

Modeling results of calcium-containing minerals precipitation in the alkaline hydrotherms of Baikal Rift Zone: calcite and dolomite

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Abstract. The calculation modeling results of the nitric hydrotherms saturation in Baikal Rift Zone with calcite and dolomite are presented. The calcite and dolomite make the carbonate barrier to thermal waters equilibrium with primary minerals of igneous rocks. In the research territory, there are three main types of geochemical thermal waters which are characterized by the saturation degree with the calcite and dolomite and the proportion of precipitating minerals phases. It has been established that nitric thermal waters-rock system has equilibrium with these minerals, which leads to bonding migrated from the rocks calcium and magnesium by the secondary formed minerals – calcite and dolomite.

1. Introduction

Previously, the assessment of preliminary results of thermal waters equilibrium with a variety of carbonate minerals was considered [1]. The assessment of water equilibrium degree with the water-bearing rocks is currently widely used by the hydrogeochemists [2]. The equilibrium degree assessment of water with water-bearing rock helps to determine the conditions of chemical composition formation [3, 4]. It is shown in the research [5] that the thermal water of Baikal Rift Zone (BRZ) is the product of long-term interaction of ancient and modern infiltration waters with the host rocks followed by large-scale redistribution of chemical elements between the water and secondary formed minerals. In the solution, the equilibrium with a variety of minerals is achieved (carbonate and aluminosilicate) which results in formation of various secondary formed minerals.

The work purpose is to determine quantitative proportion of new secondary formed mineral in order to prove the hypothesis characterized peculiar of BRZ hydrotherms chemical composition. More preciously, the study considers formation of calcite and dolomite, which formation of them is the main part in the evolution of water-rock system.

2. The geologic and thermal condition of hydrothermal systems formation

The temperature of aqueous solutions also exerts a significant effect on the chemical composition of thermal waters: when heated, the water-rocks interaction accelerates and the products of aluminosilicate hydrolysis intensely pass into the solution. At the same time, carbonate precipitation accelerates. It is supposed that the character of water composition transformation is much influenced by the temperature gradient. When temperature drastically changes, the chemical transformation is



mainly determined by the reactions in the solution. At a slow temperature change, the water–rock interaction is a determining factor.

The geochemical composition of rocks in the area where hydrotherms originate definitely influences the chemical composition of the waters. The BRZ is mainly composed of similar intrusive and metamorphic types. However, there are also geochemical traces of the existed Barguzin–Vitim ocean basin and conjugate Kelyana and Meteshikha island-arc systems. The deep fault rocks that occurred during the formation of the Sayan–Baikal Fold Belt [6] show a great geochemical diversity. These ancient geologic objects and associated geochemical redistribution of substance influence the chemical composition of modern surface and underground waters.

2. Materials and Methods

2.1. The nitric thermal waters concise description

The detailed analysis of the hydrotherms chemical composition peculiarities is presented [7]. It should be taken into account that low mineralization is of the main peculiarities of thermal water. The TDS exceeds 1 g/L, but it is usually below 0.5 g/L. Besides the TDS, the thermal waters have the same differential peculiarity as the high alkalinity (pH from 8.2 to 10), with high concentration of silicon (sometimes 120 mg/L) and fluorine (to 47 mg/L) being identified. As it has been defined, the content of fluorine perfectly correlates with carbonate ions but poorly – with sulfates. In general, five chemical types of thermal waters have been formed within BRZ – $\text{HCO}_3\text{--Na}$, $\text{HCO}_3\text{--F--Na}$, $\text{HCO}_3\text{--SO}_4\text{--Na}$, $\text{SO}_4\text{--HCO}_3\text{--Na}$ и $\text{SO}_4\text{--Na}$, which differ in chemical composition transportation, correlation with total mineralization, temperature, pH, contents of fluoride and sulfate ions. Therefore, the alkaline thermal waters of sodic type are fresh ($M < 0.5$ g/L). This fact has not been scientifically explained yet.

2.2. Investigation methods

The chemical composition data of 47 springs were used in the modeling process. The saturation index was used to define thermal waters saturation degree to individual minerals. The index of saturation is

$$L = \lg Q/K$$

where Q – ion activity product; K – solubility product. As solution is saturating in relation to any mineral, the saturation index increases to zero (equilibrium state). In case of oversaturation, its values become positive. The parameter calculation and modeling of mineral phases solution/precipitation processes were made according to methods which were developed on the basis of thermodynamics hydrogeochemical processes [8] using computer program [9]. The modeling process of minerals formation is based on the free energy minimization within the program. The method principle is the calculation of studied geochemical system equilibrium composition based on the data of its initial elemental composition according to the fundamentally principles of the equilibration chemical thermodynamics. Thus, the most probable of development system is its transition to state that corresponds to the minimum of total Gibbs thermodynamic system potential (Gibbs free energy) under given thermodynamic conditions. In this particular case, the real temperature of water and ranging from 40 to 80°C was taken into account in the calculations. When setting a model, 14 minerals which contain calcium were included in the system: CaCO_3 (κ) – calcite, $\text{CaMg}(\text{CO}_3)_2$ – dolomite, CaCO_3 (a) – aragonite, CaF_2 – fluorite, $\text{Ca}_{0.15}\text{Al}_{1.9}\text{Si}_4\text{O}_{10}(\text{OH})_2$ – montmorillonite, $\text{Ca}_{0.187}\text{Na}_{0.0205}\text{K}_{0.0205}\text{Fe}^{3+}_{0.141}\text{Mg}_{0.336}\text{Al}_{1.59}\text{Si}_{3.93}\text{O}_{10}(\text{OH})_2$ – montmorillonite, $\text{CaAl}_2\text{Si}_2\text{O}_6(\text{OH})_4$ – lawsonite, $\text{CaAl}_2\text{Si}_4\text{O}_8(\text{OH})_8$ – laumontite (zeolite), $\text{CaAl}_4\text{Si}_2\text{O}_{10}(\text{OH})_2$ – margarite, $\text{CaMg}_3(\text{CO}_3)_4$ – guntit, CaSO_4 – anhydride, $\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$ – bassanite, $\text{CaSO}_4(\text{H}_2\text{O})_2$ – gypsum, $\text{CaAl}_2\text{Si}_4\text{O}_{12}(\text{H}_2\text{O})_2$ – wairakite (zeolite).

3. Results and Discussion

3.1 The index of saturation for calcite and dolomite

In spite of nitric thermal waters low salinity (1–7 mg/L) and low calcium concentrations in the thermal waters, the equilibrium with calcite has been established. It was found that most springs are saturated to calcite and dolomite (figure 1, figure 2).

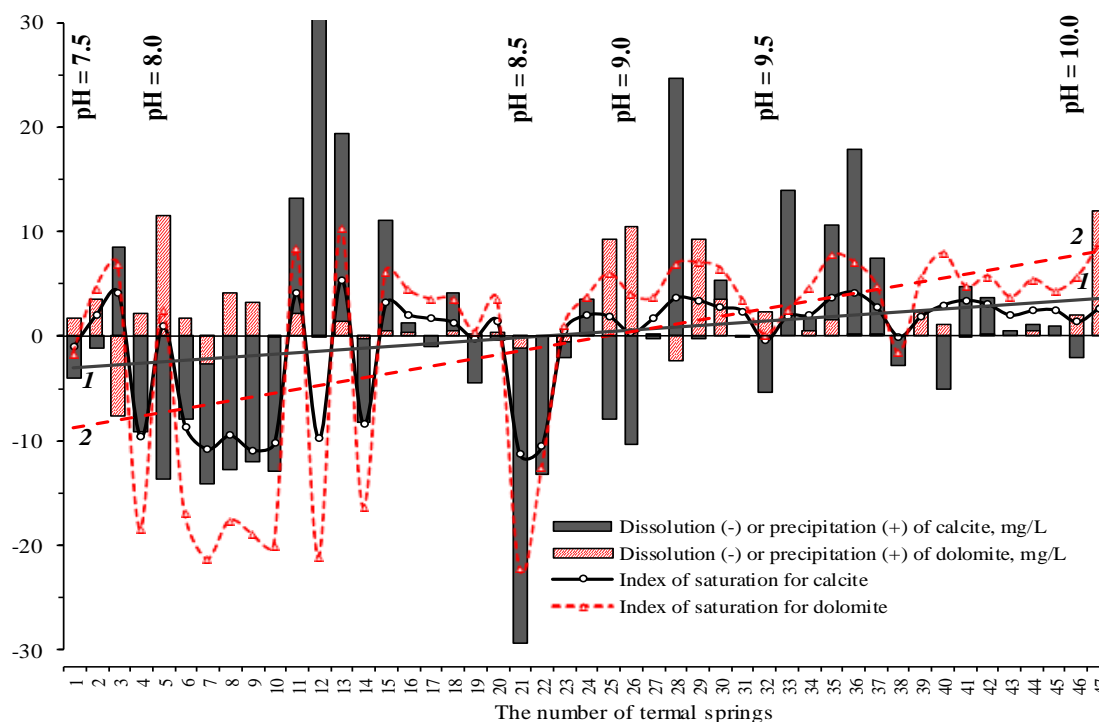


Figure 1. Dependence of saturation index values and quantity of mineral dissolution/precipitation on pH of springs.

Trend lines: 1 – for precipitate calcite quantity; 2 – for saturation index to dolomite. The number of thermal springs: 1 – Engorboyskii; 2 – Garginskii; 3 – Zmeinyi; 4 – Teplyi Klyuch; 5 – Nilova Pustyn'; 6 – Irkaninskii-2; 7 – Alginskii; 8 – Korikeiskii; 9 – Sartinskii; 10 – Busanskii-2; 11 – Irkaninskii-1; 12 – Gusikhinskii; 13 – Tochinskii-2; 14 – Busanskii-1; 15 – Tochinskii-1; 16 – Bauntovskii-1; 17 – Bauntovskii-2; 18 – Mogoiskii-1; 19 – Mogoiskii-2; 20 – Mogoiskii-3; 21 – Mogoiskii-4; 22 – Mogoiskii-5; 23 – Shurindinskii-1; 24 – Shurindinskii-2; 25 – Verkhneangarskii; 26 – Kotel'nikovskii; 27 – Bylyrinskii; 28 – Pitatelevskii; 29 – Pitatelevskii (well); 30 – Dzelindinskii; 31 – Kyrinskii-1; 32 – Dzelinda well; 33 – Kyrinskii-2; 34 – Kulinye Bolota; 35 – Tolstikhinskii; 36 – Allinskii-2; 37 – Allinskii-1; 38 – Goryachinskii; 39 – Angarkan-Sartinskii; 40 – Uluriiskii-1; 41 – Uluriiskii-2; 42 – Kuchigerskii-1; 43 – Umkheiskii-1; 44 – Umkheiskii-2; 45 – Kuchigerskii-2; 46 – Solnechnyi; 47 – Bol'sherechenskii.

The similar results were previously obtained by using calculation methods based on the stability fields of carbonate minerals. However, the data of quantitative minerals formation were obtained for the first time.

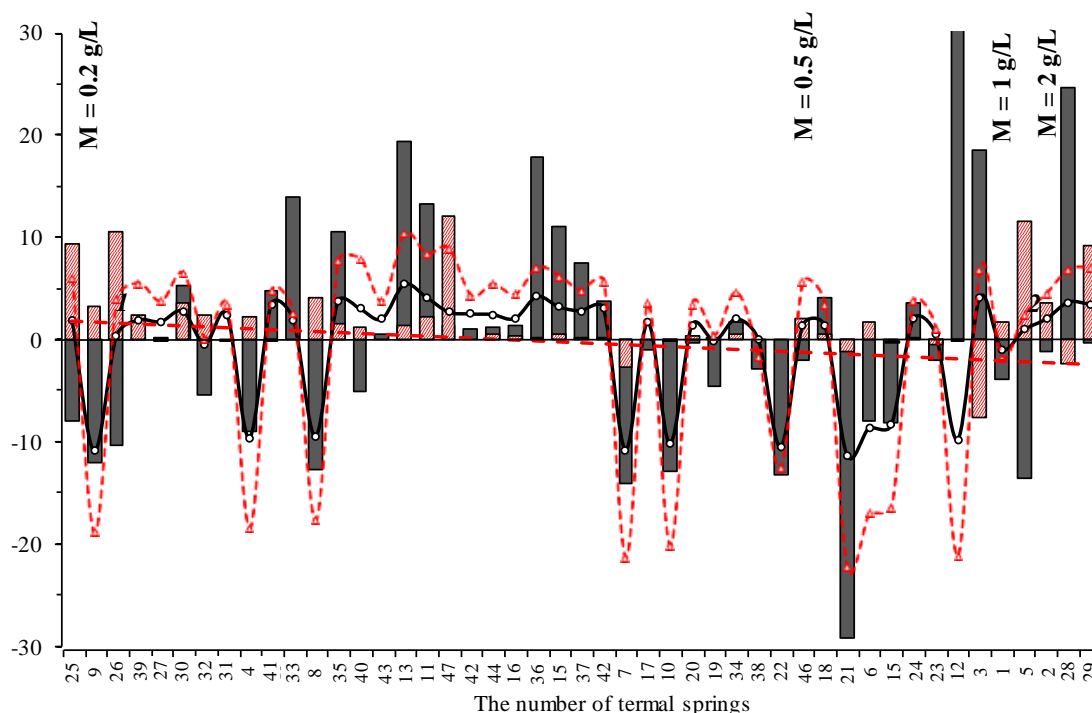


Figure 2. Dependence of saturation index values and quantity of mineral dissolution/precipitation on TDS of springs (the legend is in the figure 1).

Three types of hydrochemical springs are distinguished: 1 type – the springs with high degree of undersaturation to calcite and dolomite which are consequently dissolved due to chemical reaction; 2 type – springs that have reached the equilibrium state or oversaturation to calcite and dolomite, where both or one of the minerals are dissolved due to chemical reaction; 3 type – springs that are oversaturated to calcite and dolomite which precipitate as solid secondary formed minerals. Alongside, there are springs where one more geochemical combination can be observed: the springs are nonsaturated to calcite or dolomite but dolomite precipitates as a solid. This fact has no clear explanation and has to be more explored.

With springs pH growth calcite precipitation is likely to occur. With $\text{pH} < 8.5$, calcite dissolves while precipitating, with the amount ranging from 2 to 18 mg per liter of water solution with $\text{pH} > 8.5$. The maximum quantity of calcite is formed in the Pitalevskii spring (25 mg/L), with the TDS values being more than 2 g/L.

It should be noted that thermal water-mineral equilibrium can be achieved only under particular geochemical conditions, for example, right temperature which is necessary for calcite concentration, definite pH, etc. (figure 3). The saturation degree to calcite increases with the growth of mineralization (TDS) (figure 3a). It is related to accumulation of calcium (figure 3c) and carbonates in the solution. However, the saturation growth occurs till the particular values. Thus, the thermal waters with TDS 0.2 g/L reach equilibrium and oversaturate by calcite in the high temperature conditions. Then it is formed as a solid phase. Under standard conditions, the equilibrium with calcite is reached under slightly higher thermal water mineralization – from 0.32 g/L (figure 3d).

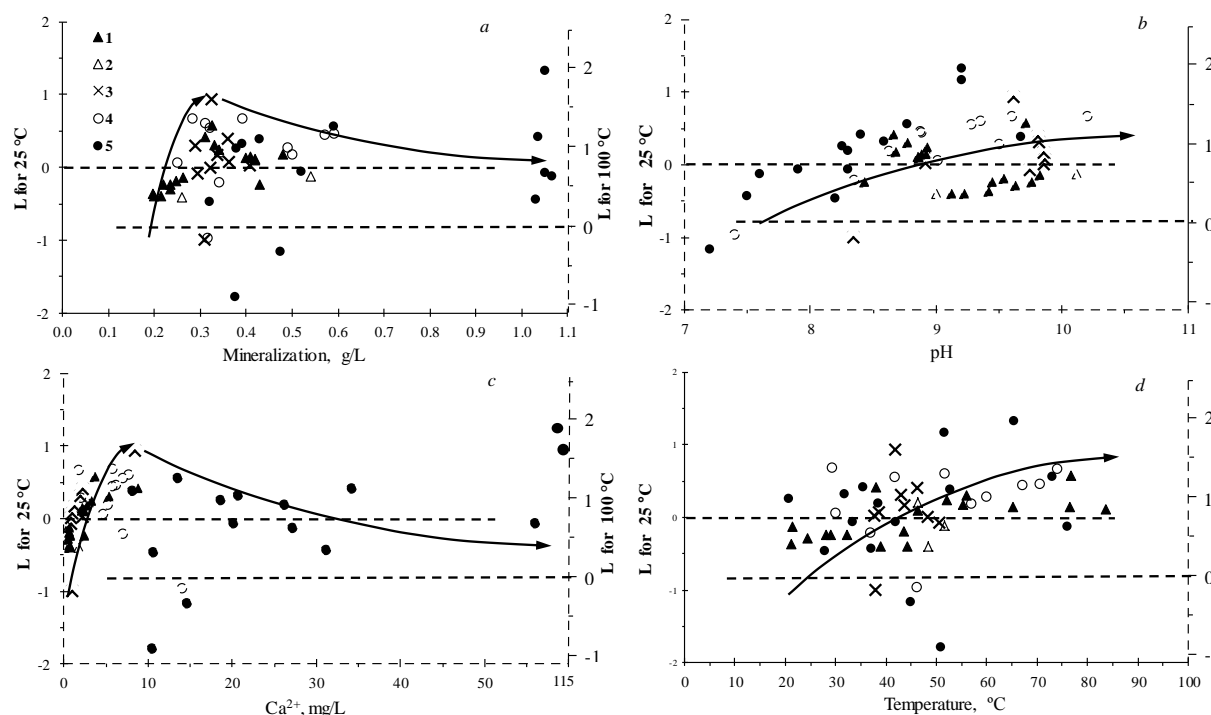


Figure 3. Dependence of thermal water saturation index (L) to calcite on general check parameters of thermal waters composition.

The chemical type of thermal waters: 1 – $\text{HCO}_3\text{-Na}$; 2 – $\text{HCO}_3\text{-F-Na}$; 3 – $\text{HCO}_3\text{-SO}_4\text{-Na}$; 4 – $\text{SO}_4\text{-HCO}_3\text{-Na}$; 5 – $\text{SO}_4\text{-Na}$.

This group includes the thermal waters with high concentration of sulfate-ion, i.e. $\text{SO}_4\text{-HCO}_3\text{-Na}$ and $\text{SO}_4\text{-Na}$ types of thermal waters. The index saturation value is lower in these thermal waters types due to less importance of carbonate component.

As carbonate dissolubility decreases due to the temperature increase, the saturation degree of nitric thermal waters to calcite and dolomite grows with depth increase. According to this, we believe that all nitric thermal waters have equilibrium with carbonate mineral at the shallow depth. Disturbance of equilibrium occurs only when they rise to the surface, cool and are diluted by fresh groundwater.

The sulfate type of thermal waters can reach the equilibrium with calcite when pH 7.5, under deep conditions when pH 8.4 – for standard conditions (figure 3b). For $\text{HCO}_3\text{-Na}$ и $\text{HCO}_3\text{-SO}_4\text{-Na}$ types of thermal waters the pH values are significantly higher (9.9) to reach equilibrium to calcite.

The equilibrium with calcite is established even at the low spring temperature. Most of $\text{HCO}_3\text{-SO}_4\text{-Na}$ thermal waters types in the field of the mineral saturation. As for $\text{SO}_4\text{-HCO}_3\text{-Na}$, it is represented by all types. The gradual decrease in saturation to calcite occurs with higher concentrations of Ca^{2+} (from 10 to 115 mg/L) and with lower values of pH. This can be observed in the $\text{SO}_4\text{-Na}$ thermal waters. It can be explained by balancing calcium with sulfate-ion in the thermal waters and insufficient amount of carbonate ion under these pH conditions.

Thus, the equilibrium and oversaturation of nitric thermal waters by calcite and dolomite lead to its formation as secondary forms minerals (authigenous). In this case, definite set of secondary formed minerals corresponds to each stage of water-rock interaction. The composition of authigenous minerals can change over time. Where being formed, the secondary formed minerals, in its formation process, bind the particular chemical elements of the solution, therefore, the content of these chemical elements is not grow. As a result, a variety of geochemical barriers appear. The geochemical barriers prevent the equilibration with primary (endogenous) minerals. First of all, it concerns Ca-, Mg-aluminosilicates of anorthite, forsterite, fayalite types, and etc., as moving elements of these minerals

form the carbonates (calcite, dolomite and others) which completely prevent the equilibrium of solutions with igneous minerals.

4. Conclusion

To sum up, the water equilibrium with the majority of host rock minerals occurs at a certain stage of water-rock system evolution. Instead of being dissolute, minerals of host rocks begin to form. Thus, not only chemical equilibrium but also dynamic balance is reached in the system. The latter ensure the equality of entering elements to solution and precipitating elements. The consequence of this equilibrium is low mineralization in the thermal water which can slightly increase over time or does not increase.

One of the main peculiarities of water-rock system is due to the fact that in the course of evolution the ratio between chemical elements is constantly changing, which, in its turn, leads to constant change of groundwater chemical composition and increases the difference between groundwater and host rock composition[10]. This is explained by the fact that one part of elements is bond by precipitated secondary minerals and the second one which remains in solution, can concentrate redundant. The water is the medium where the chemical bond between ionic pairs breaks down, redistribution of chemical bonds between the ions occurs and new ion pairs form. According to hydrodynamics laws, the new ionic pairs form other solids that are different from primary one.

Due to above, there is another peculiarity of secondary minerals formation. A mineral forms under the conditions of equilibrium with solution. Therefore, the sudden change (increase or decrease) in concentration of elements that form the mineral, is not possible in the solution. Only elements which enter the solution from nonequilibrium with water minerals are precipitate. But the solution does not change, of course, if the system keeps equilibrium-nonequilibrium state.

Acknowledgements

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