

charge balance being maintained by substitution of fluorine and/or hydroxyl for oxygen. If indeed this occurs, the O(1) site would be partly occupied, a fact consistent with a large thermal parameter. However, the infrared absorption spectrum and electron-microprobe analysis of the phase given by Appleton *et al.* (1992) suggest such substitution occurs only in very small amounts, if at all. To test this hypothesis, occupancy of the O(1) site was released. Although the occupancy of the site dropped to 0.93(4), the value is less than 2 sigma from full occupancy and there was no decrease in the *R* value. These results suggest that the site is essentially fully occupied, a result in accord with the chemical and infrared data of Appleton *et al.* (1992). The large thermal parameter may thus result from factors such as positional disorder, not uncommon in atoms occupying positions of high symmetry as O(1) in daqingshanite-(Ce) (site symmetry = $3m$).

The results of the high-precision crystal structure study described herein elucidate the huntite-daqingshanite-(Ce) relationship; the work also demonstrates that the ideal formula of Nkombwa Hill daqingshanite-(Ce) is $\text{Sr}_3(\text{REE})_1(\text{CO}_3)_3(\text{PO}_4)_1$, and that there is little or no substitution of hydroxyl or fluorine in its atomic arrangement.

KEYWORDS: daqingshanite-(Ce), crystal structure, Zambia, Nkombwa Hill

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Acknowledgements

The sample of daqingshanite-(Ce) used in this study was graciously provided by Forrest and Barbara Cureton. Support for the study from U.S. National Science Foundation grant EAR-9218577 is acknowledged.

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[Manuscript received 9 December 1993]

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MINERALOGICAL MAGAZINE, SEPTEMBER 1994, VOL. 58, PP. 496–501

Monticellite in the Gwena kimberlite (Shaba, Zaïre): evidence of late-magmatic crystallization

PRIOR to 1975 monticellite was considered a rare mineral in kimberlites but microprobe studies have now established it as a fine grained constituent in many kimberlite matrices (e.g. Clement *et al.*,

1975; Mitchell, 1978; Skinner and Clement, 1979). This paper describes the mode of occurrence and chemical composition of well-developed monticellite in the Gwena kimberlite, Shaba, Zaïre.

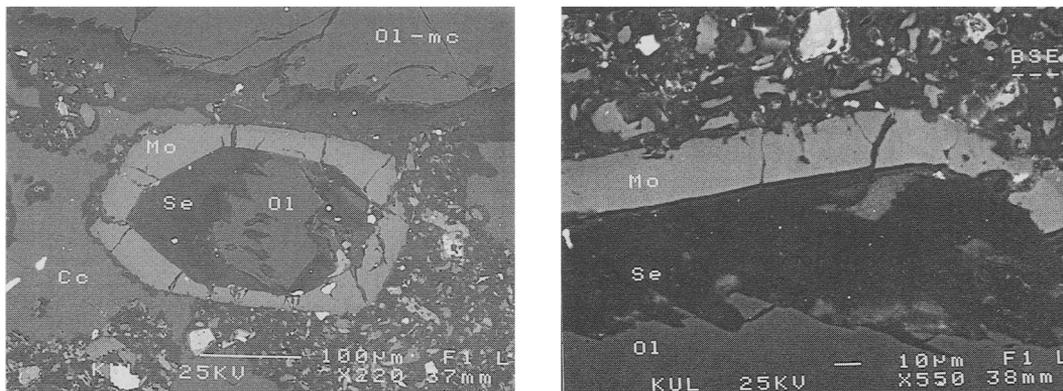


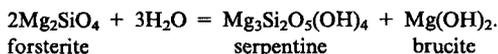
FIG. 1. (a) Electron microscope back scatter image (BSE) showing a partially serpentinized (Se) olivine microphenocryst (Ol) surrounded by a rim of epitaxial monticellite (Mo). The olivine macrocrysts (Ol-mc) is surrounded only by a rim of serpentine. (b) Back scatter image (BSE) showing a detail of a weakly zoned monticellite fringe (Mo) around a partially serpentinized (Se) olivine macrophenocryst (Ol). The matrix consists predominantly of monticellite (grey) and serpentine (dark) with minor perovskite (bright), spinel (light-grey) and ilmenite (white).

On the Kundulungu Plateau, some 20 kimberlite pipes are known, cropping out roughly along two N-S alignments. They were first described by Verhoogen (1938). A number of them contain monticellite, originally identified by Verhoogen as 'calcic olivine'. Only the western Gwena pipe (16 ha) is characterized by the exceptional presence of two different habits of monticellite.

Petrographic characteristics. The Gwena kimberlite is dark grey and remarkably fresh. It contains numerous xenoliths of both mantle (lherzolites, harzburgites, eclogites) and crustal (metamorphic and sedimentary rocks) origin.

The kimberlite has a porphyritic texture with macrocrysts of olivine, garnet, pyroxene and ilmenite, embedded in a dark, fine-grained matrix of olivine, monticellite, spinel, perovskite, serpentine and calcite. The rock can be classified as a macrocrystic hypabyssal kimberlite, following the textural classification of Clement and Skinner (1985).

Olivine morphology is varied. There are large (> 1 cm) rounded macrocrysts, small, euhedral to subhedral microphenocrysts (> 1 mm) and smaller anhedral groundmass olivines. The microphenocrysts and groundmass olivines are usually strongly serpentinized whereas the olivine macrocrysts are only moderately affected at the periphery. The olivine macrocrysts are occasionally altered to serpentine-brucite mixtures that illustrate the classical reaction achieved at c. 450°C described by Bowen and Tuttle (1949):



Morphologically, there are two types of monticellite (Fig. 1a, b): (1) Small (5–10 µm), rod-like, colourless, euhedral crystals disseminated in the matrix. The individual grains are very homogeneous and, apparently, free of inclusions. Some are partially altered to carbonate. (2) Overgrowths developed around partially serpentinized euhedral olivine microphenocrysts. The monticellite crystals have the same (epitaxial) optical orientation as the olivine cores. Their external shape is perfectly parallel to the euhedral form of the olivine cores, despite serpentinization (Fig. 1a, b).

Monticellite rims are absent from rounded olivine macrocrysts as well as from the small, anhedral groundmass olivines. This might be related to the absence of crystallographic faces suitable for epitaxial overgrowths or be due to compositional factors. Anhedral macrocrysts include refractory high Mg mantle olivine xenocrysts.

Chemical composition. Mineral analyses were performed on a Cameca CAMEBAX electron microprobe (WDS-mode, 15 kV, 15 nA, counting time 10 s, corrections by the ZAF method). The analyses (Table 1) are for isolated monticellite crystals from the kimberlite groundmass and monticellite rims surrounding olivine phenocrysts.

Both types of monticellite have similar chemical composition (Fig. 2). They are solid

TABLE 1. Representative analyses of monticellites, olivines and serpentines from Gwena kimberlite

Samples	Monticellites						Olivines				Serpentines		
	G39A	G40A	G42A	G02B	G03B	G35B	G14r	G20c	G22c	G26r	G4A	G11c	G8c
SiO ₂	37.46	36.80	36.94	37.09	35.51	36.86	40.85	41.28	41.00	40.48	40.68	39.87	39.95
TiO ₂	0.05	0.07	0.07	0.13	0.04	0.03	0.01	0.01	0.01	0.02	0.02	0.07	0.01
Al ₂ O ₃	0.12	0.01	0.08	0.09	0.04	0.03	0.03	0.04	0.05	0.03	0.30	0.46	0.52
FeO*	4.89	8.28	6.19	6.15	6.62	6.80	8.82	8.90	8.47	9.62	4.73	7.50	5.96
MnO	0.39	0.66	0.47	0.50	0.44	0.56	0.15	0.04	0.13	0.13	0.08	0.14	0.09
MgO	23.85	21.77	23.04	22.93	21.91	22.64	49.62	50.07	49.78	49.06	40.21	39.05	40.28
CaO	33.50	32.03	32.49	33.45	32.56	32.86	0.11	0.09	0.10	0.27	0.13	0.05	0.11
Na ₂ O	0.09	0.08	0.08	0.08	0.55	0.09	0.02	0.04	0.01	0.02	0.01	0.01	0.00
K ₂ O	0.00	0.01	0.03	0.05	0.51	0.01	0.00	0.00	0.00	0.03	0.00	0.00	0.01
H ₂ O	—	—	—	—	—	—	—	—	—	—	12.24	11.92	12.20
Total	100.35	99.71	99.39	100.47	98.18	99.88	99.61	100.47	99.55	99.66	98.4	99.07	99.13
mol. %													
Mo	83.4	74.0	78.8	81.0	80.6	80.0	—	—	—	—	—	—	—
Ki	11.1	19.0	15.1	14.0	14.9	14.0	—	—	—	—	—	—	—
Fo	5.5	7.0	6.1	5.0	4.5	6.0	90.8	90.9	91.2	90.0	—	—	—
Fa	—	—	—	—	—	—	9.2	9.1	8.8	10.0	—	—	—

Monticellite: A = in matrix, B = around olivine, * Total iron

Olivine: r = rim, c = core

Mo = Monticellite, Ki = Kirschsteinite, Fo = Forsterite, Fa = Fayalite

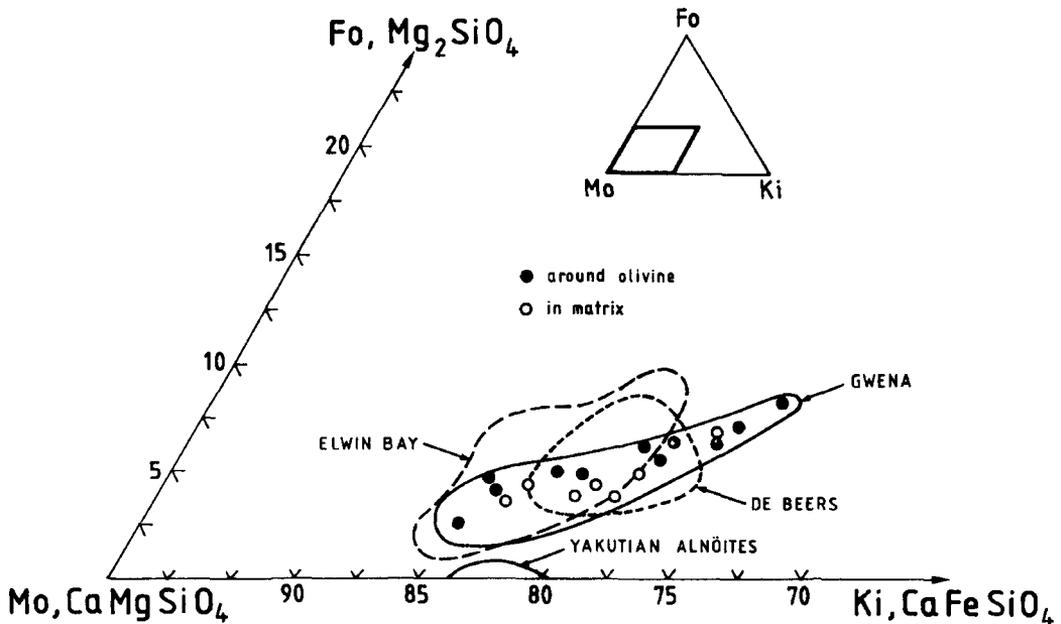


FIG. 2 Chemical composition of the Gwena monticellites plotted on the triangular diagram forsterite (Fo = Mg₂SiO₄)–monticellite (Mo = CaMgSiO₄)–kirschsteinite (Ki = CaFeSiO₄). Comparison with monticellite from Elwin Bay, Canada (Mitchell, 1978), De Beers, South-Africa (Clement *et al.*, 1975) and Yakutian alnöites (Nikishov *et al.*, 1979).

solutions of monticellite CaMgSiO_4 (74–85 mol% Mo) and kirschsteinite, CaFeSiO_4 (11–19 mol.% Ki) with 2.5–7 mol.% Fo. The $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios of the monticellites (0.84–0.88) are slightly lower than those of the olivine phenocrysts (0.88–0.91). The Gwena monticellite compositions are comparable to those of the kimberlites of Elwin Bay, Canada (Mitchell, 1978) and De Beers, South Africa (Clement *et al.*, 1975). In contrast monticellites from Yakutian alnöites (Nikishov *et al.*, 1979) essentially exhibit monticellite-kirschsteinite solid solutions without olivine (Fig. 2).

Figure 3 shows the results of a step scan profile across a partly serpentinized olivine phenocryst surrounded by a monticellite corona. The contiguous results are fully in agreement with the optical observation that the inner serpentine zone (2) must have formed by replacement of the olivine core (1). This is also indicated by the variable width of the serpentine rim, and by its highly fluctuating chemical composition, which shows variable values for Fe and Mg and, to a lesser extent, for Ca and Si. The Ca-rich monticellite corona, zone (3), in contrast, is regular in width and fairly homogeneous in chemical composition. The outer serpentine rim (4), developed on the outer surface of the monticellite corona, is more aluminous than the inner serpentine zone (2).

Conclusions. There are few descriptions of monticellite surrounding olivine in kimberlites. Nikishov and Nikishova (1966) mention the presence of monticellite (with 20–30% Ki) in the matrix as well as in reaction aureoles surrounding olivine megacrysts in the kimberlites of Yakutia (Siberia). Clement (1982) and Kornilova *et al.* (1983) report the presence of monticellite as a secondary reaction product replacing olivine.

The contact between olivine and the surrounding monticellite in South African kimberlites is irregular. According to Clement (*pers. comm.*), there is petrographic evidence for the replacement of serpentinized olivine by monticellite, thus implying a very late-stage, deuteric origin for this monticellite. At Gwena, in contrast, the contacts with the monticellite overgrowths are smooth and regular. Microprobe analyses indicate the existence of a thin rim of serpentine corroding the outer surfaces of the monticellite aureoles although serpentinization is mainly restricted to olivine since the Ca-ion monticellite cannot readily be accommodated in the serpentine lattice. This clearly suggests that at Gwena the monticellite is older than the serpentinization.

If at Gwena the monticellite crystallization were later than the serpentinization, then it would be logical to expect that the other forms of serpentinized olivine would have similar monticellite overgrowths. This is not the case. The shape of the monticellite overgrowths faithfully reflects the euhedral shape and optical orientation of the olivine phenocrysts. Such an epitaxial phenomenon might not be expected where an intervening phyllosilicate (serpentine) is present. We therefore suggest that the monticellite coronas were formed as a direct overgrowth, in crystallographic continuity (epitaxial) on the olivine phenocrysts. This could have been occasioned by physicochemical changes in the kimberlitic magma, possibly provoked by the introduction of a carbonatite component.

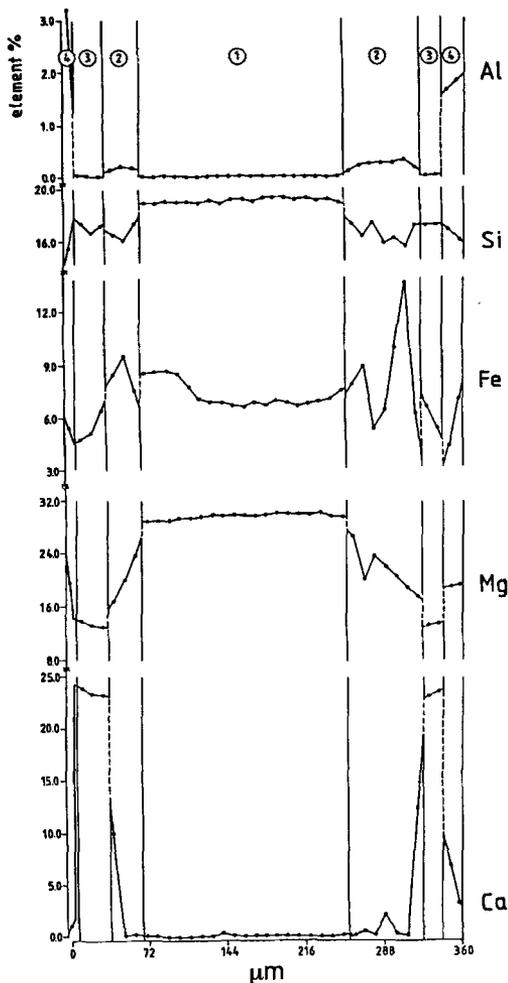


FIG. 3 Microprobe traverse across an olivine core (1) surrounded by epitaxial monticellite (3) with intervening (2) and surrounding (4) serpentine in the Gwena kimberlite.

cellite overgrowths. This is not the case. The shape of the monticellite overgrowths faithfully reflects the euhedral shape and optical orientation of the olivine phenocrysts. Such an epitaxial phenomenon might not be expected where an intervening phyllosilicate (serpentine) is present. We therefore suggest that the monticellite coronas were formed as a direct overgrowth, in crystallographic continuity (epitaxial) on the olivine phenocrysts. This could have been occasioned by physicochemical changes in the kimberlitic magma, possibly provoked by the introduction of a carbonatite component.

The similar chemical composition of the corona monticellite and the idiomorphic groundmass monticellites suggests that both types formed simultaneously, from the same Ca-enriched, late-magmatic fluid. The assemblage perovskite-monticellite-calcite in the kimberlite matrix indicates a crystallization temperature around 600°C (Wyllie, 1966). In experiments of Edgar *et al.* (1986), monticellite was stable at 12 kbar together with forsterite, phlogopite, calcite and diopside. The presence of monticellite as a common groundmass mineral reflects crystallization at low pressure (Eggler, 1989).

Cracks and cleavages in the monticellite overgrowths (Fig. 1b) presumably allowed the ingress of volatiles (H₂O) necessary for the subsequent breakdown of the olivine into serpentine at slightly lower temperatures (450–500°C) as described above.

Acknowledgements. Mr. J. Wautier of the CAMST/UCL is thanked for performing the microprobe analyses. The SEM-BSE photomicrographs were recorded with a Jeol JSM-6400 scanning electron microscope at Katholieke Universiteit Leuven.

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[Manuscript received 18 February 1993:
revised 18 May 1993]

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KEYWORDS kimberlite, monticellite, epitaxis, Gwena, Zaïre.

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MINERALOGICAL MAGAZINE, SEPTEMBER 1994, VOL. 58, PP. 501–505

Thermal behaviour of cavansite from Wagholi, India

BIRCH (1977) described isolated sky-blue rosettes of the rare vanadium mineral cavansite $[\text{Ca}(\text{VO})\text{Si}_4\text{O}_{10}\cdot 4\text{H}_2\text{O}]$ from an uncertain location in Pune district, Maharashtra, India; since then, detailed work by Arvind Bhale (Wilke *et al.*, 1989) resulted in the successful location of this mineral in one of the stone quarries at Wagholi, about 14 km from Pune. Besides the other two known occurrences from Oregon, USA, from where Staples *et al.* (1973) described this mineral and named it from its major chemical constituents Ca, V and Si, Wagholi is the only other known locality. Evans (1973) gave a detailed solution to the structure of cavansite and its polymorph pentagonite.

At Wagholi, cavansite occurs in cavities in tholeiitic basalts of the Deccan Volcanic Province. It is always associated with zeolites and other cavity minerals like calcite, okenite, apophyllite, etc. This paragenesis is very similar to that from the localities in the USA, although at Wagholi pentagonite is not recorded. Optical properties and other physical characters of cavansite from Wagholi are almost identical with those given by Staples *et al.* (1973) and the material is generally highly superior to that from Oregon in quality. The samples from Wagholi, under the microscope, show parallel extinction, R.I. ranging from $\alpha = 1.544 (\pm 0.002)$ to $\gamma = 1.550 (\pm 0.002)$ and biaxial interference figure with $2V\gamma$ around 50° , a strong dispersion $r < v$, $c = \text{Bxa}$ and length slow character. These characters are almost identical with those given by Staples *et al.* (1973) except that the pleochroism of the Wagholi material is different. Parallel to the b -axis the colour is deep blue while that parallel to the a axis is also quite strong in shades of blue instead of being colourless, particularly when the needles are thicker. The cavansite needles are pellucid and

are free from any visible inclusions even at high magnification ($\times 800$).

Confirmation of the Indian material as cavansite was obtained from the X-ray powder diffraction patterns (Cu target and Ni filter). However, it is noteworthy that the Wagholi cavansite includes a CuCl phase, tentatively identified using XRD during the search match. Though the deep bluish green colour of the mineral is likely to be due to the absorption properties of V^{2+} , the possibility that the CuCl phase contributes to the colour of this mineral needs to be examined further as the contaminant is identified only by XRD. The possibility of this phase influencing the thermal characters of cavansite is ruled out on account of its insignificant amount.

Though detailed mineralogical information is available through the papers published by Staples *et al.* (1973), Evans (1973) and Wilke *et al.* (1989), there is no record of the thermal behaviour and the positions of the water molecules and their loss on heating. The availability of large crystals prompted the present authors to undertake investigations of the thermal behaviour of cavansite using Indian samples.

The DTA, DTG and TG curves (Fig. 1) have been recorded during continuous heating up to a maximum of 1000°C on the Hungarian manufactured 'Derivatograph' (OD Type 102, MOM), at the Department of Geology, University of Poona. The X-ray diffractograms (Figs. 2*a,b,c*) were obtained on a 'Rigaku' diffraction system DMax IVC (operating voltage of 50 kV and current of 25 mA) at the Department of Archaeology, Deccan College, Pune. Sample preparation and conditions of the heating experiments are summarized in Table 1.