



Identification of anhydrous CaCl_2 and KCaCl_3 in natural inclusions by Raman spectroscopy

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ABSTRACT

Anhydrous chlorides - CaCl_2 , and KCaCl_3 (chlorocalcite) were identified as mineral inclusions in halite from the Siberian Large Igneous Province at the contact of magmatic intrusions and evaporates. Chlorocalcite was also found as daughter mineral in polyphase hypersaline inclusions. While Raman spectra of KCaCl_3 (chlorocalcite) in natural inclusions are similar to spectra of synthetic analogue, the Raman spectra of natural CaCl_2 do not correspond to the published Raman spectra of synthetic CaCl_2 . Simulations of Raman spectra using *ab initio* density-functional theory (DFT) allowed us to calculate the spectra of individual polymorphs of CaCl_2 and to discriminate anhydrous CaCl_2 phases in natural inclusions and synthetic CaCl_2 . In the spectrum of the *Pbcn* polymorph of CaCl_2 twelve different peaks could be identified at 74, 95, 99, 107, 124, 158, 164, 179, 212, 236, 244, 256 cm^{-1} in contrast to five peaks in the spectrum of the *Pnmm* polymorph of CaCl_2 at 115, 157, 160, 211 and 252 cm^{-1} . Naturally occurring CaCl_2 in inclusions in halite consist of *Pbcn* polymorph only, which probably results from a mechanical stress on cooling from magmatic to ambient temperatures. However, the Raman spectra of the synthetic CaCl_2 corresponds to the *Pnmm* phase with small contributions of the *Pbcn* phase.

Raman spectra of synthetic KCaCl_3 with main peaks at 58, 67, 90, 97, 133, 139, 147, 193 cm^{-1} agrees well with the spectra of chlorocalcite in the natural inclusions. Positions of each atom in the KCaCl_3 structure were refined using the density-functional theory. There are no imaginary phonon modes for the optimized structure, indicating that the structure of KCaCl_3 is stable. Calculated Raman spectrum is in a good agreement with the Raman spectrum of synthetic and natural KCaCl_3 samples.

1. Introduction

Highly saline paleofluids and molten salts are reported from a wide range of geological environments (e.g. Roedder, 1992). It is widely recognized, that chloride-rich brines play an important role in transport and precipitation of metals to form economic deposits in diverse geological settings, but especially in magmatic-hydrothermal and metamorphic systems (Reyf and Bazheyev, 1977; Kamenetsky et al., 2002; Newton and Manning, 2010; Lecumberri-Sanchez et al., 2015; Giuliani et al., 2018).

Fluid inclusions provide the best available means to characterize the

physical and chemical properties of fluids in fossil hydrothermal systems (Naumov et al., 1990; Andreeva et al., 1998; Bodnar et al., 2014). One of the most important high-salinity hydrothermal systems is the geochemical system $\text{NaCl-KCl-CaCl}_2\text{-H}_2\text{O}$ that often includes deep-crustal and upper mantle fluids. Chemical analysis of associated fluid inclusions and their daughter minerals can help to understand the connection between magmatic processes and the composition of magmatic-hydrothermal fluids (Audetat et al., 2008). The high salinity fluids and melts, trapped in multiphase fluid inclusions, often host one or more chloride daughter minerals at ambient temperature due to the precipitation of solid salts on cooling of the inclusions from trapping

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temperatures. Chloride daughter minerals in inclusions from magmatic-hydrothermal environments are mostly reported as NaCl (halite), KCl (sylvite) and several other chloride crystals.

Correct identification of the chloride daughter minerals in brine inclusions enables one to constrain the composition of ore-forming paleofluids and can help to understand the ways of transport and precipitation of metals from hydrothermal fluids. However, only a limited number of analytical tools can be applied for their identification due to the typically small size of the daughter minerals (usually a few microns in diameter) and their exceptionally high hygroscopicity on opening of the host inclusions. The prime analytical technique is Raman spectroscopy that provides a quick, non-destructive and easy available identification method for their identification by comparison with published Raman spectra of chlorides (see recent reviews of Frezzotti et al., 2012 and Hurai et al., 2015). Despite the ionic nature of the bonds in chloride salts with orthorhombic spatial symmetry they display a rich phonon spectra. The Raman response of the crystals was found strong enough for the structure-spectrum correlation study. Furthermore, reference spectra of several other synthetic chlorides have been reported recently: CaCl_2 (Uriarte et al., 2015), $\text{K}_3\text{NaMnCl}_6$ (Kurosawa et al., 2016) and KFeCl_3 (Koděra et al., 2017). However, there is still a lack of published Raman spectra of some less common minerals hosted in fluid inclusions or the published spectra of synthetic minerals are different from those found in fluid inclusions.

The goal of this work is to provide the Raman spectrum of synthetic KCaCl_3 and to understand the differences of Raman spectra collected from synthetic and natural CaCl_2 samples. Raman spectra of all these chloride solids have been calculated using *ab initio* density-functional theory (DFT) and compared with those of synthetic solids and those in natural inclusions. Naturally occurring anhydrous chloride minerals, found in halite and apatite from the Siberian Large Igneous Province were used for this purpose. The results of this study can be applied for a clear identification of these minerals in highly saline fluid inclusions by Raman spectroscopy.

2. Geological background

The samples with studied inclusions were taken from endogenic deposits of the Siberian Platform (Fig. 1). The Siberian Platform has been subjected to intensive magmatic activity in the Permian to Early Triassic. The Siberian Traps represent one of the most voluminous flood basalt provinces on the Earth (Burgess and Bowring, 2015). The basement of the Siberian Traps is heterogeneous and consists of metamorphosed Archean and Early Middle Proterozoic formations (Mazurov and Bondarenko, 1997). The sedimentary cover comprises Riphean and Vendian carbonate terrigenous deposits, Cambrian saliferous carbonates, Middle Palaeozoic terrigenous carbonates, Upper Palaeozoic coal-bearing rocks and Lower Mesozoic volcanoclastic sediments (Kontorovich et al., 1997).

Two main features of geology of the Siberian platform are relevant to this study. One is the widespread occurrence of a thick halite-bearing succession among the Lower Cambrian carbonates. The salt thickness is particularly important in the central and southern platform area where it reaches 350 m. The individual salt beds are 10 to 50 m thick, and are often intercalated with dolomites. The second important feature is the ubiquitous presence of dykes, sills and complex volcanic–tectonic edifices. The lateral extent of individual sills reaches up to several tens to hundreds of kilometers. The thickness of sills is highly variable from a few centimeters up to three hundred meters. The maximum total thickness of intrusive bodies within a sedimentary sequence, as determined in the northwestern part of the Siberian platform, reaches 1300 m. The emplacement of the high-temperature gas-saturated magma took place over a rather short period during the Permian and Early Triassic. The sills have caused significant alteration of the sedimentary rocks. The volcanic–tectonic edifices cut through the sedimentary cover from the Vendian to the Lower Triassic and are rooted in

the crystalline basement (Mazurov and Bondarenko, 1997). The Siberian Trap event is associated with mineral deposits of various types, including apatite-magnetite mineralization.

The huge area of the Cambrian evaporite deposits and intense magmatic activity provide a unique opportunity to study salt-magma interaction associated with different styles of magmatic intrusions:

- I. metamorphosed salts in the vicinity of trap intrusions (Kochumdek);
- II. halite-magnetite rocks from volcanogenic edifices (Korshunovsk Fe-ore deposit);
- III. chloride segregations in kimberlites (Udachnaya-East kimberlite pipe).

Samples of salts from both I and II environments are external to the magma body and have clearly an evaporite origin (Grishina et al., 1992; Mazurov et al., 2007). The nature of chloride segregations in kimberlites is intensively debated, while a co-magmatic origin of chlorides is mostly suggested (Kamenetsky et al., 2014; Kitayama et al., 2017; D'Eyrames et al., 2017), the evaporitic source of chlorides (*i.e.* xenoliths) is also proposed (Grishina et al., 2014a, 2014b; Kopylova et al., 2016).

3. Samples

Most studied inclusions are hosted by metamorphosed halite from different endogenic environments of the Siberian Igneous Province. Metamorphosed salts in the vicinity of trap intrusions were studied from a deep borehole in Kochumdek, located close to the Kochumdek River, the right tributary of the Podkamennaya Tunguska River in East Siberia. The Kochumdek sample was taken from a depth of 2900 m, 7 m above a 300 m thickness dolerite sill (Fig. 2).

Halite-magnetite rock was studied from core samples from the Korshunovsk Fe-ore deposit (Fig. 3A). Cavities filled by halite, a few to 10 cm in diameter, are common throughout the magnetite rock and contain euhedral apatite and forsterite crystals (Fig. 3B–E). Anhydrous chlorides were found in halite from cavities, as well as in spatially associated high temperature minerals, apatite and forsterite.

Samples of chloride segregations in unserpentinised kimberlites were collected from stockpiles of the Udachnaya pipe (Fig. 4).

4. Methods

From the samples described above, cleavage plates of halite and doubly polished thick sections of apatite crystals (150 to 350 μm thick) were prepared. Fluid inclusion petrography including chronological sequence of fluid inclusions was determined by optical microscopy on an Olympus BX51 microscope combined with an Olympus Color View III camera connected to a PC. The inclusions in apatite and forsterite were exposed to the surface in a water-free environment using oil-based diamond pastes to avoid the loss of water-soluble minerals. After polishing, oil was removed by Petroleum Benzene.

The microthermometric study of CO_2 inclusions was performed on a Linkam stage (model THMS600). The stage was calibrated against the melting points of pure CO_2 inclusions (-56.6°C) and pure water (0°C). Precision of these measurements is estimated to be $\pm 0.1^\circ\text{C}$. The thermometry of inclusions in forsterite and apatite was carried out on a high-temperature heating stage T-1500 (Osorgin and Tomilenko, 1990). This stage was calibrated against the melting points of synthetic standards: $\text{K}_2\text{Cr}_2\text{O}_7$ (398°C), CsCl (645°C), NaCl (800°C), Au (1063°C), and Mn (1240°C). Precision of these measurements is estimated to be $\pm 5^\circ\text{C}$.

The composition of inclusions was determined by micro-Raman spectrometry and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) on an Oxford Instruments INCA Energy 350 microanalyzer at the Analytical Center for multi-

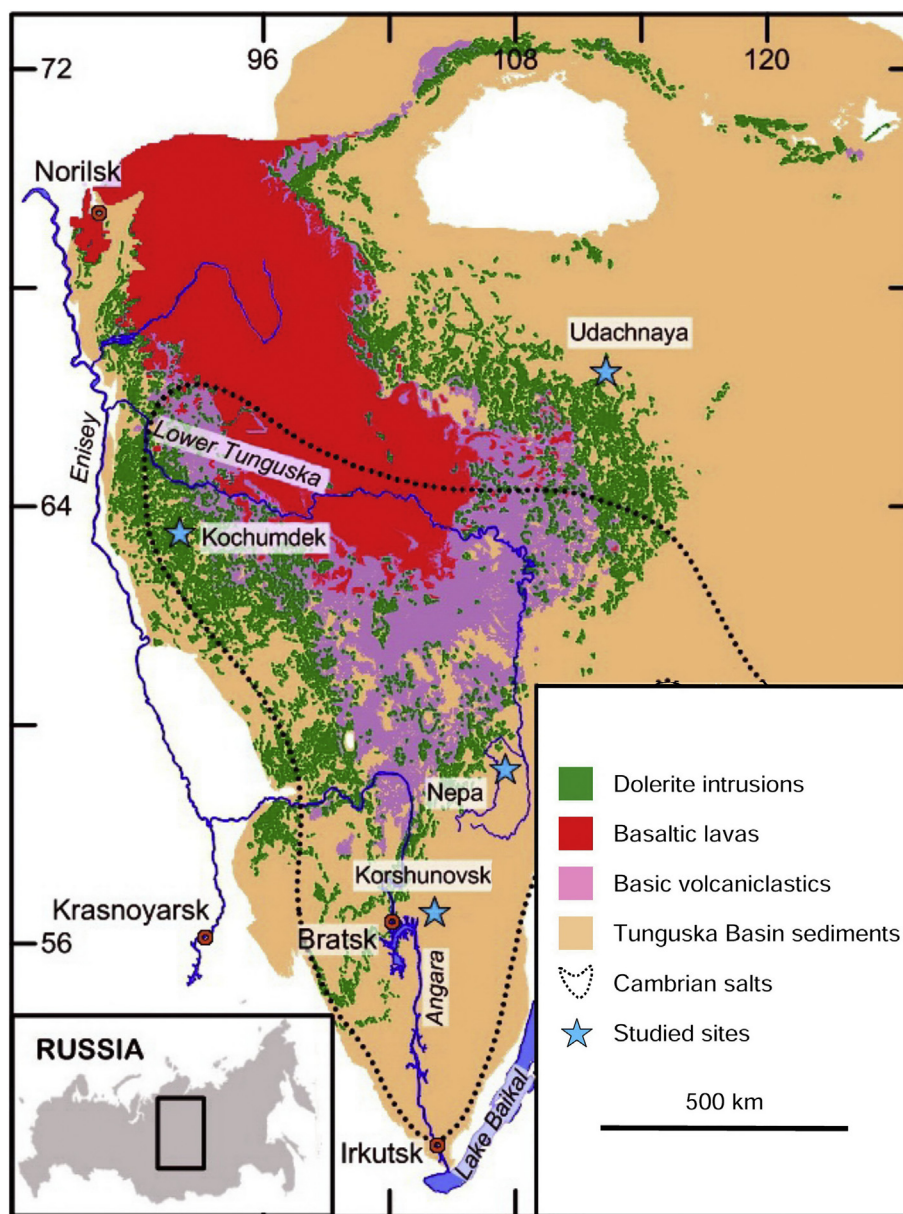


Fig. 1. Sample locations shown on the schematic geological map of the Siberian Large Igneous Province, represented by products of Permian to Early Triassic volcanism, emplaced on the Tunguska basin sediments (Archean to Upper Palaeozoic), including the extent of Cambrian saliferous carbonates. Modified from Polozov et al. (2016).

elemental and isotope research of the Siberian Branch of the Russian Academy of Science in Novosibirsk. A liquid nitrogen-free large area EDS X-Max-80 silicon drift detector is installed on a JEOL JSM-6510LV scanning electron microscope. EDS spectra were collected at an acquisition time of 60 s, an accelerating voltage of 15 kV, a beam current of 1 nA, and a spot diameter of $\sim 1 \mu\text{m}$. The EDS spectra were optimized for quantification using the standard XPP procedure included in the INCA Energy 350 software.

The Raman spectra of natural samples were recorded in Novosibirsk on a Horiba Jobin Yvon LabRam HR800 spectrometer coupled to a 1024 pixel LN/CCD detector, using as excitation source the double harmonic of Nd:YAG solid state laser with a narrow band of nominal wavelength 532 nm and a beam power 30 mW (up to 5 mW on samples; Goryainov et al., 2014). Raman spectra were collected in back-scattering geometry, using an Olympus BX41 microscope. The spectral resolution of the recorded Stokes side of the Raman spectra was set to 2cm^{-1} at Raman shift of $\sim 300 \text{cm}^{-1}$. This resolution was achieved by

using one grating with 1800 grooves/mm and equal $100 \mu\text{m}$ slit and confocal pin hole. The microscope was equipped with an Olympus $50\times$ objective lens of $\text{WD} = 0.37 \text{mm}$ and 0.75 numerical aperture, the focal spot diameter is $\sim 2 \mu\text{m}$. The lines from a Ne lamp were used to calibrate the spectrometer. An Edge filter eliminates the Rayleigh scattering which suppressed low-frequency Raman spectrum below 60cm^{-1} and attenuated the range of $60\text{--}100 \text{cm}^{-1}$. Residual laser beam permitted additional calibration and correction of each recorded spectrum. The spectra were recorded in the 10 to 3800cm^{-1} range. The accuracy and precision in the wavenumber Raman shift is $\pm 1 \text{cm}^{-1}$. PeakFit software package was used for deconvolution of Raman spectra into Voigt amplitude contours (Canberra Technical Publications).

For the preparation of synthetic KCaCl_3 sample, the following chemicals were used: KCl (Sigma-Aldrich, 99.5%), CaCl_2 (CaCl_2 , Sigma-Aldrich, 99.9%, dried 3 h at 250°C), both of reagent quality. Sample preparation consisted of mixture containing 50 mol% KCl and 50 mol% CaCl_2 (molar ratio $\text{KCl}:\text{CaCl}_2 = 1:1$). Sample was weighed in a glove

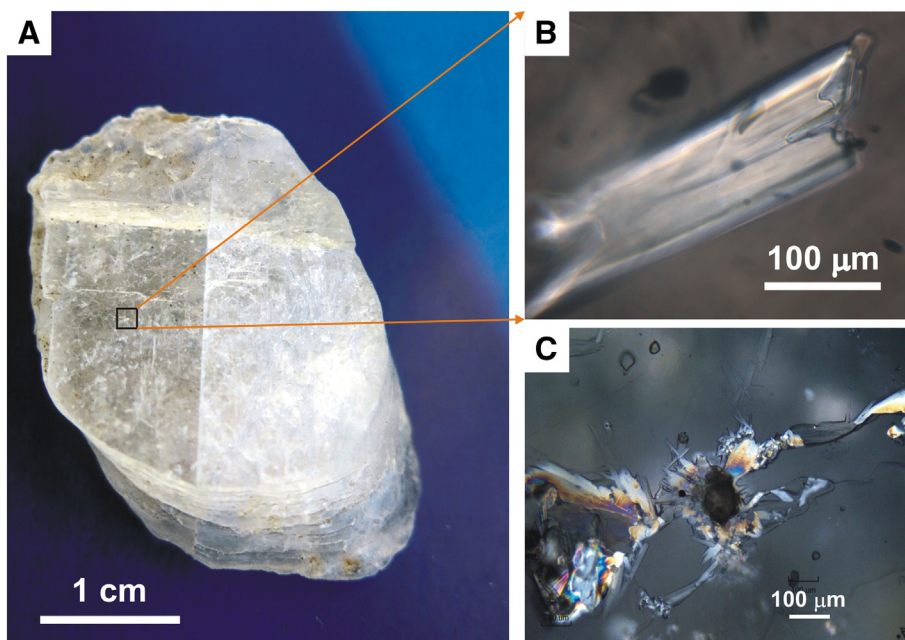


Fig. 2. Images from the rock salt of the Kochumdek borehole: A - core sample from the Kochumdek borehole; B - CaCl_2 inclusion in halite (transmitted light); C - cleavage plate surface with empty cavity of exposed CaCl_2 inclusion, surrounded by CaCl_2 -hydrates (transmitted light).

box under inert atmosphere (Ar, Messer, 99.999% purity), homogenized, then introduced in a platinum crucible and transferred into a preheated furnace at 80 °C under dried argon atmosphere. The experiment was done in tightly closed vertical resistance furnace with water

cooling. Thereafter, the sample was heated to 760 °C at rate of 5 °C/min. The mixture was kept at this temperature during 1 h and then cooled to room temperature spontaneously. At the end, the sample was homogenized and analyzed by XRD and Raman methods. The

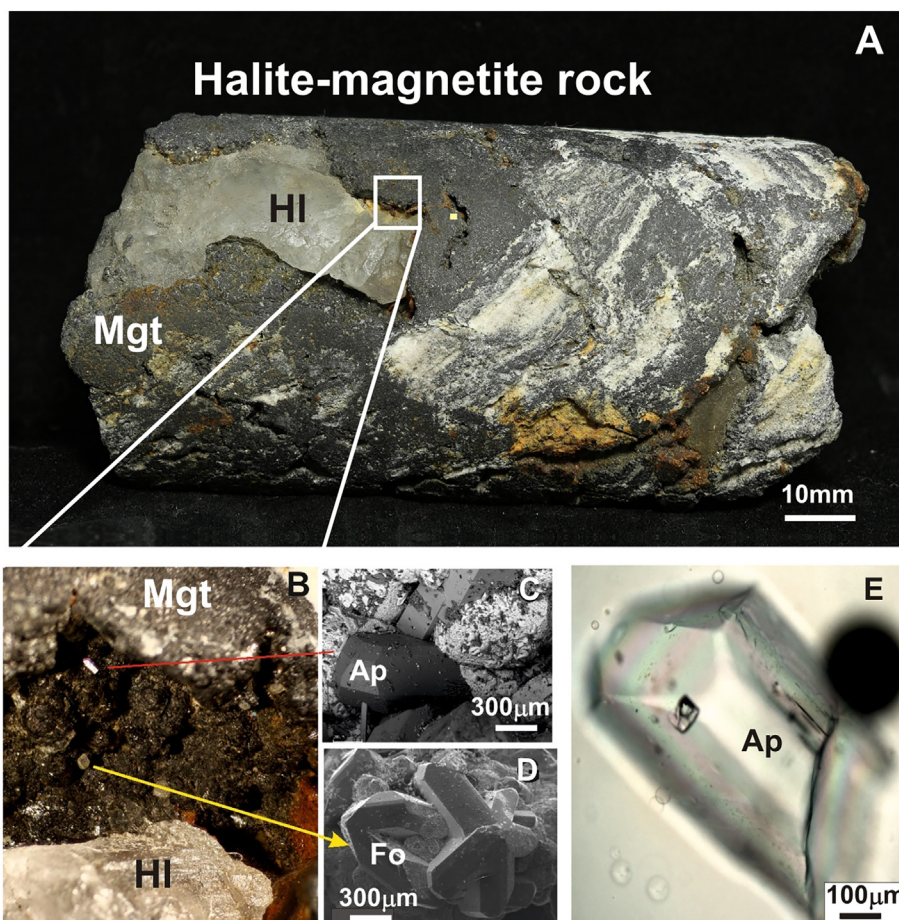


Fig. 3. Images from the studied halite-magnetite rock from the Korshunovsk FeO deposit (A) Borehole sample of with halite filling a cavity; (B) Enlarged surface of the cavity, incrustated by euhedral crystals of apatite (C) and forsterite (D) (C and D are SEM images); (E) apatite crystal mounted in epoxy with a polyphase fluid inclusion.



Fig. 4. Chloride segregation in kimberlite from the Udachnaya-East pipe.

temperature control and the data processing were performed using a computerized measuring device, developed at the Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava (Multi-component model for thermal analysis data collections - National Instruments Japan (Japan), where the data collections run on-line under Labview™ software). The temperature of the sample was controlled by a Pt-PtRh10 thermocouple, calibrated on the melting points of pure NaCl and NaF. The accuracy of the temperature difference measurement between the temperatures of primary crystallizations of the given mixtures was ± 1 °C.

The X-ray powder patterns of synthetic KCaCl_3 were collected at the Institute of Inorganic Chemistry, Slovak Academy of Sciences on a PanAnalytical diffractometer equipped with a curved Ge (111) monochromator placed in the primary beam and a linear position sensitive detector. In order to achieve a better resolution, Cu $K\alpha$ radiation was used. The XRD patterns were taken in the 2θ range of 7 – 90° at room temperature.

Micro-Raman analysis of synthetic KCaCl_3 was performed using a DXR SmartRaman spectrometer associated with a DXR Raman microscope (Thermo Fisher Scientific, U.S.A.). Raman spectra were obtained by rotating the powder sample, immersed in a sealed glass capillary. Spectra were excited at room temperature using the 532 nm line of a Nd:YAG laser, with power emission conditions of 5 mW on the sample surface. Objective lens of $100\times$ with a pinhole or slit aperture of $50\ \mu\text{m}$ was used. Each spectrum was collected with exposure time 5 s and 60 accumulations, in order to eliminate accidental contamination by cosmic radiation. Peak position was calibrated using a $520\ \text{cm}^{-1}$ band of Si-wafer and using a neon lamp.

4.1. Calculation details for Raman spectra of CaCl_2

Structural optimization, energy and Raman calculation were carried out by the CASTEP software package (Clark et al., 2005; Segall et al., 1996; Refson et al., 2006) based on *ab initio* density-functional theory (DFT). Initial structures of CaCl_2 with the space group *Pnmm* (Tomaszewski, 1992,) at ambient pressure and *Pbcn* at high pressure conditions (Liu et al., 2007) were fully optimized using the local density approximation (LDA) with Perdew-Zunger-Ceperley-Alder (PZ) exchange-correlation functional (Perdew and Zunger, 1981; Ceperley and Alder, 1980). Calculations were performed using Norm Conserving

pseudopotentials with 3s3p3d4s electrons used as valence for Ca atom and 3s3p3d electrons used as valence for Cl atom. The self-consistent field (SCF) procedure was used with a convergence threshold of $2.0 \cdot 10^{-8}$ eV/atom. To obtain ground state properties of fully relaxed structures, lattice parameters and fractional positions of atoms have been fully optimized. Cell relaxations were achieved with the convergence criterion for forces on atoms set to 0.005 eV/Å, and for total stress < 0.1 GPa, and for the maximum atomic displacement between iterations set to 0.002 Å. Energy cut off was set to be 1000 eV, and the Brillouin zone was sampled by $4 \times 4 \times 6$ k-points for CaCl_2 with space group *Pnmm* and $4 \times 4 \times 4$ points for the CaCl_2 with space group *Pbcn* using the Monkhorst-Pack scheme (Monkhorst and Pack, 1976). The phonon spectra at Γ point and Raman tensors were calculated within density functional perturbation theory and finite displacement method (Porezag and Pederson, 1996 and Refson et al., 2006), based on the crystal system type. Raman spectra were simulated by a Lorentzian distribution with fixed HWHM equal to $4\ \text{cm}^{-1}$.

4.2. Calculation details for Raman spectra of KCaCl_3

All the structural optimization, energy and Raman calculation were carried out by the CASTEP program (Clark et al., 2005; Segall et al., 1996; Refson et al., 2006) using the density-functional theory (DFT). Initial orthorhombic structure of KCaCl_3 with the space group *Pmna* (Seifert et al., 1985) was fully optimized using the local density approximation (LDA) and generalized gradient approximation (GGA) with exchange-correlation functionals Perdew-Burke-Ernzerhof (PBE) and Perdew-Burke-Ernzerhof for solids (PBEsol) (Perdew et al., 1996, Perdew et al., 2009). The coordinates of atoms were presented without estimated standard deviations (esd) (Seifert et al., 1985), so the bond length precision could not be obtained and quality of Rietveld refinement is unclear.

5. Results

5.1. Description of inclusions

5.1.1. Inclusions in halite

Halite from reaction zones between intrusive magma and salt rocks is characterized by abundant solid chloride and brine inclusions, spatially associated with dense CO_2 inclusions (Fig. 5). CO_2 -rich phase occurs as intergrowth with chlorides and in isolated monophase inclusions. KCl and KCaCl_3 mineral inclusions are ubiquitous in the environments of the three types of magmatic intrusions: at the vicinity of trap intrusions, in halite cavities of magnetite near basaltic diatremes and in halite segregations in kimberlites. Anhydrous CaCl_2 solid inclusions were found only in two localities: at Kochumdek in contact with trap intrusion and in halite cavities of magnetite in the Korshunovsk iron ore deposit.

Kochumdek deposit contains rare samples preserved contact metamorphic halite while generally metamorphic halite was removed by dissolution during intensive late hydrothermal activity (Warren, 2016). Abundant CaCl_2 solid inclusions were found often in overgrowths with KCaCl_3 solids. They are spatially associated with liquid CO_2 inclusions and mineral inclusions such as periclase, diopside, amphibole, muscovite, quartz, sulphur, chalcopyrite, pyrite and pyrrhotite. Homogenization temperatures of CO_2 inclusions to the liquid phase vary from -9 to -15 °C in halite from Kochumdek (suppl. Fig. 1). No liquid water was observed visually or by Raman spectroscopy using long acquisition times (30–60 s) and 10 accumulations in this inclusion assemblage (suppl. Fig. 2).

All the solid inclusions presented in this work are anhydrous chloride inclusions as shown by the absence of the OH-stretching band in their Raman spectrum. They have rounded, cubic, euhedral or irregular shapes (Fig. 5). The size of the inclusions varies from several to $200\ \mu\text{m}$, sometimes reaching 500 – $600\ \mu\text{m}$. Intergrowths between

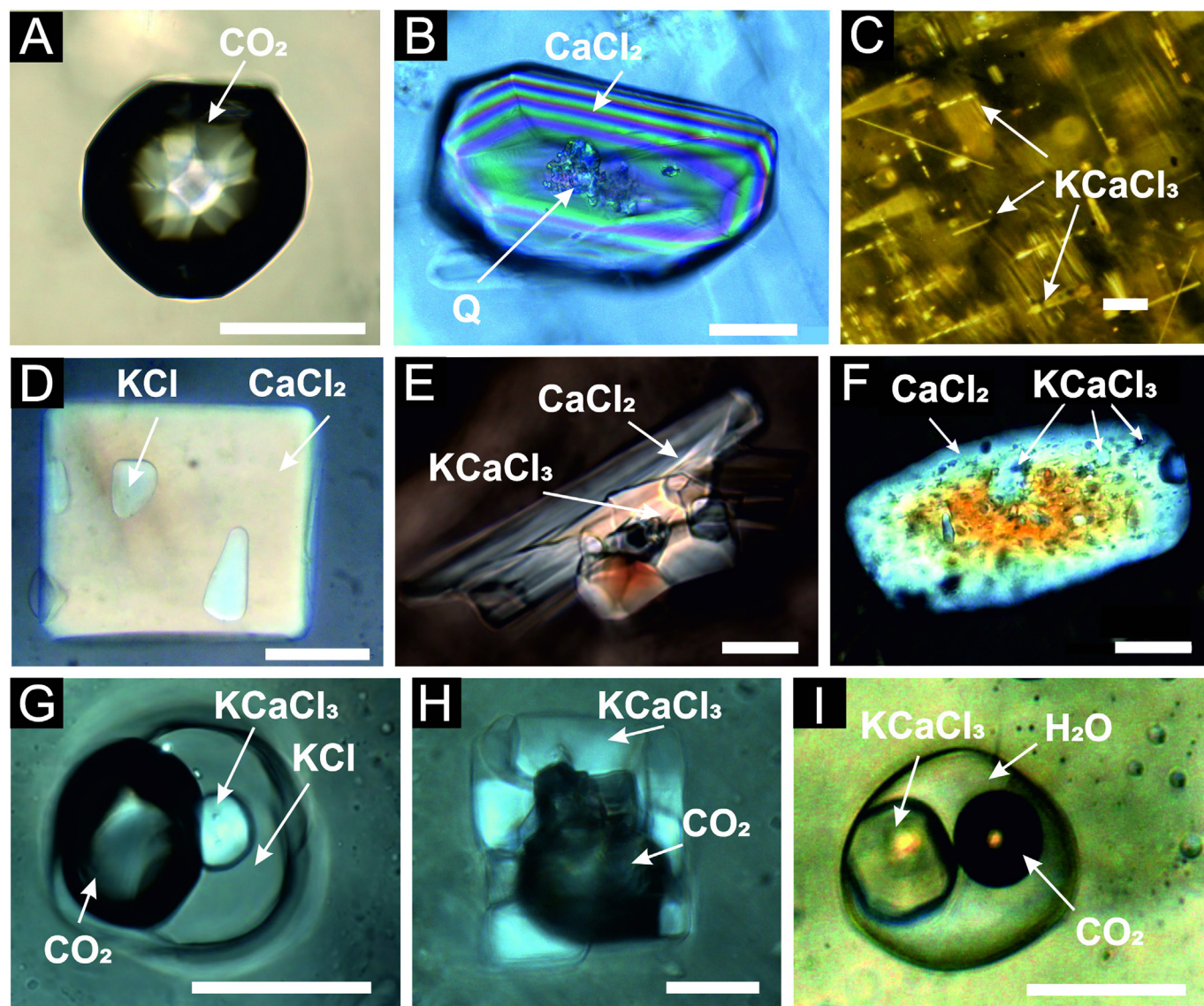


Fig. 5. Photomicrographs of representative anhydrous chloride minerals and coexisting CO_2 inclusions, in halite from different environments: contact with a trap intrusion (A-liquid CO_2 inclusion and B, C-solid CaCl_2 inclusion), coexisting in halite from the Kochumdek well. Integrowth of different chlorides from the Korshunovsk Fe-ore deposit (D, E, F). Integrowth of chlorides and CO_2 inclusions from chloride xenoliths in Udachnaya-East pipe kimberlites (G, H,) and brine inclusion with KCaCl_3 daughter mineral (I). All photomicrographs are in crossed Nicols. Scale bars are 50 μm . Q-quartz.

different individual chloride minerals are common (Fig. 5A, D, E, F).

Brine inclusions containing KCaCl_3 as daughter minerals were found in hydrothermally recrystallised halite in the environments of all types of intrusion (Fig. 5I) and in apatite from the Korshunovsk Fe ore deposit.

5.1.2. Inclusions in apatite and forsterite

Apatite and forsterite from the Korshunovsk FeO deposit contain polycrystalline inclusions that have no liquid water at room temperature. According to combined SEM-EDS and Raman analyses their major components are chloride daughter minerals and an unknown Fe-Mg-OH-bearing silicate. Forsterite from Korshunovsk is considered to be a reaction product between the basalt magma and salt-carbonate sedimentary deposits (Mazurov et al., 2007). According to EDS analyses it is quite Mg-rich ($\text{F}_{0.92-96}$).

NaCl , KCl and KCaCl_3 daughter minerals have been found in apatite hosted inclusions and only NaCl , KCl in forsterite hosted inclusions. Melting of chloride daughter minerals in apatite occurred at 400–450 °C and melting of Fe-Mg-OH-bearing daughter minerals occurs at

500–540 °C. Volume decrease of vapour bubble occurred at 600 °C, and then inclusions decrepitated. Total homogenization was observed in forsterite-hosted inclusions at 720–840 °C.

5.2. Composition of CaCl_2 -bearing anhydrous inclusions

After opening, solid chloride inclusions transformed immediately to a liquid due to deliquescent properties typical of chloride minerals. Dissolution of KCaCl_3 in moisture resulted in formation of KCl crystals and CaCl_2 solution. After precipitation generally isotropic crystals form inside the cavity of opened inclusion and mostly anisotropic crystals surround the cavity. The SEM images of products of the incongruent dissolution of KCaCl_3 show octahedral crystals in the cavity and a mixture of crystals surrounding the cavity. The elemental composition determined by EDS revealed the presence of K-Cl in octahedral crystals and Ca-K-Cl in the precipitated leachate (Fig. 6). In the case of CaCl_2 inclusions only Ca-Cl was identified by EDS analyses in the precipitated leachate around empty cavities (Fig. 2C).

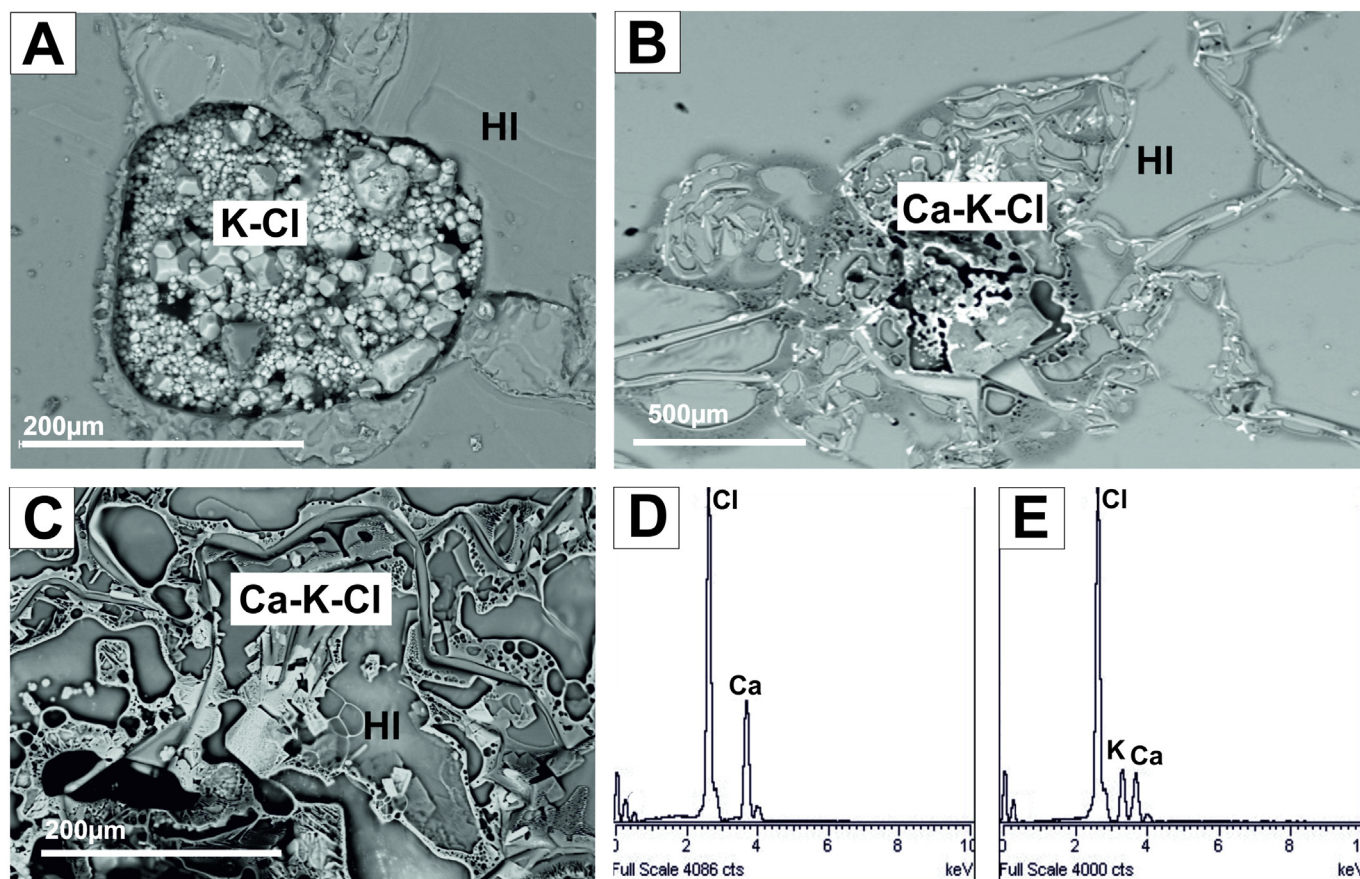


Fig. 6. Backscattered electron images of KCaCl_3 inclusions in halite exposed on air (A, B, C) and representative energy dispersive spectra of the leachate from opened inclusion (D, E), Korshunovsk FeO deposit. Abbreviation: HI—Halite.

5.3. Raman characterization of natural inclusions

KCaCl_3 (chlorocalcite) inclusions are common as daughter minerals in fluid inclusions and as individual mineral inclusions in metamorphosed halite. KCaCl_3 was also found in polycrystalline inclusions in apatite from the reaction zone of dolerites and salt deposits. The absence of water in these solids was demonstrated by the total absence of symmetric and antisymmetric O–H stretching vibrations in the $2700\text{--}4000\text{ cm}^{-1}$ spectral range of the Raman spectra (suppl. Fig. 2A). Only bands below 300 cm^{-1} have been observed with main peaks at 140 , 149 and 195 cm^{-1} wavenumbers which are remarkably constant in between the different samples and match perfectly with the Raman spectra of synthetic KCaCl_3 (see below, Fig. 7).

Similar spectra were found in CaCl_2 inclusions of samples from two different localities. The Raman spectra of natural inclusions confirms the presence of an anhydrous phase, due to the absence of bands in the water stretching region ($2700\text{--}4000\text{ cm}^{-1}$) (suppl. Fig. 2A). Spectra of inclusions from the two different localities display all same major peaks position in the low frequency region: 74 , 95 , 99 , 107 , 124 , 157 , 164 , 179 , 214 , 236 , 244 , 256 cm^{-1} (Fig. 8). Differences in the relative intensity of the Raman peaks can be seen even in between the spectra of samples from the same location. These differences in relative intensity are attributed to different orientations of the crystals in the samples and the anisotropy of the Raman scattering tensor of these crystals. Not all the bands were observed in every spectrum, particularly when Raman signal is too weak to allow minor bands to be detected above the noise level.

As can be seen in Fig. 9 the Raman spectra of natural inclusions of CaCl_2 are different from reported reference spectra of CaCl_2 $Pnmm$ polymorph (Uriarte et al., 2015). *Ab initio* calculations were performed

to understand the discrepancy of Raman spectra collected from synthetic and natural CaCl_2 samples.

5.4. *Ab initio* computations

The Raman spectra of two different CaCl_2 polymorphs with space groups $Pnmm$ and $Pbcn$ were calculated by the density functional perturbation theory. Group theory analysis predicts 6 active Raman modes for the CaCl_2 polymorph with $Pnmm$ space group: $\Gamma_{\text{Raman}} = 2A_g + 2B_{1g} + B_{2g} + B_{3g}$. The calculated Raman spectrum for this polymorph consists of 5 peaks and one shoulder (Fig. 10, top). The $Pbcn$ space group polymorph has 18 active Raman modes: $\Gamma_{\text{Raman}} = 4A_g + 5B_{1g} + 4B_{2g} + 5B_{3g}$ (Table 3), but due to the overlap and low intensity of some modes the Raman spectrum of this polymorph displays only 13 peaks (Fig. 10, bottom).

Reported XRD results of synthetic CaCl_2 nucleated inside capillaries show the presence of two dehydrated phases, the main phase is probably $Pnmm$ CaCl_2 polymorph, coexisting with the metastable $Pbcn$ CaCl_2 polymorph (Uriarte et al., 2015). Crystal structures of both polymorphs of CaCl_2 ($Pnmm$ and $Pbcn$) are plotted in Fig. 11 as a result of *ab initio* simulation. In both structures, Ca cations are 6-coordinated, whereas Cl anions are 3-coordinated.

As mentioned before, there are 6 Raman-active modes of the $Pnmm$ polymorph and 18 Raman-active modes for $Pbcn$ polymorph according to the selection rules for the Raman spectra. Thus, two CaCl_2 polymorphs can be easily distinguished with Raman scattering spectroscopy due to different numbers of bands. In addition, the intensities and wavenumbers of similar type bands (Ca–Cl stretching, bending etc.) are generally different.

In Table 1 the experimental lattice parameters are compared with

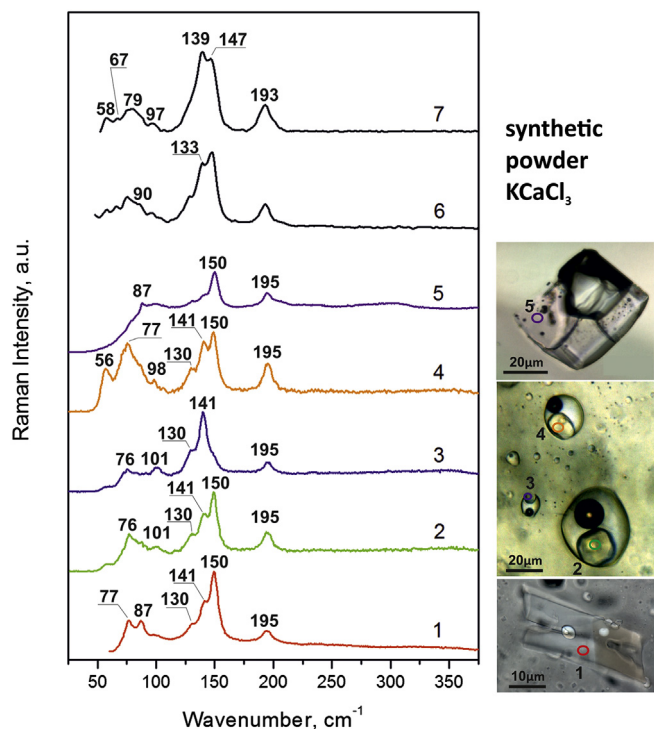


Fig. 7. Comparison of Raman spectra of KCaCl_3 from natural inclusions and synthetic powder: 1 - euhedral crystal inclusion in halite (kimberlite pipe Udachnaya-East); 2-4 - daughter minerals inside brine inclusions in halite (kimberlite pipe Udachnaya-East); 5 - daughter mineral in apatite-hosted polyphase inclusion (Korshunovsk Fe-ore deposit); 6, 7 - synthetic KCaCl_3 powder.

the ones obtained using DFT for KCaCl_3 . The calculated results are in a good agreement with the experimental data, as the mean deviation is $< 10\%$. It is well known, that LDA calculations underestimate equilibrium lattice parameters, while the GGA PBE calculations leads to larger lattice parameters (LeSar, 2013) and our calculations are in agreement with that fact. Thus, calculated bond lengths obtained using LDA are shorter than experimental and longer than experimental in the case of GGA approximation with PBEsol functional. In the case of KCaCl_3 , GGA PBEsol approximation predicted lattice constants close to experimental ones. Atomic positions in the unit cell obtained by GGA PBEsol approximations are presented in Table 2.

The Raman spectra calculated by CASTEP code are comparable with the experimental spectra of synthetic sample of KCaCl_3 (Fig. 12). There are no unstable vibrational modes (modes with imaginary frequency) for all used approximations, thus, calculated structures of KCaCl_3 are stable. It is clear that there is a good agreement between experimental spectra and the calculated one using GGA PBEsol approximation, thus, calculated lattice parameters and atomic coordinates could be used for description of crystal structure of synthetic KCaCl_3 .

6. Discussion

Due to similarities in their structure, the majority of anhydrous chlorides display similar Raman spectra. Thus, the positive identification of an unknown daughter mineral in inclusion must be supported by a good fit of all major peaks in terms of their position. This can be obtained by various approaches, including reference to Raman spectrum of a synthetic compound at ambient and/or low temperature and reference to calculated Raman spectrum based on structural data.

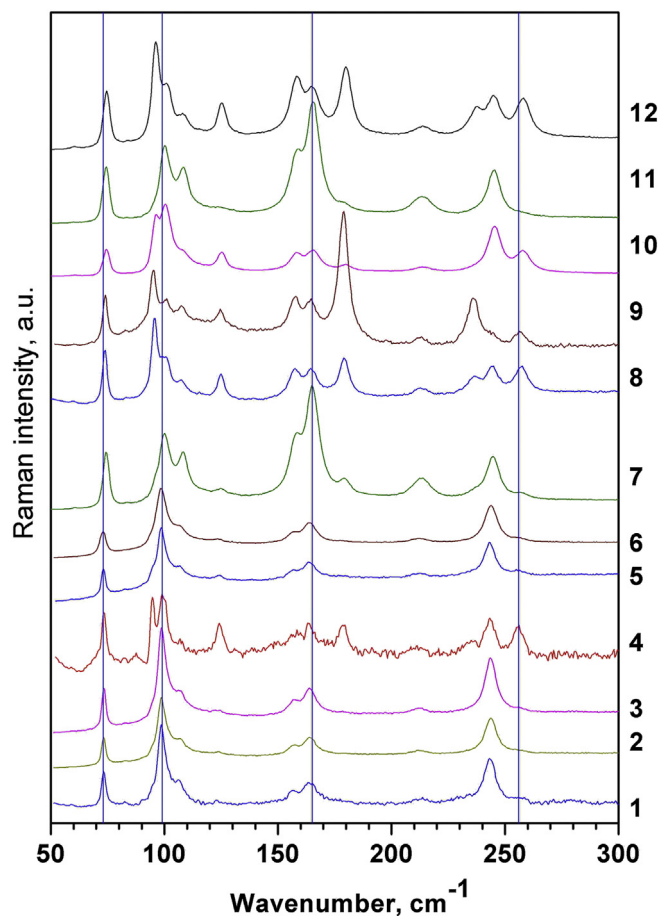


Fig. 8. Low frequency region Raman spectra of anhydrous CaCl_2 inclusions in halite from Korshunovsk FeO deposit (1–9) and Kochumdek borehole (10–12). Vertical lines show Ag modes.

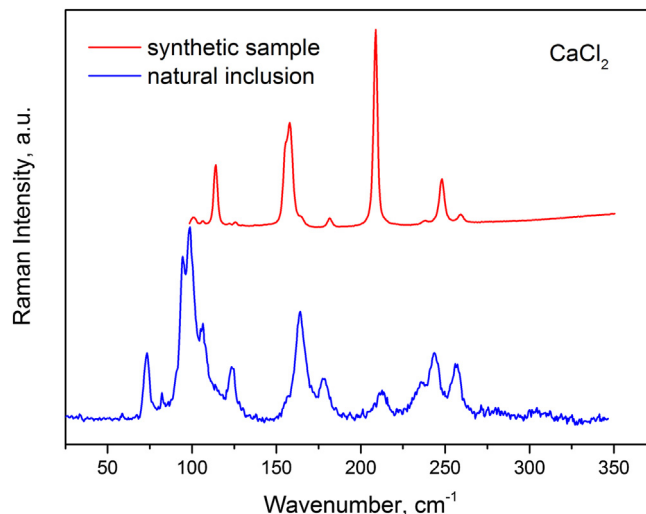


Fig. 9. Comparison of Raman spectra of synthetic CaCl_2 (Uriarte et al., 2015) and representative Raman spectra of natural inclusion in halite from the Korshunovsk Fe-ore deposit.

6.1. Identification of CaCl_2

According to the Raman spectra calculations within DFPT, we attribute the strong peaks in the published spectrum (Uriarte et al., 2015) of the synthetic CaCl_2 to phonons of the $Pn\bar{m}$ polymorph and the weak

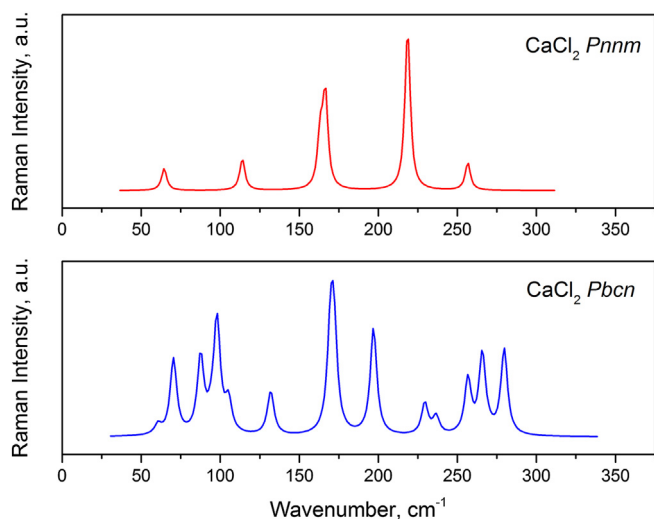


Fig. 10. Calculated Raman spectra of CaCl_2 *Pnnm* (top) and *Pbcn* (bottom) phases. Spectra was simulated for powder (non-oriented) samples.

lines to phonons of the *Pbcn* polymorph (Fig. 13). The calculated vibrational frequencies of CaCl_2 polymorphs agree well with experimental results on synthetic CaCl_2 .

In Table 3 and Fig. 14 the Raman spectrum of natural CaCl_2 in halite from the Korshunovsk Fe-ore deposit is compared to the calculated Raman spectrum of the *Pbcn* polymorph. Apparently, the peaks intensity and wavenumbers are similar to the calculated *Pbcn* polymorph. The vertical lines in Fig. 8 correspond to the symmetric A_g modes at 73, 99, 165 and 256 cm^{-1} of the calculated *Pbcn* phase. The total symmetric A_g modes often exhibit strong Raman intensity, although several B_{1g} , B_{2g} and B_{3g} modes also show a high intensity (Fig. 8). Note that, all Raman spectra from natural CaCl_2 inclusions from this study display a similar Raman shift for all major peaks in the spectra of Fig. 8. As mention before the different band.

intensities for different samples and positions within one sample are attributed to non-fixed orientation of crystals with respect to the direction of the electric field of the exciting laser beam and the anisotropy of Raman scattering tensor of the *Pbcn* phase.

The CaCl_2 (*Pnnm*) crystals show a phase transition sequence which is unique among the AX_2 compounds. In a narrow pressure range, CaCl_2 transforms from the *Pnnm* phase into four different phases: $\alpha\text{-PbO}_2$ (*Pbcn*), EuI_2 ($P2_1/c$), SrI_2 (*Pbca*), and PbCl_2 -type (*Pnma*) structures (Léger et al., 1998). The phase transition from CaCl_2 *Pnnm* structure to

Table 1

Lattice parameters and cell volume of KCaCl_3 obtained from experiment and DFT.

	experiment	LDA	PBE	PBEsol
a , Å	7.561	7.3966	7.6487	7.5362
b , Å	10.48	10.1071	10.5436	10.3498
c , Å	7.255	7.0099	7.3313	7.1748
V , Å ³	574.9	524.0478	591.2435	559.6301

$\alpha\text{-PbO}_2$ (*Pbcn*, $Z = 4$) happens at room temperature in interval 0.5–3 GPa according to the experimental work of Léger et al. (1998) and at 2.9 GPa according to quantum chemistry calculations of Liu et al. (2007).

At ambient pressure the formation of the CaCl_2 *Pbcn* phase has been described in three experimental works (Anselment, 1986; Unruh et al., 1992; Uriarte et al., 2015). Unruh et al. (1992), studied ferroelastic phase transitions in CaCl_2 *Pnnm* by Raman spectroscopy. They remark the appearance of additional Raman modes when cooling from 380 °C. These bands were attributed to the formation of another CaCl_2 phase, $\alpha\text{-PbO}_2$ -type structure (*Pbcn*), as a sequence of mechanical stress in sample induced by domain structure. The formation of this phase due mechanical stress on cooling has also been reported in CaCl_2 crystals grown from the melt by Anselment (1986) who also demonstrate the metastability of this *Pbcn* at room temperature. Finally, Uriarte et al. (2015) synthesized CaCl_2 (*Pnnm*) by dehydration of CaCl_2 solutions using 140 °C temperatures. A mixture of the two CaCl_2 polymorphs was found in the product, mainly that with the *Pnnm* structure with small contribution of the *Pbcn* phase also stable at liquid nitrogen temperatures. Positions of the weak line of the *Pbcn* phase are similar to those of additional lines in Unruh et al. (1992).

According to previous studies, pressure (Léger et al., 1998; Liu et al. (2007) and mechanical stress from cooling (Anselment, 1986; Unruh et al., 1992; Uriarte et al., 2015) seems to be the key factors in the formation *Pbcn* structure. Natural CaCl_2 inclusions in halite samples were formed at high temperatures, according to numerical calculations, the halite crystallization temperature was 600–700 °C in the vicinity of the intrusion (Kontorovich et al., 1997). This temperature interval is higher than the eutectic temperature in the system NaCl-KCl-CaCl_2 (Clark and Reinhardt, 1975) which indicates that the crystallization of CaCl_2 inclusions occurred from an anhydrous ionic salt melt. In the studied halite samples, the pressure of 0.5 GPa was estimated using the density of coexisting CO_2 liquid inclusions (this study, Suppl. Fig. 1). This pressure estimate is also applicable for the crystallization of the mineral inclusions of CaCl_2 (*Pbcn* phase) and KCaCl_3 .

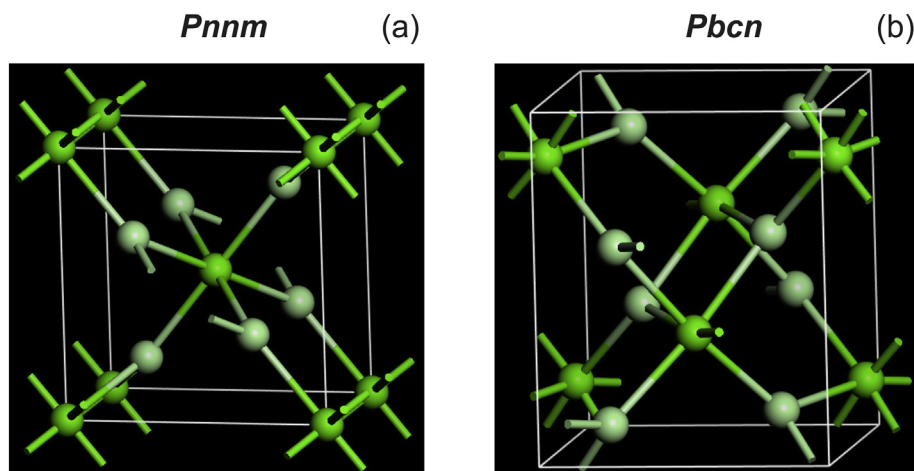


Fig. 11. Structures of two polymorphs of CaCl_2 : *Pnnm* (a) and *Pbcn* (b). In both structures, Ca cations (dark green balls) are 6-coordinated, whereas Cl anions (light green balls) are 3-coordinated. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Fractional atomic coordinates of KCaCl_3 obtained using GGA PBESol approximation.

	x	y	z
K	0.42927	0.25000	0.02403
Ca	0.00000	0.00000	0.00000
Cl1	0.19986	0.05513	0.30459
Cl2	0.53366	0.25000	0.60626

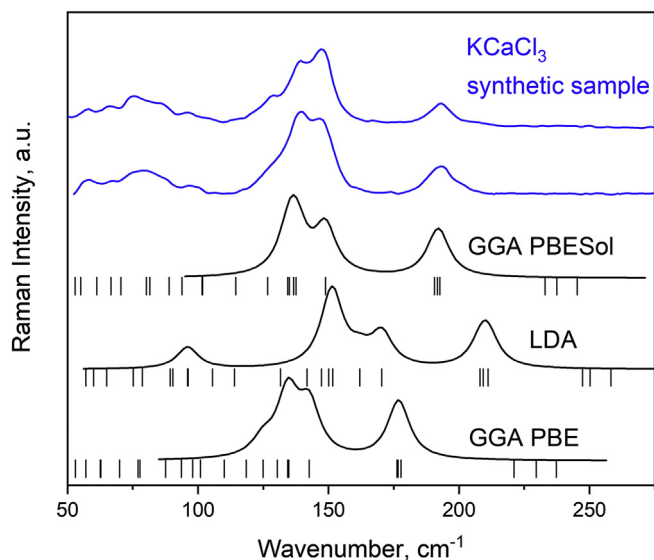


Fig. 12. Comparison of observed Raman spectra of KCaCl_3 synthetic sample with calculated using GGA PBESol, LDA and GGA PBE approximations.

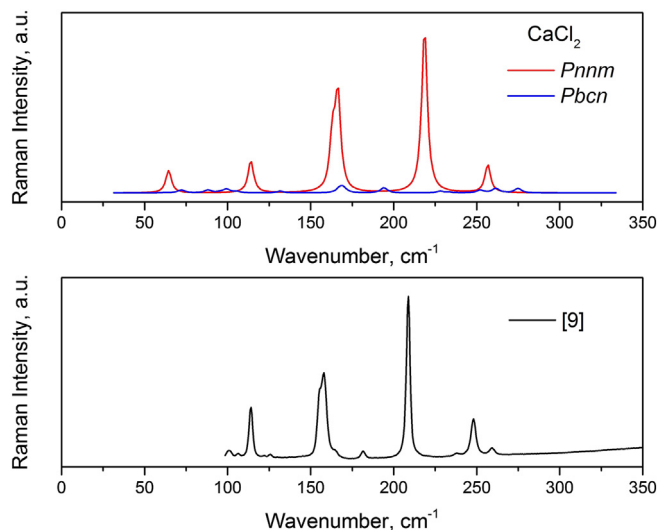


Fig. 13. The calculated Raman spectra of two polymorphs (top) of CaCl_2 and experimental Raman spectra of synthetic CaCl_2 at $-172\text{ }^\circ\text{C}$ (bottom; Uriarte et al., 2015). In order to obtain a better agreement of the simulated Raman spectra of both CaCl_2 polymorphs with the spectrum of synthetic mixture of polymorphs, the intensity of the simulated spectrum of the $Pbcn$ polymorph was reduced by 10 times.

The formation of CaCl_2 $Pbcn$ crystals structure in natural samples is attributed mechanical stress on cooling during the crystallization process from the melt ($600\text{--}700\text{ }^\circ\text{C}$). The presence of only this phase is also explain by the fact that the transition from $Pnmm$ to $Pbcn$ due to pressure begins at 0.5 GPa according to (Léger et al., 1998) which is the estimated pressure in the CaCl_2 inclusions. The natural CaCl_2 ($Pnmm$)

Table 3
The calculated phonon frequencies and irreducible representations (Irreps.) for both $Pnmm$ and $Pbcn$ CaCl_2 polymorphs relative to experimental phonon frequencies of natural and synthesized CaCl_2 .

Synthetic CaCl_2 , (Uriarte et al., 2015) exp.	Natural CaCl_2 (this work), exp.	$Pbcn$, DFT	$Pnmm$, DFT
ν , cm^{-1}	ν , cm^{-1}	Irreps.	Irreps.
		B_{3g} 61	A_g 65
	74	A_g 70	
	95	B_{1g} 88	
		B_{3g} 94	
		B_{2g} 97	
	99	A_g 98	
107	107	B_{1g} 105	
115			B_{1g} 114
125	124		B_{3g} 163
160			B_{2g} 166
	157	A_g 170	
168	164	B_{2g} 172	
182	179	B_{3g} 197	
211			A_g 218
	214	B_{2g} 229	
		B_{1g} 236	
238	236	B_{3g} 257	
	244	A_g 266	
		B_{2g} 270	
		B_{3g} 271	
252			B_{1g} 257
260	256	B_{1g} 280	

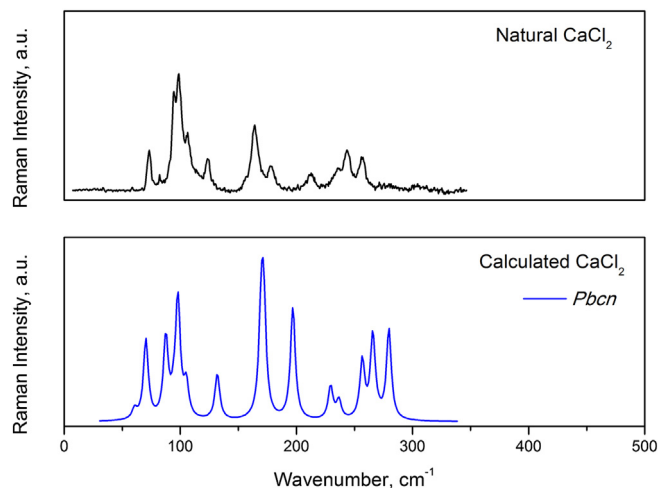


Fig. 14. The natural CaCl_2 mineral inclusions hosted by halite (Korshunovsk Fe-ore deposit) Raman spectrum (top), and calculated Raman spectrum of the $Pbcn$ polymorph (bottom).

(hydrophilite) was discredited and considered to be either antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) or sinjarite ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (Burke, 2006). However, anhydrous CaCl_2 ($Pbcn$ phase), found in halite from the Siberian Large Igneous Province, was unequivocally identified by the Raman spectroscopy in this study.

6.2. Identification of KCaCl_3

Chlorocalcite is a rare chloride mineral, that was originally found in sublimates from active volcanic fumaroles (Anthony et al., 1997), but it was also recently determined as a minor evaporite mineral at some potash deposits in China and Laos (Li et al., 2015). In fluid inclusions, chlorocalcite was first reported as daughter crystals in fluid inclusions in halite from the Prairie Formation (Lowenstein and Spencer, 1990).

Raman spectrum of solid KCl-CaCl₂ inclusion in halite at the vicinity of dolerite intrusions have been reported based on tentative identification according to SEM-EDS and ultra-microchemical analysis (Grishina et al., 1992). In non-evaporate rock environment KCaCl₃ was described from SEM-EDS in high temperature fluid inclusions in olivine gems from Zabardad (Clocchiatti et al., 1981) and chlorocalcite was documented by Koděra et al. (2017) from salt melt inclusions hosted in vein quartz in the Biely Vrch porphyry gold deposit; however, their identification was just tentative based on FIB-EDS analyses. In order to provide a tool for unequivocal identification of this mineral in our fluid inclusions, we have prepared a synthetic analogue of chlorocalcite (KCaCl₃) to determine Raman spectrum of this mineral. Furthermore, the Raman spectrum of KCaCl₃ was also calculated by *Ab initio* computations, using the structural data of (Seifert et al., 1985).

As shown in Fig. 7 the main Raman scattering bands of chlorocalcite in natural inclusions correspond to main bands and intensity of peaks of potassium calcium trichloride from the synthetic analogue as well as those calculated from structural data. The minor differences are probably related to admixtures in the natural samples and to different orientation of analyzed crystals.

7. Conclusions

Raman spectroscopy was used to prove the presence of anhydrous CaCl₂ and KCaCl₃ daughter minerals in natural inclusions hosted by high temperature halite from different endogenic environments of the Siberian Igneous Province.

The presence of chlorocalcite (KCaCl₃) was unambiguously determined by the comparison of the Raman spectra of the daughter mineral and synthetic KCaCl₃. This was further supported by *ab initio* density-functional theory (DFT) simulations which were used to calculate the theoretical structure and Raman spectra of KCaCl₃. Theoretical structure was in a good agreement with previously published data on KCaCl₃ structure and the theoretical Raman spectrum with those of natural and synthetic KCaCl₃ samples.

In case of CaCl₂, the collected Raman spectra from natural inclusions appear to be completely different from those of synthetic samples published in literature (Uriarte et al., 2015). *Ab initio* calculations enabled resolution of this discrepancy. CaCl₂ (*Pnmm*) has a phase transition sequence which is unique among the AX₂ compounds. Indeed, in a narrow pressure range CaCl₂ can crystallize in five different phases. The published Raman spectrum of synthetic CaCl₂ is mainly formed by the *Pnmm* polymorph, which is the most stable phase at room temperature and atmospheric pressure with small contributions of the *Pbcn* polymorph. Our calculated spectra of both of these polymorphs are in a good agreement with the spectra published in literature. The comparison of Raman spectra of naturally occurring CaCl₂ inclusions in halite with the calculated spectra revealed the presence of the *Pbcn* polymorph mostly. This polymorph was probably formed on cooling from magmatic to ambient temperatures.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2018.07.017>.

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