

Magnetic susceptibility, a better approach to defining garnets

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Abstract: Using a new, non-destructive method of gem testing, magnetic susceptibility, the authors show how the major end-member composition of any garnet may be confidently predicted by plotting RI against measured susceptibility. On this diagram, eight end-member garnets are plotted, so that any measured garnet can be placed in an appropriate ternary area. This method shows how previous methods of identifying garnets – by their colour, RI and spectrum – are insufficient to accurately identify chemistry in the garnet group. Furthermore, it can be done with inexpensive equipment available to most gemmologists.

Keywords: garnet, gem testing, magnetic susceptibility, refractive index, specific gravity, UV-Visible spectra

Introduction

Most gemmologists classify garnets based on their colour, refractive index (RI) and absorption spectrum^{1,2,3,4,5,6,7}. As new sources and new gem varieties of garnet are discovered, and as our information on garnet chemistry increases, problems with the present gemmological classification become more apparent⁸. The practising gemmologist needs a better means for characterization of garnets to avoid such problems. In this article, the authors will show how any gemmologist can closely infer the major end-members composition of a garnet – without expensive or high-tech equipment.

Two of the authors introduced a new method of gem testing – magnetic susceptibility – in a recent paper⁹. Due to the presence of transition metals in many garnets, the garnet group provides an interesting range of stones to which this method can be applied. Our research further confirmed that far more accurate garnet composition can be revealed in this way than was previously possible with

only conventional gemmological testing equipment. Few non-destructive tests can give a better idea of the chemistry. When the RI is plotted against magnetic susceptibility, a more complete picture of a garnet's chemistry can be made. While this new characterization technique raises questions about the current nomenclature and classification of gem garnets, we will stick to the chemistry and leave nomenclature and classification to future debate.

Most modern gemmological texts identify six garnet end-member species; the pyralspite group – pyrope, almandine and spessartine; and the ugrandite group – grossular, andradite and uvarovite^{8,10,11}. A garnet species in its theoretical pure form is referred to as an end-member, however they have not been found pure in nature. Natural garnets are always a mix of several end-members, typically with three to five species of significant quantity¹². The mineralogist recognizes fifteen garnet end-members – some of which exist only in theory¹². In this article

we will consider eight of them, adding knorringite and goldmanite to the more familiar six (*Table D*). The mineralogist names any of the mixed garnets by the name of the dominant end-member¹². Thus, although a pyrope may contain less than 50% of the pyrope molecule, it can still be the dominant component when more than two end-members are present, which is commonly the case.

Due to the difficulty of getting sufficient compositional information quickly and easily, gemmology has generally followed a different nomenclature, opting to define nine varieties of garnets: pyrope, pyrope-almandine, almandine, almandine-spessartine, spessartine, spessartine-pyrope, grossular, grossular-andradite, and andradite^{5,6,7}. Uvarovite is normally not included as it has limited gem significance. To date, gemmologists have not come to an agreement on what value of RI should mark the separation between



Spessartite garnet. Photo by R. Weldon.

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Table 1: Properties and chemical formulae of the end-member garnets considered in this paper.

End-member	RI	SG (calc.)	Volume susceptibility (k) (calc.) $\times 10^{-4}$ SI	Chemistry
Pyrope	1.714	3.582	-0.225	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Almandine	1.829	4.315	40.7	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Spessartine	1.799	4.197	47.45---	$\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Grossular	1.734	3.594	-0.225	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Andradite	1.887	3.859	30.76	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$
Uvarovite	1.865	3.850	12.9	$\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$
Goldmanite	1.834	3.765	6.9	$\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$
Knorringite	1.875	3.835	13.68	$\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$

N.B. ^{12, 18}

these arbitrary boundaries in the garnet chemistry continuum⁸. Adding further to the confusion, gemmologists classify, mostly by colour, eight commonly-used trade names of these nine varieties; chrome pyrope, rhodolite, malaia, colour-change pyrope-spessartine, tsavorite, hessonite, topazolite, Mali and demantoid⁵. Note that these are their gemmological classes, not mineralogical classes. With trade names, it becomes yet more complicated, but no more accurate.

From our studies, we do not believe that gemmologists, relying only on RI, spectrum, and colour can reliably — or consistently — allocate the correct species or varietal name to a garnet being studied. Gemmological texts often imply, for example, that tsavorite, because it is coloured by vanadium and/or chromium, is allochromatic, when in fact it is a combination of garnet end-members that creates the colour. Very often there is a third (or even more) end-member present, that while less than 10% in quantity, can yet affect the RI and colour in such a way as to lead to a false conclusion by the traditional methods. Problems with the current state of affairs will become apparent later in this paper.

History

The mineralogical literature abounds with papers on the garnets¹². Much of the information has limited relevance to gemmology in the classification and identification of gem garnets, as stones of gem quality comprise only a very small proportion of the whole, and

gemmological identification methods must be non-destructive. In a series of articles on the garnets, Manson and Stockton^{1,2,4} and Stockton and Manson^{3,5} presented an in-depth study on 202 transparent, gem-quality garnets that is invaluable to gemmologists for presentation of the chemistry and physical properties of each of the studied garnets. In their final paper of the series⁵ (p.215), they set the precedent for the garnet classifications currently in use.

Manson and Stockton obtained their accurate garnet chemistry analyses using microprobe equipment not available to the average gemmologist. It should be noted that while they measured the specific gravity (SG) of each gem, they do not use SG at all in characterizing gem garnets⁵. In fact, they state (p. 216): “Although we generally discourage the use of this property in gemmology, it nevertheless can provide some useful indications.” We will see why they may have done this later on.

Mineralogists often use another method of quantitative measurement of garnet, — its unit cell length. This measurement of the length of one edge of the unit cell, from X-ray diffraction data, is not practical for the gemmologist. Sriramadas¹³ has published eight ternary diagrams for the garnet group showing RIs and unit cell lengths on the triangles. Winchell¹⁴ notes that ternary diagrams are mostly used to estimate composition from measured physical properties, but that generally there are too few properties to uniquely define the composition. Using the

garnet group as an example, he shows how treating two physical properties as independent variables, one can plot the compositions, and yet another physical property on the same graph. In essence, one can put the information of the eight plots of Sriramadas, on one graph. Winchell¹⁴ uses RI and cell length on the Y and X axes, and shows SG variation within each ternary diagram, which now becomes a general triangle. He recognizes, as others have, that SG is not a very reliable measurement for determining chemical composition.

The Manson and Stockton papers^{1,2,3,4,5} note that virtually all gem garnets can be described by five end-members; namely, pyrope, almandine, spessartine, grossular, and andradite. Deer *et al.*¹² note that these five members usually make up more than 99% of any garnet's composition. This will be important in what follows. Stockton and Manson⁵ also note that Cr⁺³, V⁺³ and Ti^{+3,+4}, although important for colour in some garnets, can be treated as trace elements, and not as components of other end-member gem garnets, at least for this method of classification.

Johnson *et al.*⁶ add another important contribution to gem garnet chemistry with a paper on the Mali grossular-andradite garnets. These gems are ugrandites with typical yellow-green stones averaging about 80% grossular, 18% andradite and 2% pyrope. It is important to note that these are typically strongly zoned; hence, their physical properties will vary as well as their colour across the zonation. In these Mali garnets, pyrope is typically 2 to 3% with almandine and spessartine much less. They noted that mineralogists may use physical properties such as unit cell length, RI and SG to determine garnet composition from end-member values, and tested how well their data served to match determined chemistry. They found that, for the Mali garnets, RI correlated well with the garnet chemistry, while there was poorer correlation with other physical properties, especially SG which was determined hydrostatically. It would be expected that since the Mali garnets are almost entirely grossular-andradite, only one property is needed to define the

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chemistry and RI would do this.

Adamo *et al.*⁷ recently described correlations between physical properties and chemistry for 17 gem-quality garnets in both the ugrandite and pyrospite groups, and also examined IR spectral features to see what they may contribute to classification of the garnets. They concluded that IR spectra, in particular, permit discrimination between the pyrospite and ugrandite series. Their data generally agree with what was found by Manson and Stockton^{1,2,3,4,5}. Three hessonites contained from 84.5 to 92.75% grossular with andradite the other major component at 5 to 14%. Pyrospite members were under 2.1%. The two tsavorite measured showed about 90% grossular, and 4% goldmanite (vanadium garnet). Of ten pyrospites measured, grossular contents ranged from 0 to 6.15%, the andradite component was generally under 1% but in one sample was 8.3%. Uvarovite reached 1.7% in a chrome-pyrope, and goldmanite 3.65% in a colour-change pyrope-spessartine. The chromium content of a garnet may be expressed as either uvarovite or knorringite, but since knorringite is stable only at very high pressures (greater than 70-100kbar)¹², the chrome in most gem garnets is probably better considered as part of the uvarovite end member. An important exception may be in some gem chrome pyrope.

Adamo *et al.*⁷ used the same garnet nomenclature as Stockton and Manson⁵ but added the variety grossular-andradite, based on the work of Johnson *et al.*⁶

It was in 1933 that Winchell divided the garnet group into two series composed each of three major garnet species – the ugrandite series (uvarovite, grossular, andradite), and the pyrospite series (pyrope, almandine, spessartine). These two mineralogical series do not appear to be as well known to gemmologists as they should be. Although complete solid solution between natural members of each series was believed possible, there appeared to be a compositional gap between them. Modern studies on the garnets have shown there to be more miscibility between the various garnet end-members than

Table II: Some paramagnetic ions, their valencies, effective magnetic moments, and the square of the moment, which is proportional to the magnetic attraction.

Ion	Magnetic moment (experimental)	Magnetic moment squared (relative attraction)
Transition elements:		
Fe ³⁺ , Mn ²⁺	5.9	34.8
Fe ²⁺	5.4	29.2
Mn ³⁺ , Cr ²⁺	4.9	24.0
Co ²⁺	4.8	23.0
Cr ³⁺ , V ²⁺	3.8	14.4
Ni ²⁺	3.2	10.2
V ³⁺	2.8	7.84
Cu ²⁺	1.9	3.61
Ti ³⁺ , V ⁴⁺	1.8	3.24
Rare-earth elements:		
Dysprosium Dy ³⁺	10.6	112.
Holmium Ho ³⁺	10.4	108.
Erbium Er ³⁺ , terbium Tb ³⁺	9.5	90.
Gadolinium Gd ³⁺	8.0	64.
Thulium Tm ³⁺	7.3	53.
Ytterbium Yb ³⁺	4.5	20.
Neodymium Nd ³⁺ , praseodymium Pr ³⁺	3.5	12.2
Europium Eu ³⁺	3.4	11.6
Cerium Ce ³⁺	2.4	5.7
Samarium Sm ³⁺	1.5	2.2

previously thought but the two series do show structural differences and most gem garnets appear to fall within or close to one series or the other.

Magnetic measurements

Modern understanding of magnetism shows that it arises from the motion of electrons in atoms in the same way that an electrical current in a wire produces a magnetic field about the wire. Within the atom, electrons move in orbits about the nucleus and also spin. Both of these motions produce very small magnetic dipole fields, so the electrons act as very small permanent magnets within the atom. The magnetic property of any material is the resultant of the contributions of all of its atoms and how this reacts to an applied magnetic field. More on this complex subject can be obtained from Kittel¹⁵, college physics texts, or the Internet.

We will be primarily concerned with

magnetic susceptibility per unit volume, k , a bulk property of all materials, that can be directly measured. These materials can be classified in three distinct groups according to the sign and value of their magnetic susceptibility.

The orbiting electrons about an atom of any material, when in the presence of an applied field, will precess, presenting a weak opposing magnetic field. Precession is the wobble that a toy top makes when the spin axis is not in line with the vertical direction. If no other magnetic effects are present, these materials will be weakly repelled by a magnet, and k will be negative. Such materials are called diamagnetic. Most gems are diamagnetic.

In some atoms and molecules there is a net magnetization generally related to electron spin, but which in bulk is zero due to thermal motion of the atoms. However, when a field is applied they can become oriented to give a small net positive susceptibility, overcoming the

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negative value due to diamagnetism. Such materials are called paramagnetic. The elements contributing to this type of magnetism, that are relevant to gemmology, are the transition and rare-earth elements. These elements, while best known for their colour causing properties, whether as major or trace components in many gems, also have paramagnetic properties.

As shown in *Table II*, the manganese- and iron-bearing gems will have the greatest paramagnetic susceptibilities, as the rare-earth content of most gems is small. Thus, magnetic testing will indicate the presence or quantity of these elements, just as absorption spectra show their presence by the absorption of light. Paramagnetic gems are of the most interest in gem characterization and identification by means of susceptibility measurements. The table shows the square of the measured effective ion moment, because this is directly proportional to susceptibility.

Ferromagnetic materials have much larger absolute susceptibilities than diamagnetic or paramagnetic materials due to a natural alignment of magnetic moments of the individual atoms. They are further distinguished by being made up of small individual magnetic domains in which the magnetization may not be the same as a neighbour. To the gemmologist, ferromagnetic minerals, such as magnetite, are of interest where they may be present as inclusions, but are generally of less importance than paramagnetic minerals.

In the past, non-laboratory gemmologists have had only two truly quantitative, physical tests available by which to characterize gemstones. These are refractive index (RI and related birefringence) and SG. Unfortunately, RI and SG are not very independent variables, as many years ago Gladstone and Dale (quoted in Larsen and Berman¹⁶) showed that the ratio of RI to SG is approximately a constant, $(RI-1)/SG=k$. Because of the Gladstone-Dale relationship, and the fact that accurate measurement of SG is generally difficult, mineralogists and gemmologists



Figure 1: Apparatus used to measure magnetic susceptibility in this study.

often marginalize the use of SG for characterization of their materials. This is clearly one of the reasons that Stockton and Manson⁵ didn't make use of SG in their work.

By having a new, independent, quantitative physical property by which to characterize gems, the gemmologist now has much greater scope to characterize gemstones than before. Not only can we measure a gem's susceptibility, but we can also calculate what its susceptibility should be from its chemistry when known; or, with certain assumptions, calculate the quantity of a transition metal in a gemstone as shown by Hoover and Williams⁹.

Making magnetic susceptibility measurements

The basic theory behind susceptibility measurements has been described in a

previous article⁹, where the magnetic attraction (pull) between a very small Neodymium-iron-boron (NdFeB – or NIB) magnet and the flat table of a cut gem was measured on an electronic scale. If the NIB magnet pole face is smaller in diameter than the gem's table, then the pull is a direct measure of the gem's susceptibility. We have used cylindrical magnets of $\frac{1}{4}$, $\frac{3}{16}$, $\frac{1}{8}$ and $\frac{1}{16}$ inch diameters by $\frac{1}{2}$ inch long. These N42 grade NIB magnets are available from K&J Magnetics Inc. (www.kjmagnetics.com). These are inexpensive, but very strong. We recommend following the manufacturers warnings regarding use. For the best precision, the largest magnet that fits within the stone's table should be used. For all measurements shown in this paper we used a $\frac{1}{8}$ inch magnet, which allowed measurements on stones of one carat or larger. In order to convert this pull

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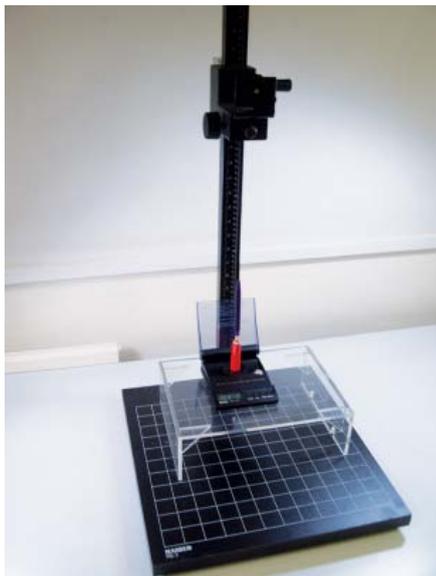


Figure 2 (above): An early prototype using a photo stand. While less precise than later set-ups, this arrangement proved useful for experimenting with the technique.

into a measure of the gem’s susceptibility one need only measure a material of known and consistent susceptibility — a standard. A standard can be any paramagnetic material in which the paramagnetic element that causes the magnetic susceptibility is equally distributed and in consistent quantity.

For our testing purposes, we used cobalt chloride (CoCl₂·6H₂O) with a pull of 0.855 ct (measured with one of our 1/8 inch (3.12 mm) magnets) and susceptibility of 9.87 × 10⁻⁴ SI units. The equation below shows the relationship to determine an unknown susceptibility from pull measurements.

<p>Equation 1 $k = C \times \text{Pull}$ where Pull = measured pull of the test stone and $C = \frac{k \text{ (of standard)}}{\text{Pull (of standard)}}$</p>

As an example, a 3.10 ct pyralspite has a pull of 1.135 ct with the 1/8 inch magnet. Its susceptibility, $k = [9.87 \times 10^{-4} \text{SI} / .855 \text{ ct}] \times 1.135 \text{ ct} = 11.54 \times 10^{-4} \text{SI/ct} \times 1.135 \text{ ct} = 13.10 \times 10^{-4} \text{SI}$.

The concept is very simple, but the measurement must be done with care and it takes some practice to become consistent. The equipment is shown in Figures 1, 2 and 3. The authors

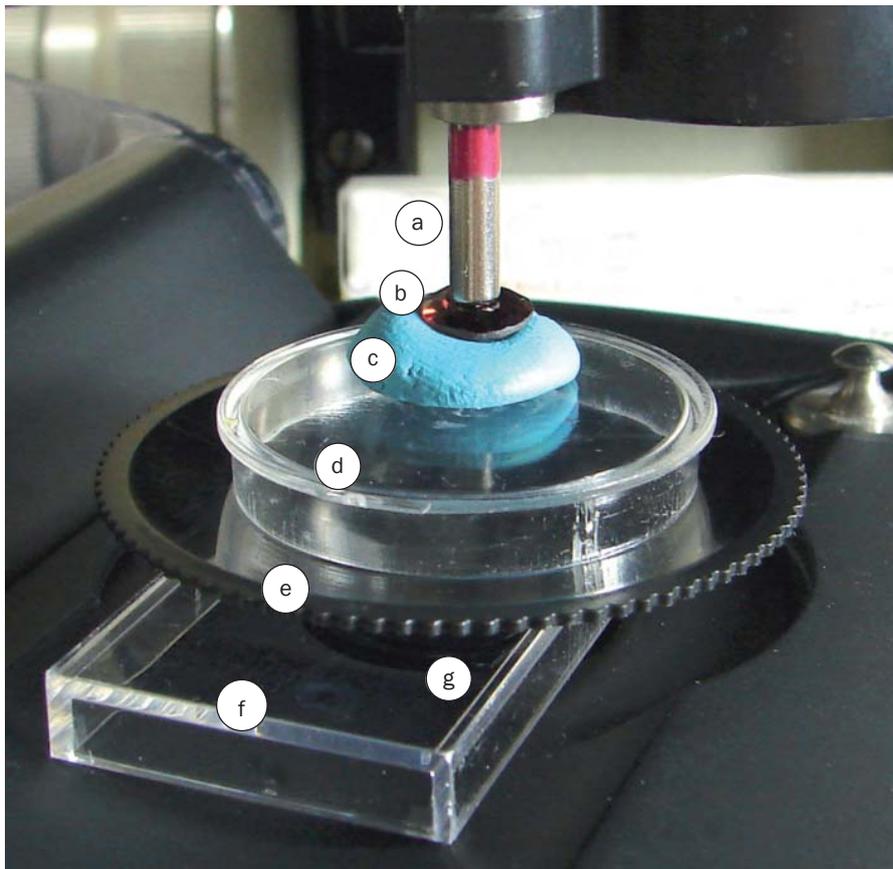


Figure 3 (right): Close-up of magnet and stone interface on scale. a) cylindrical NIB magnet; b) stone under test; c) Blu Tack ring support to hold the stone; d) non-magnetic stone support; e) scale measuring cup; f) bridge support – to avoid pressure on the scale while the stone table is made parallel to the magnet face; g) scale’s active surface (underneath the bridge).

are continuing to investigate ways to improve the apparatus and technique, but believe that their present method is quite adequate for garnet characterization.

The current apparatus is a surplus biological microscope stand containing a fine focus mechanism, and an x-y translation stage for centring the gem table with the magnet face. In place of the microscope optics is a plastic fitting with a steel bolt at its centre, to which a cylindrical magnet of whatever size needed may be placed. This holds the magnet in a fixed, stable, and rigid position. The fine focus knob raises and lowers the microscope stage by micrometres, with a macro knob for larger adjustments.

For measuring the force of the magnetic attraction, a small digital scale was placed on the microscope stage. We used a GemOro PCT50 scale, but any similar scale that measures to 0.005 ct should work. The gem is placed on a

non-magnetic pedestal, table up, and held in place with Blu Tack, then placed within the scale’s measuring cup. A number of precautions need to be observed in order to obtain accurate and reproducible measurements. First, the magnet and gem table must be absolutely clean and free of all grease, dirt and dust. An antistatic brush will help prevent static electricity from affecting measurements, as well as aid in the removal of charged dust, especially in cold climates. One needs to regularly check the magnet pole surface, as these very strong magnets tend to acquire minute specks of magnetic particles, which must be removed before measuring.

Once these precautions are satisfied, it is critical to make the magnet pole surface and the gem’s table exactly parallel. This is done by placing the gem within a bit of Blu Tack so that it is held in place along the girdle. A rigid bridge consisting of a 1/8 inch plastic sheet measuring 1 by 2 inches

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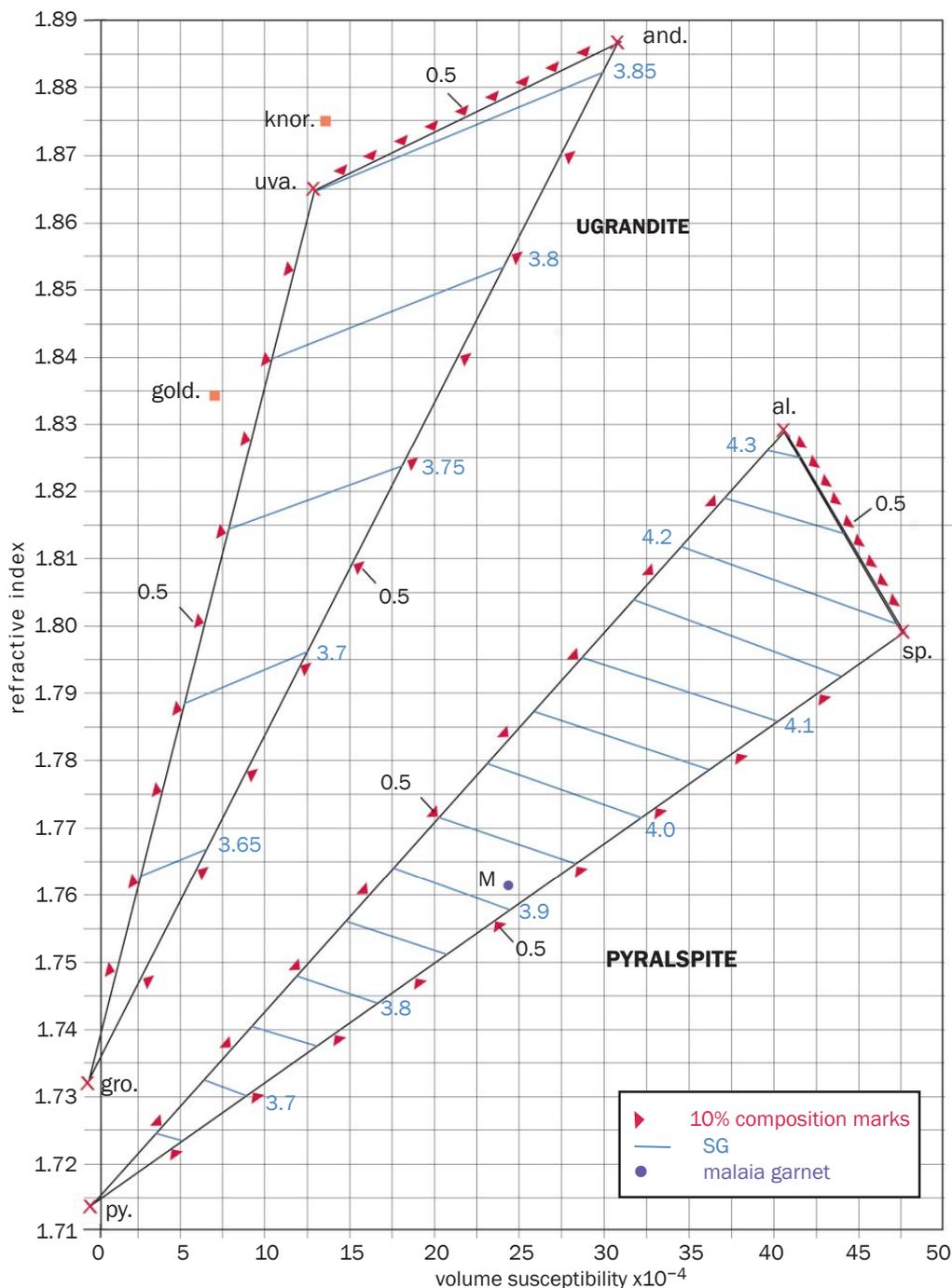


Figure 4: Plot of RI versus magnetic susceptibility for the garnet end-members pyrope, almandine, spessartine, grossular, andradite, uvarovite, goldmanite and knorringite. The pyralspite and ugrandite ternary triangles are shown with 10% triangles (red) shown along sides, and SG variations (blue) within each ternary. The purple data point (M) in the middle of the pyralspite ternary is that of a malaya garnet we measured.

is placed above the scale's recessed active surface and the measuring cup placed on this bridge. This then permits the magnet and gem table to be brought in contact and pressure put on the interface, so as to push the gem into the Blu Tack and align the two surfaces exactly parallel. With the bridge in place, the magnet is separated a millimetre or less from the gem table, and the surfaces viewed from two directions,

at about 90 degrees difference, to be sure that they are parallel. Once the surfaces are parallel, the microscope stage is lowered, the bridge removed, and the measuring cup placed back on the scale. Again, check that the table and magnet face are parallel. In practice, we have had little problem in parallelism after the bridge is removed if care is taken. Next, the magnet and gem are separated

by several centimetres, and the scale is turned on and tared. Then the microscope stage is gradually brought up to meet the magnet, and the maximum attraction measured. A magnetic attraction will show as a negative reading. Upon contact of the magnet with the gem, the scale reading will go in a positive direction. The maximum negative reading is the 'pull'. This number is then converted to k, using

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the formula (1).

A diamagnetic gem will give a very small positive measurement, due to the ‘push’ or repulsion of the stone by the magnet. For a 1/8-inch magnet, this will typically be about 0.02 ct.

As more individuals try their hand at such measurements there undoubtedly will be better methods developed for their implementation. At present, this method gives the best results for us.

Results

A ternary diagram, sometimes called a triangular plot, is a simple graphical tool to show chemical compositions in a three-component system. The diagram is an equilateral triangle where 100% of a component is plotted at each triangle point. Zero percent of that component would be at the opposite side and the centre point of the triangle would represent 33.3% of each. They are often used to determine garnet composition, and have been described and used in the papers by Manson and Stockton^{1,2,3,4,5}. The pyralspite and ugrandite groups are examples, but if other garnet end-members are important in a garnet, additional diagrams are needed. For the five principal garnet end-members, grossular, andradite, pyrope, almandine and spessartine, ten ternary diagrams would be required to cover all possibilities for three major components¹⁴. Where four components are involved it becomes a bit more complex, but details can be found in Hutchison¹⁷ (p.374 *et seq.*).

Because many physical properties of minerals have been shown to be approximately linear functions of the proportions of their components, the ternary diagrams can also show the variation of a physical property (P) with chemistry within the triangle^{14,17}, summarized in the following equation:

Equation 2

$$P = \sum p_i m_i = p_1 m_1 + p_2 m_2 + p_3 m_3 \dots$$

where p_i = the property of the i th end-member such as RI, and m_i = the mole percent of that end-member in the composition.

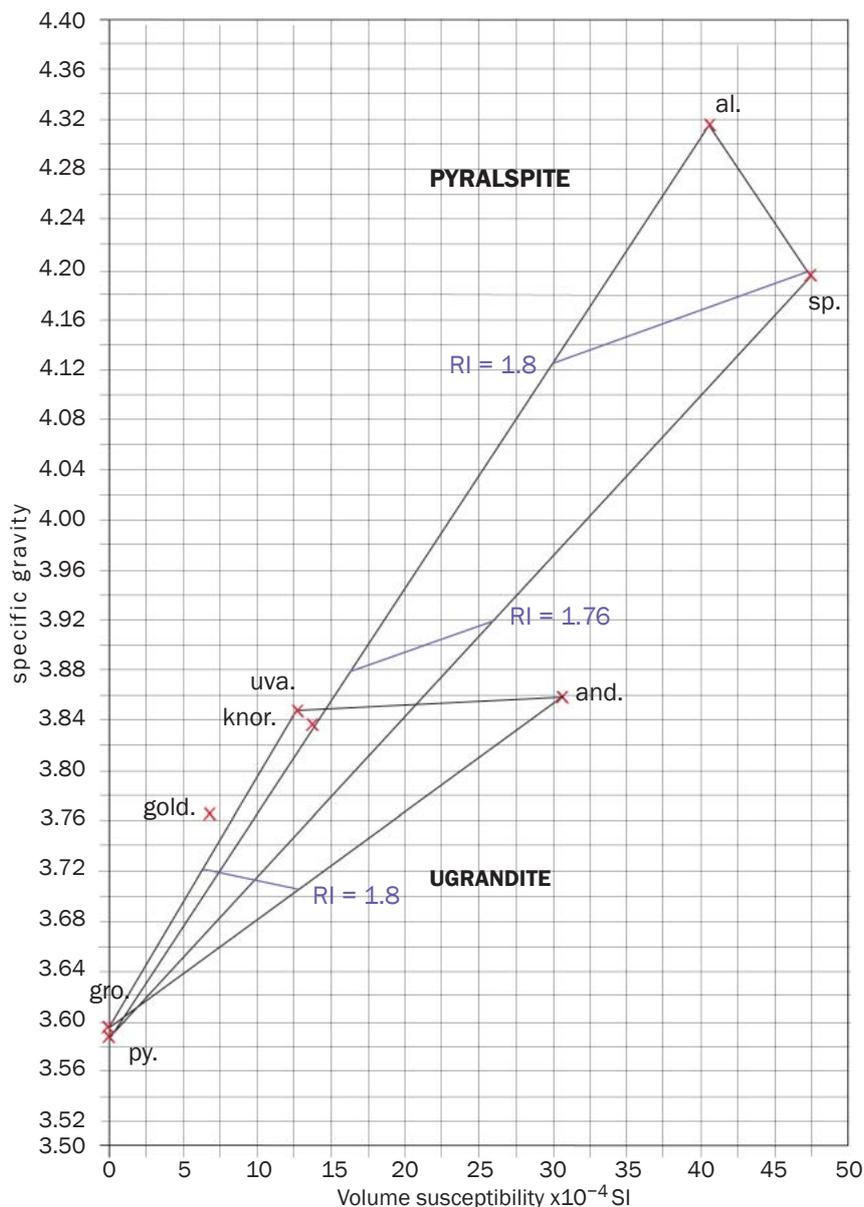


Figure 5: Plot of SG versus magnetic susceptibility for the garnet end-members pyrope, almandine, spessartine, grossular, andradite, uvarovite, goldmanite and knorringite. The pyralspite and ugrandite ternary triangles are shown with reddish purple lines indicating lines of constant RI.

Because we wish to distinguish between the various garnets, the statement by Deer *et al.*¹² (p.497) on the subject is worth reviewing: “Within the garnet group the various species are best distinguished by their RIs, SGs and cell edges in conjunction, if possible, with partial chemical data, e.g. for FeO or MnO. The entry of even small amounts of the uvarovite molecule to the ugrandite series imparts an emerald-green colour in hand specimen; chrome-pyrope is usually reddish but some show a green hue.”

Because most gemmologists are not normally able to measure the cell edge

dimension of a garnet, we will substitute the value of magnetic susceptibility for this, and plot RI against magnetic susceptibility. This provides information on the FeO and MnO that Winchell¹⁴ called for.

Proposed new garnet characterization technique

In order to effectively use the plot in Figures 4 and 5, one needs to understand how the values of each end-member garnet are shown. The gemmological properties of RI and SG, for the eight

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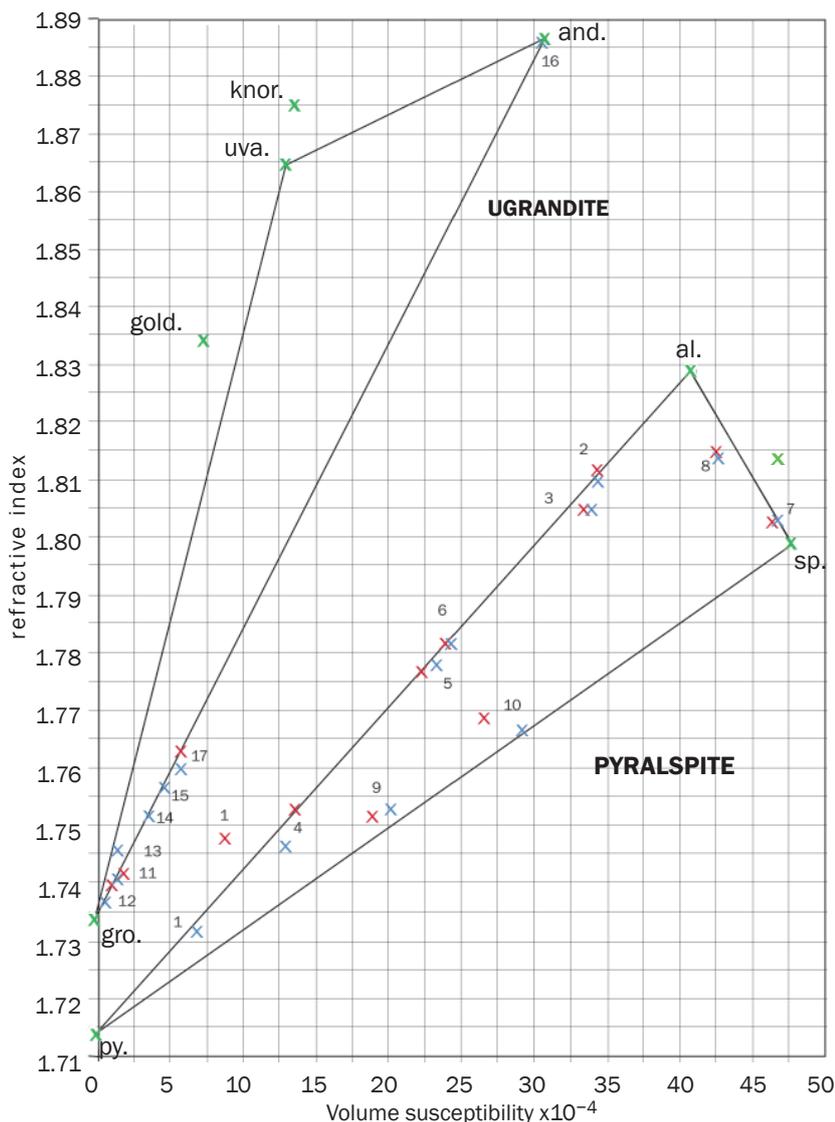


Figure 6: Plot of RI versus magnetic susceptibility for the garnet end-member data of Adamo et al.⁷ Red crosses are calculated for all end-members found, blue crosses are for the three main end-members of each series.

end-member garnets we will consider, are taken from the mineralogical literature^{12,18}. The values for their magnetic susceptibilities have been calculated based on ‘ideal chemistry’ as shown in Table I and mean measured moments from Table II by use of the Langevin equation¹⁵.

Figure 4 illustrates the basic plot used, with RI on the Y-axis and magnetic susceptibility (k) on the X-axis. Of the eight principal garnet end-members plotted, the commonest six are joined to demonstrate the ternary diagrams. These are the pyralspite and ugrandite triangles (which are no longer equilateral) with the end-member abbreviations shown at each corner. Small red triangles along each side

mark 10% intervals, with the 50% position labelled (0.5). Blue lines and numbers mark SG values, assuming only pyralspite or ugrandite components are present.

As can be seen in Figure 4, if one has a pyralspite garnet with no other garnet components, then it must plot within the pyralspite triangle, but if a measured garnet is within the triangle, how does one determine what its pyralspite composition is? Consider a malaia garnet that we measured with an RI of 1.762, and susceptibility of 24.1×10^{-4} SI. This is plotted in Figure 4 as a purple spot (M). From its position in the triangle, it is apparent that this garnet is a pyrope-spessartine-almandine. First,

one prints the illustration to a piece of paper so that lines can be drawn and measured. Additionally, this is available for downloading from one of the author’s websites (www.stonegrouplabs.com go to ‘Articles and Papers’, then ‘Garnet Chart’). The scale of the printout is irrelevant. From each apex of the pyralspite ternary, draw lines through the data point (the purple dot). Next, measure the length of the line between the pyrope apex to the opposite base, and the length between this base and the data point. When we did this, the measurements were 163 mm and 77.5 mm. The ratio $77.5/163 = 47.5$ is the proportion of pyrope in the garnet. Doing this for the other components, we find 42% spessartine, and 11% almandine. These total 100.5% when added, showing minor graphical measurement error, but still a far more accurate idea of the components than would otherwise be known. This malaia garnet would be described as approximately $Py_{47}Sp_{42}Al_{11}$. The precision of all measurements is important to accurately define the chemistry. Based on our repeat measurements we estimate that RI should be within +/- .001 and susceptibility about +/- 1×10^{-4} SI. Thus, the error bars are of similar magnitude on the graphs for the scales used, suggesting that each property measurement contributes to a similar error in chemistry.

Note that it only requires values of RI and k to be able to specify the three pyralspite components. A value of the SG, if accurate, would be able to confirm the composition, or if accurate and not in agreement would indicate the presence of one or more additional end-members.

With this understanding, it should be clear that if we take the malaia garnet and add a little andradite, but keep the pyralspite components balanced, the data point would move up in RI, with very little change in susceptibility. Adding a little grossular would pull the point down and to the left. In this figure, for clarity we have shown only the two principal garnet ternary diagrams, but clearly one could draw in all the others. Other results presented below from pyropes and almandines plot within the grossular-

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pyrope-almandine triangle, indicating that these garnets most likely contain a measurable grossular component.

These can be computed in a similar manner to pyralspites or ugrandites, by closing the lines for the relevant triangle – grossular, pyrope and almandine.

We want to emphasize that the only change that we are making to long-used mineralogical techniques¹⁴ is the substitution of magnetic susceptibility for unit cell length.

Another way to present the RI, SG, and k data is shown in *Figure 5*, which has SG on the Y-axis and magnetic susceptibility on the X-axis, giving additional insights into property variations. *Figure 5* shows that there is an overlap between the pyralspite and ugrandite groups below an SG of 3.86. The violet lines in each group mark lines of constant RI. The diagram clearly shows there is complete separation between the two groups for indices above 1.80. This is particularly important for the identification of garnets whose RI is above 1.80, where most gemmologists cannot obtain measurements. Thus, SG can be substituted for RI using this new technique. As *Figure 5* shows, andradite, almandine and spessartine can be distinguished on the SG-susceptibility chart at the higher RIs.

Using *Figure 4* as the basic diagram and by taking published compositions from the literature, we can now calculate what their RIs, magnetic susceptibilities and SGs should be. This can be done using as many end-member components as we have values for. However, in using such chemical data, one needs to be aware of the problems of calculating end-member molecules from chemical analyses as noted by Deer *et al.*¹² Conversely, we can estimate what the compositions could be, based on the measured values of the properties, for each three-component system if we have two properties, or for four-component systems if we have values of RI, susceptibility and SG. In many cases, there will be more than one combination of end-members that can fit a given physical property set. It is up to the gemmologist to choose which possibility is most probable. We believe this new

Table III: Comparison of measured and calculated properties of selected garnets from Adamo *et al.*, 2007.

Specimen number	Property	Measured	Calculated on basis of		Composition
			All end members	Three main end members	
1	RI	1.741	1.748	1.732	Py ₇₅ Al ₁₄ Sp _{0.7} An _{8.3} Uv _{1.7}
	SG	3.68	3.719	3.704	
	Susc. #		8.79	6.69	
2	RI	>1.79	1.812	1.81	Py ₁₅ Al ₈₁ Sp _{1.1} An _{2.3}
	SG	4.19	4.190	4.196	
	Susc. #		34.20	34.27	
7	RI	>1.79	1.803	1.803	Py _{0.4} Al ₁₂ Sp ₈₇ Gr _{0.4} An _{0.6}
	SG	4.13	4.207	4.212	
	Susc. #		46.34	46.62	
10	RI	1.775	1.769	1.767	Py ₃₄ Al _{1.1} Sp ₅₄ Gr _{5.4} Uv _{1.0} Go _{3.6}
	SG	4.00	3.935	3.963	
	Susc. #		26.53	29.11	
11	RI	1.738	1.742	1.741	Uv _{0.5} Gr ₉₃ An _{5.1} Py _{1.4} Sp _{0.7}
	SG	3.59	3.612	3.607	
	Susc. #		1.70	1.35	
12	RI	1.741	1.740	1.737	Uv _{1.1} Gr ₉₁ An _{0.5} Py _{2.1} Sp _{1.5} Go _{3.7}
	S.G	3.62	3.612	3.600	
	Susc.		0.94	0.45	
16	RI	>1.79	1.886	1.886	An _{99.2} Py _{0.7} Al _{0.06} Sp _{0.04}
	SG	3.88	3.857	3.857	
	Susc.		30.55	30.56	
17	RI	1.766	1.763	1.760	Uv _{0.1} Gr ₇₈ An ₁₉ Py _{2.8} Sp _{0.2}
	S.G	3.66	3.645	3.680	
	Susc.		5.76	5.68	

NB: Calculation based on equation (2)

Magnetic susceptibility all $\times 10^{-4}$ SI

technique for indirect determination of garnet chemistry, permitting better characterization of the garnet group, is a major step forward in gemmology.

Determination of properties from chemistry

As an example of using compositions to determine properties, we have plotted on *Figure 6* RI and susceptibility data calculated for the pyrope and ugrandite garnets of Adamo *et al.*⁷ using equation (2). Values in red are derived using all the end-member compositions given by Adamo *et al.*, while those in blue are for only the three main components of either the pyralspite or ugrandite subgroups,

and normalized to 100%, much as Manson and Stockton⁵ have done. The numbers on each data point correspond to those of Adamo *et al.*⁷ The end-member garnets (*Table I*) are indicated by green crosses and labelled. The pairs of red and blue crosses, generally, are fairly close. In *Table III* is a selection comparing these calculated values against measured values given by Adamo *et al.* The analyses of the ten pyralspites showed seven end-members present, but no individual specimen with all seven. Four to six end-members were found between these pyralspites, with half needing only four end-members to describe them. Grossular and andradite were the largest

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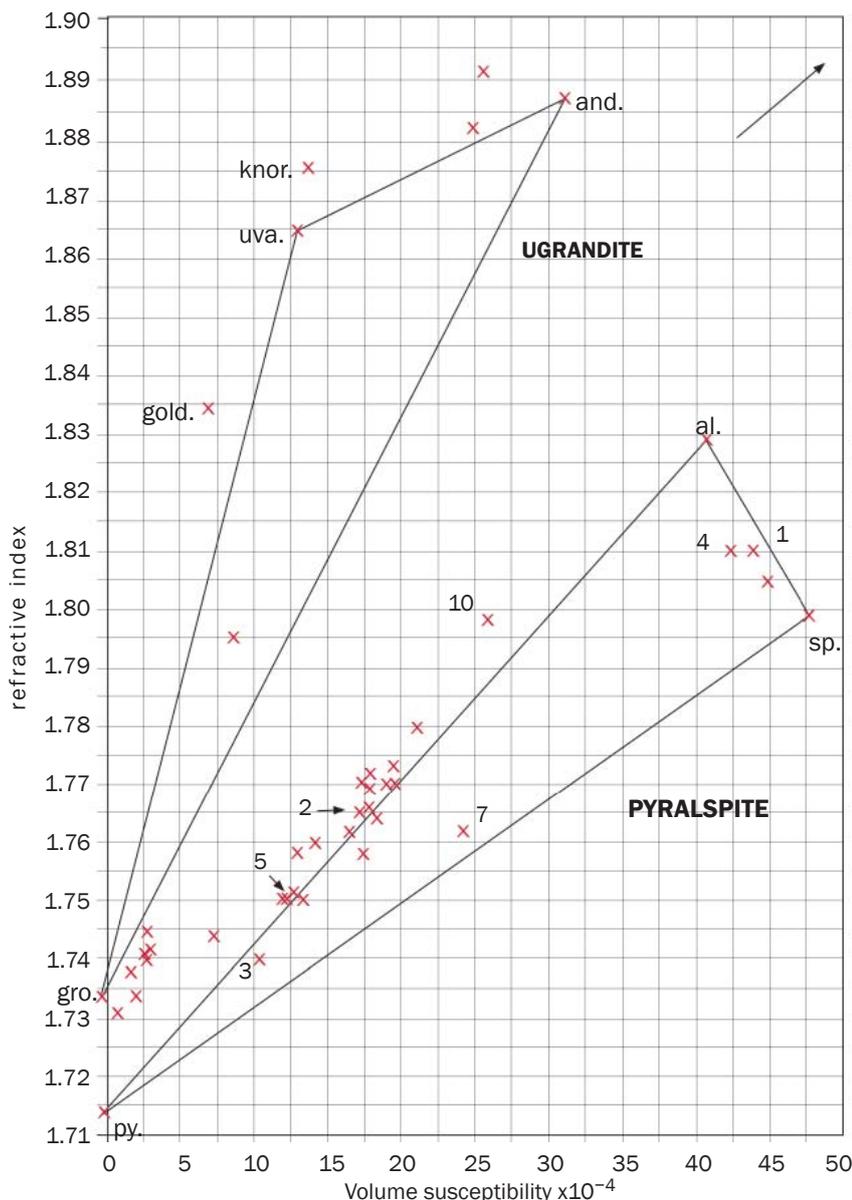


Figure 7: Plot of RI versus magnetic susceptibility for a series of garnets measured by the authors. The pyralspite and ugrandite ternary triangles are shown.

non-pyralspite components found. The chrome pyrope, specimen 1 of Adamo's list (Figure 6), shows the greatest divergence between values based on the pyralspite component (blue cross within the pyralspite ternary diagram) versus complete chemistry. This stone had 8.3% andradite, and 1.7% uvarovite mixed with pyrope, almandine and spessartine components. The shift in graph position is toward the uvarovite-andradite positions, as would be expected. The other specimens in this series, 2–10, had 2.3%, 1.6%, 4.01%, 5.04%, 1.25%, 0.98%, 0.8%, 6.1%, and 10% non-pyralspite components respectively.

In the ugrandite group specimens (Table III and Figure 6), the data show the grossular garnets stretched out on the grossular-andradite join up to about 20% andradite (specimen 17). This is a similar pattern to that found by Manson and Stockton². Some of the red crosses do not show because of overlap with the blue ones. In Table III the measured and calculated property values of a selection of the ugrandites can be compared. One andradite (16) is essentially pure and this is typical, as most natural andradites are compositionally close to the end-member¹².

The distribution of points in Figure

6 shows that for these gem garnets, measurements of the RI and susceptibility correlate with the chemical composition rather well, remembering that the red crosses represent the practical measurements. Chrome pyrope, the garnet with the widest spread between red and blue values (specimen 1), shows that it can't be well characterized as a pure pyralspite and that some additional component needs to be considered, such as andradite or uvarovite.

The data of Adamo *et al.*, although far fewer in number, illustrate what Manson and Stockton^{1,2,4} and Stockton and Manson^{3,5} found: in general, gem andradite and grossular fall close to their respective end-members in the ugrandite ternary diagram; gem almandine and pyrope fall along the pyrope-almandine line with little spessartine present; and similarly for the almandine-spessartine group. The malaia (specimen 9) and colour-change (specimen 10) pyralspite garnets are mainly spessartine-pyrope with minor almandine. These values, we believe, are well correlated, including those for SG.

Estimation of chemistry from properties

For gemmologists, the most practical and quick means of determining the composition of a garnet is through magnetic susceptibility. We have measured the RI and susceptibility of 39 gem garnets from worldwide sources and the results are given in Table IV and Figure 7. Grossulars plot close to the end-member, as do the andradites. In the pyralspite group, most almandine-pyropes show little evidence of a spessartine component, and the almandine-spessartines show little pyrope. It is only the malaia garnets that have a strong mix of all three end-members. In Figure 7 the RIs of stones below 1.79 were measured with a conventional, critical angle refractometer. Those with RI over 1.79 were measured with a deviation angle refractometer, built by one of the authors (D.H.), making use of a laser pointer light source. The accuracy of this device is estimated at ± 0.004 and because the laser wavelength is

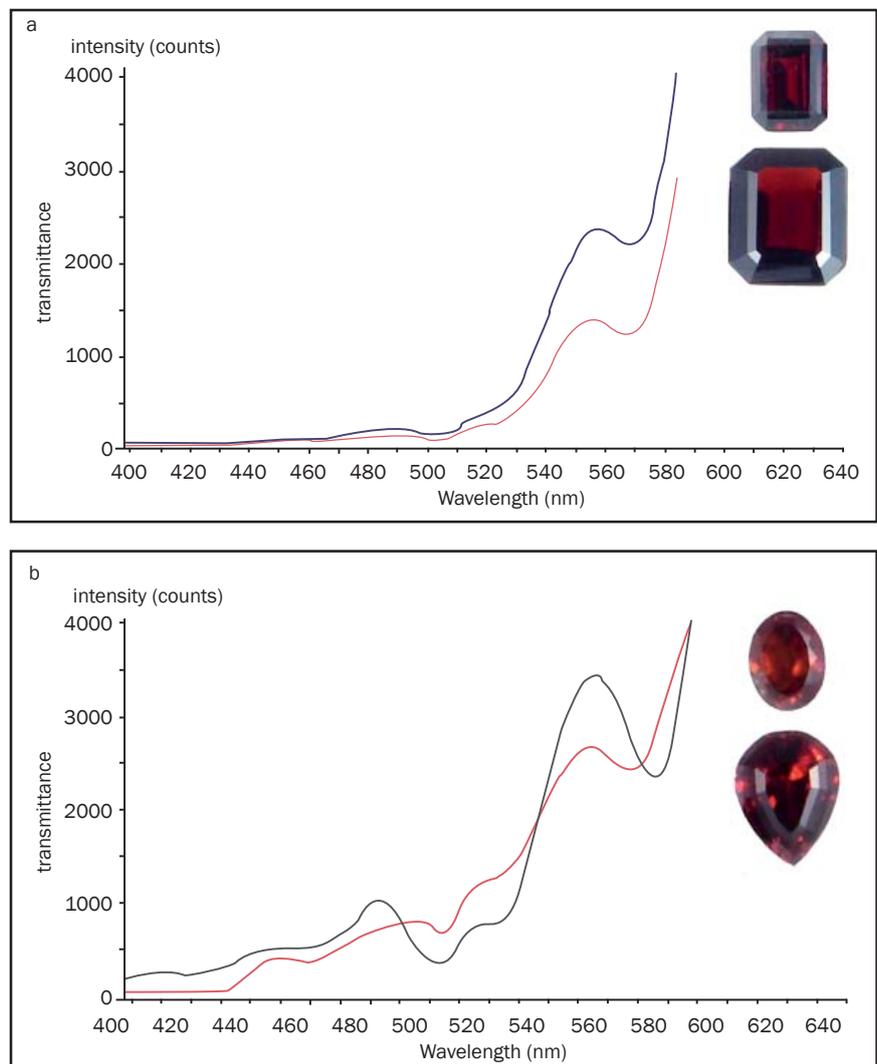
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Absorption spectra and chemistry

A thorough investigation of the use of absorption spectra to determine garnet species would require another paper; so to indicate the diagnostic limitations of this method, only a few features of the pyralspite series will be discussed. In the pyralspite garnets, it is the Mg^{2+} , Mn^{2+} and Fe^{2+} contents that determine the species. This gives us three choices when looking at a pyralspite spectrum, if, for the moment, trace elements are neglected, there is either an Fe^{2+} spectrum, a Mn^{2+} spectrum, or both. Stockton and Manson⁵ rely on the presence of the 410 and 430 nm Mn lines to indicate if any Mn is present. Rossman¹⁹ (p.218) notes: "Only the sharp 410 nm band is seen in the spectrum of many minerals with minor amounts of Mn^{2+} in the presence of greater quantities of Fe^{2+} ." This raises the question of whether Mn lines in many garnets can be identified with the hand spectroscope, as these weak lines are commonly hidden in the obscurity of the blue end of the spectrum. Pearson²⁰ also discusses the poor sensitivity at each end of the visible spectrum of the human eye and its limitations for identification of absorption lines in the blue to violet when using a hand spectroscope.

Figures 8a and 8b show pairs of similar spectra from garnets we have measured (specimens 1, 2 and 3, 4) in Figure 7. These transmission spectra were run on an Ocean Optics S2000 Spectrophotometer. The classic almandine absorption lines at about 505, 526 and 576 nm are present in all.

In Figure 8a the spectra of specimens 1 (spessartine) and 2 (pyrope) appear nearly identical. In the region between 400 and 500 nm, note that the 410 and 430 nm absorption lines used by gemmologists to identify Mn^{2+} (5) are not present. This was confirmed with the hand spectroscope, where only a cut-off at approximately 440 nm was observed. The 575 line was most apparent, the 505 was relatively strong,



Figures 8a and b: Graphs of transmission spectra for the four pictured garnets, showing similarities between pyrope and spessartine spectra. a) Red line is a 2.24 ct spessartine (no. 1); black line is a 4.19 ct pyrope (no. 2); b) Red line is a 1.61 ct oval spessartine (no. 4); black line is a 4.73 ct pyrope (no. 3).

and the 526 line could be seen by only one of the authors. No characteristic manganese lines could be seen.

In Figure 8b there are some small differences in spectra of specimens 3 (pyrope) and 4 (spessartine), especially a shift in the two troughs (absorptions) near 575 nm between the two spectra. The almandine lines are clearly prominent. The cut-off in the blue is near 430 nm, with no evidence of manganese lines at either 410 or 430 nm. There is also a weak absorption near 460 nm, but this is not recognized as a strong Mn line. There are no Mn lines visible with the

hand spectroscope. With the hand spectroscope, the authors observed only iron lines at 510 and 575, with a cut-off at approximately 430 for the 1.61 ct oval (red curve). The 526 line seen in 8b could not be distinguished with the hand spectroscope. For the 4.74 ct pear shape, two authors observed a cut-off at 400 and 430 nm, strong lines at 575 nm, a good line at 505 nm, and a weak line at 526 nm. In each of these sets, one stone is near the almandine-spessartine boundary with little pyrope, and the other primarily pyrope (Figure 7). Yet all stones have very similar colours.

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Table IV: Magnetic susceptibility and other properties of the garnets measured in this study.

No.	Species or variety	Weight ct.	Locality	Colour	RI	$k \times 10^{-4}$
1	spessartine	2.24	?	deep red	1.810	43.8
5	pyrope	3.42	Mozambique?	red	1.751	12.5
7	malaia	2.78	E. Africa	orange	1.762	24.1
10	almandine	2.57	India	deep red	1.798	25.8
14	tsavorite	2.54	E. Africa	medium bright green	1.731	0.69
15	demantoid	1.25	Russia	green	1.892	25.5
24	hessonite	3.73	Sri Lanka?	orange	1.741	2.54
25	'uvarovite'	17.97	Cab, S. Africa	fine deep green	1.795	8.53
28	rhodolite	1.55	Tocantins, Brazil	purple	1.77	17.2
29	rhodolite	7.75	unknown	purple-red	1.773	19.3

680 nm, the RI values were corrected for dispersion.

From the data given in *Figure 7*, it is apparent that these garnets can easily be separated into pyralspite or ugrandite groups based on RI and susceptibility values. If there is any question, SG should assist, due to the large density gradient between the two groups (*Figures 4* and *5*). Of greater importance is the power this gives us in identifying the chemistry of a particular gem within the pyralspite or ugrandite groups. As an example, look at the garnet labelled 5 in *Figure 7*. This 3.42 ct stone is on the almandine-pyrope line, so can be specified as approximately $\text{Py}_{68}\text{Al}_{32}$ with an RI of 1.751 and susceptibility of $12.5 \times 10^{-4}\text{SI}$. Of course, a mix of other different garnet end-members could be devised to give the same physical properties, but this is the simplest. This stone was sold as a Mozambique spessartine many years ago, but our data indicate clearly that it is predominantly pyrope. In colour, it is close to the other three adjacent pyropes.

The malaia garnet labelled 7 is an example where three end-members are present (see also M in *Figure 4*). It is approximately $\text{Py}_{47}\text{Sp}_{42}\text{Al}_{11}$, compared to the malaia measured by Adamo *et al.*⁷ (no. 9 in *Figure 6*), which was $\text{Py}_{52.7}\text{Sp}_{33.6}\text{Al}_{7.5}\text{Gr}_{6.1}$. The garnet labelled 10 was purchased as an Indian almandine,

but it falls above the almandine-grossular join, so must have some andradite or chrome garnet component. A clue to its probable composition is provided by Deer *et al.*¹² in the composition of one Indian garnet from Madras, which is $\text{Al}_{61.4}\text{Py}_{30.8}\text{An}_{5.9}\text{Sp}_{1.4}\text{Gr}_{0.5}$. This composition gives a calculated RI of 1.796 and susceptibility of 27.4×10^{-4} , remarkably close to that of the measured Indian almandine (1.798, 25.8). If one calculates the composition from its position in the pyrope-almandine andradite ternary diagram, one obtains a composition of $\text{Al}_{62}\text{Py}_{30}\text{An}_8$. This, we believe, is a good example of what can be done with this new technique.

Discussion

By plotting pairs of RI and susceptibility values for garnets as shown in *Figure 4* and following, one can directly define a garnet's chemistry based on the composition of any three selected end-member molecules. Because it has been found that 99% of most garnet compositions can be described by a combination of the five common garnet end-members^{5,12}, the probable compositions of any tested garnet are quite restricted.

Additionally, by plotting RI and magnetic susceptibility, the pyralspite and ugrandite series' ternary triangles are

quite separate and do not overlap^{12,14}. Clearly, a stone lying in the pyralspite ternary area will have a limited amount of any ugrandite component that could be present in order to fit measured physical properties.

The measurements of 39 stones plotted in *Figure 7* reveal variations in gem garnet chemistry that were not obvious from previous gemmological work^{5,6,7,10}. Looking at the pyrope to almandines near the line (join) between the pyrope and almandine end-members, it is clear that most of these have some measurable component from the ugrandite series garnets. This is evident by their plotting at higher RI values than the line along the join. If one looks at garnet chemistry given for example in Deer *et al.*¹² for pyrope, chrome-pyrope, and almandine, most analyses show a significant ugrandite component (or knorringite, in some stones) with one of these being the second largest component. This had been reported by Rouse¹⁰, but not emphasized. Our data show that this is rather common in gem garnets, and needs to be considered when discussing variations in garnet properties.

Further research and testing of this new method is called for in order to confirm results from this method with measured chemistry on more stones. The current method is good for identifying the chemistry in terms of three end-members. To combine SG measurements with the current information will increase its complexity, but could more accurately define the chemistry in terms of four end-members. For example, grossular and spessartine components in a stone can balance each other out, hiding evidence of both, as has been observed in some rhodolites.

The authors have presented a means for quantitatively measuring the magnetic susceptibility of cut gemstones as an aid in characterizing their end-member chemistry. In fact, any rough material need only have one polished surface to enable testing by this method. The simplicity of the method makes it ideal for field-testing new finds of garnet.

It is recognized that trade and varietal

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names of garnet will continue to be used for commercial purposes. However, for gemmological purposes, we believe it would be better to describe the actual end-member chemistry of a garnet derived using this new method. The technique overcomes the present RI and SG limitations as garnet identification methods. Further, it will allow new varieties to be easily defined in the garnet continuum with less confusion about their composition.

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