

Qandilite, a new spinel end-member, Mg_2TiO_4 , from the Qala-Dizeh region, NE Iraq

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ABSTRACT. Qandilite, a new species of the spinel group, has been found in a forsterite-rich rock in contact with a kaersutite-rich banded diorite from the Qala-Dizeh region, NE Iraq. Chemical analysis yielded MgO 29.62, FeO 10.32, MnO 0.76, Fe_2O_3 28.27, Al_2O_3 4.83, TiO_2 26.41, SiO_2 0.02, sum 100.23 wt. %. This analysis calculates to $[(\text{Mg}_{1.20}\text{Ti}_{0.60})][(\text{Fe}_{0.26}^{2+}\text{Mg}_{0.12}\text{Mn}_{0.02})\text{Fe}_{0.64}^{3+}\text{Al}_{0.17}]_2\text{O}_4$ with a composition of Mg_2TiO_4 63.8, MgFe_2O_4 12.8, FeFe_2O_4 23.4 mole %. Qandilite is cubic with $a = 8.4033 \pm 0014 \text{ \AA}$; cell volume 593.40 \AA^3 and space group $Fd\bar{3}m$; $Z = 8$. The seven strongest lines in the X-ray diffraction pattern are (d, I, hkl): 2.971, 30, (220); 2.53, 100, (311); 2.101, 45, (400); 1.617, 50, (333, 511); 1.486, 60, (440); 1.0938, 30, (553, 731); 0.9704, 25, (555, 751). The colour is black, lustre metallic, streak black, fracture even and the cleavage perfect on (111). It is opaque, strongly magnetic, $D_{\text{calc}} = 4.04$, $D_{\text{meas}} = 4.03$, and $\text{VHN}_{100} = 960\text{--}1045 \text{ kg/mm}^2$, with H-7. The reflection colour is grey with a pinkish tint; it is isotropic with no internal reflections. Reflectance measurement data in air and oil in the range (400–700 nm) are given. Colour values for illuminant C in air and oil in terms of CIE colour space are: $x = 0.307, 0.307$; $y = 0.311, 0.310$; $Y\% = 13.10, 3.0$; $\lambda d = 465, 460$; and $Pe\% = 2.0, 2.2$. Calculated data for the absorption coefficients (k) and refractive indices (n) in the range 400–700 nm are also presented.

KEYWORDS: qandilite, new mineral, spinel group, Qala-Dizeh, Iraq.

THE new species described herein is dominated by the compound Mg_2TiO_4 , which is recognized as an end-member of the spinel-group minerals. Its occurrence has not been previously recorded as a distinct mineral, but only as a minor component of complex spinel solid-solution series. These complex spinels are restricted to carbonatites as described by Dawson and Hawthorne (1973) from Benfontein Sills, South Africa, and Reid *et al.* (1975) from Igwisi Hill, Tanzania; the compound Mg_2TiO_4 in solid solution reaches up to 31.6 and 32.1 mole % respectively. Gittins *et al.* (1982) have recently reported the occurrence of Mg_2TiO_4 as a distinct mineral from the Kangerdlugssuaq region of East Greenland. It is found in a periclase-forsterite marble in contact with an alkalic ultramafic rock

intrusion of Caledonian age and co-exists with MgAl_2O_4 spinel and geikielite, MgTiO_3 . The physical properties, optical properties and X-ray data of Mg_2TiO_4 were not determined by Gittins *et al.* (1982) owing to the small size of the few grains found only in one specimen.

Qandilite is found in the Qandil Group of metamorphic rocks at Dupezeh mountain, Hero Town, Qala-Dizeh region, NE Iraq. In this area the Qandil Group rocks are xenoliths of Cretaceous calcareous sediments, in Eocene dioritic and gabbroic intrusions cut by small bodies of Oligocene syenite and granite. The xenoliths are composed of calc-silicate marbles and hornfelses with minor magnesian skarn like the qandilite host rock and brucite marble of the pentacite variety. The xenoliths show no relics of unmetamorphosed sediments and the grade of metamorphism lies within that of the pyroxene hornfels facies.

The mineral is named after the metamorphic Qandil Group. The data and name were approved, prior to publication, by the Commission on New Minerals and Mineral Names, IMA (1980-46). Type material is preserved at Strathclyde University, the Royal Scottish Museum in Edinburgh, the National Science Museum in Tokyo, the Ecole Nationale Supérieure de Mines and the Musée de Minéralogie in Paris.

Nature of occurrence. Qandilite is found in a forsterite skarn in contact with a banded diorite composed mainly of andesine and kaersutite with ubiquitous amounts of titanite, titaniferous magnetite, and ilmenite. The forsterite skarn is buff to cream coloured, coarsely crystalline and has a granular texture. This rock is heavily impregnated with dark-coloured minerals of qandilite, perovskite, and spinel which are homogeneously distributed throughout the rock (fig. 1). The modal analysis showed that the mineral assemblage of the forsterite skarn is composed of 74.2% forsterite ($\text{Fo}_{98}\text{Fy}_2$); 17.7% calcite; 3.4% spinel [$\text{Mg}_{1.0}(\text{Al}_{1.75}\text{Fe}_{0.21}\text{Ti}_{0.04})\text{O}_4$]; 3.0% perovskite; and 1.7% qandilite with accessory calzirtite and

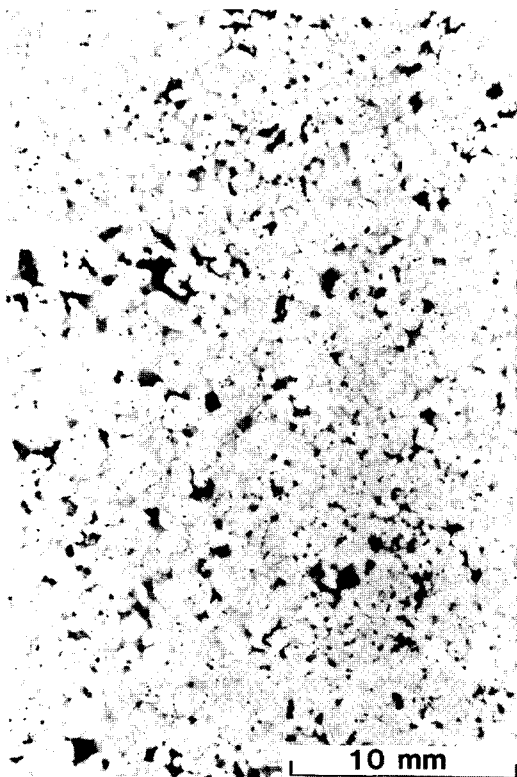


FIG. 1. Polished specimen of olivine skarn containing the abundant black-coloured minerals qandilite, perovskite, and Mg,Al-spinel.

thorianite. Chemical analysis of the qandilite host rock gave: SiO_2 29.04, TiO_2 2.34, ZrO_2 0.15, Al_2O_3 2.64, Fe_2O_3 1.56, FeO 2.41, MnO 0.14, MgO 38.88, CaO 12.20, Na_2O 0.12, K_2O 0.05, CO_2 8.80, H_2O^+ 2.14, sum 100.47 wt. %. This analysis is quite close to an analysis of olivine, magnetite, perovskite cumulate kimberlite from Middle Sill, Benfontein, South Africa (Dawson and Hawthorne, 1973).

Calcite is often found in small lenticular and irregular pockets forming the interstitial matrix between the coarse idioblastic crystals of forsterite (2–6 mm). The closely associated qandilite, perovskite, and spinel also occur in the interstitial matrix between the forsterite grains as an alternative to calcite (fig. 2). Qandilite is found in a variety of textures; in most cases it mantles perovskite and spinel and occurs intergrown with perovskite. In some instances it occurs as euhedral grains embedded in the calcite. The grain size of qandilite varies from 0.1 to 2.3 mm.

It is rather difficult to establish a reaction to explain the formation of qandilite with regard to

the other associated minerals. Nevertheless the textural evidence suggests that qandilite developed at a late stage of thermal metamorphism by introduction of Ti from the adjacent Ti-rich dioritic magma. The evidence for the magma containing an abundance of Ti is the mineral assemblage of kaersutite, titanite, titaniferous magnetite, and ilmenite in the contact diorite rock. The qandilite host rock has been subjected to hydrothermal alteration processes during a late episode of thermal metamorphism. As a result of this, forsterite is partially altered to serpentine, and spinel into a mixture of hydrotalcite and diaspore.

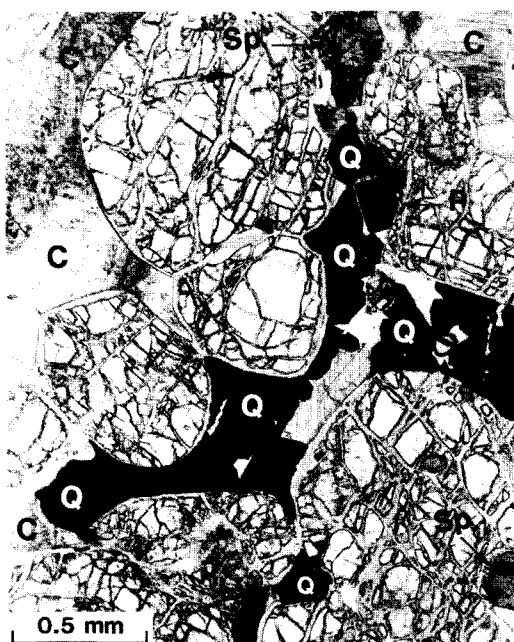


FIG. 2. Photograph in plane-polarized light showing rounded fractured serpentinized olivine surrounded by the interstitial calcite (C), qandilite (Q), perovskite (P), and altered Mg,Al-spinel (SP).

Physical and optical properties. The mineral is iron black in colour, the streak black, and the lustre metallic. The euhedral crystals have three sets of octahedral (111) cleavages; the fracture is even with a tendency to brittle tenacity. The Mohs' hardness number approaches 7. Measured VHN_{100} on eight grains free from cleavages and fractures gave: 960–1045, $\text{mean}_{16} = 998$. Specific gravity determination by Berman balance on four separate fragments gave an average measured value of 4.03 ± 0.03 which is in excellent agreement with the calculated value of 4.04. The mineral is strongly magnetic, in

fact it is similar to magnetite. It is soluble in hot HCl, but only partially soluble in cold HCl, hot H₂SO₄, and hot HNO₃.

Reflectance measurements were carried out using a Vickers M72 spectral microphotometer equipped with a continuous line-interference filter and a X10 air objective and using a Zeiss SiC standard, no. 157. The values of *R*_{oil} of this standard were calibrated to the new PCB-free Zeiss oil 518 at 23°C. The specimen and the standard were both carefully cleaned and levelled using a Lanham stage and the reflectance spectra in air and in oil were measured from 400 to 700 nm at an interval of 7 to 11 nm. Thirty-four measurements were required to cover the full range from 400 to 700 nm and the measurements were repeated five times on five independent grains. The results of these measurements provide the reflectance dispersion curves (fig. 3). Chromite resembles qandilite as is apparent on comparison of the reflectance curves (fig. 3).

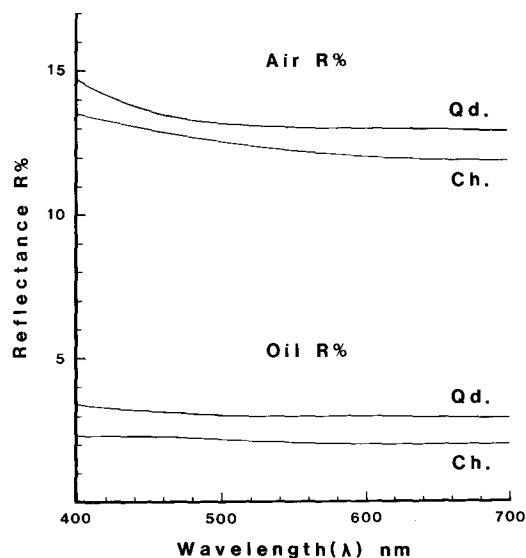


FIG. 3. Reflectance curves in air and oil of qandilite compared with chromite (IMA/COM. data file no: 1600). Qd = qandilite and Ch = chromite.

Table I contains the reflectance values in air and in oil of qandilite, compared with the published data for chromite. These reflectance values of qandilite are obtained from the smoothed spectral reflectance curves (fig. 3). The reflectance values (*R*%) in air showed great consistency in the range 500–700 nm, ranging from ±(0.01 to 0.12) and reasonable consistency in the range of 400–480 nm,

ranging from ±(0.19 to 0.47). The reflectance values (*R*%) in oil showed great consistency through the full scale range 400–700 nm, ranging from ±(0.01 to 0.08).

Table I
Spectral reflectance measurements in air and oil of qandilite compared with chromite (Simpson and Soler, 1977, IMA/COM, data file no. 1600).

λnm	Qandilite		Chromite	
	air R%	oil R%	air R%	oil R%
400	14.8	3.4	13.5	2.3
420	14.2	3.3	13.3	2.3
440	13.8	3.2	13.1	2.3
460	13.5	3.1	12.9	2.3
480	13.3	3.1	12.7	2.2
500	13.2	3.0	12.6	2.2
520	13.1	3.0	12.4	2.1
540	13.1	3.0	12.3	2.1
560	13.0	3.0	12.2	2.0
580	13.0	3.0	12.1	2.0
600	13.0	3.0	12.0	2.0
620	13.0	3.0	12.0	2.0
640	13.0	3.0	11.9	2.0
660	12.9	2.9	11.9	2.0
680	12.9	2.9	11.9	2.0
700	12.9	2.9	11.9	2.0

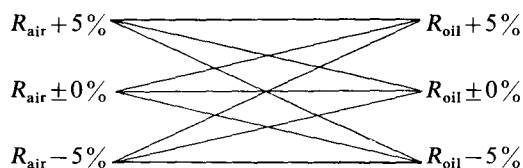
The qualitative colour of the mineral in reflected light is grey with a pinkish tint. It is isotropic and shows no evidence of internal reflections. The qualitative description of the colour of any opaque mineral is inevitably imprecise and somewhat subjective, so a system for quantitatively specifying colour has obvious advantages. The quantitative colour parameters are specified by chromaticity coordinates (*x*,*y*), dominant wavelength (*λd*); purity (*Pe*%), and luminance (*Y*%). The colour values for the mineral for the CIE (1931), illuminant C are recorded below:

<i>x</i>	<i>y</i>	<i>Y</i> %	<i>Pe</i> %	<i>λd</i>	
0.307	0.311	13.1	2.0	465	in air
0.307	0.310	3.0	2.2	460	in oil

The above values were determined both graphically and by utilizing the NISOMI computer program. The dominant wavelengths are nearly constant (460–5) and the corresponding spectral line lies between Sr and Cd blue.

The optical constants calculated were the refractive index, *n*, and the absorption coefficient, *k*. The values of *n* and *k* for a given wavelength were calculated from the reflectance *R*% in air and in oil using the Koenigsberger equations quoted by

Embrey and Criddle (1978). To assure the accuracy of calculated n and k values for each specified wavelength a value of $\pm 5\%$ of the related reflectance $R\%$ in air and in oil have been taken into consideration; this is illustrated by the diagram below:



As a result of such calculations, nine different values of n and k are obtained from the related $R\%$ values for each specified wavelength. Table II gives the range in n and k , with their representative 5% error ranges for each specified wavelength from 400–700 nm. It can be seen that the values of n at the specified wavelengths from 440–700 nm show great consistency and are equal to 2.12 ± 0.03 , whereas from 400–420 nm there is a slight deterioration. Such slight deterioration in n values at these particular wavelengths could possibly be caused by a small error in reflectance measurements in air and in oil. The reason for such error is attributed to the low intensity of light at these wavelengths

Table II.

Refractive index (n) and absorption coefficient (k) of qandilite with range due to estimated errors $R_{air} \pm 5\%$ and $R_{oil} \pm 5\%$

λ nm	5% Error range		5% Error range	
	n	n_{\min} - n_{\max}	k	k_{\min} - k_{\max}
400	2.29	2.27-2.31	0.00	0.00-0.00
420	2.20	2.18-2.22	0.19	0.00-0.19
440	2.13	2.12-2.15	0.23	0.19-0.26
460	2.13	2.12-2.15	0.23	0.19-0.26
480	2.10	2.09-2.12	0.28	0.26-0.30
500	2.11	2.10-2.12	0.23	0.19-0.26
520	2.10	2.08-2.11	0.25	0.21-0.28
540	2.10	2.09-2.12	0.24	0.19-0.27
560	2.09	2.07-2.10	0.26	0.23-0.29
580	2.09	2.08-2.10	0.25	0.21-0.28
600	2.09	2.08-2.11	0.24	0.20-0.27
620	2.10	2.08-2.11	0.23	0.19-0.26
640	2.10	2.08-2.11	0.22	0.18-0.26
660	2.10	2.09-2.12	0.18	0.13-0.21
680	2.10	2.09-2.12	0.17	0.10-0.21
700	2.11	2.09-2.12	0.16	0.07-0.20

(400–420 nm), which make measurements more susceptible to glare and other variations in source and detector.

The k values appear to be satisfactory since they do not show any extreme changes or negative values. The only negative values for k were obtained for 400 and 420 nm wavelengths. Again, this is probably due to the reflectance measurement error at these particular wavelengths. Furthermore the error in this case is compounded by the reliance on $R\%$ and n for the calculation of k , since n would also include an error if $R\%$ was inaccurate.

Table III.

X-ray data of qandilite compared with a synthetic analogue (PDF no. 3 - 858).

hkl	Qandilite			Synthetic Mg_2TiO_4	
	d_{meas}	d_{calc}	I/I_0	d_{meas}	I/I_0
111	4.853	4.852	15	4.92	40
220	2.971	2.971	30	2.99	16
311	2.533	2.534	100	2.55	100
222	2.426	2.426	5	-	-
400	2.101	2.101	45	2.10	80
331	1.927	1.928	3	1.93	1
422	1.715	1.715	15	1.72	7
333, 511	1.617	1.617	50	1.63	50
440	1.486	1.486	60	1.50	80
433, 530	1.441	1.439	5	-	-
531	1.421	1.420	5	1.43	6
620	1.329	1.329	10	1.34	2
533	1.281	1.281	20	1.29	8
622	1.267	1.267	5	-	-
444	1.2128	1.2130	10	1.22	12
551, 711	1.1765	1.1767	5	1.19	3
642	1.1226	1.1230	10	1.13	3
553, 731	1.0938	1.0941	30	1.10	20
800	1.0504	1.0505	15	1.06	8
660, 822	0.9900	0.9904	10	0.997	2
555, 751	0.9704	0.9704	25	0.979	8
662	0.9636	0.9636	5	-	-
840	0.9396	0.9396	15	0.945	7
753, 911	0.9225	0.9225	5	-	-
931	-	0.8809	-	0.885	5
844	-	0.8577	-	0.864	12
951	-	0.8124	-	0.819	4

X-ray data. The d -spacing data (Table III) were determined from powder photographs taken in a 114.6 mm diameter Debye-Scherrer camera using Co- $K\alpha$ radiation. Values of the measured d -spacing compare closely with that of synthetic $MgTiO_4$ (PDF Card 3-858). The sample was prepared in spindle form with a diameter less than 0.5 mm and

also mounted in capillaries of 0.3 mm internal diameter. No attempts were made to obviate the preferred orientation effect, simply because the mineral is cubic with perfect (111) cleavage and easily breaks into equidimensional grains during grinding. Samples were subjected to line focus and spot focus beams. The exposure times were 16 hours at 30 kV and 10 mA, and 3 hours at 36 kV and 20 mA respectively. The lines produced from the spot focus beam gave lower resolution and higher intensity and background, whereas the line focus beam gave greater resolution with relatively lower intensity and background.

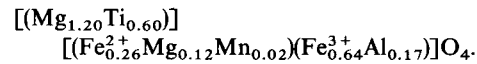
It is noteworthy that the mineral gave extreme fluorescence using Cu-K α radiation, even on short exposures of 2 hours duration. Fluorescence was greater than magnetite, which means that the cause of fluorescence is not entirely attributed to Fe, but also to Ti.

Examination of the reflections show the space group to be consistent with *Fd3m* and the data was indexed on a cubic cell $a = 8.4033 \pm 0.0014 \text{ \AA}$, using the Nelson-Reilly extrapolation method; $V = 593.4 \text{ \AA}^3$ and $Z = 8$.

Chemical compositions. Seven crystal spectrometric analyses on the microprobe from four grains gave the result presented in Table IV. The listed value for iron oxides, FeO and Fe₂O₃ in the average analysis column were independently determined by wet chemical analysis. If this iron oxide result is expressed only as FeO, the value of 35.76% is in good agreement with seven microprobe analyses whose average is 35.63%. The analyses at

the core and rim of three grains indicate that the mineral is fairly homogeneous in composition.

The derived chemical formula from the average analysis on the basis of 4 oxygen ions is: $(\text{Mg}_{1.32}\text{Fe}_{0.26}^{2+}\text{Mn}_{0.02}\text{Fe}_{0.64}^{3+}\text{Al}_{0.17}\text{Ti}_{0.60})\text{O}_4$. All the relevant spinel group end-members have an ideal formula $R^{2+}R_2^{3+}\text{O}_4$ (1), except ulvospinel with $R_2^{2+}R^{4+}\text{O}_4$ (2), where R^{2+} represents divalent cations (Fe, Mg, Mn, Zn, Ni); R^{3+} represents trivalent cations (Fe, Al, Cr, V); and R^{4+} represents tetravalent cations (Ti). The sum of the divalent cations in qandilite is equal to 1.6 and the trivalent plus tetravalent cations sum to 1.41. According to the ideal formula (1), it appears that qandilite has a considerable excess of divalent cations and an extreme deficiency in trivalent plus tetravalent cations. On the other hand by using ideal formula (2), qandilite shows a substantial deficiency in divalent cations and a great excess in tetravalent plus trivalent cations. All these inconsistencies in terms of formula are created simply because the qandilite is not a pure end-member but contains substantial amounts of magnetite and magnesioferrite which belong to the ideal formula (1) while ideal qandilite (Mg_2TiO_4) as a new end member belongs to the ideal formula (2). For this reason a new empirical formula has been calculated for qandilite by combining the ideal formulae (1 and 2):



The mineral has a composition of Mg_2TiO_4 63.8, FeFe_2O_4 23.4, and MgFe_2O_4 12.8 mole %. The

Table IV.

Electron microprobe crystal spectrometry analysis of qandilite. The iron oxide values for the grains 1 to 4 represent total iron oxides as FeO, while the listed iron oxide values for FeO and Fe₂O₃ in the average analyses were independently determined by wet chemical analyses.

Oxides Wt. %	Grain 1		Grain 2		Grain 3		Grain 4	AVERAGE ANALYSIS
	Core	Rim	Core	Rim	Core	Rim	Core	
SiO ₂	0.02	0.05	0.03	0.02	0.00	0.00	0.05	0.02
TiO ₂	25.81	26.36	26.27	27.41	26.09	27.37	25.59	26.41
Al ₂ O ₃	5.85	4.77	5.04	3.53	5.14	3.94	5.51	4.83
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃								28.27
FeO	35.54	35.36	35.48	35.57	35.81	35.21	36.47	10.32
MnO	0.74	0.74	0.73	0.79	0.77	0.76	0.78	0.76
MgO	29.31	29.78	29.66	29.95	29.62	29.86	29.15	29.62
NiO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	97.27	97.06	97.21	97.21	97.27	97.43	97.55	100.23

name qandilite stands for the dominant end member of Mg_2TiO_4 , as a new species of the spinel group. The pronunciation of the name qandilite can be represented as kandilite.

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REFERENCES

- Dawson, J. B., and Hawthorne, J. B. (1973) *J. Geol. Soc. Lond.* **129**, 61-85.
Embrey, P. G., and Criddle, A. J. (1978) *Am. Mineral.* **68**, 853-62.
Gittins, J., Fawcett, J. J., Rucklidge, J. C., and Brooks, C. K. (1982) *Mineral. Mag.* **45**, 135-7.
Reid, A. M., Donaldson, C. H., Dawson, J. B., Brown, R. W., and Ridley, W. I. (1975) *Phys. Chem. Earth*, **9**, 199-218.

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