This preliminary study focuses on using secondary ion mass spectrometry (SIMS) to measure relative carbon isotope ratios for natural and synthetic diamonds (i.e. those grown by both chemical vapour deposition [CVD] and high-pressure, high-temperature [HPHT] techniques). The synthetic diamonds (of both CVD and HPHT origin) had significantly lower relative carbon isotope values than the natural diamonds. The lowest value was obtained for the CVD synthetic diamond sample, in agreement with results from other investigators. More research is desirable on the carbon isotope variation of synthetic diamonds.

**INTRODUCTION**

Natural diamonds have been used in jewellery and for industrial purposes (e.g. abrasives) for centuries (Harlow, 1998). They constitute some of the most famous and valuable gems found worldwide. Diamonds form in the earth’s mantle, and a number of different hypotheses for their specific geological formation continue to be discussed (Stachel and Harris, 2009; Stachel and Luth, 2015) and reviewed (Cartigny et al., 2014) in the literature. The chemical and physical properties of diamonds also are widely studied subjects (Clark et al., 1979; Shirey et al., 2013; Zaitsev, 2013).

However, openly available research on the identification and formation of synthetic diamonds is much scarcer. Synthetic diamonds were first produced in the 1950s in the USA and Sweden (Angus, 2002; Martineau et al., 2004). In recent years, advances in CVD and HPHT technology—the two methods used to synthesize diamonds—have made these synthetics much more widely available and of higher quality (Figure 1).

The introduction of undisclosed synthetic diamonds into the market has become a critical issue for the diamond and jewellery industry at large (Even-Zohar, 2012; Kitawaki et al., 2013; Sheintal, 2015). Although various laboratory techniques involving spectroscopy (Fourier-transform infrared, ultraviolet-visible–near infrared and photoluminescence) and imaging (ultra-short-wave UV and cathodoluminescence) can be used to distinguish natural from synthetic diamonds, further research is required to understand their formation mechanisms (Shigley et al., 1997; Wang et al., 2003).

Rapid developments in both CVD and HPHT technology require that research keep pace to ensure synthetic diamonds can be conclusively identified in the future, and to maintain consumer confidence in the diamond trade. Isotopic studies, such as those using SIMS instrumentation that are presented in this article, provide additional information for such efforts. Other studies that have applied SIMS to diamond research—for purposes of documenting chemical zoning and distinguishing different geological sources—include those by Hauri et al. (2002), Deines and Harris (2004), Cartigny (2005), Palot et al. (2012, 2014) and Stern et al. (2014). In addition,
Wang et al. (2014) used SIMS to investigate carbon isotopes in both natural and CVD synthetic diamonds. The current study includes HPHT synthetics along with CVD and natural samples.

**SAMPLE SELECTION AND PREPARATION**

Nine faceted samples were examined for this study: five natural diamonds, three colourless HPHT-grown synthetics and one colourless CVD synthetic diamond. The geological origin of the five natural diamonds and the exact manufacturing processes of the synthetic diamonds are not known. The samples were randomly chosen from different types of diamonds found in the market. Table I provides a summary of the samples.

To prepare them for analysis, the samples were pressed into indium metal in a sample holder. They were mounted with their table surface (or other large flat surface) facing upward. Last, the prepared holder was coated with gold before being inserted into the SIMS sample chamber.

**METHODS**

SIMS is an ion-beam microprobe technique used in surface analysis. The high sensitivity, high mass-resolving power and micrometre- to nanometre-scale spatial resolution of SIMS have made it a widely used technique in advanced materials research (Benninghoven et al., 1987; de Laeter, 2001). A primary ion beam is used to ionize elements on a sample’s surface, thereby generating secondary ions that are analysed using a mass spectrometer. The SIMS method has a wide range of applications, including the analysis of carbon and nitrogen isotopes.

**Table I:** Diamond samples analysed for this study.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Weight (ct)</th>
<th>Origin</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (reference)</td>
<td>0.136</td>
<td>Natural</td>
<td>Brownish</td>
</tr>
<tr>
<td>2</td>
<td>0.088</td>
<td>Natural</td>
<td>Colourless</td>
</tr>
<tr>
<td>3</td>
<td>0.628</td>
<td>Natural</td>
<td>Grey</td>
</tr>
<tr>
<td>4</td>
<td>0.062</td>
<td>Natural</td>
<td>Green</td>
</tr>
<tr>
<td>5</td>
<td>0.028</td>
<td>Natural</td>
<td>Colourless</td>
</tr>
<tr>
<td>6</td>
<td>0.230</td>
<td>HPHT synthetic</td>
<td>Colourless</td>
</tr>
<tr>
<td>7</td>
<td>0.019</td>
<td>HPHT synthetic</td>
<td>Colourless</td>
</tr>
<tr>
<td>8</td>
<td>0.031</td>
<td>HPHT synthetic</td>
<td>Colourless</td>
</tr>
<tr>
<td>9</td>
<td>0.092</td>
<td>CVD synthetic</td>
<td>Colourless</td>
</tr>
</tbody>
</table>
The carbon isotopes in our samples were measured using a Cameca IMS 1280-HR instrument (Figure 2) at the SwissSIMS facility of the Institute of Earth Sciences at the University of Lausanne, Switzerland (Seitz et al., 2017; Siron et al., 2017). We used a 10 kV Cs+ primary beam and an ~0.6 nA current, resulting in an ~10 μm rastered beam size. An electron flood gun, with normal incidence, was used to compensate charges. We gathered 12C− and 13C− secondary ions, accelerated at 10 kV, in multi-collection mode using a Faraday cup (for 12C−) and an electron multiplier (for 13C−). A mass resolving power of ~6,000 was achieved, to overcome polyatomic interference of 13C− with 12CH−, for example (Fitzsimons et al., 1999). The Faraday cup was calibrated at the beginning of the session. Each spot analysis took ~7 minutes, including pre-sputtering (60 seconds) and automated centring of secondary ions. The results of the analyses were expressed as the isotopic signature \(^{13}\text{C}/^{12}\text{C} \times 1000\), which is a measure of the ratio of the isotopes \(^{13}\text{C}/^{12}\text{C}\), reported in parts per thousand (per mil, ‰).

Since no standard reference diamond of known isotopic composition was available for this work, accurate \(^{13}\text{C}/^{12}\text{C} \times 1000\) values were not obtainable. Nevertheless, the analyses were precise, and differences were meaningful. Natural diamond sample 1 was found to yield relatively homogeneous \(^{13}\text{C}/^{12}\text{C} \times 1000\) ratios (\(2\sigma = 0.21\%\), 18 analyses). Therefore, for the purpose of qualitative analysis in this study, sample 1 was used as an external reference diamond to which the carbon isotope ratios for all other samples were normalized. For samples 2–9, four or five separate cluster locations on their surfaces were measured to address possible sample heterogeneity. At each cluster location, three SIMS analyses were carried out. The distance between these three replicates was much smaller compared to that between different cluster locations on a sample. After every six measurements of samples 2–9, two analyses were carried out on sample 1. Instrument drift over time was corrected in post-data evaluation using third-order polynomial fitting of the \(^{13}\text{C}/^{12}\text{C} \times 1000\) signal of sample 1. In addition, a homogeneity test was conducted on the surface of sample 2, in which two orthogonal directions across the table were scanned by lines of spots. Each SIMS analysis spot measured 10 μm in diameter and had a depth of less than a few hundred nanometres, which is not visible to the unaided eye. To remove the thin gold coating required for SIMS analysis, the samples were immersed in aqua regia that was heated to 40°C. Ideally, \(^{15}\text{N} \times 1000\) also would be a candidate to distinguish synthetic from natural diamonds. There are numerous studies investigating \(^{15}\text{N} \times 1000\) in natural diamonds (Cartigny et al., 2001; Cartigny, 2005; Hogberg et al., 2016). However, the nitrogen concentrations in the synthetic samples randomly selected for this study were below the detection limit of the SIMS instrument. Natural type II diamonds also contain amounts of nitrogen that cannot be detected by SIMS. Therefore, using nitrogen isotope ratios to determine natural or synthetic origin is not applicable to general cases and was not pursued in this study. The present research thus focused on using SIMS to determine normalized carbon isotope ratios, which could be measured on a relative basis without the use of a standard. To obtain quantitative data, it would be imperative to have bulk \(^{13}\text{C}/^{12}\text{C} \times 1000\) results on a reference sample. This was not pursued in the context of this preliminary study, as the aim was to investigate only the possible separation of natural from synthetic diamonds.
RESULTS

A summary of the carbon isotopic values is shown in Figure 3. Relative \( \delta^{13}C \) for the four measured natural diamonds (samples 2–5) varied from \(-2.16 \pm 0.56\%\) to \(-1.31 \pm 0.43\%\). The three HPHT synthetic diamonds (samples 6–8) had lower relative \( \delta^{13}C \) values ranging between \(-14.55 \pm 1.21\%\) and \(-11.84 \pm 1.78\%\). The CVD synthetic diamond (sample 9) had the lowest relative \( \delta^{13}C \) value of \(-51.99 \pm 1.63\%\), which is consistent with the work of Wang et al. (2014), who found that there was no overlap of \( \delta^{13}C \) values for the natural and CVD synthetic diamonds they analysed. The low \( ^{13}C/^{12}C \) ratio for the CVD synthetic diamond might be explained by the \( ^{13}C \)-depleted methane used as a synthetic precursor to obtain good crystal quality and a flat surface on the CVD plates (Fiori et al., 2013). For HPHT-grown synthetic diamonds, the carbon source is different (commonly graphite), and fractionation in these crystals was investigated in detail by Reutsky et al. (2008). According to Cartigny (2005), there are three commonly hypothesized explanations for the different \( \delta^{13}C \) values found in natural diamonds: (1) distinct carbon sources (i.e. different geological origins), (2) primordial isotopic variability and (3) fractionation of stable isotopes at mantle temperatures.

For the purpose of evaluating synthetic vs. natural origin, we observed no significant differences in relative carbon isotope ratios in the different areas analysed on the surfaces of the individual samples (both natural and synthetic). Nevertheless, other studies have shown that growth orientation and sectorization in natural and synthetic diamonds can have an influence on \( \delta^{13}C \) and \( \delta^{15}N \) ratios (Boyd et al., 1992; Bulanova et al., 2002, Reutsky et al., 2008; Fiori et al., 2013). Figure 4 shows the minor variability of relative \( \delta^{13}C \) values in both of the line scans across the table facet of sample 2.
CONCLUSIONS

Among the samples analysed in this SIMS study, the synthetic diamonds had distinctly lower relative $^{13}$C/$^{12}$C values than the randomly selected natural samples. The data also showed that HPHT and CVD synthetic diamonds potentially can be distinguished from one another on the basis of their relative carbon-isotope ratios. More research is required to understand $^{8}$13C variability and fractionation in synthetic diamonds. In addition, this preliminary study has shown the need for a carbon-isotope standard to obtain quantitative data for comparison with other diamond carbon-isotope studies. Future research using the SIMS technique will continue to provide a deeper understanding of diamond growth, and as such is complementary to other methods being used to separate natural from synthetic diamonds.

REFERENCES


The Authors
Dr Hao A. O. Wang
Dr Laurent E. Cartier FGA
Prof. Dr Lukas P. Baumgartner
Dr Anne-Sophie Bouvier
Dr Florence Bégué
Jean-Pierre Chalain
Dr Michael S. Krzemnicki FGA

1 Swiss Gemmological Institute SSEF, Aeschengraben 26, 4051 Basel, Switzerland
Email: gemlab@ssef.ch

2 Institute of Earth Sciences, SwissSIMS, University of Lausanne, 1015 Lausanne, Switzerland