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Content Variations of Rubidium and Bromide in Sylvite Derived from Carnallite by Leaching of Magnesium Chloride

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The relationship between sylvinite and carnallite is important in the potash mine body contained carnallite, especially sylvinite overlies carnallite, the reverse of a normal depositional sequence. Trace elements are more sensitive to changes in the salt-forming environment than major elements forming mineral assemblages and bear, and are often used as genetic and metamorphism indicator in salt deposits (Herrmann, 1980; Valyashko, 1956; Cheng, 2008). The following four types of relationship between sylvite and carnallite are considered: (1) the rocks are facies equivalents deposited in different areas from essentially contemporaneous brines, (2) carnallite formed by reaction of sylvite with magnesium chloride brines, (3) sylvite derived from carnallite by leaching of magnesium chloride, (4) sylvite, as presently found, not directly related to carnallite, but formed through solution of pre-existing sylvite with subsequent crystallization. In our work, we investigated content variations of bromide and rubidium in sylvite derived from carnallite simulating dissolution processes in aqueous solution at 25℃.

In Fig. 1, OA shows the ratio of magnesium chloride to potassium chloride during the stage of halite crystallization from $MgSO_4$-deficient sea water. At 25℃, at point A, sylvite crystallization begins and, with continued evaporation, the composition of brine changes along line A-B as sylvite crystallizes. Point B lies on the boundary between the sylvite and carnallite fields. This is a reaction boundary, and sylvite is unstable in the presence of brines in the carnallite and bischofite fields. Thus, with further evaporation, unless the sylvite is removed from contact with the brine, it will be altered to carnallite. Carnallite crystallizes during evaporation to point C, where bischofite crystallization commences. Profiles 1 and 2 in Fig.1 show, respectively, the sequence of salts obtained from $MgSO_4$-deficient sea water without and with reaction of sylvite at the reaction boundary. If carnallite is dissolved in water, magnesium chloride and potassium chloride enter the solution in equimolecular proportions, as illustrated by OX, Fig.1. At 25℃, X represents a saturation point for sylvite. If the solution is evaporated, sylvite will crystallize and the solution will change in composition along XB, to carnallite saturation at B. If solution X is not evaporated, but exposed to more carnallite, magnesium chloride will continue to enter the solution, suppressing potassium chloride solubility and

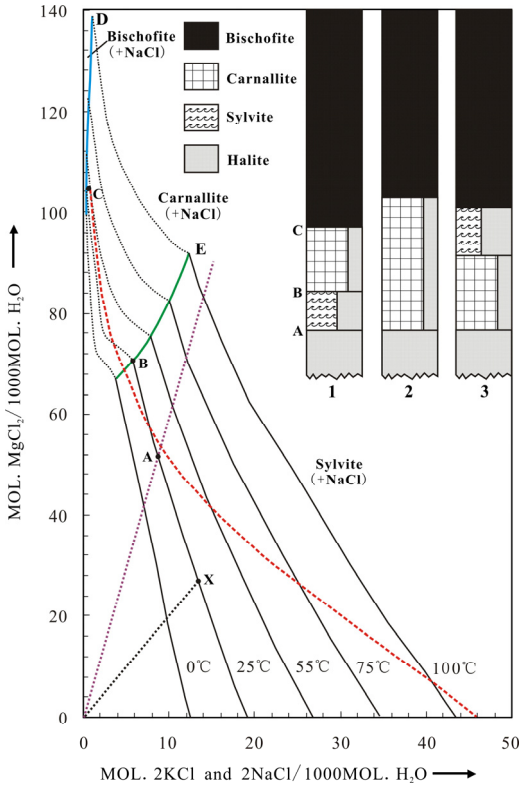

Fig. 1. The system NaCl-KCl-$MgCl_2$-H_2O at different temperatures.

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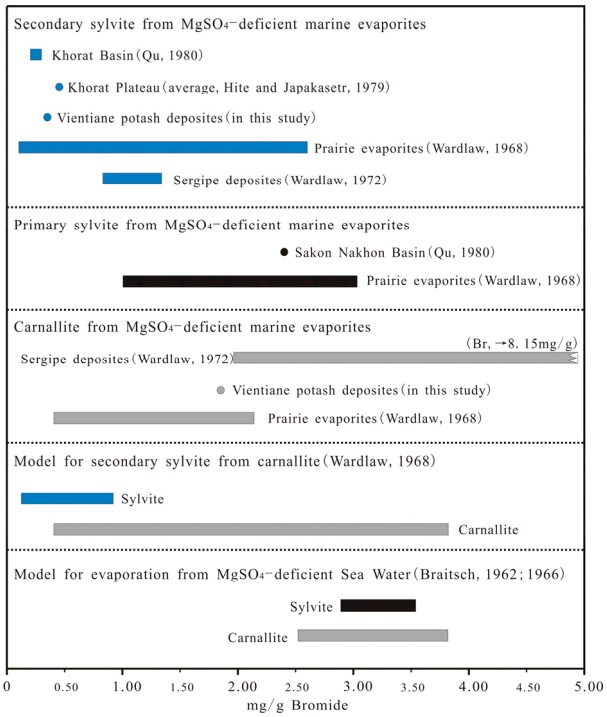

Fig. 2. Bromide values of primary sylvite and secondary sylvite from $MgSO_4$-deficient evaporates.

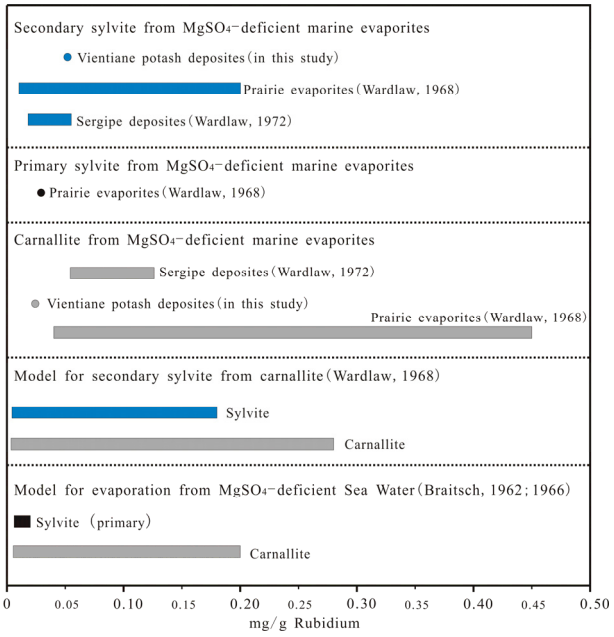

Fig. 3. Rubdium values of primary sylvite and secondary sylvite from $MgSO_4$-deficient evaporates.

causing the precipitation of sylvite. With or without evaporation, then, carnallite will react with water to form sylvite. Profiles 3 in Fig.1 show that sylvite may alter to carnallite if treated with water in which there is no evaporation at saturation with potassium chloride, but further leaching of magnesium chloride from carnallite.

To obtain sylvite derived from carnallite ore by leaching magnesium chloride, the dissolution processes of carnallite ore is simulated in aqueous solution at 25℃ in this paper. Sylvite is separated from sylvinite after the end of dissolution of carnallite ore through flotation method. In order to estimate the values of bromide and rubidium in pure solid phases in which mother liquor inclusion were removed, the amount of mother liquor solution adsorbed to the crystals/minerals surface was calculated based on Mg^{2+} concentration measurements of the crystals/minerals.

The results shows that: (1) contents of bromide and rubidium in carnallite ore, more than two third of them enter into mother liquor phases after the end of dissolution; (2) lower bromide and higher rubidium contents in the secondary sylvite from carnallite, provide a good signal for identifying secondary sylvite derived from carnallite by leaching magnesium chloride from therein, while higher bromide and lower rubidium in primary sylvite from $MgSO_4$-deficient evaporates; (3) in Fig.2, carnallite ore, from the drilling core of Vientiane potash deposits in Laos in our work, with 1850ppm bromide dissolved in fresh water, will result in sylvite with 350ppm bromide, which is close to the average value of bromide in secondary sylvite from Khorat Plateau (450ppm), which is close to the value of bromide in secondary sylvite from Sergipe deposits (830-1340ppm) and Prairie evaporites (100-2600ppm), and which is obviously lower than the value of bromide in primary sylvite from Sakon Nakon Basin (2400ppm) and Prairie evaporates (1000-3000ppm). (4) in Fig.3, carnallite ore, from the drilling core of Vientiane potash deposits in Laos in our work, with 24.3ppm rubidium dissolved in fresh water, will result in sylvite with 51.5ppm rubidium, which is close to the range of rubidium values in secondary sylvite from Sergipe deposits (18-55ppm) and Khorat Plateau (20-50ppm), and which is obviously higher than the value of rubidium in primary sylvite from normal evaporation deposits from $MgSO_4$-defficient sea water (17-20ppm).

Content variations of bromide and rubidium in sylvite derived from carnallite by leaching magnesium chloride are obviously as a good indicator to distinguish primary and secondary sylvite, the characteristics of lower Br contents and higher Rb contents in the sylvite were used to indicate secondary sylvite-forming from carnallite by leaching magnesium chloride. This research provides a good signal for indentifying secondary sylvite from unusual marine evaporates of Khorat Basin, Sergipe Basin and Congo Basin.

Key words: carnallite, primary sylvite, secondary sylvite, bromide, rubidium.

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