

Atomic force microscopy (AFM) in research of microinclusions in halite

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This paper presents and discusses results of a fluid inclusions study in blue halite from the Verkhnekamsk potassium salt deposit (Russia). The shape and morphology of the inclusions ranging from tens of micrometers to fractions of a micron in size have been investigated with an atomic force microscope. All images of sample surfaces were obtained in air and in liquid cell under room conditions. The chemical composition of inclusions $\geq 40 \mu\text{m}$ in diameter was determined with X-ray energy-dispersive analysis. Typical morphological forms of the microinclusions have been established.

1. INTRODUCTION

It is known that crystallisation of mineral individuals is accompanied by formation of various structural defects, to which belong fluid inclusions. Results of their investigation are highly informative [1]. Appearance of modern methods allows one to obtain new data on the structure and composition of substance. The strategy of studying inclusions in minerals, consisting of various techniques and fine operations, like any other method of substance investigation, requires constant improvement and development.

The shape and relief of microinclusions are generally studied with the help of standard optical methods and photographs. These methods, however, have a number of disadvantages, as they are often responsible for false pictures and imaginary or real optical artefacts, mistakes in size, shape, morphology determinations arising because of the subjectivity of researcher's perception. Optical observations strongly depend on the resolution of a microscope. Studying many aspects of daughter phases becomes reasonably simple and accurate only as the size of the inclusions increases from 5 to 50 and 500 microns [2]. The major problem is three-dimensional images of inclusions which often fail to provide sufficient amount of reliable information, especially if obtained at large magnifications approaching the resolution limit of the optical microscope.

Besides the shape and morphology, the researcher is interested in chemical and structural composition of fluid inclusions. Scanning electron microscopy combined with energy dispersive analysis provides good results for identification of daughter minerals in fluid inclusions in a variety of minerals [3]. However, using the energy dispersive analysis to study inclusions directly in salt mineral samples, in particular in halite, is substantially hindered, because accuracy of the obtained data may be reduced as a result of the possible sample degasation in the vacuum chamber under the electron beam action, which can cause noise and errors, and influence of the composition and relief of the salt matrix penetrated by the electron beam.

Scanning force microscopes are now widely used to examine surface structures of solids [4], because they provide high resolutions (to the atomic scale), possibility to study both conductive and nonconductive substances and to get three-dimensional topographic images not only in vacuum but also in gaseous and liquid media, considerably simplifying sample preparation and investigation, which is vital for many minerals including salt ones. AFM are also actively used for metric analysis at the micro- and nanometer scale [5].

We have attempted to study the shape and relief of microinclusions in halite with an atomic force microscope. The elementary composition of the fluid inclusions was determined with an energy-dispersive X-ray microanalyser after applying a special method

of sample preparation, eliminating the drawbacks mentioned above.

2. MATERIAL AND METHODS

2.1. Methods

Investigation of the shape and microrelief of the inclusions was conducted with the help of a personal atomic force microscope ARIS 3500, Burleigh Instrument Co; USA (maximum scan range 70 microns in the X and Y directions). The basic component of an AFM is a microprobe (cantilever) which is a spring of minimal hardness, bending under the action of supersmall forces. A micron-size tip integrated into the free end of the cantilever perpendicular to the surface is brought within an interatomic distance of the surface so that the atoms of the tip and the surface are affected by interatomic potentials. We used standard silicon cantilevers (Burleigh) with pyramidal silicon tips 10-15 microns in size, radius at the end 10 nanometers, hardness 0.1 Newtons/meter. The probe, engaged with the surface and sliding over it, reproduces the surface relief and registers all the three coordinates of the tip thus generating a three-dimensional image of the surface with angstrom precision. It must be stressed that the the probe's pressure on the sample does not exceed several nanoNewtons thanks to the vertical movement of the sample relative to the probe, by which the feedback system compensates changes in the relief height, so the observed surface is not damaged by the AFM probe. To monitor angstrom deflection of the cantilever from the balanced position, our AFM probe is supplied with an optical system consisting of a semiconductive laser and a foursegmented diode photodetector included into a differential circuit. The laser beam is focused on the end of the cantilever and reflected off into the center of the detector. The deflection of the cantilever is registered as a difference signal of mismatch from the photodiode windows both in the vertical and horizontal directions.

All surface images of the samples were obtained both in air and in liquid cell at room temperature. The liquid medium was unsaturated water solution of NaCl, which concentration provided the optimal rate of halite surface dissolution. The scan was performed both in the constant height and constant force of contact modes (force of interaction 10^{-8} - 10^{-9}

Newtons). In this mode, deflection of the cantilever occurs as a result of mutual repulsion of the tip and surface atoms as a consequence of the interaction between their electronic shells and coulomb repulsion of their nuclei. In our case the measured forces were limited to the magnitude of 10^{-6} - 10^{-9} Newtons. In addition, plane surfaces were scanned in the lateral force mode. We used standard scan parameters for this instrument (data points in the X and Y directions 256×256 samples, sample delay - 0.2 ms/sample, retrace delay - 0.2 ms/step, scanline delay - 3 ms/line). For metric precision, scales of the images were calibrated in the X and Y directions and in height with the help of calibrated samples (Burleigh). The obtained images were displayed on a computer monitor. To eliminate electrical noise, the images were processed with a Fast Fourier Transformation filter.

Elementary composition of the fluid inclusions with diameter $\geq 40 \mu\text{m}$ was determined with an energy dispersive spectrometer «Link» combined with REM JSM 6400 (Jeol). The inclusions were opened with a sharp steel needle and the fluid was extracted with a tapered capillary tube, based on O.Petrichenko's recommendations [6]. The content of the tube in the form of a regular spherical drop was placed on a special carbon substrate with atomic-smooth surface, carbon-coated, and analysed. Carbon was chosen as the substrate material because it is a light element that does not affect results of the analysis.

2.2. Material

The object of our study were inclusions in blue halite from a carnallite bed of the Verkhnekamsk potassium salt deposit. Halite is recrystallised, coarse-grained, with a small number of inclusions up to 1-10 mm in size. Several types of inclusions are observed. According to the aggregate state, the inclusions are classified as one-phase, two-phase (liquid-gas, liquid-solid), three-phase (liquid-gas with a solid phase), multiphase (liquid-gas with numerous xenogenic crystals and terrigenous substance), and inclusions with hydrocarbons. The liquid phase is represented by water solutions or liquid hydrocarbons. No forms typical of sedimentary halite are observed. These inclusions, individual or in small groups, are commonly found in the peripheral part of the crystals. Sometimes the inclusions are distributed among growth zones suggesting that they are primary

Table 1

The element composition of brine inclusions in blue halite from the Verkhnekamsk deposit

№	Content of elements, weight percent				
	Na	Mg	K	Ca	Cl
1	23.42	0.71	0.57	3.17	44.10
2*	-	4.04	11.40	0.77	27.80
3*	-	6.08	18.86	1.41	28.52

* - results does not include sodium

ones. Secondary inclusions (liquid and gas-liquid) are located in healed fissures. The surfaces for investigation were prepared by splitting the sample in air. The split was made in the plane of inclusion along crystallographic planes, providing opening of the inclusion and morphologically smooth surface of the halite samples.

3. RESULTS AND DISCUSSION

We used an atomic force microscope to visualize the shape and morphology of microinclusions in halite under room conditions. The majority of data were obtained in air. In order to avoid possible artefacts which can be caused by contamination of the surface, we studied only fresh splits. The desired inclusions of various sizes or groups of inclusions were previously found with the help of a binocular microscope. Prior to the analysis, liquid inclusions were freed from liquid in accordance with the AFM procedure.

The energy dispersive analysis has shown that Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^- are the major components in inclusion solutions of diagenetic halite (Table 1). Some brine inclusions contain Fe, Mn, Cr, Ag, Au as microelements. Quantitative analysis of light elements (atomic number <10) involves considerable errors [7], and so it was not carried out. The absence of Na (the dominant constituent of fluid inclusions in halite) in the results of 2d and 3d inclusions is explained by the fact that after brine was placed on the substrate, the phase of light hydrocarbons which was also present in the inclusions, readily evaporated, leaving behind thin sodium chloride films and individual carnallite crystals, and quantitative analysis of thin films fails to yield reliable results under standard conditions of experiment [7].

At first we obtained an image of halite surface free from defects and inclusions. The halite sample in Figure 1 shows indistinct banding (light bands) which was best observed in the lateral force mode and which is invisible under the optical microscope.

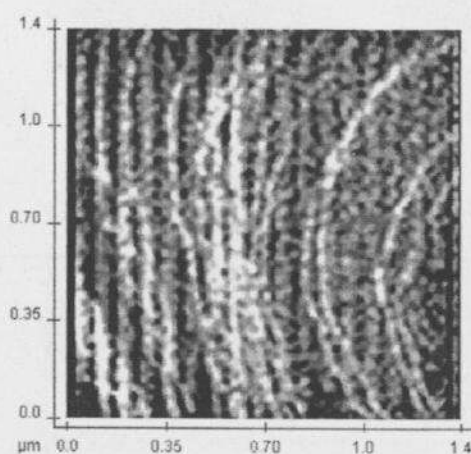


Figure 1. AFM image of banding growth of halite (lateral force mode, $1.4 \times 1.4 \mu\text{m}^2$ area).

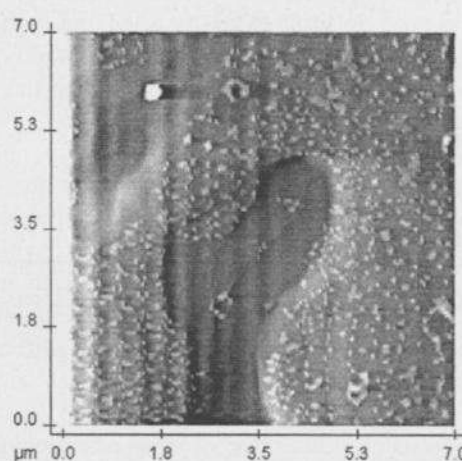


Figure 2. AFM image of halite surface with a fragment of secondary fluid inclusion in 30 minutes after opening ($7 \times 7 \mu\text{m}^2$ area).

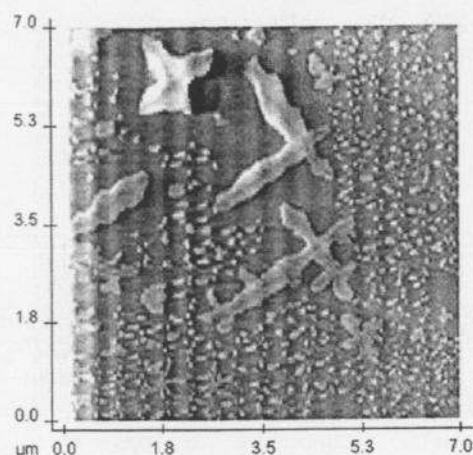


Figure 3. AFM image of halite crystals crystallised from the content of fluid inclusion ($7 \times 7 \mu\text{m}^2$ area).

The vertical lines visible in some images are artefacts (interference fringes).

The image of halite surface shown in Figure 2 is a good illustration of why inclusions should be freed from fluid and the surface around them dried. We observed a secondary inclusion without removing the fluid after its opening. Figure 3 shows halite crystals observed as dendritic crosses and cubes. They were formed on the split surface near the inclusion as a result of crystallisation of its liquid content. The image was generated in 30 minutes after the inclusion opening. We failed to see the internal relief of the inclusion, evidently because the tip went out of contact with the inclusion's surface because of the abrupt change in surface density when the cantilever immersed in the liquid. Additional observation of the inclusion in twenty four hours showed that the fluid content inside the inclusion also crystallised.

Practically all investigated primary inclusions in halite have cubic or rectangular shape in the optic axial plane. Some of the inclusions can be interpreted as negative crystals. We believe that the convolution effect of the form of the tip with the form of the object, which can cause distortion, can be ignored in this case because of the significant difference between the size of the investigated objects and the radius of the end of the tip. In this paper we would like to focus on description of three microinclusions which represent the basic morphological types observed in the halite.

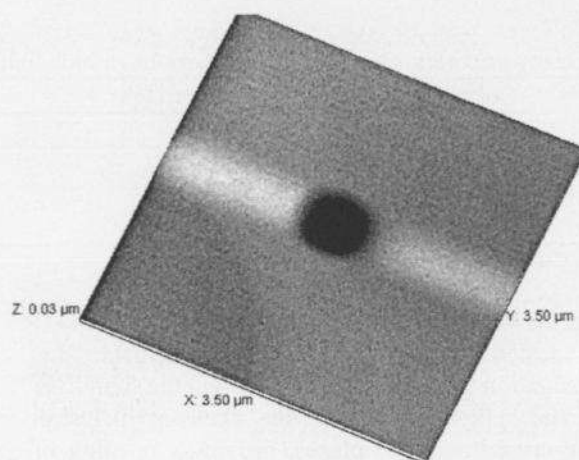


Figure 4. Three-dimensional AFM image of gaseous microinclusion ($3.5 \times 3.5 \mu\text{m}^2$ area).

1. Gas microinclusion (Fig. 4): shape close to a square, size 0.7×0.7 microns. Morphology of the walls smooth and flat. Inclusions analogous in shape to that shown Figure 4 were interpreted as negative cubic crystal in [8].

2. Fluid inclusion with solid phases (Fig. 5): shape resembles to rounded, size 27×27 micrometers. Found inside the inclusion were several radiaxial aggregates about 2.5 micrometers in size (Fig. 6). One of them is shown in Figures 7 and 8 in two- and three-dimension projections. Because of the small size of these aggregates, we failed to extract them for

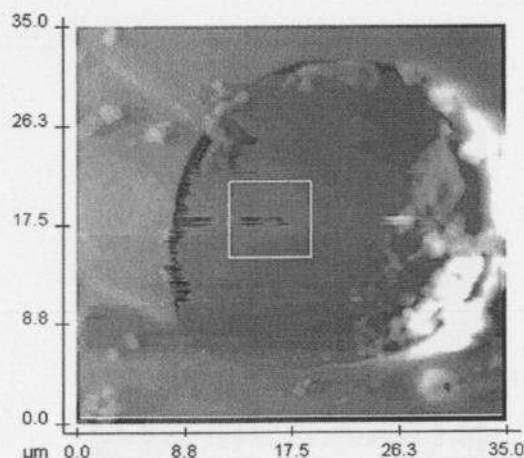


Figure 5. AFM image of a fluid inclusion with solid phases ($35 \times 35 \mu\text{m}^2$ area). The square indicates the location of solid phases.

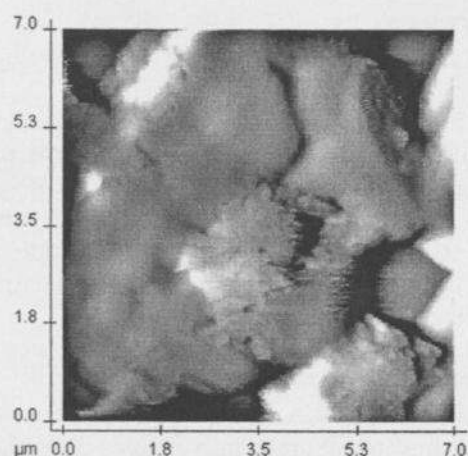


Figure 6. AFM image of solid phases found as radiaxial aggregates ($7 \times 7 \mu\text{m}^2$ area).

identification with energy-dispersive analysis. Most probably, they represent a daughter minerals anhydrite which must have precipitated from the fluid after the inclusion's entrapment, using calcium sulphate, as far as such radiaxial anhydrite aggregates can survive only in isolated space.

3. Liquid inclusion with peculiar internal morphology determined by the step configuration of the walls (Fig. 9). Such original internal morphology of the walls is characteristic of inclusions in secondary halite. Growth by steps is commonly thought to be connected with recrystallisation [8].

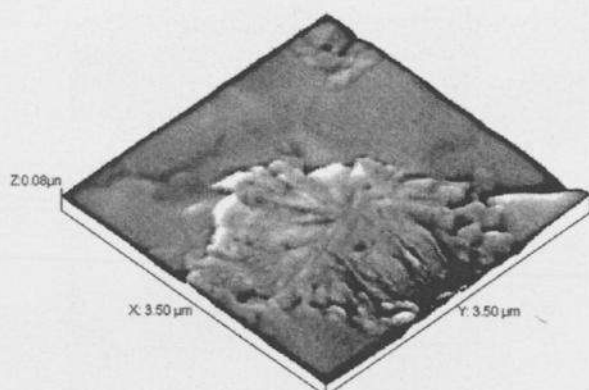


Figure 8. Three-dimensional AFM image of a radiaxial aggregate ($3.5 \times 3.5 \mu\text{m}^2$ area).

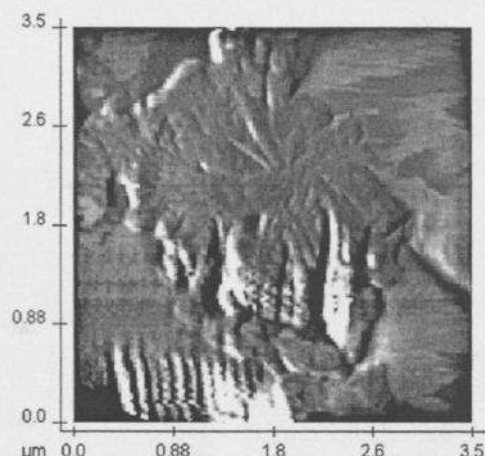


Figure 7. AFM image of a radiaxial aggregate (lateral force mode, $3.5 \times 3.5 \mu\text{m}^2$ area).

The shape of the inclusion approaches that of a negative octahedral prism. Part of the inclusions in the studied halite fragment consists of three steps varying in height around 0.4 micrometers. The configuration of the steps is symmetric. The maximal linear size of the inclusion in the visible plane is 4 micrometers.

Another way of visualizing inclusions with an AFM is *in situ* observation of halite surface dissolution. For example, Figure 10 shows visualization of an inclusion, probably gaseous, 1.4×1.4 micrometers in size.

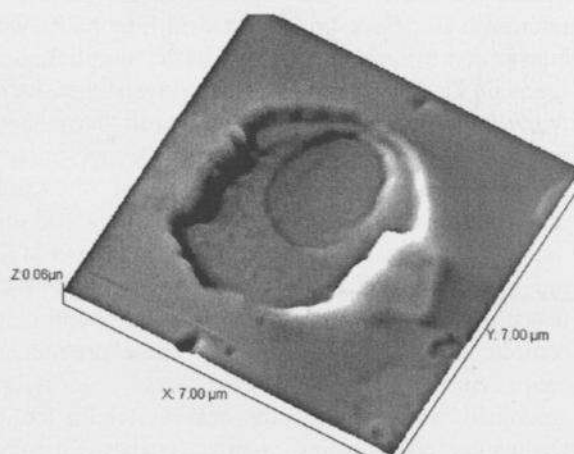


Figure 9. Three-dimensional AFM image of a liquid inclusion with step configuration of the walls ($7 \times 7 \mu\text{m}^2$ area).

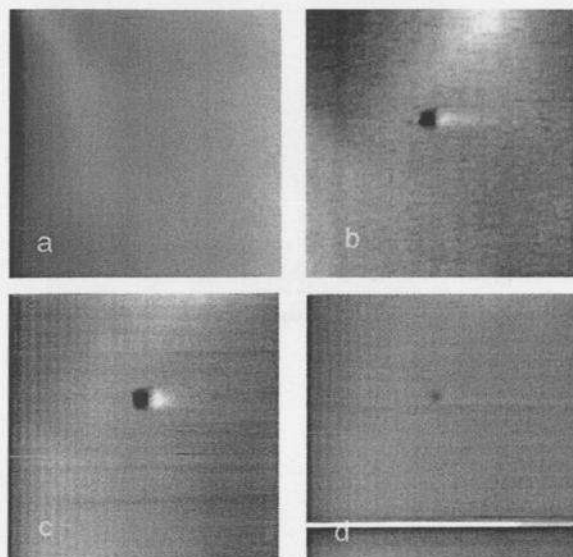


Fig. 10. Sequence of *in situ* AFM images of an inclusion in the process of halite surface dissolution. Interval between images is 2 min. The image area in each case is $14 \times 14 \mu\text{m}^2$.

4. CONCLUSIONS

The shape and morphology of fluid microinclusions and microinclusions with solid phases from tens of micrometers to fractions of a micron in size have been studied in blue halite with atomic force microscopy. The basic morphological types of the microinclusions in recrystallised halite from the Verkhnekamsk salt deposit have been established. We have attempted X-ray energy-dispersive analysis for the study of the fluid composition of the inclusions with diameter $\geq 40 \mu\text{m}$.

This work is only an attempt of using an AFM for the study of inclusions in salt minerals. Further investigations are necessary in order to obtain more complete information. But even these preliminary data demonstrate that atomic force microscopy combined with methods of local determination of elementary composition, such as energy-dispersive X-ray microanalysis, in the nearest future can provide new insights into mineralogy of salt deposits by furnishing data about the shape, relief, size and solid phases of their microinclusions and correlation of the various factors of crystal growth.

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