

MAGNETIC SUSCEPTIBILITY OF GEMSTONES Part 4

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Understanding Ternary and Winchell Diagrams:

Application to the Garnet Group

The practicing gemmologist, in contrast to the laboratory gemmologist with his high tech instruments, has too few truly quantitative measures by which to characterize an unknown gemstone; the principal measures used being the refractive index (RI) and specific gravity (SG).

Birefringence is a derivative of the refractive indices, so I don't include it in the list.

The only other quantitative properties one is apt to find in a gemmological text are hardness, and dispersion, neither of which are generally measured or used for gem characterization by the typical gemmologist. The addition of a means to quantitatively measure magnetic susceptibility adds a third important measure to the few we have available in the gemmologist's tool kit

It was a Scot, the first champion of quantitative geology, who stated years ago that "when you can measure what you are speaking about, and express it in numbers, you know something about it, but when you cannot measure it, your knowledge is of a meager and unsatisfactory kind."

That Scot was Sir William Thomson, Lord Kelvin, and his words are as relevant today as they were 127 years ago.

The advantages to the gemmologist of having a third quantitative measure is probably best exemplified by what it brings to characterization of the garnet group minerals (Hoover et al, 2008). This aspect is explored in this section.

Garnets

We all know that most natural garnets are mixtures of several species of ideal end member garnets. Table 1. shows the six principal end members recognized by gemmologists; pyrope, almandine, and spessartine comprising the pyralspite trio, and uvarovite, grossular and andradite comprising the ugrandite trio.

The calcium-vanadium garnet goldmanite, and magnesium-chromium garnet knorringite are also listed in Table 1 as they are relevant to some gem garnets.

TABLE 1. Garnet end member properties and chemistry, all from Meagher (1982) except for knorringite from Deer et al (1982, p.489); susceptibility calculated by authors.

END MEMBER	REFRACTIVE INDEX	DENSITY, (CALC.) gm/cm ³	VOLUME SUSCEPTIBILITY x10 ⁻⁶ SI	
PYROPE	1.714	3.582	-22.5	Mg ₃ Al ₂ Si ₃ O ₁₂
ALMANDINE	1.829	4.315	4070	Fe ₃ Al ₂ Si ₃ O ₁₂
SPESSARTINE	1.799	4.197	4745	Mn ₃ Al ₂ Si ₃ O ₁₂
GROSSULAR	1.734	3.594	-22.5	Ca ₃ Al ₂ Si ₃ O ₁₂
ANDRADITE	1.887	3.859	3076	Ca ₃ Fe ₂ Si ₃ O ₁₂
UVAROVITE	1.865	3.850	1290	Ca ₃ Cr ₂ Si ₃ O ₁₂
GOLDMANITE	1.834	3.765	690	Ca ₃ V ₂ Si ₃ O ₁₂
KNORRINGITE	1.875	3.835	1368	Mg ₃ Cr ₂ Si ₃ O ₁₂

A typical natural gem pyrope may have some amount of manganese, iron⁺² or calcium substituting for the magnesium, and/or some iron⁺³, chromium or vanadium substituting for the aluminum. Clearly, they can be a real melting pot of garnet species.

For simplicity these complex garnet mixes may be represented as proportions of each of the simple end members.

Remember that mineral species nomenclature is based on chemistry, so the problem for the gemmologist in characterizing any garnet is how to estimate or determine its chemistry.

This can be done, more or less directly, by determining the composition of a sample in terms of its oxide percentages, such as SiO₂, Al₂O₃, FeO, etc, perhaps by wet chemical methods or the microprobe, and from these, calculating the percentages of the various end members.

Unfortunately, there are over 200 ways of calculating the end members, and they do not give exactly equivalent results.

Later we will see the extent of this difference. However, such direct methods are not generally available to the average gemmologist.

An indirect way to determine a garnet's chemistry is to measure its physical properties, and from as many of those properties as possible, determine its chemistry based on the properties being linear functions of the respective end member properties.

This technique is often used with a measure of refractive index to determine where a garnet falls when a mix of almandine and pyrope, or where a plagioclase is between albite and anorthite, or for the scapolite group between marialite and meionite.

For this indirect technique, if one has a single property, then two end-members may be determined, if two properties are available then three end members may be determined, if three properties, four end members, etc.

Using this indirect approach, the solutions for end members can be obtained by solving simultaneous equations, or more simply by graphical techniques. This leads us to ternary, or triangle, diagrams.

In their classic work on garnets, Manson and Stockton (1981, 1982, 1984) and Stockton and Manson (1982, 1985) made use of ternary, or triangle, diagrams to show variations in the chemistry between three end members among groups of gem garnets.

If five end members are considered important for characterization, then ten ternary diagrams are needed to cover all possibilities.

Eight of the ten diagrams were published by Sriramandas (1957) showing lines of constant refractive index (RI) and constant cell constant. From such diagrams, if one measures the RI and cell constant, then the chemistry is given for a three component garnet which fits the measured properties.

However, the chemistry is not unique because different proportions of other end members could also fit the measured properties.

Fig 1
Manson-Stockton Fig7
Modified
(1982 red to purple garnets)

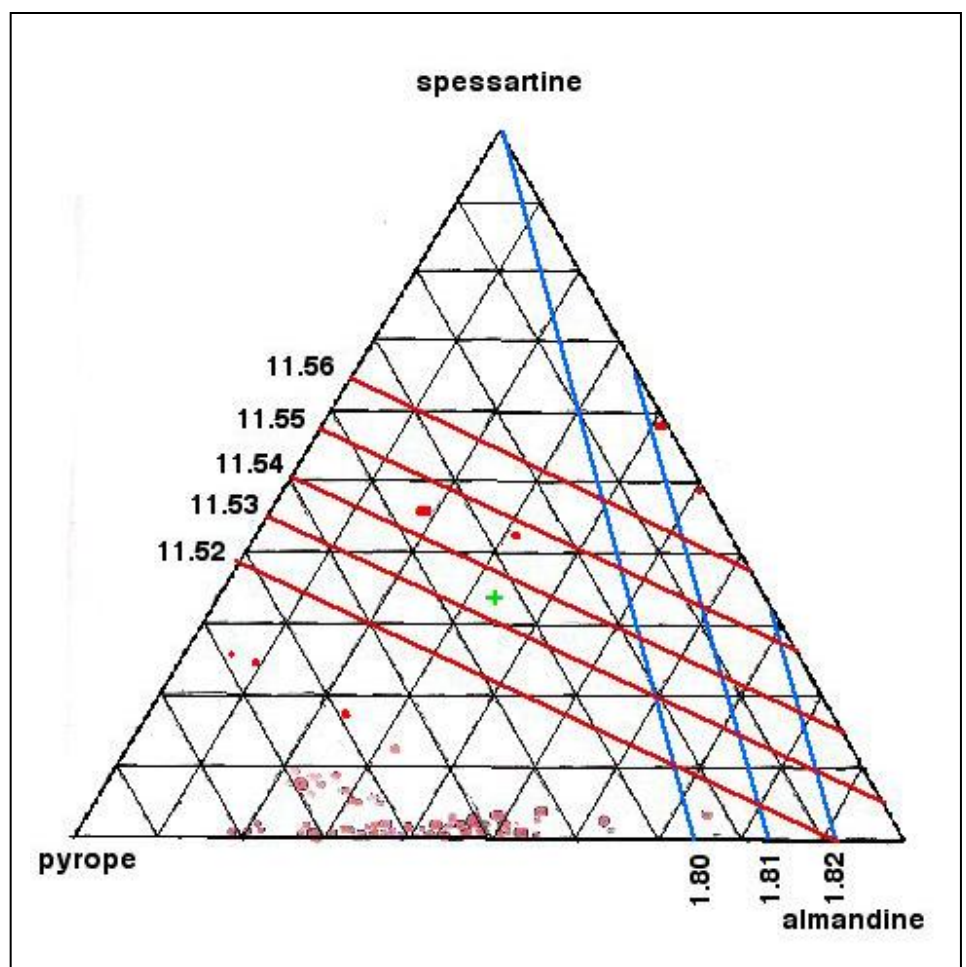


Figure 1 shows the pyrope-almandine-spessartine ternary diagram for the red to purple garnets studied by Manson and Stockton; their fig.7, modified.

For those not familiar with such diagrams the black lines represent lines of constant composition, with the peak of the triangle the 100% point, and descending in 10% intervals.

Thus any point on or inside the triangle has a specific composition in terms of the three end member points. The center, shown by the green cross, is 33.3% of each.

Instead of plotting points on the diagram, Manson and Stockton placed each separate cut stone in the proper position on the diagram and photographed it.

This shows the chemistry of each stone studied, but only for the three major components. Because all the end members must add to 100% for such a ternary diagram, they had to drop any other end members from consideration, recalculating the three to 100%.

This can give a distorted picture as we will see. Note the clustering of stones near the pyrope-almandine boundary, or join. Many of these have significant quantities of grossular which has been ignored.

The other aspect you need to know about ternary diagrams like this is that the properties can also be shown on them, since the properties are, to a first approximation, linear functions of the end member properties.

I have shown in blue a few of the lines of constant refractive index, and in red those for constant cell constant to illustrate part of one of Sriramandas' diagrams.

But, the properties so shown are valid only for a garnet with no other end members than pyrope, almandine and spessartine.

Note the two most almandine-rich stones with refractive indices of 1.803, and cell constants just below 11.52.

The stone with no spessartine content from this diagram is GIA stone 6673F. It's composition from the microprobe is almandine 75%, pyrope 22.5%, andradite 1% with traces of others. Its measured properties are RI=1.793, Cell C.=11.513.

The other stone is # 5544A, whose microprobe composition is almandine 70.5%, pyrope 20.5%, grossular 5%, spessartine 3%, with RI=1.791, cell C.=11.534.

The agreement between estimated properties and chemistry, or vice versus is not exact.

In part, this stems from dropping some end members in order to plot the diagram.

This diagram also shows that if you only have a measure of the refractive index, that you have no information on chemistry within the triangle. You are restricted to the edges of the ternary joining two of the three end members.

This makes clear what was said earlier that with only one physical property you can only determine the chemistry in terms of two end members.

It should be no surprise then that the nomenclature introduced by Manson and Stockton for the garnet group, since the only quantitative measure they used was the refractive index, is limited to descriptions of what segment of a particular join the refractive index indicates. They use color and spectral properties to select which join is appropriate. For example if a garnet has a refractive index of 1.810, it could be a spessartine with 33% almandine, or an almandine with 18% pyrope.

Thus, while Manson and Stockton could represent the measured chemistry on ternary diagrams, by using only refractive index to infer chemistry they were restricted to characterizing the garnets in terms of only two end members.

This then raises the question of how many end members are needed to characterize any given garnet? In part we can answer that by returning to the Manson-Stockton data set.

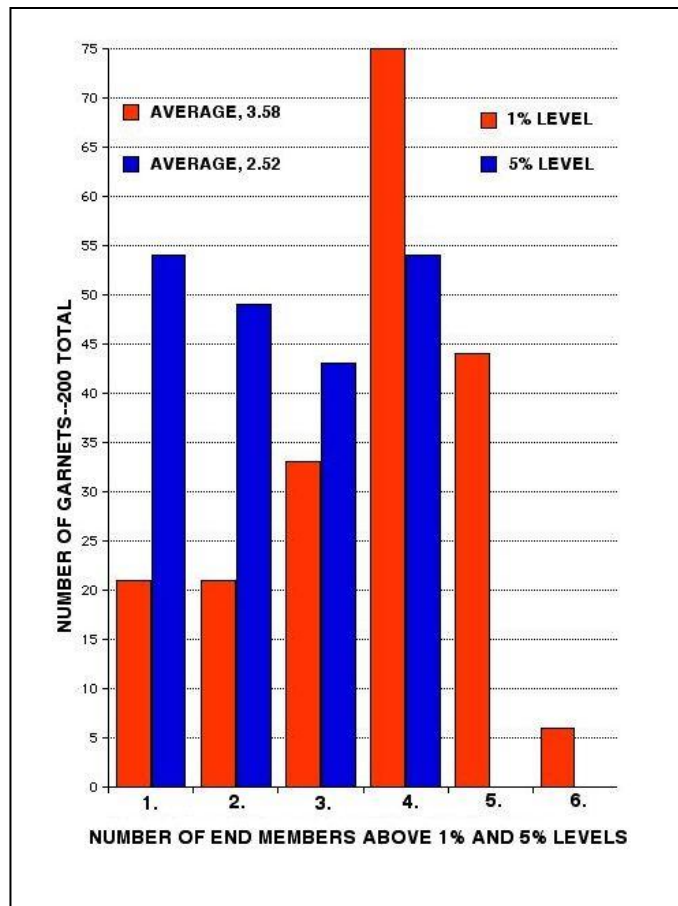


Fig 2
Manson-Stockton
End member
No's

In this figure I show, for the 200 garnets that Manson and Stockton studied in detail, the number of end members above either the 1% or 5% level. For example, the 54 garnets in which only one end member was above 5% may have had two, three, or four that were just under 5%.

Thus one end member may not necessarily constitute 95% of the stone.

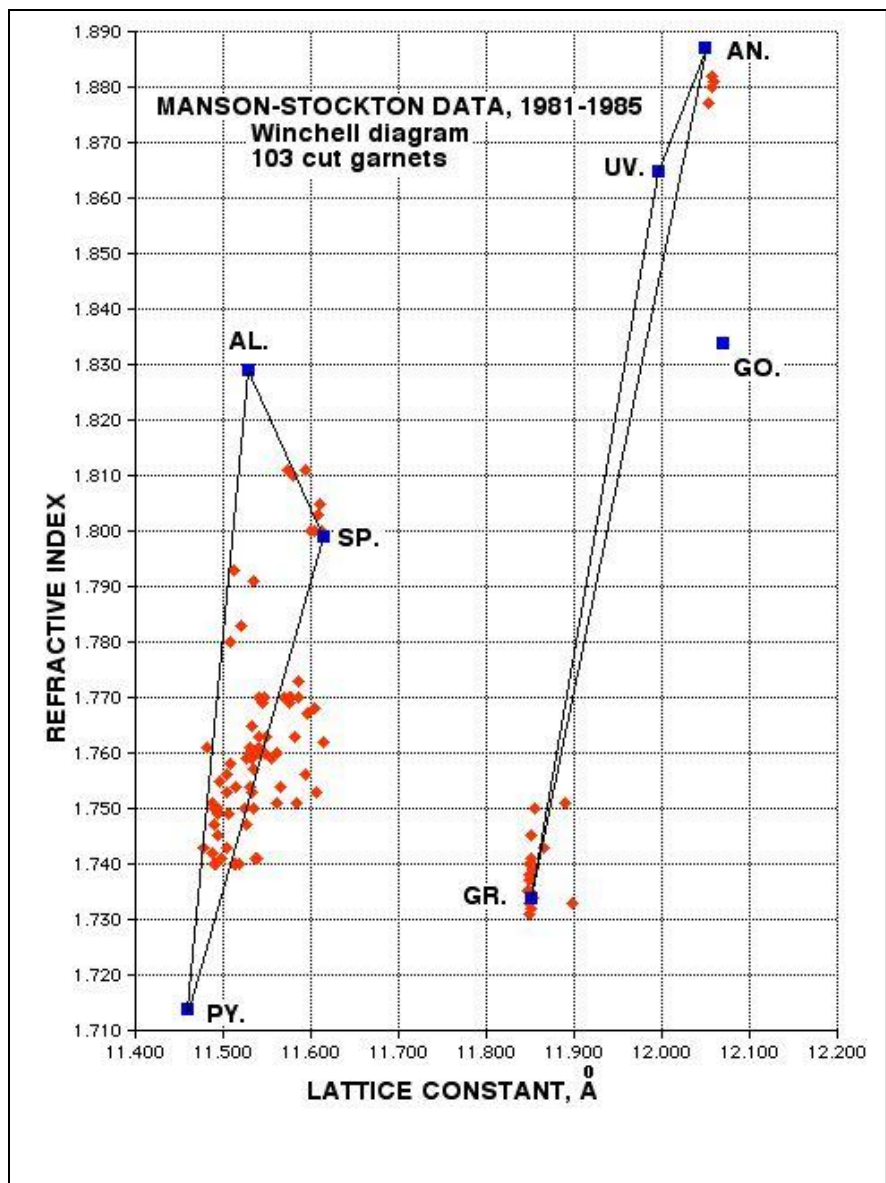
Those with only one end member above the 1% or 5% level are obviously close to pure end members.

These are mostly the grossulars and andradites.

No almandines or pyropes were in these groups. This figure then gives us a general idea that three to four end members are desired to characterize a majority of gem garnets.

This requires two to three quantitative physical properties. By using magnetic susceptibility and specific gravity with refractive index this can now be accomplished.

**Fig 3. Winchell Digram
Manson-Stockton
RI Cell Data**



Back in 1958 H. Winchell devised a different way to show the relationship between garnet chemistry and properties to eliminate the numerous ternary diagrams used previously and to better represent the relationship with properties.

This is the Winchell diagram where the refractive index and cell constant are plotted on rectilinear paper and the ternary diagrams plotted within the physical property space.

This Winchell diagram can be used to read the properties (RI and cell C.), if the chemistry is known, or usually to estimate the chemistry from the actual properties.

An example is shown in Figure 3 using the 103 garnets for which Manson and Stockton had both property data sets.

Note that it gives you a different picture of the chemistry of these stones from that of the single pyralspite ternary Manson & Stockton presented, shown in Figure 2.

In this case the ternary diagrams are no longer simple equilateral triangles. On this plot I have only shown the pyralspite and ugrandite ternaries. These are the two more important ones, but many others could be shown on this single diagram.

Now, the majority of pyralspite garnets are not clustered along the pyrope-almandine join.

This presentation permits one to visually see just where a set of real physical properties places any garnet with respect to all the end members, not just a particular three.

Remember the two garnets with an RI at 1.803 that I pointed out earlier? They now are shown with their true measured values and in relation to all the various major end members.

This is a powerful way, I believe, to look at garnet chemistry and properties. I strongly encourage each of you to work with such plots, and understand how to use them.

This plot clearly shows distinct groups of garnets. the andradite and grossular are quite distinct, and close to each end member. Within the "pyralspite" ternary it is clear that most stones are pyropes.

Note that no stones are close to either the pyrope or almandine end members, and a few stones are close to the almandine-spessartine join.

Many are no longer even within the pyralspite ternary, yet, these stones were classified by Manson and Stockton as pyrope, pyrope-almandine or pyrope-spessartine.

The Winchell diagram suggests they are not well classified as such, but in fairness to Manson and Stockton, with only RI to work with, they could not do more.

I hope it is clear that this Winchell diagram is a better tool for evaluation of garnet chemistry from physical property data than the numerous ternary diagrams and only one physical property.

Fig 4.
Manson-Stockton
RI v SG
Winchell Diagram

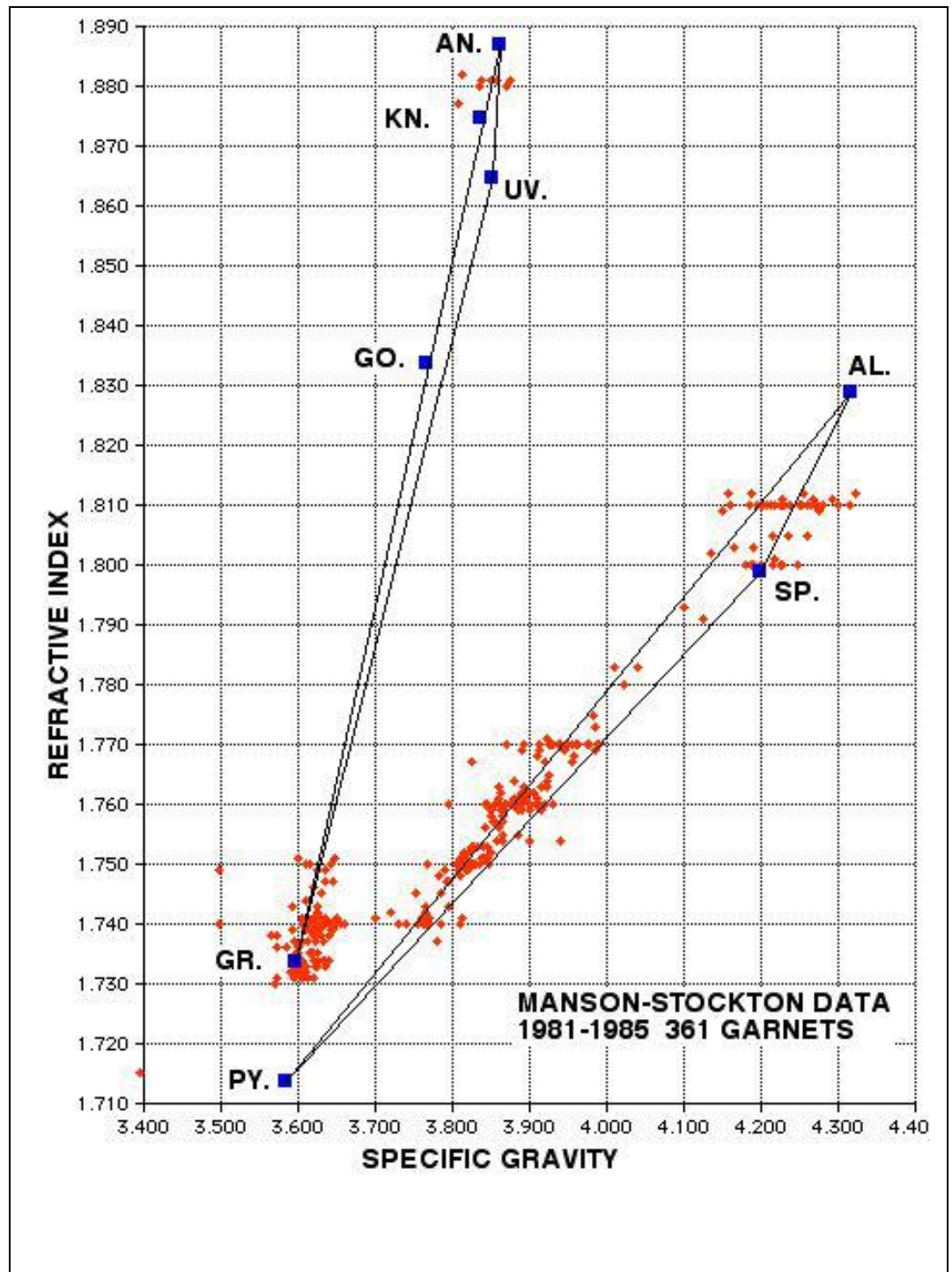


Figure 4 shows a Winchell type diagram using RI and SG data for some 361 garnets in the Manson/Stockton data set.

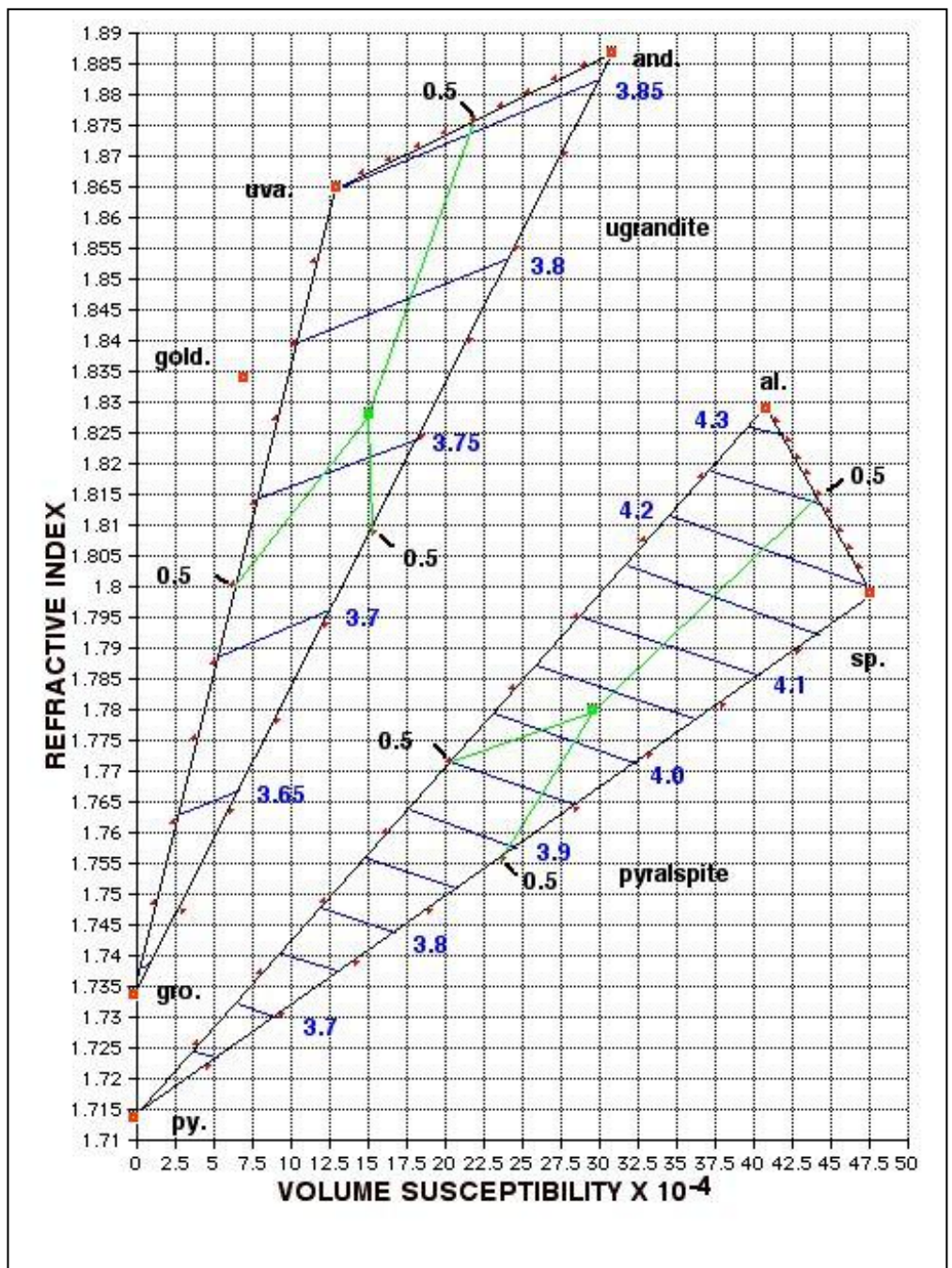
Mineralogists typically don't like to use S.G. data for estimation of chemistry because of the difficulty in measuring SG to sufficient accuracy. Manson and Stockton similarly didn't consider SG in their characterization of the garnet group.

This diagram illustrates one problem with its use, there is not much independent information given by the S.G., as shown by the very narrow ternary diagrams.

Look at the pyralspite ternary, one would need rather accurate RI and SG in order to estimate the percentages of the three pyralspite end members.

However, it is adequate for separation between the pyralspite and ugrandite group garnets, but this is normally not much of a problem.

Fig 5. Winchell Plot
RI v Susceptibility



This figure introduces the Winchell type plot that makes use of susceptibility with RI for what we believe is a distinct improvement in the way an average gemologist can estimate garnet chemistry.

In this plot you see that the pyralspite and ugrandite ternaries are quite open and distinct. I have not shown other ternaries, but you can easily visualize where they would be located.

The almandine-grossular-pyropite is an important one for many gem garnets. Within the two ternaries, I've shown the values for SG, so that it is easy to check if that property matches with the other two. However, the SG values are for a garnet composed only of the three corresponding end members.

Red ten-percent composition ticks are shown along the sides and I've indicated the center of each of the two ternaries, so that the 33.33 percent point is easily located.

Consider the pyralspite ternary and its center point. This center point, when connected to each of the 50 percent points on each join, divides the pyralspite ternary into three parts, in each of which the corresponding end member is largest.

This diagram very simply and clearly illustrates that a pyralspite garnet in which pyropite is the major component can span a refractive index range of 1.714 for pure pyropite to 1.780 for a garnet with 33.3% of each end member.

Perhaps surprising to some of you. Remember, that the SG lines shown are only for a garnet composed of just the three end member components.

Now mentally construct two more lines; joins; between the grossular and spessartine end members, and between grossular and almandine.

Better yet print out this illustration and start to work with these diagrams.

For these four end members, you have now defined four ternary diagrams, and one can calculate what the SG would be within each, just as I did for the pyralspite.

Now take any set of RI and susceptibility for a pyralspite, and you can see that there will also be a distinct composition of either the gr-al-sp, or gr-sp-py ternary that will also match that set of values.

If the garnet is composed of no more than four end members, then a measurement of the garnet's SG will fall on or between the two values on each of the ternaries. From this, one then calculates the four end member composition.

It is important for you to understand that the end member susceptibilities used in making this plot were calculated by use of the Langevin equation and an average measured

magnetic moment of the ions. Thus, for the paramagnetic end members there is some question of just how close the calculation is to reality.

If we are not correct then we may need to shift some end member values to the right or left as better data is obtained. So let's look at some actual data which we have obtained on stones of known chemistry.

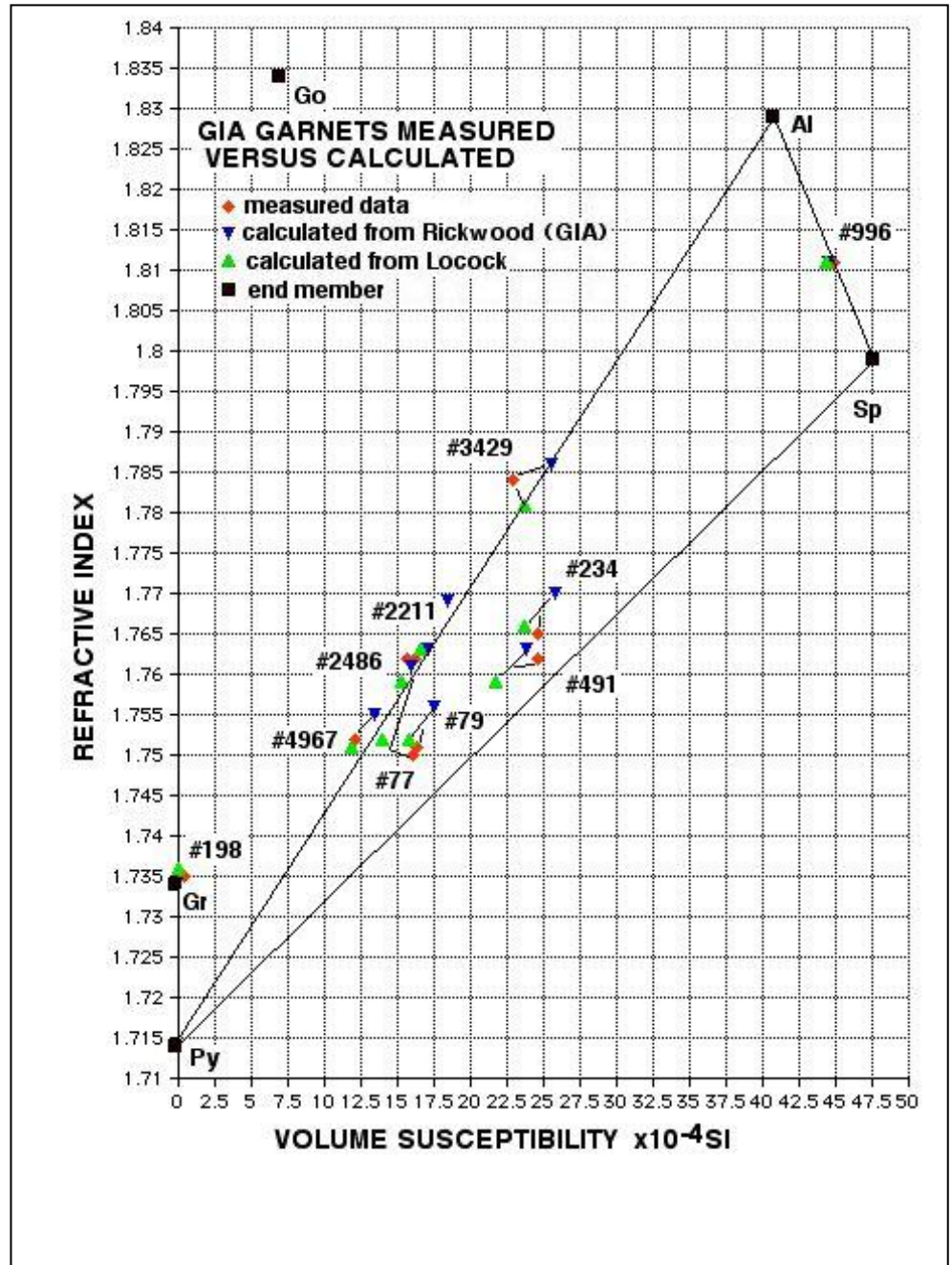


Fig 6. RI v Susceptibility
GIA's 10 garnets

Thanks to GIA, they generously loaned us ten of the garnets that Manson and Stockton studied, and on which we then measured susceptibility.

Nine were pyrospites and one a grossular.

Figure 6 shows where the measured values plot on the Winchell diagram of RI and susceptibility, and are shown by the red diamonds.

The blue triangles show the calculated RI's and susceptibilities based on the end members as calculated by Manson and Stockton from a slightly modified Rickwood procedure to get end members from measured oxide percentages.

The green triangles are the calculated properties based on the more recent procedure of Locock for determining end members.

Clearly, the garnets with the simplest chemistry, the grossular and the almandine-spessartine #996, show good agreement between measured and calculated properties.

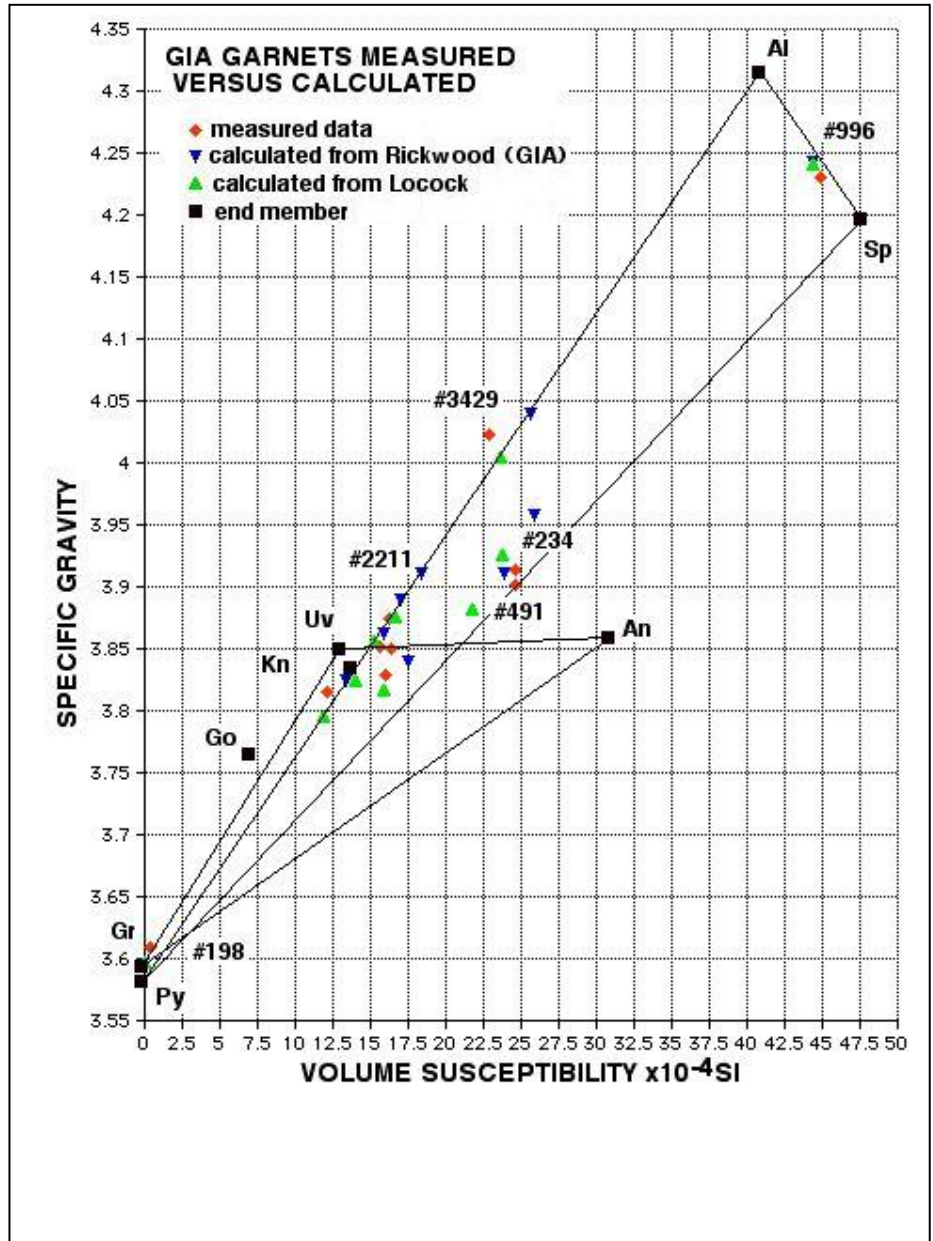
Among the centrally positioned pyrospites with a more complex chemistry the three values diverge a bit. However, the measured values appear to give an inferred chemistry that is within the general error range of end members calculated from the microprobe results.

This has given us some confidence that we have no major errors in this technology.

With the measured and calculated values for the almandine-spessartine #996 falling on the almandine-spessartine join we gain some assurance that the calculated end member susceptibilities of almandine and spessartine are close to correct.

This figure below shows a Winchell diagram of SG versus susceptibility for the ten GIA garnets shown in the prior illustration. Again you see the good agreement between the grossular and the almandine-spessartine, #996, and the scatter of the others.

Fig 7. SG v Susceptibility
GIA's 10 Garnets



But, the reason I show this is to make the point that gemologists now have the ability to use the SG as a proxy for RI when characterizing garnets with refractive indices above about 1.80. Note the relative positions of each of the calculated and measured data points on each graph. While Manson and Stockton didn't recommend the use of SG, it seems clear that it can now be well used in characterization, provided it is measured carefully.

It seems clear that the SG's measured by Manson and Stockton were quite adequate for this use.

We have similar data for three garnets from the collection of Alan Hodgkinson where the chemistry also was known.

Acknowledgements

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Appendix 1 has A4 pages of RI v Susceptibility and SG v Susceptibility

