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EXPERIMENTAL STUDY OF THE SOLID SOLUTION BETWEEN THE GROSSULAR-ALMANDINE SERIES

by

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(with 1 Table and 2 Text-figures)

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Introduction

A solubility gap has been thought to exist under natural conditions between the pyrospite and ugrandite groups of garnet. Recently, however, Frondel and ITO (1965) have indicated that a probably complete series extends, under some natural conditions, between grossular and spessartine. In experiments with synthetic garnets they found complete solid solution in this series under hydrothermal conditions (1968). Also SUWA and NAKA (1971) have recently synthesized a solid solution series between uvarovite and spessartine at high pressure. These facts suggest that no solubility gap exists between the pyrospite and ugrandite groups of garnet.

The six normal species of natural garnet have been listed already. In addition it must be considered theoretically possible to have sixteen species in garnet. Some of the unusual combinations reported have been given various names; skiagite $\text{Fe}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, calderite $\text{Mn}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, blythite $\text{Mn}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$, hanleite $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$, koharite $\text{Mg}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ and goldmanite $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$. In fact, recently, MASON et al. (1968) have found the end member of magnesium iron garnet, with the composition $\text{Mg}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, in the Coorara chondrite from Western Australia. Garnet has thus been identified for the first time as a meteorite mineral. Also NIXON and HORNING (1968) have proven that garnet from Kao Kimberlite pipe, Lesotho, Basutoland, Africa, contains a major proportion of $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$. This end member is named knorringite. MEYER (1968) also described Cr-rich pyrope as inclusions in diamonds, similar to those described by Nixon and Hornung. Pure magnesium chromium garnet has been synthesized under 20 Kb at 800°C by ROY and TUTTLE (1965) and 30 Kb at 1000°C by Hariya (1971).

Recent experiments on some garnet solid solution series and the discovery of some new natural garnet, indicate that there is no solubility gap between the pyrospite and ugrandite groups of six end members in natural garnets. From

these view points experimental study of the relationship between grossular $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and almandine $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ under high pressure conditions has been made.

Experimental method

High pressure experiments in the present study were carried out in the single stage piston cylinder apparatus. The working volume was of 1.25 cm bore and 5 cm length. The pressure transmitting medium was molten pyrex glass and the design of the pressure cell was similar to that figured by HARIYA and KENNEDY (1968). A hysteresis loop, relating piston displacement to ram thrust, on compression and decompression cycles was determined at a number of temperature. The double value of friction was applied, as a function of both temperature and pressure (HARIYA, DOLLASE and KENNEDY, 1969). Reported pressures are believed to be correct to within 1 kilobar.

Temperatures were measured with a chromel-alumel thermocouple which was in contact with platinum sample capsules.

As a starting material mixtures of the four compositions between grossular and almandine were prepared from calcium carbonate, ferrous oxalate, aluminum oxide and quartz or silica gel in stoichiometric proportions.

Post-run phase identifications were made by X-Ray powder diffraction patterns and optical microscopy. The unit cell dimensions were computed by averaging the values obtained from the reflections 642 and 640. Each composition was run for periods of 12 to 36 hours at two different pressures; 1000°C at 13 Kb and 20 Kb.

Experimental results

Intermediate garnets with compositions almandine 80 grossular 20, almandine 60 grossular 40, almandine 40 grossular 60 and almandine 20 grossular 80 were synthesized. Difficulty was experienced in crystallizing the charge to 100 per cent garnet, and in some runs small amounts of an unknown metastable phase tended to persist. Nucleation of these garnets is very difficult, probably due to the high activation energy. Nevertheless the synthetic garnets themselves, were distinctly crystalline under the optical microscope. Grains of garnet are commonly 2 to 3 μ in diameter and a few well developed aggregate crystals from 5 to 8 μ in diameter were observed. Due to their small size optical measurement was extremely difficult. The experimental results are given in Table 1.

In some synthetic iron silicates unit cell parameters and refringence change

Table 1. Synthetic data of grossular-almandine series

starting material oxide mixture	pressure (Kb)	temperature (°C)	time (hr)	unit cell dimention a Å	index n	remarks
Gro ₂₀ Alm ₈₀	13	1000	36	11.601+0.002		small amount x-phase and gl
	20	1000	36	11.572+0.002		small amount gl
Gro ₄₀ Alm ₆₀	13	1000	24	11.682+0.002		x-phase and small amount gl
	20	1000	12	11.656+0.002	1.793	
Gro ₆₀ Alm ₄₀	13	1000	12	11.745+0.002	1.769	small amount gl
	20	1000	12	11.736+0.001		
Gro ₈₀ Alm ₂₀	13	1000	24	11.803+0.001		small amount starting material and x-phase
	13	1000	24	11.800+0.002		small amount starting material and x-phase

Gro: grossular composition Alm: almandine composition gl: glass

very systematically with respect to the variation in Fe^{3+}/Fe^{2+} ratio, itself a function of f_{O_2} . If some ferrous iron was oxidized to ferric iron, during the synthesis of garnet in this study, it must be substituting for Al^{3+} ions in octahedral coordination in the garnet structure. If so, we must have two garnet solid solutions such as grossular-andradite and grossular-almandine series. From observation by optical microscope and X-Ray powder patterns, all runs show only one phase garnet solid solution.

The unit cell dimension of the synthetic garnets was determined by X-Ray diffractometer. The variation in the unit cell dimensions and refractive indices is shown graphically in figure 1. From this it may be seen that both unit cell dimensions and refractive indices of these garnets change lineally with molar composition. The unit cell $a = 11.860$ Å of the synthetic grossular end composition determined by one of the authors (HARIYA, 1968) is identical with the value $a = 11.86$ Å determined by Roy and Roy (1960). This value is used for the grossular end composition in figure 1. The unit cell $a = 11.528$ Å for almandine is taken from data on synthetic garnets compiled by Hsu (1968). The results of this study suggest that systematic changes in unit cell dimensions

and refractive indices are due to continuous solid solution between grossular and almandine.

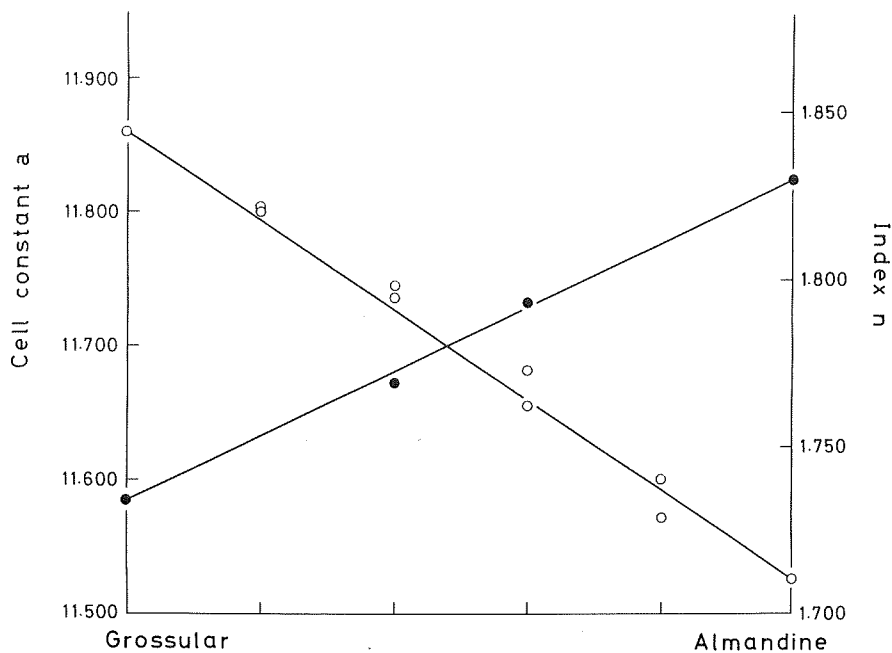


Fig. 1

Variation in unit cell dimension \circ (open circles) and refractive index \bullet (closed circles) with composition

General consideration of garnet solid solution

Garnet is a constituent mineral of a wide variety of metamorphic rocks and is also found in some granites, pegmatites and acid volcanic rocks. Numerous, recent chemical analyses of natural garnet from many different occurrences reveal an apparent solubility gap between the pyrospite and ugrandite groups. Variation in the composition of calcium and aluminum garnets termed pyrospite and ugrandite is shown in figure 2. The lack of complete solid solution between the two garnet sub-groups stands out clearly.

Ferrous iron and magnesium are interchangeable, producing a series of intermediate compositions between almandine and pyrope in the pyrospite series; similarly, a series of intermediate compositions exists between grossular and andradite in the ugrandite series. However, the difference in ionic size between calcium and ferrous iron allows limited substitution as seen from chemical analyses of natural garnets. Calcium and manganese also differ in ionic size and a solubility gap may exist between natural grossular and spessartine. However, Frondel and ITO (1965) indicate that a probably complete series

Pyrope, Almandine, Spessartine

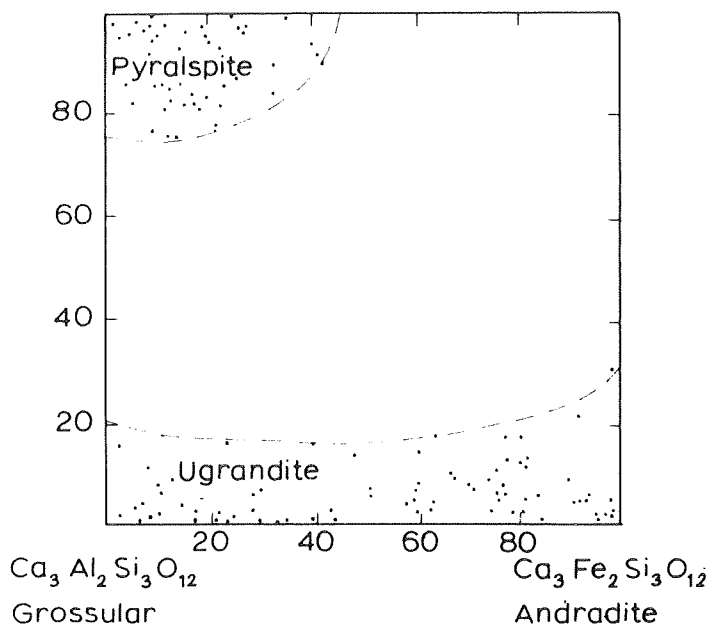
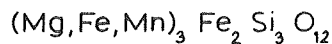
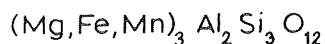


Fig. 2

Variation of the natural garnet composition. (A.N. WINCHELL)

extends, under some natural conditions, between grossular and spessartine.

Recent experimental data of Frondel and ITO (1968), and the data reported in this paper show no solubility gaps between grossular and spessartine, or between grossular and almandine. According to SUWA et al. (1971), complete solid solution is also possible between spessartine and uvarovite under high pressure conditions.

An attempt is being made to establish the relationship between synthetic pyrope and uvarovite. At pressure lower than 30 Kb and 1000°C, clinopyroxene is observed with garnet. At pressures higher than 30 Kb, clinopyroxene gradually disappears, and the garnet at still higher pressures differs from the low pressure phase. This difference is evident in the shift of reflections in X-Ray powder diffraction patterns. Thus, garnet appears to form complete solid solution between pyrope and uvarovite at high pressure.

The experimental data indicate the existence of continuous solid solution between the pyralspite and ugrandite groups under some experimental conditions. This suggests that a complete series may also extend between these two groups of garnets under some natural conditions.

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