12th International Kimberlite Conference Extended Abstract No. 12IKC-87, 2024

Laser ablation of 'diamonds-in-water' – a new technique for digging deeper

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Introduction

For the last 30 years, laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) studies of diamonds used various lasers, including 1064, 266 and 213 nm Nd:YAG or 193 nm ArF excimer lasers coupled to conventional ablation cells and mass spectrometers (e.g. Rege et al., 2005; Tomlinson et al., 2009; Watling et al., 1995). The laser beam is focused into a ~20–100 μm spot on the diamond surface and the ablated material is carried into the plasma torch, ionized and analyzed using a quadrupole mass spectrometer. This 'on-line' LA-ICPMS method allowed fast and easy measurement of many trace elements in microinclusion-bearing diamonds.

In an attempt to analyze trace element concentrations in gem-quality diamonds, barren of visible microinclusion aggregates, an 'off-line' approach was developed (McNeill et al., 2009). This technique utilized the same lasers for on-line ablation but increased the analyte levels via ablation in a closed-system cell that is not connected to a mass spectrometer, followed by solution analyses of the produced analyte. It allowed analyses of ~500 μg of ablated diamond, yielded very accurate results for microinclusion-bearing diamonds, and was also proved successful in the analyses of some gem-quality diamonds (Krebs et al., 2019; Melton et al., 2012). Moreover, it opened the way for radiogenic isotope analyses of microinclusion-bearing diamonds, especially their Sr isotopic compositions (Klein-BenDavid et al., 2014). Still, only diamonds with high total trace element abundances could be analyzed for other radiogenic isotopes. To overcome this hurdle we developed a technique of diamonds-in-water ablation using a 'powerful laser' to significantly improve the amount of ablated material and facilitate the analyses of radiogenic isotopes.

Experimental

Following the off-line concept, the ablation of diamond-in-water is conducted in a closed-system cell that is not connected to a mass spectrometer. We use a custom-modified quartz Fluorometer cell (3-Q-20, 7.0 ml, Starna Cells) as an ablation cell. Each diamond is placed in the cell and Milli-Q water (Milli-Q, 18.2 MU cm) is added before the cell is sealed in an ultra-clean environment.

The first generation used a Spectra-Physics GCR-150-30 Q-switched Nd:YAG laser (Weiss et al., 2022). The laser beam of 532 nm was spot-focused on the diamond with a power of ~150 mJ per pulse, 7 ns pulse duration, and operated at a repetition rate of 30 Hz. These ablations significantly improved the amount of ablated material and allowed a high but variable diamond ablation rate, between 3 and 14.4 mg h^{-1} (Figure 1). However as the stage speed and incremental movement in the X–Y–Z directions were controlled manually during operation, the ablation pit morphology and spatial depth were irregular and varied between ablations.

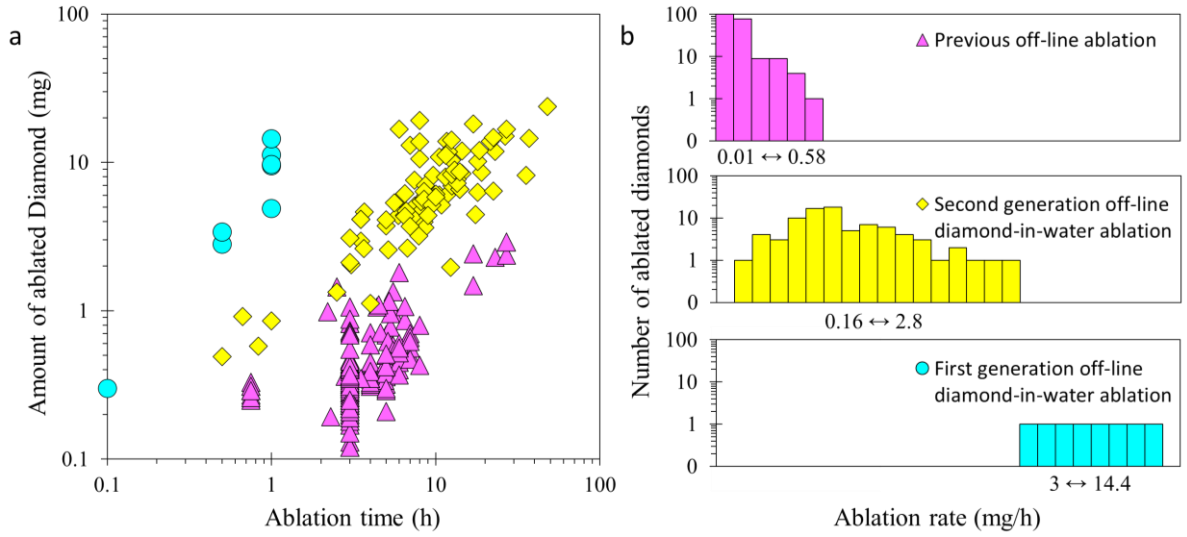

Figure 1: (a) Weight of ablated diamond *vs.* ablation time, and (b) Ablation rate of off-line diamond-in-water ablation using second generation system in the diamond processing lab at the Hebrew University (middle). For comparison, available data for diamond-in-water ablation using first generation system (bottom; Weiss et al., 2022) and previous off-line ablation methods using conventional systems for geological applications are presented (top; e.g. Klein-BenDavid et al., 2014; Krebs et al., 2019; McNeill, 2009; Melton et al., 2012; Timmerman et al., 2019; Weiss et al., 2015).

The second generation off-line ablation system in the diamond processing lab at the Hebrew University is a custom-made setup equipped with a Spectra-Physics Talon 532-20 Nd:YV04 laser. The 532 nm laser with a maximum power of 20W, generates pulses of up to 400 µJ and 25 ns pulse duration at a maximum repetition rate of 500 kHz. Based on multiple ablation runs (n=84) the new system's average ablation rate is 0.73 ±0.38 mg h^{-1}, and we have managed to ablate up to 25 mg of a diamond (Figure 1). The system is fully automated with an X–Y–Z working area of 20×20×20 mm, resolution of 0.5 µm, repeatability that is less than ±2 µm and a maximum stage speed of 5 mm s^{-1}. The combined Talon laser specifications with an automated stage designed for micromachining applications provide a highly stable and precise ablation, thus leading to a smooth pit morphology with spatial depth that is close to uniform (Figure 2).

Advantages and potential

The combination of a powerful laser and ablation in water has two major advantages. First, it provides a means to increase the volume of diamond that can be ablated relatively fast (several mg in a timely manner) and thus, the amount of analyte that can be collected and analyzed. Second, because the ablated area is underwater, the trapping efficiency is very high and allows efficient retrieval of the nanosized analyte particles. In addition, all the material trapped in the microinclusions is ablated and digested by acids, so possible elemental and isotopic fractionation induced by ablation are avoided.

Improving the amount and yield of the ablated material is a key issue that facilitates the chemical measurements of microinclusion-bearing diamonds. The new ablation technique and system provide enough material for quantitative analysis of trace elements, including all rare earth elements (REEs), even in diamonds of low element abundance levels. Using the system and analyzing the ablated material by state-of-the-art mass spectrometers we now get accurate Sr, Nd and Pb isotopic data on individual microinclusion-bearing diamonds. Also, enough diamond material can now be collected which paves the way for successful non-traditional stable isotope (Fe, Mg, K, etc.) analyses, and perhaps other isotopic systems that were limited by sample amount of such diamonds until now.

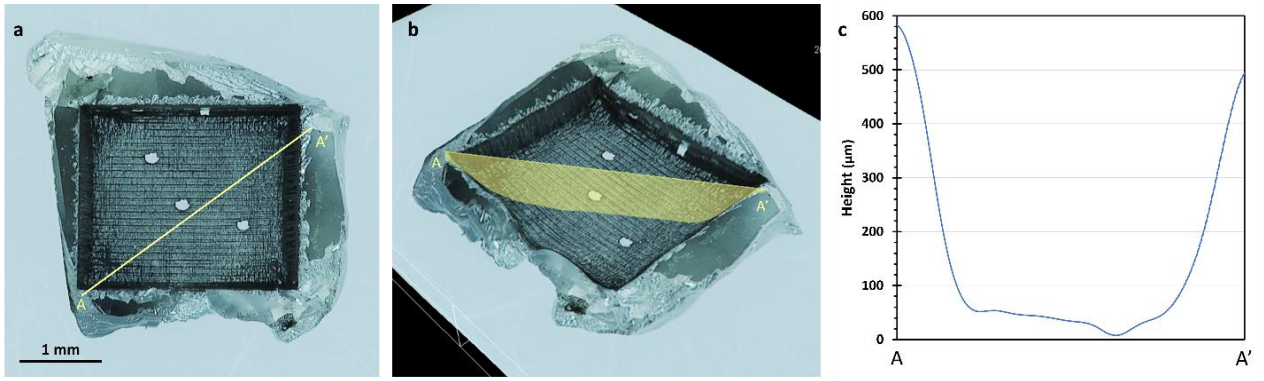

Figure 2: Process outcome of off-line diamond-in-water ablation using second generation system. (a) Photomicrograph of diamond ON-DBP-333 after ablation. The large rectangle pit that was excavated during off-line ablation compared to the much smaller pits during on-line LA-ICPMS analyses, illustrates the significant difference in diamond volume that can be quarried using the two different methods. (b, c) 3D image and a cross-section profile along A–A' in (a) showing the morphology and vertical depth variation within the ablation pit. Photos and profile were produced and measured using the 3D model function of a Hirox HR-2000 optical microscope.

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