# Megawite, $CaSnO_3$ : a new perovskite-group mineral from skarns of the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia

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# ABSTRACT

Megawite is a perovskite-group mineral with an ideal formula CaSnO<sub>3</sub> that was discovered in altered silicate-carbonate xenoliths in the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia. Megawite occurs in ignimbrite, where it forms by contact metamorphism at a temperature >800°C and low pressure. The name megawite honours the British crystallographer Helen Dick Megaw (1907–2002) who did pioneering research on perovskite-group minerals. Megawite is associated with spurrite, reinhardbraunsite, rondorfite, wadalite, srebrodolskite, lakargiite, perovskite, kerimasite, elbrusite-(Zr), periclase, hydroxylellestadite, hydrogrossular, ettringite-group minerals, afwillite, hydrocalumite and brucite. Megawite forms pale yellow or colourless crystals up to 15 µm on edge with pseudo-cubic and pseudo-cuboctahedral habits. The calculated density and average refractive index are 5.06 g cm<sup>-3</sup> and 1.89, respectively. Megawite is Zr-rich and usually crystallizes on lakargiite, CaZrO<sub>3</sub>. The main bands in the Raman spectrum of megawite are at: 159, 183, 262, 283, 355, 443, 474, 557 and 705 cm<sup>-1</sup>. The unit-cell parameters and space group of megawite, derived from electron back scattered diffraction, are: a = 5.555(3), b = 5.708(2), c = 7.939(5) Å, V = 251.8(1) Å<sup>3</sup>, *Pbnm*, Z = 4; they are based on an orthorhombic structural model for the synthetic perovskite CaSn<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>3</sub>.

Keywords: megawite, CaSnO<sub>3</sub>, lakargiite, perovskite, Raman spectroscopy, EBSD, Lakargi mountain, Russia.

### Introduction

THE discovery of lakargiite,  $CaZrO_3$  (Galuskin *et al.*, 2008*a*) and other perovskite-group minerals in the CaO-ZrO<sub>2</sub>-SnO<sub>2</sub>-TiO<sub>2</sub> system, in carbo-

\* E-mail: evgeny.galuskin@us.edu.pl DOI: 10.1180/minmag.2011.075.5.2563 nate-silicate skarn-type xenoliths in ignimbrites of the Upper Chegem caldera, led to the recognition of Sn-rich lakargiite (Galuskin *et al.*, 2008*b*) and to the discovery of a new Sn-dominant analogue which has an ideal formula CaSnO<sub>3</sub> (Galuskin *et al.*, 2010). This mineral was approved by the CNMNC/IMA in 2010 and it is named in honour of the British crystallographer Helen Dick Megaw (1907–2002) who made significant contributions to our understanding of the structure and properties of natural and synthetic perovskites (Megaw, 1945, 1946, 1952; Megaw and Darlington, 1975).

Megawite is the natural analogue of the synthetic calcium stannate perovskite CaSnO<sub>3</sub> (Megaw, 1946; Vegas et al., 1986; Kung et al., 2001; Mitchell, 2002; Zhao et al., 2004; Tsuchiya and Tsuchiva, 2006; Tarrida et al., 2009), which finds diverse applications in capacitors, sensors, electrodes for batteries and matrices for photoluminescent materials (Alves et al., 2009; Chen et al., 2010). Knowledge of synthetic CaSnO<sub>3</sub> and intermediate CaZrO<sub>3</sub>-CaSnO<sub>3</sub> solid solutions (Tarrida et al., 2009) permits megawite to be validated as a new mineral species. The characterization of megawite by electron microprobe analysis (EMPA), Raman spectroscopy and electron back scattered diffraction (EBSD) allows derivation of the composition and unitcell parameters from the typically very small (<15 µm) megawite crystals, occurring as inclusions in rock-forming minerals in the Chegem caldera skarn xenoliths.

Holotype samples of megawite are deposited in the Mineralogical Museum of Wrocław University, Poland under accession number MMUWr II16717 and in the Fersman Mineralogical Museum, Moscow, Russia under accession number 4021/1.

# Analytical methods

The morphology and composition of megawite and lakargiite were investigated using a Philips/ FEI ESEM XL30/EDAX scanning electron microscope (Faculty of Earth Sciences, University of Silesia) and a CAMECA SX100 electron microprobe (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). The composition of megawite was determined at an accelerating voltage of 15 kV, with a probe current of 40 nA using natural and synthetic standards. A detailed description of the EMPA procedure is provided by Galuskina *et al.* (2010*a*).

The small size of megawite crystals (<15  $\mu$ m) required the use of single crystal electron backscatter diffraction (EBSD) analysis to determine the crystal structure. The EBSD images were recorded using an HKL EBSD system (HKL Technology Inc., Oxford Instruments Group) on a JSM-6480 high performance scanning electron microscope (Institute of Materials Science, University of Silesia) using an accelerating voltage of 30 kV. Thin sections used for electron

microprobe analyses were repolished using an Al<sub>2</sub>O<sub>3</sub> suspension with a 20 nm particle size. To minimize charging, specimens were coated in a carbon layer several tens of nanometres thick. The calibration of the EBSD system was carried out using a Si single crystal at detector distances) of 177 mm (normal working position) and 150 mm (camera retracted position). A Nordlys II camera with a resolution of  $1344 \times 1024$  pixels was used. Either  $2 \times 2$  binning or no binning was applied for the electron backscatter pattern collection at the different detector distances. To improve the pattern quality, acquisition times of between 300 and 3000 ms and frame averaging were used. Depending on the detector distance and pattern collection time, up to 30 frames were averaged. The Channel5 software package (Oxford Instruments; Day and Trimby, 2004) was used for the interpretation of the EBSD patterns. For the 150 mm detector distance, only manual band detection was used as data reduction using the Hough transform was not effective. For the 177 mm detector distance, manual plus Hough (maximum 125 resolution) band detection was applied. In the match 54 reflectors and 7-11bands were used.

Raman spectra of single crystals of megawite were recorded using a LabRAM HR800 (Jobin-Yvon-Horiba) spectrometer equipped with an 1800 line/mm grating, a charge-coupled device (CCD) Peltier-cooled detector ( $1024 \times 256$ ) and an Olympus BX40 confocal microscope (Wrocław University of Technology). The incident laser excitation was provided by a water-cooled argon laser operating at 514.5 nm, which produced a power at the 100x objective lens of 40-60 mW. Raman spectra were recorded in 0° geometry in the range  $50-4000 \text{ cm}^{-1}$  with a spectral resolution of 2.5  $\text{cm}^{-1}$ . The collection time was 10 s and 16 scans were accumulated. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7  $\text{cm}^{-1}$ ).

# Occurrence and description of megawite

Crystals of Zr-bearing megawite were found in the spurrite zones of skarned xenolith no. 1 (20–25 m in size) in ignimbrites of the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia (Galuskin *et al.*, 2010; Fig. 1a-c). The geology of the area is described by Gazeev *et al.* (2006) and Galuskin *et al.* (2009). In addition to megawite, xenolith no. 1 is the type locality for six minerals: lakargiite,



FIG. 1. Megawite and lakargiite in skarns of the Upper Chegem caldera: (a-c) spurrite skarns from xenolith no. 1; (*a*) megawite crystals are found only inside spurrite grains (magnified fragment is shown in inset), whereas lakargiite is widespread in both spurrite and wadalite-hydrocalumite-calcite aggregate; (*b*) spurrite crystal etched in 10% HCl with megawite and wadalite inclusions (a magnified image of a megawite crystal is shown in inset); (*c*) megawite and lakargiite in a fractured spurrite crystal (see description in the text); (*d*) pseudo-cubic crystals of high-Sn lakargiite overgrowing a porous aggregate of lakargiite and srebrodolskite from the chegemite zone of xenolith no. 7; (*e*) crystals of high-Sn lakargiite with external zones of megawite growing over a fine-grained lakargiite-wadalitehibschite aggregate, burtite CaSn(OH)<sub>6</sub> also occurs in this association; (*f*) megawite and garnet forming later zones in complex pseudomorphs after zircon, from the larnite-cuspidine zone of xenolith no. 3 (a zoned crystal comprising a lakargiite core and a megawite rim is shown inset). Arabic numerals show the sites of the EMPA analyses. Abbreviations are: Meg, megawite; Afw, afwillite; Brc, brucite; Brt, burtite; Cal, calcite; Chg, chegemite; Etr, ettringite; Hgr, hydrogrossular; Hil, hillebrandite; Hcl, hydrocalumite; Lak, lakargiite; Lar, larnite; Rnd, rondorfite; Sch, schorlomite; Spu, spurrite; Srb, srebrodolskite; Tot, toturite; Wad, wadalite.

TABLE 1. Composition of megawite and lakargiite (major elements as wt.%) from Lakargi mountain

CaZrO<sub>3</sub> (Galuskin *et al.*, 2008*a*); chegemite, Ca<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub> (Galuskin *et al.*, 2009); kumtyubeite, Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>F<sub>2</sub> (Galuskina *et al.*, 2009); bitikleite-(SnAl), Ca<sub>3</sub>SbSnAl<sub>3</sub>O<sub>12</sub> (Galuskina *et al.*, 2010*a*); elbrusite-(Zr), Ca<sub>3</sub>UZrFe<sub>3</sub>O<sub>12</sub> (Galuskina *et al.*, 2010*b*); and bitikleite-(SnFe), Ca<sub>3</sub>SbSnFe<sub>3</sub>O<sub>12</sub> (Galuskina *et al.*, 2011*a*).

Zirconium-bearing megawite occurs with spurrite,  $Ca_5(SiO_4)_2(CO_3)$ ; hydroxylellestadite,  $Ca_5(SiO_4)_{1.5}(SO_4)_{1.5}(OH,F)$ ; rondorfite,  $MgCa_8(SiO_4)_4Cl_2$ ; wadalite,  $Ca_{12}Al_{10}Si_4O_{32}Cl_6$ ; minerals of the reinhardbraunsite-kumtyubeite series, Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>(OH,F)<sub>2</sub>; calcite and rarely periclase. Accessory and rare minerals are represented by the perovskite-group minerals lakargiite, CaZrO<sub>3</sub> and perovskite, CaTiO<sub>3</sub>; the garnet-group minerals kerimasite,  $Ca_3Zr_2Fe_2SiO_{12}$  and elbrusite-(Zr); and by srebrodolskite, Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, and an as yet undescribed mineral with a formula Ca<sub>3</sub>TiFe<sub>2</sub>O<sub>8</sub>. Spurrite crystals are embedded in the mass of secondary minerals among which hydrocalumite, ettringitegroup minerals, hydrogrossular, afwillite and other hydrosilicates (Fig. 1a) are widespread. Brucite develops after periclase.

Zirconium-bearing megawite crystals with either pseudo-cubic or pseudo-cuboctahedral crystal habits from the holotype sample do not exceed 15 µm in size and usually occur as inclusions in spurrite (Fig. 1a-c). The CaSnO<sub>3</sub> endmember content of holotype megawite reaches 61 mol.% (Table 1, analyses 1-3 and 6). Numerous lakargiite crystals occur between spurrite grains in wadalite-calcite-hydrocalumiteettringite aggregates (Fig. 1a; Table 1, analysis 5). Homogeneous megawite (CaSnO<sub>3</sub>  $\approx$ 56 mol.%, CaZrO<sub>3</sub>  $\approx$  34 mol.%) and lakargiite  $(CaZrO_3 \approx 67 \text{ mol.}\%, CaSnO_3 \approx 27 \text{ mol.}\%)$ crystals are commonly found in the same spurrite crystal (Fig. 1d; Table 1, analyses 6 and 7). A few grains with compositions which oscillate about the megawite-lakargiite boundary (e.g. Table 1, analysis 4) are present. Megawite and lakargiite inclusions in spurrite are characterized by CaTiO<sub>3</sub> contents of <10 mol.% (Table 1, analyses 1-4 and 6), whereas lakargiite in a wadalite-calcitehydrocalumite aggregate between spurrite crystals has >20 mol.% CaTiO<sub>3</sub> (Table 1, analysis 5).

Following the recognition in 2009 of megawite in spurrite skarns in xenolith no. 1, there were several other discoveries. Tin-rich lakargiite (with up to 30-35 mol.% CaSnO<sub>3</sub>) was found in xenolith no. 7 (10–15 m in size), which is located 1.5 km from xenolith no. 1 (see the

13	1.57	0.93	0.18	12.42	19.53	28.48	0.39	0.24	0.17	0.32	0.31	2.68	0.16	0.27	0.03
12	1.17	1.15	0.15	13.27	18.06	28.87	0.47	0.23	0.03	0.27	0.31	2.46	0.22	0.37	0.02
11	1.10	1.37	0.12	10.14	29.52	19.93	0.86	0.82	0.34	0.13	0.78	2.29	0.15	0.28	n.d.
10	0.47	0.12	0.05	0.65	29.25	39.43	0.69	0.34	0.03	0.18	0.06	0.60	0.40	0.21	0.04
6	0.65	0.54	0.04	2.42	35.41	26.73	0.89	0.54	0.05	0.29	n.d.	1.95	n.d.	n.d.	n.d.
8	0.83	0.07	0.25	0.64	60.63	1.91	1.56	n.d.	0.13	0.02	n.d.	1.18	n.d.	n.d.	n.d.
7	0.38	0.11	0.09	0.91	44.20	22.06	1.00	0.49	n.d.	0.25	n.d.	0.63	0.25	0.23	0.03
9	0.24	0.11	0.33	2.31	21.95	43.80	0.65	0.41	n.d.	0.23	0.16	0.55	0.09	0.11	0.02
5	3.18	0.55	0.04	10.51	37.13	10.05	0.82	n.d.	0.05	0.30	0.24	3.04	0.78	0.58	n.d.
4	0.28	0.25	0.20	4.35	25.37	36.30	0.91	0.35	0.09	0.22	0.50	0.54	n.d.	n.d.	0.04
3	0.44	0.18	0.08	3.33	18.18	43.99	0.56	0.38	0.05	0.35	0.56	1.24	0.18	0.21	0.03
2	0.23	0.12	n.d.	2.42	17.72	47.20	0.58	0.40	n.d.	0.34	0.48	0.93	0.34	0.21	0.04
Range	0.15 - 0.48	0.05 - 0.22	0-0.60	1.23 - 4.05	17.72 - 23.42	42.22-47.20	0.56 - 0.68	0.18 - 0.48	0 - 0.09	0.23 - 0.35	0.16 - 0.56	0.55 - 1.24	0.09 - 0.45	0.11 - 0.28	0.02 - 0.04
s.d.	0.11	0.07	0.20	0.94	1.98	1.53	0.06	0.10	0.03	0.04	0.12	0.24	0.12	0.05	0.01
-	0.30	0.15	0.22	2.87	19.89	44.24	0.62	0.32	0.04	0.28	0.39	0.85	0.23	0.21	0.03
	JO <sub>3</sub>	$Vb_2O_5$	$5iO_2$	$\Gamma iO_2$	$CrO_2$	$SnO_2$	$HO_2$	$\Gamma hO_2$	$M_2O_3$	$c_2O_3$	$Cr_2O_3$	$e_2O_3$	$a_2O_3$	Ce203	ИgO

31.98 n.d.	99.66	1.000	0.002	0.002	0.003	0.001	1.008	0.331	0.278	0.273	0.010	0.012	0.005	0.003	0.006	0.008	0.007	0.059	0.992	0.056	33	28	27	12	lith no 1
30.93 n.d.	97.98	0.987	0.002	0.002	0.004	0.001	0.996	0.343	0.262	0.297	0.007	0.015	0.004	0.004	0.001	0.007	0.007	0.055	1.004	0.023	34	26	30	10	from vand
31.10 n.d.	98.93	0.984	0.006	0.002	0.003		0.995	0.235	0.425	0.225	0.007	0.018	0.004	0.007	0.012	0.003	0.018	0.051	1.005	0.026	23	42	22	13	ملمتعدماه
28.20 0.19	100.91	0.971 0.004	0.002	0.005	0.002	0.002	0.986	0.505	0.458	0.016	0.003	0.002	0.002	0.006	0.001	0.005	0.002	0.015	1.014	-0.026	50	45	7	n	in control to
29.19 n.d.	98.70	0.983	0.004				0.988	0.335	0.543	0.057	0.004	0.008	0.001	0.008	0.002	0.008		0.046	1.012	0.007	33	53	9	~	retale writh
30.48 n.d.	97.70	0.998					0.999	0.023	0.904	0.015	0.005	0.001	0.008	0.014	0.005	0.001		0.027	1.001	0.018	2	90	1.5	6.5	and the or
29.85 0.25	100.73	$0.989 \\ 0.004$	0.003	0.003	0.003	0.001	1.004	0.272	0.666	0.021	0.002	0.002	0.003	0.009		0.007		0.015	0.996	0.010	27	67	7	4	ient levere
29.26 0.16	100.39	0.997 0.003	0.003	0.001	0.001	0.001	1.006	0.555	0.340	0.055	0.002	0.002	0.010	0.006		0.006	0.004	0.013	0.994	0.023	56	34	9	4	(V - C)
32.24 0.18	<u>99.69</u>	0.999 0.003		0.008	0.006		1.017	0.116	0.523	0.229	0.019	0.007	0.001	0.007	0.002	0.008	0.005	0.066	0.983	0.053	12	53	23	12	lith no.
30.23 0.16	99.79	$1.005 \\ 0.003$	0.002			0.002	1.012	0.449	0.384	0.102	0.002	0.004	0.006	0.008	0.003	0.006	0.012	0.013	0.988	0.046	45	39	10	9	nev aearl
29.82 0.13	99.71	1.009 0.002	0.003	0.002	0.002	0.001	1.020	0.554	0.280	0.079	0.003	0.003	0.003	0.005	0.002	0.010	0.014	0.029	0.980	0.076	57	29	8	9	of 0 and
29.89 0.14	101.04	$1.011 \\ 0.003$	0.003	0.004	0.002	0.002	1.024	0.594	0.273	0.057	0.002	0.002		0.005		0.009	0.012	0.022	0.976	0.075	61	28	9	S	opun mode
28.95 - 30.63 0.10 - 0.19																									male of sumite
$0.59 \\ 0.03$																									of the second
29.80 0.14	100.58	1.005 0.003	0.002	0.003	0.002	0.001	1.016	0.555	0.305	0.068	0.002	0.002	0.007	0.006	0.001	0.008	0.010	0.020	0.984	0.056	56	31	7	9	ita from ho
CaO SrO	Total	Ca** Sr	Th	$La^{3+}$	$Ce^{3+}$	Mg	A site	${ m Sn}^{4+}$	Zr	${ m Ti}^{4+}$	$U^{6+}$	$Nb^{5+}$	Si	Hf	Al	Sc	$Cr^{3+}$	$\mathrm{Fe}^{3+}$	B site	$\Delta e^-$	CaSnO <sub>3</sub>	CaZrO <sub>3</sub>	CaTiO <sub>3</sub>	Others <sup>§</sup>	(1) mean

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(point of analysis no. 2 is shown in Fig. 1a); (5) lakargiite associated with megawite from a wadalite-hydrocalumite-ettringite aggregate (Fig. 1a); (6–7) megawite (6) and lakargiite (7) crystals used for single crystal Raman and EBSD studies from xenolith no. 1; (8-9) porous aggregate of lakargiite (8) overgrowing Sn-bearing lakargiite (9) crystals (Fig. 1c) from xenolith no. 7; (110) thin zone of megawite on lakargiite (Fig. 1e) from xenolith no. 7; (11-12) minerals of the perovskite-group -4) several inegawire crystals wiumi spurme crystals nom venomin no. 1 from xenolith no. 3, a zoned crystal with a lakargiite core (11) and megawite rim (12) (Fig. 1e, inset); (13) megawite from xenolith no. 3 forming later zones on (1) inegawite from hototype sample of spurfice skarn, mean of 9 analyses, xenolith no. 1; (2complex pseudomorphs (Fig. 1f). The abbreviation n.d. means not detected. \* low total because of high porosity of lakargiite,

\*\* calculated on the basis of 2 cations,  $\Delta e^-$  charge difference to  $30^{2-}$ . CaSnO<sub>3</sub> as the megawite endmember, CaZrO<sub>3</sub> as the lakargiite endmember and CaTiO<sub>3</sub> as the

perovskite endmember;  $^{\$}$  CaFe $^{3+}_{0,5}Nb}_{0,5}^{5,5}O_3, CaSe_{0,5}Nb}_{0,5}^{5,5}O_3, CaFe}_{0,7}U^{6+}_{0,3}O_3, CaHfO_3 etc.$ 

geological map in Galuskin et al., 2009), and is the type locality for bitikleite-(ZrFe), Ca<sub>3</sub>SbZrFe<sub>3</sub>O<sub>12</sub> (Galuskina et al., 2010a); vorlanite, CaUO<sub>4</sub> (Galuskin et al., 2011a) and irinarassite, Ca<sub>3</sub>Sn<sub>2</sub>Al<sub>2</sub>SiO<sub>12</sub> (Galuskina et al., 2011b). Crystals of Sn-rich lakargiite (with pseudo-cubic or pseudo-cuboctahedral habits) overgrow porous, fine-grained aggregates of almost pure lakargiite, which occur with relict larnite, rondorfite, wadalite, magnesioferrite, As-bearing hydroxylellestadite and srebrodolskite (Fig. 1d; Table 1, analyses 8 and 9). Rarely, megawite occurs as rims up to 5 µm thick on Sn-rich lakargiite crystals in the highly altered parts of the chegemite-bearing skarns which contain hydrogarnet and ettringite (Fig. 1e). The megawite composition approaches the boundary with lakargiite (CaSnO<sub>3</sub>  $\approx$  50 mol.%, CaZrO<sub>3</sub>  $\approx$ 45 mol.%; Table 1, analysis 10). A phase close to burtite, CaSn(OH)<sub>6</sub> (Sonnet, 1981), which overgrows the lakargiite aggregates, (Fig. 1e) is also found in this association.

Megawite was also found in xenolith no. 3 (20 m in size), which is the type locality for toturite,  $Ca_3Sn_2Fe_2SiO_{12}$  (Galuskina *et al.*, 2010*c*); pavlovskyite,  $Ca_8(SiO_4)_2(Si_3O_{10})$  (Galuskin *et al.*, 2011*b*) and rusinovite,  $Ca_5(Si_2O_7)_3Cl_2$  (Galuskin *et al.*, 2011*c*). Xenolith no. 3 is located 10–15 m from xenolith no. 1 (see the geological map in Galuskin *et al.*, 2009). Megawite forms rims on µm-sized lakargiite crystals in larnite-cuspidine zones in skarns which contain abundant hydrogarnet and hydrosilicates (Fig. 1*f*; Table 1, analyses 11 and 12). Megawite and garnets (toturite and Sn-

bearing schorlomite) form rims on lakargiite pseudomorphs after zircon (Fig. 1*f*; Table 1, analysis 13). Megawite from xenolith no. 3 contains considerable CaZrO<sub>3</sub> and CaTiO<sub>3</sub>, and also U, Nb and Fe impurities (Table 1, analyses 12 and 13). The megawite rims on lakargiite pseudomorphs after zircon contain 0.331 Sn atoms per formula unit (a.p.f.u.) (33 mol.% of the megawite endmember); 0.278 Zr a.p.f.u. (28 mol.% of the lakargiite endmember) and 0.273 Ti a.p.f.u. (27 mol.% of the perovskite endmember); the remaining 12% is accounted for by Fe<sup>3+</sup>-bearing endmembers (Table 1, analysis 13).

Megawite crystals are transparent and pale yellow or colourless with a vitreous lustre and white streak. Megawite is biaxial, but twinning and small crystal sizes prevented the determination of the refractive indices and optic sign. The calculated refractive index of megawite is 1.89 (for pure CaSnO<sub>3</sub>). The calculated density for megawite corresponding to analysis 1 (Table 1) is  $5.06 \text{ g cm}^{-3}$ . The synthetic analogue of megawite, orthorhombic CaSnO<sub>3</sub>, is optically positive. Crystallographic orientation by analogy with lakargiite is:  $X = \beta$ ,  $Y = \alpha$ ,  $Z = \gamma$ . Megawite has good cleavage along (110) and (001) (orthorhombic indices).

Structural data for megawite were derived using EBSD (Fig. 2). The best mean angular deviation (MAD)  $\approx 0.2^{\circ}$  (an excellent fit) was obtained for a cubic model with a = 3.8 Å. However, taking into account structural data for synthetic CaSnO<sub>3</sub> and phases of the Ca(Sn<sub>1-x</sub>Zr<sub>x</sub>)O<sub>3</sub> series (Megaw 1946; Vegas *et* 



FIG. 2. Electron backscattered diffraction patterns of megawite (detector distance 177mm): (*a*) performed at point 6 shown in Fig. 1*c*; (*b*) its fitting result.

h	k	l	$d_{hkl}$	$I_{\rm rel}$	h	k	l	$d_{hkl}$	Irel
1	0	1	4.554	3	2	0	4	1.616	7
1	1	0	3.984	52	3	1	2	1.611	13
0	0	2	3.970	19	0	4	0	1.428	2
1	1	1	3.561	3	2	2	4	1.406	8
0	2	0	2.855	43	4	0	0	1.390	2
1	1	2	2.812	100	1	3	4	1.334	4
2	0	0	2.780	19	2	4	0	1.270	2
0	2	2	2.318	9	3	3	2	1.259	5
2	2	0	1.992	13	1	1	6	1.256	6
0	0	4	1.985	13	4	2	0	1.250	3
1	3	0	1.800	5	2	4	2	1.210	2
2	2	2	1.780	3	4	2	2	1.192	2
1	1	4	1.777	8	0	4	4	1.159	2
1	3	2	1.640	13	4	0	4	1.139	3
0	2	4	1.630	11	1	5	2	1.077	3

TABLE 2. Calculated XRD pattern of megawite (for Co-*K*α radiation Debye-Scherrer geometry).

*al.*, 1986; McMillan and Ross, 1988; Kung *et al.*, 2001; Mitchell, 2002; Tarrida *et al.*, 2009), structural data for lakargiite-megawite solid solutions (Galuskin *et al.*, 2008*b*) and the optical properties (megawite is an optically biaxial mineral); an orthorhombic model was chosen with a = 5.555(3), b = 5.708(2), c = 7.939(5) Å, V = 251.8(1) Å<sup>3</sup>, *Pbnm*, Z = 4. The unit-cell parameters of this structural model are based on data for the synthetic phase CaSn<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>3</sub>

(Tarrida *et al.*, 2009) and fitting gives a MAD =  $0.4^{\circ}$  (a very good fit).

Due to the scarcity of megawite and the small size of the available crystals a powder X-ray diffraction (XRD) pattern could not be collected. Calculated XRD data for analysis 1 are provided in Table 2. Values are calculated for Co- $K\alpha$  radiation and Debye-Scherrer geometry.

The Raman spectrum of megawite (Fig. 3) was obtained from the grain shown in Fig. 1c at point 6, where EMPA was also performed. After repolishing the thin section using colloidal Al<sub>2</sub>O<sub>3</sub>, EBSD images were obtained at the same point (Fig. 2). The Raman spectrum of megawite is similar to that of synthetic CaSnO<sub>3</sub> (McMillan and Ross, 1988) and synthetic perovskite of composition Ca(Sn<sub>0.6</sub>Zr<sub>0.4</sub>)O<sub>3</sub> (Tarrida et al., 2009). The following bands can be assigned (Fig. 3, spectrum 1):  $159 \text{ cm}^{-1}$  and  $183 \text{ cm}^{-1}$ (lattice soft modes); 262 cm<sup>-1</sup>, 283 cm<sup>-1</sup> (Sn–O and Zr–O bending modes); 355 cm<sup>-1</sup> and 443 cm<sup>-1</sup> (torsional modes); 474 cm<sup>-1</sup>, 557 cm<sup>-1</sup> (Sn–O and Zr–O stretching modes); 705  $\text{cm}^{-1}$  (overtone). The megawite spectrum also resembles that of Sn-rich lakargiite (Fig. 3, spectrum 2).

### Discussion

Orthorhombic perovskites of the  $CaTiO_3$ -CaZrO<sub>3</sub>-CaSnO<sub>3</sub> system are widespread in skarns that have formed within xenoliths in the



FIG. 3. Raman spectra of (1) megawite and (2) lakargite, obtained for the crystals shown in Fig. 1*c* at points 6 and 7, respectively.



FIG. 4. Ternary plot showing the perovskite group minerals from the xenoliths in terms of their CaTiO<sub>3</sub> (perovskite)-CaSnO<sub>3</sub> (megawite)-CaZrO<sub>3</sub> (lakargiite) composition: (1) xenolith 1, spurrite zone with megawite;
(2) xenolith 1 (rest of zones); (3) xenolith 3; (4) xenolith 7. The arrows, 5–8 show the trend the perovskite group composition changes: 5, 6 refer to xenolith 1; 7 to xenolith 7; and 8 to xenolith 3.

ignimbrites of the Upper Chegem caldera. High Sn contents are observed only in lakargiite, an observation which can be explained by the very similar ionic radii of <sup>[6]</sup>Zr<sup>4+</sup> (0.72 Å) and <sup>[6]</sup>Sn<sup>4+</sup> (0.69 Å) (Shannon, 1976). The holotype megawite contains substantial amounts of CaTiO<sub>3</sub> and CaZrO<sub>3</sub> in solid solution (Table 1, analysis 1; Fig. 4). Crystals of Zr-bearing megawite from the holotype sample are found in the same spurrite crystal as Sn-bearing lakargiite (Fig. 1c, 4; Table 1, analyses 6 and 7), an observation that may indicate the presence of a miscibility gap in this solid solution under the conditions in which the skarn formed (Fig. 4). Other spurrite crystals from the same sample of perovskite with megawite-lakargiite intermediate composition (Fig. 4; Table 1, analysis 4) suggest low mobility of Sn and Zr, i.e. the perovskites inherited chemical inhomogeneities in the protolith.

Megawite belongs to the early skarn mineral association at the Upper Chegem caldera, which contains lakargiite, perovskite, magnesioferrite, larnite, wadalite and rondorfite. This assemblage was formed by high-temperature contact metamorphism of carbonate xenoliths in persilicic ignimbrites (age 2.8 Ma) under larnite-facies conditions (temperature >800°C and low pressures) as described by Gazeev *et al.*, (2006) and Galuskin *et al.*, (2008*a*,*b*; 2009).

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