A study of uvarovite

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Summary. Uvarovite and its relationships with grossular and andradite have been studied in order to understand better the geochemistry of uvarovite. Syntheses have been carried out under both dry and hydrothermal conditions; a solid solution with grossular was obtained under both conditions, but with andradite only under hydrothermal conditions. The results are discussed in relation to the chemistry of uvarovite.

THE mineral uvarovite, which is the rarest of the common garnets, has never been reported as a pure end-member, but usually as a solid solution with grossular, or most commonly with andradite. The ideal uvarovite should contain 30·38 % Cr_2O_3, but chemical analyses of a number of specimens (see fig. 1) show that the Cr_2O_3 content may vary from 3·39 to 27·54 %. There appears to be a gap in the range of Cr_2O_3 composition from approximately 15 to 22 % (Deer, Howie, and Zussman, 1962), but this gap may be just the result of insufficient numbers of analyses.

Uvarovite has generally been found associated with serpentinite, chromite, metamorphic limestones, and skarn ore-bodies; it has formed from contact metamorphic processes or hydrothermal processes. In the Bushveld area, grossular and uvarovite are rarely associated with each other, although the uvarovite is usually a solid solution with grossular (Frankel, 1959). Chemical analyses show that there is considerable divergence from the ideal molecular ratio of 3:1:3, with an excess of the CaO component. Frankel postulated an accommodation of the excess CaO group in 'cavities' within the unit cell and concluded that the garnet therefore is elastic. He further noted that compositional discrepancies occurred in those garnets that contained much TiO_2 or FeO, with iron in the structure producing marked non-linear change in cell-size between grossular and uvarovite in the solid-solution series.

That uvarovite is usually really a solid solution with grossular gives

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us an apparent geological paradox, as grossular is considered a wet-forming mineral and uvarovite a dry-forming one. At least, experimental studies have indicated that grossular requires hydrothermal conditions for synthesis and uvarovite dry conditions.

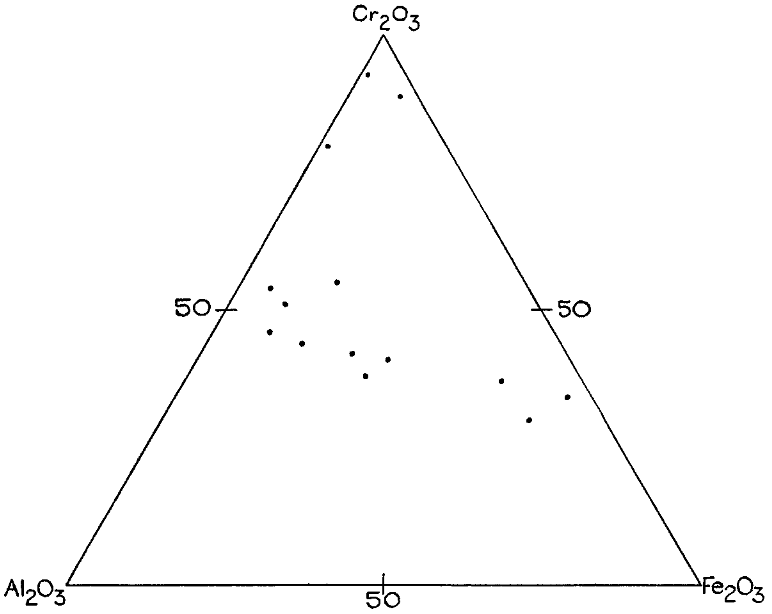

FIG. 1. Chemical compositions of chrome-bearing garnets, from data published by:
ASTM card 7–70
Betekhtin (1946)
Deer, Howie, and Zussman (1962)
Frankel (1959)
von Knorring (1951)

A number of investigators have reported synthesizing a pure uvarovite, but in all of these results α-$CaSiO_3$ and Cr_2O_3 were present as reaction products along with the uvarovite; in none of the reported experiments was uvarovite the sole phase present. There are also disagreements as to the optimum conditions of synthesis. Hummel (1950) reported obtaining uvarovite from runs at from 855 to 1400° C, with a breakdown to α-$CaSiO_3$+Cr_2O_3 at 1490° C; Gentile and Roy (1960) obtained it at 1200° C; Geller and Miller (1959) and Swanson *et al.* (1960) at 1400° C; and Glasser and Osborn (1958) reported its optimum temperature of formation as 1370±10° C (they found that 1370° was the ternary point between uvarovite, α-$CaSiO_3$, and Cr_2O_3).

This study was undertaken to determine experimentally the conditions of formation of pure uvarovite, and the relation in solid solution to grossular and andradite. The writer also wanted to find out if the compositional gap reported above might be related to conditions of formation (that is, whether there was a limit to solid solution under dry or hydrothermal conditions), or if it was more likely due to too few specimens having been analysed.

Experimental details

Spectrographic grade chemicals (oxides and carbonates) were used as starting materials. These were ground together under acetone in appropriate proportions in an agate mortar and pestle for approximately 20 minutes. Runs were made under both dry and hydrothermal conditions. Sealed platinum capsules were used in all of the hydrothermal experiments and in some of the dry ones, in the latter case to offset possible volatization of Cr_2O_3 and GeO_2 at high temperatures. Most of the dry runs were made using 0·25 mm thick platinum foil.

Dry runs were made in a platinum–13 %-rhodium-wound quenching furnace with a maximum temperature of 1500° C, a silicon carbide rod pot-furnace with a maximum temperature of 1400° C or a carbon furnace with maximum usable temperature of 1600+°C. In the work in the sub-solidus region, quick quenching was found to be unnecessary since inversion, or breakdown to other compounds, did not occur with the slower air quench. In some of the hydrothermal runs leaching of the SiO_2 appeared to occur, and excess SiO_2 was therefore added to a number of charges.

Results of the experiments were examined by X-ray powder diffraction techniques using Cr-$K\alpha$ radiation; some were also examined under the polarizing microscope.

Results

The first part of the work consisted of attempts to synthesize pure uvarovite under both dry and hydrothermal conditions. In the dry runs, using only a pure uvarovite mixture, a temperature range of from 1300 to 1600° C was used, but uvarovite was never the sole reaction product, α-$CaSiO_3$ and Cr_2O_3 always being present in varying amounts. The best results (that is to say, the runs where the relatively least amounts of α-$CaSiO_3$ and Cr_2O_3 were found) were at the temperature of 1365±5° C.

TABLE I. Results of dry runs. U, uvarovite mix; Uge, germanium uvarovite mix; A, andradite mix; G grossular mix; $\alpha\text{-CaSiO}_3$ = pseudowollastonite.

Starting material	Temperature	Duration	Products
U	1460° C	1 day	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U	1420	7 days	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U	1300	1 day	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U	1352	22 hr	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
*	1365	24 hr	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3+$garnet
U	1375	48 hr	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U	1392	25 hr	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U+seed	1392	25+143 hr	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U+KCl	1350	5 hr	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3+$tr. garnet
U+seed+KCl	1392	25 hr	garnet$+\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U	1500	24 hr	Cr_2O_3+melt+ ? SiO_2
U	1480	20 hr	Cr_2O_3+melt+tr. $\alpha\text{-CaSiO}_3$
U	1560±25	5 min	Cr_2O_3+melt
U	1610±25	15 min	Cr_2O_3+melt
U	1610±25, slowly cooled to 1200±25	15 min + 2 hr	Cr_2O_3+melt
U:A 2:8	1285	28 hr	$\alpha\text{-CaSiO}_3+(\text{Cr},\text{Fe})_2\text{O}_3$
U:A 4:6	1285	28 hr	$\alpha\text{-CaSiO}_3+(\text{Cr},\text{Fe})_2\text{O}_3$
U:A 6:4	1285	28 hr	$\alpha\text{-CaSiO}_3+(\text{Cr},\text{Fe})_2\text{O}_3$
U:A 9:1	1285	28 hr	$\alpha\text{-CaSiO}_3+(\text{Cr},\text{Fe})_2\text{O}_3$
U:A 9:1+KCl	1258	46 hr	garnet$+\alpha\text{-CaSiO}_3+R_2\text{O}_3$
U:Uge 1:1	1420	1 day	garnet
U:Uge 3:1	1420	1 day	garnet
U:Uge 9:1	1420	1 day	garnet
U:Uge 98:2	1420	1 day	garnet
U:Uge 99:1	1420	1 day	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U:Uge 98:2	1390	25 hr	garnet
U:G 5:95	1200	72 hr	$\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 1:9	1200	1 day	$\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 3:7	1200	2 days	tr. garnet$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 1:1	1200	3 days	garnet$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 7:3	1200	3 days	garnet$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 95:5	1200	1 day	garnet ?$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 98:2	1200	1 day	$\alpha\text{-CaSiO}_3+\text{Cr}_2\text{O}_3$
U:G 5:95	1225	48 hr	tr. garnet$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 2:8	1225	48 hr	garnet$+\alpha\text{-CaSiO}_3(\text{Cr},\text{Al})_2\text{O}_3$
U:G 5:95	1255	72 hr	tr. garnet$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 1:9	1258	47 hr	garnet+melt$+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 5:95	1258	47 hr	melt+tr.$(\text{Cr},\text{Al})_2\text{O}_3$
U:G 5:95	1295	94 hr	melt
U:G 2:8	1295	94 hr	garnet+melt
U:G 4:6	1295	94 hr	garnet+melt
U:G 1:1	1300	1 day	garnet+melt
U:G 6:4	1300	1 day	garnet+melt
U:G 7:3	1300	1 day	garnet
U:G 8:2	1300	1 day	garnet$+\alpha\text{-CaSiO}_3+$tr. $(\text{Cr},\text{Al})_2\text{O}_3$
U:G 95:5	1300	1 day	garnet$+\alpha\text{-CaSiO}_3+$tr. $(\text{Cr},\text{Al})_2\text{O}_3$
U:G 98:2	1300	2 days	garnet ?$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 9:1	1344	18 hr	garnet$+\alpha\text{-CaSiO}_3$
U:G 7:3	1400	47 hr	melt$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 8:2	1400	47 hr	melt$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 9:1	1400	47 hr	melt$+\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$
U:G 98:2	1400	47 hr	$\alpha\text{-CaSiO}_3+(\text{Cr},\text{Al})_2\text{O}_3$

* Products from the 1352° C run.

A glass of CaSiO_3 composition and crystalline Cr_2O_3 were produced at approximately 1480° C. A glass of uvarovite composition was not produced in these experiments. Table I gives the results of all dry runs.

Similar results were obtained under hydrothermal conditions in that pure uvarovite was not made as the only reaction product, but was accompanied by the formation of Cr_2O_3 and α-$CaSiO_3$.

The germanium analogue of uvarovite was readily synthesized under dry conditions, and its solid solution with the silicon end member was studied. There was complete solid solution with the formation of garnet as the only phase until the composition of the mixture was approximately 98 % of the silica uvarovite, when once again Cr_2O_3 and α-$CaSiO_3$ were the main phases present. By using crystals of the 98:2 silica: germania uvarovite as seeds, it was possible to make an almost pure silica uvarovite as the only reaction product in the hydrothermal runs, but not in dry runs.

As natural uvarovite is almost always a solid solution with grossular, and to a much lesser extent with andradite, the solid solution relationships with these other members of the ugrandite series were studied under both dry and hydrothermal conditions. In the hydrothermal experiments, solid solution was obtained with both andradite and grossular, but in the latter case a solid solution of $(Cr, Al)_2O_3$ and α-$CaSiO_3$ were also present. It may well be that the temperature was too low to permit the formation of garnet as the only phase (but higher temperatures could not be used as 900° C was near the upper limit of the bombs), or that leaching of SiO_2 could have played a role since the few runs made with excess SiO_2 produced garnet as the only phase, with one exception. In the runs with andradite a weak solution of hydrogen peroxide was used in the capsule as an oxidising agent to keep the iron in the ferric state. Table II gives the results of the hydrothermal experiments. It is interesting to note that an attempt to synthesize a germanium uvarovite also produced some Cr_2O_3 and a trace of what may be a germanium analogue of pseudo-wollastonite in the same run. Once again, temperature may have been the determining factor.

In the dry runs, we were unable to synthesize a garnet phase in the uvarovite–andradite series, but obtained α-$CaSiO_3$ and a solid solution between Fe_2O_3 and Cr_2O_3 instead. A solid solution between grossular and uvarovite was obtained, and in many of the runs garnet was the only phase produced, particularly where the temperature was at or near the fusion point of the mixture.

Discussion

These experimental studies show that uvarovite may be regarded as a hydrothermal mineral as well as a dry one.

Certainly, this would fit in better with much of its natural occurrences, which are usually as products of contact metamorphism. The compositional discrepancies in the solid solution with grossular mentioned earlier are probably more apparent than real, and due to too few analyses having been made.

TABLE II. Results of hydrothermal runs. All runs for 7 days at 900° C and 500 bars except where indicated (notes column). U, uvarovite mix; G, grossular mix; Uge, germanium uvarovite mix; A, andradite mix.

Starting material	Notes	Products
U:G 2:8	*	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 3:7	*	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 1:1	*	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 2:8	†	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 3:7	‡	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 1:9	§	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 1:1	†	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 4:6	‖	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 6:4	‖	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 9:1	‖	garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 98:2		garnet + Cr_2O_3 + α-$CaSiO_3$
U:G 8:2		garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 7:3		garnet + $(Al,Cr)_2O_3$ + α-$CaSiO_3$
U:G 4:6 + SiO_2		garnet + SiO_2
U:G 6:4 + SiO_2	¶	garnet
U:G 9:1 + SiO_2	¶	garnet + tr. Cr_2O_3
U:A 1:1	**	garnet
U:A 8:2	**	garnet
U:A 6:4		garnet
U:A 4:6		garnet
U:A 2:8		garnet + tr. Cr_2O_3
U:A 9:1		garnet
U:G:A 9:1:1		garnet
U + SiO_2		Cr_2O_3 + α-$CaSiO_3$ + SiO_2
U + SiO_2 + seed	**	garnet + SiO_2
U:Uge 98:2 + SiO_2		garnet
U + seed		garnet
Uge	†	garnet + Cr_2O_3 + $CaGeO_3$
U		garnet + Cr_2O_3 + α-$CaSiO_3$

* 850° C and 1000 bars
† 480 bars
‡ 450 bars
§ 920° C for 12 days
‖ 8 days
¶ 9 days at 600 bars
** 890° C

We must still ask why natural uvarovites are usually a solid solution with grossular rather than with andradite. These experimental studies indicate that, at least under hydrothermal conditions, no such preference exists; that we did not produce a solid solution between andradite and uvarovite under dry conditions is not conclusive. It is possible that this may not be the case, but that there have not been enough analyses of relevant garnets. There is a tendency to call green chrome-bearing garnets uvarovite regardless of chrome content; the stronger colour of andradite may mask the green uvarovite colour, and therefore not give an indication of the presence of chrome, whereas grossular itself is colourless and therefore would easily be coloured by the inclusion of small amounts of another garnet phase. Or, it may be that there is a preference for solid solution with grossular. If the environment was not an oxidizing one, then the iron would be in the form Fe^{2+} and go into the formation of minerals where it is divalent. Chromite, for example, is frequently found associated with uvarovite. But in contact metamorphism with limestones, oxidizing conditions could prevail, and no preference in solid solution should exist. A few uvarovites have been reported that contain an appreciable amount of Fe_2O_3 as well as Cr_2O_3 and Al_2O_3. Geller (1960) stated that the difference in ionic radii results in a limited substitution of Cr^{3+} for Fe^{3+}. But minerals that are solid solutions between andradite and grossular are very common, though the difference in ionic radii between Fe^{3+} and Al^{3+} is greater than that between Fe^{3+} and Cr^{3+}. Garnet has a high degree of covalency, and the size difference will be smaller.

Also, we have produced complete solid solution under hydrothermal conditions between uvarovite and andradite. This problem was not solved by the experimental study.

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