



## Low water contents in diamond mineral inclusions: Proto-genetic origin in a dry cratonic lithosphere



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### ABSTRACT

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

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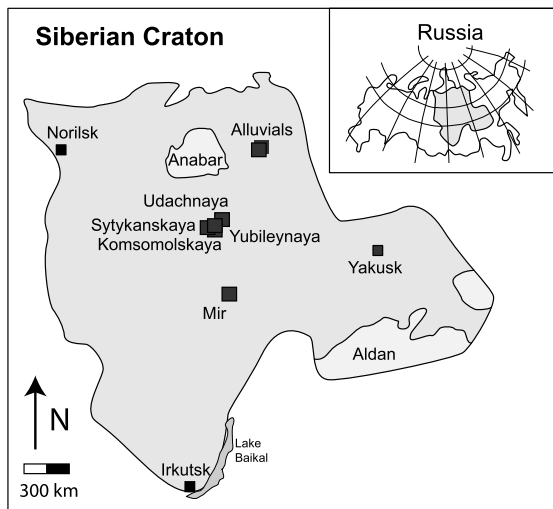
### 1. Introduction

From infrared spectroscopic studies on single-crystals of Al<sub>2</sub>SiO<sub>5</sub> minerals several decades ago (e.g., Beran and Zemmann, 1969) to the ground-breaking research of George Rossman and his students in the mid-80s and onward (e.g., Aines and Rossman, 1984; Bell and Rossman, 1992), the water contents of an increasing number of Nominally Anhydrous Minerals (NAMs) have been determined, mainly by Fourier Transform Infra-Red (FTIR) spectroscopy. It readily 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, 2010; Peslier et al., 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 and 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 H<sub>2</sub>O),

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**Fig. 1.** Map of the Siberian Craton indicating the locations of the diamonds utilized in this study.

and this was interpreted to be a major factor in the stabilization of its thickened continental roots (Peslier et al., 2010, 2012). In contrast, it was recently reported that the base of the Siberian SCLM has water-rich olivines (8–323 ppmw H<sub>2</sub>O), suggesting that water may not have as large an affect, as previously thought, on the rheology of the cratonic mantle (Doucet et al., 2014).

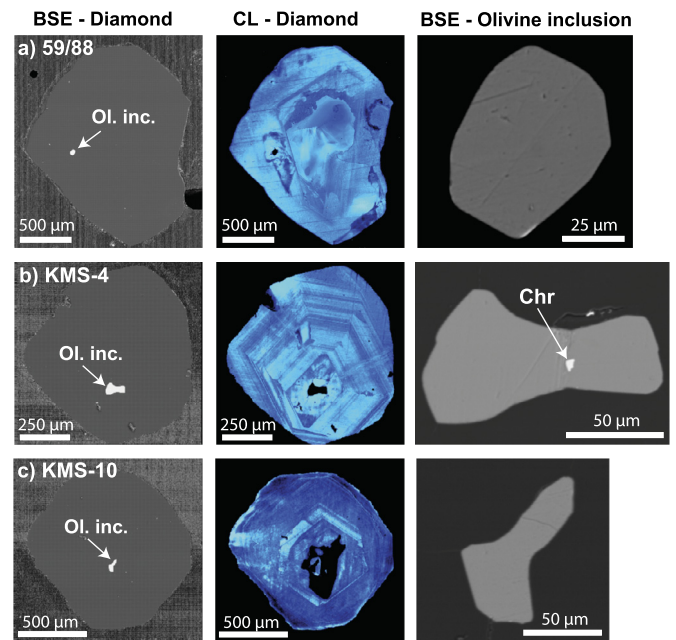
It is well appreciated that diamonds effectively represent a ‘treasure chest’ of mineral inclusions that present us with phases from the mantle that have remained pristine from their time of incorporation and/or formation in the diamond. However, previous studies have found little detectable water (<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 H<sub>2</sub>O 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, Sytykansкая, Udachnaya, and Yubileynaya 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.



**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.

### 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 (500×) 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 H<sub>2</sub>O 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-μm 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

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