

SHORT
COMMUNICATIONS

Genesis of Dawsonite Mineralization: Thermodynamic Analysis and Alternatives

B. N. Ryzhenko

*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
ul. Kosygina 19, Moscow, 119991 Russia*

e-mail: ryzhenko@geokhi.ru

Received October 20, 2005

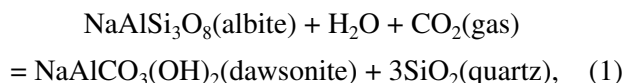
DOI: 10.1134/S0016702906080088

Although the mineral dawsonite $\text{NaAlCO}_3(\text{OH})_2$ is not well known to geologists, dawsonite mineralization is quite widely known and was documented, for example, in the Carpathians, Kuznetsk Basin, Donets Basin, Northern Caucasus, Caspian Sea area, Khibina, and Colorado. The Lower Carboniferous deposits of the Pripyat' foredeep in Belarus (sandy-clayey rocks with carbonate beds of the Visean stage filling the El'sk depression) host the Zaozerskoe dawsonite deposit [1]. The sandstones, siltstones, and mudstones of the coal-bearing Balakhonskaya Group (Lower Permian–Upper Carboniferous) contain 2- to 35-m-thick tabular and lens-shaped bodies with average dawsonite contents of 10–15% [2]. The gravitational and pore waters of these rocks are highly alkaline ($\text{pH} > 8\text{--}9$), and the chemical formula of this mineral itself suggests that it can be formed when alkaline waters interact with aluminosilicate minerals of the water-hosting rocks and/or the products of their weathering (up to gibbsite).

Proceeding from the thermodynamic analysis of the conditions currently existing at sites with dawsonite mineralization at the Berezovoyarskoe locality in the Kuznetsk basin, Shvartsev [2] has arrived at the conclusion that dawsonite is formed when the solution becomes saturated with respect to calcite (the sodium bicarbonate stage of the weathering of aluminosilicate rocks), and dawsonite is an interaction product of the aqueous solution (containing $\text{Na} > 230$ mg/l and having $\text{pH} > 7.8$ and overall mineralization of >1 g/l) with aluminosilicate minerals. At the same time, it remains uncertain whether modern alkaline waters at sites with dawsonite mineralization can be formed owing to interactions with dawsonite. Inasmuch as thermodynamics does not shed light onto all intermediate stages of the process of attaining equilibrium, the saturation of the aqueous phase with respect to dawsonite is insufficient to prove that dawsonite can crystallize from this aqueous solution. The equilibrium between dawsonite and the aqueous solution can be approached from below and above, particularly considering the fact that the

composition points of the aqueous phase from sites with dawsonite mineralization plot on both sides of the equilibrium line (Fig. 1). This alternative was the starting point for the discussion of the results of thermodynamic analysis in [2]. Below I will attempt to elucidate this problem.

Consider the chemical equilibrium between mineral phases and an aqueous solution in the system $\text{Na}_2\text{O}\text{--}\text{CaO}\text{--}\text{SiO}_2\text{--}\text{Al}_2\text{O}_3\text{--}\text{CO}_2\text{--}\text{H}_2\text{O}$ (table), in which $\text{NaAlCO}_3(\text{OH})_2$ (dawsonite) can be formed when $\text{NaAlSi}_3\text{O}_8$ (albite), $\text{NaAl}_3\text{Si}_3\text{O}_{12}\text{H}_2$ (mica), and $\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{12}\text{H}_2$ (montmorillonite) interact with a CO_2 -bearing aqueous solution.



$$K_1^\circ = (P_{\text{CO}_2})^{-1} = 10^{2.09}; \quad (P_{\text{CO}_2}) = 10^{-2.09},$$

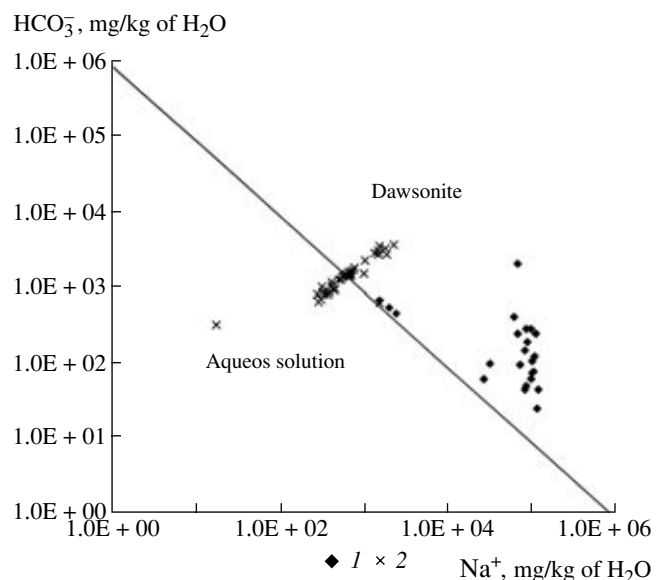
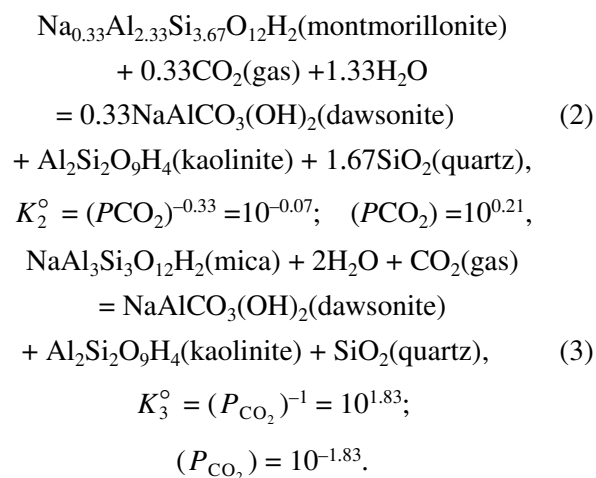


Fig. 1. Dawsonite–aqueous solution equilibrium, according to (1) [1] and (2) [2].

Gibbs free energy (J/mol, at 25°C) of minerals, gases, and aqueous species used to simulate equilibria in the system Na₂O–CaO–SiO₂–Al₂O₃–CO₂–H₂O [3–5]

OH ⁻	-157297	H ₂ O	-237144
Ca ²⁺	-552790	CaCO ₃ (calcite)	-1129258
Na ⁺	-261881	Al(OH) ₃ (gibbsite)	-1155487
CO ₂ (gas)	-394359	Al ₂ Si ₂ O ₉ H ₄ (kaolinite)	-3801800
CO ₂ (aq)	-385974	NaAlSi ₃ O ₈ (albite)	-3712020
HCO ₃ ⁻	-586940	CaAl ₂ Si ₂ O ₈ (anorthite)	-4007954
CO ₃ ²⁻	-527983	NaAl ₃ Si ₃ O ₁₂ H ₂ (Na-mica)	-5565228
HAIO ₂ ⁰	-869017	NaAlCO ₃ (OH) ₂ (dawsonite)	-1786024
AlO ₂ ⁻	-831332	SiO ₂ (quartz)	-856479
SiO ₂ (aq)	-833411	Na _{0.33} Al _{2.33} Si _{3.67} O ₁₂ H ₂	-5376367
Cl ⁻	-131290		



The equilibrium constants of reactions (1)–(3) are inversely proportional to the partial pressure of CO₂. It follows from the equations of reactions (1)–(3) that dawsonite can be formed when albite, mica, or mont-

morillonite are affected by an aqueous solution saturated with respect to CO₂ at a partial pressure equal to or more than 10^{0.21} bar (for montmorillonite), 10^{-1.83} bar (for mica), and 10^{-2.09} (for albite). Hence, dawsonite can be produced if there is a stable CO₂ source that can maintain a partial pressure of CO₂ equal to or higher than these values. The molal (*m*) concentration of the dissolved CO₂(aq) = 10^{-1.47} P_{CO₂(gas), bar, i.e., dawsonite can form at a concentration of CO₂(aq) higher than, respectively, 2400 mg/kg of H₂O (for montmorillonite), 22 mg/kg of H₂O (for mica), and 12 mg/kg of H₂O (for albite). *Waters with such concentrations of dissolved CO₂(aq) are not alkaline, and the conclusion in [2] that dawsonite is formed by alkaline waters is not universally applicable.*}

The boundaries of the stability fields of albite, montmorillonite, mica, kaolinite, and quartz are defined by

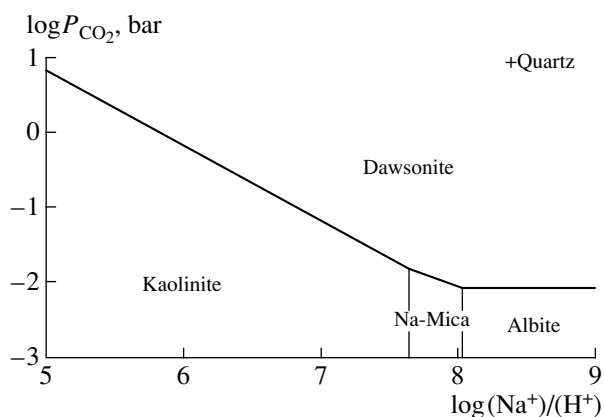


Fig. 2. Stability fields of various phase in the presence of quartz [reactions (1) and (3)–(5)] at 25°C.

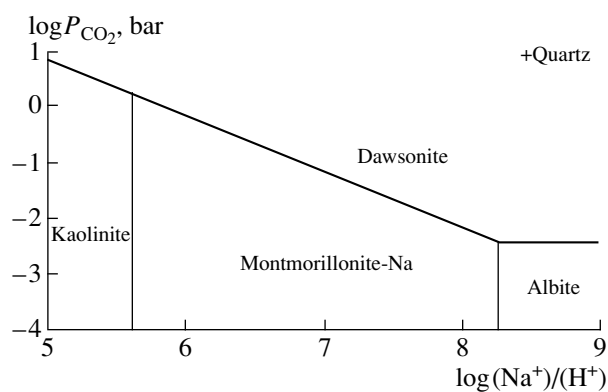
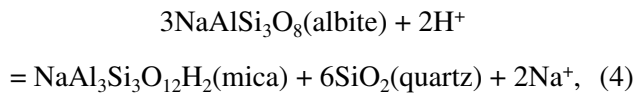


Fig. 3. Stability field of montmorillonite [reactions (2), (6), and (8)] at 25°C.

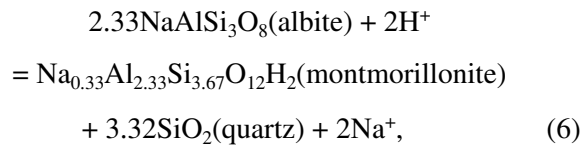
reactions (4)–(7) and are shown in the $\log P_{\text{CO}_2}$ – $\log(\text{Na}^+)/(\text{H}^+)$ diagrams of Figs. 2–4.



$$K_4^\circ = (\text{Na}^+)^2/(\text{H}^+)^2 = 10^{16.08}; \quad (\text{Na}^+)/(\text{H}^+) = 10^{8.04},$$

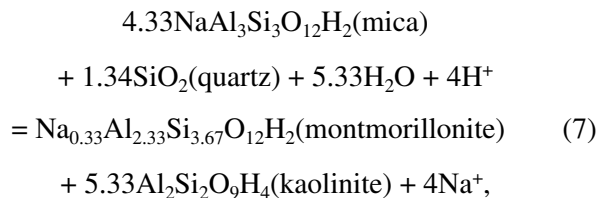
$$2\text{NaAl}_3\text{Si}_3\text{O}_{12}\text{H}_2(\text{mica}) + 3\text{H}_2\text{O} + 2\text{H}^+ = 3\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4(\text{kaolinite}) + 2\text{Na}^+, \quad (5)$$

$$K_5^\circ = (\text{Na}^+)^2/(\text{H}^+)^2 = 10^{15.29}; \quad (\text{Na}^+)/(\text{H}^+) = 10^{7.65},$$

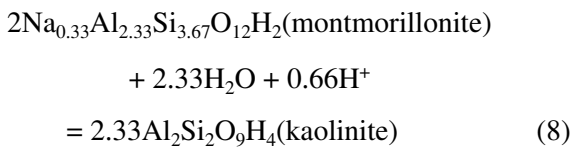


$$K_6^\circ = (\text{Na}^+)^2/(\text{H}^+)^2 = 10^{16.58};$$

$$(\text{Na}^+)/(\text{H}^+) = 10^{8.29},$$

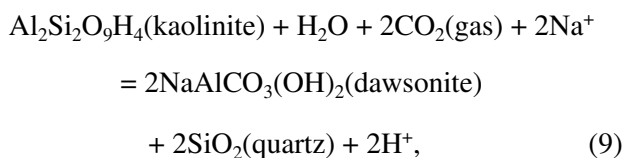


$$K_7^\circ = (\text{Na}^+)^4/(\text{H}^+)^4 = 10^{31.26}; \quad (\text{Na}^+)/(\text{H}^+) = 10^{7.82},$$



$$K_8^\circ = [(\text{Na}^+)/(\text{H}^+)]^{0.66} = 10^{3.70}; \quad (\text{Na}^+)/(\text{H}^+) = 10^{5.61}.$$

Dawsonite can be produced from kaolinite $\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4$, gibbsite $\text{Al}(\text{OH})_3$, or anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ [Eqs. (9)–(12)] only at their interaction with an aqueous solution containing simultaneously Na and carbonic acid components (CO_2 and HCO_3^-).



$$K_9^\circ = [(\text{H}^+)^2/(\text{Na}^+)^2](P_{\text{CO}_2})^{-2} = 10^{-11.64};$$

$$(P_{\text{CO}_2}) = 10^{5.82}/[(\text{Na}^+)/(\text{H}^+)],$$

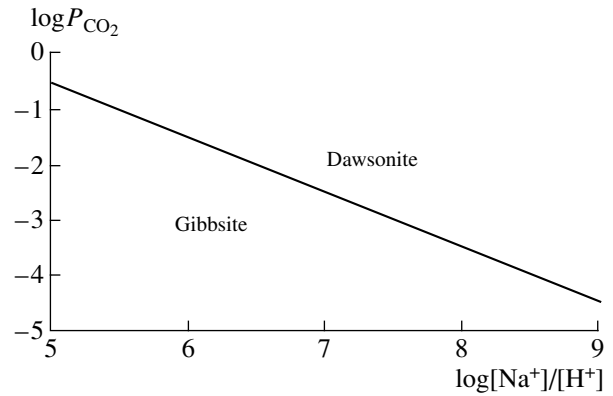


Fig. 4. Gibbsite–dawsonite equilibrium [reaction (10)].

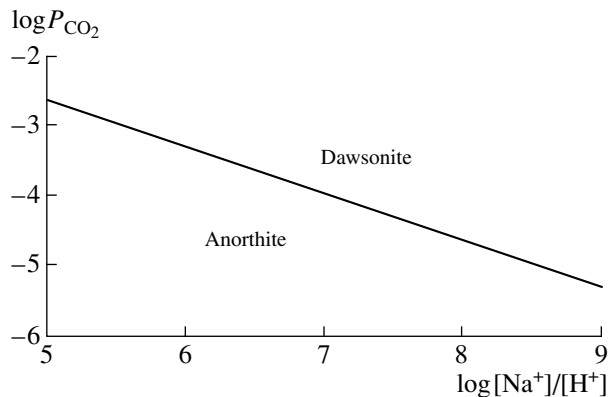
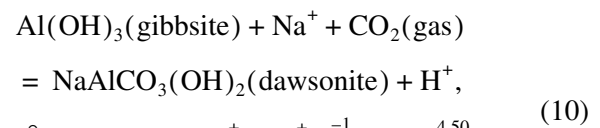
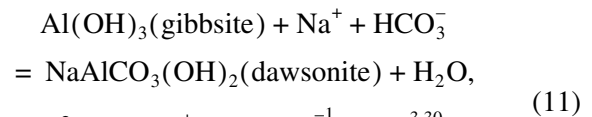


Fig. 5. Anorthite–dawsonite equilibrium [reaction (12)].



$$K_{10}^\circ = [(P_{\text{CO}_2})(\text{Na}^+)/(\text{H}^+)]^{-1} = 10^{-4.50};$$

$$(P_{\text{CO}_2}) = 10^{4.50}/[(\text{Na}^+)/(\text{H}^+)],$$



$$K_{11}^\circ = [(\text{Na}^+)(\text{HCO}_3^-)]^{-1} = 10^{3.30};$$

$$(\text{Na}^+)(\text{HCO}_3^-) = 10^{-3.30}.$$

The equilibrium constants (9)–(11) include [in explicit form for Eqs. (9)–(10) and in implicit form for Eq. (11)] the $(\text{Na}^+)/(\text{H}^+)$ ratio of activities in the aqueous solution and the partial pressure of CO_2 . Dawsonite is formed in the equilibrium association mica + quartz + montmorillonite + kaolinite [Eq. (7)] at $P_{\text{CO}_2} = 10^{5.82}/10^{7.82} = 10^{-2.0}$ bar. In the equilibrium association montmorillonite + kaolinite + quartz [Eq. (7)], dawsonite is produced at $P_{\text{CO}_2} = 10^{5.82}/10^{5.61} = 10^{0.21}$ bar (Fig. 3). The partial pressure of CO_2 needed for the gibbsite–

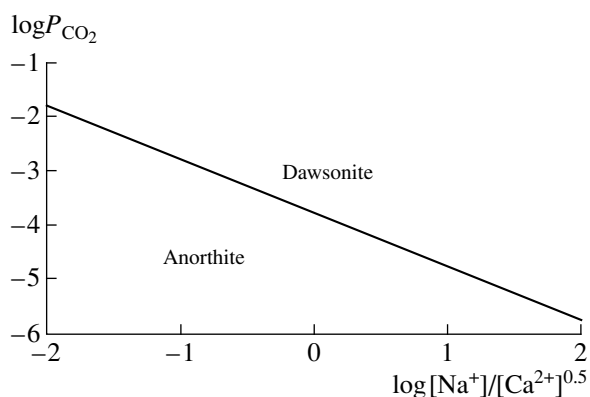
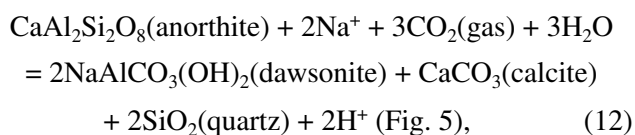


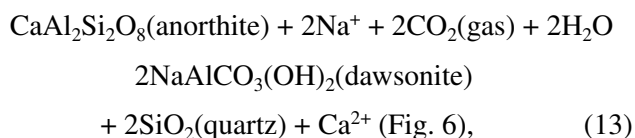
Fig. 6. Anorthite–dawsonite equilibrium [reaction (13)].

dawsonite transformation decreases with increasing $(\text{Na}^+)/(\text{H}^+)$ ratio of activities (Fig. 4).

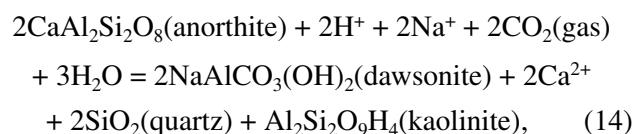
Let us consider the origin of dawsonite by the reaction of anorthite with a Na-bearing solution that is saturated with respect to CaCO_3 (calcite) [Eq. (12)] and undersaturated in it [Eqs. (13)–(14)].



$$\begin{aligned} K_{12}^\circ &= [(\text{H}^+)/(\text{Na}^+)]^2 (P_{\text{CO}_2})^{-3} = 10^{-2.09} \\ (P_{\text{CO}_2}) &= 10^{0.70} [(\text{Na}^+)/(\text{H}^+)]^{-2/3}, \end{aligned}$$

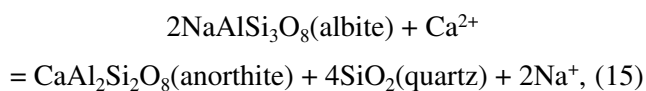


$$\begin{aligned} K_{13}^\circ &= [(\text{Ca}^{2+})/(\text{Na}^+)^2] (P_{\text{CO}_2})^{-2} = 10^{7.55} \\ (P_{\text{CO}_2}) &= 10^{-3.77} / [(\text{Na}^+)/\sqrt{(\text{Ca}^{2+})}], \end{aligned}$$



$$\begin{aligned} K_{14}^\circ &= (\text{Ca}^{2+})^2 [(\text{Na}^+)(\text{H}^+)(P_{\text{CO}_2})]^{-2} = 10^{26.73}; \\ [(\text{H}^+)/(\text{Na}^+)] [(\text{Na}^+)^2/(\text{Ca}^{2+})] (P_{\text{CO}_2}) &= 10^{-13.37}. \end{aligned}$$

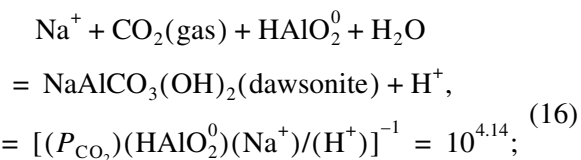
According to the reaction



$K_{15}^\circ = (\text{Na}^+)^2/(\text{Ca}^{2+}) = 10^{-3.36}$; $(\text{Na}^+)/\sqrt{(\text{Ca}^{2+})} = 10^{-1.68}$, and, thus, the partial pressure of CO_2 needed to produce dawsonite by replacing feldspars (Fig. 6) varies from

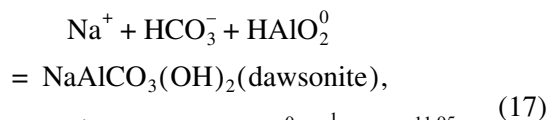
$$\begin{aligned} P_{\text{CO}_2} &= 10^{-3.77}/10^{-1.68} = 10^{-2.09} \text{ bar [Eqs. (13) and (15)] to} \\ P_{\text{CO}_2} &= 10^{0.70}(10^{8.04})^{-2/3} = 10^{-4.66} \text{ bar [Eqs. (4) and (12)].} \end{aligned}$$

Reactions forming dawsonite can also proceed in solutions undersaturated with respect to $\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4$ (kaolinite) and $\text{Al}(\text{OH})_3$ (gibbsite)



$$K_{16}^\circ = [(P_{\text{CO}_2})(\text{HAIO}_2^0)(\text{Na}^+)/(\text{H}^+)]^{-1} = 10^{4.14};$$

$$(P_{\text{CO}_2}) = 10^{-4.14}/\{(\text{HAIO}_2^0)[(\text{Na}^+)/(\text{H}^+)]\},$$



$$K_{17}^\circ = [(\text{Na}^+)(\text{HCO}_3^-)(\text{HAIO}_2^0)]^{-1} = 10^{11.95};$$

$$[(\text{Na}^+)(\text{HCO}_3^-)] = 10^{-11.95}/(\text{HAIO}_2^0).$$

The equations of reactions (16) and (17) demonstrate the conditions under which dawsonite is formed in aqueous solutions whose Al concentrations are not high enough to precipitate kaolinite and gibbsite. Gibbsite is stable when the molal concentration of HAIO_2^0 is higher than $10^{-8.64}$, and kaolinite is stable in equilibrium with gibbsite at a molal concentration of $\text{SiO}_2(\text{aq}) > 10^{-5.86}$. It is pertinent to remember that the molal concentration of $\text{SiO}_2(\text{aq})$ in an aqueous solution saturated with respect to quartz is equal to $10^{-4.01}$.

Summarizing the results of our thermodynamic simulations, it should be mentioned that dawsonite can be formed by reactions between aluminosilicate minerals and Na-bearing aqueous solutions with a $(\text{Na}^+)/(\text{H}^+)$ ratio of activities of the order of 10^5 to 10^9 , at a partial pressure of CO_2 of the order of 10^{-2} or higher (Figs. 3–5). To maintain the required values of the $(\text{Na}^+)/(\text{H}^+)$ ratio of activities (within the range of 10^5 – 10^9), it is sufficient that the Na^+ and H^+ activities vary concurrently. An alkaline solution can have a relatively low activity of Na^+ but a high activity of the HCO_3^- ion [Eq. (11)], and dawsonite can be produced by neutral and weakly acid solutions with high Na^+ activities (brines).

Dawsonite was found in Belarus in sandy–clayey rocks that occur between salt domes and are in places soaked in hydrocarbons. According to A.A. Makhnach, “...the destruction of salt domes in the Carboniferous could provide Cl- and Na-bearing aqueous solutions, and oxidizing hydrocarbons could be a source of carbon dioxide. This is corroborated by the isotopic composition of dawsonite, whose oxygen is isotopically heavy and carbon is isotopically light.” In the Kuznetsk basin, dawsonite was identified in sandstone, siltstone, and mudstone of the coal-bearing Balakhonskaya

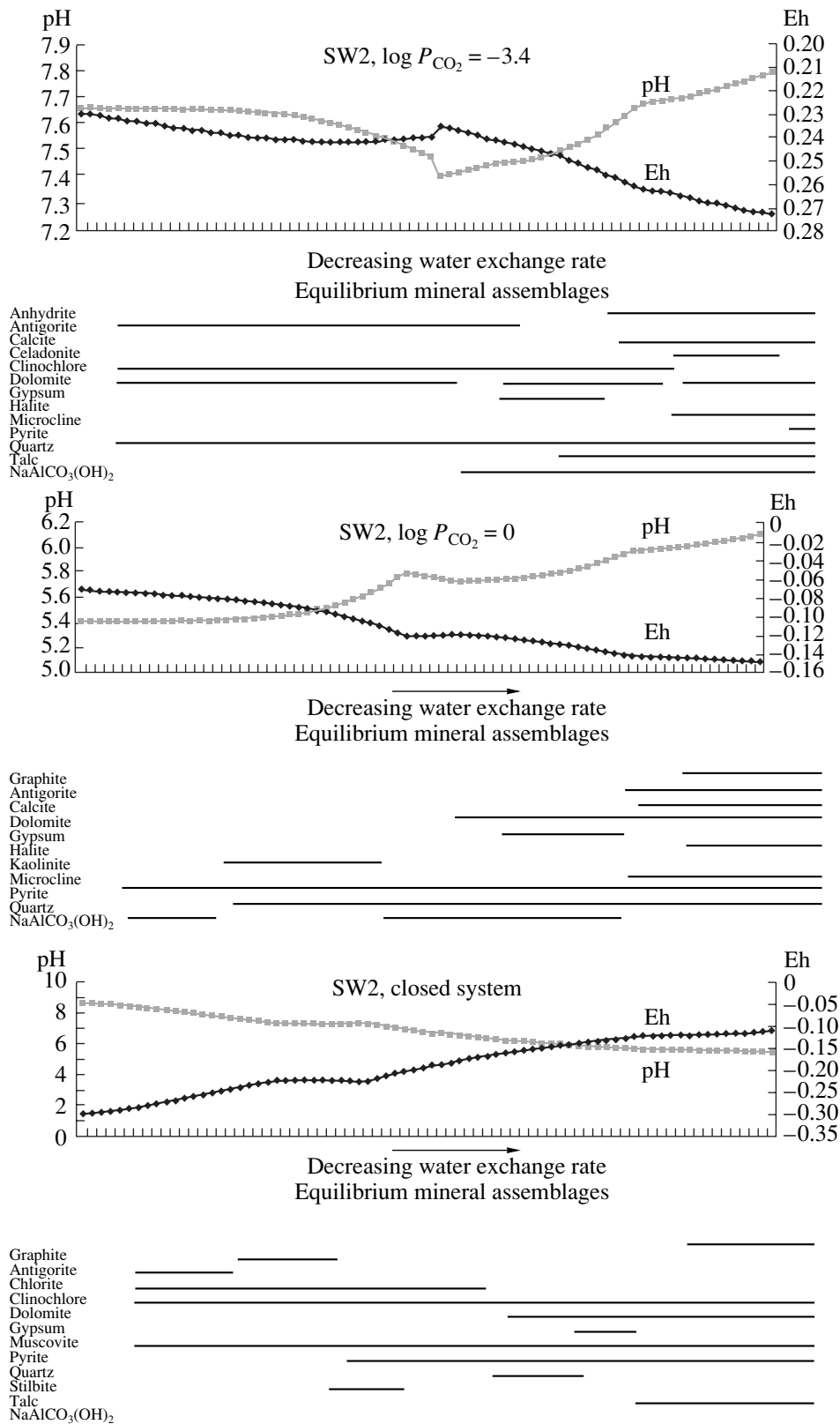


Fig. 7. System silty sand + seawater (halite precipitation stage) at 25°C.

Group [2]. I have no information on the oxygen and carbon isotopic composition of dawsonite from the Berezovoyarskoe occurrence. In principle, the coal accompanying dawsonite mineralization can be a source of carbon dioxide, because the equilibrium oxidation of carbon by oxygen dissolved in water is shifted toward CO_2 : $P_{\text{CO}_2} = 10^{71.98} \text{ m O}_2(\text{aq})$.

In order to test A.A. Makhnach's hypothesis, we simulated the interaction of aqueous solutions of seawater composition (of the stage of halite precipitation) with silty sandstone [6] and introduced dawsonite into the list of possible minerals. The simulation results indicate that dawsonite is formed when an aqueous solution of Cl–Na composition (seawater of the stage of halite precipitation) filters through a silty sandstone (Fig. 7) in a system either opened or closed with respect to CO_2 . Thereby neither the starting nor the equilibrium aqueous solutions are alkaline, which offers an alternative to Shvartsev's conclusion [2].

ACKNOWLEDGMENTS

The author thanks A.A. Makhnach and S.L. Shvartsev who initiated this research. This study was financially supported by the Russian Foundation for Basic

Research (project nos. 04-05-64673, 05-05-65098, and NSh-9542.2006.5).

REFERENCES

1. A. V. Kudel'skii, V. M. Shimanovich, and A. A. Makhnach, *Hydrogeology and Brines of the Pripjat Oil-and-Gas Basin* (Nauka Tekhnika, Minsk, 1985) [in Russian].
2. S. L. Shvartsev, "Hydrogeochemical Conditions of Formation of Dawsonite Mineralization in the Berezovoyarka Area, Kuznetsk Basin," *Geokhimiya*, No. 10, 1068–1080 (2004) [*Geochem. Int.* **42** (10), 938–949 (2004)].
3. T. Holland and R. Powell, "An Internally Consistent Thermodynamic Dataset for Phases of Petrological Interest," *J. Metamorph. Geol.* **16** (3), 309–343 (1998).
4. E. L. Shock, D. C. Sassani, M. Willis, and D. A. Sverjensky, "Inorganic Species in Geological Fluids," *Geochim. Cosmochim. Acta* **61** (5), 907–950 (1997).
5. M. V. Borisov and Yu. V. Shvarov, *Thermodynamics of Geochemical Processes* (Mosk. Gos. Univ., Moscow, 1992) [in Russian].
6. B. N. Ryzhenko and S. R. Krainov, "Rock–Water Model as a Base for Predicting the Chemical Composition of Natural Crustal Waters," *Geokhimiya*, No. 9, 1002–1024 (2003) [*Geochem. Int.* **41** (9), 915 (2003)].