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Investigation of the thermal microstructural effects of CO_2 laser engraving on agate via X-ray microtomography

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ABSTRACT

CO_2 laser micro-machining is a precise and versatile tool for brittle, low-conductive materials such as agate, a quartz mineral variety of chalcedony. Laser engraving on agate's polished surface generates a permanent white mark, noticeable to the unaided eye, resulting from several thermal microstructural effects originated by the laser's focalized heat that rapidly melts, vaporizes, and solidifies specific regions. However, few studies have attempted evaluating and quantifying such micro-scale effects during laser processing. We used a non-destructive, high-resolution method to reconstruct and analyze a 3D model of the laser engraved agate surface based on microtomography (μCT) images. Intrinsic water found in agate's microstructural defects was identified as the major cause for the development of micro-cracks, fractures, and internal porosity due to the resultant vapor pressure. Molten SiO_2 ejection also generated an external porosity composed of large, open cavities, forming the mark on the gemstone's surface. μCT images allowed the evaluation of the absolute and relative amounts of material ejected and vaporized, and both molecular water (H_2O) and hydroxyl bonds on silanole groups (SiOH), within the material's microstructure, should be considered for a precise and uniform laser engraving. The results show that μCT analysis is an accurate method for evaluating and quantifying the microstructural effects of laser engraving on the surface of silica-based materials.

1. Introduction

Brazilian southernmost state of Rio Grande do Sul is one of the world's largest producers of agate (SiO_2), an α-quartz mineral variety of successive chalcedony bands occurring as a compact material filling geodes of volcanic rocks [1–5]. Agate is mainly found in the Salto do Jacuí Mining District, in the central region of the state, where it is mined and exported in the form of gemstones through the manufacturing of several ornamental objects, thus playing an important role in the region's economy [2,6]. Several processing techniques are locally used for increasing the value of agate, including dyeing, plate slicing and polishing, water cutting, and CO_2 laser engraving [7]. CO_2 laser technology is one of the most effective micromachining tools for low-conductive and brittle materials such as ceramics and glasses [8]. Basically, electrons excite molecules of a gas mixture primarily consisting of $CO_2/N_2/He$, thus generating high-energy photons in the infrared wavelength. Lasing principles are further presented by [9–11]. A high-intensity, focalized laser beam irradiates the surface of the sample, leading to thermal events that rapidly melt, vaporize, and solidify the material. The laser beam movement is controlled via CNC mechanisms by means of an X-Y plotter system or by galvanometer mirror equipment. When processing ornamental stones, optimal parameters of the CO_2 laser can be achieved for successfully cutting marble [12] and granite [13] via the plotter equipment. As for agate, the engraving of illustrations in the surface of thin slabs is one of CO_2 laser's main applications in galvanometer equipment, particularly in the mining industries of the central state region [1,7].

The effects of CO_2 laser on silica-based materials, such as agate, are directly dependent on the processing parameters, such as laser power and beam speed [7,8]. Different settings were studied for the manufacturing of micro-lenses [14,15], surface polishing [16,17], continuous peeling [18], welding [19,20], micromachining [8,21], and engraving [7,22], resulting in various effects on the

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microstructure of the material. With the infrared radiation absorption, the vibration of the material's molecular bonds creates a heat affected zone (HAZ) corresponding to the laser paths on the surface of the sample, and it is surrounded by a much cooler region [10,18]. When applied on polished surfaces of agate plates, with specific parameters, the CO_2 laser creates a regular artificial porosity in the HAZ, which is visualized as a continuous, thin (~200–500 μm) white mark that is used for the engraving of drawings [7]. Generally, with high laser absorption, thermal expansion and contraction of the HAZ generates micro-cracks and fractures near the laser path [10]. Thermal cracks and fractures on large-scale samples of brittle, siliceous minerals such as agate were attributed to differential thermal expansion, which is given as a function of the sample size and thickness [23,24], as well as the maximum temperature and the heating and cooling rates [25,26]. Water content in the microstructure was demonstrated to have a crucial part in cracking and microstructural failure as a result of internal vapor pressure in macro-scale samples [27,28]. Engraving is one of the main laser processing technique used on agate, but few studies have investigated those effects on the material's microstructure [29], particularly in relation to the formation of thermal micro-cracks and fractures in micro-scale samples. Hence, this research focused on the micro-scale thermal laser effects evaluated by a high-resolution quantitative analysis.

Laser engraving is a flexible and precise machining method for ceramics, and new techniques for processing and measuring of its microstructural effects have been recently developed for several materials. Wang and Zeng [30] studied different processing parameters for the development of 3D carving on Al_2O_3, and Bharatish et al. [31] verified the thermal residual stresses by Micro-Raman spectroscopy. The evaluation of laser processing effects has also been performed with non-destructive methods, for instance, optical coherence tomography on ABS plastics [32]. Despite the resulting engraving effects of CO_2 laser use on agate or silica-based materials, few data could be obtained and then discussed concerning the 3D microstructural characteristics of the process [7,11,29]. The visual investigation of the engraving effect on agate usually depends on superficial scanning electron microscopy (SEM) images, not allowing an internal analysis of the HAZ in the sample. Cross-sectioning engraved agate samples for internal viewing may damage the fragile porosity and induce false micro-cracks, hence requiring the use of a non-invasive technique. In addition, the artificial laser porosity region is caused by micro-scale thermal effects, including melting and vaporization of a certain amount of material. However, the precise measurement of the vaporized volume of agate material is rather difficult to achieve by physical methods. In this research, we propose the investigation of the 3D microstructural effects of CO_2 laser engraving on the surface of agate via X-ray microtomography (μCT). High-resolution μCT images allowed a non-invasive investigation of the engraved surface of agate, the assessment of the amount of material that was vaporized and ejected, as well as the analysis of the internal porosity originated by the laser processing.

2. Experimental procedures

2.1. Agate

Agate is a variety of chalcedony, a cryptocrystalline form of silica. Agate includes varieties that are found in numerous trade names, according to the sample, design or internal layer structures, although there is no unified terminology [33,34]. Agates (Fig. 1) are found as geodes filling and occurs mostly in the central region of Rio Grande do Sul state, locally named "*umbú*" [7]. This type of geode (Fig. 1A) presents a rough external surface and generally a

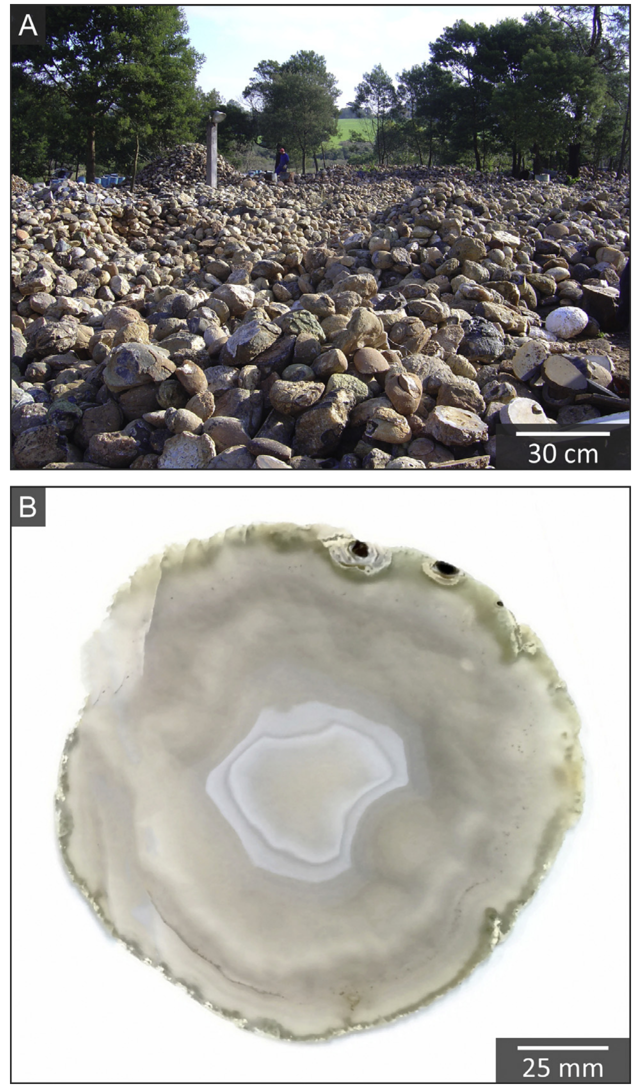

Fig. 1. Typical external and internal aspect of *umbú* agate, from Salto do Jacuí Mining District (Rio Grande do Sul state, Brazil): (A) geodes; (B) undyed, polished slab.

spherical or oval-shape. When cut, the geode reveals a grayish internal surface, making the *umbú* variety suitable for dyeing. Once classified by size, thin slabs (from 2 to 6 mm) of agate are cut, washed, and polished (Fig. 1B) for trading [7]. Before polishing, however, slabs may be tinted with different techniques using organic or inorganics dyes, *e.g.*, an agate plate can be heated in a ferric nitrate solution for red coloring [33]. For this research, an undyed agate sample from a polished thin slab was selected to preserve its natural microstructure from possible dyeing chemical reactions.

Microstructurally, agate is composed by 50–100 nm α-quartz crystallites [35], forming a nano-sized internal porosity network that allows it to be dyed by artificial means [5]. Qualitative analysis of agate's natural nano-porosity is rather difficult to accomplish due to its size, even by means of SEM or TEM [5,36]. Chalcedony is composed of 90–99 wt% of SiO_2, with up to 2 wt% H_2O, and impurities such as Fe_2O_3 or Al_2O_3 [5,36–38]. Water in chalcedony is not essential and is mostly found within internal defects, which is located in a strained and disordered region between adjacent, interlocking fibers [5]. Total water content is subdivided into direct molecular water (H_2O) and hydroxyl bonds (–OH) on silanole groups, SiOH [39]. Molecular water is entrapped into closed or