

LENAITE FROM THE GIES GOLD–SILVER TELLURIDE DEPOSIT, JUDITH MOUNTAINS, MONTANA, USA: OCCURRENCE, COMPOSITION, AND CRYSTAL STRUCTURE

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ABSTRACT

Lenaite, AgFeS_2 , a very rare silver–iron sulfide, was found in a sample in the mineralogical collection of the Natural History Museum of Florence. The sample is from the Gies gold–silver telluride deposit, Judith Mountains, Montana. Lenaite in this sample occurs as anhedral grains up to 0.2 mm across. It is steel-grey in color and has a black streak. No cleavage is observed, and the Vickers hardness (VHN_{10}) is 285 kg/mm^2 . Lenaite is greyish white, non-pleochroic, moderately anisotropic in yellowish tints, and it shows no birefractance. Reflectance values in air for R_{\min} and R_{\max} are 28.2, 30.6 (471.1 nm), 31.8, 35.8 (548.3 nm), 32.8, 36.5 (586.6 nm), and 30.9, 35.0% (652.3 nm), respectively. Lenaite is tetragonal and belongs to the space group $I4_2d$, with the following unit-cell parameters: a 5.4371(2), c 10.8479(9) Å, V 320.69(3) Å³, and Z = 4. Electron-microprobe analyses gave the chemical formula $\text{Ag}_{0.96}\text{Fe}_{1.01}\text{S}_{2.02}$. The crystal structure has been solved and refined to R = 3.63%. It consists of corner-sharing ¹⁴¹M and ¹⁴¹X tetrahedra forming cubic or pseudocubic frameworks, as in sphalerite, but with cation order. The crystal-chemical relationships with other members of the chalcopyrite group are outlined.

Keywords: lenaite, chalcopyrite, imiterite, chemical composition, physical properties, crystal-structure determination, Gies, Montana.

SOMMAIRE

Nous signalons la présence de lénaïte, AgFeS_2 , sulfure rarissime d'argent et de fer, dans un échantillon de la collection minéralogique du musée d'Histoire Naturelle de Florence. L'échantillon provient du gisement de tellurures d'or et d'argent de Gies, dans les montagnes Judith, au Montana. La lénaïte se présente en grains xénomorphes atteignant 0.2 mm. Ils sont gris-acier et possèdent une rayure noire. Nous n'avons vu aucun clivage; la dureté de Vickers (VHN_{10}) est 285 kg/mm^2 . La lénaïte est blanc grisâtre, non pléochroïque, modérément anisotrope en teintes de jaune, et elle ne montre aucune biréfractance. Les valeurs de réflectance dans l'air (R_{\min} et R_{\max}) sont 28.2, 30.6 (471.1 nm), 31.8, 35.8 (548.3 nm), 32.8, 36.5 (586.6 nm), et 30.9, 35.0% (652.3 nm), respectivement. La lénaïte est tétraogonale, groupe d'espace $I4_2d$, avec les paramètres réticulaires suivants: a 5.4371(2), c 10.8479(9) Å, V 320.69(3) Å³, et Z = 4. Les analyses, effectuées avec une microsonde électronique, ont donné la formule $\text{Ag}_{0.96}\text{Fe}_{1.01}\text{S}_{2.02}$. La structure cristalline a été résolue jusqu'à un résidu R de 3.63%. Elle contient des tétraèdres ¹⁴¹M et ¹⁴¹X à coins partagés, formant des trames cubiques ou pseudocubiques, tout comme dans la sphalérite, mais avec une distribution ordonnée des cations. Nous décrivons les relations cristallographiques avec les autres membres du groupe de la chalcopyrite.

(Traduit par la Rédaction)

Mots-clés: lénaïte, chalcopyrite, imiterite, composition chimique, propriétés physiques, structure cristalline, Gies, Montana.

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INTRODUCTION

An unnamed Ag–Fe sulfide with the formula AgFeS_2 , found in association with various Ni–Co–Fe arsenides, was described from the Tynebottom mine, Garrigill, Cumbria, England by Ixer & Stanley (1987). It occurs as lamellae up to 15 μm across in chalcopyrite. They reported it as being pale grey-buff in air, non-pleochroic and slightly anisotropic. Nekrasov *et al.* (1987) also reported a mineral with the same composition occurring as a rim 0.1 mm wide on grains of Ag-bearing chalcopyrite in the Aid and Alfa silver deposit, Siberia, Russia. Since then, Zhang & Spry (1994) described the Ag–Fe sulfide (“unnamed mineral 1”) as inclusions up to 20 μm across in a veinlet 50 μm wide coexisting with hessite and pyrite in the epithermal Gies gold–silver telluride deposit, Judith Mountains, Montana. The name *lenaite* was formally given to AgFeS_2 by Amuzinskii *et al.* (1995); they reported it as grains up to 0.2 mm in length in goethite pseudomorphs after magnesian siderite from the Khachakchanskoye silver occurrence, Lena River basin, Yakutia, Russia. It is also spatially associated with acanthite, chalcopyrite, and Ag-rich members of the tetrahedrite group in quartz–siderite veins. The optical properties given by Amuzinskii *et al.* (1995) for lenaite match those given previously for the unnamed phases by Ixer & Stanley (1987), Nekrasov *et al.* (1987), and Zhang & Spry (1994).

In the course of a revision of the mineralogical collection of the Natural History Museum of Florence (Bindi *et al.* 2005, and references therein), we discovered a sample of lenaite from the Gies deposit (catalogue number 44285/G, labeled proustitite). In this paper, we report the physical and chemical characteristics of lenaite from the Gies deposit, together with

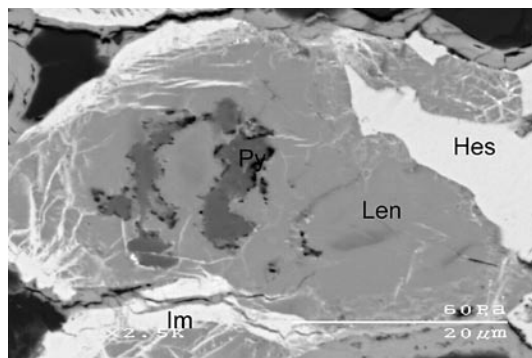


FIG. 1. Back-scattered electron image of lenaite (Len) containing inclusions of pyrite (Py) and in contact with hessite (Hes). It is also rimmed and cross-cut by imiterite (Im). Sample 90–P13; the image was obtained using Hitachi S 2460 reduced-vacuum scanning electron microscope at an accelerating voltage of 20 kV.

a determination of the crystal structure. We have also re-examined the specimen of lenaite (sample 90–P13) of Zhang & Spry (1994) by optical methods and with a scanning electron microscope.

OCCURRENCE OF LENAITE AND GEOLOGICAL SETTING

The Gies deposit is an epithermal vein system that occurs along the contact between Cretaceous–Tertiary alkaline intrusive rocks (monzonite, syenite, and tinguaitite) and Cambrian to Cretaceous sedimentary rocks (limestone, sandstone, and siltstone) in the Judith Mountains, Montana. The average grade of the deposit was about 14 g/t gold. Thirty-six ore and gangue minerals were identified by Zhang & Spry (1994) in four hypogene stages. The first three stages correlate with quartz-forming events, whereas the last three stages contain tellurides. Sulfides are found in all four stages, with lenaite occurring in stage-IV veinlets (<1 mm wide) that cross-cut minerals of stage III. In sample 44285/G, lenaite occurs as anhedral grains up to 0.2 mm across spatially associated with proustitite, tetrahedrite, tennantite, chalcopyrite, and pyrite.

A re-examination of sample 90–P13 of Zhang & Spry (1994) shows the presence of the following ore minerals: hessite, pyrite, lenaite, native gold, chalcopyrite, polybasite, tennantite, and the rare phase imiterite (Ag_2HgS_2). Lenaitite occurs in contact with hessite, pyrite, and imiterite, with the last mineral cross-cutting lenaite (Fig. 1). Imiterite has been reported previously from only two localities (Guillou *et al.* 1985, Walenta & Hess 1985).

Although fluid-inclusion studies show that stages I, II, and III formed between 270° and 320°C, there was no suitable mineral on which to conduct a fluid-inclusion study in the stage-IV lenaite-bearing material. However, we speculate that lenaite formed at less than 170°C because of the presence of coexisting hessite and Au–Ag alloy in sample 90–P13 of Zhang & Spry (1994) from stage IV and the intimate spatial association between hessite and lenaite. Coexisting Au–Ag alloy and hessite would have formed as products of the decomposition of the γ phase, a composition intermediate between hessite and petzite, which forms only below 170°C (Cabri 1965).

PHYSICAL AND OPTICAL PROPERTIES

Lenaite is steel-grey in color and shows a black streak. The mineral is opaque with a metallic luster. The micro-indentation measurements carried out with a VHN load of 10 g on sample 44285/G gave a mean value of 285 kg/mm^2 (range: 270–300), corresponding to a Mohs hardness of about 4 – 4½. This value is slightly lower than that found by Amuzinskii *et al.* (1995) for lenaite from the Khachakchanskoye ore deposit (310 kg/mm^2). In reflected light, lenaite in sample 44285/G is greyish white, non-pleochroic, moderately anisotropic

in yellowish tints, and shows no birefractance. There are no internal reflections.

Reflectance measurements were performed in air with a MPM–200 Zeiss microphotometer equipped with a MSP–20 system processor on a Zeiss Axioplan ore microscope on the 44285/G sample. Filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same conditions of focus. The diameter of the circular measuring area was 0.1 mm. Measurements of reflectivity (in %) for R_{\min} and R_{\max} are 28.2, 30.6 (471.1 nm), 31.8, 35.8 (548.3 nm), 32.8, 36.5 (586.6 nm), and 30.9, 35.0 (652.3 nm), respectively.

CHEMICAL COMPOSITION

A preliminary chemical analysis using EDS, performed on the same crystal fragment as that used for the structural study, did not indicate elements ($Z > 9$) other than Ag, Fe, S and very minor Sb, As and Cu. The chemical composition was then determined by means of a JEOL JXA–8600 electron microprobe. Concentrations of the major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with variable count-times: 30 s were used for Ag, Fe and S, and 60 s for the minor elements Sb, As and Cu. For the wavelength-dispersion analyses, the following lines were used: $\text{AgL}\alpha$, $\text{FeK}\alpha$, $\text{SK}\alpha$, $\text{SbL}\beta$, $\text{AsL}\alpha$, and $\text{CuK}\alpha$. We employed the following standards: pure silver (Ag), marcasite (Fe, S), synthetic GaAs (As), pure copper (Cu), and synthetic Sb_2Te_3 (Sb). The crystal fragment was found to be homogeneous within analytical uncertainty. The average chemical composition, together with ranges of wt.% of elements, is reported in Table 1. On the basis of four atoms, the empirical formula is $\text{Ag}_{0.96}\text{Fe}_{1.01}\text{S}_{2.02}$, which is similar to that reported by Amuzinskii *et al.* (1995): $\text{Ag}_{0.98}\text{Fe}_{0.98}\text{S}_{2.04}$.

CRYSTAL-STRUCTURE SOLUTION AND REFINEMENT

A small fragment ($15 \times 25 \times 25 \mu\text{m}$) from sample 44285/G was selected for the single-crystal X-ray-diffraction study. The data collection intensity ($3 < \theta < 50^\circ$) was carried out by means of an Oxford Diffraction Xcalibur 2 single-crystal diffractometer (enhanced X-ray source, X-ray radiation $\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$) fitted with a Sapphire–2 CCD detector. A total of 1985 frames of data were collected at room temperature as 12 sets of omega runs with an exposure time of 40 s per frame and a frame width of 0.75° . This afforded an overall data-collection of 15048 reflections (836 unique). Data frames were processed using the *CRYSTALIS* software package (Oxford Diffraction 2002) running on the Xcalibur 2 control PC. The empirical method proposed

by Blessing (1995) was applied for the absorption correction. The merging R for the data set decreased from 9.31% before the absorption correction to 5.24% after this correction. Systematic absences (hkl : $h + k + l = 2n$; $hk0$: $h + k = 2n$; $0kl$: $k + l = 2n$; hhl : $2h + l = 4n$; $00l$: $l = 4n$; $h00$: $h = 2n$; $h\bar{h}0$: $h = 2n$) are consistent with the space groups $I4_1md$ and $I\bar{4}2d$. In view of the close similarity with the minerals of the chalcopyrite group, we decided to solve the structure in the space group $I\bar{4}2d$. The positions of silver and iron atoms were determined from a three-dimensional Patterson synthesis (Sheldrick 1997a). A least-squares refinement using these heavy-atom positions and isotropic temperature-factors yielded an R factor of 8.55%. Three-dimensional difference-Fourier synthesis yielded the position of the remaining sulfur atom. The full-matrix least-squares program SHELXL–97 (Sheldrick 1997b) was used for the refinement of the structure. The introduction of anisotropic temperature-factors for all the atoms led to $R = 3.63\%$ for 651 observed reflections [$F_o > 4\sigma(F_o)$] and $R = 3.88\%$ for all 836 independent reflections. Neutral scattering curves for Ag, Fe and S were taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Inspection of the difference-Fourier map revealed that maximum positive and negative peaks were 3.85 and $3.77 e^-/\text{\AA}^3$, respectively.

In contrast with what is observed for the chalcopyrite structure (Hall & Stewart 1973), the absolute structure cannot be determined accurately. In fact, the Flack parameter is 0.53(8) for the data presented here, and 0.51(8) for the inverted structure. Experimental details and R indices are given in Table 2. Fractional atomic coordinates and anisotropic-displacement parameters are shown in Table 3.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

In their mineralogical classification Strunz & Nickel (2001) considered lenaite as a member of the chalcopyrite group. There are six members: chalcopyrite, CuFeS_2 (Hall & Stewart 1973), gallite, CuGaS_2 (Strunz *et al.* 1958), roquesite, CuInS_2 (Picot & Pierrot 1963), eskebornite, CuFeSe_2 (Delgado *et al.* 1992), lenaite,

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF LENAITE

	wt.%	range	$\sigma(\%)$
Ag	45.86	45.03 – 46.39	0.40
Fe	24.97	24.12 – 25.60	0.30
S	28.53	27.98 – 28.90	0.30
Sb	0.00	0.00 – 0.34	0.02
As	0.00	0.00 – 0.41	0.02
Cu	0.00	0.00 – 0.52	0.02
Total	99.36		

Note: Six spot-analyses on the same crystal. Sample 44285/G.

AgFeS₂ (Amuzinskii *et al.* 1995), and laforêtite, AgInS₂ (Meisser *et al.* 1999). Apart from eskebornite (space group *P42c*, Delgado *et al.* 1992) and lenaite (space group proposed *P4₂mc*, Amuzinskii *et al.* 1995), all the others are characterized by space group *I42d*, unit-cell dimensions *a* in the range 5.29 – 5.88 Å, 10.42 < *c* < 11.21 Å, and *Z* = 4. From the crystallographic point of view, however, only the crystal structure of chalcopyrite has been investigated (Hall & Stewart 1973). It consists of corner-sharing ⁴*M* and ⁴*X* tetrahedra forming cubic or pseudocubic frameworks, as in sphalerite, but with order of the cations. On the whole, the crystal structure of lenaite refined here (Fig. 2) is topologically identical to that of chalcopyrite, apart from the deviations expected from the metal size (*i.e.*, Ag with respect to Cu). Both Ag and Fe atoms are tetrahedrally surrounded by S atoms, with distances Ag–S of 2.4698(4) Å, and Fe–S of 2.2458(3) Å.

One of the most interesting structural peculiarities of the crystal structure of lenaite is the angle that the sulfur atoms subtend with the different metals. The two independent S–Fe–S angles of the iron tetrahedron are 111.38(1) and 105.72(1)°, whereas the S–Ag–S angles in the silver tetrahedron are 113.40(1) and 107.54(1)° (Fig. 3). On the other hand, Hall & Stewart (1973) showed that the coordination of iron in chalcopyrite is perfectly tetrahedral [S–Fe–S: 109.47(4) and 109.47(3)°, respectively], whereas the coordination of copper resembles a flattened tetrahedron [S–Cu–S: 111.06(3) and 108.68(4)°, respectively] in the *z* direction of the cell. The combination of distorted tetrahedrally coordinated silver and iron atoms in the crystal structure of lenaite apparently induces a strong increase in the distortion parameter σ^2 (Robinson *et al.* 1971) of the S(Ag₂Fe₂) tetrahedron. In fact, the value of this parameter, 24.05, exceeds by far that observed in chalcopyrite [$\sigma^2 = 1.40$ for S(Cu₂Fe₂): Hall & Stewart (1973)] and those observed in the stannite–kësterite join [$\sigma^2 = 2.06$ –3.51 for the S(*M*₃Sn): Bonazzi *et al.* (2003)].

By comparing the crystal structures of chalcopyrite (Hall & Stewart 1973), talnakhite (Hall & Gabe 1972), mooihoeite (Hall & Rowland 1973), and haycockite (Rowland & Hall 1975), Hall (1975) pointed out that the relative magnitude of the thermal motion for the Cu, Fe and S atoms in these minerals is remarkably consistent. Hall (1975) noted that the average isotropic

temperature-factor of the iron atoms is consistently lower than that for the copper atoms. The likely cause for this difference is the stronger covalent interaction between iron and sulfur over copper and sulfur, as indicated by the markedly shorter Fe–S bond distances with respect to Cu–S. For the lenaite sample studied here, we observed a very similar average isotropic temperature-factor for the Ag and Fe atoms (Table 3), thus indicating a similar covalent interaction between metals and sulfur atoms. It should be stressed, however, that Hall (1975) analyzed temperature factors and distortions of coordination polyhedra in order to find out possible guidelines to determine the degree of metal order in the chalcopyrite-group minerals. In the case of lenaite, since there is a strong difference in size between silver and iron, together with the marked difference in the mean number of electrons, we were able to determine the tetrahedral environment of both metals.

Table 4 shows the X-ray powder pattern calculated using the structural data obtained in this study, together with that reported by Amuzinskii *et al.* (1995) for lenaite from the type locality. It is evident that the patterns

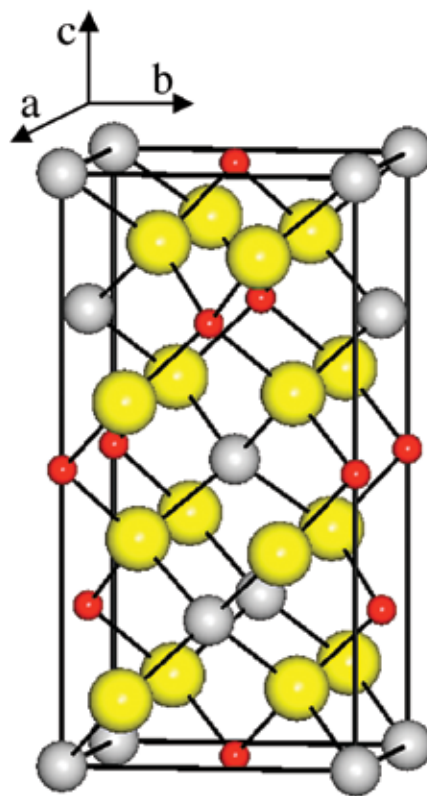


Fig. 2. The crystal structure of lenaite. Grey, red and yellow circles refer to Ag, Fe and S atoms, respectively. The unit cell is outlined.

TABLE 2. EXPERIMENTAL DETAILS FOR THE LENAITE CRYSTAL SELECTED

space group	<i>I42d</i> (#122)	theta range (°)	3–50
cell parameters		independent reflections	836
<i>a</i> (Å)	5.4371(2)	reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	651
<i>c</i> (Å)	10.8479(9)	<i>R</i> _{int} (%)	3.63
<i>V</i> (Å ³)	320.69(3)	<i>R</i> _{all} (%)	3.88
crystal size (µm)	15 × 25 × 25		
radiation	MoKα		
	40 mA, 40 kV		

TABLE 3. FRACTIONAL COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN LENAITE

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Ag	0	0	0	0.01620(6)	U_{11}	0.01586(7)	0	0	0	0.01609(5)
Fe	0	0	½	0.0152(1)	U_{11}	0.0148(1)	0	0	0	0.01505(7)
S	0.2857(1)	¼	⅙	0.0189(2)	0.0175(2)	0.0176(3)	0	0	-0.0003(2)	0.0180(1)

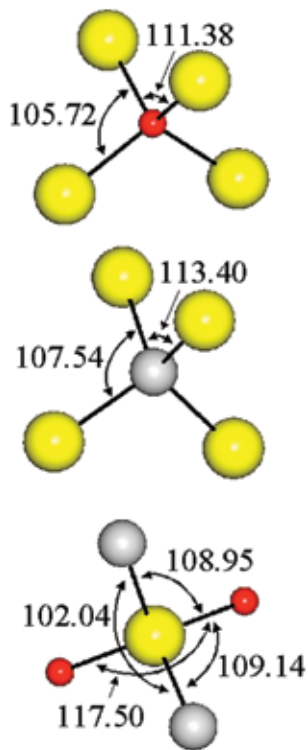


FIG. 3. Interatomic angles in lenaite. Symbols as in Figure 2. The unit cell is outlined.

differ from one another significantly. Amuzinskii *et al.* (1995) reported only 14 lines in their diffraction pattern, and the attribution of the space group $P4_2mc$ to lenaite is considered questionable. One can speculate that the original lenaite and the mineral examined here could represent two distinct species; however, the chemical composition of the two minerals is identical. On the other hand, possible reasons for the observed discrepancies could be the small amount of material (very small grain-size) available to Amuzinskii *et al.* (1995), as well as the possibility of intergrowths with other Ag-sulfides.

TABLE 4. X-RAY POWDER-DIFFRACTION PATTERN OF LENAITE

hkl	1			2		
	d_{calc} (Å)	I/I_{calc}		hkl	d_{obs} (Å)	I/I_0
101	4.8607	7	-	-	-	-
-	-	-	-	003	3.43	1
112	3.1366	100	-	112	3.15	10
103	3.0109	5	-	-	-	-
-	-	-	-	200	2.824	1
200	2.7185	12	-	201	2.726	≤ 1
004	2.7120	5	-	-	-	-
-	-	-	-	004	2.586	1
-	-	-	-	211	2.445	2
211	2.3727	6	-	-	-	-
-	-	-	-	104	2.340	≤ 2
-	-	-	-	203	2.191	1
-	-	-	-	005	2.072	1
213	2.0178	2	-	220	1.998	1
105	2.0151	2	-	-	-	-
220	1.9223	17	-	-	-	-
204	1.9200	34	-	204	1.910	4
301	1.7876	2	-	-	-	-
-	-	-	-	312	1.692	2
-	-	-	-	205	1.670	≤ 1
312	1.6390	23	-	-	-	-
116	1.6361	12	-	-	-	-
224	1.5683	4	-	-	-	-
323	1.3918	1	-	-	-	-
400	1.3593	4	-	-	-	-
008	1.3560	2	-	-	-	-
217	1.3068	1	-	-	-	-
-	-	-	-	332	1.288	< 1
332	1.2472	4	-	-	-	-
316	1.2459	8	-	-	-	-
325	1.2383	1	-	-	-	-
420	1.2158	2	-	-	-	-
404	1.2152	2	-	-	-	-
208	1.2134	1	-	-	-	-
424	1.1094	8	-	-	-	-
228	1.1081	4	-	-	-	-
512	1.0463	4	-	-	-	-
336	1.0455	2	-	-	-	-
11.10	1.0440	-	-	-	-	-

1: d values calculated on the basis of a 5.4371(2), c 10.8479(9) Å, and with the atom coordinates reported in Table 3. Intensities calculated using XPOW software version 2.0 (Downs *et al.* 1993).

2: observed powder-diffraction pattern and indexing originally reported by Amuzinskii *et al.* (1995).

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