.66 mm ⁻¹	Goof = 1.075 (all data)
$R = \Sigma(F_o - F_c) / \Sigma F_o =$	$wR^2 = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2] = 0.071$
0.025 (for <i>F_o</i>), 0.026 (for all <i>F</i>) and	$w = 1 / (\sigma^2(F_o^2) + [0.04(\text{Max}(F_o^2, 0) + 2F_c^2) / 3]^2)$
0.024 (for all <i>F</i> merged)	

TABLE 4. MELIPHANITE: ATOM COORDINATES AND
ANISOTROPIC DISPLACEMENT PARAMETERS (Å²)

Site	Wyck*	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{eq}	BVS**
Ca	8g	0.25462(4)	0.09040(4)	0.25568(5)	0.0129(2)	0.0083(2)	0.0094(2)	0.0010(2)	-0.0013(2)	0.0000(1)	0.0102(1)	1.95
Na	8g	0.23900(8)	0.08693(7)	0.75073(10)	0.0387(5)	0.0147(3)	0.0192(4)	0.0025(3)	0.0054(4)	0.0007(3)	0.0242(3)	1.13
Al	2a	0	0	0	0.0061(6)	0.0061(6)	0.0069(9)	0	0	0	0.0063(5)	3.23
Si1	2b	0	0	1/2	0.0057(3)	0.0057(3)	0.0094(6)	0	0	0	0.0069(2)	3.87
Si2	4f	1/2	0	0.00573(3)	0.0089(4)	0.0091(4)	0.0109(4)	0	0	-0.0003(3)	0.0096(2)	3.78
Si3	8g	0.25251(6)	0.88834(6)	0.97402(7)	0.0088(3)	0.0081(3)	0.0085(3)	-0.0004(2)	-0.0007(2)	0.0002(2)	0.0085(1)	4.01
Be	8g	0.24830(19)	0.89319(18)	0.47330(22)	0.0092(9)	0.0066(9)	0.0097(9)	0.0012(6)	0.0002(6)	-0.0000(6)	0.0085(6)	1.96
O1	8g	0.25297(14)	0.25601(14)	0.08835(18)	0.0076(7)	0.0126(7)	0.0078(7)	0.0001(5)	-0.0011(5)	-0.0002(6)	0.0093(3)	2.16
O2	8g	0.12502(15)	0.96902(16)	0.40747(18)	0.0083(7)	0.0118(7)	0.0124(8)	0.0025(6)	0.0019(6)	0.0018(6)	0.0108(3)	1.84
O3	8g	0.12831(15)	0.95323(16)	0.90262(18)	0.0080(7)	0.0122(7)	0.0100(7)	0.0020(6)	-0.0011(6)	0.0023(6)	0.0101(3)	2.13
O4	8g	0.37662(15)	0.95923(16)	0.40499(18)	0.0069(7)	0.0104(7)	0.0107(7)	0.0020(6)	-0.0016(6)	-0.0019(6)	0.0093(3)	1.91
O5	8g	0.37771(15)	0.96106(17)	0.90772(18)	0.0096(7)	0.0129(7)	0.0105(7)	0.0013(6)	-0.0011(6)	-0.0030(6)	0.0110(3)	1.95
O6	8g	0.25369(16)	0.89533(16)	0.13478(16)	0.0107(7)	0.0106(7)	0.0076(6)	-0.0004(5)	-0.0008(6)	0.0003(6)	0.0096(3)	1.80
F	8g	0.24825(15)	0.89211(15)	0.63154(14)	0.0155(8)	0.0157(8)	0.0104(7)	-0.0016(5)	0.0006(6)	-0.0011(6)	0.0139(4)	0.85

* multiplicity and site symmetry

** bond-valence sum using parameters of Brese & O'Keeffe (1991)

cation sites. Without this cation order, the crystal structure remains in the orthorhombic crystal system. If the interpretation of Cannillo *et al.* (1992) is correct, then their mineral is not leucophanite but a new mineral species.

Meliphanite and leucophanite are structurally related to the melilite group of minerals. Members of this group, åkermanite, gehlenite, gugiaite and hardystonite, have the general formula A_2T1T2X_7 with $A = \text{Na, Ca}$; $T1 = \text{Al, Be, Mg, Zn}$; $T2 = \text{Al and Si}$, and $X = \text{O, F}$. In addition to these minerals, several related phases have been synthesized (Armbruster *et al.* 1990). The dominant feature in the crystal structure of all these compounds is the sheet of $T1$ and $T2$ tetrahedra. The strongly bonded sheets are cross-linked into a three-dimensional structure by more weakly bonded alkali and alkaline-earth cations (A cations). To understand the relation of leucophanite and meliphanite, it is necessary to examine the topology of the layer of tetrahedra.

Within the melilite group, the crystal structures of several minerals have been refined; of particular interest in the present case are gehlenite, $\text{Ca}_2\text{Al}(\text{Si,Al})_2\text{O}_7$ (Louisnathan 1971) and gugiaite, $\text{Ca}_2\text{BeSi}_2\text{O}_7$ (Yang *et al.* 2001). These isomorphous structures have space-group symmetry $P\bar{4}2_1m$; in gehlenite, Al occupies the $T1$ site with point symmetry 4, and the $T2$ site (with point symmetry m) is occupied by $\text{Al}_{1/2}\text{Si}_{1/2}$; in gugiaite, Be occupies the $T1$ and Si the $T2$ sites. If we consider the sheet as a two-dimensional net (*e.g.*, Smith 1977, Hawthorne & Smith 1986), it may be represented by the general symbol $(5^3)_1(5^4)_1$; the vertices representing centers of tetrahedra within the layer of tetrahedra outline a pentagonal net, and there are two types of vertices, 3-connected and 4-connected. In gugiaite, Be occupies the (5^4) vertex, and Si occupies the (5^3) vertex (Fig. 5a, Table 6). In the leucophanite structure, the degree of complexity within the net increases to $(5^3)_2(5^4)_1$, with $Si1$ and Be at each of the (5^3) vertices and $Si2$ at the (5^4) vertex (Fig. 5b, Table 6). This reversal in preference of Be for a (5^3) than a (5^4) vertex was explained by Grice & Hawthorne (1989) in terms of satisfaction of local bond-valence requirements within the sheet by the addition of F. The meliphanite structure builds further on this theme, with a net topology $(5^3)_2(5^4)_3$ (Fig. 5c, Table 6). Again, Be occupies a (5^3) vertex and has a F ligand, $Si3$ occupies the other (5^3) vertex, $Si1$ and $Si2$ occupy (5^4) vertices, and Al occupies the largest tetrahedral site with a (5^4) vertex. Aminoffite (Hurlbut 1937) was initially classified in the melilite group because of its chemical similarity, $\text{Ca}_3\text{Be}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$, and it has the same crystal system and a very similar cell to that of meliphanite. Looking closely at the crystal structure, we see that the net is dramatically different, $(4.6^2)_2(6^4)$ (Fig. 5d, Table 6). In that structure, Be occupies a 3-connected vertex, (4.6^2) , as does $Si1$, whereas $Si2$ is at a 4-connected vertex (6^4) . As F stabilizes Be at 3-connected vertices in leucophanite and meliphanite, it is the (OH) group that satisfies

TABLE 5. MELIPHANITE: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Ca square anti-prism		Na square anti-prism	
Ca-O6	2.376(2)	Na-O1	2.306(2)
Ca-O4	2.395(2)	Na-O3	2.365(2)
Ca-O2	2.397(2)	Na-F	2.367(2)
Ca-O1	2.403(2)	Na-O5	2.509(2)
Ca-O6	2.462(2)	Na-O6	2.522(2)
Ca-F	2.528(2)	Na-F	2.639(2)
Ca-O4	2.699(2)	Na-O2	2.721(2)
Ca-O3	2.719(2)	Na-O5	2.838(2)
(Ca- ϕ)	(2.497)	(Na- ϕ)	(2.533)
Al-O tetrahedron			
Al-O3	1.730(2) X 4	O3-Al-O3	108.04(5) X 3
(Al-O)	(1.730)	O3-Al-O3	112.27(5) X 3
		(O-Al-O)	(110.16)
Si1-O tetrahedron			
Si1-O2	1.636(2) X 4	O2-Si1-O2	108.23(6) X 3
(Si1-O)	(1.636)	O2-Si1-O2	111.9(1) X 3
		(O-Si1-O)	(110.16)
Si2-O tetrahedron			
Si2-O4	1.628(2) X 2	O4-Si2-O4	114.32(13)
Si2-O5	1.663(2) X 2	O5-Si2-O4	108.87(8) X 2
(Si2-O)	(1.646)	O5-Si2-O4	107.98(8) X 2
		O5-Si2-O5	108.70(13)
		(O-Si2-O)	(109.97)
Si3-O tetrahedron			
Si3-O6	1.591(2)	O1-Si3-O6	115.15(10)
Si3-O1	1.611(2)	O3-Si3-O6	114.72(10)
Si3-O3	1.635(2)	O5-Si3-O6	111.54(9)
Si3-O5	1.659(2)	O3-Si3-O1	103.82(9)
(Si3-O)	(1.624)	O5-Si3-O1	104.87(9)
		O5-Si3-O3	105.77(9)
		(O-Si3-O)	(109.31)
Be- ϕ tetrahedron			
Be-F	1.565(3)	O1-Be-F	112.01(15)
Be-O1	1.597(3)	O2-Be-F	113.33(15)
Be-O2	1.657(3)	O4-Be-F	114.18(14)
Be-O4	1.662(3)	O2-Be-O1	105.84(15)
(Be- ϕ)	(1.620)	O4-Be-O1	104.74(14)
		O4-Be-O2	105.98(13)
		(O-Be-O)	(109.35)

the local bond-valence requirements for Be in aminoffite. Aminoffite should not be classified in the melilite group of structures.

The differences between the closely related minerals leucophanite and meliphanite are now well understood. They may be differentiated by powder diffraction (differing d -values at low 2θ), single-crystal X-ray dif-

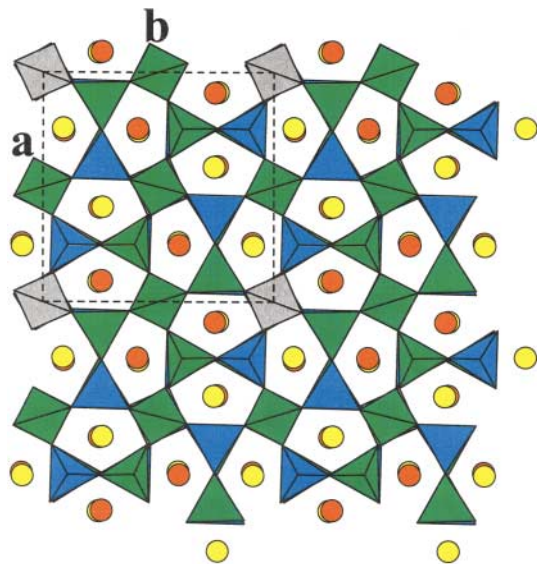


FIG. 3. The meliphanite structure projected along [001]. The (SiO_4) tetrahedra are green, (AlO_4) tetrahedra are grey and the $(\text{Be}\phi_4)$ tetrahedra are blue, the Na atoms are yellow, and the Ca atoms are orange. The unit cell is outlined. ϕ : unspecified anion.

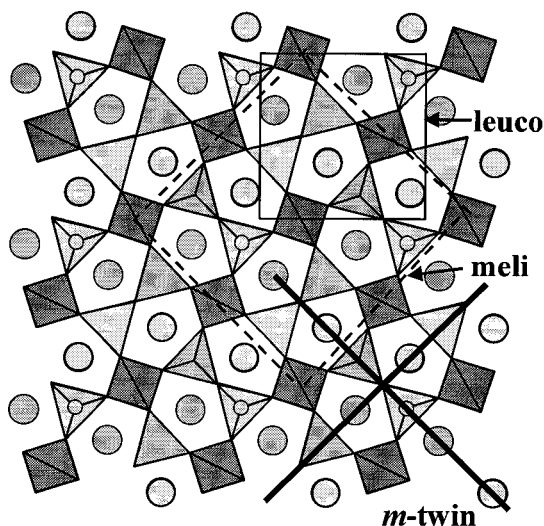


FIG. 4. The relationship in the crystal structure of meliphanite (meli) and leucophanite (leuco), shown projected along [001]. The twin plane $m\{100\}$ of meliphanite is shown.

fraction (orthorhombic P lattice in leucophanite, and a tetragonal I lattice in meliphanite) and chemical analysis (leucophanite has very little or no Al, whereas meliphanite has essential Al). It is of interest that although the two minerals are closely related, they do not coexist. This mutual exclusion is likely geochemical rather than crystal chemical, as differences in the activity of Al in the environment of growth of these minerals seem critical in their paragenesis.

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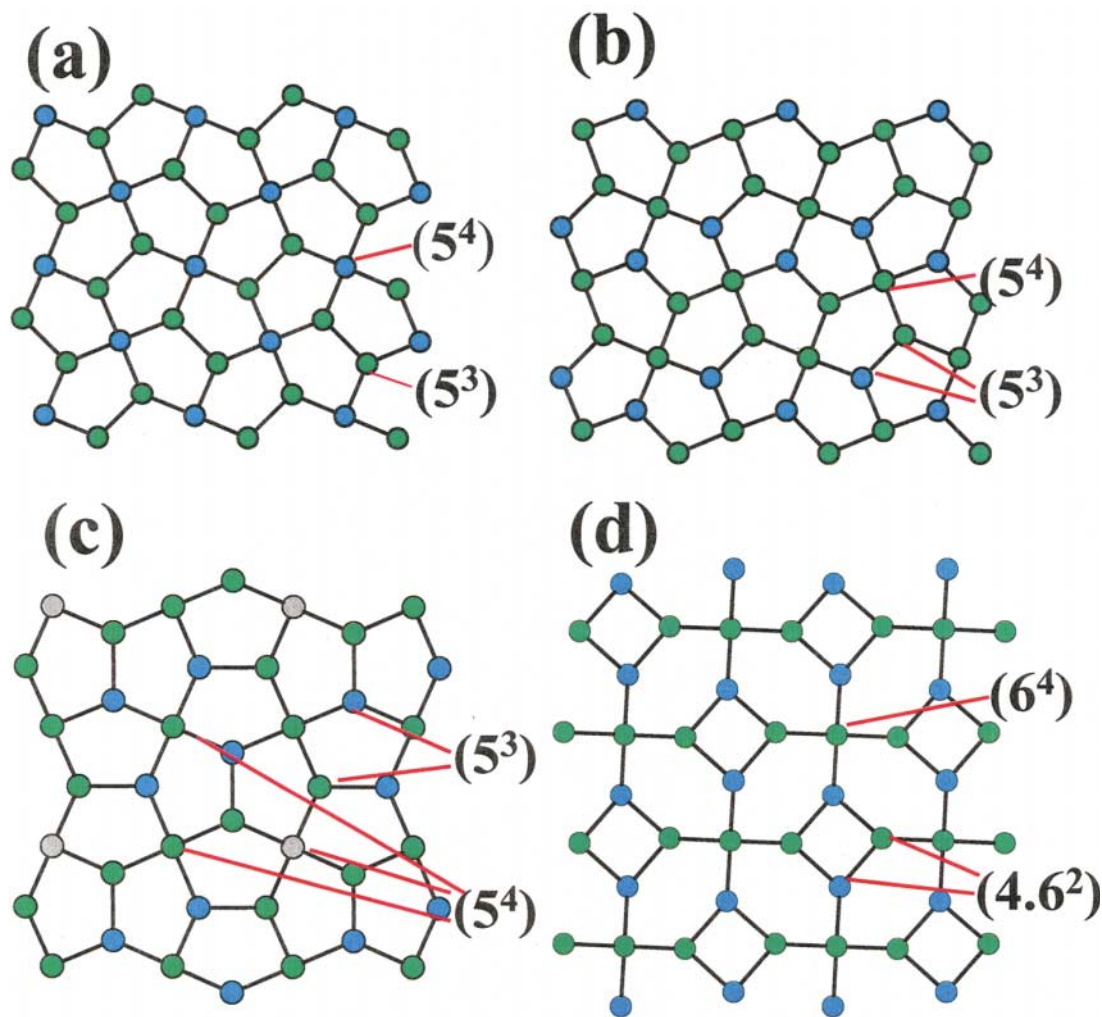


FIG. 5. Topologies of the layers of tetrahedra. The vertices, which represent centers of tetrahedra, are colored; Si is green and Be is blue. The vertices are connected to outline the polygons that define the two-dimensional net: (a) gugiaite with Be at (5⁴) and Si at (5³), (b) leucophanite with Be at (5³), Si1 at (5³) and Si2 at (5⁴), (c) meliphanite with Be at (5³), Al at (5⁴), Si1 at (5⁴), Si2 at (5⁴) and Si3 at (5³), (d) aminoffite with Be at (4.6²), Si1 at (4.6²) and Si2 at (6⁴).

TABLE 6. COMPARISON OF MELILITE-TYPE STRUCTURES

Mineral	Space Group	Cell	A	T1	T2	X	Ref*
åkermanite	$P\bar{4}2_1m$	7.84, 5.01	Ca ₂	Mg (5 ⁴)	Si ₂ (5 ³)	O ₇	(1)
gehlenite	$P\bar{4}2_1m$	7.72, 5.09	Ca ₂	Al (5 ³)	(Si, Al) ₂ (5 ³)	O ₇	(2)
gugiaite	$P\bar{4}2_1m$	7.43, 5.00	Ca ₂	Be (5 ⁴)	Si ₂ (5 ³)	O ₇	(3)
hardystonite	$P\bar{4}2_1m$	7.80, 5.00	Ca ₂	Zn (5 ⁴)	Si ₂ (5 ³)	O ₇	(4)
"soda-melilite"	$P\bar{4}2_1m$	7.63, 5.05	(CaNa)	Al (5 ⁴)	Si ₂ (5 ³)	O ₇	(5)
leucophanite	$P2_12_12_1$	7.40, 7.41, 9.99	(Ca)(Na)	Be (5 ³)	Si ₂ (5 ³) (5 ⁴)	O ₆ F	(6)
meliphanite	$I\bar{4}$	10.51, 9.89	(Ca) ₄ (Na) ₄	Be ₂ (5 ³)	Al (5 ⁴) Si ₂ (5 ⁴) (5 ³)	O ₁₀ F ₄	(7)
aminoffite	$P4_2/n$	9.86, 9.93	Ca ₃	Be ₂ (6 ^{2.4})	Si ₃ (6 ^{2.4}) (6 ⁴)	O ₁₀ (OH) ₂	(8)

*Reference: (1) Kimata & Ii (1981), (2) Louisnathan (1971), (3) Yang *et al.* (2001), (4) Bindi *et al.* (2001), (5) Louisnathan (1970), (6) Grice & Hawthorne (1989), (7) present study, (8) Huminicki & Hawthorne (2002).

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