

A Preliminary SIMS Study Using Carbon Isotopes to Separate Natural from Synthetic Diamonds

Hao A. O. Wang, Laurent E. Cartier, Lukas P. Baumgartner, Anne-Sophie Bouvier, Florence Bégué, Jean-Pierre Chalain and Michael S. Krzemnicki

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.

The Journal of Gemmology, 36(1), 2018, pp. 38–43, <http://dx.doi.org/10.15506/JoG.2018.36.1.38>
© 2018 The Gemmological Association of Great Britain

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,



Figure 1: Seven colourless and fancy-colour diamonds (weighing up to 3.03 ct) of various natural or synthetic origins are shown here. The top-right and bottom-left round brilliants are HPHT- and CVD-grown, respectively, and the other diamonds are natural. The confident separation of natural and synthetic diamonds is critical to maintaining consumer confidence in the trade. Composite photo by Luc Phan, SSEF.

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

Table I: Diamond samples analysed for this study.

Sample no.	Weight (ct)	Origin	Colour
1 (reference)	0.136	Natural	Brownish
2	0.088	Natural	Colourless
3	0.628	Natural	Grey
4	0.062	Natural	Green
5	0.028	Natural	Colourless
6	0.230	HPHT synthetic	Colourless
7	0.019	HPHT synthetic	Colourless
8	0.031	HPHT synthetic	Colourless
9	0.092	CVD synthetic	Colourless

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.



Figure 2: The SIMS instrument (Cameca IMS 1280-HR) at the SwissSIMS facility of the University of Lausanne consists of the following components: (a) sample chamber, (b) primary ion source, (c) electrostatic analyser, (d) magnet and (e) detection unit. Photo courtesy of SwissSIMS, University of Lausanne.

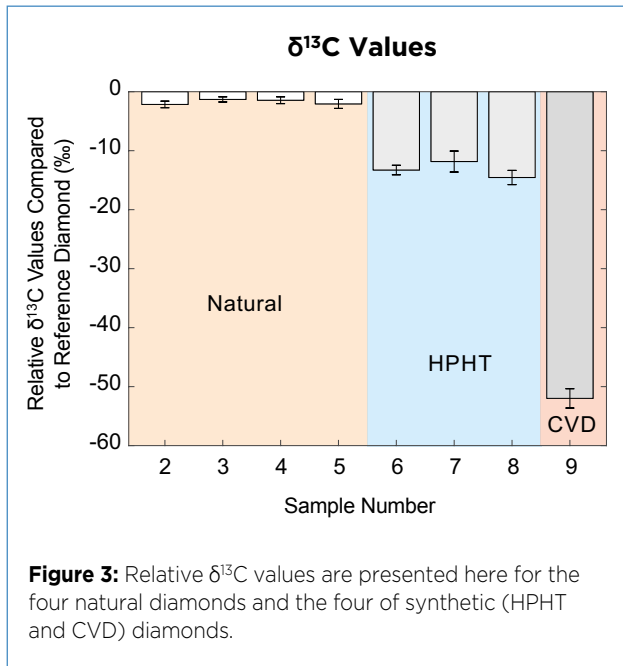
The carbon isotopes in our samples were measured using a Cameca IMS 1280-HR instrument (Figure 2) at the SwissSIMS facility of the Institute of Earth Sciences at the University of Lausanne, Switzerland (Seitz et al., 2017; Siron et al., 2017). We used a 10 kV Cs^+ primary beam and an ~ 0.6 nA current, resulting in an ~ 10 μm rastered beam size. An electron flood gun, with normal incidence, was used to compensate charges. We gathered $^{12}\text{C}^-$ and $^{13}\text{C}^-$ secondary ions, accelerated at 10 kV, in multi-collection mode using a Faraday cup (for $^{12}\text{C}^-$) and an electron multiplier (for $^{13}\text{C}^-$). A mass resolving power of $\sim 6,000$ was achieved, to overcome polyatomic interference of $^{13}\text{C}^-$ with $^{12}\text{CH}^-$, 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 $\delta^{13}\text{C}$, 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 $\delta^{13}\text{C}$ values were not obtainable. Nevertheless, the analyses were precise, and differences were meaningful. Natural diamond sample 1 was found to yield relatively homogeneous $^{13}\text{C}/^{12}\text{C}$ ratios ($2\sigma = 0.21\text{‰}$, 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 $^{13}\text{C}/^{12}\text{C}$ 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, $\delta^{15}\text{N}$ also would be a candidate to distinguish synthetic from natural diamonds. There are numerous studies investigating $\delta^{15}\text{N}$ 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 $\delta^{13}\text{C}$ 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.



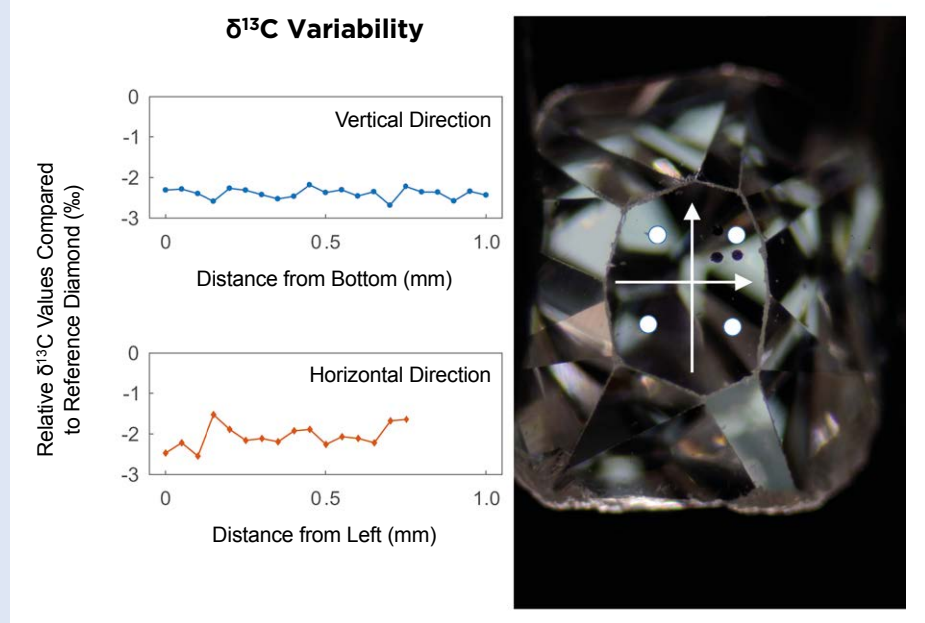
RESULTS

A summary of the carbon isotopic values is shown in Figure 3. Relative $\delta^{13}\text{C}$ for the four measured natural diamonds (samples 2–5) varied from $-2.16 \pm 0.56\text{‰}$ (2σ) to $-1.31 \pm 0.43\text{‰}$ (2σ). The three HPHT synthetic diamonds (samples 6–8) had lower relative $\delta^{13}\text{C}$ values ranging between $-14.55 \pm 1.21\text{‰}$ (2σ) and $-11.84 \pm 1.78\text{‰}$ (2σ). The CVD synthetic diamond (sample 9) had the lowest relative $\delta^{13}\text{C}$

value of $-51.99 \pm 1.63\text{‰}$ (2σ), which is consistent with the work of Wang et al. (2014), who found that there was no overlap of $\delta^{13}\text{C}$ values for the natural and CVD synthetic diamonds they analysed. The low $^{13}\text{C}/^{12}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ 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 $\delta^{13}\text{C}$ values in both of the line scans across the table facet of sample 2.

Figure 4: Sample 2, a colourless old-mine cut natural diamond of 0.088 ct ($2.53 \times 2.35 \times 2.13$ mm), exhibits only minor variability of relative $\delta^{13}\text{C}$ values in both directions across the surface of the table facet. The four white spots indicate cluster locations (three data points each) of SIMS analyses, and the arrows show the locations of the SIMS analytical traverses. Near the top-right cluster are three black spots resulting from laser ablation inductively coupled plasma mass spectrometry (performed for a separate study). Photo by SSEF.



CONCLUSIONS

Among the samples analysed in this SIMS study, the synthetic diamonds had distinctly lower relative $^{13}\text{C}/^{12}\text{C}$ 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 $\delta^{13}\text{C}$ 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

- Angus J.C., 2002. A short history of diamond synthesis. In J. Asmussen and D.K. Reinhard, Eds., *Diamond Films Handbook*, Marcel Dekker Inc., New York, New York, USA, 14–22.
- Benninghoven A., Rudenauer F.G. and Werner H.W., 1987. *Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends*. Wiley-Interscience, New York, New York, USA, 1,264 pp.
- Boyd S.R., Pillinger C.T., Milledge H.J., Mendelsohn M.J. and Seal M., 1992. C and N isotopic composition and the infrared absorption spectra of coated diamonds: Evidence for the regional uniformity of $\text{CO}_2\text{-H}_2\text{O}$ rich fluids in lithospheric mantle. *Earth and Planetary Science Letters*, **109**(3–4), 633–644, [http://dx.doi.org/10.1016/0012-821x\(92\)90121-b](http://dx.doi.org/10.1016/0012-821x(92)90121-b).
- Bulanova G.P., Pearson D.G., Hauri E.H. and Griffin B.J., 2002. Carbon and nitrogen isotope systematics within a sector-growth diamond from the Mir kimberlite, Yakutia. *Chemical Geology*, **188**(1–2), 105–123, [http://dx.doi.org/10.1016/S0009-2541\(02\)00075-x](http://dx.doi.org/10.1016/S0009-2541(02)00075-x).
- Cartigny P., 2005. Stable isotopes and the origin of diamond. *Elements*, **1**(2), 79–84, <http://dx.doi.org/10.2113/gselements.1.2.79>.
- Cartigny P., Harris J.W. and Javoy M., 2001. Diamond genesis, mantle fractionations and mantle nitrogen content: A study of $\delta^{13}\text{C-N}$ concentrations in diamonds. *Earth and Planetary Science Letters*, **185**(1–2), 85–98, [http://dx.doi.org/10.1016/S0012-821x\(00\)00357-5](http://dx.doi.org/10.1016/S0012-821x(00)00357-5).
- Cartigny P., Palot M., Thomassot E. and Harris J.W., 2014. Diamond formation: A stable isotope perspective. *Annual Review of Earth and Planetary Sciences*, **42**(1), 699–732, <http://dx.doi.org/10.1146/annurev-earth-042711-105259>.
- Clark C.D., Mitchell E.W. and Parsons B.J., 1979. Colour centres and optical properties. In J.E. Field, Ed., *The Properties of Diamond*, Academic Press, London, 23–77.
- de Laeter J.R., 2001. *Applications of Inorganic Mass Spectrometry*. John Wiley & Sons Inc., New York, New York, USA, 474 pp.
- Deines P. and Harris J.W., 2004. New insights into the occurrence of ^{13}C -depleted carbon in the mantle from two closely associated kimberlites: Letlhakane and Orapa, Botswana. *Lithos*, **77**(1–4), 125–142, <http://dx.doi.org/10.1016/j.lithos.2004.04.015>.
- Even-Zohar C., 2012. Synthetics specifically ‘made to defraud’. *Diamond Intelligence Briefs*, **27**(709), 7281–7290.
- Fiori A., Jomard F., Teraji T., Koizumi S., Isoya J., Gheeraert E. and Bustarret E., 2013. Synchronized B and ^{13}C diamond delta structures for an ultimate in-depth chemical characterization. *Applied Physics Express*, **6**(4), article 045801, 4 pp., <http://dx.doi.org/10.7567/apex.6.045801>.
- Fitzsimons I.C.W., Harte B., Chinn I.L., Gurney J.J. and Taylor W.R., 1999. Extreme chemical variation in complex diamonds from George Creek, Colorado: A SIMS study of carbon isotope composition and nitrogen abundance. *Mineralogical Magazine*, **63**(6), 857–878, <http://dx.doi.org/10.1180/002646199548970>.
- Harlow G.E., Ed. 1998. *The Nature of Diamonds*. Cambridge University Press, Cambridge, 278 pp.
- Hauri E., Wang J., Pearson D.G. and Bulanova G.P., 2002. Microanalysis of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and N abundances in diamonds by secondary ion mass spectrometry. *Chemical Geology*, **185**(1–2), 149–163, [http://dx.doi.org/10.1016/S0009-2541\(01\)00400-4](http://dx.doi.org/10.1016/S0009-2541(01)00400-4).
- Hogberg K., Stachel T. and Stern R.A., 2016. Carbon and nitrogen isotope systematics in diamond: Different sensitivities to isotopic fractionation or a decoupled origin? *Lithos*, **265**, 16–30, <http://dx.doi.org/10.1016/j.lithos.2016.06.020>.
- Kitawaki H., Yamamoto M., Hisanaga M., Okano M. and Emori K., 2013. Gem News International: Undisclosed samples of large CVD synthetic diamond. *Gems & Gemology*, **49**(1), 60–61.
- Martineau P.M., Lawson S.C., Taylor A.J., Quinn S.J., Evans D.J.F. and Crowder M.J., 2004. Identification

- of synthetic diamond grown using chemical vapor deposition (CVD). *Gems & Gemology*, **40**(1), 2–25, <http://dx.doi.org/10.5741/gems.40.1.2>.
- Palot M., Cartigny P., Harris J.W., Kaminsky F.V. and Stachel T., 2012. Evidence for deep mantle convection and primordial heterogeneity from nitrogen and carbon stable isotopes in diamond. *Earth and Planetary Science Letters*, **357–358**, 179–193, <http://dx.doi.org/10.1016/j.epsl.2012.09.015>.
- Palot M., Pearson D.G., Stern R.A., Stachel T. and Harris J.W., 2014. Isotopic constraints on the nature and circulation of deep mantle C–H–O–N fluids: Carbon and nitrogen systematics within ultra-deep diamonds from Kankan (Guinea). *Geochimica et Cosmochimica Acta*, **139**, 26–46, <http://dx.doi.org/10.1016/j.gca.2014.04.027>.
- Reutsky V.N., Borzdov Y.M. and Palyanov Y.N., 2008. Carbon isotope fractionation associated with HPHT crystallization of diamond. *Diamond and Related Materials*, **17**(11), 1986–1989, <http://dx.doi.org/10.1016/j.diamond.2008.06.003>.
- Seitz S., Baumgartner L.P., Bouvier A.-S., Putlitz B. and Vennemann T., 2017. Quartz reference materials for oxygen isotope analysis by SIMS. *Geostandards and Geoanalytical Research*, **41**(1), 69–75, <http://dx.doi.org/10.1111/ggr.12133>.
- Sheintal U., 2015. CIBJO Diamond Commission Special Report: Threat of Synthetics and Corrupting of Diamond Grading Continues to Trouble International Diamond Sector. CIBJO, The World Jewellery Confederation, 4 pp., [http://congress2015.cibjo.org/CIBJO%20Special%20Report%202015%20\(Diamond\).pdf](http://congress2015.cibjo.org/CIBJO%20Special%20Report%202015%20(Diamond).pdf).
- Shigley J.E., Moses T.M., Reinitz I., Elen S., McClure S.F. and Fritsch E., 1997. Gemological properties of near-colorless synthetic diamonds. *Gems & Gemology*, **33**(1), 42–53, <http://dx.doi.org/10.5741/gems.33.1.42>.
- Shirey S.B., Cartigny P., Frost D.J., Keshav S., Nestola F., Nimis P., Pearson D.G., Sobolev N.V. and Walter M.J., 2013. Diamonds and the geology of mantle carbon. *Reviews in Mineralogy and Geochemistry*, **75**, 355–421, <http://dx.doi.org/10.2138/rmg.2013.75.12>.
- Siron G., Baumgartner L., Bouvier A.-S., Putlitz B. and Vennemann T., 2017. Biotite reference materials for secondary ion mass spectrometry $^{18}\text{O}/^{16}\text{O}$ measurements. *Geostandards and Geoanalytical Research*, **41**(2), 243–253, <http://dx.doi.org/10.1111/ggr.12148>.
- Stachel T. and Harris J.W., 2009. Formation of diamond in the earth's mantle. *Journal of Physics: Condensed Matter*, **21**(36), article 364206, 10 pp., <http://dx.doi.org/10.1088/0953-8984/21/36/364206>.
- Stachel T. and Luth R.W., 2015. Diamond formation — Where, when and how? *Lithos*, **220–223**, 200–220, <http://dx.doi.org/10.1016/j.lithos.2015.01.028>.
- Stern R.A., Stachel T., Pearson G., Palot M., Cartigny P., Howell D. and Oh A., 2014. *Methods and Reference Materials for SIMS Diamond C- and N-Isotope Analysis*. CCIM Research Report 14-01, Canadian Centre for Isotopic Microanalysis, Department of Earth and Atmospheric Sciences, University of Alberta, Canada, 87 pp.
- Wang W., Moses T., Linares R.C., Shigley J.E., Hall M. and Butler J.E., 2003. Gem-quality synthetic diamonds grown by a chemical vapor deposition (CVD) method. *Gems & Gemology*, **39**(4), 268–283, <http://dx.doi.org/10.5741/gems.39.4.268>.
- Wang W., D'Haenens-Johansson U., Smit K., Breeding C.M. and Stern R., 2014. Carbon isotope analysis of CVD synthetic diamonds. *Geological Society of America Abstracts with Programs*, **46**(6), 268.
- Zaitsev A.M., 2001. *Optical Properties of Diamond: A Data Handbook*. Springer-Verlag, Berlin and Heidelberg, Germany, 502 pp., <http://dx.doi.org/10.1007/978-3-662-04548-0>.

The Authors

Dr Hao A. O. Wang¹

Dr Laurent E. Cartier FGA^{1,2}

Prof. Dr Lukas P. Baumgartner²

Dr Anne-Sophie Bouvier²

Dr Florence Bégué²

Jean-Pierre Chalain¹

Dr Michael S. Krzemnicki FGA¹

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