



Effects of dry grinding on the structure and granularity of calcite and its polymorphic transformation into aragonite



Tiantian Li ^a, Fengfeng Sui ^a, Fuchun Li ^{a,*}, Yuanfeng Cai ^b, Zhangdong Jin ^c

^a College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China

^b State Key Laboratory of Mineral Deposit Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, China

^c State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, Shaanxi 710075, China

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ABSTRACT

The structure and granularity of calcite were measured during dry grinding in a ball mill by X-ray diffraction, Fourier transform infrared spectroscopy and laser diffraction, and its morphology was observed by a scanning electron microscope. During the early stage of grinding (0–10 min), the median particle size and X-ray diffraction intensity of the calcite decreased, while the full width at half maximum increased as grinding progressed. During the middle grinding stage (20–300 min), the grain size and crystalline degree of ultrafine calcite particles no longer changed with time; this was attributed to aggregation, which hindered the breakage of particles. During the final grinding stage (360–720 min), a polymorphic transformation of calcite into aragonite took place.

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1. Introduction

It is well known that mechanical effects occurring during dry grinding of mineral particles can initiate significant surface and structural changes and even chemical reactions in the material [1]. Therefore, the study of temporal changes of the various characteristics of mineral particles during the dry grinding process has practical significance in the fields of food processing, pharmaceutical preparation, cosmetics manufacturing, etc. Samples used for the determination of the chemical composition and physical characteristics of materials are usually prepared in laboratories by prolonged dry or wet grinding. During such grinding, however, the physical as well as the chemical characteristics of these materials can undergo significant alterations. As a result, studying the changes of those properties in the grinding process is essential.

There are two primary methods for producing ultrafine powder materials: chemical and physical. The latter consists of dry grinding and wet grinding, with wet grinding being favorable because it entails use of dispersing agents that can restrain the aggregation among particles [2,3]. Research results indicate that the smallest grain size of quartz that can be obtained under the condition of dry grinding is about 2 μm; however, sizes of about 0.5–0.6 μm can be achieved under the condition of wet grinding [4]. In addition, with wet grinding there is little breakage of the mineral structure, in contrast to dry grinding [5]. Therefore, from the viewpoint of decreasing the grain

size of materials, wet grinding is preferable to dry grinding. Nevertheless, in practical production, one must separate solid and liquid phases and then dry the particles after the wet grinding process. The solid–liquid separation of ultrafine powder is very difficult to perform and is accompanied by the loss of ultrafine powders, some of which dissolve in the filtrate. In addition, agglomeration frequently takes place after drying. Consequently, dry grinding is used more often than wet grinding [6].

Most of the research involving dry grinding has focused on clay minerals [1,2,7]. Furthermore, there are some reports on the effects of dry grinding on quartz [4], feldspar [8], corundum [9], and calcite [10,11]. Research on dry grinding of nonmetallic minerals has concentrated on the crystal structure changes [7,8], aggregation, and changes of granularity [10,12], as well as surface properties of particles, especially specific surface area, cation exchange capacity, and Zeta potential [1,8]. As a result of the low thermal conductivity of most of nonmetallic solids, the energy delivered by the mill is not totally stored in the particle as thermal energy but is also applied to the bending and/or breaking of the crystalline solid [13]. Moreover, dry grinding also might bring about amorphization as well as formation of polymorphs of some components owing to deformation of the crystal structure [14].

In recent decades, most work on calcite has focused on the kinetics of dry grinding [11] and selection of dispersing agents for wet grinding [15]. Meanwhile, a few works have involved the crystal structure and phase transformation of carbonate minerals during the dry grinding process. For instance, it was found that calcite ground in a pebble mill for several hundred hours polymorphically transformed into aragonite

* Corresponding author. Tel.: +86 25 84395014.

E-mail address: fchli@njau.edu.cn (F. Li).

[16,17]. Among calcite, magnesite, and dolomite, only dolomite suffered considerable structural deformations during grinding for 10 h [18]. Moreover, Zhang et al. observed a phase transformation from aragonite into calcite in the process of grinding aragonite [19].

In this paper, we investigate the temporal changes of the calcite structure, granularity, and phase transition during dry grinding with a vibrating mill. The aim of this work is to study the change of the structure and phase of calcite during the dry grinding process. The results might be of useful scientific value for practical utilization of ultrafine calcium carbonate in fields such as materials, powder coatings, plastics, papers, pharmaceuticals, and cosmetics.

2. Materials and methods

The calcite sample applied in this work was of white and gray color with perfect cleavage in three directions. The sample was ground by using an agate mortar and then passed through a sieve with a pore size of 105 μm (150 mesh). Afterward, a dry grinding test was performed by using a type MM 400 vibration ball mill (Retsch, Germany) in the laboratory. The vibration mill has two 25-ml stainless steel pots, each of which has two stainless steel balls with diameters of 15 mm. At regular intervals, 0.3 g of powder was removed from the grinding pots and conserved to assay, then grinding of the residual fraction was continued. The operational parameters were as follows: The vibration mill was revolved by a motor operating at a voltage of 220 V, a current of 4 A, and a power of 150 W; the rotational speed was 1500 rpm.

Powder samples of calcite were prepared with a conventional front-packing technique. The mineral composition was analyzed using a Rigaku D/max-B (III) X-ray diffractometer at Nanjing Agricultural University. Each sample was scanned continuously at $[4^\circ (2\theta)]/\text{min}$ from 10° to $60^\circ (2\theta)$ at 35 kV and 20 mA in $0.01^\circ (2\theta)$ steps. The errors were less than 5%. The qualitative identification of mineral phases was performed using the Jade 5 program.

The calcite powder reclaimed from the X-ray diffraction (XRD) analysis was mixed with specpure KBr powder and molded into pellets. The samples were analyzed using a TENSOR27 infrared spectrophotometer (Bruker, Germany) at Nanjing Agricultural University. The spectrometer was set to scan at 1 cm^{-1} resolution with a scan range of $4000\text{--}400 \text{ cm}^{-1}$.

The particle size distribution was measured using a Mastersizer 2000 laser sizer based on light diffraction at the Institute of Earth Environment, Chinese Academy of Sciences. The measuring range was $0.02\text{--}2000 \mu\text{m}$, and the errors were less than 2%. Before determination, calcite particles were treated in 0.05 M sodium hexametaphosphate as a dispersing agent with ultrasound waves for 10 min.

An EVO18 scanning electron microscope (SEM) was used for imaging of particles at the Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences. The dried samples were coated with 8 nm of gold before SEM imaging.

3. Results and discussion

3.1. Change of calcite granularity

The median particle size of ground calcite decreased sharply during the initial stage (5 and 10 min) of grinding in comparison with starting materials, as shown in Fig. 1. After 20 and 30 min of grinding, the median particle size displayed an obvious increasing trend instead of decreasing. Subsequently, the grain size remained stable, though it did fluctuate, indicating aggregation of ultrafine calcite particles in the middle stage of the grinding process. The size distributions of calcite particles ground at different milling times are shown in Fig. 2. As seen in Fig. 2, before being ground using a vibration mill (grinding time of 0 min), the calcite powders were mostly composed of a coarse particle fraction and a fine particle fraction. The modes of the grain size of the fine and coarse fractions were about 0.6 and

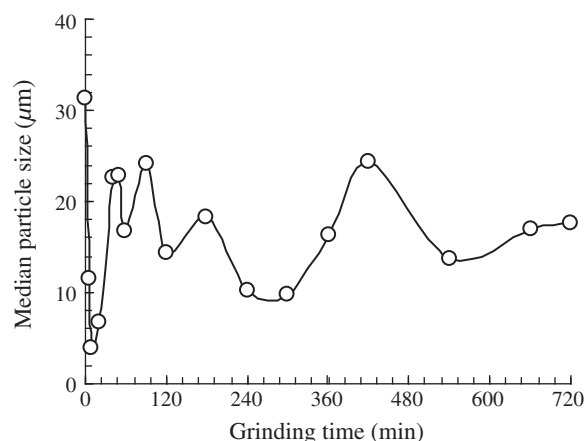


Fig. 1. The temporal change of median grain size of calcite during dry grinding.

45 μm , respectively, and their contents were about 0.4% and 4.1%, respectively. After 5 min of grinding, the fine fraction content increased while the coarse fraction content decreased. After 10 min of grinding, this process intensified, and the two fractions almost merged into one broad peak. Subsequently, a reversal appeared after 20 min of grinding; i.e., the fine fraction content decreased while the coarse fraction content increased. At this stage of grinding, the mode of the grain size of the coarse particle fraction was about 40 μm (with a content of approximately 2.4%), which was slightly smaller than that of the ground sample of 0 min. These data indicate that 10 min of grinding might be a critical point at which aggregation of ultrafine calcite particles begins. After that, the grain size distribution maintained basically a bimodal pattern. However, after grinding for 420 min, a third peak appeared in the grain size distribution, and the mode of the grain size was about 160 μm (with a content of approximately 2.0%). The large aggregates that were not dispersed by sodium hexametaphosphate were breached further by mechanical force upon grinding. Therefore, that fraction does not appear in other samples that were ground longer than 420 min. Hence, the breakage and aggregation of particles are opposing processes during grinding. Congregation among particles might consist of two stages: aggregation and agglomeration. During the aggregation stage, particles bond together via van der Waals forces (VDW) and form agglomerates, which can be dispersed by dispersing agents, whereas during the agglomeration stage, particles bond together via chemical bonds to form tight and irreversible aggregates. SEM images (Fig. 3) show that numerous ultrafine calcite particles merge together to form spherulike aggregates or agglomerates.

There are several key aspects relating to the formation of aggregates and agglomerates: (1) During impact and friction, the mineral particles absorb a certain amount of energy; this energy raises their surface energy, and they become unstable. Formation of aggregates or agglomerates can reduce this surface energy. (2) The specific surface area of calcite particles increases during the grinding process, which strengthens the adsorption capacity of particles. (3) Many broken bonds are formed in the process of fragmentation; these create new surfaces to take more charge and to enhance surface activity. Consequently, there is a tendency for particles to aggregate spontaneously to reduce the enthalpy of the system [20].

3.2. Change of calcite structure

The XRD spectrographs (Fig. 4) show eight characteristic diffraction peaks of calcite, representing eight crystal planes: (012) ($2\theta = 22.98^\circ$, $d = 3.86 \times 10^{-1} \text{ nm}$), (104) ($2\theta = 29.36^\circ$, $3.04 \times 10^{-1} \text{ nm}$), (110) ($2\theta = 35.90^\circ$, $2.50 \times 10^{-1} \text{ nm}$), (113) ($2\theta = 39.36^\circ$, $2.29 \times 10^{-1} \text{ nm}$), (202)

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