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Reconstruction of crystallisation temperature of artificially grown H-analcimes by means of the IR and fluid inclusion studies

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ABSTRACT:

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A method of reconstruction of the crystallisation temperature (Tc) of analcime has been proposed. The method is based on the compilation of two data sets: the IR absorption spectra and fluid inclusion study results. The water position in the analcime structure depends on the crystallisation temperature. Certain bands in the IR absorption spectrum are sensitive to the change in the temperature conditions of the analcime formation. Moreover, the IR absorption band positions are also influenced by the composition of the crystallisation system as well as by the crystallisation time. For more precise information about Tc, fluid inclusion studies were performed. They provide additional data about salt concentrations in the crystallisation system, water behaviour in the analcime structure and crystallisation temperature.

Key words: H-analcime, Crystallisation temperature, Temperature reconstruction, IR study, Fluid inclusion, Zeolitic structure.

INTRODUCTION

The symmetry of the analcime structure is related to the conditions of crystallisation. Depending on the environment of crystallisation, the symmetry changes from cubic to monoclinic displaying a different pattern of order-disorder for the Si/Al framework, sodium and OH_n clusters. One of the most important factors, which govern the formation of the structure, is temperature. The influence of the crystallisation temperature (Tc) on the symmetry of the structure and the relation between the symmetry and water position have been documented for artificially grown H-analcime (SŁABY 1999, 2001a, b) and corroborated by BAKAKIN (2001, in press). With decreasing Tc, water in the analcime structure forms increasingly more complicated patterns. Within a temperature range 550-350°C one or two types of water appear in the analcime structure (SŁABY 1999). Spectroscopic investigations (IR, NMR) of analcimes grown above 450°C point to only one type of hydrogen-bonded water. The second type appears in analcimes formed below that temperature. The position of this type of water is better defined. The NMR spectra of low temperature analcimes display, apart from both types of water, an additional third hydrogen environment. Although the water environment in H-analcime is also influenced by crystallisation time, activity of the species taking part in the crystallisation as well as by the source material, that is transformed by hydrothermal process, temperature seems to be the most strongly acting factor in the crystallisation system. Because of the visible relationship between the temperature of crystallisation and development of the hydrogen environments in the analcime structure, the question arises to what extent this information could be used as a geothermometer.

Approximate determination of the Tc is also possible by means of fluid inclusion study (SŁABY & *al.* 1995). Investigations of fluid inclusions in zeolites and in minerals of the zeolite-type structures (e.g. analcime, apophyllite) have been performed only rarely (cf. e.g. DOROSHENKO & *al.* 1969, LISITSYN & RUDNEV 1978, BUKHAREV & *al.* 1981, TAKENOUCHI 1988, DE VIVO & SASADA 1992). Minerals of this type are believed to be inappropriate for fluid inclusion studies. Such minerals contain loosely bound water molecules in their structures. Because of this loose binding, water from the mineral structure may be removed unintentionally during the storage of the mineral after it had been unearthed or even earlier, in the parent rock after the crystallisation of the mineral but before its collection. Decrease in the water content in the structure of the zeolite-type mineral may lead to the absorption of water into the structure from an inclusion of aqueous solution, as the structure becomes water-undersaturated. The longer the time of the "drying" of the mineral, the greater the amount of water that might escape from fluid inclusions. A similar influence may be predicted for temperature increase: any heating expels water from the mineral structure, consequently causing lowering of the liquid/vapour ratio in aqueous inclusions in the mineral.

On the other hand, aqueous inclusions in the "dried" zeolite-type minerals, which had low liquid/vapour ratios, may regain water in their vacuoles after storage in a humid environment, to convert to inclusions largely filled with liquid. This "final" content of water has no relationship to the water content at the moment of the trapping of the inclusion during the crystallisation of the mineral, on the contrary, it depends only on the humidity of the storage environment and the time of the storage under specific conditions. The water content in a fluid inclusion changes unless equilibrium of "saturation" is reached; later the stable humidity of the environment means the stable liquid/vapour ratio in the considered fluid inclusion.

The present study was performed to verify the possibility of fluid inclusion studies in minerals of the zeolite-type structure. Three main topics were of special interest: a) is it possible to obtain the homogenisation temperatures for inclusions in the minerals of the zeolite-type structures; b) whether the measurements of the homogenisation temperature of aqueous inclusions in such minerals are interpretable; c) what is the behaviour of fluid inclusions in such minerals, which were affected by the change in the water content, mainly water escape, during storage under laboratory conditions.

The aim of the present publication is to provide a discussion on various ways of reconstruction of the analcime crystallisation temperature, with use of the study results of the artificially grown zeolites for the purpose of the discussion. The crystals have been grown under controlled conditions, in a closed system.

EXPERIMENTAL

Analcime was grown as a reaction product of acid plagioclase with diluted Na_2CO_3 solution of the molalities: 0.1, 0.5. Single runs were performed with 0.1M $NaHCO_3$ solution. The source material, natural oligoclase crystals $(Na_{0.74\text{-}0.76}K_{0.02}Ca_{0.23\text{-}0.21})[Al_{1.27\text{-}1.24}Si_{2.74\text{-}2.77}O_8]$ separated from granitic rock, was mixed with the solution (ratio 1:10) and heated in copper containers, placed in cone seal pressure vessels. The autoclaves were installed with a cup at the bottom and surrounded with an external heating mantle. The arrangement gave rise to a thermal gradient of 100°C between the top and the bottom. The temperature during the runs was monitored continuously by means of an external Ni-CrNi thermocouple. The temperature of the reaction was extrapolated from the autoclave calibration curve. The vessels were air-cooled after every run. The pressure medium used in the vessels was water. P-T conditions of the runs were as follows: the pressure was fixed usually at 1.8 kbar (sample R-1 and R-2 at 2 kbar), the temperature of the runs varied between 300 and 550°C (300, 350, 380, 400, 450, 480, 500, 550 °C). The durations of the runs were chosen arbitrarily to fall within the range 8-40 days. The last duration was longer than that used by CERMIGNANI & ANDERSON (1983) to establish equilibrium between plagioclase and carbonate solution under similar temperature. A summary of the run conditions for the analcime used for the present investigation is presented in Table 1.

Solid products of the reaction were checked by means of X-ray powder diffraction, scanning electron microscopy and microprobe analysis. The products in all of the runs were analcimes with plagioclase relics. The relics displayed albite composition.

The water environment in all of the analcime samples was determined by means of the IR method. The infrared absorption spectra were measured with an IR Nicolet (Magna – IR 550) spectrometer (KBr pellets; 1:100 – sample/KBr). The range of recorded spectra was set to be 4000-400 cm^{-1}. The OH stretching vibration region of the spectra was deconvoluted by means of square interpolation assuming Gauss-shaped bands. For every band in the deconvoluted spectrum half-width, relative shift, maximum and integrated intensities were assigned.

The analcime crystals did not need to be polished for the fluid inclusion studies, because they were transparent enough and their faces were glossy, and consequently the fluid inclusions inside the crystals were clearly visible. The grains were carefully split in two parts in the Chaixmeca microscope crushing stage to obtain more preparations, because the properties of the host mineral precluded multiple heating and the procedure: one preparation – one inclusion investigated, had to be maintained. The heating runs were performed by means of the Fluid Co., Inc. (USA) heating/freezing microscope stage. The accuracy of the temperature measurement was ±1 to ±1.5°C for the routine procedure, whereas for rapid heating it worsened to ±2 or even ±3.5°C. The routine procedure applied a temperature increase rate of 5 or 10°C per minute, the rapid heating had a rate of 25 or 30°C per minute. The accuracy of the temperature measurements during the freezing runs was ±0.1 to ±0.2°C. Routine physico-chemical interpretation plots were applied (Roedder 1984).

Some preparations were dried at a constant temperature of 280°C (this temperature was selected arbitrarily) in the heating stage until the volume of the fluid

Run temperature (°C)	Salt concentration in the solution W/M=10	Duration of the synthesis, days	IR study - OH stretching area, selected bands			
			Band (cm^{-1})	Integrated intensity	Band (cm^{-1})	Integrated intensity
300 R-1	0.1M Na$_2$CO$_3$	8				
300 R-2	0.1M Na$_2$CO$_3$	40				
350	0.1M Na$_2$CO$_3$	30	3636	41,91	3562	33,13
350	0.1M Na$_2$CO$_3$	30	3629	48,64	3564	27,38
350	0.5M Na$_2$CO$_3$	30	3636	55,58	3568	25,3
380	0.1M Na$_2$CO$_3$	12	3634	42,42	3566	44,58
380	0.1M Na$_2$CO$_3$	30	3636	49,48	3565	40,83
400	0.1M Na$_2$CO$_3$	12	3622	12,78	3562	39,7
400	0.1M NaHCO3	30	3629	62,87	3564	49,48
400	0.5M Na$_2$CO$_3$	8	3627	69,7	3565	4,2
400	0.1M Na$_2$CO$_3$	12	3626	28,8	3560	47,2
430	0.5M Na$_2$CO$_3$	12	3629	23,28	3562	52,3
430	0.1M Na$_2$CO$_3$	20	3630	31,66	3564	50,3
450	0.5M Na$_2$CO$_3$	30	3633	70,2	3564	57,8
450	0.1M Na$_2$CO$_3$	12	3628	18,53	3558	53,3
500	0.1M Na$_2$CO$_3$	30	0	0	3556	29,9
550	0.1M Na$_2$CO$_3$	30	0	0	3555	29,9

Tab. 1. Summary of experimental run conditions and IR spectroscopic data for experimentally grown analcimes

phase, after a certain decrease, became constant. This process lasted from 3 to 5 hours. Afterwards, these preparations were placed in an air-tight closed vessel with water at the bottom, above the water level. Under those conditions the preparations were kept for one year at room temperature i.e. at 20-22°C.

RECONSTRUCTION OF Tc FROM THE IR DATA

IR absorption spectra of analcime grown under hydrothermal conditions within the temperature range 350-550°C show, in the OH stretching vibration area, a three-part broad band with a maximum around 3450 cm^{-1}. The values for the remaining constituent bands (after deconvolution) fluctuate around 3260 cm^{-1} and 3560 cm^{-1}. The tripartite pattern appears for the samples crystallised near 550°C as well as near 350°C, irrespective of higher or lower sodium activity in the solution. The position of the peak at ~3450 cm^{-1} is not very sensitive to thermal condition of the sample synthesis. The position and integrated intensity (peak area) of the second band around 3260 cm^{-1} changes as the synthesis time, temperature and sodium activity in the system vary. This peak vanishes in the samples crystallised during 8-12 days. Higher sodium activity pushes more OH clusters bonded with the r_{OH} = 0.93Å in the structure. Temperature acts in exactly the same way. Therefore the peak area increases in accordance with temperature and growth in sodium activity, reaching the same value for analcime crystallised at 450°C in 0.5M Na_2CO_3 solution as for analcime crystallised at 550°C in 0.1M Na_2CO_3 solution. Although the position of the peak changes with temperature, the variation does not consistently follow fluctuation in the thermal conditions of the synthesis. The most sensitive to temperature change, and relatively insensitive to sodium activity in the hydrothermal system, is the OH_n hydrogen-bonded cluster with the r_{OH} almost equal to the value for the free water molecule, that is represented by the third band.

Apart from the tripartite band, another peak occurs in the OH stretching area near 3630 cm^{-1}. This peak points to the second type of water in the analcimes synthesised at and below 450°C (SŁABY 1999). The integrated intensity and the position of this peak display certain connections with the thermal condition of analcime formation.

For further consideration of the usefulness of the IR spectra in the Tc reconstruction, two bands showing temperature dependence on the synthesis conditions, one at ~3560 cm^{-1} and the other at ~3630 cm^{-1}, have been chosen (Text-fig. 1a,b). Interdependence of the positions of both of the peaks is also clearly visible (Text-fig. 1c). Information on the position and integrated intensity of both of the bands, together with temperature of analcime synthesis, is shown in Table 1.

The dependence between the position of both of the bands and temperature, as well as between the integrated intensity of the peaks and temperature, is shown in Text-fig. 2. Additionally the correlation between peak position and amount of OH groups, responsible for the appearance of the band, is shown.

Almost all of the projection points belonging to the hydrogen-bonded groups with r_{OH} = 0.93 A (~3560 cm^{-1}) show good correlation between the band position and temperature, and similarly very good correlation

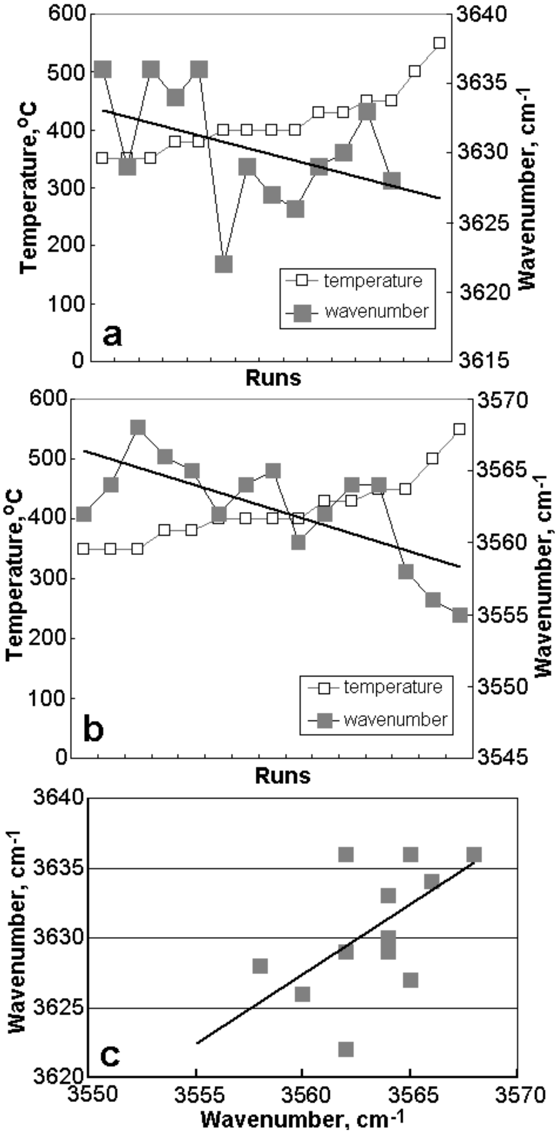

Fig. 1. Changes in the values of the selected IR bands (OH stretching area) of analcime crystals compared to the thermal conditions of their formation; a) first type of water, b) second type of water, c) mutual relation of both bands position referring to the two types of water

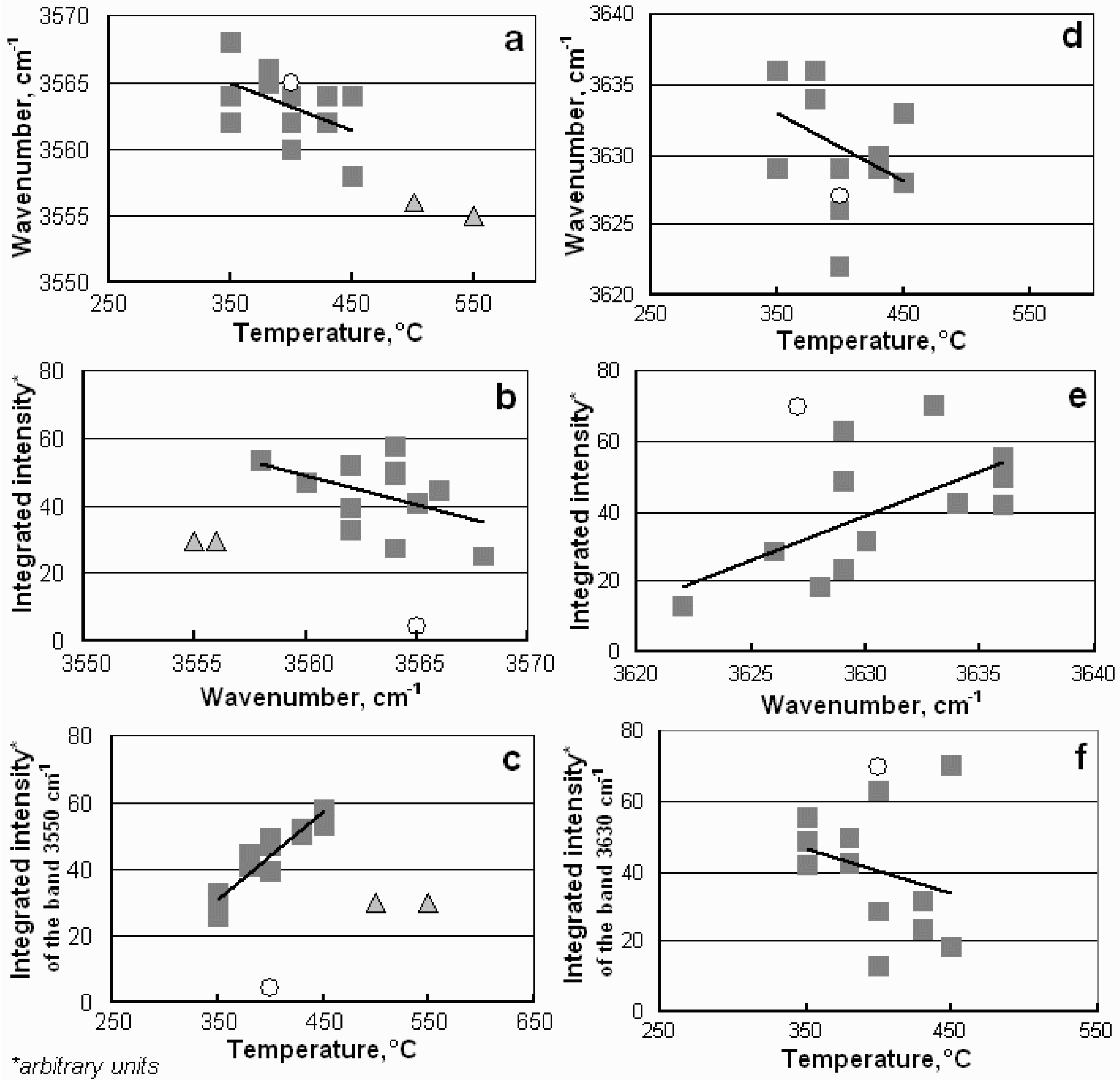

Fig. 2. Interdependence between spectroscopic data (wavenumber and integrated intensity) and Tc (triangles – samples grown at 500°C and 550°C, circle – sample with run duration 8 days, squares – remaining samples)

between the peak area and temperature (Text-fig. 2a, c). The correlation between the frequency of the band and the amount of OH groups with similar length of hydrogen bonding is rather poor (Text-fig. 2b). Three points fall completely outside all of the trends and have accordingly been given different symbols in the figures. Two of them present analcimes crystallised at 500°C and 550°C. The structure of both of them seems to be cubic, in contrast to the remaining samples showing a lower symmetry (SŁABY 2001a, b). Analcime crystals with cubic symmetry should posses three crystallographically equivalent water environments (H – occupancies 1/3, 1/3, 1/3). All three bands in the tripartite spectrum nearly converge to one. The position of the band maximum, 3555-3556 cm $^{-1}$, reaches its minimum within the entire data set (Table 1). The integrated intensity for the band is very low. The number of groups showing deviation from cubic symmetry is low. The third point represents the analcime crystallised during eight days, clearly under non-equilibrium conditions. There is almost no water in this position, although the value of the band fits exactly to those occurring in the analcime crystals grown during 30 days.

The increase in Tc causes a systematic shift of the ~3560 cm^{-1} band toward lower values. The amount of OH clusters, appearing in the structure, grows markedly with Tc decrease. Both of the trends, especially integrated intensity versus temperature (Text-fig. 2c), are independent from the sodium concentration and anion speciation in the solution during analcime crystallisation.

The dependence of the position and amount of the second type of water on Tc is shown in Text-figs 2 d, e, f. The two samples grown at 550°C and 500°C do not reveal any traces of this type of hydrogen-bonded water. Due to the lack of the second type of water they have been disregarded. Comparing the analogous diagrams constructed for the first and second type of water, the correlation between parameters in the case of second type of water is poorer. Furthermore, although the position of the band shows a similar relation to Tc as the band at ~3560 cm^{-1}, the other relation is different. Increasing Tc generates a shift of the band position toward lower values. The correlation between the wavenumber and Tc is influenced by the duration of analcime crystallisation as well as by the sodium concentration in the solution. A short run duration lowers the band value. Synthesis in the environment enriched in sodium, while keeping the temperature constant, increases the band value. The anion speciation plays also an important role in the formation of analcime structure. The general relationship Tc versus integrated intensity shows water content increase with Tc decrease. The correlation is rather poor. The same parameters that influenced band frequency (time, solution composition) also govern the amount of OH groups penetrating into the structure. Short duration of the crystallisation time (non-equilibrium conditions) resulted in an enormous increase in the second type of water in the structure. An analcime structure grown long enough to approach equilibrium (keeping the solution composition constant) shows a distinctly lower amount of the second type of water. However in individual cases the non-equilibrium growth was accompanied by the opposite effect that is a shortage of water in the structure. Higher sodium concentration in the solution (keeping Tc constant) promotes an increase in the water amount in the structure.

RECONSTRUCTION OF Tc FROM THE FLUID INCLUSION STUDIES

Fluid inclusions appropriate for the microscope observations were found in 16 crystals of analcime, seven from the run lasting 8 days (Tc=300°C, 0.1M Na_2CO_3 solution, denoted R-1) and nine from the run lasting 40 days (Tc=300°C, 0.1M Na_2CO_3 solution, denoted R-2). A total of 31inclusions was investigated.

Although crystallisation times in the experiments R-1 and R-2 were different, analcime crystals from both experiments contained three identical types of inclusions:

– type A: one-phase fluid inclusions, filled with aqueous solution (Text-fig. 3a);

– type B: two-phase inclusions with prevailing liquid phase and very small vapour bubbles occupying 3-5 vol.% of the inclusion vacuole (Text-figs 3b-c);

– type C: two-phase liquid-vapour inclusions with large vapour bubbles occupying 25-30 vol.% of the inclusion vacuole (Text-figs 3d-e).

Inclusions trapped in crystals from the R-l experiments were very small (1-2 μm), whereas those from the R-2 experiments were distinctly larger (>5 μm). Inclusion of the types A and B occurred deep inside crystals. Those of the type C have been found in the zones near the crystal surface. Cryometric measurements yielded values of the NaCl equivalent of 8 wt. % for the inclusion types A and B, and 5 wt. % for the type C.

During heating the inclusions of the type A (10 inclusions investigated) either decrepitated at various temperatures (4 inclusions), or bubbles formed inside their vacuoles at temperatures from 130 to 250°C (6 inclusions). These vapour bubbles did not disappear during further temperature increase, thus the homogenisation of these inclusions was not observed. Inclusions of the type B (7 inclusions investigated) homogenized at temperatures from 110 to 120°C in the liquid phase, when the heating was rapid, i.e. at the rate of 25 to 30°C per minute. It is noteworthy that these values of the homogenisation temperatures could be obtained only during the first runs for each inclusion. The second run of rapid temperature increase yielded distinctly higher homogenisation temperatures, from 180 to 250 °C for various inclusions. On the other hand, during the slow heating the bubbles increased in the inclusions, and homogenisation was not reached (as observed in 3 other inclusions). Inclusions of the type C (11 inclusions investigated) displayed a behaviour similar to that of the type B inclusions. Fast heating caused their homogenisation at temperatures from 310 to 370°C, usually in the liquid phase (5 inclusions), though two inclusions homogenized in the gaseous phase. During the slow heating of four other type C inclusions they did not become homogeneous. In this case the bubble volumes gradually increased, reaching 70 to 80 vol. % of the total volume of the inclusion, so that the liquid phase formed only thin rims poorly visible under the microscope, and wetting the walls of the vacuoles,.

Sodium concentration obtained by means of the cryometric method (as NaCl equivalent) from the type A and B inclusions fits exactly to the maximum sodium content in the solution after complete release of this element from plagioclase. The sodium concentration from the type C inclusions, though distinctly higher than that in the post-reaction solution, could also provide valuable information about the analcime crystallisation process. This is because the Na profiles through analcime crystals show a remarkable decrease in sodium

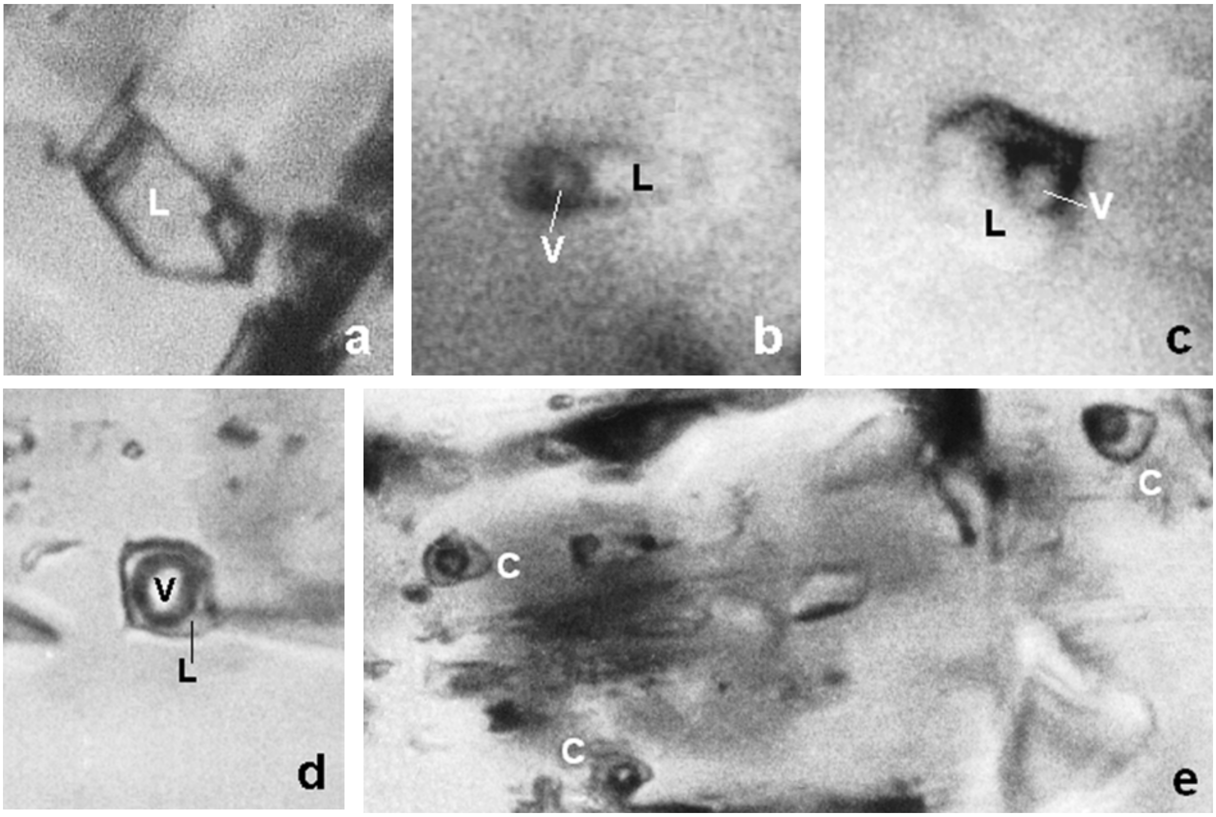

Fig. 3. Fluid inclusions in artificially grown analcime: a – one-phase inclusion of the type A, inclusion length 12 μm; b, c – two-phase inclusions of the type B, inclusion lengths ca. 3 μm; d, e – two-phase inclusions of the type C, inclusion sizes ca. 6 μm; L – liquid solution, V – vapour phase

content, which in turn is a consequence of crystallisation in a closed system. We believe that actual crystal composition and the trapped fluid reflect the decrease in alkalis in the solution during crystallisation, due to incorporation of sodium into the crystallising phase.

Knowing the true values of the inclusion trapping temperature (300°C) and trapping pressure (2 kbar) we could evaluate the meaning of the homogenisation temperatures (Text-fig. 4). The homogenisation temperatures of the type B inclusions (110 to 120°C) for the 10 wt. % NaCl solution indicated the isochores 1.04 g/cm^3 and 1.03 g/cm^3 respectively. These isochores at 2 kbars yielded the estimated trapping temperature of 285°C (the first isochore) and 295°C (the second one), which may be a good approximation of the true trapping temperature i.e. the crystallisation temperature. The decrease of the estimated temperature of the value of 5 to 15°C, when compared to the temperature of crystallisation, probably had a peculiar cause, which will be discussed later.

Only the homogenisation temperatures of the type B inclusions yielded a good approximation to the temperature of crystallisation. The homogenisation temperatures of the type C inclusions (310–370°C) were higher than the crystallisation temperature of the host minerals. This means that they cannot be used for direct reconstruction of the formation conditions of the investigated synthetic analcime. The up to 15% temperature difference may have several different causes, such as: a) temperature gradient during the crystal growth, b) migration of a limited volume of water into the inclusion vacuole during cooling of the autoclave, c) measurement error during inclusion homogenisation with a high heating rate. If possibility (b) is valid, the usefulness of the inclusions in the minerals with the zeolite-type structure for fluid inclusion studies seem to be limited by the time that has elapsed from crystallisation of the mineral to its investigation. In this case the evolution of the type B inclusions on cooling of the autoclave would be indicated by the arrow B in Text-fig. 4. The concentrations of the mineral-forming solutions, derived from the cryometric studies of the type B inclusions are explainable by the course of the hydrothermal process in the autoclave.

The type A inclusions contained a solution of the same concentration as in the type B inclusions, albeit gas bubbles were absent. The same concentration suggested a common origin of these two types of fluid inclusions and the absence of any further change (after

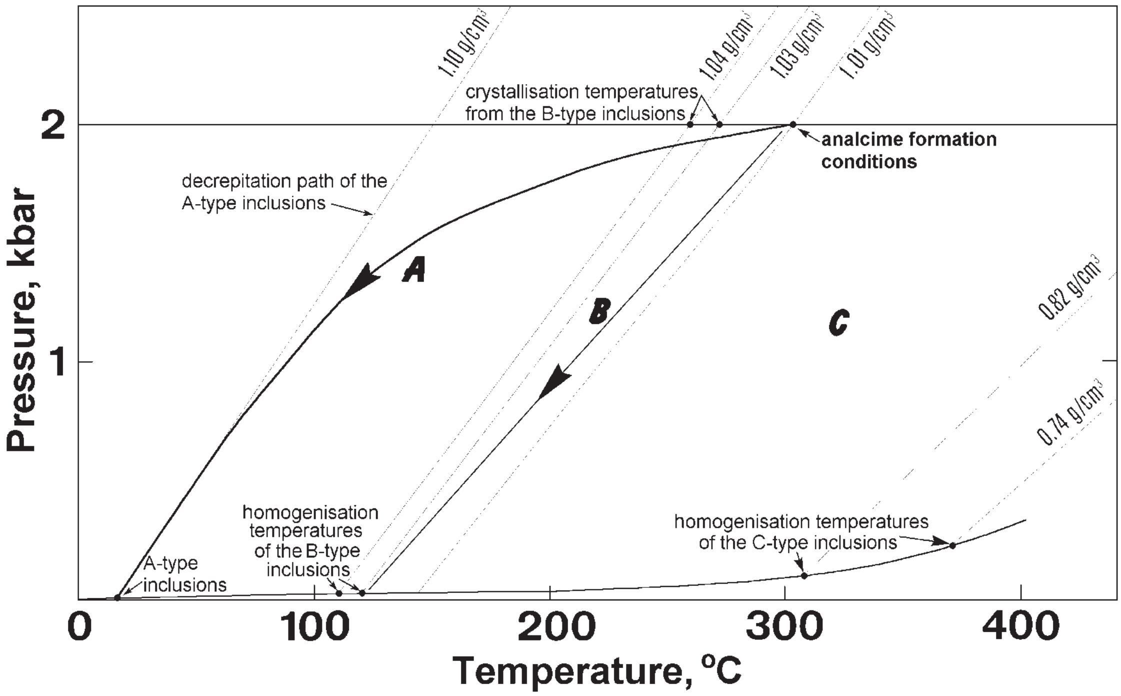

Fig. 4. Temperature – pressure plot for the 10% NaCl aqueous solution with the probable evolution paths of the fluid inclusions of the types A, B and C

the inclusion trapping) in the solution composition in the type A inclusions. These inclusions occurred in the inner parts of the analcime crystals, like the type B inclusions. The most reasonable mechanism to explain the formation of the type A inclusions, is necking down of the regular type B inclusions. After splitting in parts of a type B inclusion, its part which we observe presently as the type A inclusion, would be in fact a liquid-filled section of the type B inclusion. This phenomenon should occur at low temperature (<50°C or even <40°C), otherwise we should observe small contraction bubbles in the type A inclusions. In the neighbourhood of the type A inclusions there were found dark flat objects, which probably are rich in gas counterparts of the one-phase liquid type A inclusions. If necking down occurred, the evolution path of the type A inclusions is shown by the arrow A (Text-fig. 4).

The type C inclusions were found in the outer parts of the analcime crystals. Their homogenisation temperatures clearly indicate leakage of water from the inclusion vacuole. In this case their evolution would be indicated by the arrows C (Text-fig. 4). The salt concentrations in the solutions of these inclusions (ca. 5 wt. %) is much lower than in the solutions of the type A and B inclusions. If the type C inclusions formed by leakage of water from the vacuoles of the original inclusions, which formed under the same conditions as the type B inclusions, it is reasonable to suppose that, during this selective leakage, the concentration of the solution remaining in the inclusion vacuole increased. Taking into account the proportion of the vapour bubbles in the inclusions of the types B and C, one may suppose that the increase in concentration reached at least 20%, i.e. the original salt concentration should be close to 4 wt. %.

FINAL REMARKS

The interrelation between the water environment in the analcime structure estimated by means of the IR method, and Tc seems to be well documented. The parameters (frequency and integrated intensity) of both of the selected bands could provide approximate information about the thermal conditions of analcime crystallisation. Taking into consideration the relationships between Tc and the spectroscopic data (water position, water amount) one can conclude that reconstruction of the temperature crystallisation needs additional information about the crystallisation system as well as about the structure of the crystallised analcime. The additional information is especially useful when the second type of water is considered. The most essential information about the crystallisation conditions is the solution composition. This can be obtained by means of fluid inclusion study. The next information which could be very useful, albeit difficult to estimate, is the duration of anal-

Fig. 5. Water loss by an inclusion in analcime on heating at 280°C and regaining of water by the same inclusion during a one-year storage; a – untreated inclusion, b – "dried" inclusion, c – inclusion after the storage period; L – liquid solution, V – vapour phase, the inclusion size 8 μm

cime formation. Some properties of the water environment in the structure could give us approximate information about it. The most important information is about the symmetry of the structure, although this information we can receive partly from water environment studies. Water environment precisely describes the structure symmetry. Recognition of the water template in the analcime structure only with the help of IR is not sufficient. Furthermore, the experiment have been carried out within a very narrow range of Tc. The water template for the analcime crystallised at lower temperature is much more complicated (BAKAKIN 2001, in press).

The two-phase type B inclusions that occurred in the inner parts of the investigated analcime crystals, synthesized at 300°C and 2 kbar, yielded homogenisation temperatures, which were the basis of estimations of the trapping temperature (285-295°C) close to the crystallisation temperature. Thus these inclusions may be used in the determination of the formation conditions of a zeolite-type mineral. The behaviour of fluid inclusions in the minerals of the zeolite-type structures, which were affected by the change in the water content, mainly water escape (i.e. "dried"), during storage under laboratory conditions in water saturated air at room temperature, is typical (Text-fig. 5). After a relatively long time (months) the inclusions regain water in the inclusion vacuole. The "dried" inclusions preserved a liquid phase constituting 20 to 30 % of the vacuole volume, in some cases even less (liquid phase became invisible). After one year in humid air, water was partly introduced into the inclusion vacuoles and the amount of the liquid phase ranged from 50 to 60% of the inclusion vacuole.

The above investigations proved the common leakage of water from the solutions trapped in inclusions in analcime. The leakage occurred through the crystal lattice of the mineral. However, proper handling of the inclusions occurring in the inner parts of the mineral grains, may result in interpretable data. Nevertheless, the usefulness of inclusions in the minerals of the zeolite-type structure probably is limited to the specimens which crystallized recently, perhaps even only to those from presently active hot springs. This conclusion is supported by the experiment, that demonstrated the migration of water through the crystal lattice even at room temperature.

Compilation of the two data sets from the spectroscopic and fluid inclusion studies seems to be a reasonable method for analcime Tc estimation. Both data sets are necessary to draw reasonable and definite conclusions about the process. Precise information on the water template pattern in the analcime structure could help to predict the water behaviour in the structure and would provide thereby useful information for the interpretation of fluid inclusion data. Determination of solution composition by means of fluid inclusion study is the introductory information, to which should be added the determination of the water environment in the analcime structure. In both methods the duration of analcime crystallisation influences the accuracy of Tc determination. The estimation of that factor is difficult, but not impossible. Some information on analcime growth rate is available in the literature. Moreover, it is necessary to take into account the length of the period that has elapsed from the mineral crystallisation until its unearthing, and the duration and conditions of the laboratory storage, because both inclusion contents and water in the mineral structure are sensitive to conditions differing from those that obtained during the mineral crystallisation.

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