

A PRELIMINARY COMPARATIVE RAMAN MAPPING STUDY OF CONTRASTING ZIRCON/DIAMOND/GRAPHITE RELATIONS AT KOKCHETAV, KAZAKHSTAN

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Abstract: This contribution reports on the different Raman behaviour observed in two micro-inclusions of carbon in zircons from the Kokchetav Massif, Kazakhstan, involving different degrees of metamictisation of the host zircon and possibly also of the diamond.

Zircons in gneiss from the Kokchetav Massif, Kazakhstan, an ultra-high pressure metamorphic (UHPM) terrain created during a Palaeozoic continental collision, contain inclusions of diamond [e.g. 1,2] formed by crystallization of a COH-rich multicomponent supercritical fluid at 4-7 GPa [2].

Several zircons extracted from sample K210-LD, a garnet-biotite feldspathic gneiss collected in the vicinity of Kumdikol Lake, were examined by Raman mapping with a green 514.5 nm laser and a RENISHAW *inVia Reflex*[®] spectrometer under identical operating conditions.

Zircon 'K' contains one 14- μm wide diamond grain visible at the surface. This zircon is bluish-grey and transparent, and yields typically strong Raman spectra (Fig. 1), as it is hardly metamict (e.g. bands at 1006 & 972 cm^{-1}). In stark contrast, zircon 'G' is brownish-grey and semi-opaque. Not only is the Raman intensity reduced to be small or invisible, but also the 1006 cm^{-1} band is downshifted to 996 cm^{-1} (Fig. 1), precisely as is the case of strongly metamict zircons [3]. The diamond in zircon 'K' is subhedral and yields a slightly downshifted Raman band at 1329 cm^{-1} (Fig. 2). The diamond-like phase in 'G' (mineral X) reveals a band downshifted to 1323 cm^{-1} that is much less intense than that of the diamond in 'K'. Disordered graphitic carbon (1580 cm^{-1} with defect bands at 1357 & 1621 cm^{-1}) surrounds mineral X in 'G', but not the diamond in 'K' (Fig. 3).

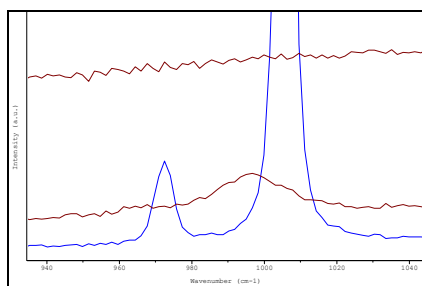


Fig. 1 (zone 940-1040 cm^{-1}) Raman spectrum of zircon 'K' (blue) and two spectra from 'G' (brown); the latter vary from eighteen times less intense to zero intensity. Raw data.

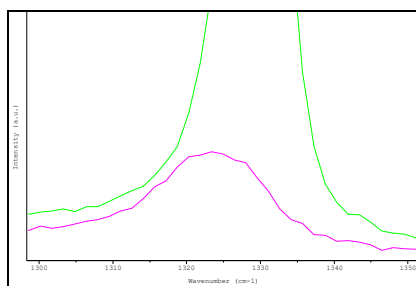


Fig. 2 (zone 1300 – 1350 cm^{-1}) Spectra of diamond in 'K' (green), and mineral X in 'G' (magenta), which is at least eight times less intense. Raw data.

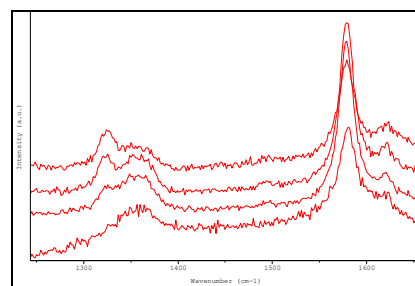


Fig. 3 (zone 1250-1650 cm^{-1}) Spectra of disordered graphitic carbon around mineral X in zircon 'G' (red). Note here the extra variable intensity of the mineral X band at 1323 cm^{-1} .

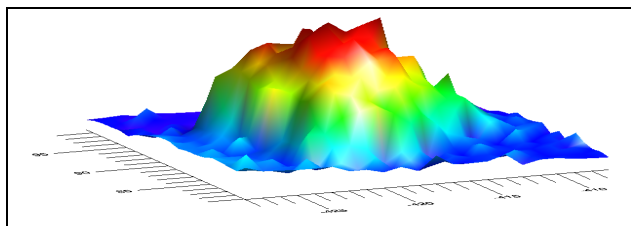


Fig. 4. A topographic map of the upper surface of the diamond in 'K' acquired with the autofocus facility of the *inVia Reflex* apparatus. The diamond appears in relief (summit at $4.2 \pm 0.4 \mu\text{m}$ higher) due to its greater hardness. The polished zircon figures in blue

Concerning zircon 'G', the intensity of the band at 1006 cm^{-1} increases close to the polyphase carbon inclusion (Fig. 5) and also at the outer grain boundary of the zircon, revealing more crystalline (*i.e.* less metamict) inner and outer rims where less alpha-radiation occurred. Inside the inclusion, the distribution of graphite is ring-like (Fig. 6) with mineral X occurring asymmetrically within the core (Fig. 7). These figures are "component score" maps of the degree of similarity of a chosen spectral zone of one selected relatively intense spectrum (*e.g.* the blue pinnacle in Fig. 5).

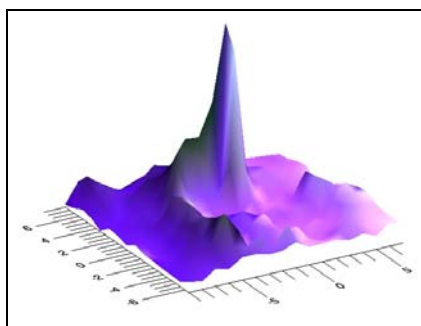


Fig. 5. 3D map of zircon's Raman band at 996 cm^{-1} around the inclusion in zircon 'G'.

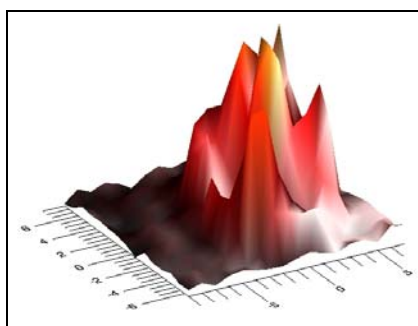


Fig. 6. 3D map of graphite's Raman band at 1580 cm^{-1} inside zircon 'G'.

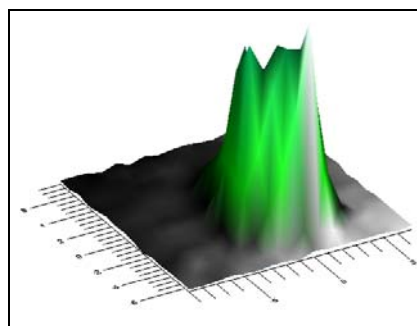


Fig. 7. 3D map of mineral X's Raman band at 1323 cm^{-1} inside zircon 'G'.

The downshifting of the normal Raman band of diamond from 1332 cm^{-1} to 1329 cm^{-1} in the diamond in 'K' and to 1323 cm^{-1} in mineral X in 'G', as well as the decrease in intensity, suggest that diamond in 'K' is intermediate between normal diamond and mineral X. This trend could be explained by several non-exclusive hypotheses: (a) defects caused by metamictisation of diamond; (b) defects caused by abundant nanometric oxide inclusions known within diamonds from Kokchetav [2]; (c) defects caused by impurities such as B, N & P; (d) disordering by another mechanism; (e) transformation into another polymorph of carbon such as lonsdaleite [*cf.* 4].

Defects in minerals commonly cause a highly fluorescent background and this is precisely the case of the spectra of the diamond in 'K' and mineral X in 'G'; indeed the 3D map of the background intensity alone is very similar to Fig. 7; this is compatible with the defect hypotheses (a, b & c). Furthermore the presence of graphite around diamond is conventionally explained by transformation by depressurisation during exhumation which, in this case, could have been facilitated by metamictisation. Thus, globally, metamictisation of diamond appears to be the strongest contender, such that mineral X would be strongly metamict diamond.

References:

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