

Thermodynamic and Hydrogeochemical Formation Conditions of Brochantite As a Crystalline Hydrate: A Case of the Udokan Copper Deposit

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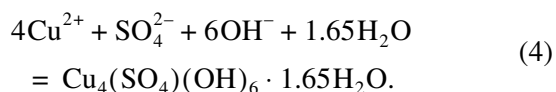
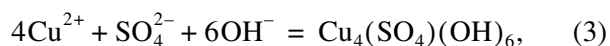
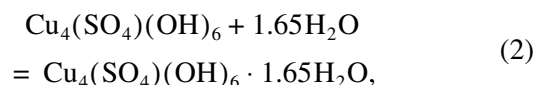
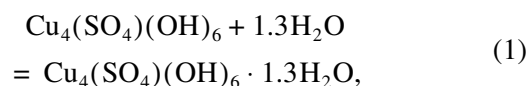
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Brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$ is an abundant secondary (mostly anhydrous) mineral in oxidation zone of copper deposits. Brochantite as a crystalline hydrate $\text{Cu}_{15}(\text{SO}_4)_4(\text{OH})_{22} \cdot 6.6\text{H}_2\text{O}$ [8] (or $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 1.65\text{H}_2\text{O}$ in recalculated form [4]) has been found for the first time at the Udokan cupriferous sandstone deposit. The mineral was defined as cryogenic, i.e., the permafrost phase. The formation of crystalline hydrate was accounted for by the deficiency of free water in frozen rocks and high copper concentration in the mineral-forming solution. Later on, thermodynamic prerequisites were also considered responsible for this process. In terms of thermodynamics, if $\text{Cu} : \text{H}_2\text{O} = 4 : 1.65$, this mineral may only be precipitated from a solution with a Cu concentration of >8.56 kg/l. As is known, mineralization of the most concentrated brines does not reach 1 kg/l.

Assumption of the thermodynamic control of brochantite formation was based on general premises, because the main thermodynamic functions (free energy and enthalpy) of this mineral were absent in the literature. In a recent work [4], the analytically calculated free energy of brochantite formation is reported, but no data on enthalpy are given. The ΔG° value is calculated with traditional approaches applied to ΔH° [5]. The calculation is based on the linear relationship $y = ax + b$ between thermodynamic functions and the number of water molecules in a mineral. Here, y is the sought function (ΔG_f° or ΔH_f°) of crystalline hydrate species, a is the increment of this function per 1 mol H_2O , b is the function of the anhydrous species under standard conditions, and x is number of water mole-

cules in the chemical formula of the given mineral. Thus, the data on the anhydrous species and one hydrate species are sufficient to calculate thermodynamic functions for other crystalline hydrates of the same series. The calculations in [4] were based on the data on anhydrous and hydrous (1.3 H_2O) brochantites [5]. The calculated ΔG_f° for brochantite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 1.65\text{H}_2\text{O}$ is -1957 kJ/mol, or -467.7 kcal/mol (ΔG° and ΔH° values are given in this paper in kcal/mol). The a value in the ΔG_f° calculation for cryogenic brochantite equals -20.167 [4]; i.e., it is nearly three times lower than the absolute value given for other minerals. Our calculations gave approximately the same discrepancy for copper minerals with crystallization water reported in [5].

To determine approximately the thermodynamic functions and ascertain geochemical formation conditions for the crystalline hydrate form of brochantite (hereafter, hydrate brochantite), let us consider the following reactions:



If hydrate species are formed from anhydrous species, the free energy of crystalline hydrates per 1 mol H_2O must shift to a greater value (in absolute value) than $\Delta G_f^\circ \text{H}_2\text{O}$ (-56.69); otherwise, ΔG° of the reaction would be positive, and thus crystalline hydrate cannot

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Table 1. Free energy and enthalpy of anhydrous and hydrous brochantite species at 25°C, kcal/mol

Func- tion	Number of water molecules in brochantite					
	0	1.0	1.30	1.65	2.0	3.0
ΔG_f°	-434.3	-492.4	-509.8	-530.1	-550.4	-608.5
ΔH_f°	-525.4	-597.0	-618.5	-643.6	-668.6	-740.2

be formed. According to reaction (1) and based on reference free energy values [5], $\Delta G^\circ = 46.70$. In this case, hydrate brochantite cannot be formed by hydration under standard conditions and must be dehydrated after precipitation from solutions as a result of interaction between ions.

Using other copper crystalline hydrates—bonattite $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and chalcantite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ —as examples in comparison with anhydrous chalcocyanite (CuSO_4), we will show that the a value (with allowance for its sign) must be not higher than $\Delta G_f^\circ \text{H}_2\text{O}$. According to data in [10], the free energies of materials in these pairs differ by -176.37 and -291.04 (or -58.79 and -58.21 per 1 mol), respectively. Thus, the obtained a values are lower than the free energy of H_2O . Therefore, the considered compounds may form and remain stable at a temperature of 25°C. This implies that the ΔG_f° value of hydrous brochantite with 1.3 H_2O reported in [5] is unreliable, and the estimate presented in [4] is unsatisfactory. Our testing has shown that the ΔG° value of reaction (2) is actually equal to 60.33. This value rules out the formation of hydrate brochantite. The ΔG_f° value of posnjakite $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$ [10] also does not satisfy the necessary condition, because the difference with the ΔG_f° value of brochantite in this case is -53.92 .

It should be noted that the thermodynamic functions for brochantite presented in [1] markedly differ from the internally consistent data reported in other sources [5, 10, and others]. Therefore, our calculations are based on data from [10] as the most commonly accepted ones for brochantite in thermodynamic computations.

To estimate thermodynamic functions of hydrate brochantite, the a values were taken approximately as the average of values calculated for other copper crystalline hydrates ($\Delta G^\circ = -58.06$ and $\Delta H^\circ = -71.6$). Based on the obtained thermodynamic functions (Table 1), the ΔG° value of reactions (1) and (2) is equal to -1.78 and -2.27 , respectively, indicating that the considered copper hydrates may form and remain stable under standard conditions. Enthalpy of reactions (1) and (2) is -4.27 and -5.42 , respectively.

The free energy of anhydrous brochantite formation (reaction 3) and hydrate brochantite precipitation (reac-

tion 4) is -93.35 and -95.62 , respectively, while enthalpy is equal to -41.07 and -46.49 , respectively. Hence, the ΔG° value of hydrous brochantite formation is lower, and therefore formation of hydrous species is preferential. Enthalpy of this reaction is lower as well, and therefore the formation of hydrous brochantite in the negative temperature field that consumes the heat of the exothermic reaction, is more favorable in terms of thermodynamics. The calculations were performed under standard conditions. However, as has been shown in [3], the increments of thermodynamic functions within a temperature range of -10°C to $+25^\circ\text{C}$ remain virtually the same.

To ascertain the level of Cu concentration necessary for the formation of anhydrous and hydrous brochantites according to reactions (3) and (4), we calculated their solubility products (SP), which are $10^{-68.42}$ and $10^{-70.08}$, respectively. With allowance for SP, the formation of cryogenic brochantite at stoichiometric proportions of mineral-forming components requires an equilibrium Cu^{2+} activity equal to $10^{-6.37}$ mol/l (or 27.1 $\mu\text{g/l}$). This concentration is only less than one order of magnitude higher than the average copper concentration in groundwater of the supergene zone (5.58 $\mu\text{g/l}$ [7]) and is much lower than in the geochemical halos and oxidation zone at copper deposits.

As mentioned above, hydrate brochantite was first found in the Udokan cupriferous sandstone deposit. The ore levels of this deposit are located in permafrost up to 800–1000 m thick, where the temperature of rocks falls to minus 7–8°C. The ore mineralization is hosted in metamorphic rocks of the Early Proterozoic Udokan Group composed of quartz–feldspar and feldspar–quartz metasandstones and metasilstones with quartz–sericite and carbonate cement that are intercalated with metamorphosed magnetite-bearing sandstone, mudstone, conglobreccia, and sandy limestone [6].

The oxidation zone at the deposit is variable in thickness, sinking down to 700–800 m along faults. Precryogenic and cryogenic epochs of oxidation are distinguished. According to [9], the preglacial stage produced sulfates, carbonates, oxides, and hydroxides. The cryogenic epoch that started in the Late Pleistocene is characterized by a sulfate-rich oxidation zone with the basic sulfates containing crystallization water. Malachite and brochantite are the major minerals among the diverse supergene minerals. The percentage of sulfates increases with depth.

In terms of hydrochemistry, water in the region and deposit fits the fresh type with TDS content up to 100 mg/l, near-neutral pH value, and hydrocarbonate (less frequently, chloride–hydrocarbonate, sulfate–hydrocarbonate, calcic, or calcic–sodic) composition. The water in active layer is closely related and compositionally similar to the surface water. The Cu concentration in the surface water of geochemical halos reaches 0.350 mg/l. The adit water is slightly acid (the TDS content up to 200 mg/l, Cu concentration up to

Table 2. Hydrochemical indices (mg/l), activity products, and water saturation at the Udokan deposit (based on anhydrous brochantite and hydrate brochantite)

Index	Water samples										
	1	2	3	4	5	6	7	8	9	10	11
pH	6.89	6.93	7.02	6.98	7.12	7.15	7.19	7.21	7.07	5.5	5.9
SO ₄ ²⁻	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.5	79.2
Cu (total)	0.259	0.237	0.321	0.266	0.252	0.215	0.126	0.066	0.004	5.28	15.8
Cu ²⁺	0.127	0.103	0.117	0.105	0.069	0.055	0.029	0.015	0.001	4.18	11.89
Mineralization	10	16	16	16	23	18	16	16	13	59	146
AP based on brochantite	1.6E-71	3.8E-71	2.2E-70	8.2E-71	1.0E-70	6.4E-71	9.1E-72	7.4E-73	4.9E-78	2.1E-73	4.4E-68
Saturation of solution (AP/SP) with minerals											
Brochantite	0.004	0.010	0.058	0.022	0.026	0.017	0.002	0.0002	1.3E-09	5.5E-05	11.57
Hydrobrochantite	0.192	0.457	2.645	0.986	1.202	0.770	0.109	0.009	5.9E-08	0.003	529.10

Note: E-71 = 10⁻⁷¹, etc.

15.8 mg/l). The activity product (AP) of the ions incorporated into brochantite has been calculated for water of the geochemical halo in the Sekushchii area of the deposit (Table 2, samples 1–9) and for adit water (samples 10 and 11).

As follows from the calculations, the water of the geochemical halo is saturated with hydrate brochantite, while the adit water is appreciably oversaturated with this mineral (Table 2). According to a computation with the HydroGeo program [2], precipitation of hydrate brochantite may be as much as 16.8 mg/l of solution.

If we accept the initial ΔG_f° of brochantite and the equation parameters suggested in [1], the free energy of brochantite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 1.65\text{H}_2\text{O}$ will be equal to -498.1 and the SP value will be $10^{-46.63}$, which correspond to the equilibrium Cu^{2+} activity of $10^{-4.24}$ mol/l (or 3.65 mg/l) in a stoichiometric mineral-forming solution. However, at the calculated ΔH_f° of brochantite equal to -608.9 , enthalpy of the reaction will be 68.4. In our opinion, this value rules out formation of this mineral at a negative temperature.

Thus, a lower free energy of crystallization water than that of free water is a necessary thermodynamic condition for the crystallization of brochantite and other hydrates. It is evident that such minerals may form and remain stable only at a certain temperature. Occurrence of hydrous brochantite at the Udokan deposit is related to hydration at negative temperatures in the oxidation zone and justifies its definition as a cryogenic mineral. Despite only approximate calculation of thermodynamic functions, it is clear that concentrated copper solutions are not necessary for precipitation of hydrate brochantite and its anhydrous counterpart.

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