

GEOCHEMISTRY

Tobermorite–Plombierite Metasomatites of the Gumeshevsk Skarn–Porphyry Copper Deposit, Middle Urals

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Although calcic hydrosilicates with tobermorite-type structure (tobermorite, plombierite, and tacherenite) are rare minerals, they are rather typical of low-temperature mineral assemblages in some Ca-silicate rocks [1–3 and others]. Owing to defect structure and micrometer-size crystals, minerals of the tobermorite group are studied insufficiently, and each finding attracts interest. Most often, these minerals fill fissures. At the Gumeshevsk skarn–porphyry copper deposit, we detected them as massive metasomatite bodies.

The Gumeshevsk deposit is situated 60 km south of Yekaterinburg at the contact of a minor quartz diorite intrusion with marble [4]. According to traditional classification [5], skarns at this deposit are represented by low-temperature facies. The typical zoning of bimetasomatic columns appears as follows: propylitized diorite–amphibole epidosite–amphibole–epidote–garnet endoskarn (often with pyroxene)–actinolite–garnet exoskarn (occasionally with pyroxene)–andradite exoskarn–marble. Diverse ore-bearing metasomatites of the retrograde stage formed after marbles, skarns, diorites, aluminosilicate schists, and serpentinites are extremely widespread.

The light cream-colored massive tobermorite–plombierite metasomatite was found in Borehole 3871 (southern flank of the deposit) at a depth of 531.9–532.8 m. This rock contains numerous thin (from 0.001 to 2–3 mm) metasomatic veinlets of one or two minerals of the thaumasite–ettringite series (thaumasite-type mineral). The tobermorite–plombierite rock contacts

with a complex hydroxyllellstadite metasomatite reported in [6] at the top of the skarn body and with foshagite–hydroxyllellstadite metasomatite at the bottom. Contacts between these rocks are sharp, and their temporal relationships remain unclear. At a depth of 530.4 m, the metasomatic zone comes into contact with epidotized quartz diorite. No cores are available from deeper levels. Marble or wollastonite (andradite–wollastonite) skarn likely was a protolith for the entire metasomatic zone as indicated by discrete (3–5 vol %) relict grains of andradite ($f = 0.81–0.83$), vesuvianite, pyrite, diopside, and tremolite. The content of pyrite, chalcopyrite, and valleriite dissemination is no more than 1 vol %. The bulk composition of the metasomatite with veinlets, which cannot be separated, is as follows (wt %): SiO₂ 31.05, TiO₂ 0.01, Al₂O₃ 0.18, Fe₂O₃ 2.27, MnO 0.04, MgO 0.89, CaO 34.27, P₂O₅ 0.17, CO₂ 6.17, S 2.90, H₂O⁺ 17.31, H₂O[–] 4.68, Cu 0.08, total 100.42. Na₂O and K₂O were not detected.

The representative compositions of the most important phases of the metasomatite are presented in the table. The analyses were performed with a JSM microscope equipped with LINK ISIS. Since the intergrowths of calcic silicates are often microporous and they contain amorphous primary carbon, the sum total in analyses may be somewhat underestimated. The IR spectra of calcic silicates taken with a Specord-75 device are typical of such minerals. The powder X-ray patterns of two characteristic areas of the metasomatite were obtained with a Rigaky diffractometer. The X-ray images were recorded in the step-by-step regime (CuK_α, 40 kV, 40 mA, exposition at each point 2 s), which provided high reliability of the results obtained and the accurate calculation of mineral unit cell. The finely dispersed phases were studied with TEM, using the crystal microdiffraction method combined with semiquantitative microprobe analysis. Photography and calculation of the unit cell parameters were performed by V.T. Dubinchuk (All-Russia Institute of Mineral Resources, Moscow).

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Representative chemical compositions of minerals and phases of tobermorite–plombierite metasomatite

Component	1	2	3	4	5
Chemical composition, wt %					
SiO ₂	12.70	43.83	44.08	48.18	49.51
Al ₂ O ₃	–	0.16	–	–	0.16
MgO	–	–	–	0.59	0.36
CaO	30.69	30.45	31.06	39.19	24.25
Na ₂ O	–	0.21	–	–	0.53
K ₂ O	–	–	–	–	0.20
SO ₃	17.78	–	–	–	–
Cl	–	–	–	–	0.6
Total	61.17	74.65	75.14	87.96	75.61
Crystallochemical formula, f.u.					
Ca	3.00	4.45	4.53	5.23	
Na	–	0.06	–	–	
Si	1.16	5.98	6.00	6.00	
Mg	–	–	–	0.11	
Al	–	0.03	–	–	
S	1.22	–	–	–	

Note: (1) Thauasite-type mineral of the first generation in the veinlet, (2, 3) plombierite I, (4) plombierite II, (5) silicate gel. Intergrowths with tobermorite are possible in (2–4). (–) Concentrations below the detection limit. Contents of FeO, TiO₂, MnO, and F are below the detection limit.

The metasomatite is a fine-grained multiphase, aggregate of plombierite I, X-ray amorphous silicate gel, and a small amount of thauasite-type mineral of the first generation. Plombierite I is intergrown with tobermorite. The content of tobermorite commonly is not great. However, this mineral dominates locally. In addition, a small amount of tacherenite and cubic CaO is present. Metasomatic veinlets consist of thauasite-type mineral of the second generation that contains insignificant quantity of plombierite II.

The metasomatite is composed of very fine (from 0.1 to 30–50 μm) mineral grains. Therefore, their microscopic study is a difficult task. The optic examination of crystals in the plombierite–tobermorite aggregate has shown that the mineral is optically negative ($n_g \sim n_p = \sim 1.550$, $2V = 0.001–0.002$). These parameters fit tobermorite rather better than they do plombierite [2]. Plombierites of various generations are typically characterized by different chemical compositions (table). Judging by the low sum totals, plombierite I from the Gumeshevsk deposit likely pertains to the variety with the highest H₂O content [1]. The elevated Ca content (>5 f.u.) in plombierite II (table) is rather rare for natural plombierite, but this is typical of synthetic mineral [7]. The elevated Ca content in plombier-

ite may be a consequence of its highly defective structure.

According to IR spectroscopy, the structure of plombierite is not only more perfect but also more condensed ($\nu\text{SiO} = 973 \text{ cm}^{-1}$) than the structure of plombierite II ($\nu\text{SiO} = 969 \text{ cm}^{-1}$). The main reflection of plombierite (13.90 Å and 13.76 Å at intensity of 48 and 52, respectively) is observed in the X-ray patterns of two samples. The unit cell parameters of plombierite are as follows, Å: $a = 5.632 \pm 0.004$, $b = 3.674 \pm 0.002$, $c = 27.923 \pm 0.017$, and $V = 577.85 \text{ Å}^3$; $a = 5.627 \pm 0.006$, $b = 3.662 \pm 0.004$, $c = 28.002 \pm 0.035$, and $V = 576.92 \text{ Å}^3$.

Tobermorite is identified in the samples not only by a single characteristic line near 11 Å on X-ray pattern but also by microdiffraction pattern of crystals. We failed to determine a reliable chemical composition of tobermorite because of its intimate intergrowths with plombierite and very fine size of grains. Tobermorite has also been identified with high-voltage electronography (A.P. Zhukhlistov, analyst). Reflections of tobermorite are as follows (d is given in Å, intensity of lines is given in parentheses): 5.97 (medium), hkl 201; 3.638 (weak, medium), hkl 115; 3.300 hkl (weak), hkl 123; 3.077 (strong), hkl 220; 2.97 (medium), hkl 222; 2.807 (medium, weak), hkl 400; 2.73 (very weak), hkl 402; 2.51 (weak), hkl 404; 2.145 (weak, medium), hkl 423; 2.00 (medium, weak), hkl 425; 1.838 (medium), hkl 040; 1.622 (weak, medium), hkl 620. The pseudorhombic unit cell ($a = 11.228$, $b = 7.352$, and $c = 22.54 \text{ Å}$) is typical of this mineral.

The thauasite-type mineral differs from the holotypical thauasite by the Ca/Si/S ratio and low contents of carbonate groups (~50% of carbonate groups is in the holotypical thauasite). The first generation occurs as tiny grains and their aggregates filling interstitial space between silicate phases of the metasomatite. The second generation is represented by crystalline aggregate (up to ~0.1 mm) in metasomatic veinlets. The representative composition of this mineral is given in the table. The mineral is optically uniaxial and negative: $n_o = 1.503(1)$, $n_e = 1.475(2)$, and N_o is directed along the crystal elongation. X-ray patterns are typical of thauasite. The unit cell parameters for two samples calculated from X-ray patterns on the basis of “common” thauasite are as follows, Å: $a = 11.046 \pm 0.005$, $b = 10.419 \pm 0.006$, $V = 1100.99 \text{ Å}^3$ and $a = 11.038 \pm 0.007$, $b = 10.39 \pm 0.01$, and $V = 1097.42 \text{ Å}^3$. Some analyses of thauasite-type mineral yield ~0.1 wt % Al₂O₃, indicating that this presence contains both ettringite end member and ettringite nuclei overgrown by thauasite-type mineral. According to [7], the growth of thauasite crystals on ettringite nuclei, which is a characteristic feature of the former mineral, lowers its crystallization temperature to 4°C.

The silicate gel consists of submicrometer-sized particles with a variable Ca/Si ratio (table) and carbon particles. The average gel composition at all points of

the sample is characterized by a stable Ca/Si ratio (~1/2). Microparticles of the silicate gel were studied with a TEM using the crystal microdiffraction method in combination with semiquantitative chemical analysis. Plombierite, tobermorite, tacherenite, and lime (CaO) have also been identified as crystalline phases of micrometer- and submicrometer dimensions. The submicrometer-sized prismatic crystals of tacherenite and plombierite partly occur as chaotically oriented intergrowths. Because the finding of lime in hydrothermally altered rocks is unusual, we specify that the detected cubic phase has unit cell parameters of CaO and “calcic” composition. The appearance of lime is probably related to the gel crystallization that should be accompanied by the formation of metastable phases. The retention of lime crystals can be caused by submicrometer size of crystals and appreciable influence of surface tension.

Tacherenite ($\text{Ca}_{12}\text{Al}_2\text{Si}_{18}\text{O}_{69}\text{H}_{36}$) was identified in the Urals for the first time. According to the microdiffraction pattern of crystals, the unit cell parameters of tacherenite from the Gumeshevsk deposit are as follows, $a = 17.60 \text{ \AA}$, $b = 3.65 \text{ \AA}$, $c = 26.70 \text{ \AA}$, and $\beta = 116.6^\circ$ (the unit cell parameters have been optimized based on the criterion of minimal unit cell size). The above parameters are close to those reported in [8]. The semiquantitative analysis of tacherenite yielded elevated Na content ($\text{Na} > \text{Ca}$) that is atypical of this mineral.

The rock under consideration was formed under low-temperature conditions over the course of at least two (probably very close in time) stages. The tobermorite–plombierite aggregate of the first generation, which alternated with numerous colonies of X-ray amorphous silicate gel, was formed at the first stage. The sharp prevalence of plombierite over tobermorite and tacherenite was probably caused by deficiency in Al, because Al-free tobermorite is very rare in nature [2]. The temperature of tobermorite crystallization might be ~130–170°C, whereas plombierite crystallized at 90–100°C [8]. The absence of Al or only traces of this element in the plombierite–tobermorite intergrowths indicate that the temperature of tobermorite crystallization was shifted toward the low-temperature range of the aforementioned interval [8]. An appreciable portion of crystalline phases arose in the course of crystallization of the amorphous $\text{SiO}_2\text{–CaO–H}_2\text{O}$ gel. The Ca/Si ratio of 1/2 in gel fits the Ca/Si ratio of solutions where tobermorite ($\text{Si} > \text{Ca}$) crystallized from [8]. It may be suggested that low Al content in the solution hampered crystallization of tobermorite, and especially hampered tacherenite. As a result, the mainly amorphous

Ca-silicate gel precipitated from the solution instead of tobermorite. When the temperature decreased to ~100°C, plombierite started to crystallize, because Al is unnecessary for this mineral. The first stage completed with crystallization of thaumasite-type mineral of the first generation. The filling of fissures with aggregate of thaumasite-type mineral of the second generation and low-crystalline plombierite is related to the second stage.

Thus, the hypogene massive and very fine-grained metasomatite of the Gumeshevsk deposit contain plombierite in association with the subordinate tobermorite, thaumasite-type mineral, Ca–Si–H₂O gel ($\text{Ca/Si} = 1/2$), and an admixture of tacherenite and cubic CaO. The metasomatite is crosscut by numerous metasomatic veinlets composed of thaumasite-type mineral with an admixture of plombierite and tobermorite of the second generation. This metasomatite is confined to a complex hydroxyllellstadite metasomatite body described previously. A certain analogy between these metasomatites and the products of alteration of wollastonite skarn at the Arimao Norte deposit in Cuba [9] may be drawn.

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REFERENCES

1. A. E. Zadov, N. V. Chukanov, N. I. Organova, et al., *Zap. Ross. Mineral. Ob-va* **124** (2), 36 (1995).
2. A. E. Zadov, N. V. Chukanov, N. I. Organova, et al., *Zap. Ross. Mineral. Ob-va* **130** (2), 26 (2001).
3. S. Merlino, E. Bonaccorsi, and T. Armbruster, *Eur. J. Mineral.* **13**, 577 (2001).
4. A. I. Grabezhev, *Petrologiya* **12**, 176 (2004) [*Petrology* **12**, 149 (2004)].
5. V. A. Zharikov, in *Genesis of Endogenic Ore Deposits* (Nedra, Moscow, 1968), pp. 220–302 [in Russian].
6. A. I. Grabezhev, V. G. Gmyra, and G. V. Pal'gueva, *Dokl. Akad. Nauk* **394**, 659 (2004) [*Dokl. Earth Sci.* **395**, 196 (2004)].
7. H. F. W. Taylor, *Cement Chemistry* (Academic Press, New York, 1990; Mir, Moscow, 1996).
8. G. Cliff, J. A. Gard, G. W. Lorimer, and H. F. W. Taylor, *Mineral. Mag.* **40**, 113 (1975).
9. M. A. Litsarev, N. I. Organova, P. Khranach, et al., *Zap. Ross. Mineral. O-va* **127** (6), 68 (1998).