

## Mavlyanovite, $\text{Mn}_5\text{Si}_3$ : a new mineral species from a lamproite diatreme, Chatkal Ridge, Uzbekistan

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### ABSTRACT

Mavlyanovite, ideally  $\text{Mn}_5\text{Si}_3$ , is a new mineral from a lamproite diatreme close to the upper reaches of the Koshmansay river, Chatkal ridge, Uzbekistan. It occurs together with unnamed manganese silicophosphide and manganese silicicarbide minerals in round to ovoid segregations, up to 10 cm in diameter, in volcanic glass. Segregations of hexagonal prismatic mavlyanovite up to 1–2 mm occur in interstices in the matrix and tiny inclusions (1–2  $\mu\text{m}$ ) of alabandite and khamrabaevite occur within mavlyanovite. It is opaque with a metallic lustre, has a dark-grey streak, is brittle with a conchoidal fracture and a near-perfect basal cleavage.  $\text{VHN}_{100}$  is 1029–1098  $\text{kg/mm}^2$  (Mohs hardness  $\sim 7$ ). In plane-polarized reflected light, mavlyanovite is a pale-brownish-grey against the accompanying unnamed manganese silicicarbide (white). Reflectance values and colour data are tabulated. Average results of 19 electron microprobe analyses give Mn 70.84, Fe 6.12, Si 22.57, Ti 0.15, P 0.18, total 99.86 wt.% leading to an empirical formula of  $(\text{Mn}_{4.66}\text{Fe}_{0.40})_{5.06}(\text{Si}_{2.91}\text{Ti}_{0.01}\text{P}_{0.02})_{2.94}$  based on 8 a.p.f.u. The calculated density is 6.06  $\text{g/cm}^3$ , (on the basis of the empirical formula and unit-cell parameters from the structure determination). Mavlyanovite is hexagonal ( $P6_3/mcm$ ) with  $a$  6.8971(7),  $c$  4.8075(4) Å,  $V$  198.05(3) Å<sup>3</sup> and  $Z = 2$ . The structure has been determined and refined to  $R_1 = 0.017$ ,  $wR_2 = 0.044$ , GoF = 1.16. Mavlyanovite is the naturally-occurring analogue of synthetic  $\text{Mn}_5\text{Si}_3$  which is the parent aristotype structure of the Nowotny intermetallic phases studied extensively by the material-science community. It is also the Mn-dominant analogue of xifengite  $\text{Fe}_5\text{Si}_3$ . The mineral name honours Academician Gani Arifkhanovich Mavlyanov (1910–1988), for his contributions to the understanding of the geology of Uzbekistan.

**KEYWORDS:** mavlyanovite, alabandite, khamrabaevite, manganese silicicarbide, xifengite.

### Introduction

THE new mineral species mavlyanovite with an ideal formula of  $\text{Mn}_5\text{Si}_3$  occurs together with suessite, native iron, moissanite, diamond, chromitel, unnamed manganese silicicarbide, unnamed manganese silicophosphide, khamrabaevite, alabandite and other high-pressure and high-temperature minerals in a lamproite diatreme on

the right bank of the upper reaches of the Koshmansay river, Chatkal ridge, Uzbekistan, N 41.5°, E 70.3°.

Mavlyanovite is named in honour of Academician Gani Arifkhanovich Mavlyanov (Гани Арифханович Мавлянов) (1910–1988), who made a huge contribution to the understanding of the geology of Uzbekistan. The mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (2008-026). Type specimens are preserved in the Geological Museum of the

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State Committee on Geology and Mineral Resources, 4, Furkat St., Tashkent, Uzbekistan, and in the Natural History Museum, London, United Kingdom as BM 2008, 31.

## Occurrence

Mavlyanovite was found in lamproitic rocks associated with a diamond-bearing diatreme. Yusupov (1993) first reported the presence of diamond in these rocks in an assemblage dominated by the metal-Si-C system. The structures and textures within these rocks, including rounded breccia fragments, reflect the explosive transport mechanism. The mineral association of diamond, moissanite, chromite, suessite, native Cr and unnamed manganese silicicide and manganese siliciphosphide phases, suggests a source in the sub-continental upper mantle (Lutkov *et al.*, 2007). The mineralogy reflects high-pressure and high-temperature conditions, typical of both upper-mantle and explosive-shock processes. Diamondiferous lamproites, recently described from other regions of Eurasia (Egorov *et al.*, 2006), together with carbonatites from Tibet, across Junggar to the Tianshan in Xinjiang, Kyrgyzstan, Tajikistan and Uzbekistan (Djuraev and Divaev, 1999; Lutkov *et al.*, 2007; Woolley and Church, 2005; Woolley and Kjarsgaard, 2008), point to the existence of a distinct layer in the lithosphere that is accessed *via* deep trans-crustal faults from where source material is brought to the surface by explosive processes. Some of the minerals may have formed only during the transport towards eruptions (in the pipe itself), others originate from the protolith of the source region (e.g. chromite) or may have become entrained when passing through the crust (xenocrysts).

Mavlyanovite is identical to unnamed mineral 0528 in the MINERAL database, described by Tatarintsev *et al.* (1990), (English abstract in Jambor and Puziewicz, 1992), for which 'Mineral 2' has a formula identical to that of mavlyanovite and was associated with unnamed  $(\text{Mn,Fe})_7\text{Si}_2$  in inclusions of unaltered glass in a volcanic breccia in the Volnovakha River basin, eastern Azov area, Ukraine. The assemblage here also includes graphite, khamrabaevite, moissanite and alabandite. Mavlyanovite is clearly different from brownleeite, isometric  $\text{MnSi}$ , discovered within an interplanetary dust particle that is believed to have originated from comet 26P/Grigg-Skjellerup (Nakamura-Messenger *et al.*, 2008).

## Physical properties

Mavlyanovite occurs together with unnamed manganese siliciphosphide and manganese silicicide minerals in spherical to ovoid segregations up to 10 cm in diameter, in volcanic glass. Segregations of hexagonal prismatic mavlyanovite up to 1–2 mm occur in the interstices of the matrix, and tiny inclusions (1–2  $\mu\text{m}$ ) of alabandite and khamrabaevite occur within mavlyanovite. The inclusion species were identified compositionally from electron probe microanalysis. Mavlyanovite is opaque with a metallic lustre, has a dark-grey streak, is brittle with a conchoidal fracture and a near-perfect basal cleavage.  $\text{VHN}_{100}$  is 1029–1098  $\text{kg/mm}^2$  (Mohs hardness  $\sim 7$ ). Accurate density measurements could not be obtained because of the small grain size and intergrown nature, but on the basis of the empirical formula and the unit-cell parameters from the crystallographic study, the calculated density is 6.06  $\text{g/cm}^3$ .

## Optical properties

Samples containing mavlyanovite were prepared for optical investigation using standard diamond polishing techniques (Stanley and Laflamme, 1998). In plane-polarized reflected light from an unfiltered quartz-halogen lamp at about 3100 K (Fig. 1), mavlyanovite is a pale-brownish-grey against the accompanying unnamed manganese silicicide (white). It is weakly birefractant but not pleochroic and displays moderate anisotropy with greyish-brown rotation tints and no internal reflections. In crossed polars the mineral does not display parallel extinction, otherwise it conforms to uniaxial norms.

Reflectance data were obtained in air from 400–700 nm using a Zeiss Axiotron microscope equipped with a Crystal Structures (Lanham) specimen-standard levelling superstage and a J & M Tidas diode array spectrometer at the Natural History Museum, London. Measurements were made relative to a Zeiss WTiC standard using Cavendish Instruments *Onyx* software at intervals of 0.823 nm. The results are given in Table 1.

## Chemical composition

Chemical analyses were carried out at the Natural History Museum using a Cameca SX100 electron microprobe operated in wavelength dispersive

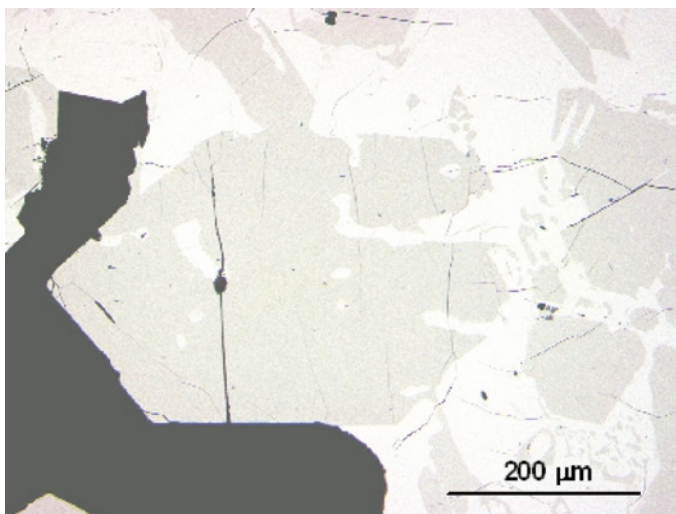


FIG. 1. Digital reflected light image (oil immersion) illustrating an almost hexagonal basal section of mavlyanovite (light-brownish-grey) in association with the white, unnamed manganese silicicarbide.

mode with an accelerating voltage of 20 kV, a probe current of 20 nA and a probe diameter of  $\sim 2 \mu\text{m}$ . The following standards were used: pure Mn and Fe (99.9% pure supplied by Johnson Matthey), diopside (Si),  $\text{MnTiO}_3$  (Ti) and InP (P). X-ray lines measured were Mn- $K\alpha$ , Fe- $K\alpha$ , Si- $K\alpha$ , Ti- $K\alpha$  and P- $K\alpha$ . Results are given in Table 2. The empirical formula for mavlyanovite, calculated from the arithmetic mean of 19 analyses (based on 8 a.p.f.u.) is:  $(\text{Mn}_{4.66}\text{Fe}_{0.40})_{5.06}(\text{Si}_{2.91}\text{Ti}_{0.01}\text{P}_{0.02})_{2.94}$ . The end-member formula is  $\text{Mn}_5\text{Si}_3$ , in which Mn = 76.52 wt.% and Si = 23.48 wt.%.

### Structure determination

A black euhedral prismatic crystal of mavlyanovite ( $0.025 \text{ mm} \times 0.040 \text{ mm} \times 0.285 \text{ mm}$ ) with hexagonal forms, was mounted on an Enraf-Nonius Turbo-CAD4 diffractometer equipped with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) operating at 45 kV and 40 mA. Preliminary precession photography (Polaroid) indicated sharp diffraction maxima and a reciprocal lattice consistent with primitive hexagonal symmetry. No superstructure reflections were observed in longer (45 min) exposures. The high diffraction quality of this crystal was confirmed by profiling of reflections in slow  $\omega$ -2 $\theta$  scans on the CAD4, which showed narrow, well-behaved lineshapes.

Information relating to the data collection and structure determination is shown in Table 3.

Unit-cell parameters and orientation matrix were determined from the setting angles of 25 reflections in the range  $9.0$ – $19.4^\circ$  located by four-position centring (SET4). Intensity data were collected in the range  $3.41$ – $29.89^\circ$  using  $\omega$ -2 $\theta$  scans, with scan-speeds inversely proportional to intensity. Peak profiles were examined for all reflections to check for aberrant lineshapes, although none was observed. Three standard reflections were used to monitor beam intensity and crystal orientation every 4 h. Variations in beam intensity were  $< \pm 1\%$ , and no misorientation was observed. Raw intensities of 2070 reflections (average  $I/\sigma(I) = 153.85$ ) were corrected for Lorentz and polarization effects. Semi-empirical (psi-scans of nine reflections) and analytical absorption corrections ( $\mu = 16.19 \text{ mm}^{-1}$ ) made no difference to the reflection merging ( $6/mmm$ ), which remained low at  $R_{\text{int}} = 0.022$ . Corrected intensities were converted to structure factors. A total of 124 unique reflections, all with  $I > 2\sigma(I)$ , was used for structure determination (data completeness to  $29.89^\circ = 100\%$ ).

Data reduction and structure determination were carried out in space group  $P6_3/mcm$  using the *WinGX* program suite (Farrugia, 1999). All atoms of the asymmetric unit were found by Direct Methods (*SHELXS*, Sheldrick 2008) and

TABLE 1. Reflectance data and colour values for mavlyanovite.

$\lambda$ nm	$R_o$	$R_e$
400	42.7	40.5
420	43.2	41.0
440	43.7	41.5
460	44.2	42.0
480	44.8	42.7
500	45.4	43.3
520	46.1	43.9
540	46.7	44.5
560	47.3	45.2
580	48.0	45.8
600	48.6	46.5
620	49.3	47.1
640	49.8	47.7
660	50.4	48.2
680	50.9	48.7
700	51.4	49.4
470	44.5	42.4
546	46.9	44.7
589	48.3	46.1
650	50.1	48.0
Colour values		
A illuminant		
x	.456	.457
y	.409	.409
Y%	47.7	45.6
$\lambda_d$	589	589
P <sub>e</sub> %	7.0	7.4
C illuminant		
x	.319	.320
y	.324	.325
Y%	47.3	45.1
$\lambda_d$	580	580
P <sub>e</sub> %	4.7	4.9

their coordinates and anisotropic displacement parameters ( $U_{ij}$ ) refined using *SHELXL* (Sheldrick, 2008). No attempt was made to refine Mn/Fe ratios for the two Mn sites because Mn and Fe atomic numbers differ by only one unit, corresponding to a single electron. This minimal contrast is unlikely to be resolved by X-ray diffraction, particularly in the present case where Mn:Fe = 0.92:0.08. Before settling on a fully Mn-Si ordered structure model, we carried out trial refinements sequentially for Mn-Si mixed

TABLE 2. Electron microprobe data for mavlyanovite.

	Wt.%	Range (wt.%)	Formula based on 8 atoms
Mn	70.84	(70.48–71.1)	4.66
Fe	6.12	(5.93–6.42)	0.40
Si	22.57	(22.51–22.68)	2.90
Ti	0.15	(0.09–0.19)	0.01
P	0.18	(0.15–0.21)	0.02
Total	99.86	7.99	

Average results of 19 electron microprobe analyses.

occupancy on Mn(1), Mn(2) and Si sites, even though synthetic  $Mn_5Si_3$  has no Mn-Si disorder. A mixed Mn-Si site occurs in the silicicarbide  $Mn_8Si_2C$  (Spinat *et al.*, 1975). However, these refinements gave standard errors on site occupancies that were larger than the deviations from fully-ordered states, e.g.  $X_{Si} = 0.008(10)$  and  $0.011(14)$  for Mn(1) and Mn(2), respectively. Refinement of Mn at the Si site was unstable. Consequently, we proceeded with refinement of the fully-ordered structure.

Reflection weighting (*SHELXL*) was used in the last stages of refinement:  $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$  where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ , and final values for  $a = 0.0271$  and  $b = 0.5066$ . Finally, an overall extinction coefficient was refined: 0.022(4). The highest peak in the final difference-Fourier map was  $2.2 \text{ e.}\text{\AA}^{-3}$  at the centre of the nominally vacant Mn(2)<sub>6</sub> octahedron and at a distance of  $2.02 \text{ \AA}$  from Mn(2). The deepest hole was  $-0.56 \text{ e.}\text{\AA}^{-3}$  at  $1.40 \text{ \AA}$  from Mn(2). Final agreement indices for a fully anisotropic, ordered model (10 refined structural parameters), an overall scale factor and an extinction correction are:  $R_1(\text{obs}) = R_1(\text{all}) = 0.017$  and  $wR_2(\text{obs}) = wR_2(\text{all}) = 0.044$  (all reflections are 'observed', having  $I > 2\sigma(I)$ ). The Goodness-of-Fit is 1.16. Atom coordinates and anisotropic displacement parameters of mavlyanovite are given in Table 4. A table of structure factors has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from [www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html).

X-ray powder-diffraction reflection data (Table 5) were calculated using the program *Powder Cell* (Kraus and Nolze, 1996) version 2.3, as the powder data obtained yielded a mixture of mavlyanovite and the two as yet unnamed minerals, with peak overlaps yielding incorrect

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TABLE 3. Information relevant to X-ray data collection and structure refinement of mavlyanovite.

Empirical formula ( $\Sigma = 8$ )	(Mn <sub>4.66</sub> ,Fe <sub>0.40</sub> ) <sub>5.06</sub> (Si <sub>2.90</sub> Ti <sub>0.01</sub> P <sub>0.02</sub> ) <sub>2.93</sub>
Formula weight	358.9 g mol <sup>-1</sup>
Temperature	293(2) K
Radiation, wavelength	Mo-K $\alpha$ , 0.71073 Å
Crystal system	hexagonal
Space group	<i>P</i> 6 <sub>3</sub> / <i>mcm</i>
Unit-cell parameters	$a = b = 6.8971(7)$ Å $c = 4.8075(4)$ Å $V = 198.05(3)$ Å <sup>3</sup>
Volume	2
Z	2
Density (calculated)	6.06 g.cm <sup>-3</sup>
Absorption coefficient	16.19 mm <sup>-1</sup>
<i>F</i> (000)	334
Crystal dimensions	0.025 mm × 0.040 mm × 0.285 mm
$\theta$ range for data collection	3.41–29.89°
Index ranges	$-9 \leq h \leq 9$ , $-9 \leq k \leq 9$ , $-6 \leq l \leq 6$
Reflections collected	2070
Average $I/\sigma(I)$	153.85
Independent reflections	124 [ $R_{\text{int}} = 0.022$ , $R_{\sigma} = 0.007$ ]
Reflections with $I > 2\sigma(I)$	124
Completeness to $\theta_{\text{max}}$	100%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	124/0/12
Goodness-of-fit on $F^2$	1.16
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.017$ , $wR_2 = 0.044$
Extinction coefficient	0.022(4)
Largest diff. peak and hole	2.20 and $-0.56$ e Å <sup>-3</sup>

intensities and inaccurate cell parameters. An unsuccessful attempt was made to extract meaningful intensities from a Gandolfi experiment using the prismatic crystal for which the structure was determined. Consequently, we advocate use of the calculated values.

## Description of crystal structure

Mavlyanovite (hexagonal, space group *P*6<sub>3</sub>/*mcm*) is the naturally-occurring analogue of synthetic Mn<sub>5</sub>Si<sub>3</sub> (Åmark *et al.*, 1936; Aronsson, 1960),

which is the parent aristotype structure of the Nowotny intermetallic phases (Nowotny, 1963; Parthé *et al.*, 1965; Shoemaker and Shoemaker, 1978; Cenxual and Parthé, 1986) that have been studied extensively by the material-science community. Mavlyanovite is also the Mn-dominant analogue of xifengite Fe<sub>5</sub>Si<sub>3</sub>, which appears to be of extraterrestrial occurrence (Yu, 1984). Furthermore, xifengite is one of the iron silicides considered to be possible lower-mantle phases (Errandonea *et al.*, 2008). The occurrence of primary mavlyanovite in mantle rocks is,

TABLE 4. Atom coordinates, anisotropic and equivalent isotropic displacement parameters for mavlyanovite.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>eq</sub>
Mn(1)	1/3	2/3	0	0.0060(3)	0.0060(3)	0.0038(3)	0.0030(2)	0.0053(3)
Mn(2)	0.23459(9)	0	1/4	0.0071(3)	0.0054(3)	0.0089(3)	0.0027(2)	0.0073(2)
Si	0.59779(15)	0	1/4	0.0057(4)	0.0046(5)	0.0091(5)	0.0023(3)	0.0066(3)

TABLE 5. Calculated X-ray powder diffraction data ( $I/I_{\max} > 10\%$ ) for mavlyanovite.

$d$ (Å)	$I/I_0$	$hkl$
2.987	12	200
2.404	11	002
2.258	44	210
2.230	29	102
2.044	100	211
1.991	30	300
1.972	67	112
1.401	16	222
1.307	22	213
1.303	13	410
1.268	15	402
1.070	15	502

therefore, consistent with high-pressure stability. The structure of xifengite was not determined directly, but inferred from a comparison with the X-ray powder diffraction data of synthetic  $\text{Mn}_5\text{Si}_3$  for which an isotropic structure is published (Åmark *et al.*, 1936; Aronsson, 1960).

Aspects of the mavlyanovite structure are shown in Fig. 2. There are two non-equivalent Mn atoms and one Si atom in the asymmetric unit. The structure comprises a single type of polyhedron: a 9-coordinate  $\text{Si}[\text{Mn}(1)_4 \text{Mn}(2)_5]$  polyhedron.  $\text{SiMn}_9$  polyhedra share faces to form a six-membered ring in the centre of which is a vacant octahedral cavity defined by six  $\text{Mn}(2)$  atoms. Adjacent sheets of six-membered rings are stacked by operation of the  $6_3$  screw axis to produce a tunnel-like structure parallel to  $[001]$  (Fig. 1). Anisotropic displacement parameters of  $\text{Mn}(2)$  and Si show slight elongation parallel to  $[001]$  whereas that of  $\text{Mn}(1)$  is slightly oblate within the  $(001)$  plane. The Si–Mn bond lengths are:  $\text{Mn}(1) = 2.4215(3)$  Å ( $\times 4$ ),  $\text{Mn}(2) = 2.4135(9)$  Å ( $\times 2$ ),  $\text{Mn}(2) = 2.505(1)$  Å ( $\times 1$ ) and  $\text{Mn}(2) = 2.6675(6)$  Å ( $\times 2$ ). The Si–Si non-bonded distance is  $2.756(1)$  Å. The vacant  $\text{Mn}(2)_6$  octahedral site has edge-lengths of  $2.802(1)$  and  $2.8974(4)$  Å. The structure refinement registered a small residual positive electron density ( $2.2 e.\text{\AA}^{-3}$ ) at the centre of the  $\text{Mn}(2)_6$  octahedron. This octahedron can be occupied by carbon in derivative Nowotny phases (Parthé *et al.*,

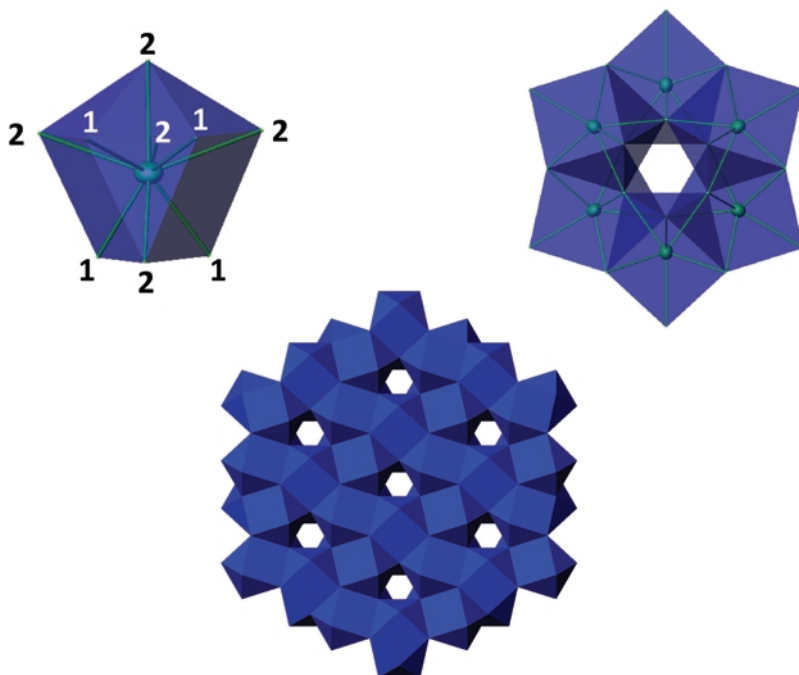


FIG. 2. Crystal structure of mavlyanovite. Shown here are the  $\text{SiMn}_9$  polyhedron (upper left), a single six-membered ring of polyhedra (upper right) and a  $[001]$  view of the structure. The Si displacement ellipsoid (upper left) is shown at the 99.9% level. The numbers associated with the upper left diagram are 1 =  $\text{Mn}(1)$ , 2 =  $\text{Mn}(2)$  atoms.



1965). Carbon also occurs in sixfold, trigonal-prismatic coordination in silicicarbides (e.g. Spinat *et al.*, 1975). Therefore, it seems probable that the residual electron density at the centre of the  $Mn(2)_6$  octahedron corresponds to a small amount of carbon at this site, although it was not possible to refine a meaningful occupancy, due to correlation with  $U_{iso}$ . Investigation of the possible role of mavlyanovite as a host of mantle carbon is planned in the near future.

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