SCIENTIFIC COMMUNICATION

NOTES ON FLUID INCLUSIONS OF VANADIFEROUS ZOISITE (TANZANITE) AND GREEN GROSSULAR IN MERELANI AREA, NORTHERN TANZANIA

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Tanzanite is a trade name for a gem-quality vanadiferous zoisite of deep sapphire-blue colour discovered in Merelani area, Tanzania in 1967. This mineral was first described as a strontium -bearing zoisite by Bank, H. & Berdesinski, W., 1967. Other minor occurrences of this mineral has been reported in Lalatema and Morogoro in Tanzania and in Lualenyi and Lilani in Kenya (Naeser and Saul 1974; Dolenc 1976; Pohl and Niedermayr 1978).

Crystals of tanzanite occur mainly in boudinaged pegmatitic veins and hydrothermal frac-

Fig. 1. Tanzanite-bearing horizon in the graphite-rich diopside gneiss. The yellow colour indicates hydrothermal alteration, which can be used in prospecting for tanzanite. Length of photo ca. 8 m.

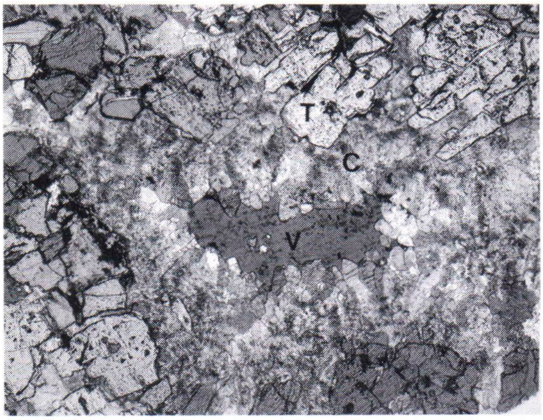

Fig. 2. Typical tanzanite-bearing cavity. T = tanzanite, C = colloformic calcite, V = empty void. One polarizer in and the length of picture is 1.9 mm.

ture fillings in a brecciated and hydrothermally altered graphite-bearing diopside gneiss in a mineral association containing in addition to tanzanite, grossular, quartz, diopside, graphite, calcite, and to a minor quantity hematite and sphene (Fig. 1). The hydrothermally altered graphite-bearing diopside gneiss lies concordantly or slightly oblique between pelitic, semi-pelitic and psammitic gneisses. These metasedimentary sequences are bordered on both sides by dolomitic limestones.

Fluid and mineral inclusions were studied in tan and blue tanzanites taken from pockets (Fig. 2) in Alli Juliyawatu and De Souza mines. Primary unleaked fluid inclusions are rare in tanzanites and almost all of the fluid inclusions are secondary. Heating experiments were performed with Leitz 350 microscope hot stage (20°—350°C) and Leitz 1350 microscope hot stage (350°—1100°C). The temperature measurements were calibrated with organic melting point standards. Two ordinary blue filters were used to display clearly the colour change of tanzanite from tan to blue during heating. The phase volume proportions of the capillary primary fluid inclusions were measured with an ocular screw micrometer at room temperature (24°C).

The chemical formula of tanzanite has been given as $Ca_2Al_3Si_3O_{12}OH$ (Ghose & Tsang 1971). The chemical compositions of tanzanites studied are given in Table 1.

Unit cell dimensions, measured by X-ray diffraction, are a = 16.21, b = 5.55, c = 10.03 ± 0.01 Å in agreement with Hurlbut (1969). Zoisite shows diffraction symmetry mmmPn-a, which limits the possible space groups to Pnma if centric or $Pn2_1$ if acentric (Dallace 1968). The most striking property of tanzanite is its pleochroism, which changes from trichroic to dichroic on heating; normally its pleochroism varies: X = red-violet, Y = c = deep blue, Z = a = yellow-green. It is optically positive with 2V = 53°, and indices of refraction are α = 1.693, β = 1.694 and γ = 1.702 (Na light). The hardness is 6.5—7.0 (Mohs), and specific gravity is 3.35 (cf. also Bank 1969; Hurlbut 1969 and Strunz 1969).

Tanzanite seems to occur in two generations: brown (older) and blue (younger) type; the blue

Table 1. Microprobe and wet chemical analyses of zoisite, tanzanite and grossular from Merelani, Tanzania.

	Zoisite	Tanzanite			Grossular	
	148-EM◦	73-EM*	73C-EM◦	73R-EM◦	191-EM*	92-EM◦
SiO_2	40.69	39.99	40.61	40.68	40.43	40.83
Al_2O_3	35.68	34.24	33.39	33.27	21.85	22.36
Fe_2O_3	0.00	0.06	0.00	0.01	0.15	0.07
FeO	—	0.00	—	—	—	—
MgO	0.04	0.04	0.04	0.06	0.25	0.29
CaO	23.46	24.40	23.47	23.39	36.18	35.40
Na_2O	0.01	0.09	0.07	0.05	0.56	0.00
K_2O	0.01	0.06	0.01	0.02	0.04	0.00
MnO	0.00	0.04	0.03	0.03	0.25	0.32
TiO_2	0.03	0.05	0.04	0.01	0.32	0.31
P_2O_5	—	0.07	—	—	0.05	—
H_2O+	—	1.15	—	—	0.16	—
H_2O-	—	0.01	—	—	0.00	—
F	—	0.05	—	—	0.00	—
V_2O_3	0.01	0.26	0.28	0.34	0.10	0.22
Cr_2O_3	0.00	0.00	0.02	0.03	0.00	0.03
NiO	0.00	0.00	0.00	0.00	0.00	0.00
—O=F	—	0.02	0.00	—	0.00	—
Total	99.93	100.49	97.96	97.89	100.34	99.83

* Wet chemical analysis. Analyst: Risto Saikkonen, GSF
◦ Microprobe analyses. Analyst: Seppo Sivonen, Oulu University
— not determined

Fig. 3. Natural tanzanite with well developed crystal faces in a graphite-rich diopside gneiss. Crystal length is 0.7 cm.

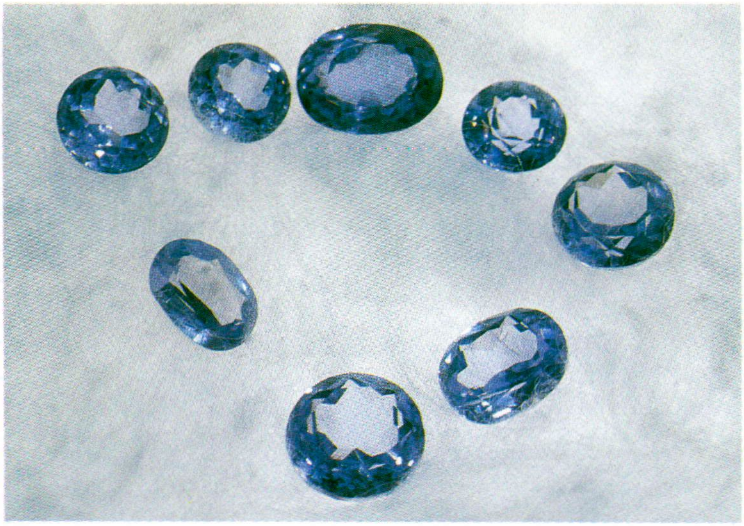

Fig. 4. Cut tanzanite crystals. (0.5—1.2 carats). By courtesy of Tanzanian Gemstone Industry.

type having more pronounced pyramidal faces. The latter, though more rare, is less fractured therefore admired for its cut (Fig. 3 & 4). The colour of tanzanite is attributed to V^{3+}, that substitutes Al^{3+}, but changes from V^{3+} to V^{4+}, when heat-treated (Hurlbut 1969). Although, Malisa and Koljonen (1986) proposed that the colour change occurs from honey yellow or khaki brown to sapphire blue when hydrated vanadium ion looses water on heating (e.g. $HV_2O_5^- \rightarrow VO^{2+}$). Most of the primary fluid inclusions have leaked and their present filling varies: gas alone or aqueous liquid and solids. Only the inclusions of negative crystal shape were studied in this work. At room temperature these primary inclusions were petrographically determined to be composed of liquid, two solid transparent phases, an opaque phase, and a gas bubble (Fig. 5). An opaque phase probably graphite, was observed in some of the inclusion cavities.

The two solid transparent phases are interpreted as true daughter minerals because their phase

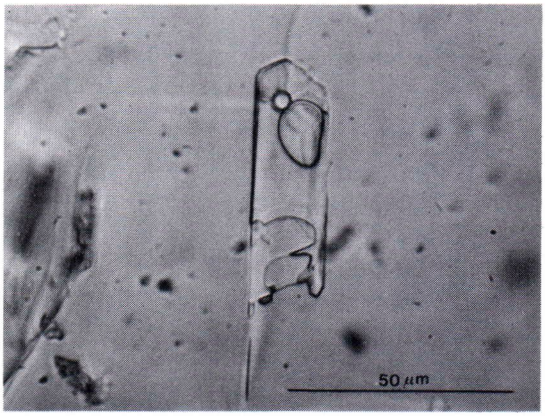

Fig. 5. Typical negative crystal shaped primary fluid inclusion cavity in tanzanite. Inclusion length 69 μm. Phase composition at room temperature: liquid, ovoidal gas bubble, small spherical unknown solid phase and several unknown daughter mineral crystals. The opaque mineral grain on the bubble is out of focus.

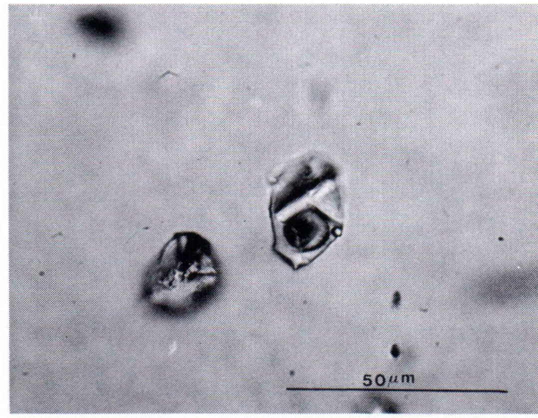

Fig. 7. Pseudo-secondary or secondary (?) fluid inclusions. Filling same as in Fig. 6.

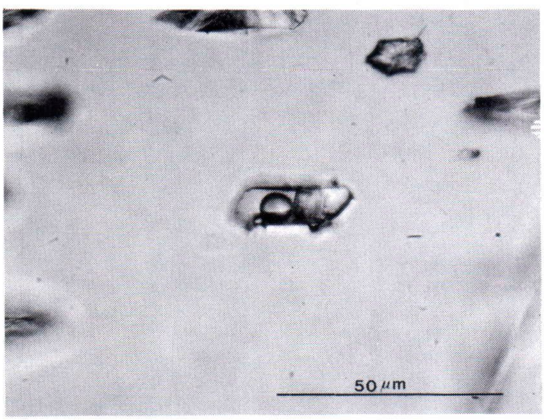

Fig. 6. Pseudo-secondary or primary (?) inclusions. Filling: (black) gas, liquid and solid phases, one of them is a carbonate mineral.

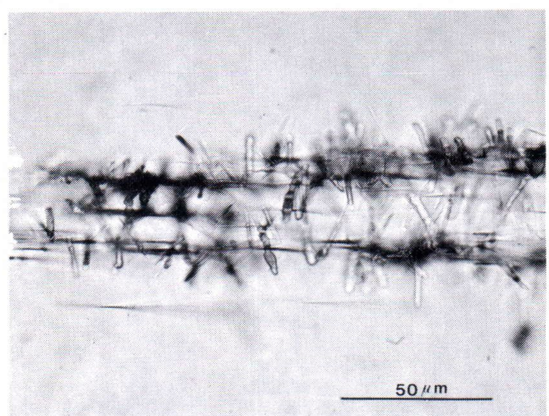

Fig. 8. Secondary fluid-filled fractures radiating from the tubes. These inclusions result from natural etching. They may have formed in the calcretization process.

volume proportion in different inclusion cavities is nearly the same (cf. Figs. 5, 6, 7 and 8). Inclusions homogenize to liquid at temperatures between 37° and 51°C (Fig. 9). These homogenization temperatures suggest chemical composition in the system CH_4-C_2H_{10}, perhaps even the presence of higher hydrocarbons such as C_3H_8 and/or C_4H_{10} (see Konnerup-Madsen *et al.* 1979, Fig. 7a).

Only one inclusion was measured to homogenize at 242°C to gas. This may be a leaked inclusion. At this temperature, the decrepitation of the larger inclusion cavities begins and continues up to 440°C. At 350°C, the daughter minerals begin to dissolve, but they did not completely dissolve even when heated for 12 hours at 440°C. Some of the primary inclusions in natural blue tanzanite are surrounded by liquid or gas-

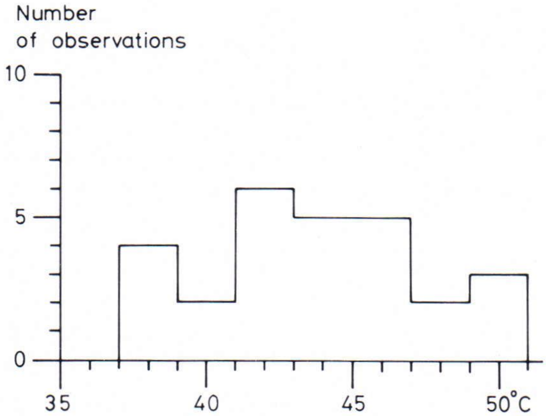

Fig. 9. Homogenization temperatures to liquid of primary fluid inclusions in tanzanites. Total of 27 measurements.

filled microcracks resembling natural decrepitation cracks. Since they seem to be absent from the tan-coloured tanzanites, it would appear that the blue tanzanite was originally tan coloured, but changed colour as the temperature rose in the cooled surrounding rocks after the crystallization (cf. Malisa et al., 1984). In some cases, rock temperatures presumably never caught up with fluid temperatures during a late reheating event and thus the tanzanite did not become blue throughout. Secondary fluid inclusions are situated in former fracture and cleavage planes of tanzanite. Their phase composition is usually similar to that of the primary inclusions.

Green vanadian grossular occur often in association with tanzanite in the hydrothermally altered zone. These garnets of gem-quality contain graphite flakes and secondary fluid inclusion cavities. These fluid inclusions contain a homogeneous liquid hydrocarbon (?) filling without a vapour bubble at room temperature but with two anisotropic daughter mineral phases. Most of these inclusions (primary and secondary) are naturally decrepitated with distinct decrepitation halos surrounding them causing a gas phase to be present even at room temperature. These decrepitated inclusions are petrographically similar to the fluid inclusions found in naturally blue tanzanite.

Fluid inclusion data imply that tanzanites crystallized in a hydrocarbon-rich fluid. Mineral inclusions within tanzanite were identified by microscopic and x-ray methods as calcite, gypsum, and graphite. In addition to these the following minerals were determined petrographically to form inclusions in tanzanite: rutile, sphene, xenotime, diopside, quartz and tremolite-actinolite as needles. Using X-ray diffraction, Dunn (1975) identified the black mineral inclusions observed in tanzanite by Eppler (1969) as graphite and suggested that the (0001) crystal face of the inclusions lies parallel to the (010) face of tanzanite. Gübelin and Weibel (1976) also verified the presence of tremolite-actinolite as inclusions in tanzanite.

A few crystals also have primary calcite inclusions at their base. Calcite, gypsum and possibly other carbonate inclusions usually occur in late fracture and cleavage planes and, occasionally, these planes exhibit secondary fluid inclusions with similar phase ratios.

Inclusions are of practical values to the gemmologist describing and identifying gem-quality materials, but in the case of tanzanite they provide additional gemmological information as well. Thermometrical data show that the hue of the blue colour obtained in heat-treatment of tanzanites depends on temperature. At 400°C the faintly tan blue colour closely resembles the colour of naturally blue tanzanite. At 800°C the colour becomes deep blue and at 1000°C violet blue. Decrepitation of the fluid inclusion cavities begins as low as 240°C. For this reason, one must pick crystals with few inclusions for heat-treatment. However, tan-coloured tanzanites with abundant needle-like inclusions could impart striking chatoyant effects, equal to those of chrysoberyl and quartz cat's eyes, to cabochon-cut tanzanites.

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