Gem-quality zoisite from Merelani (Northeastern Tanzania): review and new data

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Abstract

The Merelani area (NE Tanzania) is the unique locality in the world for tanzanite, a violetish blue gem-quality variety of vanadium-rich zoisite. However, other coloured (brown, yellow, orange, etc.) zoisite occurs in this deposit, closely associated with tanzanite. This study reports a review and new data on physical and chemical properties of this material, obtained investigating five gem-quality samples, ranging in colour from yellowish brown and greenish yellow to violetish blue, by means of classical gemmological methods and by XRD, EMP and LA-ICP-MS analyses. The results confirm that the major element concentration of all the samples is almost identical, so their different colour is mainly dependent on the variation of some minor and trace elements. In particular, the main chromophore element is V but also the V/Ti ratio plays a significant role in the colour characteristics. All the faceted gems have been subjected to heat treatment in order to observe a possible change of their colour. The various coloured zoisite gems become permanently blue and change their pleochroic scheme from trichroic to dichroic at ~ 500 °C, except for the blue specimen which is dichroic before and after heating and does not show any change of colour. The oddness of this sample could be due to an undeclared previous heat treatment, made to enhance the colour. All these characteristics observed in zoisite from Merelani derive from the geological history that makes it one of the most interesting and significant gem deposit of the world.

Key words: zoisite; tanzanite; crystal chemistry; heating treatment.

Introduction

Zoisite is the orthorhombic polymorph of a sorosilicate showing the ideal composition $Ca_2Al_3[(Si_2O_7][SiO_4]\cdot O(OH))$ and, together with the monoclinic form clinozoisite, was originally assigned to the epidote-group (Deer et al., 1986). More recently, according to the last report of the

"Subcommittee on Epidote-Group Mineral Nomenclature" established by the International Mineralogical Association (IMA), only clinozoisite was considered as a member of this group because it includes solely monoclinic minerals (Armbruster et al., 2006). However, the crystal structure of zoisite (space group *Pnma*) indeed resembles that of monoclinic epidote minerals, which are composed by endless octahedral chains parallel to the *b* axis and cross-linked by isolated SiO_4 tetrahedra and Si_2O_7 groups forming large irregular non-equivalent cavities (A1 and A2), normally occupied by Ca. Orthorhombic zoisite has only one type of octahedral chain with two non-equivalent octahedra (M1,2 and M3) whereas the monoclinic forms have two types of octahedral chains with three non-equivalent octahedra M1, M2, and M3 (Franz and Liebscher, 2004 and references therein).

Zoisite, discovered in the Saualpe Mountains of Carinthia (Austria) in 1805, was named after the Italian born nobleman Sigmund Zois, an eminent businessman financing many mineral-collecting expeditions. The mineral is formed in rocks subjected to low to medium grade metamorphism, often resulting from the deterioration of plagioclase. The most famous gem-variety of zoisite is "tanzanite", a gem name given to the violetish blue coloured vanadium-bearing zoisite. It was discovered in 1967 at the locality of Merelani (near the town of Arusha, northeastern Tanzania) and named after its country of origin by the famous New York jeweler, L.C. Tiffany. Prior to the discovery of tanzanite the only zoisite used as ornamental stone was the opaque pink Mn^{3+}-bearing variety from Norway called "thulite".

Nestled between the mountains of Meru and Kilimanjaro, in the center of the Great Rift Valley region, the Merelani mining deposit is the only commercial source of tanzanite in the world. Most of the gem-quality of this mineral occurs in fault zones within outcrops of gneisses and schists together with small quantities of transparent zoisite crystals of various colours (brown, yellow, green, pink, colourless) that, for marketing expediency, have been sometimes labelled brown tanzanite, yellow tanzanite, green tanzanite and so on. However, all the authors quoted in literature (e.g. Wilson et al., 2009 and reference therein) agree that the name "tanzanite" must be applied only to the blue violet variety of zoisite, disregarding if the colour is natural or it is the result of heating. The colour in most gem- quality samples of tanzanite available on the market is in fact produced by heat-treatment whose response varies on the basis of the different contents of vanadium, chromium, and titanium (Barot and Boehm, 1992). However, a small quantity of blue natural samples (around 10%, according to Smith, 2011) is still mined.

Many studies have been reported in literature on tanzanite and other coloured zoisite samples from Merelani since their discovery, but they mainly emphasize the economic interest (e.g. Dirlan et al., 1992) as well as the physical properties (Hurlbut, 1969; Faye and Nickel, 1971; Koziarska et al., 1994). A review on the state of the art about the Merelani tanzanite mines, even including the history as well as geological and mineralogical data, was recently published by Wilson et al., 2009. However, apart the dissertation presented for the degree of PhD at the University of Stellenbosch (South Africa) by B. Olivier (2006), the chemical data are still rather scarce and are mainly devoted to the discussion of the role played by some chromophore ions on colour variations. Therefore, the aim of the present paper is to combine the investigation on gemmological and other physical properties with a complete chemical characterization both on major and trace elements, including REE. For this purpose, we have investigated five gem-quality zoisite from the Merelani area, ranging in colour from yellowish brown, greenish yellow to violetish

blue. The samples have been characterised by traditional gemmological tests combined with EMPA-WDS and LA-ICP-MS measurements in order to determine their optical, physical and chemical properties.

Geology and Occurrence

The area of Merelani mineralization zone lies along the Lelatema fault system which is occupied by late Proterozoic metasedimentary rocks, mainly composed of graphitic gneisses, dolomitic marbles and schists. After the Pan-African tectonothermal event (about 600 Ma ago), hot hydrothermal solutions, rich in Ca, Mg, CO_2, SO_3 and other trace elements (V, U, Sr, Zn and heavy REE), injected into local faults and fissures reacted with the bedrocks giving origin to a mineral association containing tanzanite and other zoisites, green grossular ("tsavorite"), diopside, quartz, graphite and calcite (Malisa, 2003). Tanzanite mineralization occurred ca 585±28 Ma ago with P-T conditions estimated at ca 5-6 kbar and 650±50 °C (Olivier, 2006).

After the discovery of tanzanite and its marketing in the United States from 1968, private prospectors and local miners worked the Merelani Hills deposits until 1971. In this year, the tanzanite mines were nationalized, but production over the next 20 years was erratic, due to haphazard mining and theft. In 1990, the mining area, approximately 5 km long x 1 km wide, was divided into four government-controlled main sections, or blocks, designated A, B, C, D. The government awarded mining contracts for the blocks to different joint ventures but allowed also offers from individual people. Anyhow, although all production is supposed to be sold only to authorized dealers, it is very difficult a complete monitoring of trade. Tanzanite was firstly mined by the open pit method but now more than 90% of mining is underground. The Tanzanian government nets approximately US $20 million annually from the

mining of tanzanite and, at the current production rates and estimated resources, the tanzanite deposit has a life expectancy of around 20 years (Olivier, 2006; Zancanella, 2007; Wilson et al., 2009).

Materials and Methods

In the present work we have investigated five rough samples of zoisite from the Merelani area, ranging in colour from yellowish brown to greenish yellow up to violetish blue. From this material, we have obtained five faceted gems, weighting from 0.22 to 2.44 ct.

The faceted samples were examined in order to describe the optical properties (optic character, refractive indices, pleochroism), specific gravity and ultraviolet fluorescence. Refractive indices were measured with a Kruss refractometer using sodium light (589 nm) from a Leitz lamp, and methylene iodide saturated with sulphur and C2I4 as a contact liquid (R.I.=1.81), whereas pleochroism was determined using a Plus calcite dichroscope. A Mettler hydrostatic balance was used to determine the density of the stones, whereas the ultraviolet fluorescence was investigated with a short (254 nm) and long (366 nm) wavelength ultraviolet Wood lamp. The faceted gems were also heated up to 800 °C, using a Gossen Metrawatt GmbH oven operating in oxidizing atmosphere, in order to observe a possible change of colour. The experiments were divided into steps of 50 °C and the annealing time for every steps varied from 15 to 120 min with the increase of the temperature.

The unit cell parameters were measured on selected crystals obtained from the five rough samples. The intensities of the reflections were collected by a Philips PW-1100 automated four-circle diffractometer, using a graphite-monochromated MoKα X-radiation. The X-ray data were processed with the routine LAT program available in the PW1100 software. Full details on the data collection procedure are given

in Ungaretti et al. (1981).

Quantitative chemical analyses in wavelength-dispersion mode were performed on fragments of the rough samples, using a JEOL JXA-8200 electron microprobe (EMPA-WDS).The system was operated with an accelerating voltage of 15 kV, a beam current of 5 nA, a spot size of about 1 μm, and a counting time of 60 s on the peaks and 30 s on the backgrounds. A series of minerals were used as standards: olivine for Mg, wollastonite for Si and Ca, ilmenite for Ti, fayalite for Fe, anorthite for Al, rhodonite for Mn, celestine for Sr and pure V and Cr for these latter elements. The detection limit is 0.01 wt% for all the elements. The results were processed for matrix effects using a conventional ΦρZ routine in the JEOL series of programs.

Laser-ablation-inductively coupled plasma-mass spectroscopy measurements (LA-ICP-MS) were performed on the same mounts used for EMPA-WDS. The probe was constituted by an Elan DRC-e mass spectrometer coupled with a Q-switched Nd:YAG laser source (Quantel Brilliant), whose fundamental emission (1064 nm) is converted to 266 nm by two harmonic generators. The ablated material was analysed by an Elan DRC mass spectrometer, using helium as a carrier gas, mixed with an Ar downstream of the ablation cell. Calibration was performed using NIST SRM 610 glass as an external standard in combination with an internal standardization based on Ca, previously determined by EMPA-WDS. Data were collected using a spot size of 40 μm with a precision and accuracy both better than 10% for concentrations at the ppm scale.

Results

Physical properties

The physical properties of the zoisite samples here investigated are summarized in Table 1. The colour of the samples ranges from yellowish brown to greenish yellow up to violetish blue. The samples 1, 3, 4, and 5 responded to the heat treatment by turning violetish blue at approximately 450-550 °C (Figure 1). Instead, the specimen 2 showed no change in colour preserving the violetish blue colour.

The refractive indices and the birefringence of the examined faceted samples range over 1.687-1.702 and 0.008-0.013, respectively, whereas the density varies from 3.35 to 3.46 g/cm^3, in agreement with the range reported by Deer et al. (1986) for zoisite.

Both density and refractive indices do not show any change during heating but some variations can be observed in the pleochroic scheme. In particular, the untreated samples 1, 3, 4 and 5 are all trichroic but become dichroic after the heat treatment (Table 1). On the contrary, sample 2 is dichroic before and after the heat treatment.

The lattice constants of all the examined samples are in the range reported by Franz and Liebscher (2004) for orthorhombic epidote minerals (Table 1). The data are scattering and do not suggest any correlation between the cell parameters and Fe content as observed, for example, by Myer (1966) and Liebscher et al. (2002) both on natural and synthetic zoisite crystals.

Chemical composition

Major-element composition is reported in Table 2 as the average result of EMP analyses performed on grains selected on the basis of the absence of optical inclusions and microcracks. The content of H$_2$O was calculated assuming OH=1. All the crystals are essentially unzoned and the chemical composition does not vary significantly with the different colours and is very close to the idealized formula Ca$_2$Al$_3$[Si$_2$O$_7$][SiO$_4$]·O(OH) with an almost stoichiometric content of Si (Si=2.999-3.039 *apfu*) and Al (Al=2.961-3.026 *apfu*). On the contrary, the content of Ca is slightly lower than the stoichiometric value (Ca=1.909-1.955 *apfu*). From Table 2 it also appears that samples 2 and 5 have a content of Al lower than that of samples 1,

Table 1. Physical properties of zoisite samples from Merelani (Tanzania).

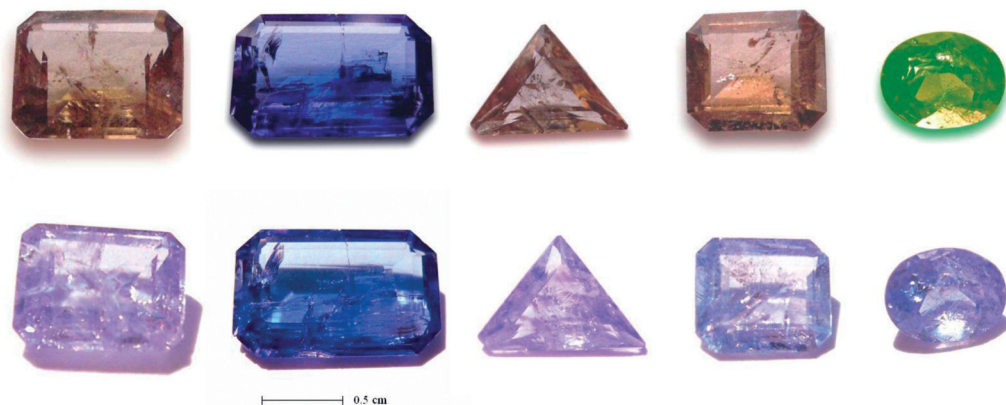| Sample		1	2	3	4	5
Colour	Before heating	Yellowish brown	Violetish blue	Yellowish brown	Yellowish brown	Greenish yellow
	After heating (450-550 °C)	Violetish blue	Violetish blue	Violetish blue	Violetish blue	Violetish blue
Diaphaneity		Transparent	Transparent	Transparent	Transparent	Transparent
Optic character		Biaxial positive	Biaxial positive	Biaxial positive	Biaxial positive	Biaxial positive
Refractive indices		n_x=1.690(2) n_y=1.692(2) n_z=1.698(2)	n_x=1.690(2) n_y=1.693(2) n_z=1.700(2)	n_x=1.687(2) n_y=1.690(2) n_z=1.700(2)	n_x=1.690(2) n_y=1.693(2) n_z=1.701(2)	n_x=1.692(2) n_y=1.695(2) n_z=1.702(2)
Birefringence		0.008	0.010	0.013	0.011	0.010
$2V_z$		30°	33°	29°	31°	33°
Pleochroism	Before heating	Trichroism: reddish violet (X), blue (Y), yellowish brown (Z)	Dichroism: reddish violet (X), blue (Y and Z)	Trichroism: reddish violet (X), blue (Y), yellowish brown (Z)	Trichroism: reddish violet (X), blue (Y), yellowish brown (Z)	Trichroism: reddish violet (X), greenish blue (Y), greenish yellow (Z)
	After heating (450-550 °C)	Dichroism: reddish violet (X), blue (Y and Z)	Dichroism: reddish violet (X), blue (Y and Z)	Dichroism: reddish violet (X), blue (Y and Z)	Dichroism: reddish violet (X), blue (Y and Z)	Dichroism: reddish violet (X), blue (Y and Z)
Density (g/cm³)		3.35(1)	3.40(1)	3.46(1)	3.46(1)	3.35(1)
Cell parameters		a(Å)=16.1899(4) b(Å)=5.5479(2) c(Å)=10.0308(4) V(Å³)=900.9(6)	a(Å)=16.1974(3) b(Å)=5.5474(1) c(Å)=10.0312(4) V(Å³)=901.3(3)	a(Å)=16.1936(7) b(Å)=5.5504(2) c(Å)=10.0395(4) V(Å³)=902.3(5)	a(Å)=16.1932(6) b(Å)=5.5502(1) c(Å)=10.0400(3) V(Å³)=902.3(4)	a(Å)=16.1910(4) b(Å)=5.5498(1) c(Å)=10.0398(2) V(Å³)=902.1(4)
UV fluorescence		Inert	Inert	Inert	Inert	Inert

Figure 1. Photograph of the faceted zoisite gems from Merelani, before (first line) and after (second line) heating. From left to right nos. 1, 2, 3, 4, 5 samples. See text for details.

3, 4. These results are related to the different content of some other minor and trace elements substituting for calcium and aluminium in the structural sites. In particular, the most significant is the probable substitution of Ca by Sr in the A-sites and that of Al by V^{3+} and Cr^{3+} in the octahedral sites (Hutton, 1971; Franz and Liebscher, 2004). In all the examined samples there is a negative correlation between Ca and Sr as well as between Al and (V+Cr) contents. Sample 2 contains the highest amount of calcium and the lowest amount of strontium. On the contrary, the minor amount of aluminium determined in this sample is coupled by a slight enrichment in vanadium and chromium. Some minor elements, including Sr and the possible chromophores for zoisite (Ti, V, Cr, Mn, Fe) were also analysed, together with REE and other trace elements, by means of laser ablation ICP-MS. The comparison between these analytical data and the results obtained by EMPA suggests a general agreement.

Table 3 presents the data, obtained by LA-ICP-MS technique and expressed in ppm, for Sc, Ti, V, Cr, Mn, Fe, Ga, Sr, Y, Zr, Ba, Th, U and REE. Li, Be, B, Na, K, Co, Ni, Cu, Zn, As, Rb, Nb, Mo, Ag, Cd, Sn, Sb, Cs, W, Tl, Pb, Bi were also

sought, but their abundances were found generally less than 1 ppm in all the samples. The intergrain variation is within typical LA-ICP-MS analytical precision for trace elements, as derived from measurement on BCR-2 standard (accuracy 2σ), for concentration at ppm level. Detection limits for each element can be found in Miller et al. (2012).

The data relative to the chromophore elements of the first transition series (Ti, V, Cr, Mn, Fe) are plotted in Figure 2, according to the increase of the atomic number. The obtained histogram emphasizes that vanadium is the main chromophore element in all the analysed samples (Figure 2), ranging from 1316 ppm (=0.19 wt% as V_2O_3) in the greenish yellow zoisite up to 2625 ppm (=0.39 wt% as V_2O_3) in blue one which also displays the highest content of Cr (224 ppm). Both these values are slightly higher than the average values (V=1872 ± 85 ppm; Cr=131±6 ppm) of 42 analyses of blue samples reported by Olivier (2006). Frei et al. (2004) obtained a value of 0.3 wt% of V_2O_3 in blue coloured zoisite (tanzanite), in good accordance with the data of Hurlbut (1969) and Smith et al. (1987). On the contrary, our blue sample is depleted in Ti (43 ppm) and Fe (8 ppm) in

Table 2. Major and minor elements composition of the five zoisites here investigated.

Sample	1		2		3		4		5	
Oxides (wt%)	average*	st. dev.	average*	st. dev.	average*	st. dev.	average*	st. dev.	average*	st. dev.
SiO_2	39.83	0.11	40.04	0.27	40.08	0.10	40.16	0.17	39.98	0.06
TiO_2	0.04	0.01	0.01	0.02	0.03	0.01	0.04	0.01	0.06	0.01
Al_2O_3	34.03	0.22	33.92	0.22	34.16	0.27	33.20	0.27	33.98	0.29
Cr_2O_3	0.04	0.02	0.07	0.00	0.03	0.01	0.05	0.02	0.03	0.02
FeO	0.01	0.01	0.00	0.00	0.01	0.00	0.02	0.02	0.01	0.01
MnO	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01
MgO	0.06	0.01	0.04	0.00	0.03	0.00	0.06	0.01	0.03	0.01
CaO	23.63	0.20	24.36	0.22	23.83	0.07	23.88	0.07	23.87	0.22
V_2O_3	0.21	0.02	0.39	0.11	0.24	0.03	0.20	0.03	0.20	0.03
SrO	0.20	0.03	0.13	0.02	0.16	0.01	0.21	0.04	0.27	0.02
H_2O**	1.99		2.00		2.00		1.98		1.99	
Total	100.06		100.97		100.57		99.81		100.44	

Stoichiometric formulae on the basis of 13 oxygens

Si *apfu*	3.004		2.999		3.007		3.039		3.007	
Ti	0.002		0.001		0.002		0.002		0.003	
Al	3.026		2.995		3.021		2.961		3.012	
Cr	0.002		0.004		0.002		0.003		0.002	
Fe	0.001		0.000		0.000		0.001		0.001	
Mn	0.001		0.001		0.000		0.000		0.001	
Mg	0.007		0.004		0.004		0.007		0.003	
Ca	1.909		1.955		1.916		1.936		1.923	
V	0.013		0.024		0.014		0.012		0.012	
Sr	0.009		0.006		0.007		0.009		0.012	
OH	1.000		1.000		1.000		1.000		1.000	

* Average data of five spot analyses; **H_2O calculated assuming OH=1.

comparison with the mean values quoted by Olivier (2006) for tanzanite (Ti=606±14 ppm; Fe=28±4 ppm). The greenish yellow zoisite (no. 5) has the highest content of Ti (267 ppm) and Fe (37 ppm) respect to all the other samples. The green coloured samples analysed by Olivier (2006) also show the highest content of titanium (Ti=707±39 ppm; average of 24 analyses) compared with other coloured samples (blue, orange, "golden") and with the colourless ones.

As regards to manganese, it is always low in our samples, ranging from 15 ppm in the sample 2 to 64 ppm in the yellowish brown sample 1. Olivier (2006) obtained from the microprobe analyses a particularly high content of Mn (up to 0.51 wt% as MnO) in the orange samples, inferring that this element can play as main chromophore. Also the blue samples investigated by Olivier (2006) may contain Mn (MnO=0.19 wt% as average of 55 specimens), although in
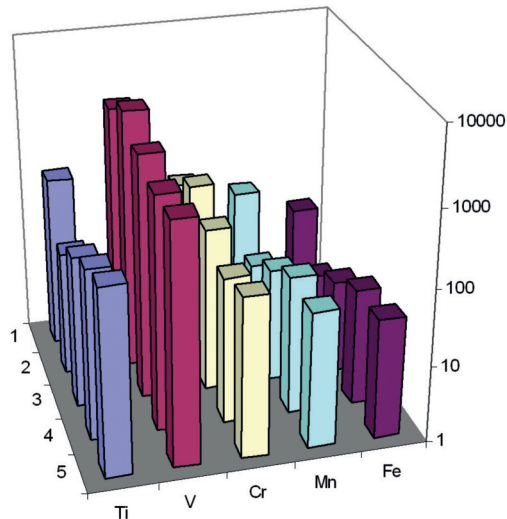
Figure 2. Histogram on a logarithmic scale showing the variation of selected elements (Ti, V, Cr, Mn, Fe) in the samples here examined.

almost half of the analysed samples MnO ranges from 0.08 wt% to a no detectable value (LA-ICP-MS). This result suggests that the contribution of Mn to colour is not significant, at least in blue coloured zoisites.

Among the elements of the first transition series it is also included scandium, which is not considered a chromophore: its abundance is almost constant in the three yellowish brown samples (18-20 ppm) but it decreases in the greenish yellow (11 ppm) and blue (4 ppm) samples. Gallium is not considered a chromophore element but, as already observed by Olivier (2006), there are some differences in its concentration within the different coloured samples. Our blue coloured zoisite (no. 2) has a Ga concentration of 140 ppm, very close to the result reported by the mentioned author as average concentration (139 ppm). The content of Ga varies from 127 up to 155 ppm in the yellowish brown samples, whereas decreases down to ~104 ppm in the greenish yellow. All these values are lower than those reported by

Olivier (2006) as average of orange (280 ppm) and "golden" (199 ppm) zoisite, whereas are closer to the average value of 134 ppm determined in green samples. Strontium is not a chromophore element so, despite its high quantity, it does not influence the colour of zoisite. However, Zancanella (2004) indicated a rough correlation of colour with the ratio V/Sr: according to this author the dark blue tanzanite contains 3800-4900 ppm of V and ~1000 ppm of Sr, while paler blue zoisite contains equal amounts of vanadium and strontium (~1300-2000 ppm). Yellow zoisite contains more strontium (~2000-3000 ppm) than vanadium (<1000 ppm). In the present case, we can observe that the high vanadium content (2625 ppm) of the examined blue samples is indeed coupled with an amount of strontium lower (1266 ppm) than that of the other samples (1451-2549 ppm), but it is impossible to find a true correlation between these elements and the colour. Blue sample (no. 2) also differs from the other ones examined for a lower content of

Table 3. Trace elements in the five zoisite samples from Merelani here investigated.

Sample	1	2	3	4	5
Element (ppm)*					
Sc	19	4	18	20	11
Ti	186	43	95	173	268
V	1374	2625	1571	1139	1316
Cr	103	224	140	81	118
Mn	64	15	31	63	60
Fe	29	8	17	34	37
Ga	127	140	118	155	104
Sr	1753	1266	1451	1913	2549
Y	76	96	66	52	88
Zr	13.5	1.3	6.6	11.8	13.5
Ba	13.1	0.6	21.1	7.8	22.7
La	46	87	15	51	65
Ce	106	172	38	101	142
Nd	64	68	26	51	81
Sm	17.7	12.4	8.6	12.6	20.7
Eu	4.5	3.3	2.9	4.0	5.0
Gd	16.1	9.2	8.8	11.4	19.2
Tb	2.7	1.8	1.7	1.9	3.1
Dy	15.2	13.2	10.9	10.3	17.5
Er	5.7	8.8	5.2	3.5	6.9
Yb	3.7	7.8	4.7	2.4	4.5
Lu	0.47	0.96	0.55	0.25	0.50
Th	12	0.9	4.4	7.8	9.1
U	32	5.3	16	22	16

* Average data of three spot analyses.

barium (0.6 ppm) that, like strontium, is accommodated into the A sites by a homovalent substitution for calcium (Frei et al., 2004). On the contrary, two tanzanite samples (Mir 1, 2) analysed by the last authors have a barium content (17.5 and 12.9 ppm, respectively) that is in the range of our 1, 3, 4, 5 gems (~ 8-23 ppm). The inspection of Table 3 shows that blue sample is also depleted in the content of Th and U (0.9

and 5.3, respectively) when compared with the other gems (Th=4-12; U=16-32 ppm) and with Mir 1 and 2 (Th=17.5 and 6.78, U=17.6 and 24.3 ppm, respectively). However, all the samples deviate from the 1:1 Th/U ratio, typical of most zoisite and epidote and display a general enrichment of U indicating an enhanced mobility of this element under highly oxidation conditions (Frei et al., 2004).

Rare earth elements (REE) are expected to enter the A-sites of zoisite as substituting for Ca. On the basis of the combination of structural and physical data with the elastic strain model, Frei et al. (2003) suggest that REE prefer the A1-site, with the only exception of La and Ce, which can be incorporated into the A2-site in significant amount. All the examined samples show comparable rare earth elements (REE) distribution patterns (Figure 3) with an enrichment of LREE relatively to middle (M-)REE (La_N/Sm_N=1.09-4.33) and to heavy (H-)REE (La_N/Yb_N=2.17-14.40) but the total REE content is higher in blue sample (ΣREE=384 ppm) than in the other ones (ΣREE=123-365 ppm). The inspection of Table 3 indicates that in all the examined samples a significant contribution to the total REE budget is given by La, Ce and Nd, in good agreement with the data reported by Olivier (2006). In the C1-normalized diagram of REE (Figure 3), the patterns of our samples are compared with those of tanzanite Mir 1, and 2 analysed by Frei et al. (2004). The REE fractionation in Mir 1 and 2 is more moderate (La_N/Sm_N=1.33 and 0.87, La_N/Yb_N=6.36 and 3.11, respectively) than in our blue sample (La_N/Sm_N=4.33; La_N/Yb_N=7.44) but they display a more pronounced negative Eu-anomaly (Eu_N/Eu_N*=0.59 and 0.72 vs Eu_N/Eu_N*=0.95) and a lower content of REE (ΣREE=295 and 217 vs 384 ppm). The REE distribution pattern also reports the C1-normalized value of Y that it is commonly included within this group owing to its similarity in the atomic radius as well as in chemical behaviour (Henderson, 1984). This assumption is confirmed also in the present case,
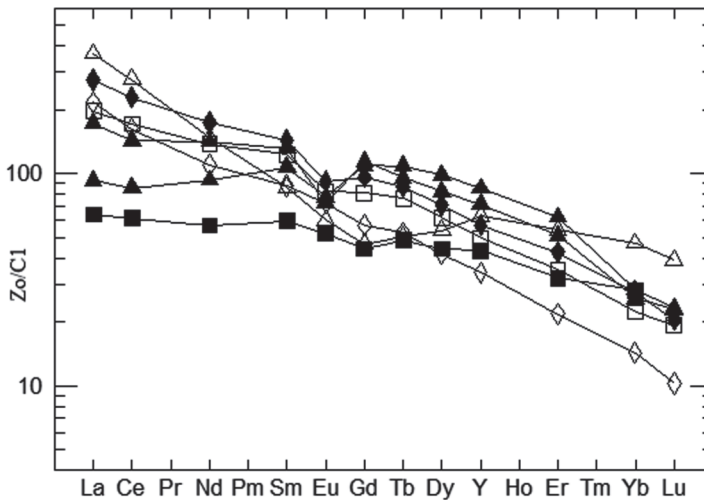
Figure 3. REE and Y patterns normalized to the C1 values of Anders and Grevesse (1989) for all the analysed samples. Symbols: open triangles: no. 2; open and full squares: nos. 1 and 3, respectively; open and full diamonds: nos. 4 and 5, respectively; full triangles: tanzanite Mir 1 and Mir 2 (Frei et al., 2004).

because Y matches well the REE fractionation pattern and has the higher contents in blue and greenish yellow samples (96 and 88 ppm, respectively) that also contain the higher concentration of REE.

Discussion

Many studies quoted in literature (e.g. Faye and Nickel, 1971; Schmetzer and Bank,1979; Zancanella, 2004) suggested that the colour change of the zoisite from Merelani through heat treatment occurs approximately at ~500 °C and is permanent. This implies the disappearance of a strong absorption band at ~450nm (~22,000 cm^{-1}) producing a transmission window in the blue part of the visible spectrum that accounts for much of the colour change (Faye and Nickel, 1971). Such a feature has been tentatively explained in terms of change of the oxidation state of transitions metal ions such as vanadium or titanium (Faye and Nickel, 1971; Hutton, 1971; Schmetzer and Bank, 1979; Olivier, 2006),

although the interpretation is still controversial. The colour change in coloured zoisite after heating also implies a change in the pleochroic scheme: they are trichroic but became dichroic, i.e., the Y and Z axis colours become more or less identical, after the heat treatment (Franz and Liebscher, 2004 and reference therein).

Both these features were observed in our samples 1, 3, 4, 5, that became blue and dichroic after heating, but not in the blue sample 2 that is already dichroic and, after the thermal annealing, does not show any change in the tonality of its colour and in the pleochroic scheme (Table 1; Figure 1). This result is quite unusual because untreated blue samples from Meralani are commonly described in literature as trichroic and suggests to consider the possibility that our blue sample could have been subjected to an undeclared heating treatment just after mining. This is in fact a very common procedure at Merelani, made with the commercial purposes to enhance the quality and the quantity of the mined

blue zoisite. However, rare natural blue coloured samples, showing dichroism before and after the heat-treatment, have been already described in literature (Hurlbut,1969; Faye and Nickel, 1971). The last authors suggested the possibility that they could have been subjected during the crystal growth to higher thermal conditions. Unfortunately we do not know where exactly the examined gems were collected and their "history" after mining. So it is not possible to establish any correlation between their physical and chemical properties and the various geological features, including the mined depth and the possible association with V-bearing grossular (tsavorite). However, we can notice that sample 2 is significantly different from the other ones in the content of all those elements that are unanimously considered chromophores i.e. Ti, V, Cr, Mn, Fe. In particular, it has a content of vanadium higher than that of all the other samples. The high content of this element, originating from the abundant organically derived graphite situated within the gneisses outcropping in this area, is in fact considered the most distinguishing chemical feature of zoisite samples from Merelani and is considered the dominant colouring agent. According to the data reported in literature, the natural blue colour of tanzanite is mainly due to the presence of trivalent vanadium (V^{3+}) substituting for Al^{3+} (Deer et al., 1986 and reference therein). In fact, studies on colour-zoned zoisite samples performed by Olivier (2006) show that there is a strong correlation between the colour and V content and that the higher content of this element was located on the blue/colourless contact. The author infers that, during zoisite crystallization or recrystallization, V migrated in a mobile state through the crystals, although subsequent changes in the oxidation conditions probably prohibited its complete movements through the minerals. According to the same author, the content of chromium throught coloured zoisite samples of Merelani mimics that of vanadium but at a lower concentration (<15

times). However, the presence of chromium does not seem to have a significant influence on the colour variation of zoisite. The unique exceptions are bluish green and green samples whose colours are due to a combination of $V^{3+}+Cr^{3+}$ or to Cr^{3+} only, respectively (Schmetzer and Bank, 1979; Barot and Boehm, 1992). The blue sample 2 distinguishes itself from the other ones for a higher content of chromium. It also differs in the titanium content that, together with vanadium, could indeed control the colour of zoisite. In fact, spectroscopic and EPR analyses (Olivier, 2006) emphasize the influence of the Ti^{4+}/Ti^{3+} ratio, as well as the Ti^{3+}-Ti^{4+} intervalence charge-transfer, on the colour of blue and green zoisite, respectively. The V/Ti ratio appears to be related to the colour characteristics: the content of V is almost 60 times higher than that of Ti in blue sample whereas it decreases from 16 to 5 times in the yellowish brown and greenish yellow samples. The blue samples has also the lowest concentration of manganese and iron but most authors do not consider relevant these cations with regard to the colour of zoisite from Merelani.

Olivier (2006) suggests that both Ce and Nd could act, at least within the orange zoisites, as chromophores. In certain minerals, Ce is in fact associated with a colourless to yellow colouration whereas Nd produces an orange to lilac colour. Our blue and greenish yellow samples (nos. 2 and 5, respectively) show Ce and Nd amounts higher than those of the other yellowish brown samples (Table 2). Recently, Wilson et al. (2009) reported that not only in zoisite, but also in other minerals (i.e. axinite, tremolite, diopside and grossular) from Merelani area, was found a distinctive content of neodymium (~20 ppm), which has not seen in these specimens from other countries. Although it is not possible to infer the contribution of Ce and Nd to the colour of zoisite, the behaviour, as well as the source, of these elements, could be worthy of further investigations.

Conclusion

The results obtained by the investigation on the physical and chemical properties of five different coloured gem-quality zoisite specimens from Merelani deposit can be summarized as follows: I) the major element concentration of all the samples is almost identical, so their different colour is mainly dependent on the variation of some minor and trace elements; II) the main chromophore element is V but also the V/Ti ratio plays a significant role with regard to the colour characteristics; III) the gems become permanently blue and change their pleochroic scheme from trichroic to dichroic at ~500°C, except for the blue one which is dichroic before and after heating and does not show any change of colour; IV) the distinctive behaviour of the last mentioned sample could be the consequence of an undeclared heat treatment made with the purpose to achieve a better colour or, alternatively, this odd sample could have been interested by different P/T conditions during the crystal growth; V) on the basis of their behaviour after heating, we can attribute to all the studied samples the gem name "tanzanite".

The data recorded during this study expand the knowledge about zoisite from Merelani but also highlight that further and more detailed investigations are still required to understand definitively why so many colours of this mineral come from such a small area and to give new insights on forming processes.

Acknowledgement

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