

## HYDROTHERMAL HALITE IN THE Pb-Zn MINERAL ASSOCIATION OF THE SASA DEPOSIT (NORTH MACEDONIA)

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**Abstract:** The present study was performed to describe an occurrence of hydrothermal halite in the Sasa ore field. The occurrence of halite in hydrothermal systems is not a rare occurrence, considering the different types of hydrothermal processes. The occurrence of hydrothermal halite embedded in calcite crystals has not been established so far. In the Sasa ore field calcite is the most important of all non-ore minerals. It occurs together with dolomite, rhodochrosite, siderite, barite, quartz, calcedony, opal, and so on. Halite crystals are in form of dendrites. The morphology of natural halite is largely dominated by the cube {100}; the {110} and {111} forms are rarely present. When crystals grow by evaporation from aqueous solution the perfection of the cube faces is usually lost. Owing to the high values of the supersaturation appear dendritic branches developing in the <111> directions. Dendrite forms when water rich in NaCl flows between microscopic layers of calcite. Halite crystals are long from 4.08 to 22.35 and wide from 1.24 to 2.42  $\mu\text{m}$ .

**Key words:** halite; calcite; hydrothermal; Sasa

### INTRODUCTION

In the Sasa ore field calcite is the most important of all non-ore minerals. It occurs together with dolomite, rhodochrosite, siderite, barite, quartz, calcedony, opal, and so on. (Šijakova et al., 2006). The occurrence of hydrothermal halite embedded in calcite crystals has not been established so far.

The occurrence of halite in hydrothermal systems is not a rare occurrence, considering the different types of hydrothermal processes. Subsurface brines at supercritical temperatures, especially in the deeper parts of thermally active mid-ocean ridges, are extremely common. In two publications (Hovland et al., 2018a,b) a large part of the investigations are summarized so far on serpentinization processes in which chlorides are formed and later in sedimentary basins halite crystallizes from the chlorites. Opposing arguments for the idea that halite is formed in other environments are given in the

papers of Aftabi and Atapour (2018). The importance of the Wilson cycle in the context of halite formation in sedimentary basins, rather than magmatic and metamorphic processes, is summarized in the papers of Hovland et al. (2006a). Hovland's model relies on the idea of the existence of subsurface saline solutions that are superheated (supercritical temperatures) transforming into saline fluids from which halite precipitates at lower temperatures and pressures.

A supercritical fluid is defined as any substance at a temperature and pressure above its critical point. In such a state, it can be transported through solid rock as a gas and dissolve the materials to form a liquid. Moreover, near the critical point, small changes in pressure or

temperature result in significant changes in density. The critical point (CP), also called the critical state, specifies the conditions (temperature, pressure, and sometimes composition) at which a phase boundary ceases to exist. Under certain pressure/temperature conditions, supercritical water cannot dissolve/keep common sea salts in solution (Simoneit et al., 1994; Hovland et al., 2006a). When brines with seawater are heated in pressure cells in the laboratory, they pass into the supercritical region at a temperature of 405°C and a pressure of 300 bar (Seawater CP). Then a particle "cloud" is formed through the beginning of the "shock crystallization" of NaCl and Na<sub>2</sub>SO<sub>4</sub>. An abrupt phase transition occurs when the solubility of previously dissolved salts drops to near zero over a temperature range of only a few degrees and is associated with a significant decrease in density. The resulting solids in the "cloud" consist of amorphous microscopic NaCl and Na<sub>2</sub>SO<sub>4</sub> particles with sizes between 10 and 100 nm. During these processes, larger amounts of underground salts can be formed in fractures and cracks, and perhaps even in the deeper parts of salt structures (Al-Zoubi et al. 2001, 2002).

In supercritical conditions, the ability of saline solutions to carry larger amounts of hy-

drothermal hydrocarbons before the onset of supercritical conditions also improves (Bellissent-Funel, 2001). Supercritical water has an increased capacity to dissolve organic compounds and reduced properties for building ionic solutions due to its loss of water-hydrogen bonding (Simoneit et al., 1994). The large amounts of deep underground salt found in the Red Sea, in the Mediterranean Sea and the Danakil Depression, formed through the influence of magmatic processes during the formation of a hydrothermal phase in seawater at depths where it became supercritical (Hovland et al., 2006). This salt, they claim, was precipitated deep underground via "shock crystallization" from a supercritical effusive phase and thus formed massive accumulations (mostly halite) typically in crystal fractures that facilitated deep circulation.

More recently (Hovland et al, 2018, a, b) theorized that serpentinization is the dominant source of halite in the Mediterranean. To this day (Holness et al., 1997; Driesner et al., 2007; Gruen et al., 2014) the hydrothermal source model for widespread halite from a supercritical brine source (in active magmatic regions) has not been widely accepted by the geological community (Aftabi and Atapour, 2018).

## ANALYTICAL METHODS

Several samples of calcite were taken from the Sasa deposit. Four of them were selected for our investigation.

For reliable characterization of the mineral species in our research following analytical methods were used: ICP-MS, SEM-EDS and XPRD.

Chemical composition is determined with ICP-MS. This method provides a rapid and precise means of monitoring up to 50 elements simultaneously for minor and trace-levels. The ICP-MS technique is widely regarded as the most versatile analytical technique in the chemistry laboratory. When the sample solution is introduced into the spectrometer, it becomes atomized into a mistlike cloud. This mist is carried into the argon plasma with a stream of argon gas. The plasma (ionized argon) produces temperatures close to 7.000 °C, which thermally excites the outershell electrons of the elements in the sample.

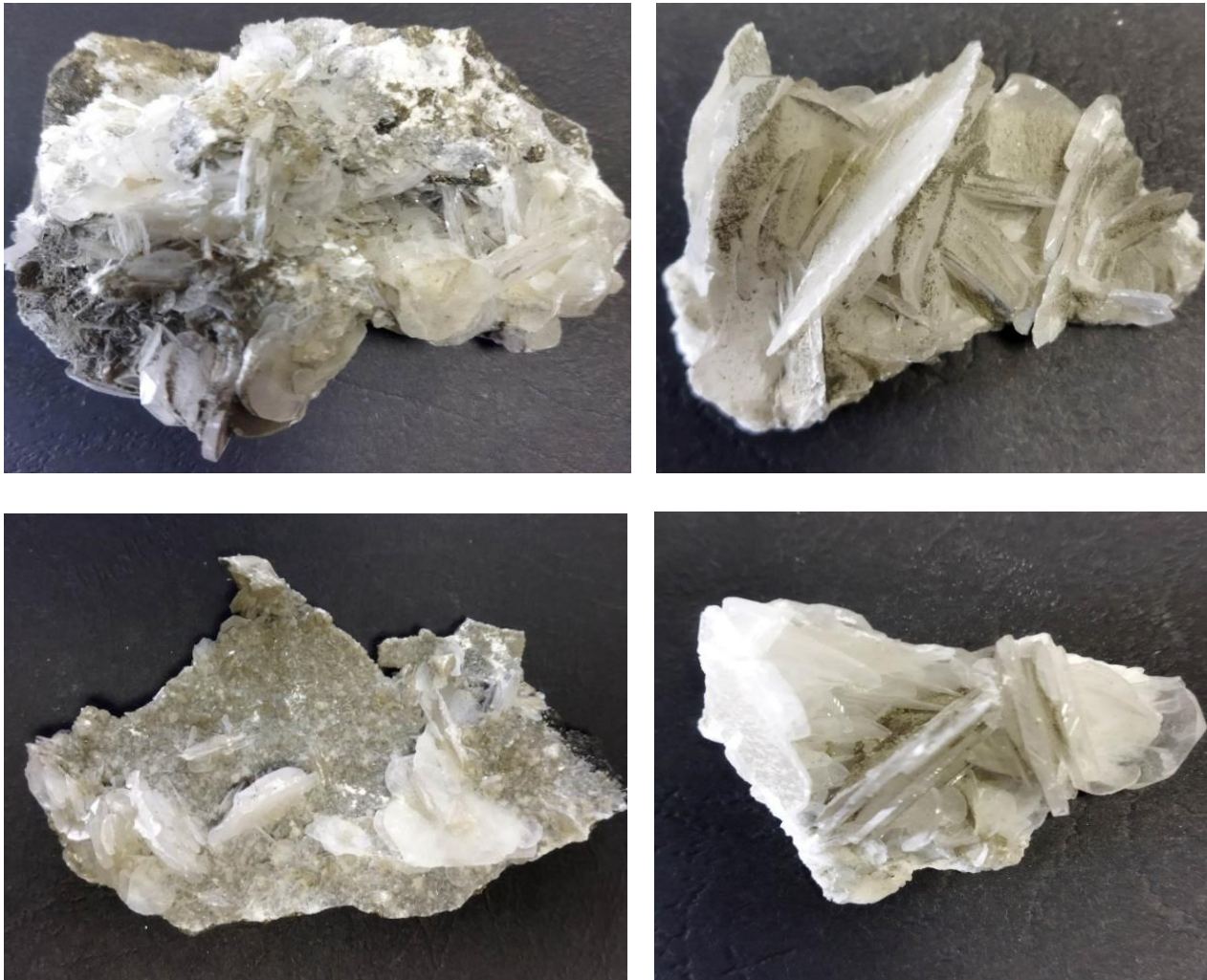
**SEM-EDS** analyses and electron micro-photographs were conducted using a VEGA3LMU scanning electron microscopy (SEM) increasing  $2 \times 1000\ 000$ . The study utilized semi-quantitative analysis using appropriate standards. The standards used are as follows: O : SiO<sub>2</sub>; Na : albite; Mg : MgO; Al : Al<sub>2</sub>O<sub>3</sub>; Si : SiO<sub>2</sub>; P : GaP; Ca : wollastonite; Ti : Ti; Fe : Fe; Br : KBr.

**XPRD** analyses were carried by conventional X-ray diffraction (XRD) techniques on samples used a Shimadzu XRD-6100 diffractometer with Cu (1.54060 Å) radiation operating at 40 kV and 30 mA. The powdered sample was scanned over the 10 – 70° range with step size of 0.02°/min and scanning speed of 2°/min. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

## RESULTS AND DISCUSSION

Macroscopic characteristics on the calcite are given in Figure 1. Calcite from the Sasa ore field occurs in good rhombohedral crystals of different size. The colour is white. Cleavage is perfect on {1011}. The occurrence of hydrothermal halite embedded in calcite crystals has not been established

so far. The presence of halite crystals is not visible macroscopically. The presence of halite dendritic crystals from Sasa was determined by SEM-EDS. In some places halite is isomorphically mixed with syl-vite.



**Fig. 1.** Macroscopic characteristics of calcite crystals

SEM image of calcite and halite crystals from Sasa are given in Figure 2. Halite appears in the dendrites form. Dendrites are long from 4.08 to 22.35 and wide from 1.24 to 2.42  $\mu\text{m}$ . Dendrite forms when water rich in NaCl flows between microscopic layers of calcite.

Investigations of the dendritic structure of halite are made by Nobuhiko J. Suematsu et al.,

2021; Dino Aquilano et al., 2016; P. N. Southgate, 2006).

Chemical composition of calcite by ICP-MS is presented in Table 1.

Our investigation shows proportional depends between elements in calcite samples (Figures 3 and 4). XRPD patterns of the examined calcite from Sasa are given in Figure 5.

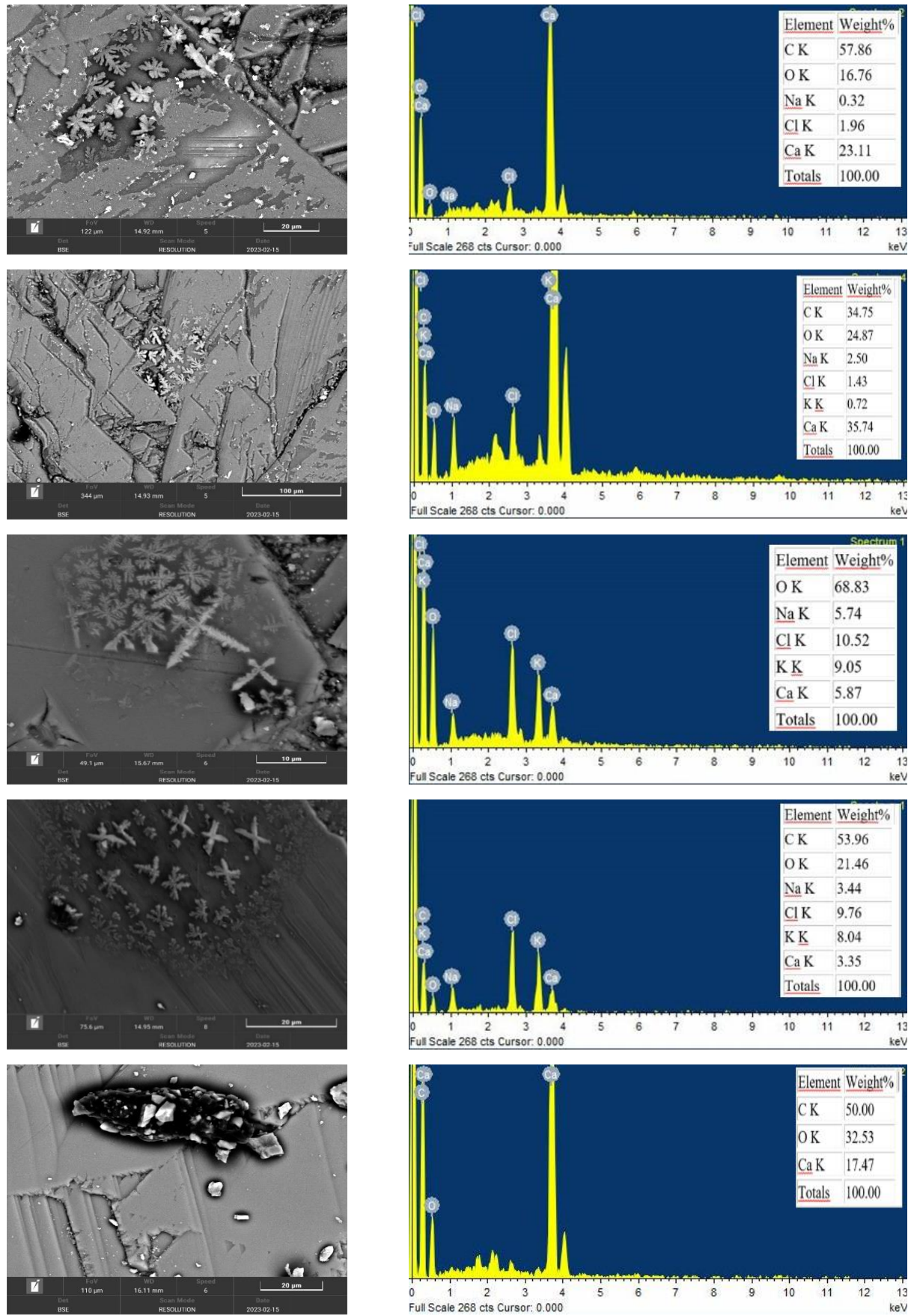


Fig. 2. SEM image and EDS spectrum of halite and calcite from Sasa

Table 1

*Chemical composition of calcite from Sasa by ICP-MS*

	Sample 1	Sample 2	Sample 3
<b>Oxides (%)</b>			
Al <sub>2</sub> O <sub>3</sub>	0.019	0.013	0.023
FeO	0.111	0.083	0.087
K <sub>2</sub> O	0.108	0.071	0.081
CaO	55.2	54.3	53.6
MgO	0.319	0.110	0.180
MnO	0.355	0.618	0.458
Na <sub>2</sub> O	0.531	0.499	0.565
TiO <sub>2</sub>	<0.0001	<0.0001	<0.0001
P <sub>2</sub> O <sub>5</sub>	<0.001	<0.001	<0.001
SO <sub>2</sub>	0.166	0.258	0.131
LOI	43.6	44.1	40.4
<b>Elements (ppm)</b>			
Sn	<1	<1	1.22
Cd	<1	<1	<1
Sb	<1	<1	<1
As	5.5	2.8	3.8
Cu	6.2	2.2	3.4
Ba	<1	<1	<1
Be	<1	<1	<1
Bi	<1	<1	<1
B	25	5.6	20.1
V	1.4	1.3	2.5
Co	0.94	0.61	0.67
Li	0.93	2.1	0.21
Mo	0.242	0.184	0.155
Ni	2.9	3.2	2.5
Pb	<1	<1	8.80
Pd	<1	<1	<1
Se	<1	<1	<1
Ag	2.1	2.3	3.3
Sr	21.1	29.4	16.9
Si	<1	<1	<1
Tl	<1	<1	<1
Cr	2.0	1.0	1.4
Zn	17.8	14.1	11.6
<b>Chlorides (%)</b>			
NaCl	1.00	0.94	1.06
KCl	0.2	0.13	0.15

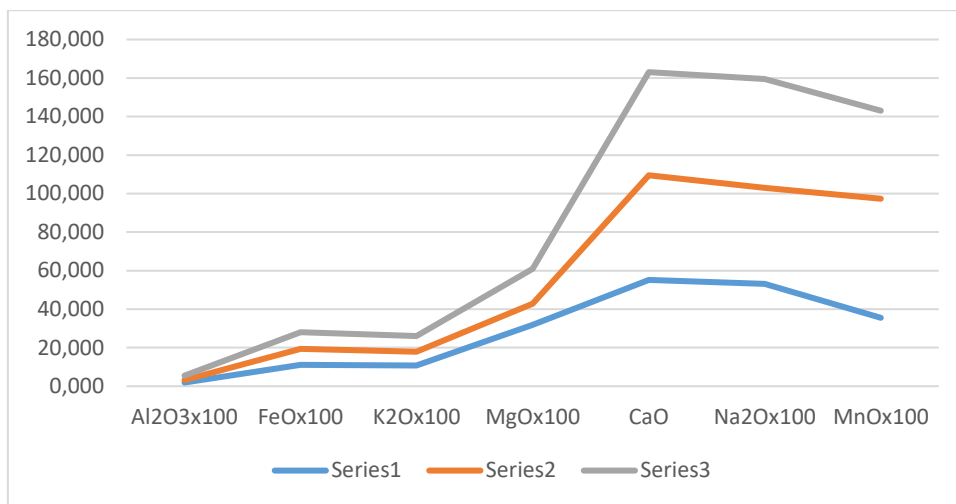


Fig. 3. Proportional dependences between Al<sub>2</sub>O<sub>3</sub>, CaO, K<sub>2</sub>O, MgO, FeO, Na<sub>2</sub>O and MnO

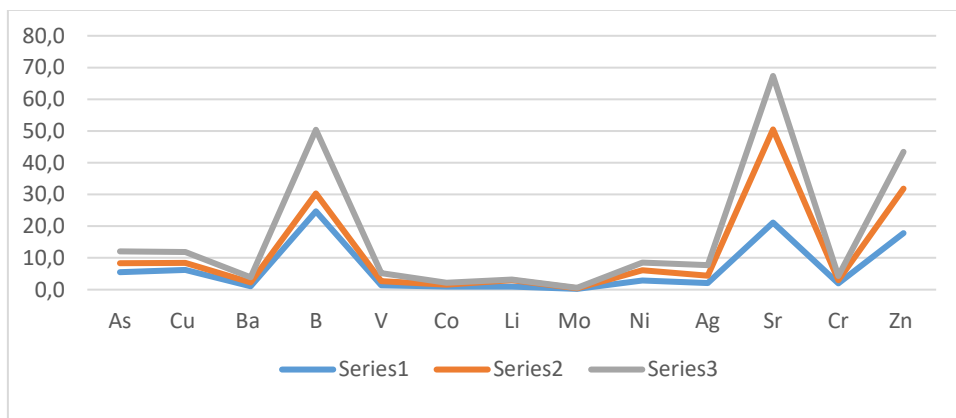


Fig. 4. Proportional dependences between As, Cu, Ba, B, V, Co, Li, Mo, Ni, Ag, Sr, Cr and Zn

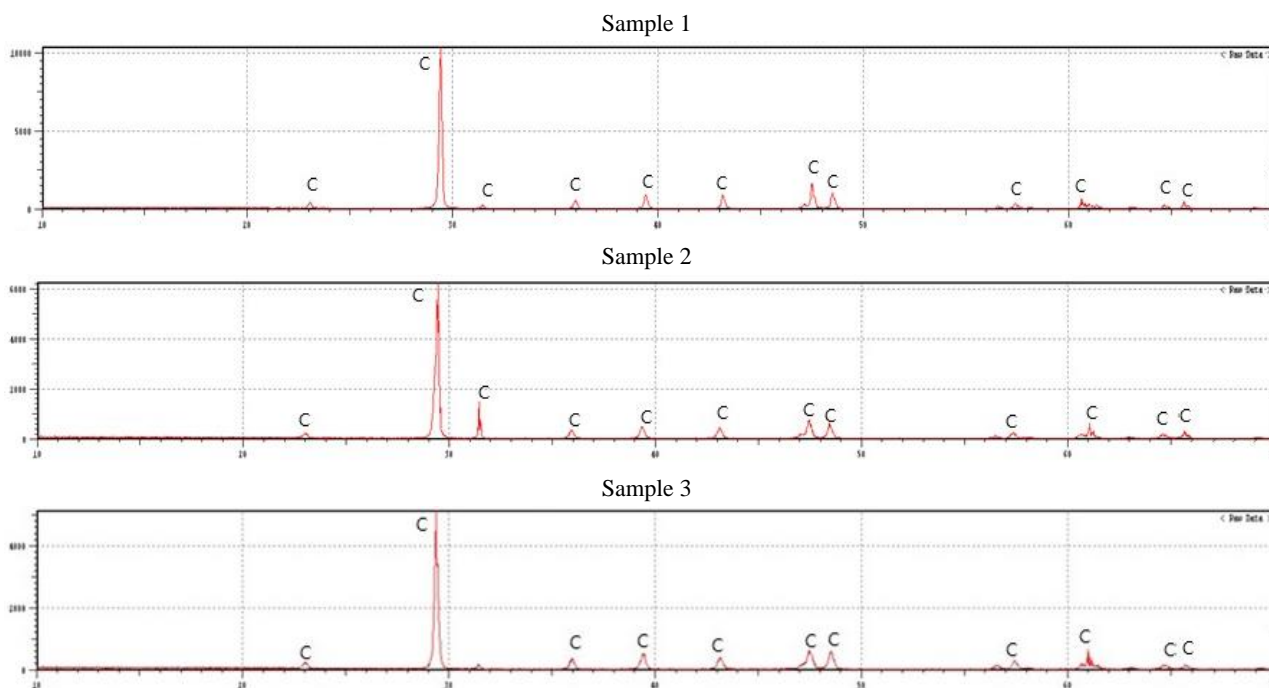


Fig. 5. XRPD pattern of the examined calcite from Sasa

## CONCLUSION

The occurrence of halite in hydrothermal systems is not a rare occurrence, considering the different types of hydrothermal processes. The occurrence of hydrothermal halite embedded in calcite crystals has not been established so far. In the Sasa ore field calcite is the most important of all non-ore minerals. It occurs together with dolomite, rhodochrosite, siderite, barite, quartz, calcedony, opal and so on. A proportional dependence has been established between elements in calcite crystals. Halite appears in the

dendrites form. Dendrites are long from 4.08 to 22.35  $\mu\text{m}$  and wide from 1.24 to 2.42  $\mu\text{m}$ . The morphology of natural halite is largely dominated by the cube {100}; the {110} and {111} forms are rarely present. When crystals grow by evaporation from aqueous solution the perfection of the cube faces is usually lost. Owing to the high values of the supersaturation appear dendritic branches developing in the  $\langle 111 \rangle$  directions. Dendrite forms when water rich in NaCl flows between microscopic layers of calcite.

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## Резиме

**ПОЈАВА НА ХИДРОТЕРМАЛЕН ХАЛИТ ВО МИНЕРАЛНАТА АСОЦИЈАЦИЈА  
НА Pb-Zn ВО НАОЃАЛИШТЕТО САСА (СЕВЕРНА МАКЕДОНИЈА)****Тена Шијакoва-Иванова, Иван Боев**

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**Клучни зборови:** халит; калцит; хидротермалност; Саса

Појавата на халит во хидротермалните системи не е ретка појава, имајќи ги предвид различните типови на хидротермални процеси. Појавата на хидротермален халит вграден во калцитните кристали од Саса досега не е утврдена. Во рудното поле Саса калцитот е најважен од сите нерудни минерали. Се јавува заедно со доломит, родохрозит, сидерит, барит, кварц, халцедон, опал и така натаму. Утврдена е пропорционална зависност помеѓу елементите во калцитните кристали. Калцитните кристали имаат инклу-

зии со ниска соленост (0,94–1,06 wt% NaCl). Во морфологијата на природниот халит во голема мера доминира хексаедарската форма {100}; формите {110} и {111} ретко се присутни. Кога кристалите растат со испарување на воден раствор, совршенството на хексаедарот обично се губи. Поради високите вредности на презаситеноста се појавуваат дендритски гранки кои се развиваат во правците <111>. Кристалите на халит се долги од 4,08 до 22,35  $\mu\text{m}$  и широки од 1,24 до 2,42  $\mu\text{m}$ .