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Characterization of inner structure of limestone by X-ray computed sub-micron tomography

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HIGHLIGHTS

- X-ray computed tomography (CT) is used to visualize limestone inner structure.
- Limestone containing coarser cement of calcite with fluid inclusions is studied.
- Characterization of material is performed by classical petrographic methods.
- 3D distribution of fluid inclusions and air voids in volume is shown by CT.
- CT data are correlated with light microscopy and 3D EDS analysis using FIB-SEM.

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ABSTRACT

Limestones are fundamental industrial and building materials. Sparry calcite as a principal petrographic component of limestones can contain fluid inclusions. A certain amount of fluid inclusions directly influences decrepitation which plays an important role in decarbonisation processes.

In this paper, a limestone with a high content of fluid inclusions and carbon was investigated. Presence of chlorine and alcalic elements was confirmed with microthermometry, mineralogical and chemical analyses. X-ray computed tomography with sub-micron resolution (CT) was applied to obtain a 3D distribution of cavities. CT data were correlated with some light microscopy images and also with the same sample's tomography data which were gathered using the 3D X-ray energy dispersive spectroscopy (3D EDS) by a scanning electron microscope equipped with a focused ion beam (FIB-SEM). The latter further determined dolomites and metals in the CT data of limestone.

1. Introduction

Limestone is a very important industrial rock and a raw material. It is used for the production of lime and cement and also serves as a desulphurization of flue gases of large energy sources. It is also used as a filler in the manufacture of paper with high white balance requirements, in the chemical industry and, last but not least, as a fertilizer. Limestones occur in various sedimentary basin environments, hence they differ in their geological age, crystallinity, petrographic structure, chemical purity and in the porous structure as a result of lithofacial conditions. All of these properties influence not only their behaviour during firing process but also the reactivity with acids in the process of mutual reactions. Many scientific works have been focused on finding and describing the relationship of limestone properties to their behaviour [1–3].

In the process of firing of limestones, some volumetric changes occur, which significantly affects the decarbonation process, especially in shaft kilns. There is only a very small number of publications dealing with this issue and searching for some more general dependence of the limestone properties on their volume changes during firing. Wolter et al. carried out a relatively extensive study in this area on 21 limestone samples [4]. However, the available

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works deal mostly with the expansion of pure calcite grains, possibly also with the influence of various impurities on this quantity. This relatively frequently observed phenomenon is related to the volumetric changes of limestone during firing, e.g. a loss of compactness due to the development of net cracks, so called decrepitaion.

The process of decrepitation has been investigated by various authors, especially from the viewpoint of the influence of a particle size [5]. This phenomenon makes some types of limestone absolutely unusable for the production of lime. A similar issue was observed in the case of flue gas desulphurization by the fluid combustion technology [6].

The only reasonable way to explain the "decrepitation" of limestones is to take into account the presence of fluid inclusions in sparry carbonate minerals, mostly calcite that is a coarse crystalline component of limestones. Fluid inclusions are common objects in natural minerals. They originate as defects during the growth of crystalline lattice leaving voids which are filled by ambient solution (fluids). Consequently, natural crystal/mineral phases precipitate from this solution. Sparry calcite in most limestones is formed from simple pore-filling cement among allochems (particles forming structural framework of limestones – intraclasts, oolites, fossils and pellets of microcrystalline calcite). The sparry calcite crystallizes from pore solutions and its amount differs according to a particular type of limestones. Thanks to the presence of a particular genetic type of calcite cement, it is possible to observe various properties and behaviour of limestone within industrial processing.

One of standard methods for investigation of nature of fluids trapped inside inclusions is optical microthermometry. This method is based on the phase transitions during temperature changes and also on the interpretation and thermodynamic calculations of fluid properties [7,8]. In studies of micro and nanostructures of rocks, nano-detection methods are applied. The scanning electron microscopy (SEM) is commonly used for obtaining information about the morphology of the sample surface [9]. The transmission electron microscopy (TEM) shows a connection between fluid inclusions and crystal structure defects [10]. A sample can be only observed layer by layer, which are removed by a focused ion beam (FIB). The electron microscopy can be further supported by a quantitative analysis such as energy dispersive X-ray spectroscopy or wavelength dispersive X-ray spectroscopy [10,11]. They provide a good resolution below 1 nm [12], thus they enable the observation of structures in more detail than the previously mentioned petrographic methods.

Density discontinuities in materials have been studied using X-ray computed tomography (CT) [13,14]. CT is a non-destructive method applied for 3D visualizations of materials' inner structure [15,16]. A sample is placed on a rotational table and scanned with the X-ray from many angles of rotation to get X-ray projections [17]. On the basis of these projections, virtual slices through the sample are reconstructed. The slices are stacked together to get 3D data. Gray values in slices correspond to the linear attenuation coefficient of the material. Based on different X-ray attenuations, different materials can be distinguished, segmented and quantified [18,19]. Modern laboratory CT devices are capable of reaching a voxel resolution (voxel is a volumetric element of CT data) of hundreds of nm [20,21]. Nevertheless, an observation with a small voxel size is only possible with adequately small samples due to a smaller field of view.

CT has been applied in various fields in geology, from hydrology, soil science, geodynamics up to planetary science. This technique is used to visualize the distribution and determination of a volume fraction in different phases of rock [22,23]. It has been applied for the detection of nano-inclusions of solids and fluid inclusions in diamonds [24], for the detection of cracks in rocks [25] and even for the identification of phases inside fluid inclusions [26]. The CT is often combined with various petrographic methods [11,24,25].

This paper introduces a novel approach for investigation of the limestone's inner structure. It is focused on the identification and quantification of air voids and fluid inclusions, which play an important role in the decrepitation of limestone during firing. For this investigation, the laboratory-based X-ray computed tomography that provides a sufficiently high resolution and sensitivity to image fluid inclusions was applied. CT data reveal some parameters (such as the volume fraction of inclusions and their 3D distribution) which have not been determined so far by any other method. This approach was demonstrated on a selected limestone sample which was subjected to both chemical and mineralogical analyses and to microthermometry. To interpret the CT data correctly, also the two following techniques were used. Firstly, the light microscopy (LM) was used to verify the inclusions detected in CT data. Secondly, the serial-sectioning 3D analysis with X-ray energy dispersive spectroscopic analysis (3D EDS) by a scanning electron microscope equipped with a focused ion beam (FIB-SEM) was applied as a supplementary method for the determination of sample composition. As a consequence, this paper presents a unique combination of these three imaging techniques which were implemented on one sample in a special order showing a correlation between the outputs.

2. Materials

26 samples of limestones coming from various locations and geological units were collected. They differ in structure, petrographic character and chemical composition. Chemical and mineralogical analyses were made on all samples, the procedures were the same as described further in Section 3.1. The LM was applied on samples which might contain fluid inclusions. For the investigation, a sample which contained coarser cement of calcite (sparry calcite) and plenty of fluid inclusions was selected. The statement was based on the highest amount of chlorine and the LM (Fig. 1).

The examined sample was a hard, compact limestone classified as bioclastic grainstone according to Dunham classification [27]. It had been taken from a limestone deposit near Koněprusy, Czech Republic, from Lower Devonian sedimentary sequence of the Czech Karst area. The sample was prepared in several forms corresponding to the employed methods: homogenized powder of the rock

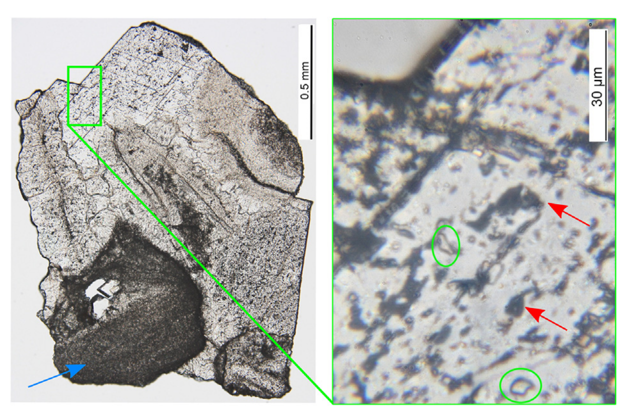

Fig. 1. Fragment of the double-sided polished limestone section from LM shows an enormous number of fluid inclusions spread within dotted brighter areas of sparry calcite. Among tiny black dots in calcite (defects in crystal lattice, pointed by red arrow), dominate the fluid inclusions (circled in green). Dark areas (pointed by the blue arrow) present allochems. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)