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SYNTHESIS OF PYROPE-KNORRINGITE SOLID SOLUTION SERIES

A E RINGWOOD

Research School of Earth Sciences, Australian National University, Canberra, A.C T. (Australia)

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The garnet solid solution series between pyrope $Mg_3Al_2Si_3O_{12}$ and knorringite $Mg_3Cr_2Si_3O_{12}$ has been synthesized from oxide mixtures at pressures of 60–80 kbars and 1400–1500°C. Lattice parameters and refractive indices of solid solutions vary linearly with (molecular) composition within the limits of measurement. The lattice parameter of pure knorringite is 11 600 Å and its refractive index is 1.83 The genetic significance of mineral inclusions in natural diamonds is discussed, particularly in the light of the very high knorringite contents often found in garnet inclusions It is suggested that the most common mineral assemblage occurring as inclusions in diamonds (olivine + knorringite-rich garnet + enstatite) might be explained in terms of subduction into the mantle of olivine + chrome-spinel + enstatite cumulates originally formed by crystallization of mafic magmas within the oceanic crust The cumulate assemblage experienced alteration by circulating hydrothermal solutions, resulting in the introduction of some carbonate and serpentine minerals. During subduction, this assemblage was partially melted at depth below 150 km, accompanied by reduction of carbonate, to form a reconstituted assemblage consisting of olivine + knorringite-rich garnet + enstatite ± diamond.

1. Introduction

It has long been known that the pyrope-rich garnets occurring in garnet lherzolite and garnet harzburgite xenoliths in diamond pipes contain substantial amounts of chromium, mostly in the range 3–10 wt % Cr_2O_3. Similar garnets occur individually within diamond pipes. Many of these possess low calcium contents, so that the chromium component must be present as the $Mg_3Cr_2Si_3O_{12}$ molecule. In a study of garnets from the Kao kimberlite pipe, Lesotho, Nixon and Horming [1] discovered a garnet crystal containing 17 4% Cr_2O_3, equivalent to 34% of the $Mg_3Cr_2Si_3O_{12}$ molecule, which they named *knorringite.* A similar garnet was discovered as an inclusion in diamond by Meyer [2].

Detailed studies of mineral inclusions within natural diamonds by Meyer and Boyd [3] showed that after olivine, the next most common inclusion found was garnet Moreover, the great majority of these garnets were high-Cr, low-Ca types, containing up to 50% of the knorringite molecule. Parallel studies by Sobolev and co-workers [4,5] (see also Gurney and Switzer [22]) revealed similar results. One garnet inclusion in a diamond contained 20.3% Cr_2O_3, 2.2% CaO and 55 mol.% of the knorringite molecule (N.V. Sobolev, personal communication). Moreover, the latter workers found very rare individual high-Cr garnets in Siberian diamond pipes.

Further studies of Meyer and Boyd [6,7] and Sobolev et al. [5] demonstrated that the high-Cr garnets from natural diamonds also possessed higher 100 Mg/(Mg + Fe) ratios (mostly 85–92) than the garnets from garnet lherzolites (mostly 75–85) occurring as xenoliths in diamond pipes. The combination of high Cr_2O_3, low CaO (0.7–3.4%) and high 100 Mg/(Mg + Fe) ratios for the most abundant class of garnets occurring in diamonds as compared to the corresponding characteristics of the vast majority of garnets occurring in garnetiferous mafic and ultramafic rocks clearly points to highly specialized conditions of origin and may provide clues to the origin of many natural diamonds.

Previous accounts of efforts to synthesize knorringite have been somewhat ambiguous. In a one-page note in which the syntheses of many minerals were described, Coes [8] mentions the synthesis of $Mg_3Cr_2Si_3O_{12}$ in one line of the text. No further details were provided In a subsequent, much more detailed account of his researches on high-pressure mineral syntheses [9], there is no mention of the synthesis of $Mg_3Cr_2Si_3O_{12}$. Rovsha [10] reported the synthesis of pyrope containing up to 20% knorringite at 50–60 kbars and 1600°C Bykova and Genshaft [11] attempted to synthesize the pyrope-knorringite series in the pressure range 30–80 kbars at 1200–1500°C. They state that they failed to synthesize garnets containing more than 30–40% of the knorringite component. In apparent contradiction to this statement, they mention the successful synthesis of pure knorringite at 37 kbars. The very large uncertainty quoted in the lattice parameter (11.92 ± 0.05 Å) implies a poorly crystallized and characterized product. Moreover, this value disagrees so grossly with the actual lattice parameter of knorringite determined below (11.600 ± 0.001 Å), that Bykova and Genshaft's statement should be regarded with reserve.

2. Experimental

Attempts to produce glass starting materials in compositions containing more than 50 mol.% knorringite were unsuccessful, owing to devitrification during quenching. Accordingly, oxide mixes of appropriate composition were prepared by intimately mixing magnesium oxide, silicic acid, chromic oxide and aluminium hydroxide, pelletizing and heating in air at 1100°C for three hours, followed by regrinding. Mixtures were made up with the following compositions: $Mg_3Cr_2Si_3O_{12}$, $Mg_3Cr_{1.8}Al_{0.2}Si_3O_{12}$, $Mg_3Cr_{1.5}Al_{0.5}Si_3O_{12}$ and $Mg_3CrAlSi_3O_{12}$.

The high-pressure apparatus used consisted of a pair of Bridgman anvils possessing 1.5-inch diameter faces. This apparatus had previously been used by Liebermann et al. [12] in the synthesis of large samples of stishovite and resembles a scaled-up version of the apparatus described by Nishikawa and Akimoto [13]. Whilst the device is well-suited to measurement of phase equilibria below 1100°C, we found that it did not possess pressure stability in runs carried out above 1200°C. In such runs, calibration studies based upon the fayalite olivine-spinel and coesite-stishovite equilibria showed that pressure on the samples decreased with time owing to relaxation of stress distribution within the gaskets. Accordingly, we were unable to achieve our objective of a detailed study of the *P*, *T* stability relationships of chromium-rich garnets. However, we were successful in synthesizing and characterizing the solid solution series.

Samples were contained in platinum capsules and subjected to pressures estimated to range between 60 and 80 kbars for periods of 15–60 minutes. Runs were carried out either at 1400°C or 1500°C. Temperatures were measured by Pt-Pt 13% Rh thermocouples next to the charges. After completion of runs, the samples were quenched by terminating the power, and were then removed from the apparatus for study by X-ray and optical methods.

3. Results

Two runs at 60 and 80 kbars (estimated) upon the $Mg_3CrAlSi_3O_{12}$ composition at 1400°C for 15 minutes produced ~95% garnet, which also contained minute inclusions of pyroxene and corundum solid solution. One run on $Mg_3Cr_{1.5}Al_{0.5}Si_3O_{12}$ composition at 70 kbars (estimated), 1500°C for 30 minutes also produced ~80% garnet; the remaining phases consisting of pyroxene and corundum solid solutions. A third run at 1000°C, 80 kbars, for 60 minutes yielded about 30% garnet plus pyroxene and corundum solid solutions. Kinetic factors clearly favoured the formation of the latter metastable assemblage despite its lower density. Two runs on the $Mg_3Cr_{1.8}Al_{0.2}Si_3O_{12}$ composition at 70 and 80 kbars (estimated) yielded 50–80% of garnet, the remaining phases consisting of corundum solid solution + pyroxene. Eight runs on pure $Mg_3Cr_2Si_3O_{12}$ composition

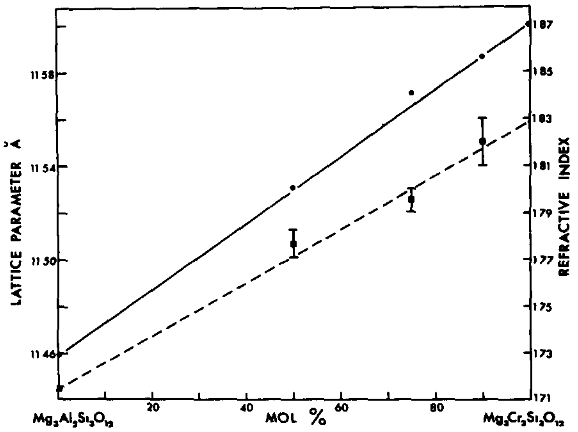

Fig 1. Lattice parameters (solid circles) and refractive indices (squares) of pyrope-knorringite solid solutions.

TABLE 1

Lattice parameters and refractive indices of pyrope-knorringite solid solutions

Composition	Lattice parameter (Å)	Refractive index
$Mg_3Al_2Si_3O_{12}$	11.460 ± 0.001	1.714
$Mg_3AlCrSi_3O_{12}$	11.537 ± 0.002	1.768 ± 0.005
$Mg_3Al_{0.5}Cr_{1.5}Si_3O_{12}$	11.571 ± 0.002	1.795 ± 0.005
$Mg_3Al_{0.2}Cr_{1.8}Si_3O_{12}$	11.586 ± 0.002	1.82 ± 0.01
$Mg_3Cr_2Si_3O_{12}$	11.600 ± 0.001	1.83 ± 0.01 (extrapolated)

yielded erratic results under apparently identical experimental conditions. The best result in a run at 1400°C, ~70 kbars, for 15 minutes yielded ~70% of garnet plus ~30% of pyroxene and corundum. Two runs were seeded with garnet from previous runs without noticeable improvement in the final yield of garnet.

The garnets so formed were deep green and isotropic. Refractive indices and lattice parameters are given in Table 1 and displayed in Fig. 1. The substantial uncertainties in refractive indices are caused by the presence of large numbers of small inclusions which greatly increase the difficulties of measurement This factor rendered it impossible to obtain a measurement upon pure $Mg_3Cr_2Si_3O_{12}$.

Except for a small deviation at the $Mg_3Cr_{1.5}Al_{0.5}Si_3O_{12}$ composition, the lattice parameters of the garnet solid solutions vary linearly with composition. Likewise, the refractive indices of the garnets varied linearly with composition within the (substantial) experimental error. The lattice parameter of $Mg_3Cr_2Si_3O_{12}$ garnet is 11.600 ± 0.001 Å, in good agreement with the value of 11.62 Å estimated by Sobolev et al. [4] by extrapolation of data on natural garnet solid solutions. The refractive index of $Mg_3Cr_2Si_3O_{12}$ garnet is found to be 1.83 ± 0.01 (Fig. 1) also in good agreement with Sobolev et al.'s estimate of 1.82.

4. Discussion

The present study has been confined to the synthesis and characterization of the pyrope-knorringite series. Without further data upon the *P*, *T* stability relationships of these garnets, it may be premature to discuss their significance in connection with the genesis of natural diamond. Nevertheless, some generalizations may be in order

Minerals and mineral assemblages occurring as inclusions in natural diamonds have been discussed by Sobolev et al. [4,5], Meyer and Boyd [3,6,7], Meyer and Svisero [14] and Prinz et al. [15]. Three principal classes of genetically related mineral inclusions have been recognized: (1) olivine ($Fo_{92\text{-}95}$) + Cr-rich, Ca-poor garnet + Ca-poor enstatite, (2) olivine + pyrope garnet + enstatite + diopside-(garnet lherzolite assemblage), and (3) pyrope-almandine garnet + omphacite (eclogitic assemblage). The above references indicate that assemblage (1) is much more abundant than the other two and our subsequent discussions will consider its significance.

An important characteristic is the low calcium content of the Cr-garnets, mostly ranging from 0.7% to 3.7% CaO. This range is distinctly lower than the calcium contents of garnet in garnet lherzolite xenoliths from kimberlites (usually 4–8% CaO). Sobolev et al. [5] concluded that these Ca-poor, Cr-rich garnets were unlikely ever to have been in equilibrium with assemblages containing Ca-rich clinopyroxene. This conclusion is further supported by the extremely low calcium contents of most enstatites found as inclusions in diamonds [14]. It seems then, that many, or most diamonds have formed in equilibrium with an assemblage of olivine + Cr-rich, Ca-poor pyrope + orthopyroxene. This assemblage, moreover, is characterized by a high 100 Mg/(Mg + Fe) ratio. For olivines and enstatites, this ratio is usually between 92 and 95 (molecular). The data of Meyer and Boyd [6], Meyer and Svisero [14] and Sobolev et al. [5] show that the 100 Mg/(Mg + Fe) ratios in garnet inclusions from diamonds are usually significantly higher (85–92) than observed in the garnets from lherzolite xenoliths in kimberlites (75–85).

A further important distinction, as noted earlier, is the high chromium content of garnets found as inclusions in diamonds, as compared with the garnets from garnet lherzolite xenoliths. Olivine inclusions in diamonds likewise contain much higher Cr_2O_3 contents than olivine from ultramafic xenoliths [6].

These characteristics are clearly of considerable genetic significance. Many previous workers [16] have proposed that diamonds crystallized from kimberlite parent magmas. The latter are believed to have formed by small degrees of partial melting of a garnet pyrolite or garnet lherzolite assemblage within the mantle. The kimberlite magma would thus have been saturated with olivine, garnet, enstatite and diopsidic pyroxene and should therefore have precipitated these minerals during subsequent crystallization. It is accordingly difficult to understand the paucity of clinopyroxene in the minerals included in diamonds in the absence of evidence for an appropriate reaction relationship which could have delayed crystallization of clinopyroxene. Moreover, olivine and orthopyroxene cumulates from kimberlite magmas would not possess 100 Mg/(Mg + Fe) ratios as high as 92–95. Finally, the high chromium contents of garnet inclusions in diamond are inexplicable on the basis of this hypothesis: Nicholls and Ringwood (unpublished experiment) have measured the partition coefficient for chromium between liquidus pyrope-rich garnet and an olivine tholeite magma * at 30 kbars, and at 1100 and 1200°C under conditions of high water vapour pressure. The partition coefficient for chromium between garnet and liquid was found to be about 5. Kimberlite magmas typically contain about 0.1% Cr_2O_3. Even allowing for a generous uncertainty in partition coefficients, it does not appear possible for garnets containing up to 20% Cr_2O_3 to have crystallized from such a parental magma. Indeed, this statement could be extended to embrace all classes of magmas so far observed (or inferred) to occur at the surface of the earth.

It seems to the author that the high chromium contents, high 100 Mg/(Mg + Fe) ratios and low calcium contents of the most abundant mineral assemblage occurring as inclusions in natural diamonds point towards another mode of origin. Such an assemblage could have been derived from olivine + orthopyroxene + chrome-spinel + minor sulphides which precipitated as cumulates from mafic magmas at comparatively shallow levels, e.g., in magma chambers within the oceanic crust or within the uppermost suboceanic mantle. These cumulates might have experienced minor alteration and introduction of carbonates (e.g. magnesite, dolomite, calcite) and hydrated phases (e.g., serpentine, talc) by circulating hydrothermal solutions. Moreover, they may have retained some of the parental liquid from which they crystallized as an intercumulus phase. Such cumulates are likely to have possessed a much higher Fe^{2+}/Fe^{3+} ratio than that of the parental magma from which they crystallized.

Oceanic crust and uppermost mantle containing these cumulate assemblages was later subducted deep into the mantle (see also [23,24]). At depths exceeding 150 km, partial melting caused by viscous dissipation occurred, accompanied by metamorphic re-equilibration to form an assemblage of Cr-rich, Ca-poor garnet, olivine and orthopyroxene. Loss of the melt phase markedly increased the 100 Mg/(Mg + Fe) ratio of the residual, unmelted assemblage. A change of redox state, caused by the higher Fe^{2+}/Fe^{3+} content of the cumulates (as compared to parental magma) and the presence of some FeS, caused partial reduction of CO_3^{2-} (present as $MgCO_3$) to precipitate diamond within its P, T stability field. The wide range of carbon isotopic compositions observed in natural diamonds [18] appears to be compatible with this hypothesis. Likewise, it is consistent with the conclusion of Fesq et al. [19] based upon trace element studies of natural diamonds, that diamonds crystallized in the presence of an H_2O-CO_2-rich picritic magma (the partial melt) in the presence of an immiscible FeS phase.

5. Synthesis of chromium kyanite solid solutions

Sobolev et al. [20] have described chromium-rich kyanites from grospydite xenoliths in a kimberlite from Yakutia, containing up to 18 mol.% of the theoretical end-member Cr_2SiO_5. High-Cr kyanites are also known from kyanite eclogite inclusions in South African diamond pipes. The stability of chromium-bearing kyanites has been investigated experi-

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* The composition of this magma is that of *olivine tholeite B*, as given by Green and Ringwood [17]

mentally by Seifert and Langer [21]. These authors observed a solubility of Cr_2SiO_5 in kyanite (Al_2SiO_5) amounting to 24 mol.% Cr_2SiO_5 at 20 kbars and 31 mol.% at 30 kbars. The extent of solid solutions was not strongly temperature-dependent but increased markedly with pressure in the composition range investigated. Dr. N.V. Sobolev previously carried out some high-pressure/high-temperature experiments on Al-Cr kyanite compositions during a visit to Canberra. Disequilibrium assemblages were generally observed, but electron microprobe analyses revealed the presence of some kyanite crystals containing up to 70 mol.% Cr_2SiO_5.

An attempt to prepare chromium-rich kyanites was made in the course of the present investigation. Starting materials consisted of intimate mixtures of Cr_2O_3, $Al(OH)_3$ and silicic acid, pelletized and sintered at 1100°C for 3 hours Samples so prepared were subjected to pressures of approximately 70 kbars at 1500°C for 20 minutes

The composition $AlCrSiO_5$ formed a well-crystallized single phase kyanite-type solid solution under these conditions, possessing refractive indices, $\alpha = 1.855 \pm 0.005$ and $\gamma = 1.905 \pm 0.005$. A more chromium-rich composition $Al_{0.5}Cr_{1.5}SiO_5$ crystallized dominantly to kyanite-type solid solution. However, the presence of abundant small inclusions made it difficult to obtain the refractive indices accurately. Values obtained were $\alpha = 1.915 \pm 0.01$, $\gamma \sim 1.98$. Attempts to produce pure Cr_2SiO_5 kyanite failed, even when seeded with small amounts of Cr-kyanite solid solutions from other runs. The refractive index data imply the existence of a complete range of kyanite solid solutions extending from Al_2SiO_5 at least to $Al_{0.5}Cr_{1.5}SiO_5$ under the P, T conditions of the experiments.

Postscript and acknowledgements

This paper was written in December 1976 and the results summarized in the Annual Report of the Research School of Earth Sciences, Australian National University, pp. 92–93, 1976. It was sent on February 7, 1977, to Dr. N. Dobretsov of the Institute of Geology and Geophysics, Novosibirsk, for inclusion in a Festschrift in honour of Academician V.S. Sobolev. Late in February, I received Earth and Planetary Science Letters 34 (1977) 30 and noticed a paper written independently by Clark and Carswell, which proposed a hypothesis parallel in some respects to the hypothesis presented herein. Because of the uncertain date of publication of the Russian book and the likelihood that it will be inaccessible in an English language version for some time, it seemed appropriate to submit the same paper to Earth and Planetary Science Letters.

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