Raman spectra of diamond abrasives and possible artefacts in detecting UHP microdiamond

Steger, S., Nasdala, L.*, Wagner, A.

Institut für Mineralogie und Kristallographie,
Universität Wien, Althanstraße 14,1090 Wien, Austria
**e-mail: lutz.nasdala@univie.ac.at*

Diamond, even if present only in minute amounts in geological samples, is easily identified using Raman micro-analysis. The Raman spectrum of diamond is dominated by a single first-order band near 1332 cm^{-1} with a narrow FWHM (full width at half band-maximum) of ca. 1.6 cm^{-1} (Solin and Ramdas 1970). The spectral parameters of this band, however, may vary appreciably. First, band down-shifts associated with FWHM increases are observed in irradiation-damaged diamond (for instance, band positions below 1310 cm^{-1} and FWHMs exceeding 40 cm^{-1} were reported by Jamieson et al. 1995), upon tensile stress (Knight and White 1989), at particle sizes of smaller than 2 μm (Yoshikawa et al. 1995), and at elevated temperatures (Herchen and Capelli 1991). Compressive stress, in contrast, results in band up-shifts associated with FWHM increases (Sharma et al. 1985; Knight and White 1989). Lastly, Raman spectral parameters may also show moderate variations due to the presence of chemical impurities (Surovtsev et al. 1999).

The analytical proof of the presence of microdiamond in metamorphic rocks is considered an important indicator of UHP (ultra-high pressure) metamorphism, with peak pressures exceeding 4 GPa (Sobolev and Shatsky 1990). In contrast to coesite (whose formation is assigned undoubtedly to UHP metamorphism), however, the reliability of diamond as UHP indicator is discussed controversially. First, there exist hypotheses of metastable diamond formation, such as from fluid inclusions. Second, diamond detected in sections of metamorphic rocks is not necessarily of metamorphic origin but its presence may be due to sample contamination, for instance by remnants of diamond tools or abasives.

The second point above has been addressed already in several Raman spectroscopic studies (Menneken et al. 2007; Perraki et al. 2009) in which authors investigated possible differences in the Raman spectral characteristics of UHP microdiamond and abrasives. To the best of our knowledge, changes of Raman spectral parameters of diamond abrasives upon their practical use have not been considered thus far. This question is addressed in the present work. Our main objectives included the questions as to which degree the mechanical impact during the usage of diamond-based abrasives and tools might result in the formation or release of stress, and whether or not fresh and spent abrasives and tools yieled different diamond Raman spectra.

Diamond grains embedded in tools (saw and drill) were found to yield moderately broadened Raman bands (band positions 1330.5–1332 cm^{-1}; FWHMs 2–4 cm^{-1}), without systematic differences between new and used tools. In contrast, we found surprisingly strong differences between the Raman spectra of fresh synthetic powder abrasives and their used analogues. Unused powders generally yield broadened and down-shifted diamond bands, indicating significant amounts of tensile stress, whereas data for used powders are much closer to those of unstessed diamond (Fig. 1a). This spectral trend is in notable difference to that of UHP diamond from the Saidenbach location (Fig. 1b). Measurements on 5–30 μm sized diamond crystals included in zircon yielded moderately broadened and up-shifted Raman signals (Fig. 1b); similar results for the Saidenbach UHP diamond were obtained by Perraki et al. (2009). For the Kokchetav UHP diamond, both down-shifted (Korsakov et al. 2005) and up-shifted Raman bands (Perraki et al. 2009) have been reported. Down-shifted Raman bands were observed by Menneken et al. (2007) for diamond from the Jack Hills and

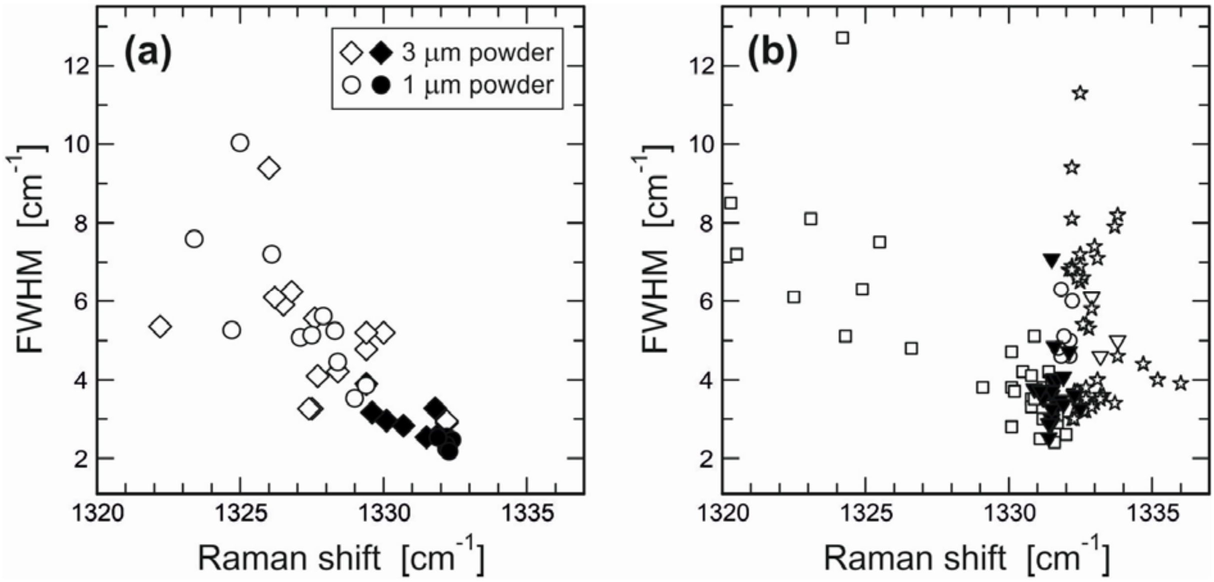

Fig. 1. *Plots of Raman spectral parameters of the main diamond band. (**a**) Two diamond-based MRB abrasives (Resin bond diamond powder, Mant USA, Inc.; open symbols = fresh powders; full symbols = used powders). (**b**) UHP microdiamond (full symbols = present work; open symbols = data from Menneken et al. 2007 and Perraki et al. 2009; ▽▼= Saidenbach, Erzgebirge, Germany; □ = Jack Hills, Western Australia; ○= Rhodopes, Greece; ☆= Kokchetav, Northern Kazakhstan).*

by Smith and Godard (2013) for diamond from Straumen, Norway. Note that the remarkably strong band down-shift and broadening of diamond abrasives observed in the present study has not been reported before. The statement of Smith and Godard (2013) who considered significantly or strongly down-shifted Raman bands "to be especially important in favouring a true geological origin", is hence inconclusive. Our results indicate that (i) simple position-FWHM relationships may be insufficient for detecting reliably diamond contaminants, and (ii) the degree of usage of abrasives needs to be considered in interpreting analytical results.

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