

# Vanadium-bearing gem-quality tourmalines from Madagascar

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**Abstract:** Gemmological, microscopic, chemical and spectroscopic properties of green, vanadium-bearing gem-quality tourmalines from southern Madagascar are presented. The samples are iron- and lithium-free and are designated as calcic aluminous dravites. They reveal a small compositional variability for sodium, calcium, magnesium and aluminium. Positive correlations between Na and Al and between Ca and Mg are present, always with Al > 6 atoms per formula unit and Mg < 3 atoms per formula unit.

Vanadium is the main transition metal present with smaller amounts of chromium and these cause the green coloration. Absorption bands in the UV-Vis range are assigned to V<sup>3+</sup> on octahedral aluminium sites.

Mineral inclusions in the tourmalines were characterized by laser Raman microspectroscopy and quantitative microprobe analyses. The commonest are bytownite plagioclases, but quartzes and zircons are also present as well as cavities and healed fractures containing liquid and two-phase fillings (liquid/gas). Non-homogeneous irregularly shaped grains consist of a mixture of hydrous aluminium silicates and iron hydroxides.

The tourmalines from Madagascar are compared with iron-free or almost iron-free gem-quality tourmalines, mainly from East Africa. Correlation diagrams of Na, Ca, Mg and Al show two different population fields, a) with Al > 6 and Mg < 3 atoms per formula unit (aluminous dravites) and b) with Al < 6 and Mg > 3 atoms per formula unit (uvites). The main isomorphic replacement within this solid solution series occurs between the tourmaline end-members oxy-dravite, Na(Mg<sub>2</sub>Al)Al<sub>6</sub>(BO<sub>3</sub>)<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>O, and uvite, CaMg<sub>3</sub>(MgAl<sub>3</sub>)(BO<sub>3</sub>)<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>, and is represented by the substitutional scheme  $Na^+ + 2Al^{3+} + O^{2-} \leftrightarrow Ca^{2+} + 2Mg^{2+} + (OH)^-$ .

**Keywords:** calcic aluminous dravite, electron microprobe analysis, isomorphic series, vanadian tourmaline, UV-visible absorption spectra



## Introduction

Recently, a parcel of rough crystals and crystal fragments of a green mineral (Figure 1) were purchased as garnets from a German dealer in a local gem market in Madagascar. The transparent material of gem quality was indicated to originate from a new locality in southern Madagascar close to the occurrence of green, vanadium-bearing grossular (tsavorite) in the Gogogogo – Bekily area (see Mercier *et al.*, 1997). According to their crystal shape, their pleochroism and their optical properties (measured on rough crystal faces), the crystals were quickly identified as tourmaline.

Numerous tourmaline occurrences are known in Madagascar and the island is famous for multi-coloured and colour-zoned tourmalines, mostly elbaite and liddicoatite (Pezzotta, 2001; Dirlam *et al.*, 2002). A more detailed examination of the parcel of our tourmalines indicated that they are vanadium-bearing dravites, and since vanadium-bearing dravites of gem quality are, according to the knowledge of

from East Africa (Kenya and Tanzania) have been known in the gem trade since the end of the 1970s, and this light to intense green gem material has frequently been misnamed 'chromium-tourmaline' in the trade (see Schmetzer *et al.*, 1979; Schmetzer and Bank, 1979; Keller, 1992; Simonet, 2006). Just recently, vanadium-bearing gem-quality uvites from Zambia with a special trapiche inclusion pattern have been described by Hainschwang *et al.* (2007).

## Materials and methods

From the original lot purchased in Madagascar containing several hundred tourmalines, about 30 rough crystal fragments were available for the present study. The larger part of the lot was faceted for commercial purposes and about 40 tourmalines were obtained from this part after cutting (Figure 2). Furthermore, a parcel of about 20 rough or sawn impure tourmaline fragments which had been rejected during the faceting process were available.

Standard gemmological methods were used to determine the refractive indices (RI), optical character, specific gravity (SG) and fluorescence under long- and short-wave ultraviolet radiation of 20 faceted stones. Standard microscopic techniques were used to examine the internal features under different lighting conditions for all rough, sawn and faceted samples, both with and without immersion liquids.

To determine the chemical composition of the tourmalines, we selected five samples for microprobe analysis using a Cameca Camebax SX 50 electron microprobe. For each tourmaline, we obtained 10 point analyses from traverses across the samples. To obtain qualitative data for water and lithium, two rough crystal fragments were powdered for wet chemical analysis. Lithium was determined by atomic absorption spectroscopy (AAS) and the water content was analysed by Karl-Fischer titration.

For the examination of boron contents (which, like lithium and water, cannot be determined routinely by electron microprobe)



**Figure 1:** Rough crystal fragments and faceted vanadium-bearing tourmalines from southern Madagascar. The crystal showing striations on a prism face (lower right) measures about 8 x 13 mm; the faceted triangular stone weighs 0.23 ct and measures 4.2 x 4.1 mm.

the present authors, not described in detail from Madagascar, the present study was undertaken to evaluate the properties of this new tourmaline material in detail.

Vanadian tourmalines (dravites and uvites)

and for trace element analysis we selected two faceted tourmalines for laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS) using a pulsed Excimer ArF laser with a characteristic wavelength of 193 nm and special optics to homogenize the energy distribution across the laser beam combined with the Perkin Elmer ELAN 6100 ICPMS quadrupole instrument. As indicated above, further trace element analyses, e.g. for lithium, were also performed by mass spectroscopy.



**Figure 2:** Faceted vanadium-bearing tourmalines from southern Madagascar. Weights of samples between 0.33 ct and 0.60 ct, the largest tourmaline (lower right) measures 4.4 x 6.5 mm.

Polarized UV-Vis-NIR (300-880 nm) absorption spectra were recorded for seven rough or faceted samples using a Perkin-Elmer Lambda 19 spectrophotometer. Unit cell dimensions were determined for one of the crystals analysed by electron microprobe using an automatic four-circle single crystal diffractometer and refined with powder data using  $\text{CuK}_{\alpha 1}$  radiation with Si as internal standard.

To identify the inclusions present in the tourmalines, we examined 15 faceted samples by laser Raman microspectroscopy using a Renishaw 1000 system. In addition, we selected 12 heavily included crystal fragments which had been rejected for faceting. From these 12 tourmalines polished thin sections of 20-25  $\mu\text{m}$  thickness were prepared to enable microscopic examination and quantitative microprobe analyses of mineral inclusions, and to carry out Raman microspectroscopy of selected

inclusions which had already been measured by electron microprobe.

## Results

### *Visual appearance and gemmological properties*

The tourmaline crystals available for the present study mostly were irregular fragments without any crystal faces. Only a few samples showed prism faces, occasionally with striations parallel to the *c*-axis (Figure 1). All rough and faceted samples were homogeneously green without any distinct colour zoning (Figures 1 and 2).

Gemmological properties are summarized in Table I. Only small variations of refractive indices and specific gravity were observed. The pleochroism of all samples is distinct with a yellowish green coloration parallel to the *c*-axis and a more intense, slightly bluish green perpendicular to *c*. In short-wave ultraviolet light a weak to medium greenish yellow, slightly chalky fluorescence is present, but all samples are inert in long-wave UV.

### *Chemical composition*

Chemical properties of five analysed samples are summarized in Table II. No compositional zoning of significance was detected within the single tourmaline crystals. All samples are sodium-, calcium- and magnesium-bearing aluminium tourmalines. Lithium is present only in trace amounts (average 0.004 wt.%  $\text{Li}_2\text{O}$ ), and iron and manganese contents were at the detection limit of the electron microprobe. Distinct amounts of vanadium and chromium are present, with vanadium content always exceeding that of chromium.

The five tourmaline crystals examined by electron microprobe showed variation in their sodium, calcium, magnesium and aluminium contents. The compositional variability between different elements and especially a correlation between specific cations is, however, elucidated in more detail after calculation of the numbers of atoms per formula unit (apfu) according to the generally accepted structural formula of tourmaline on

Table I: Physical and gemmological properties of V-bearing tourmalines from Madagascar.

Colour	Green
Pleochroism parallel <i>c</i> perpendicular <i>c</i>	Yellowish green Bluish green
Refractive indices $\omega$ $\epsilon$	1.638 – 1.640 1.618 – 1.620
Birefringence	0.020
Specific gravity	3.04 – 3.05
Unit cell dimensions <sup>1</sup> $a_0$ (Å) $c_0$ (Å)	15.9215 (1) 7.1867 (1)
Spectroscopic properties (nm) Absorption maxima    <i>c</i> Absorption maxima $\perp$ <i>c</i> Intensity relations	599, 441 610, 418, 370 (shoulder) 610 > 599 ; 441 > 418
UV fluorescence: short-wave long-wave	Weak to medium greenish yellow, slightly chalky Inert
Commonly-observed inclusions	Quartz, plagioclase (bytownite), zircon, solid multiphase inclusions consisting at least of hydrous aluminium silicates and iron hydroxides, cavities and healed fractures containing liquid and two-phase inclusions (liquid and gas)
Rarely-observed inclusions	Rutile, graphite, xenotime

<sup>1</sup> Refined powder data determined for sample D.

the basis of 31 anions (Table II).

According to the standard formula of magnesium-bearing aluminous tourmalines,  $(\text{Na,Ca},\square)(\text{Mg,Al})_3(\text{Mg,Al})_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{O,OH,F})_4$ , where the symbol  $\square$  represents a vacancy in the structure, we have to consider site occupancies of five cation-polyhedra, i.e. for Na,Ca, $\square$  = X-site, Mg,Al = Y-site, Mg,Al = Z-site, B, and Si (see Tourmaline structure box). Various natural tourmalines with magnesium-aluminium disorder have been described, for which both cations, Al and Mg, are distributed within the two relevant octahedral Y- and Z-sites (Hawthorne *et al.*, 1993; Pieczka, 1999; Bloodaxe *et al.*, 1999; Da Fonseca-Zang *et al.*, 2001; Ertl *et al.*, 2003; Pertlik *et al.*, 2003; Marschall *et al.*, 2004; Novak *et al.*, 2004). This is more or less common and not an exceptional case (Grice and Ercit, 1993). For an exact determination of order/disorder and site occupancies of Mg and Al of our tourmaline crystals, which cannot be derived from analytical data, a crystal structure refinement

would be necessary, but this is beyond the scope of the present paper. Thus, for simplicity of discussion of site populations in our samples, in which the amount of aluminium always exceeds 6 atoms per formula unit ( $\text{Al} > 6$  apfu), we only consider the sums of magnesium and aluminium (Al + Mg) on the octahedrally coordinated Y- and Z-sites.

For all our samples, the sum of aluminium in Y- and Z-sites is  $>6$  and the sum of magnesium in Y- and Z-sites is  $<3$ , with  $\text{Al} + \text{Mg} \approx 9$ , i.e. close to the theoretical value. The silicon tetrahedron is occupied mostly with Si but also a small almost constant substitution of about 0.1 atoms Al for Si is present. This feature has already been reported from vanadium-bearing gem-quality tourmalines from East Africa (MacDonald and Hawthorne, 1995), and is also common for iron-bearing members of the schorl-dravite series (Grice and Ercit, 1993). The boron content is almost equal to the theoretical value of 3, which indicates that no tetrahedral boron on Si-sites is present.

**Table II:** Chemical composition of V-bearing tourmalines from Madagascar.

Microprobe analyses (average of 10 point analyses each, wt.%)

Specimen	A	B	C	D	E
SiO <sub>2</sub>	36.64	36.36	36.41	36.21	36.11
TiO <sub>2</sub>	0.49	0.53	0.58	0.58	0.60
B <sub>2</sub> O <sub>3</sub> <sup>1</sup>	10.67	10.67	10.67	10.67	10.67
Al <sub>2</sub> O <sub>3</sub>	34.18	33.55	33.48	33.23	33.09
V <sub>2</sub> O <sub>3</sub>	0.17	0.19	0.19	0.19	0.20
Cr <sub>2</sub> O <sub>3</sub>	0.04	0.11	0.07	0.03	0.06
FeO <sup>2</sup>	0.01	0.02	0.01	0.02	0.01
MnO	0.01	0.02	0.01	0.01	0.02
MgO	10.63	10.75	10.96	10.99	10.96
CaO	1.58	1.75	1.93	2.36	2.43
Na <sub>2</sub> O	1.56	1.49	1.48	1.37	1.36
K <sub>2</sub> O	0.05	0.06	0.06	0.05	0.05
Li <sub>2</sub> O <sup>3</sup>	0.00	0.00	0.00	0.00	0.00
F	0.48	0.50	0.51	0.40	0.38
H <sub>2</sub> O <sup>4</sup>	3.00	3.00	3.00	3.00	3.00
-O=F	-0.20	-0.21	-0.21	-0.17	-0.16
Total	99.31	98.79	99.15	98.94	98.78

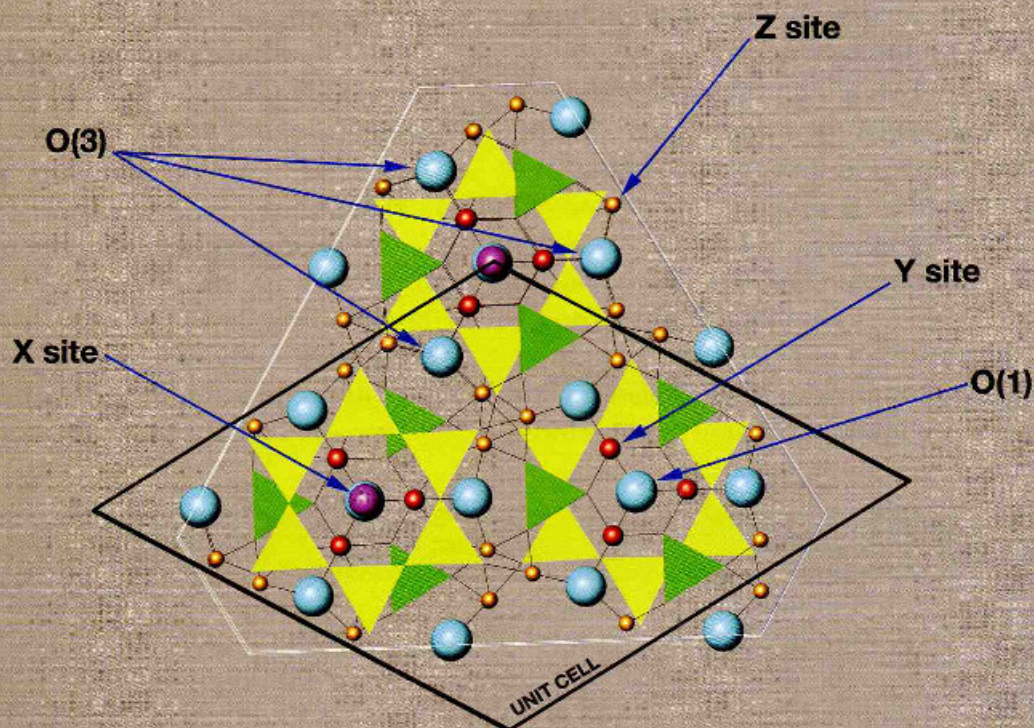
<sup>1</sup>Average analyses of two samples by LA-ICP-MS. <sup>2</sup>Total iron as FeO.<sup>3</sup>Average analyses of two samples by wet chemical methods, LA-ICP-MS gave 0.004 Li<sub>2</sub>O. <sup>4</sup>Average analyses of two samples by wet chemical methods.

Number of ions based on 31 (O, OH, F)

Specimen	A	B	C	D	E
Si	5.910	5.901	5.893	5.881	5.877
Al	0.090	0.099	0.107	0.119	0.123
Sum T site	6.000	6.000	6.000	6.000	6.000
B	2.970	2.988	2.980	2.990	2.997
Al	5.914	5.896	5.896	5.901	5.892
Ti	0.059	0.065	0.071	0.071	0.074
V	0.022	0.024	0.025	0.024	0.026
Cr	0.005	0.015	0.008	0.004	0.008
Sum Z site	6.000	6.000	6.000	6.000	6.000
Mg	2.557	2.600	2.645	2.661	2.658
Fe	0.002	0.003	0.002	0.002	0.001
Mn	0.002	0.003	0.003	0.002	0.003
Li	0.003	0.003	0.003	0.003	0.003
Al	0.493	0.421	0.384	0.340	0.333
Sum Y site	3.057	3.030	3.037	3.008	2.998
Na	0.487	0.468	0.465	0.433	0.429
K	0.010	0.012	0.012	0.010	0.011
Ca	0.273	0.305	0.335	0.411	0.424
Sum X site	0.770	0.785	0.812	0.854	0.864
OH	3.228	3.247	3.239	3.250	3.258
F	0.246	0.257	0.261	0.207	0.194

Approximate formula: (Na<sub>0.4</sub>Ca<sub>0.4</sub>□<sub>0.2</sub>)(Mg<sub>2.6</sub>Al<sub>0.4</sub>)Al<sub>6</sub>(BO<sub>3</sub>)<sub>3</sub>(Si<sub>5.4</sub>Al<sub>0.1</sub>)O<sub>18</sub>(OH<sub>3.228</sub>F<sub>0.25</sub>O<sub>0.5</sub>)

## Tourmaline structure



*Tourmaline structure projected parallel to the (0001) plane; yellow: (SiO<sub>4</sub>)-tetrahedra, green: planar (BO<sub>3</sub>)-groups, purple: X-sites, red: Y-sites, orange: Z-sites, blue: V- and W-sites (representing O(3)- and O(1)-sites). From Simmons (2002), reproduced by permission of Litographie, LLC, East Hampton, CT, USA.*

To understand the different schemes of isomorphic replacement within the oxydravite, dravite and uvite solid solution series discussed in this paper, it is helpful to consider the tourmaline structure in detail. A general summary is given in various textbooks and monographs (see, e.g., Dietrich, 1985; Deer *et al.*, 1986; Klein, 2002; Simmons, 2002).

The tourmaline structure (see above) consists of (Si<sub>6</sub>O<sub>18</sub>)-rings of six edge-sharing (SiO<sub>4</sub>)-tetrahedra, which are linked to planar (BO<sub>3</sub>)-groups. These structural elements of silicon- and boron-polyhedra are linked to each other by different cations on X-, Y- and Z-sites of the tourmaline structure.

The X-site is coordinated by nine anions and the Y- and Z-sites are octahedrally coordinated. The Y-octahedron is somewhat

larger than the Z-octahedron. In the present case, the X-site contains Na, Ca or vacancies, and the Y- and Z-sites are occupied by Mg and Al.

The formula unit of tourmaline contains 31 anions which are located at eight different lattice sites at the corners of the different coordination polyhedra of the tourmaline framework. Six of these eight different lattice sites contain only oxygen, and only two of these eight sites, designated O(1) and O(3), can also contain hydroxyl-groups and fluorine, (OH) and F.

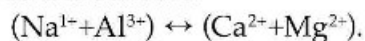
The O(3)-sites, which are also designated as V-sites, can only contain oxygen and hydroxyl-groups, and the O(1)-sites, which are also designated W-sites, can contain oxygen, hydroxyl-groups and fluorine.

This is typical for members of the schorl-dravite series (see, e.g., Grice and Ercit, 1993; Bloodaxe *et al.*, 1999). At the X-site, the sums of Na and Ca are consistently below the ideal maximum value of 1, which means that vacancies are present at this site.

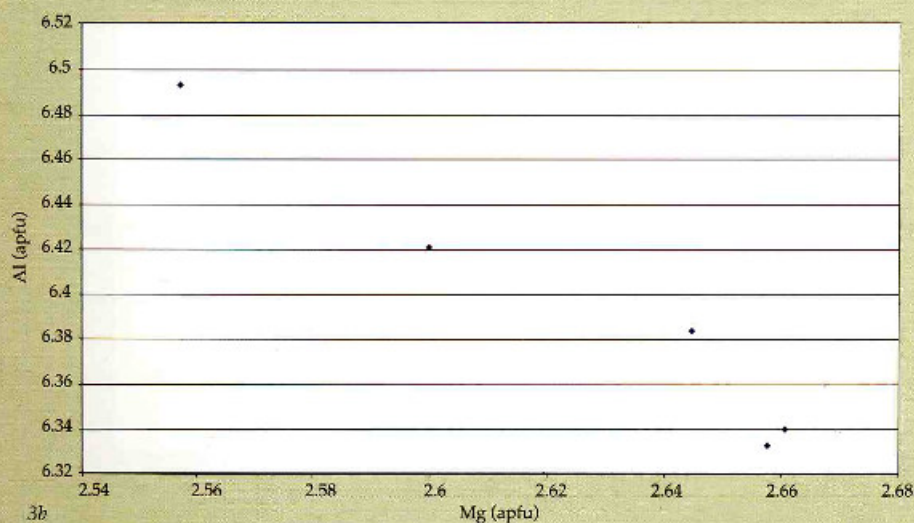
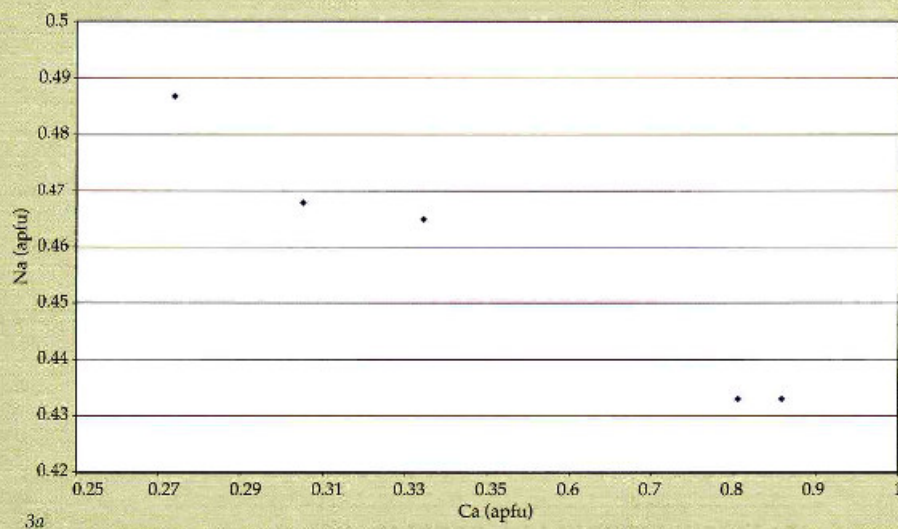
As already mentioned, the main compositional variables in the five tourmalines are Na, Ca, Mg and Al.

For the X-site a negative correlation is found between the site occupancies of sodium and calcium (Figure 3a), and for the (Y+Z)-sites, a negative correlation is found between the site occupancies of magnesium and aluminium (Figure 3b). Comparing the site populations of cations between X

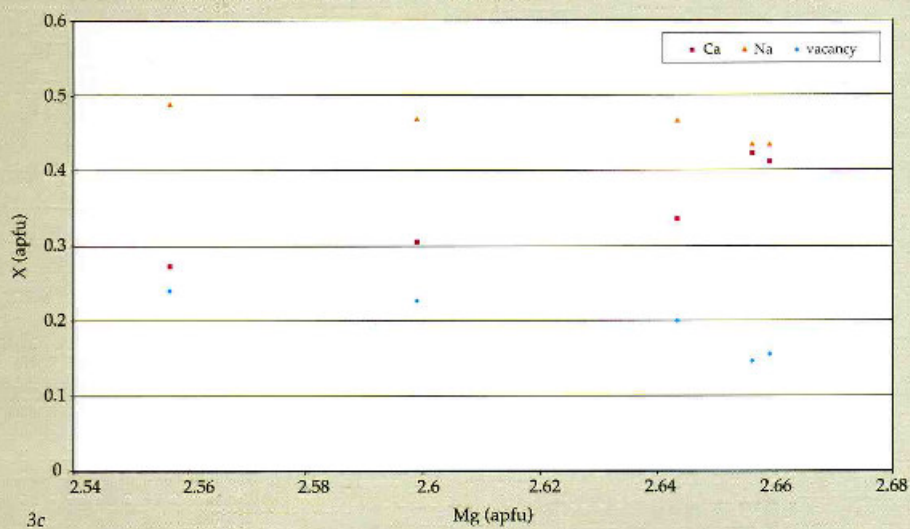
and (Y+Z) polyhedra, positive correlations are observed between magnesium and calcium and between aluminium and sodium (Figures 3c,d), and there are negative correlations between magnesium and sodium and between aluminium and calcium. Vacancies on the X-site show a positive correlation with Al-contents and a negative correlation with Mg-contents (Figures 3d and c). These data indicate a coupled isomorphic replacement of four cations on X- and (Y+Z)-sites (Figure 3e) according to the scheme



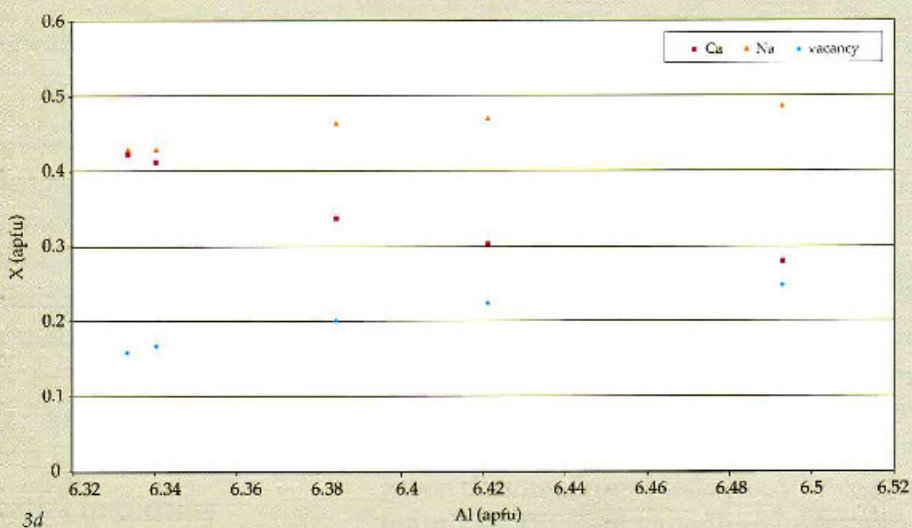
This heterovalent substitution scheme is similar to the known isomorphic replacement



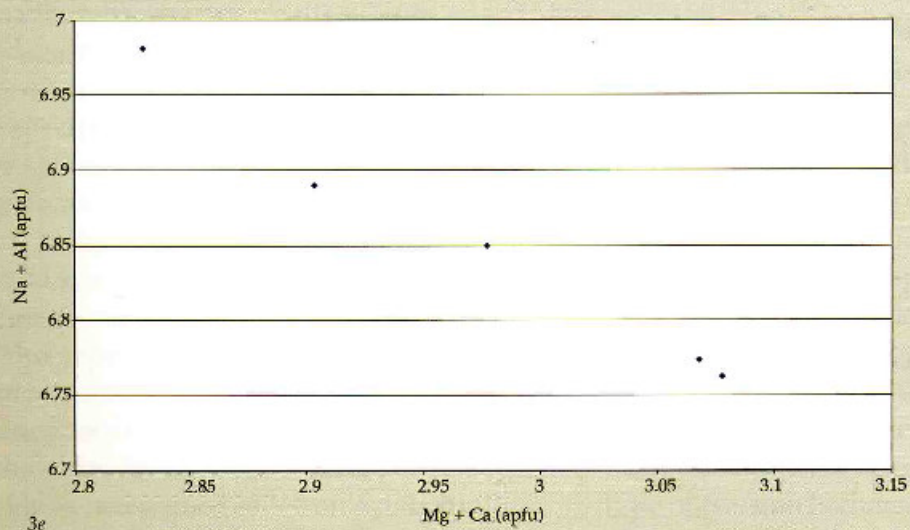
**Figure 3:** Correlation diagrams of site populations of various major components in X-, Y- and Z-sites of vanadium-bearing tourmalines from southern Madagascar.



3c

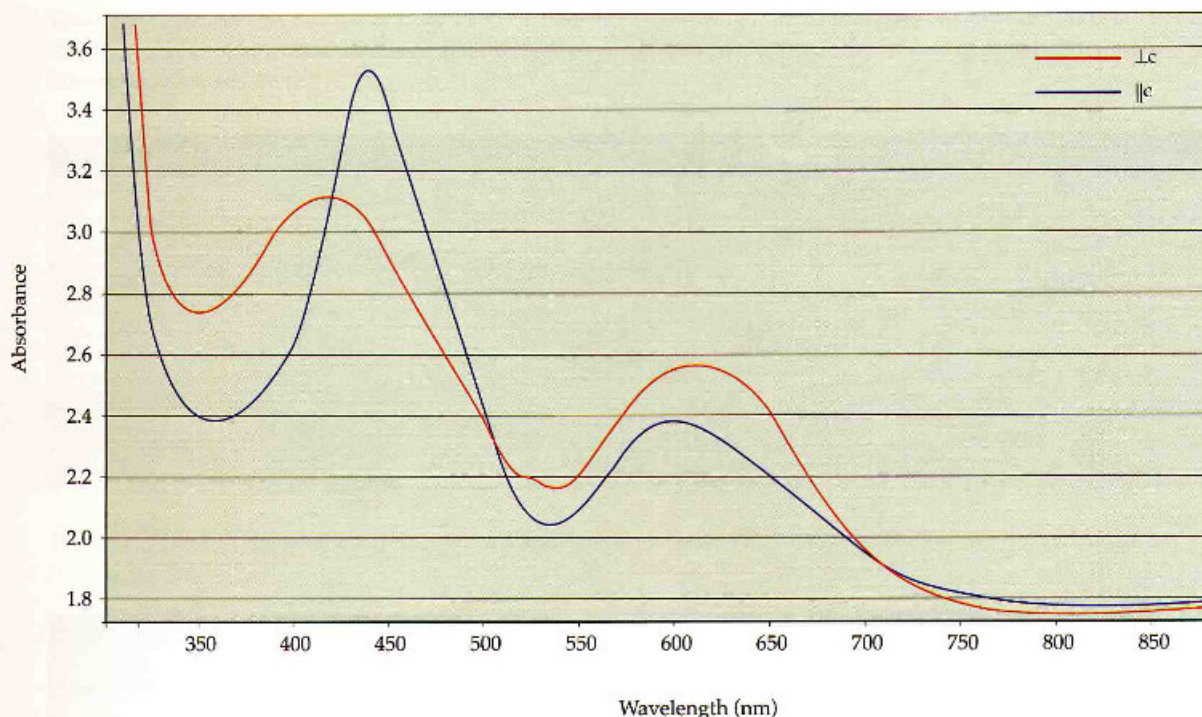


3d



3e

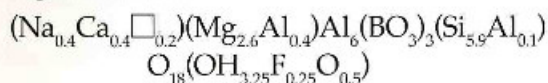




**Figure 4:** Polarized UV-visible absorption spectrum of a vanadium-bearing, iron-free tourmaline from southern Madagascar.

within the dravite – uvite solid solution series (for further details see Discussion and Table V).

An approximate, somewhat simplified formula (where traces of transition metals are omitted) for an average composition for the five analysed tourmaline crystals from Madagascar reads:



### **Spectroscopic properties and cause of colour**

The absorption spectrum of the green vanadium-bearing tourmalines from Madagascar consists of two strong absorption bands with maxima at 599 and 441 nm in the spectrum parallel to *c* and maxima at 610 and 418 nm in the spectrum perpendicular to *c* (Figure 4). In some samples in addition to these major absorption bands, an additional shoulder is seen at 370 nm in the spectrum perpendicular to *c* (not shown in Figure 4).

This type of spectrum is consistent with the data reported in the literature for vanadium-bearing tourmaline from East Africa (Schmetzer, 1978, 1982); the stronger absorption bands were assigned to  $\text{V}^{3+}$  on octahedrally coordinated aluminium-sites (Z-sites) of the

tourmaline structure.

The absorption bands of chromium in dravite occur at 588 and 417 nm, which are in the same spectral range as those of vanadium (Manning, 1969; Schmetzer, 1978; Nuber and Schmetzer, 1979; Halvorsen and Jensen, 1997; Simonet, 2000) and, thus, the two superimposed absorptions cannot be separated. Consequently, the colour of the green dravites from Madagascar is caused mainly by trivalent vanadium on aluminium sites, with some enhancement from the traces of chromium.

### **Features seen with the microscope, identification of inclusions**

The tourmaline samples from Madagascar contain numerous, mostly irregularly shaped solid inclusions (Figure 5) as well as cavities with liquid and two-phase inclusions (liquid/gas). These two-phase inclusions were homogenized under microscopic illumination, i.e. the gas bubble disappeared after a slight increase of temperature. On cooling to room temperature, the gas bubbles reappeared and the inclusions were again two-phase. This type of reaction is characteristic for two-phase inclusions consisting of liquid and gaseous  $\text{CO}_2$ .

**Table III:** Chemical composition of plagioclase inclusions in V-bearing tourmalines from Madagascar (data of samples A and C represent bytownite grains with high and low albite/anorthite contents, respectively; data of sample B represent a grain of intermediate composition).

Microprobe analyses (wt.%)			Number of ions based on 8 O				
Inclusion	A	B	C	Inclusion	A	B	C
Na <sub>2</sub> O	3.17	2.72	2.04	Na	0.283	0.242	0.183
K <sub>2</sub> O	0.13	0.11	0.06	K	0.008	0.006	0.004
CaO	14.48	15.35	16.80	Ca	0.715	0.757	0.830
Al <sub>2</sub> O <sub>3</sub>	30.99	32.13	32.95	Al	1.683	1.743	1.790
SiO <sub>2</sub>	49.98	48.92	47.59	Si	2.303	2.251	2.195
Total	98.75	99.23	99.44	Total	4.992	4.999	5.002

**Table IV:** Chemical composition of fine-grained multiphase inclusions in V-bearing tourmalines from Madagascar (ranges, wt.%).

	Hydrous aluminium silicates	Hydrous iron aluminium silicates <sup>3</sup>	Iron hydroxides
No. of analyses	4	5	5
SiO <sub>2</sub>	46.34 – 60.03	43.96 – 63.73	1.38 – 2.81
TiO <sub>2</sub>	0.01 – 0.07	0.02 – 0.04	0.09 – 0.19
Al <sub>2</sub> O <sub>3</sub>	26.21 – 35.95	9.21 – 23.06	2.67 – 3.20
Fe <sub>2</sub> O <sub>3</sub> <sup>1</sup>			76.39 – 77.21
FeO <sup>2</sup>	0.54 – 2.18	7.24 – 16.32	
MnO	0.01 – 0.11	0.01 – 0.16	0.02 – 0.10
MgO	0.29 – 0.72	1.35 – 3.58	0.30 – 0.37
CaO	0.09 – 0.40	0.28 – 0.78	0.33 – 0.47
Na <sub>2</sub> O	0.09 – 0.41	0.16 – 0.29	0.10 – 0.15
K <sub>2</sub> O	0.08 – 0.32	0.87 – 1.75	0.03 – 0.05

<sup>1</sup>Total iron as Fe<sub>2</sub>O<sub>3</sub>, <sup>2</sup>Total iron as FeO.

<sup>3</sup>Possibly a mixture of hydrous aluminium silicates and iron hydroxides.

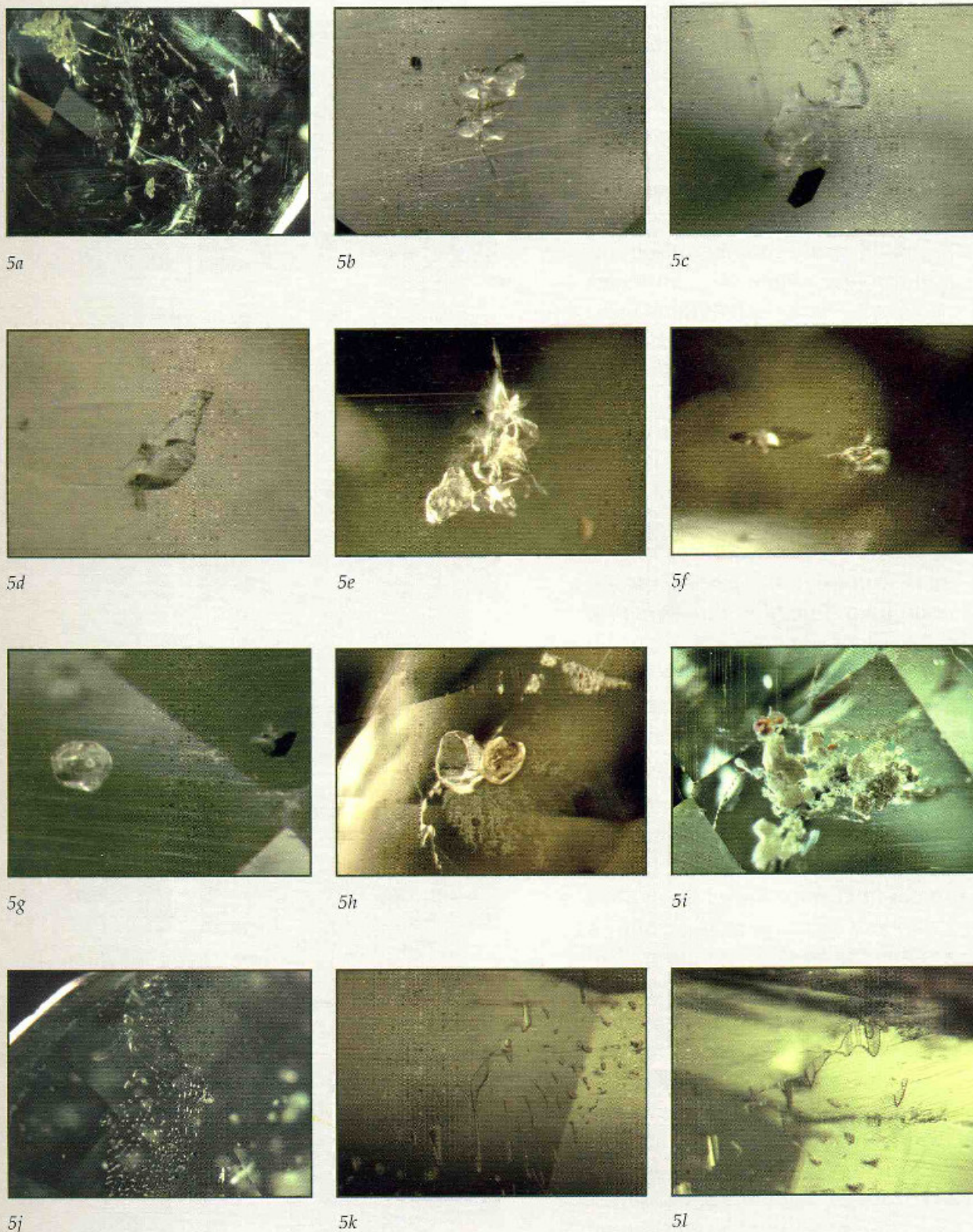
For the identification of solid inclusions, Raman microspectroscopy of inclusions in faceted gems was combined with optical microscopy of polished thin sections and electron microprobe analyses of solids localized in these thin sections. In addition to optical microscopy in reflected and transmitted light, numerous back-scattered electron (BSE) images were obtained using the electron microprobe to evaluate homogeneity within included solids. This technique is very sensitive to compositional variations between the tourmaline host and its inclusions, and especially to compositional variations within non-homogeneous mineral grains. In addition,

mineral grains in thin sections analysed by electron microprobe were also submitted to Raman microspectroscopy.

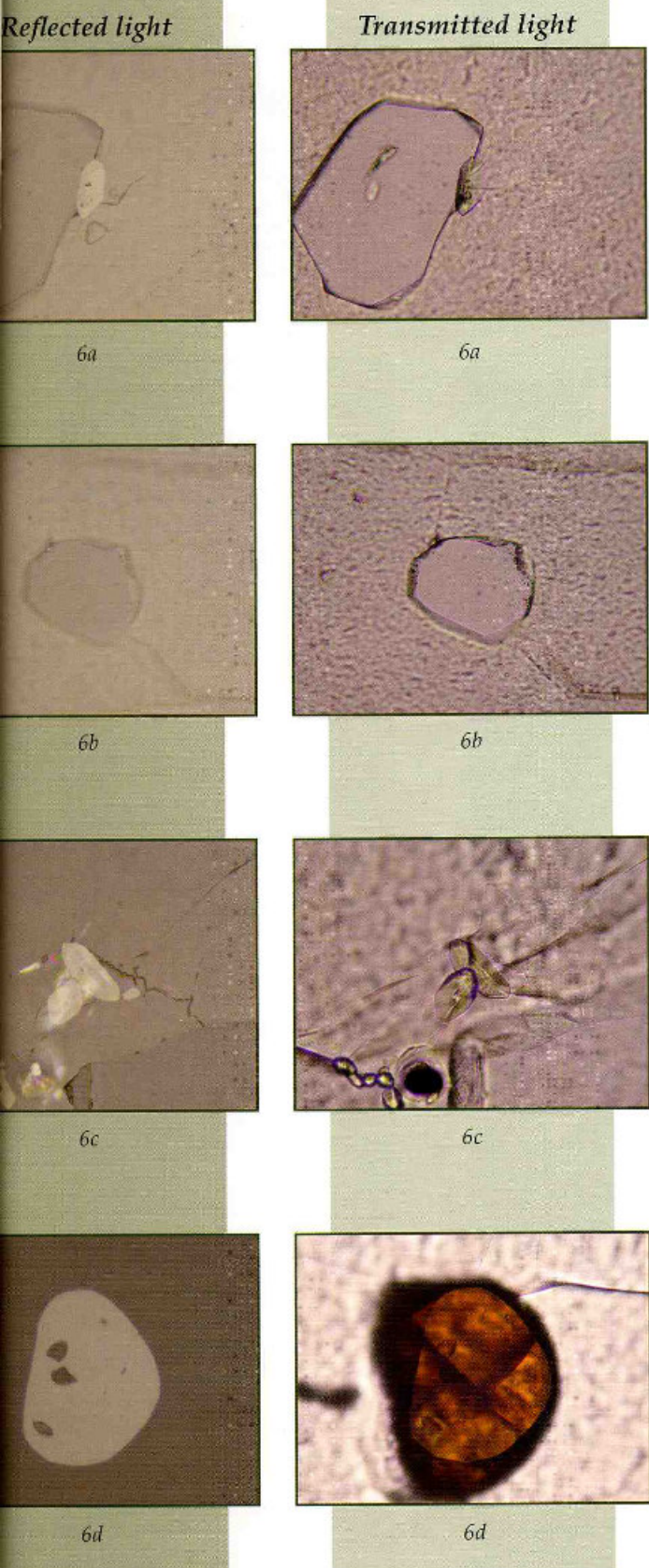
As a result, we were able to identify several minerals present as crystals with specific external forms or as single irregularly shaped mineral grains. In addition, non-homogenous inclusions consisting of several mineral phases within a single grain were also recorded.

*a. Single mineral phases (Figures 5-8).*

Irregularly shaped plagioclase grains and euhedral quartz crystals are common inclusions. Numerous zircon crystals were also observed, frequently in close contact



**Figure 5:** Inclusion patterns of vanadium-bearing tourmalines from Madagascar as seen with the gemmological microscope: (a) general overview with aggregate of irregularly shaped, non-homogeneous grains consisting of hydrous aluminium silicates and iron hydroxides (upper left), cavities with liquid and two-phase (liquid and gas) filling, 80 $\times$ ; (b) aggregate of irregularly shaped plagioclases, 40 $\times$ ; (c) aggregate of irregularly shaped plagioclases and black graphite platelet, 80 $\times$ ; (d) irregularly shaped plagioclase, 80 $\times$ ; (e) aggregate with quartzes, plagioclase and zircons with tension cracks, 60 $\times$ ; (f) euhedral zircon crystals with tension cracks, 80 $\times$ ; (g) euhedral quartz crystal (left) and black graphite (right), 80 $\times$ ; (h) quartz and xenotime (right), 80 $\times$ ; (i) aggregate of irregularly shaped, non-homogeneous grains consisting of hydrous aluminium silicates and iron hydroxides, 80 $\times$ ; (j) cavities with liquid and two-phase (liquid and gas) filling, 60 $\times$ ; (k) cavities with liquid and two-phase (liquid and gas) filling, 80 $\times$ ; (l) cavities with liquid and two-phase (liquid and gas) filling, 80 $\times$ .



**Figure 6:** Mineral inclusions in vanadium-bearing tourmalines from Madagascar as observed in polished thin sections in reflected (left column) and transmitted light (right column): (a) plagioclase and zircon, width of photo 0.35 mm; (b) quartz, width of photo 0.15 mm; (c) zircons, width of photo 0.15 mm; (d) rutile, width of photo 0.15 mm.

with plagioclase or quartz grains. Less common are black graphite platelets, rutile and xenotime.

Quantitative analyses of 22 plagioclase grains in seven tourmaline host crystals were obtained and some representative analyses are given in *Table III*. All plagioclases represent a continuous compositional range from albite<sub>28.4%</sub> anorthite<sub>71.6%</sub> to albite<sub>18.1%</sub> anorthite<sub>81.9%</sub>, i.e. all analysed plagioclase grains are in the compositional range of bytownite.

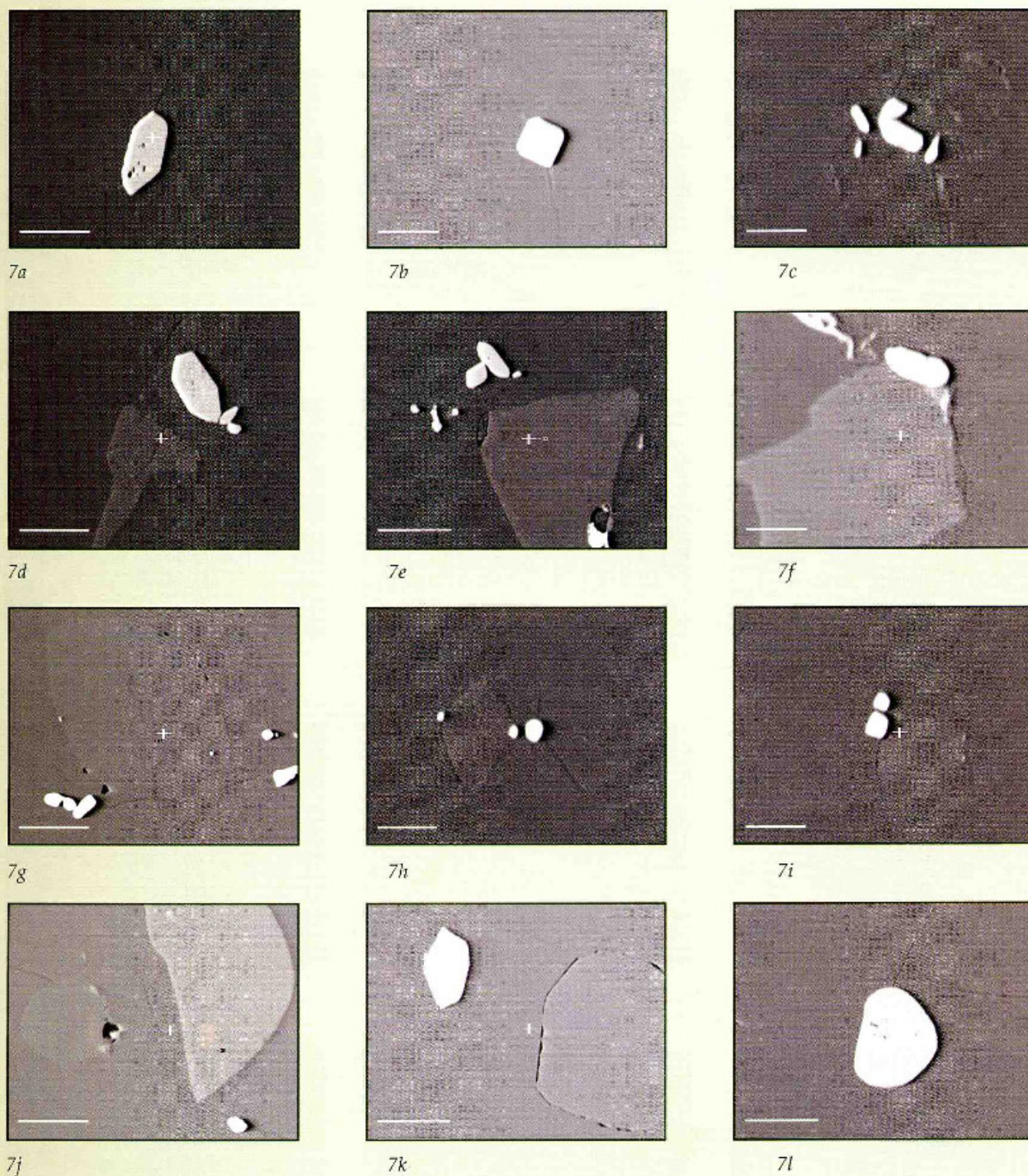
- b. *Non-homogeneous inclusions* (Figures 5 and 9). Fine-grained admixtures of several minerals are present in off-white to pale yellow, irregularly shaped grains in many tourmalines. In thin sections, they are visible as intensely intergrown colourless to off-white and reddish-brown phases (Figure 9), but were too small to identify unambiguously.

Quantitative microprobe analyses of several small to extremely small particles (*Table IV*) indicated that they are:

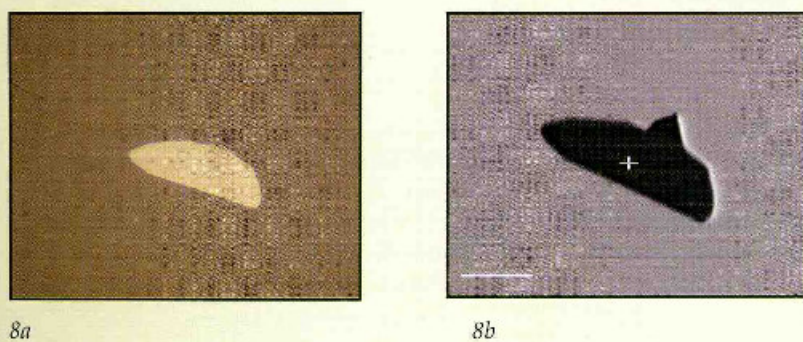
- hydrous Al-silicates, most probably clay minerals such as kaolinite (off-white to colourless component) and
- Fe-hydroxides with smaller amounts of Al and Si, most probably limonitic iron hydroxides (reddish-brown component)

Several grains or phases contain iron, aluminium, and silicon as major components, with smaller amounts of magnesium and potassium (*Table IV*). However, we were unable, even by a combination of quantitative electron microprobe analyses and Raman spectroscopy of the same grains to clarify if these inclusions represent

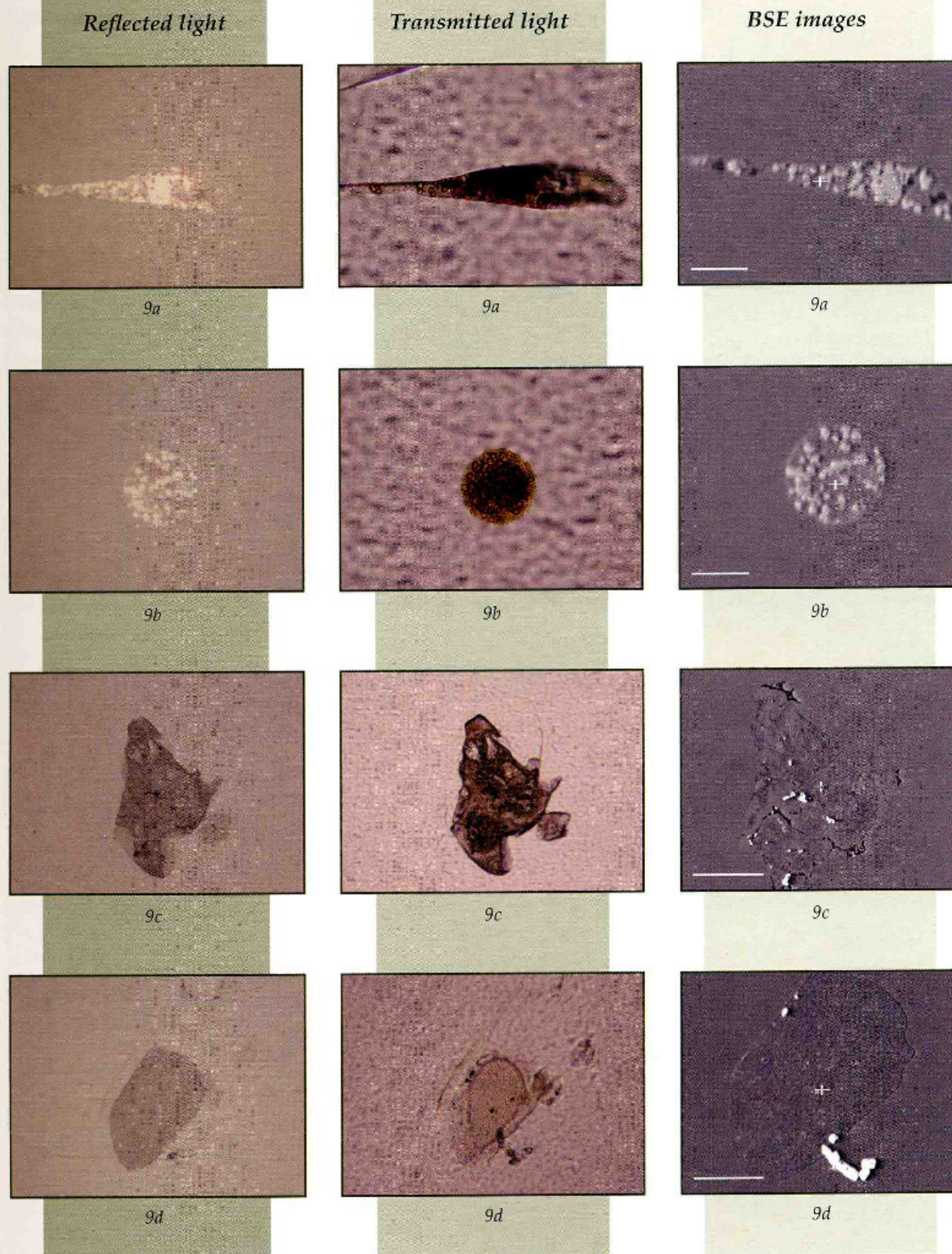
- hydrous Fe-Al-silicates which are admixtures of the two phases specified above, namely hydrous Al-silicates and Fe-hydroxides, or
- hydrous Fe-Al-silicates which are separate mineral species.



**Figure 7:** Back-scattered electron (BSE) images of mineral inclusions in vanadium-bearing tourmalines from Madagascar as observed in polished thin sections: (upper row) zircons; (second row) plagioclases and zircons; (third row) quartzes and zircons; (lower row) plagioclase, quartz and zircon (left), quartz and rutile (centre), rutile (right). Zircons and rutiles show bright electron images. The bars at the bottom left of the images represent 50  $\mu\text{m}$  in a, d, e, g, j, k and l, and 20  $\mu\text{m}$  in b, c, f, h and i.



**Figure 8:** Inclusion of graphite (bright) in reflected light (a, width of photo 0.15 mm) and back-scattered electron (BSE) image of graphite (dark) (b, the bar at the bottom left of the image represents 20  $\mu\text{m}$ ) in vanadium-bearing tourmaline from Madagascar.



**Figure 9:** Non-homogeneous mineral grains in vanadium-bearing tourmalines from Madagascar as observed in polished thin sections in reflected (left), in transmitted light (middle) and as back-scattered electron (BSE) images of the same grains (right). In the two grains pictured in 9a and 9b, iron hydroxides are dominant and hydrous aluminium silicates are subordinate mineral phases (width of all four photos 0.15 mm, the bars at the bottom left of the BSE images represent 20  $\mu\text{m}$ ). In the two grains pictured in 9c and 9d, hydrous aluminium silicates are dominant and iron hydroxides are subordinate mineral phases (width of all four photos 0.35 mm, the bars at the bottom left of the BSE images represent 100  $\mu\text{m}$  in 9c and 50  $\mu\text{m}$  in 9d).

Table V: Properties of some magnesium-bearing gem quality tourmalines from East Africa and Madagascar.

Locality	Analysed samples	Colour	V <sub>2</sub> O <sub>3</sub> (wt.%)	Cr <sub>2</sub> O <sub>3</sub> (wt.%)	FeO <sup>a</sup> (wt.%)	Al (apfu)	Mg (apfu)	Designation
Landanai, Tanzania <sup>1</sup>	3	pale green to intense green	0.14 – 0.30	nd	nd	<6	>3	uvite
Gerevi Hills, Tanzania <sup>1</sup>	3	pale brown or green	0.11 – 0.36	nd	nd to 0.10	>6	<3	calcic aluminous dravite
Umba Valley, Tanzania <sup>1</sup>	1	green	0.44	0.15	nd	>6	<3	calcic aluminous dravite
Kwale District, Kenya <sup>1</sup>	4	green to intense green	1.78–4.03	nd to 0.55	nd	>6	<3	calcic aluminous dravite
Tsavo Park, Kenya <sup>1</sup>	1	green	0.08	0.53	0.02	>6	<3	calcic aluminous dravite
Lualenyi, Kenya <sup>1</sup>	1	brownish green	0.37	nd	0.17	>6	<3	calcic aluminous dravite
Voi-Taveta area, Kenya <sup>2</sup>	4	yellow	nd	nd	nd	>6	<3	calcic aluminous dravite
Lelatema (?), Tanzania <sup>3</sup>	2	green	0.04 – 0.06	0.36 – 0.64	nd	>6	<3	calcic aluminous dravite
East Africa <sup>4</sup>	9	pale green to intense green	0.18 – 1.54	0.03 – 0.17	nd	<6	>3	uvite
Umba Valley, Tanzania <sup>5</sup>	2	green	0.05	0.22 – 0.34	nd to 0.06	>6	<3	calcic aluminous dravite
Yellow Mine, Taita-Taveta District, Kenya <sup>6</sup>	4	yellow, green, blue green	nd to 0.03	0.01 – 0.43	nd to 0.03	>6 ≈6	<3 ≈3	calcic aluminous dravite calcic dravite
John Saul Mine, Taita-Taveta District, Kenya <sup>6</sup>	2	yellow green, yellow pink	0.01 – 0.14	0.06 – 0.09	0.07 – 0.92	>6	<3	calcic aluminous dravite
Mukongonyi, Taita-Taveta District, Kenya <sup>6</sup>	1	yellow brown	0.01	0.06	0.17	>6	<3	calcic aluminous dravite
Kavungu Mine, Jivunda, Zambia <sup>7</sup>	2	green	0.28 – 0.35	0.06 – 0.15	nd – 0.01	<6	>3	uvite
Southern Madagascar <sup>8</sup>	5	green	0.17 – 0.20	0.03 – 0.11	0.01 – 0.02	>6	<3	calcic aluminous dravite

<sup>a</sup> Total iron as FeO. apfu = atoms per formula unit. nd = not detected.

<sup>1</sup> Schmetzer *et al.* (1979). <sup>2</sup> Hänni *et al.* (1981). <sup>3</sup> Bank and Henn (1988). <sup>4</sup> MacDonald and Hawthorne (1995).

<sup>5</sup> Halvorsen and Jensen (1997). <sup>6</sup> Simonet (2000). <sup>7</sup> Hainschwang *et al.* (2007). <sup>8</sup> this paper.

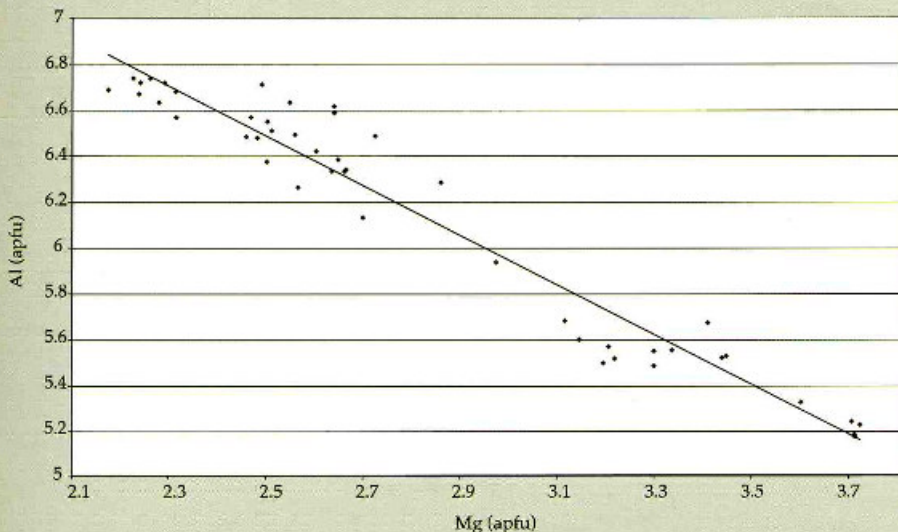
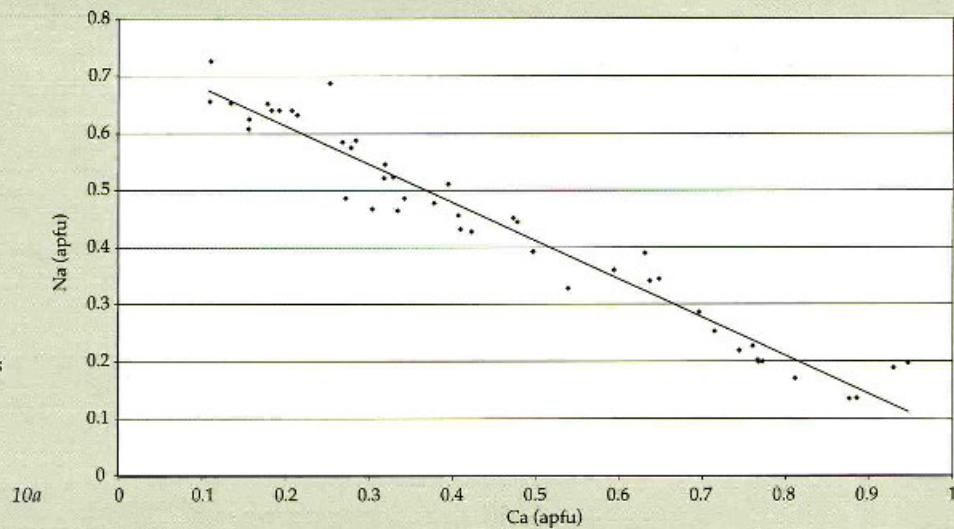
# Discussion

## Properties of magnesium-bearing tourmalines from East Africa, Zambia and Madagascar

Magnesium-bearing gem-quality tourmalines have been described from different localities in East Africa and recently also from Zambia (see Table V). On the basis of colour-causing trace elements, we can divide such tourmalines into three groups:

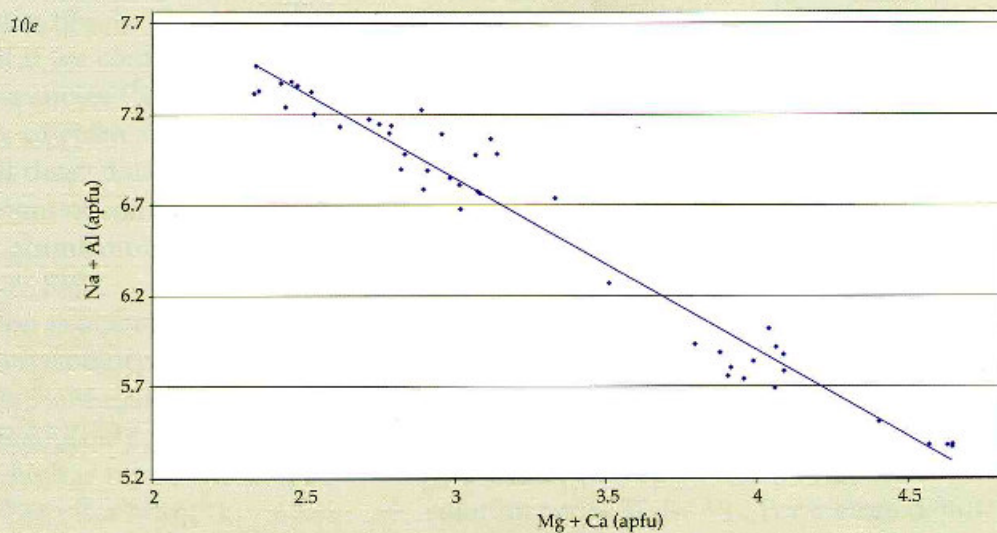
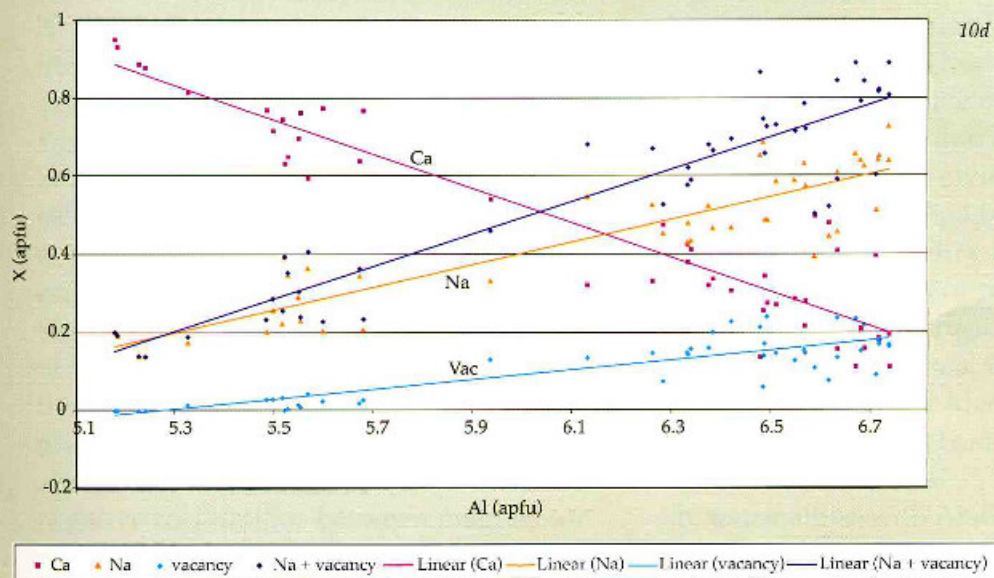
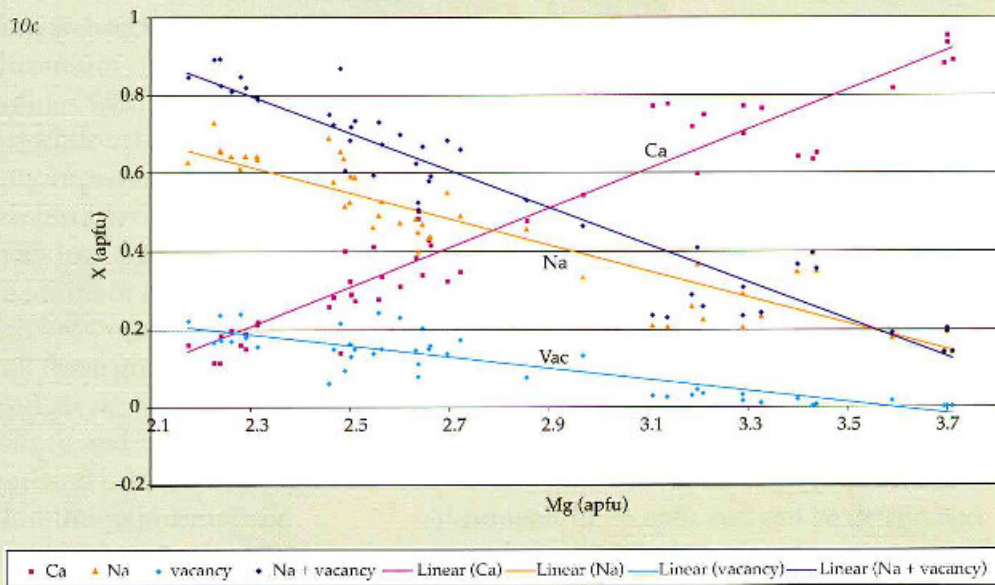
- a. those samples with vanadium concentrations up to 4.03 wt.%  $V_2O_5$  with distinctly smaller or no chromium content. According to our analytical results, the gem material from Madagascar belongs to this group.
- b. a second group of localities supplied tourmalines with higher chromium than vanadium contents. The highest chromium content reported to date has been 0.64 wt.%  $Cr_2O_3$ .  
The colour intensity of any tourmaline

Figure 10: Correlation diagrams of site populations of various major components in X-, Y- and Z-sites of magnesium-bearing gem quality tourmalines from East Africa, Zambia and southern Madagascar; the diagrams are based on 37 analyses of tourmalines from East Africa, four analyses of tourmalines from Zambia and five analyses of tourmalines from southern Madagascar.



10b





from either group is directly related to its vanadium or chromium contents.

- c. In those tourmalines with vanadium or chromium and additional small iron and/or titanium contents, brownish green or brown colours may also be observed. Tourmalines with small iron and/or titanium contents, but without vanadium or chromium, are yellow, yellowish brown or brown.

The samples of all three groups with different coloration mentioned above, i.e. with  $V > Cr$  or with  $Cr > V$  or with Fe and/or Ti (without V or Cr), are sodium- and calcium-bearing, magnesium-rich aluminium tourmalines.

All these magnesium-bearing tourmalines show variation in their Na, Ca, Mg and Al contents and correlation diagrams have been plotted for the five samples from Madagascar, 37 analysed tourmalines from various literature references in East Africa and four samples from Zambia (see again *Table V*). In *Figure 10a*, there is a clear negative correlation between the site occupancies of sodium and calcium (X-site), and for the (Y+Z)-sites, there is also a negative correlation between the site occupancies of magnesium and aluminium (*Figure 10b*). Comparing the site populations of cations between X and (Y+Z) polyhedra, there are positive correlations between magnesium and calcium and between aluminium and sodium (*Figure 10 c,d*), and negative correlations between magnesium and sodium and between aluminium and calcium (*Figure 10 c,d*). Vacancies on the X-site show a positive correlation with Al-contents and a negative correlation with Mg-contents (*Figure 10 c,d*). These trends are also observed if we compare the sum of sodium and vacancies (Na + vacancy) with magnesium, calcium and aluminium (*Figure 10 c,d*). All these data indicate a coupled replacement of sodium or (sodium + vacancies) and aluminium by calcium and magnesium (*Figure 10e*).

This substitution is heterovalent and is the same as the known isomorphic replacement within the dravite  $NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$  – uvite  $CaMg_3(MgAl_5)(BO_3)_3Si_6O_{18}(OH)_4$  solid solution series, which is represented by the scheme  $(Na^{1+}+Al^{3+}) \leftrightarrow (Ca^{2+}+Mg^{2+})$ .

The magnesium-bearing calcic tourmalines can be subdivided into two population fields. A first subgroup with  $Al < 6$  and  $Mg > 3$  apfu (atoms per formula unit), is consistent with the traditionally accepted composition and formula of uvite. A second subgroup consists of tourmalines, also with distinct calcium contents, but with  $Al > 6$  and  $Mg < 3$  apfu. The material from Madagascar belongs to this second subgroup, the samples of which can be designated as calcic aluminous dravites. Only one calcium-bearing sample (from the Yellow Mine, Kenya) had Mg-contents of  $\approx 3$  as well as Al-contents of  $\approx 6$  apfu and can be designated as calcic dravite. So far, no calcium-free dravites have been analysed from the different localities in East Africa, Zambia and Madagascar (see again *Table V*), neither within the bright green, vanadium- or chromium-bearing, nor within the yellow to brown, low-iron gem tourmalines. Vacancies on X-sites are more abundant in the group with  $Al > 6$  (aluminous dravites) than in the group with  $Al < 6$  (uvites) where they are fewer or almost negligible.

According to Henry and Guidotti (1985), tourmalines of the two subgroups mentioned above originate from two different types of host rocks:

- tourmalines with  $Al < 6$  and  $Mg > 3$  apfu (uvites) originate from metacarbonates and meta-pyroxenites
- tourmalines with  $Al > 6$  and  $Mg < 3$  (aluminous dravites) mainly originate from low-Ca meta-ultramafics and Cr,V-rich metasediments, but they also come from metapelites and metapsammities which may or may not coexist with an Al-saturating phase.

The different genetic origins of tourmalines of the two subgroups may well be the cause of their differences in composition.

Comparing the chemical compositions of gem-quality magnesium-bearing tourmalines from East Africa, Zambia and Madagascar with the formulae of different tourmaline end-members as proposed by Hawthorne and Henry (1999), we only have to consider the formulae and isomorphic replacement schemes of lithium- and iron-free members of the rather complex tourmaline solid solution series (*Table VI*). For a more detailed

**Table VI:** Formulae of iron- and lithium-free tourmaline end-members and isomorphic replacement schemes.Formulae of tourmaline end-members<sup>1</sup>

Name (see box)	X-site	Y-site	Z-site	T	B	V	W
Dravite	Na	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Oxy-dravite*	Na	Mg <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
Olenite	Na	Al <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	O <sub>3</sub>	(OH)
Uvite	Ca	Mg <sub>3</sub>	MgAl <sub>3</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Oxy-uvite*	Ca	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
Calcic magnesium-foitite*	Ca <sub>0.5</sub> □ <sub>0.5</sub>	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Magnesium-foitite*	□	Mg <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)

Isomorphic replacement schemes<sup>1</sup>

End-member	Dominant replacement scheme	End-member
Oxy-dravite*	Al <sup>3+</sup> + O <sup>2-</sup> ↔ Mg <sup>2+</sup> + (OH) <sup>-</sup>	Dravite
Oxy-uvite*	Al <sup>3+</sup> + O <sup>2-</sup> ↔ Mg <sup>2+</sup> + (OH) <sup>-</sup>	Uvite
Olenite	Al <sup>3+</sup> + O <sup>2-</sup> ↔ Mg <sup>2+</sup> + (OH) <sup>-</sup>	Dravite
Dravite	Na <sup>+</sup> + Al <sup>3+</sup> ↔ Ca <sup>2+</sup> + Mg <sup>2+</sup>	Uvite
Oxy-dravite*	Na <sup>+</sup> + Al <sup>3+</sup> ↔ Ca <sup>2+</sup> + Mg <sup>2+</sup>	Oxy-uvite*
Dravite	Na <sup>+</sup> + (OH) <sup>-</sup> ↔ Ca <sup>2+</sup> + O <sup>2-</sup>	Oxy-uvite*
Dravite	Na <sup>+</sup> ↔ 0.5 Ca <sup>2+</sup> + 0.5 □	Calcic magnesium-foitite*
Oxy-dravite*	Na <sup>+</sup> + O <sup>2-</sup> ↔ □ + (OH) <sup>-</sup>	Magnesium-foitite*

\* Hypothetical end-members. <sup>1</sup>The symbol □ represents vacancies on X-sites.

discussion of possible Na,Ca substitution schemes in iron-bearing aluminium tourmalines, the reader is referred to the papers of Burt (1989), Henry and Dutrow (1990), Hawthorne (1996) as well as Hawthorne and Henry (1999).

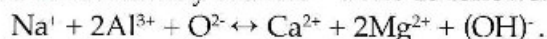
It is evident that the tourmalines from East Africa, Zambia and southern Madagascar are sodium-calcium aluminium-magnesium tourmalines with the number of aluminium atoms per formula unit between 7 and 5 [ $7 > \text{Al}(\text{apfu}) > 5$ ] and the number of magnesium atoms per formula unit between 2 and 4 [ $2 < \text{Mg}(\text{apfu}) < 4$ ]. Sodium and calcium, on the other hand, both vary between 1 and 0 apfu. This is the known compositional range for Mg-bearing tourmalines, samples with Mg < 2 apfu (compositional miscibility gap between oxy-dravite and olenite) or with Mg > 4 apfu are extremely rare or unknown (see, e.g., Dunn, 1977; Dunn *et al.*, 1977; Foit

and Rosenberg, 1979). Consequently, the tourmalines are members of a solid solution series between the end-members oxy-dravite, Na(Mg<sub>2</sub>Al)Al<sub>6</sub>(BO<sub>3</sub>)<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>O, and uvite, CaMg<sub>3</sub>(MgAl<sub>3</sub>)(BO<sub>3</sub>)<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>. It is important to underline, that within the two end-members of this series, 1 Na apfu is replaced by 1 Ca apfu, and, in addition, 2 Al apfu are replaced by 2 Mg apfu. Charge balance within this series is maintained by dehydroxylation.

For this solid solution series the isomorphic replacement scheme does not correspond to any common replacement schemes between dravite and other magnesium-bearing tourmaline end-members given in Table VI. However, by a combination of the schemes oxy-dravite – dravite (identical with oxy-uvite – uvite): Al<sup>3+</sup> + O<sup>2-</sup> ↔ Mg<sup>2+</sup> + (OH)<sup>-</sup> and dravite – uvite (identical with oxy-dravite – oxy-uvite):

Na<sup>+</sup> + Al<sup>3+</sup> ↔ Ca<sup>2+</sup> + Mg<sup>2+</sup> we can derive an isomorphic replacement scheme between the

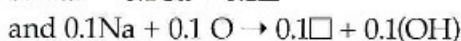
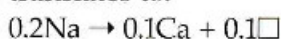
end-members oxy-dravite – uvite as follows:



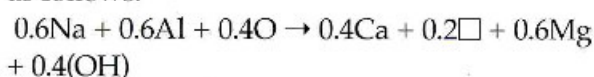
This scheme is dominant for the tourmaline solid solution series oxy-dravite – uvite and represents the compositional variability observed for the gem material from East Africa, Zambia and southern Madagascar.

In detail, to explain the average composition of our samples from Madagascar,  $(\text{Na}_{0.4}\text{Ca}_{0.4}\square_{0.2})(\text{Mg}_{2.6}\text{Al}_{0.4})\text{Al}_6(\text{BO}_3)_3(\text{Si}_{3.9}\text{Al}_{0.1})\text{O}_{18}(\text{OH}_{3.25}\text{F}_{0.25}\text{O}_{0.5})$  and starting from a tourmaline end-member with oxy-dravite composition, the first substitution is in the oxy-dravite – uvite series:  $0.3\text{Na} + 0.6\text{Al} + 0.3\text{O} \rightarrow 0.3\text{Ca} + 0.6\text{Mg} + 0.3(\text{OH})$  (Table VI, lower box, rows 5 and 2).

To derive the vacancies in the X-site, we have to add two further substitutions, which are formally represented by the series dravite – calcic magnesium-foitite and oxy-dravite – magnesium-foitite (Table VI, lower box, rows 7 and 8), which for the Madagascar tourmalines translates to:



where the symbol  $\square$  indicates vacancies on X-sites. These three substitutions sum as follows:



To complete the explanation of the composition of the Madagascar tourmalines, we have to consider the replacement of a small fraction of silicon by aluminium according to:  $\text{Si}^{4+} + \text{O}^{2-} \rightarrow \text{Al}^{3+} + (\text{OH})^-$ , in the present case  $0.1\text{Si} + 0.1\text{O} \rightarrow 0.1\text{Al} + 0.1(\text{OH})$ .

## Summary

The green gem-quality tourmalines from southern Madagascar are calcic aluminous dravites with limited compositional variability consisting mainly of coupled isomorphic replacement between (Na,Al) and (Ca,Mg), and vacancies on X-sites. The tourmalines are essentially iron- and lithium-free, but contain small amounts of vanadium and chromium, with  $\text{V}_2\text{O}_3 > \text{Cr}_2\text{O}_3$  which is the cause of the green coloration.

Common solid inclusions are plagioclase

(with a compositional variability within the bytownite field), quartz and zircon.

Irregularly shaped grains consist of a mixture of at least two minerals, namely hydrous aluminium silicates and iron hydroxide. We were unable to confirm whether more mineral phases – perhaps hydrous iron aluminium silicates – may be present within this admixture. Isolated cavities and healed fractures containing liquid and two-phase inclusions (liquid and gas) are also common.

## Acknowledgements

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