Gemstones of the Garnet Group – about mixed crystals and solid solution
柘榴石家族 – 混合晶體和固態溶體

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Fig. 1 A selection of garnets in many colours, representing the gem varieties. *These garnets are part of the Prof. H.A. Hänni collection, owned by SSEF, the Swiss Gemmological Institute. Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
精選多種顏色的柘榴石，代表不同的品種。

柘榴石不斷為我們帶來驚喜，因為其顏色多樣化，而且不同品種柘榴石的顏色、折射率和密度的差異亦很大。本文介紹柘榴石家族的主要類型，並解釋它們的主要相似點及不同之處。

Introduction

Garnets continually surprise us with their large range of colours and the wide variation in their diagnostic features of colour, refractive index and density (Deer et al. 1982; Rouse, J.D., 1986, Hänni, 1987). This paper seeks to introduce the main gem types of garnets and explain their main similarities and differences. Garnets are widely used in jewellery and are very popular as they come in so many colours (Fig. 1).

General remarks

Each mineral is defined both by its crystal structure and by its chemical composition, thus by its internal array and by the material used to build the crystal lattice. The individual building blocks of the crystal structure are ions, which are positively or negatively charged atoms of a variety of chemical elements which occupy sites in the crystal structure. During crystallisation (Fig. 2), the ions order themselves into the garnet structure which possesses cubic symmetry.
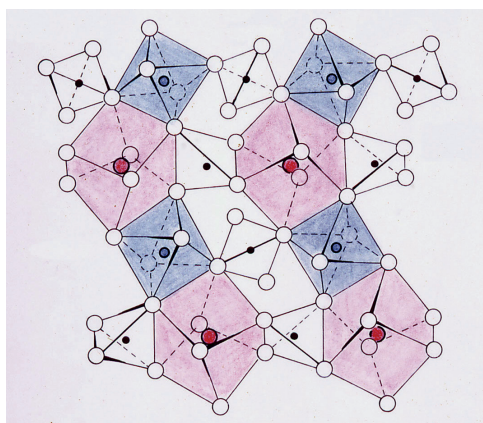
Fig. 2 A model of the garnet structure with positions of ions. In red are the ions with 8 coordination with oxygen (e.g. Mg^{2+}, Fe^{2+}, Ca^{2+}), in blue those with 6 coordination with oxygen (Al^{3+}, Fe^{3+}, Cr^{3+}) and in black those with 4 coordination (Si^{4+}) as SiO_4. The white circles represent oxygen ions. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
包含離子位置的柘榴石結構模型。紅色是離子及其與氧的8個配位（例如Mg^{2+}, Fe^{2+}, Ca^{2+}），藍色是離子及其與氧的6個配位（Al^{3+}, Fe^{3+}, Cr^{3+}），黑色是與4個配位（Si^{4+}）的SiO_4離子。白色圓圈代表氧離子。

Although all garnets have the same crystal structure, this can be made up of different, but similar ions. Because of this, a large number of garnet types occur. Studies have been carried out on naturally occurring garnets to determine which chemical elements participate in the structure and

in what amounts (DEER et al, 1982). The results are best presented in the form of a chemical formula. The formula, like a recipe, shows which elements (as single ions) are present and in what relative quantities. These quantities are indicated by the small number (index) after and just below the abbreviated name (or symbol) of the element. Crystals of tangible dimensions contain many billions of the smallest unit of the mineral formula. The smallest possible amount of garnet is formed by one formula unit cell, termed a molecule.

The following idealised and chemically pure so called end-members are of significance for the description of the gem garnets (Table 1). These chemically pure types occur solely as synthetic crystals. In nature only crystals representing a mixture of the above types are generally found. Many more garnet end members exist than those mentioned here, such as Hibschite, Morimotoite etc. (see Wikipedia, 2019)

The garnets can be classified into two chemical groups. These are named using the first letters of the members of the participating garnet types. The PYR-AL-SPITE group is composed of the aluminium-containing Pyrope, Almandine and Spessartine garnets. The U-GR-ANDITE group is composed of the calcium-containing garnets Uvarovite, Grossular and Andradite. Apart from the uniform crystal structure, the garnets show distinct chemical similarities.

All their chemical formulae contain:
3 divalent ions (e.g. Mg^{2+}, Fe^{2+}, Mn^{2+}, Ca^{2+})
2 trivalent ions (e.g. Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+})
3 SiO_4-groups

Beside the well known types of the PYRALSPITE and UGRANDITE groups additional types can be visualised with constituent ions fitting the general garnet formula. For example, the minerals knorringite (Mg, Cr) and goldmanite (Ca, V) have been synthetically produced. Furthermore, silicate-free garnets, such as YAG and GGG can be synthetically prepared and these are, or have been, used in part as diamond substitutes.

On the basis of their typical chemical composition, each idealised pure garnet type possesses characteristic physical properties (Table 2).

Formation of mixed crystals

The chemically pure end-members previously described correspond to theoretically idealised compositions which are very rarely found in nature. Natural garnets are virtually always composed of "mixtures" of the end-members. When garnet crystals are formed in nature, there are usually several different types of divalent and trivalent ions available. For example a natural garnet will use Mg^{2+} and Fe^{2+}. Pyrope molecules and almandine molecules are thus formed simultaneously. A so-called mixed crystal crystallises whose composition will lie somewhere between that of pyrope and almandine, depending on the proportion of Mg^{2+} and Fe^{2+} ions used in the formation of the crystal. Pyrope and almandine can form a complete series of mixed crystals, or a solid solution series. Fig. 3 shows the relationship between refractive indices and densities and the mixing ratio within the pyrope-almandine series. The values for the intermediate mixed crystals lie between the extreme values of the end-members.

Table 1: The pure garnet end members 純柘榴石端員

Name	Formula	8 coord.	ionic radius	6 coord.	ionic radius	lattice constant
Pyrope	$Mg_3Al_2(SiO_4)_3$	Mg^{2+}	0.65 Å	Al^{3+}	0.51 Å	11.46 Å
Almandine	$Fe_3Al_2(SiO_4)_3$	Fe^{2+}	0.83 Å	Al^{3+}	0.51 Å	11.53 Å
Spessartire	$Mn_3Al_2(SiO_4)_3$	Mn^{2+}	0.83 Å	Al^{3+}	0.51 Å	11.62 Å
Knorringite	$Mg_3Cr_2(SiO_4)_3$	Mg^{2+}	0.65 Å	Al^{3+}	0.51 Å	11.62 Å
Grossular	$Ca_3Al_2(SiO_4)_3$	Ca^{2+}	0.97 Å	Al^{3+}	0.51 Å	11.85 Å
Hydrogross	$Ca_3Al_2(SiO_4)_2(OH)_4$	Ca^{2+}	0.97 Å	Al^{3+}	0.51 Å	12.00 Å
Andradite	$Ca_3Fe_2(SiO_4)_3$	Ca^{2+}	0.97 Å	Fe^{3+}	0.63 Å	12.05 Å
Uvarovite	$Ca_3Cr_2(SiO_4)_3$	Ca^{2+}	0.97 Å	Cr^{3+}	0.62 Å	12.00 Å
Goldmanite	$Ca_3V_2(SiO_4)_3$	Ca^{2+}	0.97 Å	V^{3+}	0.64 Å	12.07 Å

Tab. 1 Garnet end members with their composition, coordination in the lattice, ionic radius and unit cell dimensions in Ångström units.

Table 2: Refractive indices and densities of the pure garnet end-members 純柘榴石端元的折射率和密度

Species	n	D	H	colour
Pyrope	1.714	3.582	7 1/4	colourless
Almandine	1.830	4.318	7 1/2	dark red
Spessartine	1.800	4.190	7 1/4	yellow
Grossular	1.734	3.594	7 1/4	colourless
Hydrogrossular	1.675	3.130	7	colourless
Andradite	1.887	3.859	6 1/2	green-yellow
Uvarovite	1.860	3.900	7 1/2	green-black
Goldmanite	1.834	3.765		green
Knorringite	1.875	3.835		green or rather red as a small component in pyrope

Tab. 2 Garnet end members with their refractive index n, density D, hardness H, and colour.

Fig. 3 Solid solution series of pyrope-almandine showing dependence in values with changing chemical composition, a typical two component system. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
固態溶體系列的鎂鋁-鐵鋁榴石顯示出隨著化學成分的變化的依賴值，這是一種典型的雙複合系統。

This illustration gives examples of mixed crystals comprising only two colours from colourless to dark red. Increasing amounts of almandine (Fe) raises the SG and RI and augments the red colour.

Most naturally occurring garnets are mixed crystals composed of two or more end-members from different sources in varying mixing ratios. Usually mixed crystals are optically homogeneous and can be considered to be solidified solutions: the gemstone in the middle of Fig. 3 has 40% almandine that is diluted in 60% pyrope.

Some garnet types possess only limited miscibility with other types. It has been found that the garnets within the Pyralspite group exhibit a large amount of miscibility (Fig. 4); so too do the garnets within the Ugrandite group. On the other hand, miscibility between members of the Pyralspite and the Ugrandite group is very limited. Areas of mixed proportions which do not occur in nature are termed "miscibility gaps". In Fig. 5 a graphical attempt is made to show the miscibilities between the main garnet types. The length of each arrow indicates the extent of miscibility with the opposite member. In this kind of two dimensional graphical representation, mixtures of three or more end-members (as occur in nature) cannot be shown.
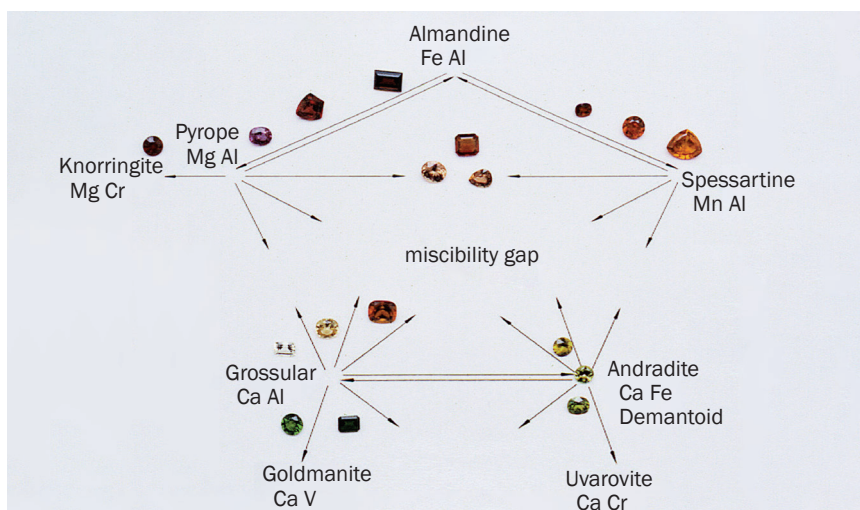

Fig. 4 Members of the solid solution series of pyrope-almandine-spessartine can be understood as a blend of three differently composed substances that constitute a uniform entity. The mixture on the right represents a pyrope-almandine-spessartine mix. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
鎂鋁-鐵鋁-錳鋁榴石固態溶體系列的成員可以理解為構成統一實體的三種不同組成物質的混合物。右邊的混合物代表一種鎂鋁-鐵鋁-錳鋁榴石混合物。

True gem garnets

The following are some examples of garnets which will be examined in more detail. The principle of miscibility of divers chemical garnet compounds possessing the same crystal structure can result in the formation of a large number of different mixed crystal compositions and appearances. Their colour, refractive indices and densities can be regarded as functions influenced by the values of the participating end-members. The type of garnet formed during crystallisation depends on the available material, local geological factors and physico-chemical factors. The naming of individual garnet types often preceded the technique of non-destructive chemical analysis. The results of quantitative analyses now permit the determination of the kind of end-members involved and their

Fig. 5 Pentagon-graph representing the relationship between the members of the garnet group in respect of the solid-solution situation among the members. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
五角形圖表示關於柘榴石家族成員之間的固態溶合情況。

relative amounts of the components. Fig. 5 shows an attempt to display graphically the situation of two families in a pentagon diagram. Pyraslpite and Ugrandite are separated by a miscibility gap. The reason is that calcium-containing garnets possess larger unit cells than those without calcium (compare the lattice constants in Table. 1).

Pyrope-Almandine garnets

The most common garnets are red stones of the pyrope-almandine series (Fig. 6). A pleasing red colour is shown when the colourless pyrope contains a 10-40% almandine component. Higher almandine contents result in too dark a colour. Pure almandine is very dark red.
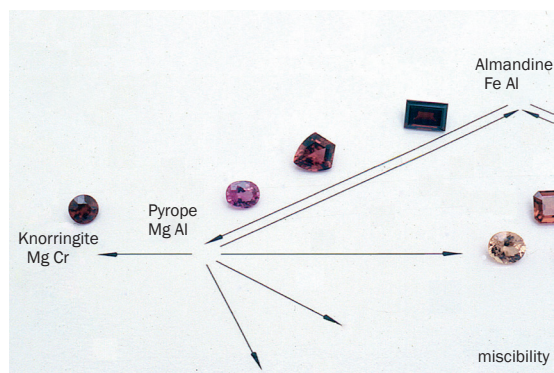
Fig. 6 Detail of the pentagon-graph representing the relationship between the members of pyrope-almandine solid-solution situation members. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
五角形圖細部表示鎂鋁-鐵鋁榴石成員間的固態溶合關係。

Rhodolite is a light purple-red pyrope-almandine variety with a 10-15% almandine component. A few percent of the almandine molecules is enough to have a strong effect on the colour. This is the reason why the absorption spectrum of light rhodolite exhibits the almandine bands at 575, 527 and 505 nm. Pyrope, which is colourless when pure, can be coloured by the presence of other idiochromatic (or self-coloured) garnet types than almandine. This may be the case with spessartine (yellow) and knorringite (red) which are also miscible with pyrope. Blood-red chromium pyrope (like "Cape ruby", or the stones from Bohemia) contains a small portion of knorringite molecules together with a little almandine. Fig. 7 shows a qualitative ED-XRF spectrum of a garnet with constituent main elements Mg, Al, Si, Cr and Fe. Some garnets, mainly composed of pyrope-almandine mixtures, also contain a few percents of grossular, spessartine or andradite molecules. The latter two can influence colour.

Classification systems for red to violet garnets with due consideration of the gemmological instruments used in determination have been published in Gems & Gemology by Stockton & Manson (1981) and Hanneman (1983).
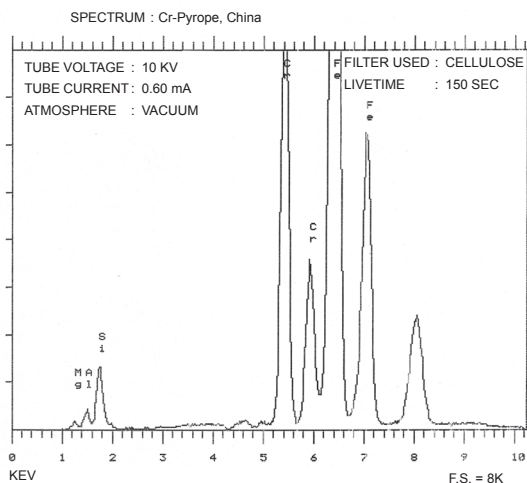
Fig. 7 An Energy-Dispersive X-Ray Fluorescence spectrum (ED-XRF). Peak heights do not reflect real relative concentrations because excitation conditions favour transitions elements. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
能量色散X-射線熒光光譜（ED-XRF）。峰值高度不反映實際相對濃度，因為其激發條件對於過渡元素有利。

A peculiarity of mainly Indian pyrope-almandines is their high content of titanium that gives rise to the formation of rutile needles. In fact, rutile is a widespread inclusion seen in these garnets. When the concentration of needles is high, star stones can be produced. Many cabochons then show stars with 4 or 6 branches depending of the orientation in which they are cut.

Spessartine and spessartine-rich garnets

Pure, yellow spessartine seldom occurs in nature in crystal sizes of interest to the gem cutter. An occurrence in Ramona, California produced light orange-yellow stones with a spessartine component of over 90%. Similarly pure spessartines were found in the Kunene river area (N-Namibia). Further recent spessartine finds have been made in Madagascar and Nigeria. More commonly, almandine-rich spessartines are encountered, which are coloured dark orange to reddish-brown by virtue of the almandine content (Fig 8). Almandine-spessartines cannot be distinguished from pyrope-almandines solely on the basis of refractive index and density. Studies using the spectroscope have to be undertaken in order to recognise the higher spessartine content, illustrated by the appearance of the absorption bands at 432, 424 and 412 nm. Stones with a very high spessartine content will display the weaker absorption lines at 573, 520, 504 and 480 nm, also due to manganese.
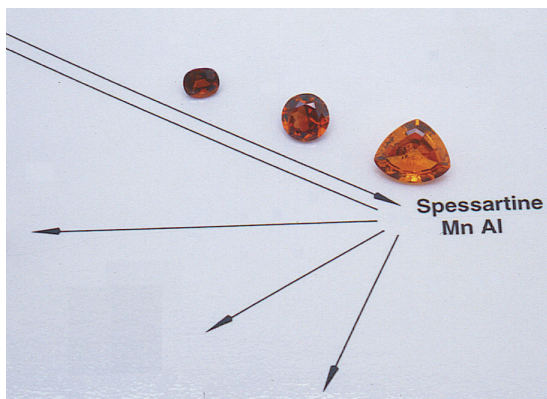
Fig. 8 Detail of the pentagon-graph representing the relationship between the spessartine-almandine members of the pyralspite group. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
五角形圖的細部代表鋁榴石系列中錳鋁-鐵鋁-榴石成員之間的關係。

A peculiar phenomenon can be seen on rare occasions when spessartine-pyrope mixed crystals contain traces of vanadium (or a goldmanite component, which means the same). In blue-rich daylight they appear blue-green or olive-green, and in red-rich incandescent light they turn to purple or brownish-red – in fact they show an alexandrite effect. (Fig. 9). Such colour-changing material is also referred as to garnet with alexandrite effect (Krzemnicki et al, 2001). When the vanadium content is over 1.7 wt% the mixture stays on the blue side.


Fig. 9 Pyrope-spessartines with some vanadium may show a distinctive colour change depending on the spectral character of the lighting. Upper: warm light, lower: cold light. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
含有釩的鎂鋁-錳鋁榴石可能會因應照明的光譜特徵而顯示出獨特的顏色變化。上：暖光；下：冷光。

Blue garnet is pretty rare and is found mainly in Madagascar and Tanzania. A blue intermediate member (Fig. 10) found in Nandagala, Tanzania was analysed by microprobe and gave spessartine 40%, pyrope 34%, grossular 15%, goldmanite 7% (Flöss, 2011). Similar materials stem from Bekily, Madagascar. But the majority of the stones found

in both localities have less than 1.7 wt% V_2O_3 and may exhibit a change of colour. Thus they do not stay on the blue side in both lights.
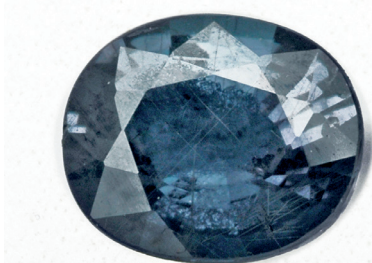
Fig. 10 A rare blue garnet of 0.66 ct from Bekily, Madagascar, with 2.1 wt% V_2O_3. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
來自馬達加斯加貝基利的稀有藍色柘榴石，重量為0.66克拉，含有2.1%重量的V_2O_3。

Pyralspite mixed crystals

Spessartine from the Umba Valley (Tanzania) forms mixed crystals with pyrope, almandine and small amounts of grossular. Such three-component stones possess a mixture of yellow, colourless and red, ending up with "tea" colours and are called malaia or umbalite garnets in the trade (Fig. 11). The orange to reddish-brown mixed crystals are typically made up of colourless pyrope (40-70%) and minor grossular, yellow spessartine (15-40%). Small amounts of almandine (5-20%) supply the red component to the colour and govern the darkness of the stones (see Fig. 4 container on the right).

Fig. 11 Pyrope-almandine-spessartine mixed members with an additional admixture of grossular from the Umba valley (Tanzania) are called malaia garnet. Photo The octagonal stone weighs 2.6 cts. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
鎂鋁-鐵鋁-錳鋁榴石的混合成員與來自翁吧山谷（坦桑尼亞）的，一種含鈣鋁榴石混合物，被稱為馬來柘榴石。圖中八邊形的原石重2.6克拉。

Grossular and grossularite

We are now discussing the lower part of the pentagon graph in Fig. 5., i.e. garnets with calcium as divalent ions as a major component. Grossular in its pure state is colourless, but through mixture with idiochromatic garnet types, mixed crystals with red, yellow, green and brown colours occur (Fig. 12). The andradite, uvarovite and goldmanite molecules are the main donors of colour. Small portions of iron-

rich types (almandine, andradite) lead to yellow, orange and brown colourations. The vanadium bearing grossular is green and is called Tsavolite in the trade. The majority of grossulars contain iron, and have a yellow to brown and greenish colour. The largest crystals originate from Mali and weigh up to 1 kilogram.
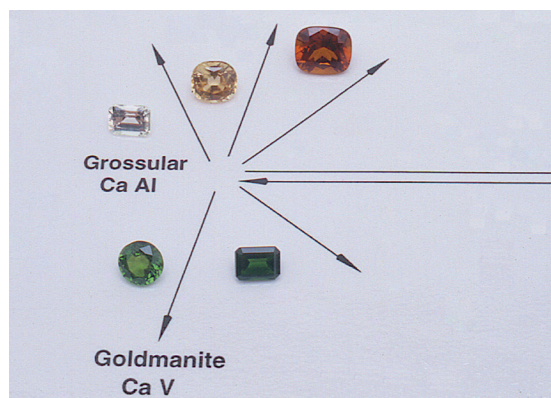

Fig. 12 Detail of the pentagon-graph representing the relationship between the grossular members of the garnet group in respect of their miscibility with other Ca-garnets. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
五角形圖的細部，表示柘榴石組中的鈣鋁榴石成員與其他
鈣-柘榴石的混溶性之關係。

Hessonites are representatives of yellow to orange-brown varieties of grossular. Their distinctive optical peculiarity is a granular structure, which appears swirly under the microscope. The granular structure is due to hessonite's polycrystalline structure (Fig. 13). Grain sizes are typically around ¼ of a millimetre.
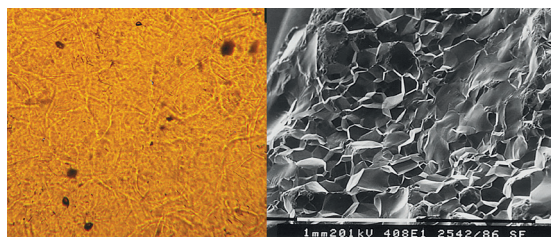
Fig. 13 Scanning electron microscopic picture of a break structure (broken surface) of polycrystalline grossularite, showing the granular structure. Crystallite sizes are in the ¼ mm area. Left side gemmological binocular, right side SEM picture. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
電子顯微鏡的掃描圖片中多晶質鈣鋁榴石的破損面結構，
亦顯示出其顆粒狀結構。微晶尺寸在¼ mm區域內。左側
由雙目顯微鏡拍攝的照片；右側由掃描式電子顯微鏡SEM
拍攝的照片。

Hessonites are therefore not single crystals but polycrystalline compositions, as sometimes seen with other grossulars, too. Grossularite (or massive grossular) is the correct name for this form. Green varieties of grossular (with Cr or V) can also possess

a polycrystalline structure. A similar polycrystalline grossular may be pink or green and is known as "Transvaal jade". Another form of green grossularite has been found in Pakistan and is sometimes mistaken for jade. Many grossularites are not necessarily composed solely of grossular grains, but can contain other minerals, such as vesuvianite or chromite. As they are an assemblage of diverse minerals they are defined as a rock. Variations, therefore, range from the single crystal grossular to grossularite and to a grossular-rich rock. The densities of the latter can be quite different from those of pure grossular.

At present, the most significant grossulars are the green tsavolites, mainly found in Tsavo national park in Kenya, and in Tanzania (Fig. 14). The green colour of these tsavolites is due to the elements vanadium and/or chromium. These elements occur in grossular as either the goldmanite (V) or uvarovite (Cr) molecules. The vanadium-containing molecule is usually represented in higher concentrations than that with chromium.


Fig. 14 A selection of crystals and cut grossulars with vanadium, or a goldmannite component. The facetted tsavolite left in the front row weighs 3.8 cts. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
精選的含釩（或金銀礦成分）鈣鋁榴石晶體和已切割的寶
石。前排左方的刻面鉻釩鈣鋁榴石重3.8卡拉。

Andradite and demantoid

Fig. 15 shows the andradite corner of the pentagon graph. Pure andradite is idiochromatically yellowish-green and exhibits a strong dispersion, giving the mineral its name, demantoid (diamond-like). Deposits are known in Russia, Namibia, Iran, China and others. Demantoids of gem quality were mined at a deposit in the Urals until the beginning of the century. This deposit is now being worked again and Russian demantoids are in high demand by collectors. We have, however, observed that since 2004 heat treated demantoids have become numerous in the trade. They can be easily recognised by discoid fractures that adhere to horse tail inclusions. A strong emerald green colour stems from a chromium content or uvarovite content. Andradites with a more yellowish to brown colour are also known as topazolites.
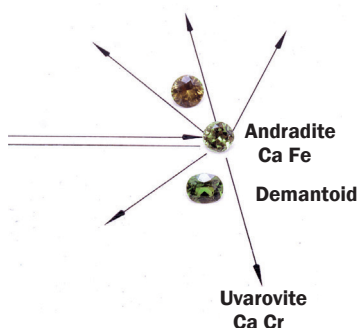
Fig. 15 Detail of the pentagon-graph representing the relationship between the andradite-uvarovite members of the ugrandite group. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
五角形圖的細部顯示鉻鈣铁榴石群的鈣鐵-鈣鉻榴石成員之間的關係。

Conclusions

Garnets form a fascinating mineral group, and supply us with gemstones of widely differing appearances. Transparent single crystal gems of all colours including the rare blue are much in demand, and garnets are, usually, not treated.

Most of these colours stem from the natural mixing of different types during crystallisation. A broad spectrum of colours is formed by the various combination possibilities of two or more of the different idiochromatic and colourless types. Polycrystalline aggregates (the so called massive form) and stones with potential asterism can be used as cabochon material. An andradite-grossular type from Mexico (Fig. 16) actually exhibits a magnificent iridescent play-of-colour (Azuki et al., 1984). The basic brown colour of these andradite-grossular crystals is also called rainbow-garnet. It is covered by a thin layer of minute scales able to produce interference colours. Crystal faces are thus only slightly polished as the iridescent layer is usually only on the surface and less than a millimetre thick!
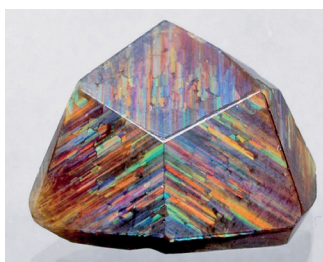
Fig. 16 A rare iridescent andradite from Mexico with a play of colour due to fine lamellae of different composition. Sample approx 2 cm across. *Photo © H.A. Hänni, SSEF Swiss Gemmological Institute*
來自墨西哥的稀有的帶暈彩鈣鐵榴石，因不同成分的薄層狀片而產生變彩。樣品約2厘米寬。

Due to the large number of varieties, obvious difficulties in nomenclatural occur. As colour is one of the main features of many gemstones, most names designate a definite colour variety (like rhodolite or tsavolite). Chromophore chemical elements often colour different garnet types in the same way. Thus, we can encounter different mineralogical types exhibiting the same colour. Chromium grossular, vanadium grossular and chromium demantoid clearly illustrate this point. The correct identification of garnet mixed crystals requires, in many cases, a laborious and non-destructive chemical analysis (e.g. ED-XRF) to determine the quantities of the end-member components involved. Garnet nomenclature based on such analyses are mineralogically correct and in agreement with the results obtained by gemmological identification techniques (refractive index, density and absorption spectrum). In the case of a light orange malaia garnet composed of e.g. 45% pyrope, 35% spessartine, 11% almandine and 9% grossular, the designation PYRALSPITE garnet or spessartine-rich pyrope are both correct. Unfortunately, neither of these two names gives us any idea as to the colour. The addition of a colour description would be helpful. The simplest and obviously correct designation is "orange-coloured garnet", but this term would also include spessartine and hessonite. Therefore trade names such as (in this case) "malaia garnet" can be very helpful.

Acknowledgement

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