

Glaucocroite-tephroite intergrowth from the Kanoiri mine, Kanuma City, Tochigi Prefecture, Japan

By

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Abstract Glaucocroite ($(\text{Ca}_{0.87}\text{Mn}_{1.03}\text{Fe}_{0.06}\text{Mg}_{0.04})\Sigma_{2.00}\text{Si}_{1.00}\text{O}_4$) bodies hosted by a calcian tephroite ($(\text{Mn}_{1.69}\text{Ca}_{0.13}\text{Fe}_{0.11}\text{Mg}_{0.07})\Sigma_{2.00}\text{Si}_{1.00}\text{O}_4$) are found in the form of intergrowth in a thermally metamorphosed manganese ore from the Kanoiri mine, and interpreted as an exsolution product. The ore includes a manganoan grossular ($(\text{Ca}_{1.60}\text{Mn}_{1.39}\text{Fe}^{2+}_{0.02})\Sigma_{2.01}(\text{Al}_{1.97}\text{Fe}^{3+}_{0.03})\Sigma_{2.00}\text{Si}_{3.00}\text{O}_{12}$), alabandite ($(\text{Mn}_{0.93}\text{Fe}_{0.05})\Sigma_{1.00}\text{S}$) and a minor zincian galaxite ($(\text{Mn}_{0.58}\text{Zn}_{0.26}\text{Fe}_{0.14})\Sigma_{0.98}\text{Al}_{2.02}\text{O}_4$). The implications of the exsolution product and of the association of alabandite with zincian galaxite are considered.

Introduction

In Japan many bedded manganese ore deposits occur chert-dominant portions of Jurassic accretional bodies. Some of them underwent thermal effects principally due to later granitic intrusions, resultantly producing various manganese minerals.

Such deposits are representatively seen in the area covering the western part of Tochigi Prefecture and the adjacent part of Gumma Prefecture, where chert with bedded manganese ore deposits crops out extensively, accompanying a large amount of mudstone with minor limestone and greenstone. They are intruded by Cretaceous granitic bodies, all of them having more extensive subsurface distribution (WATANABE *et al.*, 1970). In the area were worked more than 200 manganese ore deposits of various dimensions belonging to this type, but none of them survives at present.

The ore deposit of the Kanoiri mine is one of the examples undergoing strong thermal effect of granite, which was seen in one of the galleries. The author visited the mine in 1958 and collected some specimens. Since preliminary examinations of one of the highest grade ores visually composed of tephroite and alabandite indicated that the former had larger cell parameters suggesting the higher CaO content, it is now re-examined and eventually leads to the find of glaucocroite as exsolved bodies hosted by a calcian tephroite with which a manganoan grossular and a zincian galaxite were found as minor constituents.

Glaucocroite is a rare olivine reported from only three localities, Franklin, New Jersey (PENFIELD and WARREN, 1899; LEAVENS *et al.*, 1987), Anakit, Lower Tungska (PERTSEV and LAPUNINA, 1974), and Wessel mine, South Africa (DIXON, 1985; VON

BEZING *et al.*, 1991). The present glaucochroite is characterized by the less calcic nature than ideal CaMnSiO_4 forming an exsolution texture partnered with a calcian tephroite. The present work is for the preliminary description on the chemical compositions of the above-stated minerals and considers the implications of exsolution composed of two olivine intergrowth and of association of alabandite with a zincian galaxite.

Occurrence

The ore deposit of the Kanoiri mine is located about 17 km WNW of Kanuma Station, Nikko Line, Eastern Japan Railway Co., or latitude N $36^{\circ}37.7'$ and longitude E $139^{\circ}31.5'$. It was worked for manganese between 1950 and 1961. There is only one orebody in recrystallized chert with minor biotite hornfels partially intercalating with it as thin seams. The orebody is considered to be a small, tabular and slender mass in the original state but is intensely folded and faulted. It is elongated to NNE-SSW direction along which the dimension was about 20 m. The width and thickness are highly variable due to the pinch-and-swell structure, but even in the most swollen part the width and thickness do not exceed 3 m in both directions.

The ore minerals are tephroite, rhodonite, bustamite, spessartine, manganoan hedenbergite and alabandite in the order of decreasing quantity. All of them are rather coarse-grained except for manganoan hedenbergite and spessartine in the lower grade ores. The examined ore (NSM-M21775) was collected in a stope near the norther end of the orebody, where a porphyritic biotite granite appeared in the floor of stope. The ore is a piece of massive tephroite aggregate composed of white to grey white grains of a few mm in maximum dimension with black alabandite grains of smaller dimension, and the aggregate is intersected by calcite veinlet composed of coarser-grained colourless grains with a typical mozaic texture. Besides the described ore was collected another massive tephroite ore comprising alabandite grains in the same manner as the present one in an ore pile. It looks identical with the present one but is accompanied by a massive aggregate of calcite not in vein-form, which includes isolated tephroite and alabandite grains. The chemical study on tephroite in this ore is under way. Except these tephroites, all the tephroite ores from this mine involve rhodonite and/or bustamite and the tephroite has lower CaO and MgO and higher FeO contents. It is unfortunate that no material substantially connecting the described ore including the intergrowth with any other ores or wallrocks is found. The granite is in direct contact with recrystallized chert and massive rhodonite ore in the stope. In the dump of materials from the stope is found minor wollastonite attached to quartz of recrystallized chert origin. One of the likely order of arrangement of minerals and rocks reconstructed by the observation of ores directly responsible for the handled materials is tephroite-calcite-wollastonite-chert-granite. It is worthy of note that despite the common occurrence of pyroxenoids in the ores from the orebody including the stope, none of them is found in the examined material.

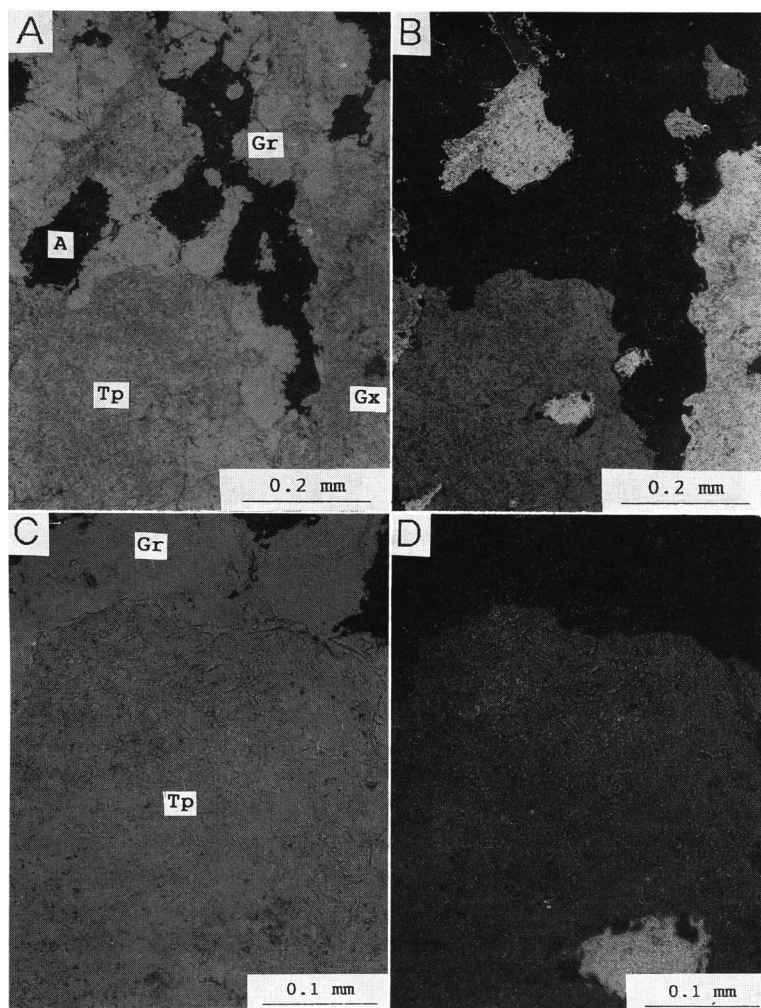


Fig. 1. Photomicrographs of tephroite grains including minute intergrown bodies of glaucocroite (Tp) with alabandite (A), grossular (Gr) and galaxite (Gx).

- A) one polar, moderately enlarged
- B) crossed polars, ditto
- C) one polar, highly enlarged
- D) crossed polars, ditto

Under the microscope, four phases are discriminated in the ordinary magnification rate. Coarse-grained tephroite has rather smooth boundaries and alabandite grains have a smoother outline to tephroite and uneven to grossular (Fig. 1A and B), which is far clearer than tephroite. Besides them tiny light brown grains of galaxite are present within tephroite grains or in direct contact with all the other three. Under

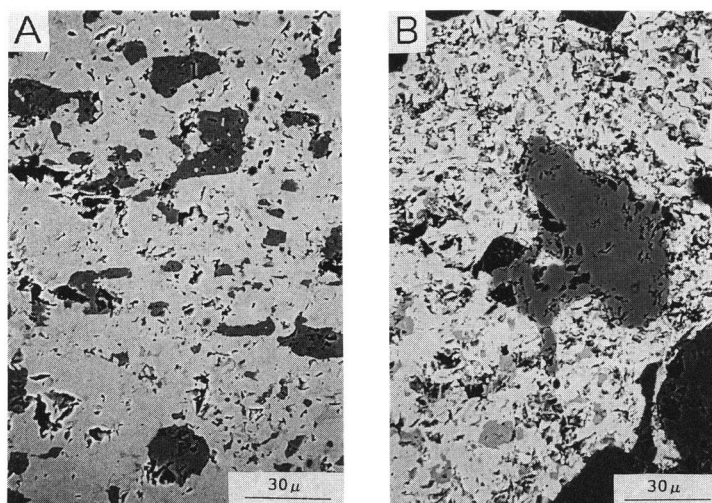


Fig. 2. Back-scattered electron images.

- A) glaucochroite bodies (grey) in tephroite (white)
- B) galaxite (medium grey) in association with glaucochroite (light grey)-bearing tephroite (white) and garnet (dark grey). Note the finer grain size of glaucochroite bodies as compared with the previous figure.

higher rate of magnification, tephroite grains host very minute bodies of glaucochroite. They are noticeable around the grossular grains in direct contact (Fig. 1C and D). With the aid of back-scattered electron image, most of their outlines are found to be rather angular elongated polygons or their jointed form in appearance (Fig. 2A). The size of minute bodies is discernibly variable. It is coarser in tephroite grains in direct contact with tephroite only, whereas finer in tephroite grains in direct contact with grossular and galaxite (Fig. 2B). The larger the size of bodies the fewer the number of them, and vice versa. The extinction of the bodies is simultaneous with the host.

Chemical Compositions Glaucochroite, Tephroite, Grossular and Galaxite

Glaucochroite, tephroite, spessartine, alabandite and galaxite were analysed by using Link Systems Energy dispersive X-ray spectrometer. The chemical analyses of glaucochroite and tephroite are given in Table 1.

Among the available chemical analyses of glaucochroite the present material is the most Ca-poor one (Table 2). Within one grain of glaucochroite, the compositional variation is practically insignificant. The compositional peculiarity suggests it to have a different origin from those of known glaucochroites, which are the products of skarn formation or a reaction mineral.

The tephroite analyses indicate a slight compositional variation (Table 1). But

Table 1. Chemical analyses of glaucocroite and tephroite (1.~4.: the present study).

	1.	2.	3.	4.	5.
Weight percentages					
SiO ₂	31.90	32.09	30.47	30.42	29.24
MnO	39.80	38.74	60.35	60.39	40.02
FeO	2.30	2.16	4.28	3.82	17.98
MgO	0.78	0.79	1.72	1.72	4.02
CaO	25.04	25.90	3.49	3.80	2.51
total	99.82	99.68	100.31	99.79	99.71*
Mole ratios (basis: O=4)					
Si	1.00	1.00	1.00	1.00	1.01**
Mn	1.06	1.03	1.68	1.69	1.15
Fe	0.06	0.06	0.12	0.11	0.55***
Mg	0.04	0.04	0.08	0.07	0.20
Ca	0.84	0.87	0.12	0.13	0.06

1. Glaucocroite. Kanoiri mine. The most Ca-poor analysis.

2. Glaucocroite. Kanoiri mine. The most Ca-rich analysis.

3. Tephroite. Kanoiri mine. The most Ca-poor analysis.

4. Tephroite. Kanoiri mine. The most Ca-rich analysis.

5. Tephroite (referred to as knebelite). Kaso mine. After YOSHIMURA (1939). *includes Al₂O₃ 1.68, Fe₂O₃ 1.66, BaO 1.68, Na₂O 0.04, K₂O 0.15, H₂O⁺ 0.13, CO₂ 0.60. **includes Al 0.02, ***includes Fe³⁺ 0.04. (after deducting Ba, alkalis, Al and Si as feldspar)

all of them are characterized by the higher CaO contents. One of the most Ca-rich tephroite known to date was from the Kaso mine (YOSHIMURA, 1939) (Table 1) located about 4 km SSE of the Kanoiri mine, where the grade of thermal metamorphism is slightly lower than that at the Kanoiri mine. A join combining the chemical compositions of two olivines is drawn in the Ca₂SiO₄-Mn₂SiO₄-(Mg, Fe, Zn)₂SiO₄ triangular diagram (Fig. 3).

The chemical analysis of garnet indicates it to be a highly manganoan grossular, that is, SiO₂ 38.35, Al₂O₃ 21.45, MnO 20.99, MgO 0.04, FeO* 0.78, CaO 19.12, total 100.72%. The empirical formula is (Ca_{1.60}Mn_{1.39}Fe²⁺_{0.02})_{Σ2.01}(Al_{1.97}Fe³⁺_{0.03})_{Σ2.01}(Al_{1.97}Fe³⁺_{0.03})_{Σ2.00}Si_{3.00}O₁₂ (basis: Si=3). ITO and FRONDEL (1968) confirmed the existence of continuous solid solution between synthetic grossular and spessartine. Also, the analysis informs the distinct exclusion of Fe²⁺ despite the formation of solid solution to almandine. Manganoan grossular described by SHIMAZAKI (1977) from the Kuga mine, Yamaguchi Prefecture, Japan, contains FeO* (total iron oxides) up to 7.3% in weight, and more than 90% of it is calculated as FeO. Though the absolute quantity of Fe is not so large in the present assemblage, it is more preferentially incorporated into olivine and alabandite to manganoan grossular. Alabandite is slightly ferroan. The ratio Mn/(Mn+Fe) is about 0.95, which is slightly larger than those in olivines. The chemical analysis gives Mn 38.18, Fe 3.00, S 38.18, total 100.66%, corresponding to (Mn_{0.95}Fe_{0.05})_{Σ1.00}S_{1.00} (basis: S=1).

Table 2. Chemical compositions of glaucochroite

	1.	2.	3.	4.	5.	6.	7.
Weight percentages							
SiO ₂	31.90	32.09	32.5	33.1	32.5	31.89	32.11
Al ₂ O ₃						0.93	
MnO	39.80	38.74	37.6	32.6	34.4	37.34	37.91
FeO	2.30	2.16			3.2	0.66	
MgO	0.78	0.79	0.5	2.4	1.1	1.07	
ZnO			1.0	1.8			
CaO	25.04	25.90	28.3	30.7	28.5	27.61	29.97
total	99.82	99.68	99.9	100.6	99.7	99.50	99.99
Mole ratios (basis: O=4)							
Si	1.00	1.00	1.01	1.01	1.01	0.99	1
Al						0.03	
Mn	1.06	1.03	0.96	0.84	0.91	0.98	1
Fe	0.06	0.06			0.08	0.02	
Mg	0.04	0.04	0.04	0.11	0.05	0.05	
Zn			0.04	0.04			
Ca	0.84	0.87	0.94	1.00	0.95	0.92	1

- 1. Kanoiri mine. The most Ca-poor analysis. Same as 1. in Table 1. The present study.
- 2. Kanoiri mine. The most Ca-rich analysis. Same as 2. in Table 1. The present study.
- 3. Franklin, New Jersey, U.S.A. NMNH# C6172. The most Ca-poor analysis in LEAVENS *et al.* (1987).
- 4. Franklin, New Jersey, U.S.A.. NMNH# R3494. The most Ca-rich analysis in LEAVENS *et al.* (1987).
- 5. Anakit, Lower Tungksa, U.S.S.R. After PERTSEV and LAPUNINA (1974).
- 6. Wessels mine, Kalahari Manganese Field, South Africa. After VON BEZING *et al.* (1991).
- 7. Theoretical CaMnSiO₄.

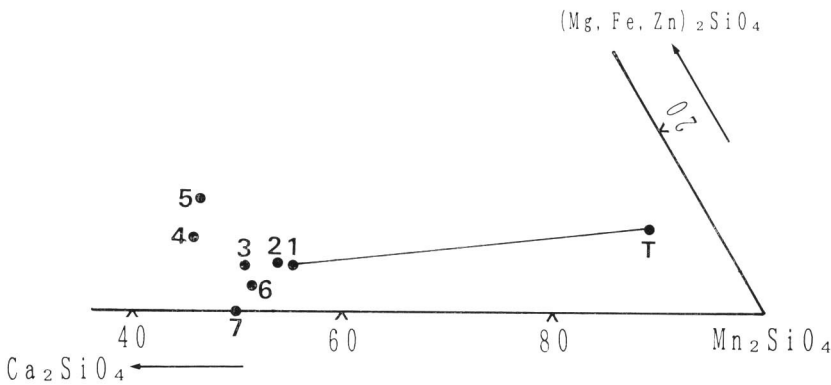


Fig. 3. Chemical compositions of glaucochroite (1.~7.) and calcian tephroite (T). The numbers correspond to those in Table 2 and T to No. 4 in Table 1. The most Ca-poor glaucochroite and the most Ca-rich tephroite are joined tentatively.

The chemical composition of galaxite is unusual. The chemical analysis gives MnO 23.64, FeO 5.63, ZnO 12.09, Al_2O_3 59.00, total 100.36%, corresponding to $(\text{Mn}_{0.58}\text{Zn}_{0.26}\text{Fe}_{0.14})_{\Sigma 0.98}\text{Al}_{2.02}\text{O}_4$ (basis: O=4). Mg is preferentially incorporated into olivines though minor in quantity, and excluded by galaxite despite its capability to admit MgAl_2O_4 molecules under various geological conditions including contact metamorphic ones of higher grade.

X-ray Powder Study

X-ray powder diffraction study was made on the tephroite involving the minute bodies of glaucochroite. The obtained diffractions are principally composed of those of tephroite with larger unit cell parameters ($a=4.908$, $b=10.772$, $c=6.302\text{\AA}$) than the ordinary one ($a=4.878$, $b=10.560$, $c=6.226\text{\AA}$) (JCPDS Card No. 19-788) reflecting the higher CaO content and of some of stronger peaks corresponding to those of glaucochroite by PERTSEV and LAPUTINA (1974) (Table 3). Since several peaks of glaucochroite are covered by those of tephroite, the unit cell parameters were not derived.

Interpretations of the Associations of two Olivines and Alabandite-zincian Galaxite

The intergrowth of glaucochroite bodies hosted by tephroite with the same optic orientation is undoubtedly the product of exsolution derived from a highly calcian tephroite formed under a higher temperature condition and subsequent cooling, although the experiments dealing with the binary system Ca_2SiO_4 - Mn_2SiO_4 (GLASSER, 1961) indicate the formation of solid solution between above two components with the range $\text{Mn}/(\text{Mn}+\text{Ca})=0.25\sim 1$ at higher temperatures. But the described exsolution is to indicate the existence of a solvus in the subsolidus region within the range $\text{Mn}>\text{Ca}$ in the phase diagram of GLASSER (1961). LEAVENS *et al.* (1987) have re-examined glaucochroite from the original locality with the expectation to find the association of glaucochroite with tephroite but could not have it. However, their schematic diagram on CO_2 pressure-temperature relation to indicate possible reactions involving the formation of glaucochroite is correctly given together with the explanatory sentence attached to it, i. e., the breakdown of olivine solid solution into glaucochroite+calcian tephroite below a critical temperature, although the breakdown was firstly predicted by BURT (1972), one of the authors just referred to. As already stated, all the available chemical analyses of glaucochroite (Table 2) have higher CaO contents than the present material. Therefore, the co-existence of such high Ca glaucochroites with tephroite seems unlikely unless it is formed under an entirely different condition allowing a prolonged cooling and delivering any resultant compositional changes.

The present assemblage contains such aluminous minerals, manganoan grossular

Table 3. X-ray powder pattern of tephroite-glaucocroite intergrowth, synthetic Mn_2SiO_4 , and glaucocroite.

1.			2.			3.		
I	$d_{\text{obs.}}$	$d_{\text{cal.}}$	I	d	hkl	I	d	hkl
2	5.597*					50	5.634	020
10	5.407	5.384	50	5.28	020			
5	4.476	4.468	40	4.43	110			
						50	4.258	021
15	4.096	4.093	60	4.03	021			
						20	3.949	101
10	3.873	3.872	50	3.85	101			
						70	3.694	111, 120
53	3.645	3.644	70	3.61	111			
			40	3.58	120			
						20	3.239	002
10	3.151	3.151	50	3.11	002			
7	2.966*					100	2.975	130
85	2.893	2.898	80	2.853	130			
						30	2.819	022
20	2.723	2.720	60	2.681	022			
20	2.699*	2.693			040	100	2.703	131
85	2.632*	2.632	80	2.593	131	60	2.643	112
100	2.574*	2.575	100	2.545	112	30	2.575	041
5	2.475	2.476	50	2.431	041	50	2.449	122
15	2.454	2.454	40	2.437	200			
2	2.398	2.393	50	2.375	210			
10	2.379	2.379	60	2.349	122			
5	2.361	2.361	60	2.320	140			
5	2.236	2.237	50	2.219	211	20	2.258	211, 220
		2.233			220			
						20	2.198	132
5	2.136	2.133			132			
2	2.102	2.104	20	2.086	221			
2	2.044	2.047			042	30	2.043	150
						20	1.961	113, 231
			20	1.937	150			
10	1.905	1.906			212			
			50	1.878	113			
2	1.850*		40	1.850	151	100	1.854	222, 240
50	1.821	1.822	80	1.802	222			
50	1.816	1.817			123			
		1.814	60	1.791	240	20	1.800	
2	1.742	1.743	50	1.720	241			
5	1.700	1.701	40	1.691	133			

1. Tephroite-glaucocroite intergrowth. Kanoiri mine. Asteriskd diffractions are due to or inclusive of those of glaucocroite. Diffractometer method. Cu/Ni radiation. The present study. Calculated cell parameters of tephroite: $a=4.908$, $b=10.772$, $c=6.302$ Å.
2. Synthetic Mn_2SiO_4 . Cr radiation. Guinier camera method. JCPDS Card No. 19-788. Given cell parameters: $a=4.878$, $b=10.560$, $c=6.226$ Å.
3. Glaucocroite. Anakit, Lower Tungksa, U.S.S.R. After PERTSEV and LAPUNINA (1974). Fe radiation. Camera method.

and zincian galaxite, although the latter is quantitatively very small. Among the associated minerals with them is involved alabandite but not sphalerite despite the existence of zinc in the galaxite. One of the explanation is that zinc was initially involved in rhodochrosite accompanying argillaceous material and the formation of zincian galaxite antedated that of alabandite. That is, when sulphur was supplied at the site of alabandite formation, zinc was no longer left in any reactive form. Despite the existence of minor Mg in the olivines, galaxite is essentially devoid of MgAl_2O_4 molecule. Although the compositional informations on galaxite in this mode of occurrence are not always complete, it seems that such a zincian galaxite is rare in contact or regionally metamorphosed manganese ores, while sphalerite is rather common in contact metamorphosed manganese ores especially in lower grade siliceous ores generally including manganese-bearing pyroxenoids. Also, it is worthy of note that as far as examined by the author this is a rare example of the association of manganese-bearing spinel with manganese-bearing garnet.

Seeing from the present assemblage of glaucocroite, the reconstructed sequence of mineral formation is considered as follows. The initial state of mineral assemblage responsible for the formation of glaucocroite was a limestone lens comprising rhodochrosite-rich parts just before the metamorphism. The ascending temperature gave rise to the recrystallization of carbonates that accompanied the formation of tephroite solid solution after the supply of siliceous material from the granite side in a limited quantity. At this time the temperature was high enough to allow the formation of tephroite solid solution, i. e., above the maximum temperature of the head of solvus. Although the shape of solvus has not been determined yet, the decreasing temperature generated the exsolution texture composed of calcian tephroite as host and glaucocroite as guest.

As to the formation of glaucocroite, many theories have been presented to date, such as those by TILLEY (1946), PERTSEV and LAPUTINA (1974), BURT (1972), and LEAVENS *et al.* (1987). All of them include the expressions in which glaucocroite is the product of reactions of minerals that existed as stable associations under different conditions, and the changes of conditions lead to the formation thereof. Although it is uncertain which state was a parental one, a calcian rhodochrosite or purer rhodochrosite plus calcite, it is very likely that the present glaucocroite was derived from a highly calcian tephroite solid solution directly coming from one or both of above-stated carbonate associations after the supply of silica under a higher temperature condition.

Besides the carbonates, the initial assemblage had contained such a clay mineral as illite as an impure material in the carbonates. The manganoan grossular is the product of a simple contact metamorphism of calcite+rhodochrosite+illite association as well as the associated zincian galaxite. Since the quantity of supplied silica was so limited, such silica undersaturated phases as olivines and galaxite were formed.

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