A Tale of Two Garnets: The Role of Solid Solution in the Development Towards a Modern Mineralogy

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ABSTRACT

This article reviews the development of mineralogy as a science by focusing largely on the common silicate garnets of general formula $\{X_3\}[Y_2](Si_3)O_{12}$. It tells of a number of important discoveries, analyses and proposals by various scientists relating to crystallography, crystal structures, isomorphism and solid solution starting in Europe in the late 1700s. The critical recognition of the importance of ionic size in determining crystal-chemical properties and solid-solution behavior is emphasized. The two garnet species "pyralspite" and "(u)grandite", which were considered to represent two independent solid-solution series, were introduced by N.H. Winchell and A.N. Winchell (1927) in their well-known book "Elements of Optical Mineralogy". Critical comments on the assumptions behind the classification scheme have been pointed out for at least 50 years, but it remains in use. There is more, though, behind this garnet classification scheme than just simple terminology. There are a long series of scientific discoveries and advances that are largely forgotten by the broader mineralogical community. They begin, here, with the work of the "father of crystallography", René-Just Haüy, concerning the microscopic nature of crystals around 1780 and include later discoveries and proposals by Mitscherlich, Beudant, Wollaston and Koop relating to isomorphism and solid-solution behavior all before 1850. A second key era started with the discovery of X-ray diffraction in 1912 that allowed the atomic structures of crystals and furthermore atomic and ion radii to be determined. In terms of isomorphism and solid solution, the proposals and studies of Vegard, Zambonini, Wherry, A.N. Winchell and the "father of crystal chemistry" Goldschmidt are briefly discussed. The recognition of the sizes of atoms and ions, along with an understanding of chemical bonding behavior in crystals, was critical in the establishment of what can be termed "modern mineralogy", a quantitative science as it is largely understood today that emerged by roughly the mid 1930s. The silicate garnet system pyrope-almandine-spessartine-grossular-andradite-uvarovite shows extensive homovalent substitutional solid solution over two structural sites and complete compositional variation between "pyralspite species" and "ugrandite species" has been documented. Thus, the prerequisites behind the terms "pyralspite" and "(u)grandite", as originally formulated and often accepted even today, are incorrect and use of this classification is not recommended. Diffraction determinations of the volumes of garnet end members and volumes of mixing of garnet solid solutions give physical insight into solid-solution behavior. Today, investigations of local structural and crystal-chemical properties, together with determinations of lattice strain and thermodynamic mixing properties of silicate solid solutions, are leading to an ever more quantitative understanding of mineral behavior from the microscopic to macroscopic level.

Key words: Garnet, Mineral Classification, X-ray Diffraction, Crystal Structures, Atomic Theory, Isomorphism, Substitutional Solid Solution, Lattice Strain, Volume

INTRODUCTION

Mineralogists, as a group, are quite zealous regarding terminology and classification. Since the beginnings of mineralogy a large number of articles, monographs, and textbooks have been devoted to the classification of minerals. Indeed, science begins with observation and description of the natural world and classification follows. In terms of the common rock-forming silicate garnets, general formula $\{X_3\}[Y_2](Z_3)O_{12}$, where dodecahedral {X}, octahedral [Y], and tetrahedral (Z) represent the three special crystallographic cation sites and their polyhedral coordination in space group $Ia\bar{3}d$[1]. One learns of the pyralspite and (u)grandite garnets and their solid-solution behavior. The two names were introduced by the father and son team of Newton Horace Winchell (1839-1914) and Alexander Newton Winchell (1874-1958) in their well-known book “Elements of Optical Mineralogy” (1927 – first edition 1909) and repeated in its later editions. They wrote, “If a mineral species is a natural substance which varies between definite natural limits in chemical composition then there are probably two and probably only two species in the garnet group, since three of the types commonly recognized belong to one continuous series and the other three to another. Neither species has received a name, but designations may be coined from the abbreviations of the names of the chemical species, as follows:

Pyralspite . . .	Pyrope	$Mg_3Al_2Si_3O_{12}$
	Almandite	$Fe_3Al_2Si_3O_{12}$
	Spessartite	$Mn_3Al_2Si_3O_{12}$
Ugrandite . . .	Uvarovite	$Ca_3Cr_2Si_3O_{12}$
	Grossularite	$Ca_3Al_2Si_3O_{12}$
	Andradite	$Ca_3Fe_2Si_3O_{12}$”.

With time, as often is the case, terminology evolves and changes and it often becomes less precise. One reads in mineralogy textbooks of the two sets or sub-groups, namely the Ca

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[1] The use of the general formula $\mathbf{E}_3\mathbf{G}_2Si_3O_{12}$ is recommended by Smith et al. (1998).

garnets and the (Mg, Fe, Mn) garnets (Deer et al., 2013), the two garnet groups (Klein and Dutrow, 2007), and the Pyralspite and Ugrandite series (Perkins, 2011; Okrusch and Matthes, 2014). Today in the modern electronic era, in the crowd-sourced Wikipedia, one finds the two solid-solution series pyrope-almandine-spessartine and uvarovite-grossular-andradite as well as Pyralspite garnets and the Ugrandite group (http://en.wikipedia.org/wiki/Garnet). Geiger (2008) noted that the prerequisites behind the classification were not correct and that its use can lead to an incorrect understanding of the crystal-chemical and thermodynamic properties of silicate garnets in general. Grew et al. (2013), in their comprehensive review and discussion of terminology for the garnet supergroup, argue against the use of pyralspite and ugrandite as species names. Indeed, critical comments on this classification (e.g., Sobolev, 1964; Nemec, 1967), and presentations of garnet compositions that violated the assumptions behind it, have been pointed out for at least 50 years. In spite of this, it remains ingrained in textbooks and the mineralogical literature.

There is, though, much more behind the pyralspite and ugrandite classification scheme than just a simple terminology for the common silicate garnets. There are a long series of scientific discoveries and advances that have been largely forgotten by the broader mineralogical community. They concern mainly the physical concepts, as well as the scientific fields, of crystallography, atomic theory, isomorphism and solid-solution behavior. All of these subjects and their interrelationships were central in the development of modern crystal chemistry and mineralogy (as well as metallurgy and inorganic chemistry) in the sense that they are known today and in how they evolved into quantitative sciences starting in the first part of the 20th century. Alexander Newton Winchell (Fig. 1), a former president of the Mineralogical Society of America (1932) and a Roebling Medal recipient (1955), among others scientists (see below), made contributions towards understanding isomorphism and solid-solution behavior in minerals.

This article reviews briefly and reconstructs the development of mineralogy as a science starting around 1770 and retells early work on isomorphism and solid-solution behavior within the framework of the common silicate garnets. The critical recognition of the importance of atomic or ionic size, and not just mass and valence, in determining solid-solution behavior in minerals is emphasized. A tale of two garnets is really a tale of crystals and the long quest to understand their chemical and physical properties at a microscopic level and ultimately to relate them to their macroscopic properties.

A HISTORY OF CRYSTALLOGRAPHY, CRYSTAL STRUCTURES AND CRYSTAL CHEMISTRY

Molécules Intégrantes, Early Atomic Theory, Isomorphism, and Substitutional Solid Solutions: The Birth of Mineralogy as a Science

The history of mineralogy can, in a simple sense, be divided (see Schneer, 1995 and Hazen, 1984 for a more complete treatment) into two parts and is taken to start, here, in the late 1700s. It begins with the concepts of *molécules intégrantes*, atomic theory, isomorphism, and the phenomenon of solid solution and how they started, evolved and were interrelated in study[2]. Treatments of the history of crystallography and the theories of crystal structures are numerous and each emphasizes certain scientific viewpoints or results over others or the contributions of one scientist over another, but the general interpretation is similar. Two books that discuss the subject at length, starting from the earliest times, include Burke (1966) and Authier (2013). The history of crystallography in its entirety is reviewed in a number of separate articles in Lima-de-Faria (1990) and chemical crystallography prior to the discovery of the diffraction experiment by Molcanov and Stilinovic (2014). Some of the major discoveries and theories, especially relating to the history of atomic theory, isomorphism and solid solution, which are discussed in short form here, are taken from the first two sources. In addition, a number of key original and review publications are presented.

The concepts of *molécules intégrantes* (integrant molecules), atomic theory, isomorphism, and solid-solution behavior were developed just following the age of enlightenment in Europe starting in the late 1700s and research followed into the first part of 1800s. During this period, a diverse range of scientists was trying to interpret and understand in a microscopic sense the nature of gases and liquids and, of interest here, crystals. Some investigators thought that crystals were made up of tiny microscopic second-order particles that were of identical shape and chemistry, but the exact nature of these particles was not fully clear. Here, the views of the prolific natural scientist, botanist, mineralogist and "father of crystallography", the Frenchman René-Just Haüy (1743-1822), reigned supreme. He argued in 1792 that crystals, reflecting their consistent forms and obeying the crystallographic law of rational intercepts, consisted of so-called integrant molecules. In a physical sense, these integrant molecules could be considered as identical juxtaposed microscopic polyhedra that serve as the very tiny building blocks of crystals (see Fig. 2 for the case of garnet, which was the subject of Haüy's first mineralogical memoir in 1782). They were "the smallest corpuscles which would be obtained if mechanical division was pushed to its ultimate limit, had we sufficiently sharp tools" (Authier, 2013) and each crystal form had its own characteristic integrant molecule. It followed, in other words, from Haüy's

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[2] From very early on the fields of chemistry and mineralogy were closely linked. Medieval and later scientists were often trained in theology and medicine and they studied the four sciences of the Quadrivium: arithmetic, geometry, astronomy and harmony (Schneer, 1995).

theory that "every chemical substance possesses a characteristic crystalline form, and that substances differing in chemical composition cannot occur in the same form" (Kraus, 1918). Haüy's view dominated the field for a number of years and it appeared to explain well the observed variety of crystal forms and the law of rational intercepts (e.g., Burke, 1966). His work was clearly of benchmark importance for the fields of crystallography and mineralogy because it set out the idea of a space lattice for the first time. However, in spite of the theory's attractiveness, contradictions and doubts on its correctness began to arise with further careful measurements on crystal forms and the angles between faces, as well as through the study of the chemistry of synthetic crystals and minerals. Here, scientists such as William Hyde Wollaston (1766-1828), François Sulpice Beudant (1787-1850) and Eilhardt Mitscherlich (1794-1863) made important contributions and discoveries (Burke, 1966).

Beudant, a former student of Haüy, researched (1817) the crystal forms of iron, copper and zinc sulfates crystallizing from solution. Haüy had proposed that these three different sulfates consisted of different integrant molecules namely, an acute rhombohedron, an irregular oblique-angled parallelepiped and a regular octahedron, respectively. Beudant wanted to investigate how much of another chemical component copper sulfate could accept without changing its crystalline form, for example. He found, surprisingly, that crystals containing 90% copper sulfate and only about 10 % iron sulfate yielded crystals having the same external rhombohedral form as pure iron sulfate. This finding, as well as other similar results for various crystal systems by other workers, was difficult to interpret using integrant molecules and these results produced heated debate among scientists throughout Europe (Burke, 1966).

It was the discovery and explanation, though, of isomorphism by the German chemist Mitscherlich that ultimately doomed Haüy's crystal theory[3]. What are isomorphs and what is isomorphism[4]? The latter is a concept that for many years played an important role in mineralogy, though rather confused and variously defined (e.g., McConnell, 1943; Whittaker, 1981; Jaffe, 1988). The term isomorphism today is largely unused and forgotten and mostly relegated to older mineralogical and crystal chemistry textbooks. According to Mitscherlich (1819; 1821), "An equal number of atoms, if they are bound in the same way, produce similar

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[3] See, for example, "Slaying the crystal homunculus" (Cahn, 1999) as well as Burke (1966) and Melhado (1980). The discovery of dimorphism and polymorphism by Mitscherlich in his studies on calcite and aragonite as well as sulfur crystals also contributed to the rejection of the theory of *molécules intégrantes*. Morrow (1969), taking a dissenting minority opinion, argued that W.H. Wollaston (see below) discovered isomorphism. Goodman (1969) discusses the views toward the atomic theory of Dalton in the 1800s and on how Wollaston vacillated in his interpretations on it.

[4] Different garnet species represent, with their well-pronounced {110} faces, textbook examples of isomorphs and garnet can form an isomorphic series in the classic sense meant by Mitscherlich (Fig. 3).

crystal forms, and the crystal form depends not on the nature of the atoms but on the number and method of combinations" (translated in Authier, 2013, page 331) or Mitscherlich's last definition, "Substances possessing an analogous composition, which crystallize in the same form (or in similar forms) and which are capable of mixing in all proportions, are isomorphous" (Morrow, 1969). And here it must be remembered that the precise physical nature of an atom prior to about 1900 was not known. John Dalton (1766-1844), often considered to be the "father of atomic theory", first presented his generalized ideas around 1803 based on his research on gases and liquid solutions (e.g., Dalton, 1803a,b). Mitscherlich accepted Dalton's theory, but "professed ignorance of the shape or constitution of these atoms" (Burke, 1966).

The discovery of isomorphism[5], which was based on Mitscherlich's study of the compounds KH_2PO_4 and $(NH_4)H_2PO_4$ as well as KH_2AsO_4 and $(NH_4)H_2AsO_4$, was of great consequence because isomorphous species can form substitutional solid solutions or as they are sometimes called mixed crystals (from the German *Mischkristalle*). In fact, the terms isomorphism and (substitutional) solid solution were used interchangeably for many years and among mineralogists the latter is used today[6]. The phenomenon of solid solution was difficult to explain using Häuy's theory[7]. Morrow (1969) traces the discovery or observation of mixed crystals back to 1772 starting with the work of Rome De L'Isle. According to Burke (1966), Beudant, with his investigations such as the one noted above, and Wollaston should be given credit for the recognition of solid solution in crystals. W.H. Wollaston, an English medical doctor turned natural scientist, made thought provoking very early proposals on the microscopic nature of crystals. It was known that it was not possible to fill space completely with a tetrahedron or octahedron, for example, in the sense of Haüy's theory. Thus, Wollaston wrote, "all difficulty is removed by supposing the elementary particles to be perfect spheres, which by mutual attraction have assumed that arrangement which brings them as near to each other as possible" (Wollaston, 1813, p. 54). He even constructed polyhedral models of various forms based on a close packing of hard spheres (Fig. 4), including some with two different types of spheres (i.e., alloy or solid solution).

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[5] Haüy wrote to Brochant, "if Mitscherlich's theory is correct, mineralogy would be the most wretched of the sciences" (Kraus, 1918). However, as noted by Kraus, further careful work after Mitscherlich's proposal, using more precise goniometers, showed that there are small differences in the angles between faces of isomorphous crystals of differing chemistry. "It was recognized rather early that the original idea of absolute identity of form, expressed by Mitscherlich, must be modified, absolute identity giving way to striking similarity of form." (Kraus, 1918). Thus, Haüy's pronouncements were in a certain sense partly correct.

[6] The crystallographic community recommended some time ago against using the term isomorphy and, thus, by extension isomorphism (see Lima de Faria et al., 1990).

[7] Haüy recognized that isomorphs and isomorphism occurred, but his interpretation of the phenomenon was incorrect (see Burke, 1966, or Melhado, 1980, for example).

The debate on the theory of isomorphism, both pro and con, following Mitscherlich's investigations was intense and much was at stake. For example, the well-known polymath, scientist, priest (wikipedia.org/wiki/William_Whewell) and professor of mineralogy at Cambridge University (i.e., Trinity College), William Whewell (1794-1866), waded into the debate in a publication from 1831. He argued in favor of the theory of isomorphism partly based on his analysis of published garnet compositions and stoichiometric arguments. Although it appears that his proposed garnet stoichiometry was not fully correct, his analysis foresaw the nature of solid solution in silicate garnet in terms of the major cation substitutions at the X- and Y-sites. The problem was to obtain a stoichiometric formula based on 'wet' chemical analyses, which were sometimes rather inexact, from a solid-solution composition garnet. Whewell came to the conclusion that the divalent cations Fe^{2+}, Mn^{2+}, Ca and Mg (X-site) belong together as do Al and Fe^{3+} (Y-site) in the garnet crystal-chemical formula.[8]

Following this often controversial but rich period of crystallographic research, further major developments with regard to the understanding of the internal structures of minerals was rather limited for a long time. It is important to note that the concept of single spherical atoms in crystals was pushed aside in many chemical and mineralogical studies. Research focused more on studying the masses and valences of elements and a more molecular approach or view, as starting largely from Haüy's work, was connected with crystals (Burke, 1966, page 124).

There was work done to better understand the phenomenon of isomorphism and the nature of "atomic" volumes in substances. Prior to the discovery of X-ray diffraction in 1912, neither a unit-cell shape and its volume nor the size of an atom in a modern sense could be measured directly. There was, though, another experimental means to determine "atomic" volumes. Here, the work of the German chemist H.F.M. Kopp (1817-1892), perhaps best known for the Kopp-Neumann rule governing heat capacity behavior, was important and he contributed to a further understanding of isomorphism and/or solid-solution behavior. His proposals, indeed, turned out to be quite foretelling (see later discussion), because he argued that similar or equal "atomic" (or smallest particle) volumes in crystals was a prerequisite for isomorphism[9]. He came to this conclusion through extensive measurements and analysis of a large number of isomorphic substances in which their "atomic volumes" were obtained by dividing their "atomic weights" by their specific gravity (Kopp, 1840; 1841). Otto (1848 - p. 126) wrote of "Kopp's Law"

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[8] As a matter of note, the general problem of assigning cations to certain crystallographic or structural sites from a chemical analysis, maintaining stoichiometry, and in calculating various end-member garnet components for a solid solution still exists today (see Locock, 2008).

[9] "Isomorphe Körper haben gleiches Atomvolum" und "Die kleinsten Theilchen isomorpher Körper sind nicht nur in der Form (Mitscherlich's Entdeckung), sondern auch in der Größe einander gleich" (Kopp, 1840, p. 3).

concerning the similar sizes of chemical atoms in isomorphous substances. The most renowned American mineralogist of the 19th century, James D. Dana (1813-1895), following upon the results and analysis of Kopp, also studied isomorphism and the nature of "atomic volume" for various minerals (Dana, 1850).

The situation in both chemistry and mineralogy was still quite confused, though, with regard to the nature and precise meaning of chemical formulae and atomic and molecular weights. The terms atoms and molecules were being used interchangeably, along with other expressions for the tiny particles thought to compose matter. For the sale of brevity, suffice it to state that the proposals of Stanislao Cannizzaro (1826-1910), an Italian chemist, at the world's first international conference of chemistry at Karlsruhe, Germany in 1860[10], were quite noteworthy. Cannizzaro's research, using the earlier hypothesis of another Italian, Amedeo Avogardo (1776-1856), who worked on gases, led to a better and more precise understanding of the difference between atomic and molecular weights and how chemical formulae and reaction stoichiometries are to be expressed. It was an important step towards the development of modern atomic theory as understood today. In terms of minerals, the concept of integrant molecules was further weakened, although it must be noted, here, there does exist the very important class of molecular crystals especially in field of chemistry and the question of crystal structures was still open into the early 20th century. After this key conference at Karlsruhe, an internationally agreed upon table of modern atomic weights was adopted.

A further development regarding the possible nature of crystal structures and isomorphism can attributed to William Barlow (1845-1934), a geologist with an interest in crystallography (he derived the 230 space groups in 1894 slightly after E.S. Fedorov and A.M. Schoenflies), and William Jackson Pope (1870-1939), a chemist and crystallographer at Cambridge University. Several papers, both singled authored (i.e., Barlow) and together, were published on atomic theory, composition and crystal structures and one work from 1906 is especially significant. In this manuscript Barlow and Pope analyzed the possible structure of various crystals, mostly organic but also a couple of silicates, using models consisting of closest packed hard spheres. They wrote, "A crystal is the homogeneous structure derived by the symmetrical arrangement in space of an independently large number of spheres of atomic influence" and "a homogeneous structure or assemblage is one in which every point or unit possesses an environment identical with that of an infinitely large number of other similar points or units in the assemblage if the

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[10] See deMilt (1951).

latter is regarded as indefinitely extended throughout space."[11] Later in the manuscript in terms of isomorphism they wrote, "It would seem that for two elements to be isomorphously replaceable one by the other, their spheres of atomic influence must be much more nearly of the same magnitude than if they are merely to possess the same valency." Barlow and Pope discussed briefly the plagioclase feldspars as an isomorphous mixture stating, "They (albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$, – C.A.G.) have, however, the same valency volume, namely, 32, and by removing from the albite assemblage the group NaSi, of valency volume 5, it can be replaced without remarshalling, and indeed with but little disturbance of the crystalline structure, by the group CaAl, of the same valency volume."

The various pre-diffraction proposals on atomic size and volume and their importance set the stage for more quantitative investigations in the 20th century.

Modern Atomic Theory, Crystal Structures, Isomorphism, and Substitutional Solid Solutions: The Beginnings of Modern Mineralogy

It took time for the modern atomic revolution to come, but when it came it hit like a tsunami. In terms of crystals and their internal structures, the breakthrough was the discovery of X-ray diffraction in 1912 by M. Laue (1879-1960) and colleagues and crystal structure analysis by another father and son team, namely W.H. Bragg (1862-1942) and W.L. Bragg (1890-1971), as discussed recently in Eckert (2012) and Authier (2013). The Braggs, especially the son, using the new method soon after 1912, determined the crystal structures of a number of minerals with simple structures such as diamond, halite and sphalerite (ZnS)[12]. These discoveries and investigations and the scientific developments arising from the X-ray diffraction experiment can be considered as defining the second part of the history discussed here. It can be argued that they marked the beginning of modern mineralogy[13], and it was physicists who made the breakthrough. In addition to the discoveries of diffraction and crystal structure analysis at roughly the same time, the fundamental physical concept of an atom came to light with the Rutherford-Bohr model.

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[11] Barlow and Pope, as other scientists before them and at the same time, did not understand the forces that acted on the atoms. They did propose the existence of both attractive and repellent forces acting between atoms, but ascribed them to gravity and kinetic energy, respectively.

[12] Gibbs et al. (2014) discuss the still widespread acceptance of the molecular crystal model for Earth materials at this time even after the determination of these simple structures and notably NaCl rock salt.

[13] The term "modern" obviously changes with time and some mineralogists soon recognized the revolutionary importance of the new scientific advances in the study of matter. See, for example, three presidential addresses to the Mineralogical Society of America entitled "The modern study of minerals" (Washington, 1925), "Isomorphous substitution of elements in minerals" (Phillips, 1932) and "The new mineralogy" (Winchell, 1933).

Unit-cell parameters can be measured via diffraction and the molar volume of a crystalline phase can be determined from the relationship:

$$V = \frac{N_o}{Z}\left\{\vec{a}\cdot\left[\vec{b}\times\vec{c}\right]\right\} \qquad (1),$$

where N_o is Avogadro's number (6.023 x 10^{23} mole^{-1}), Z is the number of formula units in the unit cell and $\vec{a}, \vec{b}$ and $\vec{c}$ are the lattice vectors. The scalar triple product of the lattice vectors determines the volume of the unit cell. One also has the relationship:

$$V = \frac{ZM}{N_o \rho} \qquad (2),$$

□□□□□ M is the molecular weight (g/mol) of the atoms in the unit cell and ρ is density (g/cm^3). Moore (1990) wrote that (2) is "Perhaps the earliest known and most important relationship between the underlying parameters for any crystalline substance….". He also states it neatly divides chemical crystallography into the pre- and post-diffractions eras. When determinations for the different parameters are available, this equation can be used as a check for their correctness. It has, for example, been used to test if analytical measurements of composition of a crystalline phase, which can be rather complex, are complete and correct.

Not long after 1912 many different scientists were undertaking diffraction investigations and measurements were even made on solid solutions. A notable example for the latter was the work of Vegard (1921). He studied several simple binary solid solutions including the system KCl-KBr. His powder diffraction measurements showed that the reflections for the $K(Cl_{0.50}Br_{0.50})$ composition were sharp and that their positions were located between those of end-member KCl and KBr (Fig. 5). This demonstrated, first, that the crystal involved "direct atomic substitution" and that it was not a physical mixture of two intergrown phases. Second, he showed that the unit-cell edge, a, and the "molecular volume" along the KCl-KBr binary obeyed the "law of additivity", that is, they varied in a linear and continuous fashion. The expression defining, what is now termed Vegard's law, the unit-cell parameter for a binary solid solution AB is:

$$a_{A_{(1\,-\,X_B)}B_{X_B}} = a°_A(1 - X_B) + a°_B(X_B) \qquad (3),$$

where X_B is the mole fraction of component B and $a°_A$ and $a°_B$ are the unit-cell parameters (or lattice parameters) of the two end-member components A and B, respectively.

It is difficult from today's more "enlightened" understanding to fully grasp the cloud of uncertainty in which mineralogists (and others as well) considered the important class of silicates during this period. This is reflected in the 1922 article of the well-known physicist, physical chemist and metallurgist G. Tammann (1861-1938) entitled "On the Constitution Question of Silicates". His article introduces and addresses the question of whether silicates could be molecular in structure analogously to the large group of organic carbon-based compounds! Of course, the nature of chemical bonding in crystals and certainly silicates was unknown and had to wait a few years for a full and correct interpretation (e.g., Pauling, 1929)[14]. Interestingly, Tammann ultimately concluded, using simple specific heat capacity data on several silicates, as well diffusional behavior of various compounds and the known crystallization behavior of some silicates from melts, that a transfer of molecular theory from organic chemistry to the silicates was not valid.

A few classically trained mineralogists did soon, though, understand the link among post-1900 atomic theory, crystal structures, and isomorphism. Wherry (1923) discussed the key role that atomic volume plays in determining isomorphism in various silicates. He wrote, "It has long been held that in order to be able to replace one another, elements must be chemically analogous and of equal valence" and then followed with "It now seems more probable that the principle requisite of isomorphous replaceability is that the elements in question must possess approximately identical volumes, at least in simple compounds, the crystal structures of which represent fairly close packing of the constituent atoms". Similar views on isomorphism were also published by Zambonini (1922) and Zambonini and Washington (1923), where emphasis was placed on heterovalent isomorphism, i.e., [Na,Si]-[Ca,Al] exchange in plagioclase. These proposals and interpretations, though beset by only a rough knowledge of atomic sizes and/or volumes, a great uncertainty of the nature of silicate crystal structures, and in chemical bonding[15], were new. The situation was far from certain, though, with the acknowledged crystal chemist and crystallographer R.W.G. Wyckoff (1923) ending his exposition on isomorphism with "Enough has been said to show that too few data are at hand to give an adequate explanation of isomorphous mixing, even in the relatively simple example of albite and anorthite."

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[14] See Gibbs et al. (2014) for a recent discussion of bonding behavior and ionic radii in minerals and a historical summary of their development.

[15] Wherry (1923), harking back to the question put forward by Tammann (1922), noted that the lack of isomorphism between carbonates and silicates is a result of the volume (size) difference between carbon and silicon!

Another classical mineralogist who recognized the importance of the property of atomic size in terms of isomorphism turns out to be A.N. Winchell, who is primarily known for his extensive work and books on the optical properties of minerals (N.H. Winchell and A.N. Winchell, 1927, and later editions). Winchell published an article in 1925 in the journal *Science* entitled "Atoms and Isomorphism" in which he presented his ideas and analysis.[16] Winchell began his article with the statement, "Atoms were formerly known only by their weights and chemical properties. …. I shall try to show that one of the properties of atoms depends upon their sizes rather than their weights."[17] He listed four isomorphous mineral groups namely: I. $CaCO_3$, $MgCO_3$, $FeCO_3$, $MnCO_3$, and $ZnCO_3$, II. $CaSO_4$, $SrSO_4$, $BaSO_4$, and $PbSO_4$, III. $MgFe_2O_4$, $FeFe_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$, and IV. $MgFe_2O_4$, $MgAl_2O_4$, and $MgCr_2O_4$ and discussed the possible nature of the exchange among cations of the same valence.

In further more detailed discussion, he used the structure of NaCl as a model to discuss atomic substitution in crystals. Winchell wrote, "If any atoms other than those of Na or Cl exist in a NaCl crystal (not merely mechanically enclosed) they must either replace some of the atoms of the NaCl space lattice, or be small enough to find places between these, as very fine sand can find places between the grains of very coarse sand, even though the latter are in contact. Both these cases probably occur in crystals, but it is plainly only the first case which can lead to an isomorphous series". He wrote, further, "With a gradual increase in the relative number of Br atoms a series can be imagined extending from pure NaCl to pure NaBr." He also wrote, "Now, if crystals are close-packed space lattices built out of atoms, and if isomorphous systems can be formed only by the replacement in the space lattice of one kind of atom by another, it is evident that the size (or domain) of the atoms must be very important in determining what atoms can mutually replace one another in such systems. This principle, that atoms must be of nearly the same size in order to be able to form isomorphous systems in various compounds, seems far more important than the old idea that the atoms must be of the same valence."

Winchell also discussed the two silicate garnet species, which at this time he termed the "two garnet systems". He wrote, "The members of each system are mutually miscible (in crystals) in all proportions, since Al, Fe and Cr are similar in size, and also Mg, Fe and Mn, but the members of one system show only partial miscibility with members of the other system, since Ca has nearly twice the volume of Mg, Fe or Mn."

It is exactly these views on atomic mixing and isomorphism that were put on a more quantitative and extended basis by the work of the well-known geochemist and mineralogist

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[16] The "Web of Science" shows zero citations.

[17] Winchell, as Wherry (1923), uses "atomic radii" (see W.L. Bragg, 1920). Landé (1920) published a short list of ionic radii for the alkali metals and halogens.

Victor Moritz Goldschmidt (1888-1947)[18]. Goldschmidt (1926a, b), together with the help of co-workers, published a list of ionic radii and he laid out his ideas on atomic exchange in crystals. Goldschmidt and his co-workers were able to determine the ionic radii of various metals by determining the unit-cell dimensions of various AX and AX_2 oxide and fluorine compounds, using the results of Wasastjena, published in 1923, who determined the ionic radii of F^- (1.33 Å) and O^{2-} (1.32 Å) anions from optical considerations (see Mason, 1992). To summarize briefly, for example, Goldschmidt stated that extensive miscibility in minerals could occur below the melting point when the difference between the ionic radii of the exchangeable "atoms"[19] is not greater than 15%. Based on this extensive and careful research, Goldschmidt is considered one of the "fathers of modern crystal chemistry" (Mason, 1992).

Returning to the slightly earlier paper of Winchell (1925), he also addressed the role of temperature in affecting solid-solution behavior, for example with the alkali feldspars $NaAlSi_3O_8$ and $KAlSi_3O_8$ and he wrote, "It is an interesting fact that, in this case and in some others, two substances, whose unlike atoms differ so much in size that the isomorphism is only partial at ordinary temperature, exhibit perfect isomorphism at high temperature, as if the expansion of the space lattice due to heat were sufficient to permit free replacement of the small atoms by larger ones at high temperature, even though that is impossible at low temperatures." The sizes of atoms and ions are common knowledge today, as taught in introductory chemistry and mineralogy courses, but this was not the case in the mid-1920s. Winchell understood early on the relationships between crystal form, structure, composition and the nature of solid solution on an atomic basis. The importance of solid solution in many minerals is further reflected in his extensive investigations of their optical properties (i.e., Elements of Optical Mineralogy, 1927, and later editions). The early proposals of Wherry, Zambonini and Winchell, and especially the extensive investigations and analysis of Goldschmidt and coworkers, were an essential development in mineralogy because they extended the interest and emphasis of atoms in minerals and crystals beyond just their masses and charges to their sizes (radii), as had been done for many years following the discoveries of Mitscherlich.

In the second half of the 1920s the study of crystals at an atomic level was moving fast, physical understanding was increasing greatly and the first silicate structures were determined. Interestingly, in completing the circle in terms of a common theme of this paper it turns out, once again, that garnet is fundamental. In 1925 the crystallographer and mineralogist G. Menzer

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[18] Neither Winchell nor Goldschmidt, for example, adopt the term solid solution, but instead use isomorphism to denote it. Goldschmidt wrote, "Als Isomorphie bezeichne ich im folgenden die Erscheinung, daß Substanzen analoger chemischer Formel Analogie der Krystallstruktur aufweisen."

[19] Krystallbausteine.

(1897-1989)[20] determined, using the new technique of X-ray diffraction, the crystal structure of grossular. His study was one of the first correct determinations of a silicate structure[21]. Menzer followed in 1928 in a classic and extensive work, where he showed that the six common end-member silicate garnets (i.e., pyrope, almandine, spessartine, uvarovite, andradite, and grossular), which were known to be isomorphous, were also isostructural with one another. Modern mineralogy had taken its first steps.

By the middle of the 1930s the state of the field was largely established, as it is essentially known today. For example, W.L. Bragg (1930) reviewed the crystal structures of many of the rock-forming (alumino-)silicates, with the notable exception of the feldspars, that within the span of previous five years had been determined. Grimm and Wolff published in 1933 a long and quantitative review article discussing the physical and chemical state of atoms and ions, the different types of bonding behavior, chemical complexes and the crystal chemistry of various crystalline phases.

A TALE OF TWO GARNETS: COMPOSITIONAL RANGE OF THE COMMON AND "NOT-SO-COMMON" SILICATE GARNETS

Natural Garnets

The pyralspite and (u)grandite classification scheme of Winchell and Winchell (1927) is based on the earlier compilation and analysis of many garnet compositions of Boeke (1914). Figure 6, taken from the former authors, is slightly modified from Boeke (1914). The lower part of the figure shows the reported range of garnet compositions between grossular and andradite (grandite), while the cluster of data in the upper left shows the composition range of the pyralspite species.[22] Of particular relevance is the apparent lack of garnet compositions falling between the pyralspite and grandite fields, and hence, the classification of two different silicate garnets.

There is, of course, a multitude more of chemical analyses on garnet available today than in 1914 and the compositional range of natural silicate garnets has been researched and "mapped" out to great detail (e.g., Grew et al., 2013). What do the data say in terms of the range of compositions within the system pyrope-almandine-spessartine-grossular-andradite-uvarovite? To

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[20] The garnet menzerite-(Y), ideal end member $\{Y_2Ca\}[Mg_2](Si_3)O_{12}$, was named in his honor by Grew et al. (2010).

[21] The crystal structures of α and β quartz were also published in 1925 by W.H. Bragg and R.E. Gibbs. W.L. Bragg and West (1927) wrote (p. 452), "It (i.e., Menzer's analysis of the garnet structure - CAG) was the first analysis of a complex silicate to be made, and illustrates the characteristic features of these compounds in a very striking way."

[22] The ferric-iron contents of many of the pyralspite compositions are too high and are due to problems with the older 'wet' chemical analyses.

give the simple and long-known answer first, there is compositional variation between the pyralspite and (u)grandite "species". Extensive, if not complete, substitutional solid solution is observed between and/or among a number of the end-member garnet components. A number of examples of early, published garnet compositions, which by no means are intended to be complete, given by crustal metamorphic and higher-pressure upper mantle garnets are briefly discussed.

Lee (1958) described a largely andradite-spessartine-(grossular) garnet from Pajsberg, Sweden in a rock consisting of rhodonite, garnet and clinopyroxene. A recalculation of the crystal-chemical formula in terms of various garnet end members, using the calculation scheme of Locock (2008), is given in Table 1. Lee also described later a largely spessartine- grossular garnet from the Victory Mine at Gabbs, Nevada (Lee 1962). The garnet occurs in "the sheared and feldspathized portion of a granodiorite" and its composition is also listed in Table 1. Ackermand et al. (1972) described almandine-grossular-rich crystals, which are compositionally zoned, from epidote-bearing gneisses and mica schists from the Western Hohe Tauern, Austria. The garnets crystallized at the greenschist to low-temperature amphibolite facies and one sample composition (123 - core) is listed in Table 1. Indeed, there are a number of reports of garnet approaching roughly 50-50 mole % almandine-grossular composition in quartzofeldspathic gneisses (e.g., Ashworth and Evirgen, 1984 - rim composition of their garnet M.56.4 E is given in Table 1). All these crustal garnets show extensive solid solution between pyralspite and (u)grandite.

The validity of the pyralspite-(u)grandite classification is further contradicted by garnets from higher pressure rocks. Sobolev et al. (1973) describe several suites of chromium-bearing garnets sampled from kimberlites. These garnets show a range of Cr_2O_3 concentrations and a few samples show compositions approximating the pyrope-uvarovite binary. Their sample S-1 has roughly 41 mole percent pyrope-almandine and 46 mole percent uvarovite (Table 1). O'Hara and Mercy (1966) noted a violation of the Winchells' classification scheme in their study of "calcic pyralspites" found in kyanite eclogite xenoliths from the Roberts Victor kimberlite mine in South Africa. A garnet from rock sample 37077 has the composition of very roughly $Py_{25}Alm_{25}Gr_{50}$ (Table 1). Sobolev et al. (1968) described, in detail, a wide range of grossular-rich pyrope-almandine garnets in so-called grospydite xenoliths from the Zagadochnaya kimberlite in Yakutia, Russia. Later, he and colleagues described more nearly binary grossular-pyrope garnets in high pressure diamond-bearing crustal carbonate-silicate rocks of the Kokchetav Massif in Kazakhstan (Sobolev et al., 2001). The core composition of these garnets is given in Table 1.

Finally, it goes without saying that ultra-high-pressure majoritic-bearing garnets (Smith and Mason 1970 - with majorite end member as $\{Mg_3\}[SiMg](Si_3)O_{12}$) - described long after the pyralspite-(u)grandite scheme was proposed, are not at all covered by the pyralspite-ugrandite classification scheme. Actually, it may be the case that many, possibly even the bulk of silicate garnet in the Earth is not covered by the scheme, because the transition zone is composed of approximately 40% majoritic garnet (e.g., Irifune, 1987)!

Synthetic Silicate Garnets

In addition to the analysis afforded by natural garnets, quantitative information on the possible compositional range of silicate garnet can be obtained by experimental laboratory investigations. Interestingly, Boeke (1914, p. 153) wrote more than 100 years ago that equilibrium investigations would “provide the final word” on this question. In the lab, unlike nature, the composition of a thermodynamic system can be chosen and P and T fixed exactly. The first laboratory test of Boeke’s assertion was only possible nearly 5 decades later in the late 1950s following technical developments in high-pressure devices. The synthesis and phase relations of grossular, pyrope and almandine and their solid solutions, which are not stable at 1 atm, could now be investigated. Chinner et al. (1960) were probably the first to show that extensive solid solution between pyrope and grossular, as well as between pyrope and almandine, was possible. Their first results on these two binaries were later confirmed a number of times in different investigations. In addition, a number of other binary garnet solid solutions have been synthesized in the lab including almandine-grossular, spessartine-grossular, spessartine-pyrope, spessartine-uvarovite, andradite-grossular, grossular-uvarovite, and almandine-spessartine (Fig. 7). Of course, various ternary, quaternary and higher-order compositions within the six-component system pyrope-almandine-spessartine-grossular-andradite-uvarovite have been synthesized and their phase relations studied as well.

Conclusion: The pyralspite-(u)grandite and other garnet classification schemes

Geiger (2008) wrote, “The Pyralspite-Ugrandite classification scheme has outgrown its usefulness in terms of describing and understanding the silicate garnets in terms of their compositions and stabilities. ... It is concluded that the Pyralspite-Ugrandite classification for silicate garnets should largely be dropped - or at best be used for purely mnemonic purposes. It should not be used to interpret solid-solution behavior, the occurrence of certain garnet compositions in nature or the lack thereof, or to infer major differences in bonding and crystal-chemical behavior between the two groups.” This has been done in some studies on garnet.

Are other classifications better and/or are they even necessary and, if so, to what scientific extent? Sobolev (1964), following along the lines of Boeke (1914) some five decades later, in an analysis of a large number of natural garnet compositions, proposed a classification scheme different than that of the Winchells. He recognized four main species, almandine-pyrope, almandine-spessartite, spessartite-grossularite, and grossularite-andradite with a possible fifth species for titanium-bearing garnet. Sobolev's diagram for the ternary system almandine-pyrope-spessartine, for example, shows compositions of natural garnets essentially spanning the entire compositional range between pyrope and almandine and between almandine and spessartine, but with very limited compositional variation between spessartine and pyrope. Boeke (1914) noted for all intents and purposes the same. The ternary almandine-pyrope-spessartine in both works is characterized by a large compositional gap at the pyrope-spessartine binary that extends into the ternary system. This behavior is not correct however. Research starting around the late 1970s demonstrated that natural largely pyrope-spessartine garnets[23] (and nearly ternary pyrope-spessartine-almandine compositions), though rare, do occur in nature (Table 1). Interestingly, they are often referred to as color change garnets that are typically characterized by pink to pinkish orange colors (Schmetzer et al., 2001), but in a few instances they may have a blue-green (e.g., Schmetzer and Bernhardt, 1999) or even a deeper blue color in daylight[24]. Localities for these garnets are in East Africa (Umba mining region), Sri Lanka and Madagascar. There should be complete solid solution over the whole pyrope-almandine-spessartine ternary at high temperatures and pressures.

Summarizing, garnet compositions falling between the pyralspite and (u)grandite fields do occur. This conclusion was reached before (e.g., Sobolev, 1964; Nemec 1967). The pyralspite and (u)grandite species or series and the like (various sources) have no validity. There is little scientific reason or justification for using any mineralogical classification for the common silicate garnets that is based on the reported degree of solid solution among or between the various end-members. In a detailed contribution on the question of garnet classification, Grew et al. (2013) list all the common silicate garnets, as well as others, into a single supergroup. The various garnet species names simply correspond to the dominant end-member component in a solid-solution crystal.

THE PRESENT STATE OF THE FIELD

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[23] Wherry (1923) noted that the absence of any natural pyrope-spessartine garnets at that time had a chemical and not a volume origin!

[24] With their discovery, the color of natural silicate garnet spans the entire color range of the visible light spectrum – violet, blue, (cyan), green, yellow, orange and red (also colorless or white, as well as black, garnets can be found).

Substitutional Solid Solutions: Atomic Size and Volumes, Structural and Thermodynamic Properties, and the Role of Strain

The structural and crystal-chemical properties of the common silicate garnets, both (nearly) end-member and solid-solution compositions, and the relationships among them have been analyzed by X-ray single-crystal diffraction methods (e.g., Novak and Gibbs, 1971; Armbruster et al., 1992; Merli et al., 1995) and using various spectroscopies (Geiger, 2004) many times. The experimental results show that the "pyralspites" and "ugrandites" are separated by certain characteristic structural behavior such as bond length (Fig. 8; see also Novak and Gibbs, 1971). The whole story does not, though, end here.

There are two points to be addressed. The first has to do with chemistry. The thermodynamic stability or occurrence of a phase with respect to another phase or phase assemblage is a function of temperature, pressure and composition of the system, as discussed above. Considering the enormous range of P-T conditions existing in the Earth, one can conclude that the occurrence of any given silicate garnet is determined by the different bulk-composition systems that occur in nature. The relatively few number of garnet compositions falling between the pyralspites and (u)grandites (Figs. 6 and 8) reflects the lack of appropriate bulk compositions necessary for these garnets to crystallize. This simple fact is sometimes forgotten or overlooked.

The second point is structurally and thermodynamically related. It involves the important effect that the size of atoms has on solid-solution behavior, a main theme of this manuscript. The size of the mixing atoms is reflected in the macroscopic thermodynamic properties, for example, in the volume of mixing behavior for say a garnet solid solution. Volume can measured with high precision and accuracy, provided good crystals can be synthesized. It often turns out that many solid solutions, including those of garnet, do not strictly obey Vegard's law - eqn. (3). Unit-cell edges and molar volumes can show slight deviations from linearity across a binary (i.e., ideality in a thermodynamic sense, $\Delta\ ^{mix,ideal}$). This gives rise to an excess volume of mixing, $\Delta\ ^{excess}$, as defined by

$$\Delta V^{excess} = \Delta V^{mix,real} - \Delta V^{mix,ideal} = \Delta V^{mix,real} - \sum X_i V_i^o \qquad (4),$$

where $\Delta\ ^{mix,real}$ is the real or measured volume of mixing and V_i^o the volume of the different end-member phases. For silicate substitutional solid solutions with random or nearly random atomic mixing, $\Delta\ ^{excess}$ often deviates from $\Delta\ ^{mix,ideal}$ in a positive manner and is seldom negative (Geiger, 2001). When atomic ordering occurs, $\Delta\ ^{excess}$ can be negative in behavior.

ΔV^{ex} behavior can be described to first order using a so-called symmetric mixing model, where $\Delta V^{excess} = W^{V} \cdot X_A(1 - X_A)$ and W^V is the volume interaction parameter and X_A the mole fraction of component A. Figure 9a shows excess volumes, □□□□□□□□□̣□□̣□$^{\square}$, for six binary aluminosilicate (i.e., $X_3Al_2Z_3O_{12}$) garnet solid solutions as a function of the volume difference, ΔV, where $\Delta V = \left(V_B^o - V_A^o\right) / V_{\overline{BA}}$ with V_B^o the molar volume of the larger component, V_A^o that of the smaller component and $V_{\overline{BA}}$ the mean of the two. W^V is a positive function of ΔV, but the choice between linear and quadratic behavior is difficult to make. Computer simulations on hypothetical binary aluminosilicate garnet solid solutions, made with empirical pair potentials, show, however, that quadratic behavior is expected (Fig. 9b - Bosenick et al., 2001). It was also shown by these authors that the excess enthalpy of mixing, ΔH^{excess}, behaved similarly (cf., Davies and Navrotsky, 1983). This quadratic dependence of the Δ ^{excess} and ΔH^{excess} for binary homovalent solid-solution systems is an important result with regard to understanding thermodynamic mixing behavior.

The recent experimental and computational modeling results build upon the earlier works from the 1910s to 1930s discussed above in terms of atomic size and solid-solution behavior and they are a quantitative extension of them. It is expected that size difference(s) among the mixing cation determines the thermodynamic behavior for solid solutions in the system pyrope-almandine-spessartine-grossular-uvarovite-andradite[25] (see Ganguly and Kennedy, 1974, for early work on garnet in this direction and for other solid-solution phases Davies and Navrotsky, 1983). Table 2 lists the difference in molar volume, ΔV_M, between various garnet end members for the 15 binaries of the six-component system (Fig. 7). Garnets for three binaries in Table 2 have not been found in nature nor synthesized in the laboratory. It must be noted, though, that in comparing the various ΔV_M values that different types of structural cation mixing in garnet occurs, involving either the X- and Y-site or both. The structures and local microscopic strain, and therefore thermodynamic mixing behavior, appear to respond differently depending upon which crystallographic site(s) solid solution takes place (Woodland et al. 2009). They argue that binaries involving the mixing of trivalent cations at the Y-site often, but not always, show negative ΔV^{ex} behavior.

Consider further pyrope-grossular, $\{Mg_{3-x}Ca_x\}Al_2Si_3O_{12}$, garnets, because they have been intensively studied and their structural-property relationships are the best understood. This binary is characterized by substantial positive nonideality in all the macroscopic thermodynamic

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[25] Fyfe (1951) in his paper "Isomorphism and Bond Type" discussed the role of chemical bonding in affecting solid-solution behavior in various phases. Other physical factors can also play a role such as atomic valence, electronegativity differences, and electronic effects such as crystal field stabilization energies.

mixing functions ΔG^{mix}, ΔH^{mix}, ΔS^{mix} and ΔV^{mix} (Dachs and Geiger, 2006). ΔH^{mix} behavior (Newton et al., 1977) is important in terms of stability, as this function is what largely controls the miscibility gap along the pyrope-grossular join (Fig. 10). Complete solid solution between pyrope and grossular is only achieved at high temperatures and pressures[26], whereas there should be unmixing at lower temperatures for more pyrope-rich compositions (Dachs and Geiger 2006).[27] What on a local scale is causing the destabilizing positive ΔH^{mix} behavior, which should lead to exsolution of Ca-rich and Mg-rich garnets? The answer is microscopic lattice strain. This was measured using X-ray powder diffraction measurements on a series of synthetic $\{Mg_xCa_{1-x}\}_3Al_2Si_3O_{12}$ solid-solution garnets (Dapiaggi et al., 2005; see also Du et al., 2016). These high-resolution synchrotron measurements allow a quantitative determination of minor variations in powder reflection line widths that, in turn, give information on elastic strain. The results show that strain is smallest for end-member grossular and pyrope, which have no local structural heterogeneity caused by Ca and Mg mixing. Intermediate compositions, on the other hand, show reflection broadening reflecting their local structural heterogeneity. This produces elastic strain that is asymmetric in nature across the binary, which is similar in behavior as ΔH^{mix} (Dapiaggi et al., 2005). The simplest crystal-chemical interpretation is that it is easier to incorporate a smaller Mg cation (0.89 Å – Shannon, 1976) in a larger volume grossular-rich host than a larger Ca (1.12 Å) cation in a smaller volume pyrope-rich garnet. The actual physical situation at the local level is more complicated, though, because it involves the distortion of strongly bonded SiO_4 and AlO_6 groups that are edged-shared to $(Mg/Ca)O_8$ dodecahedra (see Bosenick et al., 2000). It is this distortion and/or stretching of strong bonds that significantly affects ΔH^{mix}. It follows that, for the six aluminosilicate binary solid solutions (Fig. 7), pyrope-grossular garnets are the most nonideal (Bosenick et al. 2001).

IMPLICATIONS AND FUTURE RESEARCH

Much has been learned about the chemical and physical properties of minerals over the past 250 years, but the scientific quest is certainly far from over. Most rock-forming minerals, which are largely silicates, are substitutional solid solutions. Their macroscopic thermodynamic properties, and thus their stabilities in the Earth, are a function of complex local structural and crystal-chemical properties. Both the microscopic and macroscopic realms and the link between

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[26] It is interesting, furthermore, to note that complete solid solution between pyrope and grossular is possible although the difference in radii between Mg and Ca is greater than 15%.

[27] Reports of exsolution in natural garnet exist (e.g. Wang et al., 2000), but more definitive study is required, especially with regard to the crystallographic and microscopic aspects.

them are required to achieve a full understanding of solid-solution behavior. What is, briefly, the state of the research field today? A number of issues were already discussed in Geiger (2001). New understanding on microscopic structural properties is coming from a variety of different spectroscopic measurements, which are continually increasing in sophistication, and are also being made at different temperatures and pressures (for garnet see Geiger, 2004, and for a review of spectroscopic methods, in general, see Henderson et al., 2014). Diffraction- and spectroscopic-based results are highly complementary and go hand-in-hand in describing crystal properties over different length scales.

Local crystal-structure properties are also now being investigated computationally. There are a number of different approaches (*e.g.* static lattice energy with empirical pair potentials, quantum mechanical first principle, Monte Carlo, molecular dynamics, pair distribution function analysis) that allow ‘simulation experiments’ (Geiger 2001). Indeed, many experimental tools are decidedly blunt when it comes to investigating atomistic-level properties and computer simulations have opened up a whole new area of research. In some cases, even first principle calculations are now possible on relatively complex crystal structures with larger unit cells. However, the study of many key silicate solid solutions (e.g., garnets, micas, amphiboles, pyroxenes), especially those containing transition metals, still remains a serious challenge.

In terms of theory, little is understood about the precise nature of local strain fields and the nature of their interactions and what their associated elastic energies are in a solid solution beyond minor-element substitution levels. At minor concentration levels of atomic substitution, physical models describing strain energy and element partitioning behavior, for example, have been formulated under simplified assumptions (e.g. Eshelby, 1954; 1955; Nagasawa, 1966; Brice, 1975). However, constructing physical models to describe strain is very difficult for complex, low-symmetry anisotropic structures, as in many silicates. In addition to strain fields and elastic energies, electronic and magnetic behavior in solid solutions and their effect on macroscopic physical properties are poorly known. For example, it is not well understood: i) how bonding character (Gibbs et al., 2014) may vary slightly across a homovalent binary solid solution (see Geiger, 2008, for the case of aluminosilicate garnet), ii) how magnetic properties and phase transitions behave as a function of composition, iii) how magnons and phonons can interact and, thus, affect macroscopic thermodynamic behavior, and iv.) how electronic high spin-low spin transitions behave as a function of pressure, temperature and composition.

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FIGURES

Figure 1. Alexander Newton Winchell mineralogist, former president of the Mineralogical Society of America (1932) and Roebling Medal recipient (1955), as taken from Emmons (1959).

Figure 2. Haüy's illustration (1801 – PL. II, figures 11 and 13) showing how the dodecahedron (left), a typical habit of silicate garnet with rhombic {110} crystal faces, is constructed by the progressive decrement of one row of *molécules intégrantes* (right).

Figure 3. Natural crystals of uvarovite (Photo Credit: Quebul Fine Minerals), grossular (Photo Credit: Peter Cristofono), andradite (Photo Credit: Dr. Didier Descouens), almandine (Photo Credit: ©JohnBetts-FineMinerals.com), spessartine (Photo Credit: Tom Loomis ©Dakota Matrix Minerals, Inc.), as well as synthetic Cr-bearing pyrope (Geiger et al., 2000) with all showing rhombic dodecahedral {110} faces (left to right and top to bottom). These garnet crystals exhibit a text-book example of isomorphs (i.e., crystals with the same form but different composition) and they form an isomorphic series (see text) or in current terminology a substitutional solid-solution series or group.

Figure 4. Illustration showing various packings, mostly of spheres, as constructed by Wollaston (1813), to account for the form of certain crystal structures. Note especially those packings (i.e., 7, 8, 9, 11,14) showing different shaded spheres.

Figure 5. Debye-Scherrer diffraction films showing reflections for the phases KBr, K(Br,Cl) and KCl and their assigned indices below (from Vegard, 1921).

Figure 6. The pyralspite-grandite system as first defined by Winchell and Winchell (1927), using the data of Boeke (1914). Garnets represented by open circles and falling between the two garnet groups in this diagram were discussed by Boeke. Several of them, but not all, were considered to be poorly analyzed or represented contaminated garnets (i.e., other phases were present).

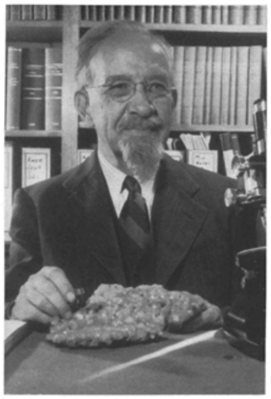
Figure 7. Octahedron showing the six component silicate garnet system Py = pyrope, Al = almandine, Sp = spessartine, Gr = grossular, An = andradite, and Uv = uvarovite (modified from Geiger, 2008). Binary compositions shown by the solid lines have been synthesized in

the laboratory, the dotted lines represent joins where seldom-occurring natural garnets approaching the binary compositions have been found and garnets along those joins shown by dashed lines have yet to be synthesized or found in nature. Various multicomponent garnets can be found in this system or its subsystems. The molar volume for the different end-members is given in J/bar.

Figure 8. Cation-oxygen bond-length behavior as a function of the unit cell edge, a_o (Å), from X-ray single-crystal refinements on 281 silicate garnets (Merli et al., 1995). Z-O is the tetrahedrally coordinated cation-oxygen bond length, Y-O is the octahedrally coordinated cation-oxygen bond length and <X-O> is the average dodecahedral coordinated cation-oxygen bond length of X-O(2) and X-O(4). Note the difference in the change in length behavior between PYR and GRO versus GRO and AND (PYR = pyrope, GRO = grossular, AND = andradite and SCH = schorlomite) and the gap in garnet compositions between PYR and GRO.

Figure 9. Excess volumes of mixing for six different binary aluminosilicate solid solutions, expressed using a symmetric solution model with W^V, versus a volume difference term, ΔV (as defined in the text), as determined experimentally (left - Geiger, 2000). Both linear and quadratic fits to the data (squares) are shown. Excess volumes for three different aluminosilicate garnet solid solutions, expressed using a symmetric solution model with W^V, versus a volume difference term, here defined as $\Delta V = V_{Large} - V_{Small}$, as determined computationally (right - Bosenick et al., 2001). Note also the difference in units.

Figure 10. Calculated *T-X* phase diagram for pyrope-grossular, $(Mg_xCa_{1-x})_3Al_2Si_3O_{12}$, solid solutions at P = 1 atm (model M1-G from Dachs and Geiger, 2006).



Alexander Newton Winchell
1874–1958

Figure 1

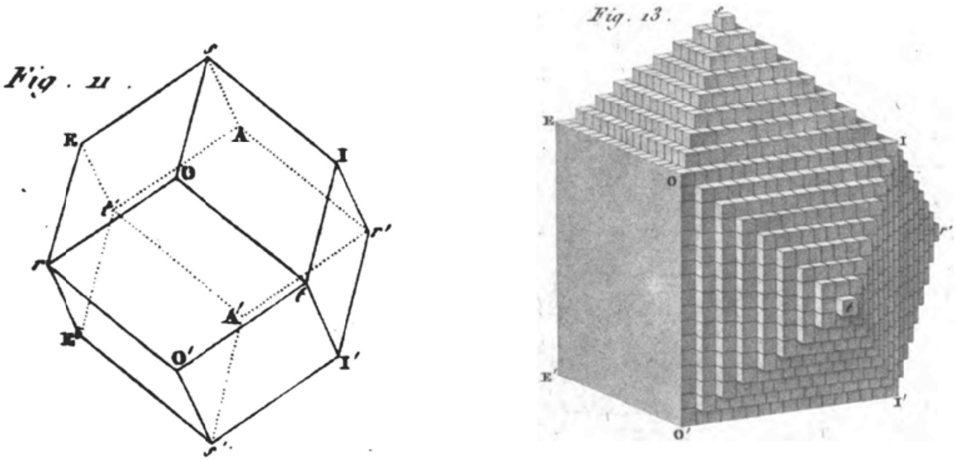


Figure 2

Figure 3

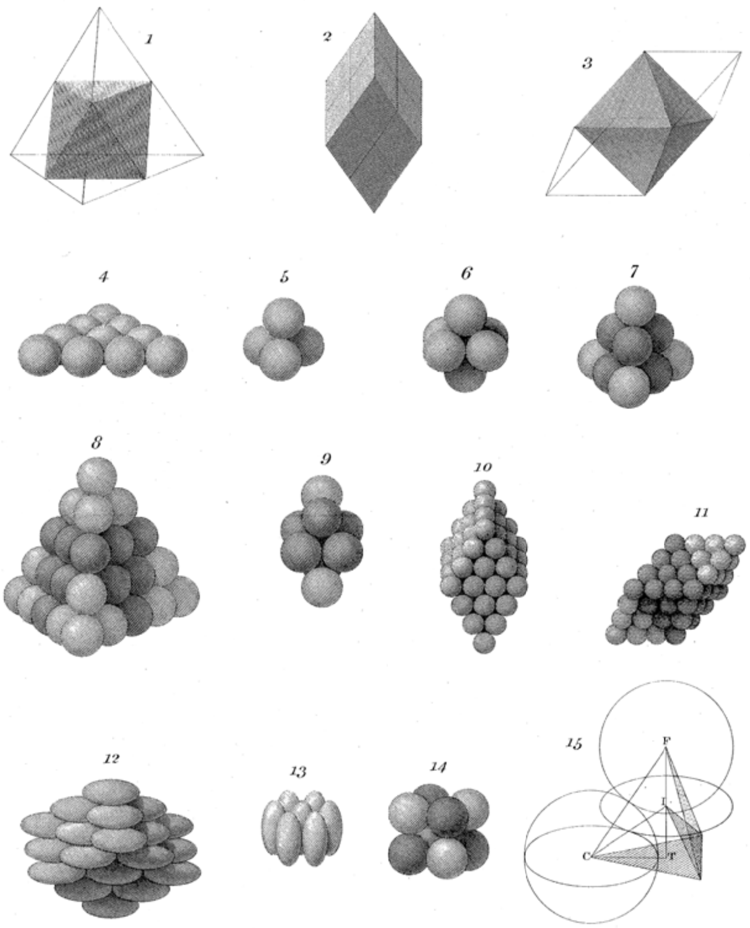
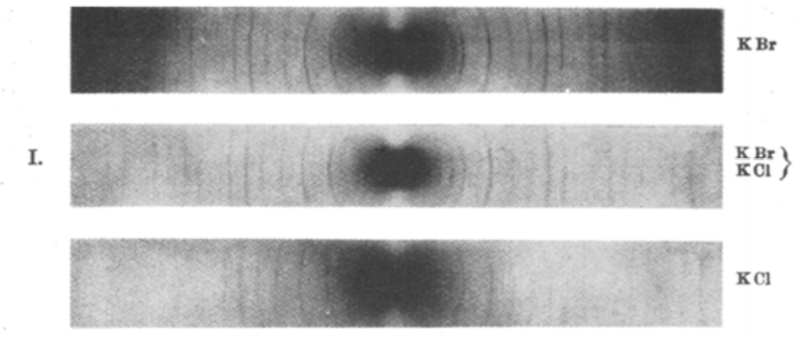


Figure 4


KBr
I.
KBr
KCl
KCl

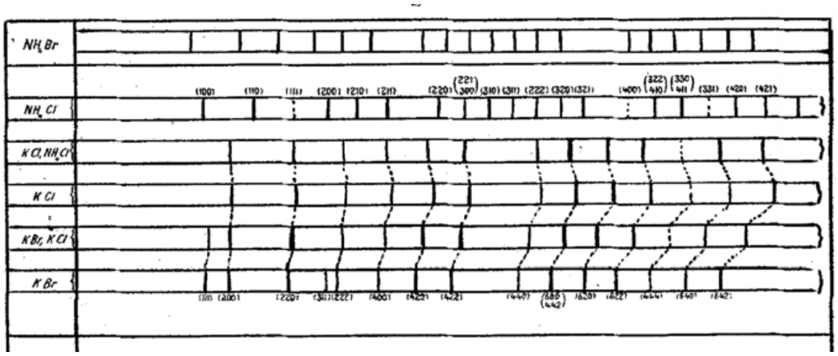

NH4Br
NH4Cl
KCl, NH4Cl
KCl
KBr, KCl
KBr
(100) (110) (111) (200) (210) (211) (220) (221/300) (310) (311) (222) (320) (321) (400) (322/410) (330/411) (331) (420) (421)
(111) (200) (220) (311) (222) (400) (420) (422) (440) (600/442) (620) (622) (444) (640) (642)

Fig. 5

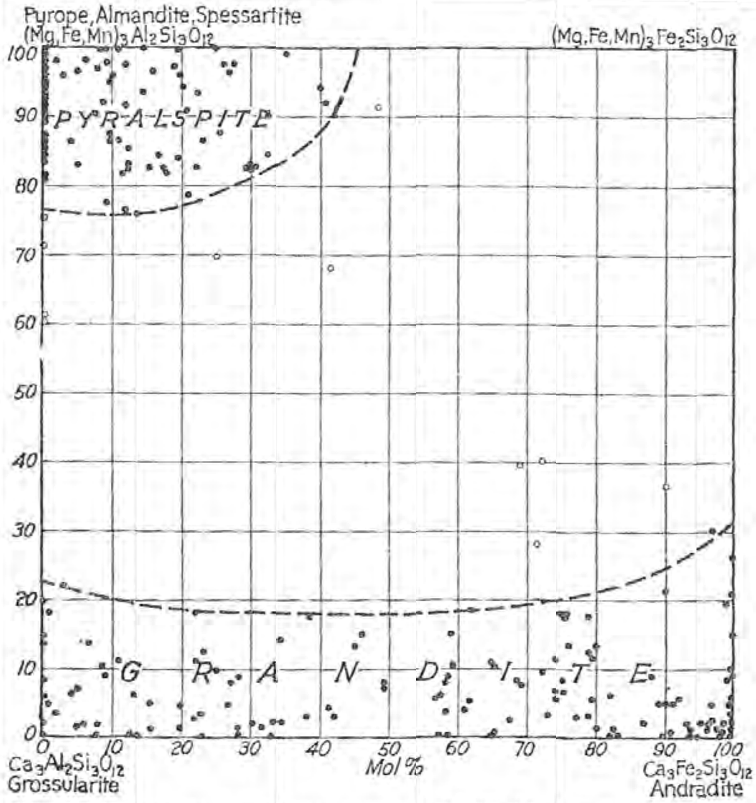


FIG. 185.—Variations in composition in garnet. Modified from Boeke: *Zeit. Kryst.*, LIII, 1914, p. 149.

Figure 6

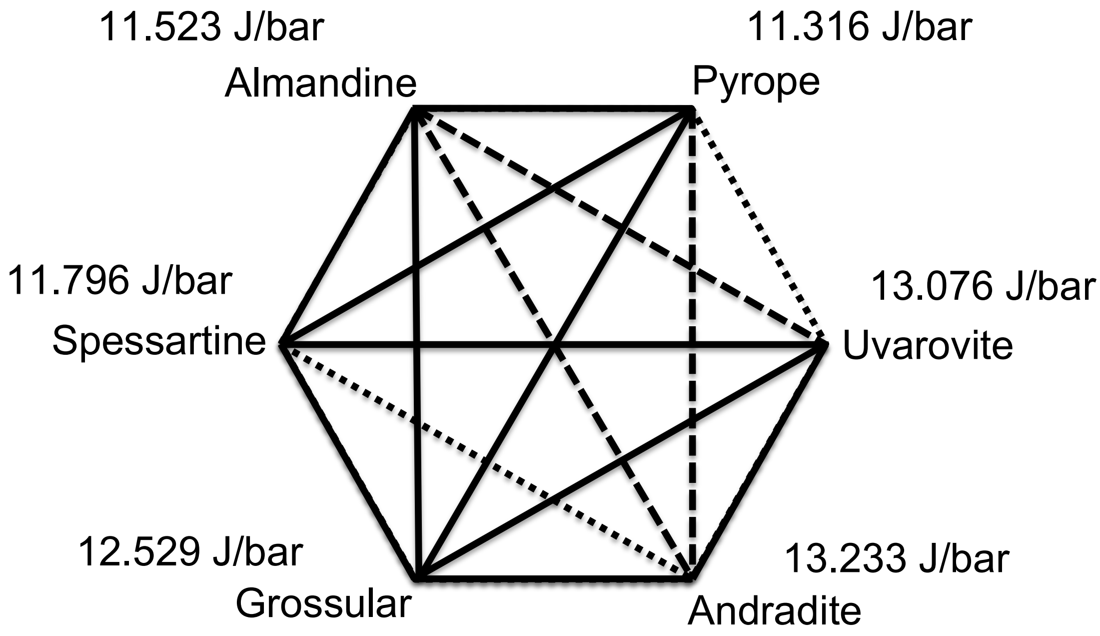

11.523 J/bar
Almandine
11.316 J/bar
Pyrope
11.796 J/bar
Spessartine
13.076 J/bar
Uvarovite
12.529 J/bar
Grossular
13.233 J/bar
Andradite

Figure 7

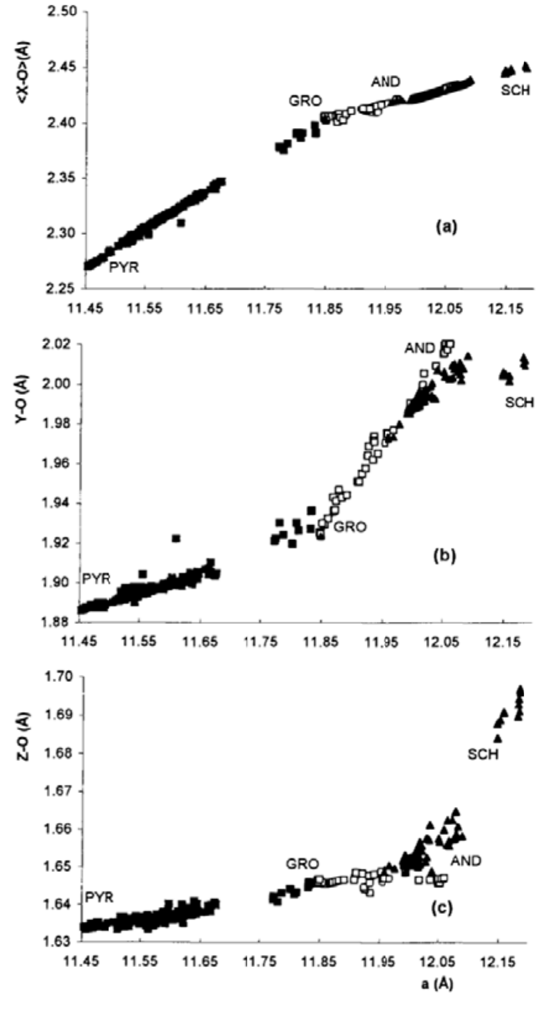

<X-O>(Å)
2.50
2.45
2.40
2.35
2.30
2.25
GRO
AND
SCH
PYR
(a)
11.45
11.55
11.65
11.75
11.85
11.95
12.05
12.15
Y-O (Å)
2.02
2.00
1.98
1.96
1.94
1.92
1.90
1.88
AND
SCH
GRO
PYR
(b)
Z-O (Å)
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.63
SCH
GRO
AND
PYR
(c)
a (Å)

Figure 8

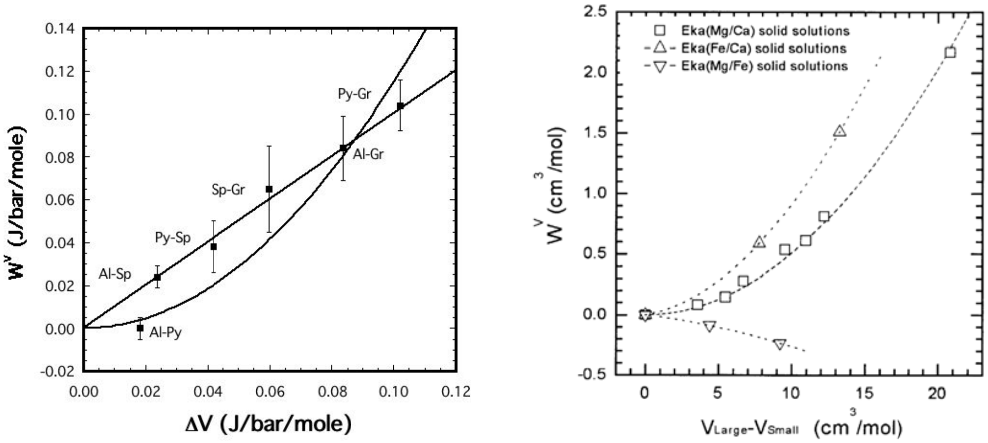

0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
W^v (J/bar/mole)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
ΔV (J/bar/mole)
Py-Gr
Al-Gr
Sp-Gr
Py-Sp
Al-Sp
Al-Py
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
W^v (cm^3/mol)
0
5
10
15
20
V_Large-V_Small (cm^3/mol)
Eka(Mg/Ca) solid solutions
Eka(Fe/Ca) solid solutions
Eka(Mg/Fe) solid solutions

Figure 9

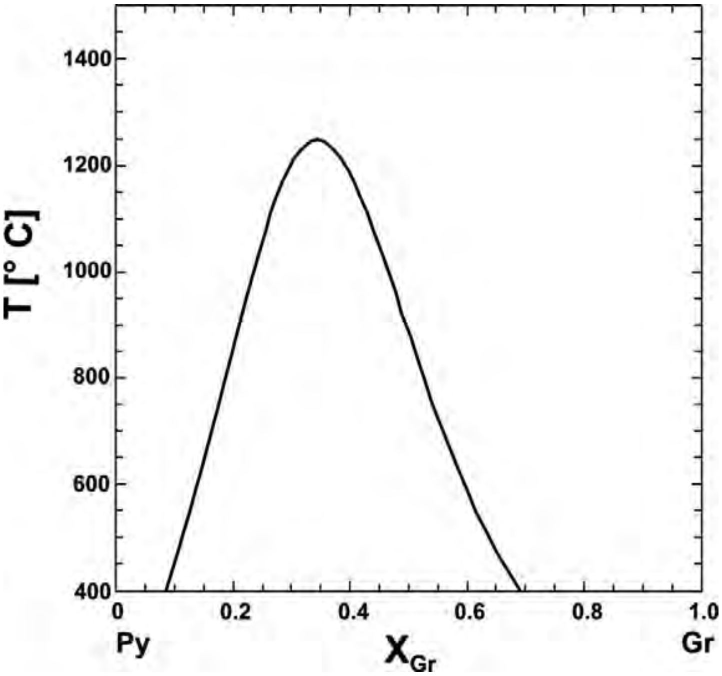


Figure 10

Table 1. Crystal chemical formulae of selected natural garnet solid solutions calculated following Locock (2008).
An = andradite, Sp = spessartine, Gr = grossular, Al = almandine, Py = pyrope, Uv = Uvarovite. Remainder means unassigned.

End-Member	Formula	An-Sp #2955[1]	Sp-Gr "A"[2]	Gr-Al 123(core)[3]	Gr-Al M.56.4 E (rim)[4]	Uv-Py S-1[5]	Gr-Py-Al (table)[6]	Gr-Py (table)[7] (core)	Py-Sp (M1)[8]
Hutcheonite[9]	$\{Ca_3\}[Ti_2](SiAl_2)O_{12}$	0.19%	0.54%					0.46%	0.03%
Majorite	$\{Mg_3\}[SiMg](Si_3)O_{12}$					4.91%			
Morimotoite	$\{Ca_3\}[TiFe](Si_3)O_{12}$					0.37%			
Morimotoite-Mg[10]	$\{Ca_3\}[TiMg](Si_3)O_{12}$			0.78%		0.68%			
Uvarovite	$\{Ca_3\}[Cr_2](Si_3)O_{12}$					45.92%	0.18%		0.26%
Goldmanite	$\{Ca_3\}[V_2](Si_3)O_{12}$								0.32%
Spessartine	$\{Mn_3\}[Al_2](Si_3)O_{12}$	26.94%	44.07%	3.14%	3.57%	0.75%	0.30%	2.39%	30.29%
Pyrope	$\{Mg_3\}[Al_2](Si_3)O_{12}$	0.42%		0.75%	1.52%	29.88%	27.59%	35.92%	60.97%
Almandine	$\{Fe_3\}[Al_2](Si_3)O_{12}$	1.17%	3.20%	43.82%	41.74%	11.57%	23.17%	0.36%	2.97%
Grossular	$\{Ca_3\}[Al_2](Si_3)O_{12}$	6.56%	38.12%	47.04%	46.25%	5.58%	46.02%	58.39%	4.08%
Andradite	$\{Ca_3\}[Fe_2](Si_3)O_{12}$	61.70%	3.20%	0.29%	5.58%			1.67%	

[1] Lee (1958); [2] Lee (1962); [3] Ackermand et al. (1972); [4] Ashworth and Evirgen (1984); [5] Sobolev et al. (1973); [6] O'Hara and Mercy (1966); [7] Sobolev et al. (2001); [8] Schmetzer et al. (2001); [9] the species hutcheonite (Ma and Krot, 2014) replaces the hypothetical end-member schorlomite-Al of Locock (2008); [10] a hypothetical end-member composition.

Table 2. Difference in molar volume, ΔV_M, between end-member garnets for the 15 binaries in the six component system pyrope-almandine-spessartine-uvarovite-grossular-andradite. Garnets for those binaries in italics have neither been found in nature nor synthesized in the laboratory.

Binary	Difference in Molar Volume (J/bar)
andradite-pyrope	1.918
uvarovite-pyrope	1.760
andradite-almandine	1.710
uvarovite-almandine	1.553
andradite-spessartine	1.437
uvarovite-spessartine	1.280
grossular-pyrope	1.214
grossular-almandine	1.006
grossular-spessartine	0.733
andradite-grossular	0.704
uvarovite-grossular	0.547
spessartine-pyrope	0.480
spessartine-almandine	0.273
almandine-pyrope	0.207
andradite-uvarovite	0.157