Colour-change garnets from Madagascar: comparison of colorimetric with chemical data

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ABSTRACT: In this study 24 colour-change garnets from Madagascar have been studied to gain data for a correlation between chemical composition and colorimetric calculations. All samples belong to the pyrope-spessartine solid solution series. They contain some traces of vanadium (0.27 to 1.61 wt% V_2O_3), which is responsible for the colour-change in these garnets. Based on visual observations, the investigated samples were separated into five groups of different colour-change behaviour when examined under daylight and incandescent light. Generally, most garnets changed from bluish-green in daylight to purple in incandescent light, although some changed from yellowish-green to pink and brownish-green to brownish-red. Two samples remained almost unchanged, i.e. blue and brown respectively. The visual separation in five groups is consistent with differences obtained by colorimetric calculations. The colorimetric calculations are presented in the CIELab colour space. Comparing colour behaviour with chemical analyses results in a correlation with several intrinsic chemical factors, mainly vanadium, chromium, manganese, magnesium and iron.

Keywords: chemistry, CIELab colour space, colorimetry, colour-change garnet, Madagascar, vanadium

395

Introduction

The colour-change effect is well known by gemmologists and highly appreciated in the gem trade. The term was originally used for alexandrite, a variety of chrysoberyl, changing its colour appearance distinctly under different 'white' illuminations, e.g. daylight and incandescent light. Gem-quality garnets displaying colour change were first mentioned from East Africa (Crowningshield, 1970; Jobbins *et al.*, 1975). In the following years similar garnets were further reported from Umba valley and Tunduru in Tanzania (Schmetzer and Ottemann, 1979; Schmetzer and Gübelin, 1980; Stockton, 1982; Hänni, 1983; Manson and Stockton, 1984; Stockton, 1985; Koivula and Kammerling, 1988) and from Athiliwewa and Embilipitiya in Sri Lanka (Johnson and Koivula, 1996b; Johnson and Koivula 1998a). However, commercial quantities of colour-changing garnets have entered the gem trade only recently due to the discovery of new gem deposits in south west Madagascar (area of Ilakaka and Bekily; Johnson and Koivula, 1998b); most faceted stones are less than 1 ct.

Generally, colour-change garnets are greenish-blue to almost blue in daylight and purplish to purple in incandescent light (Johnson and Koivula, 1998a). Some change

Materials and methods

For this study, 24 colour-changing garnets (21 faceted and 3 rough specimens labelled A-D, F-J and L-Z) ranging from 0.25 ct to 2.38 ct have been investigated. They were chosen to represent the largest possible range of colour (*Figure 1*). For comparison we also included a spessartine garnet (K) of light orange colour. All samples, including the spessartine, originate from the recently discovered secondary gem deposit near the town of Bekily in southern Madagascar (W. Spaltenstein, L. Aubert, A. Leuenberger, D. Bontempi, all pers. comm., 1999 and 2000).

Apart from standard gemmological testing for internal strain (polariscope), refractive index, specific gravity and fluorescence to long and short-wave ultraviolet radiation, the colour of each sample was determined using daylight and tungsten light (incandescent light). For tungsten light observations, a calibrated light source of 2800 K (similar to CIE illuminant A) was chosen.

In the standard visual observation routine, all samples were placed about 50 cm from the observer and colour was observed when looking straight through the table facet. For daylight measurements, the samples were shielded from direct sunlight and only exposed to diffuse daylight. For colour determination in tungsten light, the light source was slightly inclined to the table facet, as this

is the customary way to examine gemstones in the trade.

UV-VIS spectrometric data (800-350 nm) of all specimens were taken with a Varian Cary 500 spectrophotometer, using a scan rate of 60 nm/min in the transmission mode. Based on these absorption spectra, the colorimetric data (CIELab coordinates) were calculated using Mathematica® (calculations kindly provided by G. di Pietro, Institute for Scientific Photography, University of Basel) and our own CIELab calculation program.

Figure 1: *Some of the investigated colour-change garnets from Madagascar under tungsten illumination. Photo by M.S. Krzemnicki, © SSEF*

The chemical compositions of 18 samples were obtained using a Cameca SX-50 electron microprobe and a JEOL-JXA 8600 electron microprobe with an acceleration voltage of 15 kV and a beam current of 10 nA (Geochemical Laboratories, ETH Zürich and MPI University of Basel); well-characterized oxides and silicates of Al, Si, Ca, Mn, Fe, V, Cr, Ti, Mg were used for standardization. The chromium content in weight percent oxide was corrected for peak overlaps by interfering vanadium-$K\beta$ using the formula:

$$Cr_2O_3 \text{(corrected)} = Cr_2O_3 \text{(initial)} - 0.1 \times V_2O_3$$

All quantitative chemical data were further corrected for matrix effects by ZAF-type on-line procedure.

Table I: Gemmological properties of the studied colour-change garnets

Samples:	24 colour-change garnets
Weight:	0.25 to 2.38 ct
SG:	3.748 to 4.104
RI:	1.745 to negative reading (> 1.785)
Polariscope:	anomalous double refraction
UV LW:	inert
UV SW:	inert
Colour in light:	daylight: blue, greenish-blue, brownish-green, yellowish-green
	incandescent: purple, brownish-red, pink
Colour-change:	very slight to distinct
Saturation:	medium to strong
Transparency:	transparent
Lustre:	bright vitreous

their colour from yellowish-green to pink or pale brown (Johnson and Koivula, 1998b).

In the first detailed gemmological study of colour-change garnets from Madagascar, Schmetzer and Bernhardt (1999) separate colour-change garnets into two groups according to their chemistry. Most colour-change garnets are intermediate members of the pyrope-spessartine solid solution series containing minor amounts of vanadium and/or chromium (Jobbins *et al.*, 1975; Stockton, 1982; Manson and Stockton, 1984; Stockton and Manson, 1985; Koivula and Kammerling, 1988; Johnson and Koivula, 1996b; Johnson and Koivula, 1998b; Schmetzer and Bernhardt, 1999). All studied colour-change garnets from Madagascar belong to this group (Johnson and Koivula, 1998b; Schmetzer and Bernhardt, 1999). Only a few colour-change garnets were found to be chromium-rich (Schmetzer *et al.*, 1980).

The colour-change effect has been studied for decades (see references in Bosshart et al., 1982; Liu et al., 1999), mainly concentrating on alexandrite. A comprehensive description of colour-change materials (minerals and artificial products) is given by Liu et al. (1999). They compared colorimetric calculations with standard gemmological observation techniques for colour description. Previously Schmetzer et al. (1980) had studied the relationship between the colour change of different materials and the chemistry and/or crystal structure of a mineral.

In this study, the authors would like to integrate these two research approaches by presenting data on colour-change garnets from Madagascar, with emphasis on the correlation of chemical data with colorimetric calculations and colour observation.

Physical properties

The gemmological properties of the colour-change garnets (sample K, spessartine, excluded) are summarized in *Table I.* The distinct variations in RI (from 1.745 to > 1.785) and SG (3.748 – 4.104) are due to extensive exchange of magnesium by manganese in the samples (members of the pyrope-spessartine solid solution). Chemical analyses revealed a close correlation of RI (and SG) with the chemistry of colour-change garnets (*Figure 2*). Previous studies on colour-change garnets (Jobbins *et al.*, 1975; Stockton, 1985; Johnson and Koivula, 1996a, 1996b; Johnson and Koivula, 1998b; Koivula and Kammerling, 1988; Schmetzer and Bernhardt, 1999) reported RI values between 1.757 and 1.770, a distinctly smaller range than that in the present sample selection.
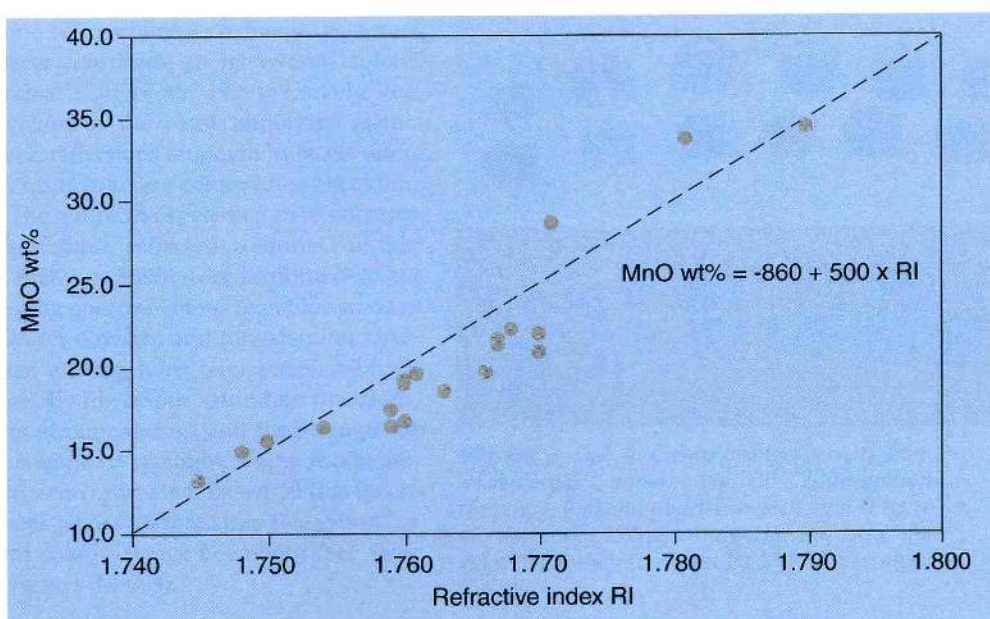
Figure 2: Correlation of manganese content (MnO wt%) versus refractive index of colour-change garnets from Madagascar. A qualitative correlation line has been drawn to show the direct relationship between main component content (i.e. manganese) and optical property (RI). A similar diagram can be obtained by plotting Mn content against SG.

All samples remained inert when exposed to long and short-wave ultraviolet radiation. Under the polariscope they showed slight to moderate anomalous extinction, resulting from internal strain within the garnet structure. Regularly oriented long prismatic crystal inclusions, often in a three-dimensional lattice array were found to be rutile.

Visual colour determination

The colour of all samples was determined by a consistent observation technique (see section 'Materials and methods'), similar to that in common practice in gemmological laboratories and in the trade. Nevertheless, visual colour determination of a faceted

Table II: The colour-change behaviour of the studied garnets from Madagascar

Group	Samples	Daylight	Tungsten light	Colour change	References
Group I	J	blue	blue with purplish hue	very slight hue change	9, 11
Group II	A, B, D, F-I, L-N, Q, T-W, Y, Z	blue-greenish blue	purplish-blue – purple	moderate – distinct	1, 2, 4, 6, 7, 11, 12
Group III	P, R. S	yellowish-green	pink – light purple	slight – moderate	3, 5, 6, 7, 11, 12, 13
Group IV	C, X	brownish-green	brownish-red	moderate	6
Group V	O	brown	reddish-brown	very slight	

References:
1. Jobbins et al., 1975
2. Johnson and Koivula, 1996a
3. Johnson and Koivula, 1996b
4. Johnson and Koivula, 1998a
5. Johnson and Koivula, 1998b
6. Koivula and Kammerling, 1988
7. Liu et al., 1999
8. Manson and Stockton, 1984
9. Schmetzer and Ottemann, 1979
10. Schmetzer et al., 1980
11. Schmetzer and Bernhardt, 1999
12. Stockton, 1982
13. Stockton and Manson, 1985

gemstone still remains a challenge, as several aspects contribute to its overall colour appearance (Liu *et al.*, 1999). Usually, the body colour is the most important factor. However, reflections on pavilion facets often display quite different colour hues (Stockton, 1982). The cut of the specimen may enhance or reduce these reflected colours. For this study, each specimen was attributed to its dominating spectral colour (e.g. blue in daylight) under daylight and tungsten illumination, just adding hues (e.g. purplish-blue). Additionally the colour saturation (medium, medium strong, strong) and the strength of colour change (very slight, slight, moderate, distinct) were estimated. Based on this the 24 specimens were separated into five groups of different colour-change behaviour (see *Table II* and *Figures 3 and 4*).

- *Group I* garnets remain blue under both illuminations; only a slight change of colour hue is observed (sample J, *Figure 5*). The colour saturation is strong (Schmetzer and Ottemann, 1979).

- *Group II* garnets change their colour moderately to distinctly from bluish to purplish (daylight/tungsten light). Their colour saturation ranges from medium to strong. In the gem trade, these colour-change garnets are commercially the most important (Schmetzer and Bernhardt, 1999). Samples A, B, D, F-I, L-N, Q, T-W, Y, and Z (a total of 17) belong to this group.

Figures 3 and 4: *Colour-change garnets from Madagascar under daylight illumination (Figure 3, top) and under tungsten light (Figure 4, bottom). Colours slightly adjusted by AdobePhotoshop®. Photos by M.S. Krzemnicki, © SSEF.*

- *Group III* garnets change their colour from yellowish-green to pink (Koivula and Kammerling, 1988; Schmetzer and Bernhardt, 1999). The colour saturation is medium to medium strong, the colour-change slight to moderate (samples P, R, S).

- *Group IV* garnets change their colour moderately from brownish-green to brownish-red. The colour saturation is strong (samples C, X).

399

Figure 5: *Almost blue garnet from Madagascar (sample J, group I) in daylight. This sample displays only a very slight change of colour hue when examined under tungsten light. Photo by M.S. Krzemnicki, © SSEF.*

Figure 6: *Brown garnet from Madagascar (sample O, group V) in daylight. This sample displays only a slight change of colour hue towards reddish-brown when examined under tungsten light. Photo by M.S. Krzemnicki, © SSEF.*

Colour-change garnets from Madagascar: comparison of colorimetric with chemical data

- *Group V* garnets change their hue slightly from brown (daylight) to reddish-brown (tungsten) (sample O, *Figure 6*). The colour saturation is strong.

The following results and interpretations of colorimetric and chemical data are discussed in relation to the visual separation in groups I-V.

Chemical data

Quantitative chemical analyses (WD-XRF) and calculated end member mol% (Deer *et al.*, 1992) of some of the colour-change garnets from each group are given in *Table III*. All samples (except sample K, a nearly pure spessartine) are intermediate members of the pyrope-spessartine solid solution series. Apart from the major MgO and MnO components, they are characterized by a significant

grossular component (CaO up to 7.31 wt%, i.e. 13.8 mol% grossular), and a rather smaller iron content from 0.52 up to 3.10 wt% FeO). In the analyses, all iron is presented as FeO (i.e. Fe^{2+}, almandine component). Due to the low iron concentrations an estimation of Fe^{3+} based on Droop (1987) is not reliable, although small amounts of Fe^{3+} might be present (andradite component).

All samples (except spessartine, sample K) contain distinct amounts of vanadium (from 0.27 in sample R to 1.61wt% V_2O_3 in sample J) and chromium (from 0.11 in sample R to 0.95 wt% Cr_2O_3 in sample M). Only in sample M (group II) is the uvarovite component (Cr_2O_3) slightly higher than the goldmanite component (V_2O_3). In all other samples vanadium content exceeds that of chromium by a factor of 2 to 5.

Table III: Electron microprobe analyses of some colour-change garnets from Madagascar

	Group I Sample J	Group II Sample M	Group II Sample A	Group III Sample R	Group IV Sample C	Group V Sample O	Spessartine Sample K
RI	1.763	1.767	1.748	1.760	1.781	neg.	neg.
SG	3.832	3.893	3.748	3.871	4.068	4.104	4.168
Oxide weight%							
MgO	10.45	11.78	15.25	10.49	4.21	0.87	b.d.
MnO	18.49	21.31	14.75	18.89	33.69	34.41	42.27
CaO	7.31	3.01	4.65	5.09	1.73	3.11	0.21
FeO	0.65	2.84	0.96	2.29	0.52	3.10	b.d.
Cr_2O_3	0.38	0.95	0.17	0.11	0.24	0.26	b.d.
V_2O_3	1.61	0.91	0.43	0.27	1.30	0.44	0.01
TiO_2	0.06	0.03	0.04	0.11	0.25	0.51	b.d.
Al_2O_3	21.12	20.48	22.70	21.67	19.99	20.06	20.88
SiO_2	38.63	38.81	41.47	40.22	37.22	37.65	36.65
Total	98.70	100.12	100.42	99.14	99.15	100.41	100.02
Endmember mol%							
Pyrope	39.3	42.6	55.4	40.1	16.9	3.6	0.0
Spessartine	39.5	43.8	30.5	41.0	76.9	80.1	99.4
Almandine	1.4	5.8	2.0	4.9	1.2	7.1	0.0
Uvarovite	1.1	2.9	0.5	0.3	0.8	0.8	0.0
Goldmanite	4.9	2.8	1.3	0.8	4.2	1.4	0.0
Grossular	13.8	2.1	10.4	12.8	0.1	6.9	0.6

For this table, only representative analyses of the studied colour-change garnets from Madagascar were chosen.

Cr_2O_3 was corrected for interference with vanadium – Kß, see section 'Materials and methods'.

b.d. – below detection limit. Endmember calculation after Deer *et al.*, 1992

neg. – negative RI, i.e. above upper limit of the TIR-refractometer at 1.785

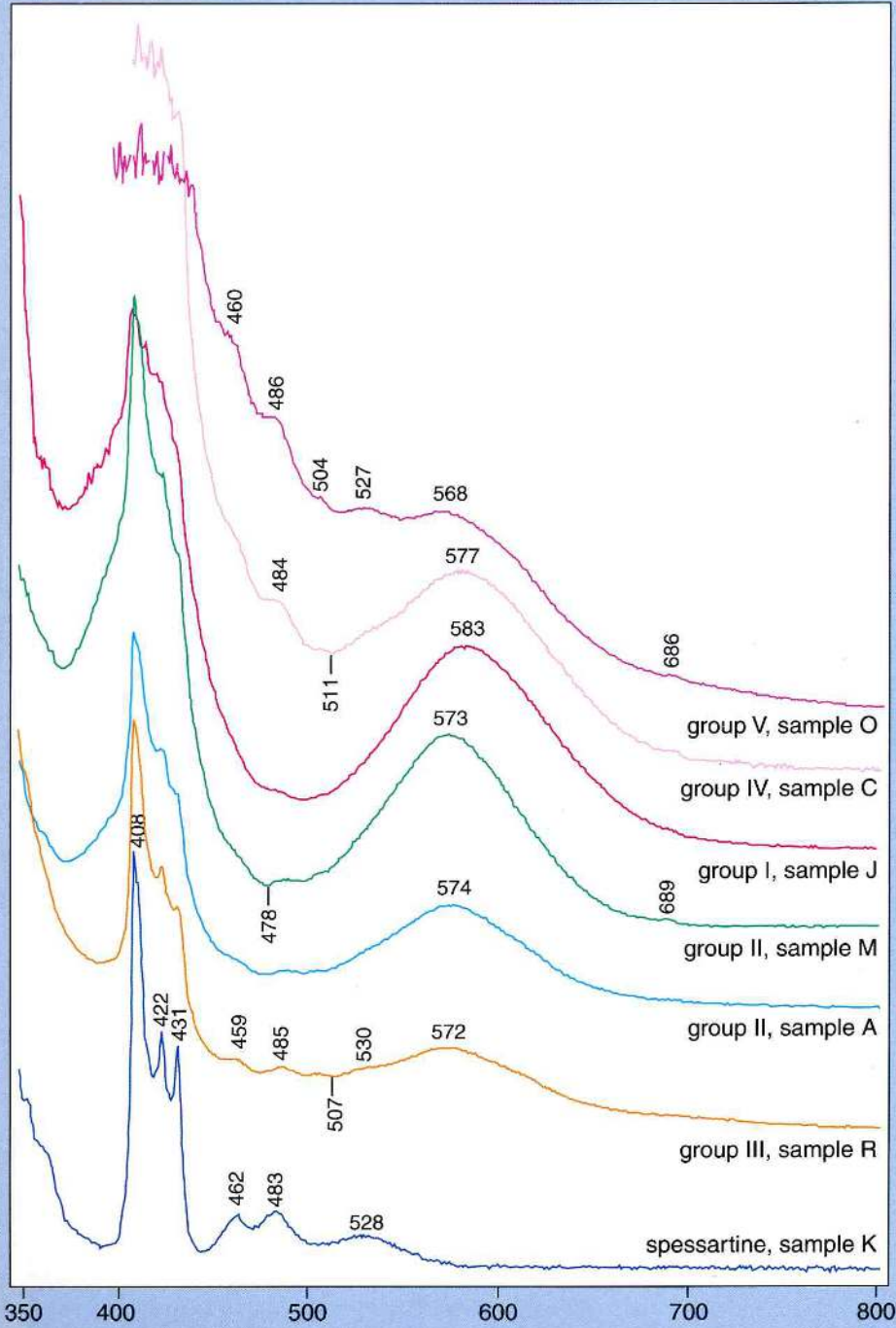**UV-VIS spectra of colour-change garnets from Madagascar**

460

486

504 527 568

484 577

511 583

686

573

group V, sample O

group IV, sample C

group I, sample J

408

478

689

574

group II, sample M

group II, sample A

422
431

459 485 530 572

507

group III, sample R

462 483

528

spessartine, sample K

350   400   500   600   700   800

Figure 7: UV-VIS spectra of colour-change garnets (groups I-V) compared with spessartine.

Spectrometric data in the UV-visible range

The colours of the present suite of stones are made up of the contributions of each of the solid solution components or garnet end members. Pyrope is colourless and has no absorption bands in the visible region of the spectrum. Pure spessartine is orange and shows its presence even in low quantities by

the well known set of absorption bands (see below). Iron, vanadium and chromium contribute to the observed colour as chromophore elements (Nassau, 1983), modifying the basic colour set by the main constituents (pyrope and spessartine). *Figure 7* shows representative UV-VIS absorption spectra of garnets from the different colour change groups (I-V, see *Table III*). They are compared with the spectrum of

Table IV: *Comparison of colorimetric with chemical data of garnets from Madagascar.*

Sample	Colour group	Hue angle Ω(D65)	Ω(A)	Hue angle difference $\Delta\Omega$	Saturation δ(D65)	δ(A)	Chemistry MnO wt%	V_2O_3 wt%	End-members Spessartine mol%
J	I	210.3	243.2	32.9	48.2	46.0	18.49	1.61	39.5
A	II	161.9	340.0	178.1	3.4	12.8	14.75	0.43	30.5
B	II	158.5	340.6	177.9	7.0	11.5	15.47	0.49	32.0
T	II	137.3	350.1	147.1	3.5	8.0	13.13	0.38	27.6
Q	II	175.9	319.0	143.1	6.3	7.3	n.a	n.a	n.a
L	II	1.79.7	321.4	141.7	5.1	7.6	21.93	0.93	46.8
U	II	192.2	326.8	134.6	4.3	12.1	16.71	0.90	34.7
W	II	183.4	316.7	133.2	12.8	14.6	20.80	1.20	47.9
G	II	193.2	315.8	122.6	9.4	14.0	19.55	1.14	43.0
I	II	190.3	306.7	116.4	12.3	13.1	22.16	1.24	48.7
H	II	171.9	285.1	113.2	17.0	6.6	16.33	0.77	34.6
V	II	212.7	314.8	102.1	6.1	13.4	16.34	0.94	34.7
F	II	210.6	305.3	94.7	11.0	16.5	19.59	1.08	41.8
D	II	212.8	297.7	84.9	13.4	17.9	19.11	1.19	40.6
Y	II	221.3	288.6	67.3	3.8	5.3	19.63	0.87	42.6
Z	II	219.2	281.9	62.7	6.9	8.4	21.60	1.31	47.9
M	II	265.3	324.7	59.5	7.6	25.7	21.31	0.91	43.8
N	II	257.9	311.3	53.4	10.5	21.3	17.36	0.80	36.2
P	III	125.0	35.9	89.2	14.4	11.2	n.a.	n.a.	n.a.
S	III	103.1	59.8	43.3	17.1	15.6	18.90	0.29	40.7
R	III	84.1	42.9	41.2	14.5	17.9	18.89	0.27	41.0
C	IV	84.6	49.4	35.2	27.3	31.8	33.69	1.30	76.9
X	IV	85.2	51.8	33.3	12.8	14.6	28.63	0.89	58.6
O	V	58.3	52.5	5.8	51.3	59.1	34.41	0.44	80.1
K	Spessartine	72.2	65.7	6.6	29.6	33.7	42.27	0.01	99.4

The table has been arranged in order of decreasing hue angle differences $\Delta\Omega$ within each group of colour-change behaviour.

The colorimetric data (hue angle Ω and saturation δ) are given for both illuminants D65 (daylight equivalent) and A (tungsten equivalent).

n.a. – not analysed chemically by electron microprobe.

spessartine of light orange colour. All spectra show characteristics of spessartine with Mn^{2+} peaks (see e.g. Manson and Stockton, 1984; Schmetzer and Bernhardt, 1999) at 408, 422, 431 nm (or complete absorption around 431 nm). All colour-change garnets (group II-IV) show a distinct broad absorption band with a maximum at about 573 nm. This maximum has been attributed to V^{3+} probably with some Cr^{3+} (see Schmetzer and Ottemann, 1979; Manson and Stockton, 1984; Schmetzer and Bernhardt, 1999). The absorption minimum for garnets changing from bluish to purple is located about 476 nm, whereas garnets with a yellowish-green to pink colour-change have a minimum around 507 nm (Schmetzer and Bernhardt, 1999). Two different spectral characteristics may result in garnets displaying only a very slight change of colour hue (group I and group V). The blue garnet (sample J, group I, *Figure 5*) has the highest vanadium content (1.61 wt% V_2O_3) of all the samples and shows a similar spectrum to colour-change garnets. However, the maximum of the broad absorption band is centred about 583 nm, and is thus slightly above the narrow range between 562–577 nm defined by Schmetzer and Bernhardt (1999) for alexandrite-like colour change materials. The brownish garnet (sample O, group V, *Figure 6*) shows distinct superposition of the characteristic V-absorption band by Fe^{2+} (almandine component) and Mn^{2+} (spessartine component). Due to this no distinct minimum in the range of 507–476 is present. This results in only a very slight change of colour hue, although the vanadium content is the same as in the colour-change garnets of group II (see *Table III*).

Colorimetric calculation

By means of colorimetric calculations, somewhat subjective colour descriptions can be displayed as coordinates in a colour space. In accordance with previous studies (Liu *et al.*, 1994, 1999) the CIELab space was chosen to calculate colour coordinates, as it is a uniform colour space which takes into account the chromatic adaptation of the human eye. In the CIELab space, colour differences are proportional to the distances of the represented colour coordinates (for a detailed discussion of colorimetry in gemmology, please refer to Liu *et al.*, 1999).

Colour is always an integration of hue (spectral colour, e.g. blue), saturation (depth of colour, weak to strong) and brightness (from light to dark). Based on the UV-VIS transmission spectra of our samples, we calculated L* (brightness) and a*, b* (colour coordinates, determining the colour hue) in the CIELab colour space (*Table IV* and *Figure 8*). Formulae can be obtained in any standard colorimetry textbook (Kuehni, 1997) or on the internet (e.g. http://www.cs.rit.edu/~ncs/color/t_convert.html).

The saturation δ of a colour is the distance between the colour coordinates (a*, b*) to the centre point (0, 0) and thus:
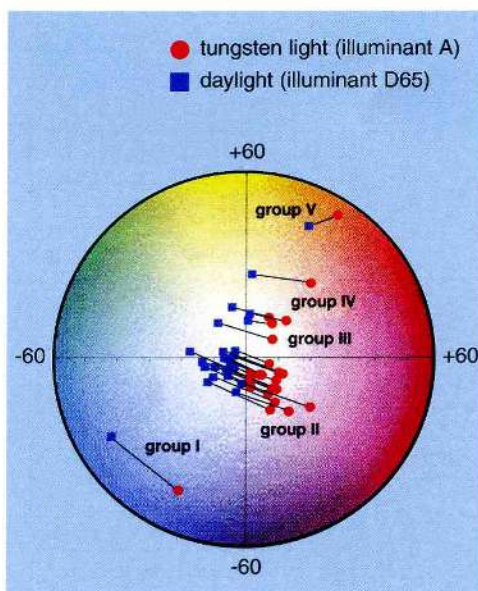
$$\delta = \sqrt{(a^2 + b^2)}$$

Figure 8: Colour coordinates of all studied colour-change garnet samples (see Table III) in the CIELab colour space. Daylight coordinates in blue, incandescent coordinates in red. The lines connect the colour coordinates of each sample calculated with illuminants D65 (daylight equivalent) and A (tungsten light equivalent).

In 1986 the 'Commission International de l'Eclairage CIE' proposed several standard illuminants (theoretical light sources); these include D65 for daylight (light emitted by a blackbody at 6504 K) and A for incandescent (tungsten) light (2856 K). Based on these illuminants and on so-called matching functions (2° standard colorimetric observer), which take into account the ability of the human eye to adapt chromatically between different 'white' light sources, the CIELab coordinates for the samples under each illumination were calculated using our own computer program. All equations and data for variables (i.e. illuminants and matching functions) were found on the internet (see references).

Using a simple trigonometric equation, colour hue angles Ω for each sample under the illuminant D65 and A were calculated:

$$\Omega = \arctan (b/a)$$

The difference between hue angles $\Delta\Omega$ of each sample is an expression of the calculated colour change behaviour of a gemstone under daylight and incandescent light, respectively.

$$\Delta\Omega = |\Omega D65 - \Omega A|$$

Comparison of colorimetric data with chemical data

The colour appearance of the samples were well reproduced by the calculated colour hue values (*Figure 8*) and we think colorimetry may become a more important tool for colour investigation in gemmology.

A close examination of the calculated hue angle differences $\Delta\Omega$ (*Figure 9*) fits well with the visual separation into five groups of colour-change behaviour (I-V, see *Table II*).
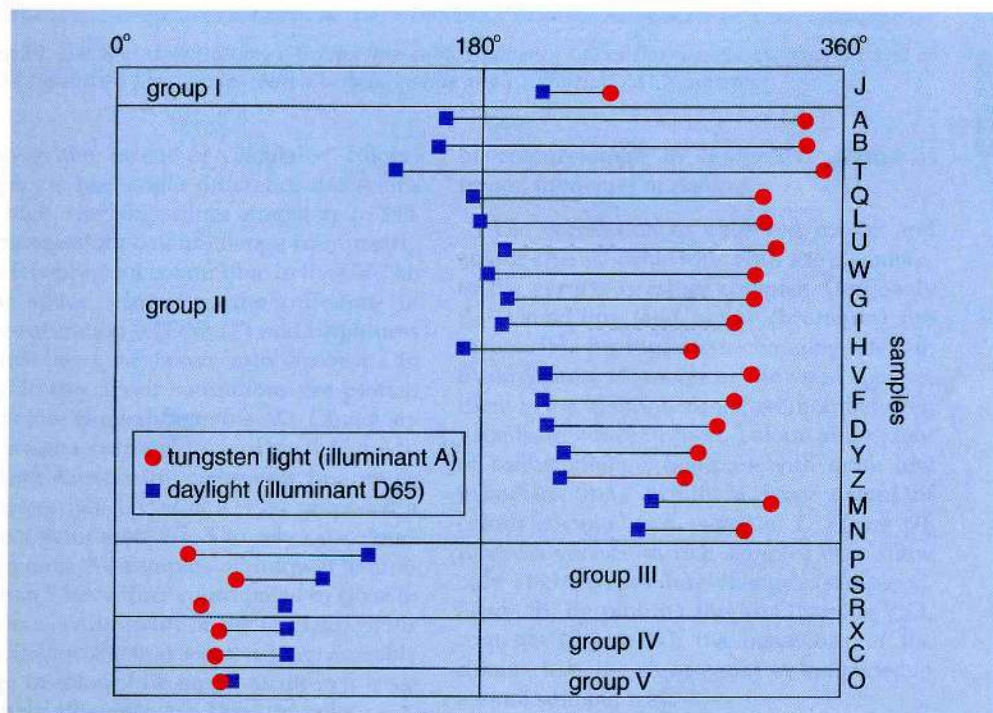
Figure 9: Calculated hue angle differences $\Delta\Omega$ of the garnets, listed in five groups of colour-change behaviour and arranged in order of $\Delta\Omega$. In daylight, all samples tend in direction to the hue angle 180° (blue-green). Samples such as A, B and Q are characterized by very large $\Delta\Omega$ but visually appear with a rather slight to moderate colour-change due to their low colour saturation (compare with Figure 10).
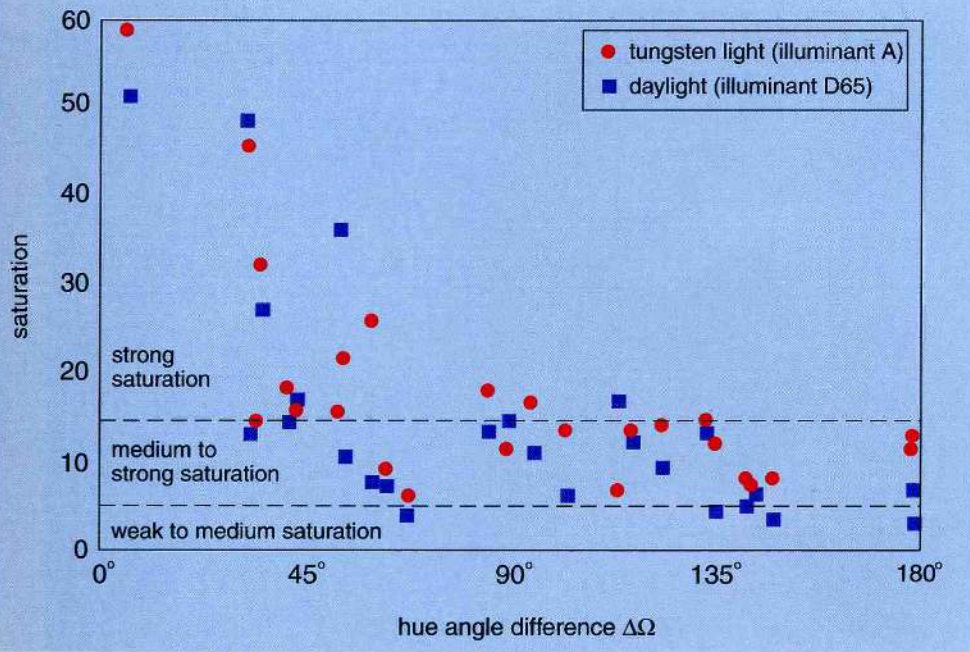
Figure 10: *Calculated saturation δ versus hue angle difference ΔΩ of the garnets. A general trend of reduced saturation for samples with a very large hue angle difference ΔΩ is apparent.*

However, the extent of calculated colour-change, i.e. hue angle difference ΔΩ seems quite high, reaching values almost up to 180, and representing colour-change from nearly red to its opponent colour blue in the CIELab colour space. However, the influence of colour saturation δ (*Table IV*) and brightness L^* must also be taken into account. In *Figure 10* the colour saturations are plotted against hue angle differences ΔΩ. Obviously there is a general trend toward weak to medium saturations with increasing hue angle differences ΔΩ. Liu *et al.* (1999) proposed a minimal saturation δ = 5 to rely on colour-change data. All samples with lower saturation than 5 have their coordinates so close to the white centre point of the CIELab colour space (*Figure 8*), that even a barely visible change in colour hue might result in a large hue angle difference ΔΩ. Thus the colour saturation δ of a sample is highly relevant to the visual extent of any colour-change. The calculated values of hue angle differences ΔΩ should be compared only between samples with similar saturation to describe the extent

of colourchange in qualitative terms as minor, moderate or distinct.

The correlation of observed colour and colour-change behaviour with the chemistry of the garnets is rather complex. Obviously the vanadium (and some chromium) are responsible for the colour-changing effect in these garnets. However, as shown in *Figure 9*, there is not a simple direct relation between vanadium concentration, colour and extent of colour change. Samples with quite low vanadium may exhibit a large extent of colour change (e.g. sample T, *Figure 9*), whereas vanadium rich samples may show only slight colour hue changes (sample C, *Figure 9*). By plotting the MnO versus V_2O_3 contents (*Figure 11*), the behaviour of the colour-changing garnets may be explained in a more suitable way.

In *Figure 11*, no evident correlation between manganese Mn^{2+} and vanadium V^{3+} ions can be expected, as they are substituting for Mg^{2+} and Al^{3+} on two different lattice positions. However, by attributing to each

Colour-change garnets from Madagascar: comparison of colorimetric with chemical data
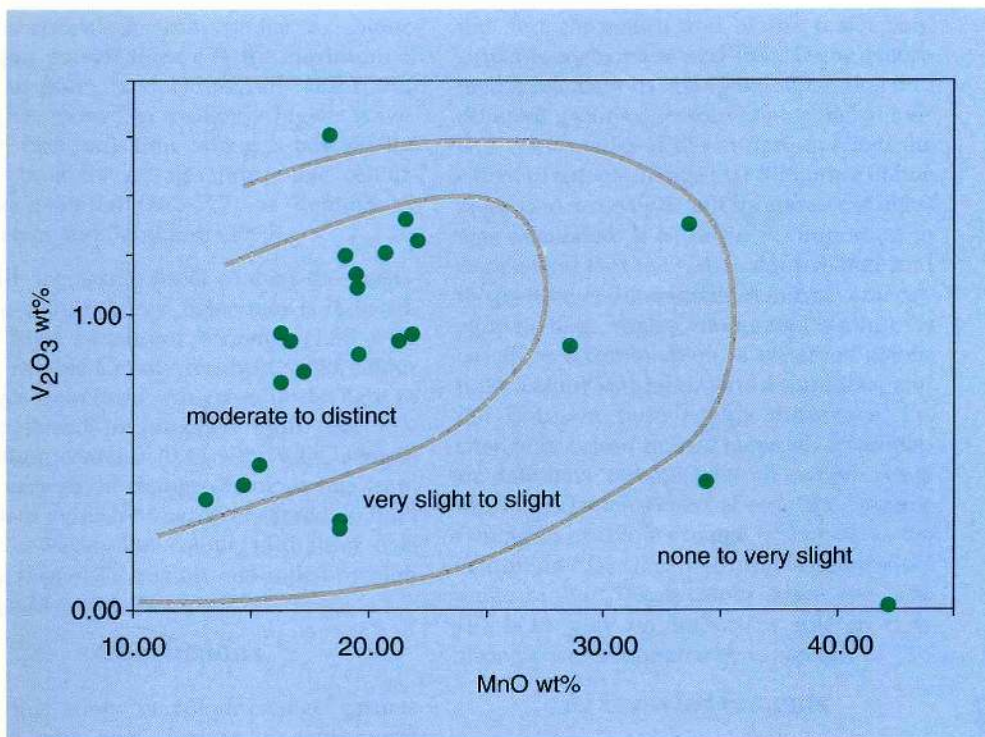
Figure 11: *Bivariate diagram of V_2O_3 versus MnO for colour-change garnets of the pyrope-spessartine series. Three main fields of colour change strength have been introduced qualitatively. The limits of the fields represent a gradual transition rather than steps of different colour-change behaviour.*

sample the observed extent of colour change (i.e. none to very slight, very slight to slight, moderate to distinct), we gain a qualitative diagram with three fields of colour-change behaviour for vanadium bearing garnets of the pyrope-spessartine solid solution series. The limits of these fields should rather be thought of as gradual intervals, e.g. from a slight to moderate colour change, rather than as steps from one field to the other. Garnets of the pyrope-spessartine series containing no vanadium and/or chromium display no colour change at all (e.g. sample K). Their colour saturation δ is correlated to the manganese content (*Figure 10*). Samples characterized by a MgO/MnO ratio of about 1 are potentially colour-change garnets. When containing only low concentrations of vanadium and/or chromium (below about 0.5 wt% V_2O_3) they display a slight to moderate colour change from greenish in daylight to pink in tungsten light (*Figure 11*). The

colour saturation remains weak to moderate. The vanadium concentration has to exceed 0.5 wt% V_2O_3 to result in a moderate to distinct colour change from bluish in daylight to purplish in tungsten light and a medium to medium strong colour saturation (*Figure 11*). According to Schmetzer and Otteman (1979) and Schmetzer and Bernhardt (1999), there is an upper limit for the vanadium concentration (about 1.60 wt% V_2O_3, sample J), above which only a slight, if any colour change can be observed. The garnet remains more or less blue under both lighting conditions with strong colour saturation (*Figure 11*). The saturation of all previously mentioned samples is basically proportional to the vanadium concentration. To understand the absence of colour change in vanadium-rich pyrope-spessartine garnets, we assume that above a critical vanadium concentration the lattice parameters are slightly modified by the goldmanite component. Although still showing

an absorption spectrum similar to colour-changing garnets (*Figure 7*), the maximum of the vanadium (and chromium) absorption band has moved to a slightly higher wavelength (583 nm), thus taking it beyond the upper limit for an alexandrite-like colour-change material (562–577) as defined by Schmetzer and Bernhardt (1999).

With increasing MnO content the potential for colour-change behaviour is reduced. Even high vanadium contents (1.30 wt% V_2O_3, sample C) only result in slight colour changes from brownish-green in daylight to brownish-red in tungsten light. For low vanadium contents (0.44 wt% V_2O_3, sample O), a very slight change of colour hue from brown to reddish-brown is observed. In both cases however, the colour saturation δ is strong (*Figure 10*), mainly controlled by high manganese contents.

Conclusions

In this study of colour-change garnets from a new gem deposit in south west Madagascar the complex relationship between chemistry and colour-change effect has been investigated. The study shows that several intrinsic chemical variables such as the content of vanadium related to chromium, manganese, magnesium and iron contribute to the variations in the visual appearance of these garnets under different 'white' illuminations (daylight and incandescent light). A qualitative diagram for colour-change garnets (*Figure 11*) of the pyrope-spessartine series has been introduced. The diagram shows several fields of different colour change behaviour. Leaving the field of moderate to distinct colour-change due to higher vanadium or manganese concentrations results in a drastically reduced colour-change behaviour (or no colour-change at all), coupled with a high colour saturation. Similar garnets with low vanadium (and chromium) contents display only a weak colour-change coupled with low colour saturations. To conclude, the observed variations of the colour-change effect in garnets is generally an effect of chemical variations in the concentrations of the trace elements, vanadi-um and chromium and of the major constituents manganese and iron. Using colorimetric calculations, the visual separation into different groups of colour-change behaviour was confirmed and the saturation δ and the extent of colour-change (ΔΩ difference of hue angle under daylight and incandescent light) was calculated. It is, however, important to understand that the term colour-change and its qualitative differentiation into several categories (e.g. slight, moderate, strong), is based on a combination of observed colour hues, colour saturation and brightness, and not only on pure colour difference, i.e. change of colour hues. Therefore, colorimetric data have to be used with caution when drawing conclusions about the degree (strength) of colour-change (*Figure 9*), as the saturation δ (see *Figure 10*) and brightness (L* value in the CIELab colour space, see *Table IV*) both play an important role in how strongly the colour-change is perceived.

References:

Bosshart, G., Frank, E., Hänni, H.A., and Barot, N., 1982. Colour-changing kyanite from East Africa. *Journal of Gemmology*, **18**, 205-12

Commission International de l'Eclairage, 1986. *Colorimetry*, 2nd edn. CIE Publication No. 15.2, Vienna

Crowningshield, R., 1970. A rare alexandrite garnet from Tanzania. *Gems & Gemology*, **13**, 174-7

Deer, W.A., Howie, R.A., and Zussman, J., 1992. *An Introduction to the Rock-Forming Minerals*, 2nd edn. Longman Scientific and Technical, Essex

Droop, G.T.R., 1987. A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analysis, using stoichiometric criteria. *Mineralogical Magazine*, **51**, 431-5

Hänni, H.A., 1983. Weitere Untersuchungen an einigen farbwechselnden Edelsteinen. *Z.Dt.Gemmol.Ges.*, **32**(2/3), 99-106

Jobbins, E.A., Saul, J.M., Tresham, A.E., and Young, B.R., 1975. Blue colour-changing gem garnet from East Africa. *Journal of Gemmology*, **14**, 201-8

Johnson, M.L., and Koivula, J.I. (Eds) 1996a. Gem news: Color-change garnet. *Gems & Gemology*, **32**(1), 53

Johnson, M.L., and Koivula, J.I. (Eds) 1996b. Gem news: A second Sri Lankan locality for color-change garnet. *Gems and Gemology*, **32**(4), 285-6

Johnson, M.L., and Koivula, J.I. (Eds) 1998a. Gem news: 'almost blue' Sri Lankan color–change garnets. *Gems & Gemology*, **34**(2), 138-40

Johnson, M.L., and Koivula, J.I. (Eds) 1998b. Gem news: Color-change pyrope-spessartine garnet, also from Madagascar. *Gems & Gemology*, **34**(3), 222-3

Koivula, J.I., and Kammerling, R.C. (Eds), 1988. Gem news: Change of color-garnets. *Gems & Gemology*, **24**(3), 176-7

Kuehni, R.G., 1997. Color: *An Introduction to practice and principles*. John Wiley and Sons, New York

Liu, Y., Shigley, J., Fritsch, E., and Hemphill, S., 1994. The 'Alexandrite effect' in gemstones. *Color and Research Application*, **19**(3), 186-91

Liu, Y., Shigley, J.E., Fritsch, E., and Hemphill, S., 1999. A colorimetric study of the alexandrite effect in gemstones. *Journal of Gemmology*, **26**(6), 371-85

Manson, D.V., and Stockton, C.M., 1984. Pyrope-spessartine garnets with unusual color behavior. *Gems & Gemology*, **20**(4), 200-7

Nassau, K., 1983. *The physics and chemistry of color – the fifteen causes of color*. John Wiley and Sons, New York

Schmetzer, K., and Ottemann, J., 1979. Kristallchemie und Farbe Vanadium-haltiger Granate. *Neues Jahrbuch für Mineralogie, Abhandlungen*, **136**(2), 146-68

Schmetzer, K., Bank, H., and Gübelin, E., 1980. The alexandrite effect in minerals: chrysoberyl, garnet, corundum, fluorite. *Neues Jahrbuch für Mineralogie, Abhandlungen*, **138**(2), 147-64

Schmetzer, K., and Bernhardt, H.-J., 1999. Garnets from Madagascar with a colour change of blue-green to purple. *Gems & Gemology*, **35**(4), 196-201

Stockton, C.M., 1982. Two notable color-change garnets. *Gems & Gemology*, **18**(2), 100-1

Stockton, C.M., and Manson, D.V., 1985. Editorial Forum: Unusual color-change garnet. *Gems & Gemology*, **21**(2), 116-17