Low water contents in diamond mineral inclusions:

Proto-genetic origin in a dry cratonic lithosphere

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20 **ABSTRACT**

21 The mantle is the major reservoir of Earth's water, hosted within Nominally Anhydrous
22 Minerals (NAMs) (e.g., Bell and Rossman, 1992; Peslier et al., 2010a, b; Nestola and Smyth,
23 2015), in the form of hydrogen bonded to the silicate's structural oxygen. From whence cometh
24 this water? Is the water in these minerals representative of the Earth's primitive upper mantle or
25 did it come from melting events linked to crustal formation or to more recent metasomatic/re-
26 fertilization events? During diamond formation, NAMs are encapsulated at hundreds of
27 kilometers depth within the mantle, thereby possibly shielding and preserving their pristine water
28 contents from re-equilibrating with fluids and melts percolating through the lithospheric mantle.
29 Here we show that the NAMs included in diamonds from six locales on the Siberian Craton
30 contain measurable and variable H₂O concentrations from 2 to 34 parts per million by weight
31 (ppmw) in olivine, 7 to 276 ppmw in clinopyroxene, and 11-17 ppmw in garnets. Our results
32 suggest that if the inclusions were in equilibrium with the diamond-forming fluid, the water
33 fugacity would have been unrealistically low. Instead, we consider the H₂O contents of the
34 inclusions, shielded by diamonds, as pristine representatives of the residual mantle prior to
35 encapsulation, and indicative of a protogenetic origin for the inclusions. Hydrogen diffusion in
36 the diamond does not appear to have modified these values significantly. The H₂O contents of
37 NAMs in mantle xenoliths represent some later metasomatic event(s), and are not always
38 representative of most of the continental lithospheric mantle. Results from the present study
39 also support the conclusions of Peslier et al. (2010a) and Novella et al. (2015) that the dry nature
40 of the SCLM of a craton may provide stabilization of its thickened continental roots.

41 **1. Introduction**

42 From infrared spectroscopic studies on single-crystals of Al₂SiO₅ minerals several decades
43 ago (e.g., Beran and Zemann, 1969) to the ground-breaking research of George Rossman and his
44 students in the mid-80s and onward (e.g., Aines and Rossman, 1984; Bell and Rossman, 1992),
45 the water contents of an increasing number of Nominally Anhydrous Minerals (NAMs) have
46 been determined, mainly by Fourier Transform Infra-Red (FTIR) spectroscopy. It readily
47 became apparent that due to solid/fluid interactions in the SCLM (Sub-Continental Lithospheric

Mantle), minerals of almost all species have incorporated water into defects, dislocations, and actual structural positions (e.g., Bell et al., 1995; Beran and Libowitzky 2006; Peslier et al., 2010b, 2012; Doucet et al., 2014). These discoveries have resulted in a re-evaluation of the ‘water budget’ of the Earth, with the result that there is far more water within the minerals of the Earth’s mantle (~84 vol. %) than in all the seas and oceans on the surface (Nestola & Smyth, 2015). However, previous studies have presented conflicting results concerning the vertical distribution of water in NAMs from the Kaapvaal and Siberian SCLMs. It was demonstrated with olivines from peridotitic xenoliths that the base (>6 GPa) of the Kaapvaal craton had water-poor olivines (<10 ppmw H₂O), and this was interpreted to be a major factor in the stabilization of its thickened continental roots (Peslier et al., 2010a, 2012). In contrast, it was recently reported that the base of the Siberian SCLM has water-rich olivines (8-323 ppmw H₂O), suggesting that water may not have as large an affect as previously thought on the rheology of the cratonic mantle (Doucet et al., 2014).

It is well appreciated that diamonds effectively represent a ‘treasure chest’ of mineral inclusions that present us with phases from the mantle that have remained pristine from their time of incorporation and/or formation in the diamond. However, previous studies have found little detectable water (<5 ppmw) in inclusions within diamonds (Matsyuk et al., 1998; Matsyuk and Langer, 2004, Novella et al., 2015).

The present study seeks to re-examine possible H₂O quantities within mineral inclusions in diamonds from several kimberlites and alluvial deposits on the Siberian Craton, as representatives of the water content of minerals at depth within the SCLM. Two main queries will be addressed: 1) is the water in the inclusion phases related to mantle processes involving diamond-forming fluids? Or 2) is the water in these inclusions a better representation of the minerals at diamond-formation depths (e.g., >150 km) and at the time of diamond formation? Here new secondary ion mass spectrometry (SIMS) data are reported on 42 analyses – 26 olivine; 6 pyroxene; 10 garnet - from a suite of 24 diamonds, from 6 kimberlite locales on the Siberian Craton - 5 kimberlites and an alluvial site (**Fig. 1**).

2. Methodology

2.1. Diamond sample locales

Diamonds were obtained from the Komsomolskaya, Mir, Sytykanskaya, Udachnaya, and Yubilenaya kimberlite pipes, and from alluvial diamond placers from the NE portion of the Siberian craton (Fig. 1). These diamonds all had single-crystal octahedral to cubo-octahedral morphologies and varied in size from 1 to 3 mm. In general, diamonds were selected with inclusions completely isolated within the diamond; however, some diamonds were also selected where the inclusions were apparently connected to the edge of the

diamonds by small cracks/fractures. This was done in order to evaluate the potential for post-encapsulation addition or loss of H in the mineral inclusions (open-systems). No evidence for post-encapsulation modification was observed.

2.2. Mineral Inclusion Preparation

The diamonds were polished with a diamond-impregnated wheel turning at 15,000 revolutions per minute, in order to expose the mineral inclusions, sometimes with two or more inclusions being exposed together on one polished surface (**Fig. 2**). With mineral inclusions in diamonds, the possibility exists for cracks leading from the inclusions through the diamond, allowing for open system behavior. The polished surfaces containing the NAMs were carefully examined under high-power (500X) microscopy. In addition, close examination with cathodoluminescent (CL) imaging on the electron microprobe was used to detect even healed cracks, similar to that by Taylor and Anand (2004). Such precautions were performed on all the diamonds (Fig. 2); several inclusions contained minor cracks that were observed to be localized, not going to the diamond surface (i.e., closed-systems). Some appeared to join the surface, indicating possible open-system behavior and were not used for this study. In addition, internal cracks were also examined during the SIMS analyses, where contamination of the inclusion with

H₂O was diligently searched for. Only those inclusions that had no possibility for post-formational contamination were analyzed.

2.3. *Electron Microprobe Analysis*

Silicate inclusions within the diamonds from Siberia were analyzed for major- and minor-element chemistry using a CAMECA SX-100 electron microprobe (EMP) housed at the University of Tennessee. The analyses were performed using wavelength dispersive spectrometers (WDS), with an accelerating voltage of 15 keV, beam current of 20 nA, a 1- μ m diameter beam, and standard PAP corrections. Counting times were 20 s for Si, Mg, Fe, Na, and Al; 30 s for Ca, Cr, K, and Mn; and 40 s for P. The instrument was calibrated daily using both natural and synthetic standards. The detectability limits for all elements were 100-300 ppmw. A cathodoluminescence (CL) detector on the EMP was utilized for creation of the overall nitrogen-zonation pattern of the diamonds and for detailed examination of potential for cracks emanating from the inclusions, particularly common with sulfide inclusions.

2.4. *Secondary Ion Mass Spectrometry (SIMS)*

The water concentrations of the inclusions were determined with a Cameca IMS 7f –GEO secondary ion mass spectrometer (SIMS) at Caltech. The analytical protocol is similar to that in Mosenfelder *et al.* (2011). Specifically, a rastered +10 keV Cs⁺ primary beam of ~4-5 nA was used to sputter C-coated samples across areas of ~40 x 40 μ m. Secondary ions (¹²C⁻, ¹⁶O¹H⁻, ¹⁸O⁻, ¹⁹F⁻, ³⁰Si⁻, ³²S⁻, and ³⁵Cl⁻) of -9 keV from the center areas of ~10 μ m in diameter were collected sequentially under high-mass-resolution conditions. The mass-resolving power (MRP) was set at ~5500, sufficient to resolve all the interferences to the ions of interests (such as ¹⁷O⁻ to ¹⁶O¹H⁻). A normal-incidence electron gun (NEG) of -9 keV was sufficient to neutralize the positive charge build-up from the Cs⁺ bombardment.

Olivine and pyroxene standards were chips of samples studied by Mosenfelder *et al.* (2011) and Mosenfelder and Rossman (2013). Pyrope to almandine garnets from Garnet Ridge, AZ were used as secondary standards. Doubly polished slabs were analyzed using a Nicolet Continuum Infrared Microscope connected to a Thermo-Nicolet iS50 Magna FTIR (Fourier Transform Infra-Red) spectrometer. Multiple points were analyzed to check homogeneity of water in these standard grains. FTIR spectra in the O-H vibrational region (from about 3000–

136 3900 cm⁻¹) were baseline corrected by manually applying spline fits using the built-in routine in
137 Nicolet's OMNIC software. The reproducibility of baseline-correction among the operator and
138 with the calibration paper of Bell et al. (1995) is ~20-30 %. The OH abundances are calculated
139 using the integral molar absorption coefficients from Bell et al. (1995, 2003).

140 **3. Results**

Fig. 2. Representative photomicrographs and CL images of diamonds and their NAM inclusions, analyzed in this study. Cracks from the inclusions to the surface were closely monitored by CL and SIMS for any water-bearing phases. For the diamonds used, none were detected.

The NAM inclusions in the diamonds examined consisted mainly of olivine, with lesser numbers of clinopyroxenes and garnets (both peridotitic and eclogitic; **Fig. 3**). The major- and minor-element compositions of the mineral inclusions are given in **Table 1**. As can be readily seen in Fig. 3, the olivines have forsterite (Fo) contents from 92.4 to 94.1, typical of harzburgitic-olivine diamond inclusions (e.g., Sobolev et al., 2009), and they have water contents ranging from 2 to 34 ppmw, with an average of 13 ppmw. The SIMS data for H₂O in the entire

42 diamond-inclusion data-set are given in **Table 2**. Olivine inclusions show a hint of two populations for water contents: 2-16 and 23-34 ppmw. In addition, water contents analyzed in 3 separate olivine inclusions within a single diamond show some variation – e.g., Ud-301, 3 separate olivines with 9, 15, 31 ppmw water (Table 2). This is a particularly important feature to note, and is discussed in detail below with regards to H-diffusion in diamond. There are also variations in olivine water contents between different localities, but all concentrations are at the low end of the range of that observed in olivines from mantle xenoliths (Fig. 4a) (Peslier et al., 2010b; Doucet et al., 2014; Hui et al., 2015).

The clinopyroxenes are of both peridotitic and eclogitic origin; two eclogitic clinopyroxenes from one diamond have 244 and 275 ppmw H₂O, whereas the peridotitic ones are lower, with 7 to 101 ppmw water (Fig. 4b; Table 2). These latter values are at the low end of the range for clinopyroxenes from cratonic peridotitic xenoliths worldwide (16-400 ppmw H₂O; Peslier et al., 2012; Hui et al., 2015). Garnets have a close grouping of water contents at 11 to 17 ppmw (Fig. 4c). The low-water contents of the garnets are also typical of garnets from mantle-peridotite xenoliths (Bell and Rossman, 1992; Peslier et al., 2010b, 2012); indeed, there does not appear to be a real difference between eclogitic versus peridotitic garnets (Table 2), but the spread of garnet water values is small in any case.

The majority of the following discussion is directed to the olivine inclusions, largely because it is the major mineral in the mantle and the one that likely controls mantle rheological properties. In addition, of the three minerals studied, the largest amount of published data exists on olivine, mostly on mantle-xenolith olivine-H₂O contents, with only a few observations on H₂O in olivine inclusions in diamonds (all ≤5 ppmw; Matsyuk and Langer, 2004; Novella et al., 2015).

4. Discussion

The Siberian SCLM can be broadly divided into two components: 1) depleted mantle (e.g., harzburgite-dunite), and 2) fertile/enriched mantle (e.g., lherzolite). The former resulted from melt extraction during large-scale (30 %) partial melting in the Archean to early Proterozoic. The latter component is the result of post-melting re-fertilization by a variety of metasomatic processes, which is generally accompanied by increases in clinopyroxene and garnet abundances

Fig. 3. Diamond inclusion chemistry. **a)** Forsterite versus water concentrations for olivine diamond inclusions; **b)** MgO versus Na₂O for clinopyroxene diamond inclusions, on plot from Taylor and Neal (1989). Note that one inclusion is eclogitic and the other is peridotitic. The third clinopyroxene inclusion analyzed, but not presented here, has high MgO (>20 wt. %) indicative of a peridotitic paragenesis. **c)** Compositions of garnets in diamondiferous xenoliths, on typical ternary. Note that two inclusions are peridotitic in origin and two are eclogitic in origin. Water contents of pyroxenes and garnets in ppmw are shown in b) and

(e.g., Ionov et al., 2010). Depleted harzburgite and dunite melt residues are characterized by high Fo olivine (>92) with Fo increasing with higher degrees of melting. All olivine inclusions in diamonds analyzed here have high Fo (>92.4) and low water (<34 ppm) contents, consistent with the composition of olivine in mantle xenoliths interpreted to represent refractory residues in the Siberian SCLM (Doucet et al., 2013, 2014).

The mantle of the Earth is dominated by olivine and its polymorphs, but the water budget of olivines in the upper mantle, based upon peridotite xenoliths, is limited to <200 ppmw (Bell and Rossman, 1992; Peslier et al., 2010b). However, at depths in the mantle of 410–660 km, the so-called Transition Zone, Pearson et al. (2014) have reported that ringwoodite can contain 1.4 wt.% H₂O, and perhaps even higher, in support of the prediction of Smyth (1987), and experimental studies (Kohlstedt et al., 1996; Thomas et al., 2014).

4.1. Water in NAMS in mantle xenoliths

The ranges of H₂O contents for the NAMS in Siberian cratonic mantle xenoliths are 6–323 ppmw in olivine, 100–272 ppm in clinopyroxene, and 0–23 ppm in garnet (**Fig. 4**). In contrast, olivine megacrysts forming in equilibrium with proto-kimberlitic melts in the mantle have an average water concentration of 152 ppm (e.g.,

Bell et al., 2004; Peslier et al., 2010b; Matveev & Stachel 2007). Furthermore, Sokol et al. (2013) showed that the water content of olivine equilibrated with carbonate-silicate $\pm$ chloride melt could be as high as 500-750 ppmw water. This suggests that olivine in equilibrium with metasomatic melts percolating through the mantle should have higher water contents than those analyzed from diamond inclusions in this study. Our measured low water contents in olivines from diamond mineral inclusions are similar to observations of Peslier et al. (2010a) for the base of the mantle lithosphere under the Kaapvaal craton. This suggests that the high-water concentrations analyzed in xenolithic NAMs from the base of the Siberian craton are likely a function of later metasomatic alteration, perhaps even related to the proto-kimberlitic melts (Doucet et al., 2014). Of course, this is based upon the supposition that dry olivine on the base of a growing craton will facilitate its stability. Our data support craton stabilization being due, in part, to low-water contents in lithospheric-mantle, as first suggested by Pollack (1986).

The large quantity of data on the H₂O contents of NAMs in mantle xenoliths segues into our study of these same NAMs isolated inside diamonds. Here we will address: a) hydrogen diffusion in diamond as negligible; b) the H₂O contents in mineral inclusions in diamonds are likely not representative of the diamond-forming fluids; and c) the H₂O contents of diamond-inclusion NAMs are representative of the mantle mineralogy at the time of the mineral encapsulation in the diamond (i.e., the inclusions are protogenetic).

4.2. Hydrogen diffusion

A critical factor that could be a real “show-stopper” for water in NAMs, including those in diamonds, is the kinetics of H (water) movement through these minerals and through the diamond hosts. Are the water contents of NAMs in diamonds their original values, or has H diffusion in the diamond modified their values? In other words, do the NAMs in diamonds lose or gain H by diffusion through the diamond host? Experimentally the diffusion rate of H in diamond is the subject of controversy. Connell et al. (1998) performed doping of diamond with muonium, a light isotope of hydrogen with similar properties, using synthetic Chemical Vapor Deposition (CVD) and HTHP diamonds (High Temperature High Pressure). They determined that H effectively does not diffuse through diamond up to the limit of their experiments at 1473 K. Popovici et al. (1995) determined H diffusion through a 500 nm thin layer on a natural IIA diamond, with the condition of diffusion being those used routinely during CVD growth. They determined that H diffusion is appreciable, at least, several orders of magnitude less than in

Fig. 4. Diamond-inclusion water concentrations for (a) olivine, (b) clinopyroxene, and (c) garnets, compared with data compiled for cratonic xenoliths from the Kaapvaal, Siberian, and Tanzanian cratons (Peslier et al., 2010b; Peslier et al., 2012; Doucet et al., 2014; Hui et al., 2015). Also note that for olivines in cratonic xenoliths in (a), the sample set in the first bin (0-20) has been capped at 25 for ease of illustration but extends to $n = 43$. Similarly, data for garnet in mantle xenoliths in the first bin in (c) extends to $n = 34$.

237 olivine, pyroxene, and garnet, but the same as for N. Their estimate is $2.4 \times 10^{-13} \text{ cm}^2/\text{sec}$. **Figure 5** is based upon this diffusion rate. Even with a minute K_d , this model predicts virtually complete re-equilibration in a Ga. There would seem to be further considerations that can affect this re-equilibration.

Natural diamond crystals contain vacancies, vacancy complexes, micro-voids, and dislocations, in addition to a myriad of N-aggregation zones. Nitrogen occupies various strategic positions in the diamond structure that hinders H diffusion. A major contribution is the presence of a single-N substitutional atom, which can substantially block H diffusion (Shiryaev et al., 2007). It is to be expected that the diffusion rates will be greatly influenced by such structural and foreign-component factors.

Another, albeit simplistic, approach to this enigma considers the driving force for the H diffusion. If the mantle host-rock for the diamonds has a lower activity of H (water) than that of the NAM inclusion, there would be a reason to suspect H diffusion as a factor. However, in post-diamond

formation, the peridotite and eclogite host rocks can realistically have a higher water activity, thus driving the possibility of increased water in the NAMs. If the inclusion in the diamond experienced a closed-system, the hydrogen content represents a dry mantle condition at the time of the diamond formation. An open-system and the hydrogen content represents a dry condition after the diamond formation. In either case, the result is for low values for the water in the NAM inclusions, such as we have determined.

All natural diamonds contain cathodoluminescent-revealed N-aggregation zonations, which point to the obvious fact that these features survived the high temperature and pressure of diamond formation and residence in the mantle, in spite of the determined N diffusion in diamond being about the same as that of H. And the same may exist for H diffusion – i.e., the water in the NAM inclusions have remained unchanged since their initial encapsulation. A further thought involves the observed fact that multiple inclusions of olivine in several of the diamonds examined in the present study have contrasting, yet similar, water contents (e.g., Ud-301, with 3 separate olivines with 9, 15, and 31 ppmw water (Table 2). This would not be expected if the inclusions had re-equilibrated with the surrounding mantle. In fact, this evidence alone strongly suggests that the diamond inclusions have been shielded within the diamonds, thus, representing the composition of the mantle at the time of diamond formation, or alternatively represent equilibration with diamond-forming fluids (discussed below).

Finally, at lithospheric-mantle temperatures and pressures, hydrogen diffusion is rapid in NAMs, particularly for olivine (e.g., Mackwell and Kohlstedt, 1990; Ingrin and Blanchard 2006). Hydrogen diffusion in Fo90 olivine at mantle P and T has been shown to occur on the scale of hours (Demouchy and Mackwell, 2006), and water profiles in olivine from xenoliths in kimberlite magmas have been used to estimate ascent rates of hours from mantle to crust (Peslier et al., 2008). This suggests that fine-grained (<100 μm) olivine inclusions in diamond might equilibrate with the diamond-forming fluid, and that indeed, the water fugacity of diamond-forming fluids is significantly lower than previously expected. However, an important concept is that H diffusion may not be the same as dehydrogenation of NAMs. A portion of the H in the NAM is there for charge compensation in the host phase (e.g., the substitution of $\text{Al}^{3+} + \text{H}^+ = \text{Si}^{4+}$ in pyroxene). To move the H out, some other chemical change must occur to maintain charge balance, etc. If the secondary process is difficult to accomplish, then the H may not leave as readily as H "diffuses" through a phase.

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300 4.3. Diamond-forming fluids

Fig. 5. The effect of diffusive re-equilibration of hydrogen depends on the partition of hydrogen between an olivine inclusion and the diamond host, as indicated by the K_d values near each curve in the figure. The effect is smaller when K_d is smaller (lower hydrogen concentration in diamond). Input: Olivine inclusion radius = 50 μm ; Diamond radius = 1000 μm ; Diffusivity = $10^{-13} \text{ cm}^2/\text{s}$.

Diamonds have been interpreted to have formed from metasomatic fluids with a large range compositions from carbonatitic end-members rich in Na, Ca, Mg, Fe, Ba, water (~6 wt.%), and carbonate (e.g., Klein-BenDavid et al., 2009), to a saline aqueous end-member rich in K, Cl, and water (14-20 wt.%) (e.g., Klein-BenDavid et al., 2009; Logvinova et al., 2008). As an aside, these fluids occur mostly in fibrous diamonds, formed by rapid growth probably within the kimberlitic melt and may not

represent the mantle conditions for

318 diamond growth. To test the scenario that the diamond-forming fluids are in equilibrium with the
 319 olivine inclusions from the present study, we calculate the water content of a melt in equilibrium
 320 with the olivine inclusions, using the experimental data of Novella et al. (2014) and Sokol et al.
 321 (2013).

322 In **Figure 6**, the calculated concentration of water in olivine is plotted against the
 323 concentration of the equilibrium melt. The partition coefficients used during these calculations
 324 are for silicate (Novella et al., 2014) and carbonatitic (Sokol et al., 2013) melt compositions.
 325 The concentrations of water in olivine analyzed in our study suggests that equilibrium melts, if
 326 indeed they were either silicate or carbonatitic in composition, would have had between 0.1 and
 327 4.5 wt.% water (Figure 6b). However, the generally low concentration of water in olivine
 328 (average 14 ppm H_2O ; Fig. 4a) suggests that this estimate is more likely $\ll 1$ wt. %. Therefore,
 329 the low concentrations of water in olivine inclusions and equilibrium fluid/melt can be

interpreted as either: 1) the water fugacity of diamond-forming fluids is likely significantly lower (i.e., $<<1$ wt. %) than previously expected, not a sensible conclusion; or 2) mineral encapsulation into diamond is sufficiently rapid to prevent equilibration between the NAMs included in the diamond with the diamond-forming fluid. [Of course, we cannot rule out some small contribution from the fluid.] This extremely low water content for the supposed diamond-forming fluid is in direct opposition with both observational data (e.g., Navon et al., 1988; Klein-BenDavid et al., 2009; Logvinova et al., 2008; 2015) and experimental evidence, which suggests that diamond growth is enhanced in carbonatitic melts with >5 wt.% water (Pal'yanov et al., 1999; 2005). It is commonly agreed that diamonds form from a metasomatic fluid rich in C-O-H-N-S (Haggerty, 1986), i.e. water, carbonate, sulfate, and minor nitrogen. The plethora of evidence leads us to believe that the water content of the NAM inclusions should represent the status of the mantle mineralogy at the moment of a rapid encapsulation in the diamonds.

4.4 *Syngeneses versus protogeneses for diamond inclusions*

One of the major premises in the study of mineral inclusions in diamonds is that they form at the same time and by the same process (i.e., syngeneses) as the diamonds that host them (e.g., Richardson et al., 1984). Indeed, many studies on the origin of diamonds base interpretations on the chemistry of the included NAMs (e.g., Shirey et al., 2013), which are generally assumed to be syn-genetic. In contrast to this origin for the inclusions is the possibility that they were simply encapsulated by the growing diamond, having formed considerably before the diamond – i.e., protogenetic. In particular, several studies (e.g., Sobolev et al., 1998; Taylor et al., 2000, 2003;) have described large chemical variations between inclusions within a single diamond. Evidence also has been given for the lack of epitaxy between the inclusions and the diamond (Bruno et al., 2014; Nestola et al., 2014), all casting doubt on the co-genesis i.e., syngeneses of the diamond inclusions. This present study also address this question of genesis and timing, with the conclusion that these diamond inclusions are protogenetic .

The present study has demonstrated that water contents of olivine garnet, and most of the clinopyroxene in diamond inclusions are obviously considerably less than those in most mantle xenoliths. Does this reflect the water content of these minerals in the SCLM before they were encapsulated (proto-genetic) or the water content of the metasomatic diamond-forming fluids as they formed (syn-genetic)? The observation of variations in the water contents of olivines

Fig. 6. a) Olivine composition versus metasomatized and depleted composition, interpreted by Doucet et al. (2014) for Siberian cratonic-mantle xenoliths. **b)** Modelled concentration of water in equilibrium with carbonatitic and silicate melts. Partition coefficients used are from Sokol et al. (2013) and Novella et al. (2014), respectively.

within one diamond (see for example UD-301 olivines in Fig. 2a) and between the OH⁻ absorption bands of olivines from the same diamond (see diamond D-14 from Novella et al., 2015) favors the former hypothesis. Water concentrations of olivine and clinopyroxene inclusions in diamond also vary between and within locales, which is best interpreted as the inclusions simply representing the water content of the mantle prior to encapsulation (protogenetic) – not the water in the diamond-forming fluids. The NAMs of a significant proportions of mantle xenoliths, on the other hand, must have acquired their water from some later source, and do not always record the water budget of the considerably dryer SCLM of the Siberian Craton, at the time of diamond formation. In fact, the hydrous nature of the diamond-forming fluids are expected because melt and fluid inclusions are water-rich (e.g., Navon et al., 1988; Klein BenDavid et al., 2009; Logvinova et al., 2015), which cannot be reconciled with an almost anhydrous diamond-forming process. Our observations are consistent with a relatively rapid encapsulation of the NAMs by the diamonds, and adds support to our contention that most diamond inclusions are protogenetic.

5. Summary

We present the first substantial data-set of the H₂O contents of well-characterized NAM inclusions within diamonds. We have illustrated that olivine and pyroxene inclusions from the Siberian SCLM contain significantly lower water contents compared to those in most cratonic mantle xenoliths and to inclusions from the much deeper transition zone. Several conclusions

are derived from this observation: 1) the unrealistically low water fugacity that the olivine H₂O contents imply effectively negates equilibrium of the NAM inclusions with the diamond-forming fluid. We conclude that the H₂O contents of the NAM diamond inclusions represent the accurate nature of the ancient mantle at the time of the diamond formation. This conclusion adds support to our contention that most diamond inclusions are protogenetic. 2) The H₂O contents of NAMs in most mantle xenoliths are not indicative of the Siberian SCLM, but represent some later fluidizing event(s). The xenolith record reflects that kimberlites preferentially sample metasomatized water-rich zones of the SCLM, which they may use as channels to ascend through (Doucet et al, 2014). Diamonds, on the other hand, protected their inclusions from later water addition. 3) The Siberian SCLM is similar to the base of the Kaapvaal cratonic root (Peslier et al., 2010a) in that both are characterized by low olivine-water contents. The latter therefore probably play a role in the strength of cratonic roots.

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