Decoupled water and iron enrichments in the cratonic mantle: a study on peridotite xenoliths from Tok, SE Siberian Craton

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ABSTRACT (418 words)

Water and iron are believed to be key constituents controlling the strength and density of the lithosphere and, therefore, play a crucial role in the long-term stability of cratons. On the other hand, metasomatism can modify the water and iron abundances in the mantle and possibly triggers thermo-mechanical erosion of cratonic keels. Whether local or large scale processes control water distribution in cratonic mantle remains unclear, calling for further investigation. Spinel peridotite xenoliths in alkali basalts of the Cenozoic Tok volcanic field sampled the lithospheric mantle beneath the southeastern margin of the Siberian Craton. The absence of garnet-bearing peridotite amongst the xenoliths, together with voluminous eruptions of basaltic magma, suggests that the craton margin, in contrast to the central part, lost its deep keel. The Tok peridotites experienced extensive and complex metasomatic reworking by evolved, Ca-Fe-rich liquids that transformed refractory harzburgite to lherzolite and wehrlite. We used polarized Fourier transform infrared spectroscopy (FTIR) to obtain water content in olivine, orthopyroxene (opx), and clinopyroxene (cpx) of 14 Tok xenoliths. Olivine, with a water content of 0-3 ppm H$_2$O, was severely degassed, probably during emplacement and cooling of the host lava flow. Orthopyroxene (49-106 ppm H$_2$O) and clinopyroxene (97-300 ppm H$_2$O) are in equilibrium. The cores of the pyroxene grains, unlike olivine, experienced no water loss due to dehydration or addition attributable to interaction with the host magma. The water contents of opx and cpx are similar to those from the Kaapvaal, Tanzania and North China cratons, but the Tok opx has less water than previously studied opx from the central Siberian craton (Udachnaya, 28-301 ppm; average 138 ppm). Melting models suggest that the water contents of Tok peridotites are higher than in melting residues, and argue for a post-melting (metasomatic) origin. Moreover, the water contents in opx and cpx of Tok peridotites are decoupled from iron enrichments or other indicators of melt metasomatism (e.g., CaO and P$_2$O$_5$). Such decoupling is not seen in the Udachnaya and Kaapvaal peridotites but is similar to observations on Tanzanian peridotites. Our data suggest that iron enrichments in the southeastern Siberian craton mantle preceded water enrichment. Pervasive and large-scale, iron enrichment in the lithospheric mantle may strongly increase its density and initiate a thermo-magmatic erosion. By contrast, the distribution of water in xenoliths is relatively “recent” and was controlled by local
metasomatic processes that operate shortly before the volcanic eruption. Hence, water abundances in minerals of Tok mantle xenoliths appear to represent a snapshot of water in the vicinity of the xenolith source regions.

KEYWORD: peridotite, water, lithospheric mantle, stability, FTIR
The longevity and the stability of the oldest continental domains (also known as ‘cratons’) are commonly attributed to the presence of a buoyant, cold and “dry” layer in their lithospheric mantle (Boyd, 1989; Hirth et al., 2000; Peslier et al., 2010). This layer is composed of residual peridotites formed by high degrees of melt extraction, responsible for iron- and water-depletion. Such cratonic peridotites are less dense (Herzberg and Rudnick, 2012) and more viscous (Dixon et al., 2004; Hirth et al., 2000) than the surrounding asthenosphere, made up of fertile peridotites richer in iron and containing more water. The cratonic keel is thus physically isolated from the convective mantle and preserved from delamination, providing its longevity (Jordan, 1978; O’Neill et al., 2008; Sleep, 2003).

Studies on cratonic mantle xenoliths worldwide show that most of these peridotites experienced metasomatic re-enrichment in incompatible elements (Carlson et al., 2005; Ionov et al., 2010; Pearson et al., 1995a; Shimizu et al., 1997; Simon et al., 2003), which is often associated with deformation (Boyd and Mertzman, 1987; Ionov et al., 2017). This post-formation modification of the cratonic keel may lead to its erosion (or rejuvenation) (Foley, 2008; Lee et al., 2011; Liu et al., 2019), which may affect either the entire keel, like in the North China Craton (Gao et al., 2002; Griffin et al., 1998; Menzies et al., 2007; Rudnick et al., 2004), or the cratonic margins, like in the Siberian craton (Ionov et al., 2005a; Ionov et al., 2005b), the Colorado Plateau (Lee et al., 2001), the Tanzanian craton (Lee and Rudnick, 1999; Rudnick et al., 1994) and cratons in Greenland (Bernstein et al., 1998; Bernstein et al., 2007).

At least three processes may cause or facilitate the destruction of cratonic keels: (1) convective removal driven by shear stress imposed by mantle flow in the asthenosphere (Cooper and Conrad, 2009; King, 2005), (2) rheological weakening through hydration of the mantle lithosphere by ingress of melt or fluids (Dasgupta et al., 2007; Li et al., 2008) and (3) thermo-magmatic erosion due to enrichment in Fe and heating during modal metasomatism (also referred to as “refertilization”) (Foley, 2008). Iron and water appear to be key constituents controlling the stability and the longevity of the lithospheric mantle because they strongly affect its density and strength, respectively.
Water in the mantle primarily resides in nominally anhydrous minerals (NAMs) such as olivine, pyroxenes, and garnet (Asimow and Langmuir, 2003; Bell and Rossman, 1992; Hermann et al., 2007; Hirth and Kohlstedt, 1996; Kovács et al., 2012; Kovacs et al., 2010). Water enters these anhydrous minerals, typically as protons (H\(^+\)) bonded to structural oxygen in intrinsic crystal defects (Bell and Rossman, 1992; Rossman, 1996; Smyth et al., 1991). Olivine tends to be stronger if its water content decreases (Mackwell et al., 1985), which may explain why cratonic roots remain strong and resistant for billions of years (Dixon et al., 2004; King, 2005; Mackwell et al., 1985; Peslier, 2010; Pollack, 1986).

The notion of craton-wide dehydration has been questioned by recent studies of water distribution in the cratonic mantle. Water content in minerals shows a clear correlation with metasomatism, especially with iron enrichment, but this correlation seems to be related to local processes (Doucet et al., 2014; Hui et al., 2015; Peslier et al., 2010; Peslier et al., 2012). In the case of the Kaapvaal craton, the enrichment in water is limited to the shallow parts of the cratonic lithosphere (Peslier et al., 2010; Peslier et al., 2012). For the Siberian craton, the water enrichment occurs above the lithosphere-asthenosphere boundary, in laterally-limited regions, probably near shear zones. Water enrichment is associated with modal metasomatism and iron enrichment (Doucet et al., 2014), possibly triggered by asthenospheric volatile-rich silicate melts (Berkesi et al., 2019). By contrast, the water enrichment in the Tanzanian craton is limited to highly-metasomatized peridotites sampled by the Labait volcano (Hui et al., 2015). The North China Craton exhibits elevated water content (Li et al., 2015; Xia et al., 2017) probably caused by metasomatism by aqueous fluids that were likely introduced by subduction (review by Liu et al., 2019). Even if the distribution of water in the cratonic mantle indeed strongly affects the long-term stability of continents (Pollack, 1986), this distribution and the related processes need to be better constrained.

In this study, we report the water content of olivine, orthopyroxene (opx) and clinopyroxene (cpx) of 14 peridotite xenoliths from the Tokinsky Stanovik volcanic field (Tok), located in the Aldan shield on the southeastern (SE) margin of the Siberian craton (Fig. 1). The xenoliths are well-characterized spinel peridotites, some of which experienced pervasive iron enrichment and modal metasomatism shortly before the eruption of host basalts (Ionov et al., 2005a; Ionov et al., 2005b). The absence of garnet-facies peridotite among the Tok
xenoliths confirms the geophysical data suggesting the lost of the deep keel beneath the SE margin of the
Siberian craton (Priestley and Debayle, 2003), in contrast to the central Siberian craton where the lithosphere-
asthenosphere boundary is 220 km deep according to both xenolith studies (Boyd et al., 1997; Ionov et al., 2010)
and geophysical data (Priestley and Debayle, 2003).

The new water data, obtained in this study by polarized FTIR, are compared with the data from an FTIR-
study on the spinel and garnet peridotites from the Udachnaya kimberlite in the central Siberian craton (Doucet
et al., 2014) to provide an overview of the distribution of water in the lithospheric mantle of the Siberian Craton.
The water content in olivine, opx, and cpx are examined in light of available data on the chemical compositions
of bulk rocks and minerals to constrain the processes controlling the distribution of water in the cratonic mantle.
Finally, the effects of water and iron on the longevity and local erosion of the Siberian craton and the
implications of these results for cratons, in general, are reviewed.

GEOLOGICAL SETTING

Neoproterozoic to Paleozoic sediments and Permian-Triassic flood basalts cover the Siberian craton,
except for the Anabar and Aldan shields in its northern and south-eastern parts (Fig. 1), where gneisses and
granulites with ages up to 3.0–3.6 billion years (Ga) are exposed (Jahn et al., 1998; Nutman et al., 1992;
Paquette et al., 2017; Zonenshain et al., 1990). The Archean and Paleoproterozoic blocks amalgamated in the
mid-Proterozoic (1.8–2.0 Ga) (Rosen et al., 2005). The oldest Re-Os ages for mantle xenoliths from the Siberian
craton are 3.3 Ga (Pearson et al., 1995a; Pearson et al., 1995b), but Re-Os and Lu-Hf data suggest that the main
components of the lithospheric mantle formed in two stages about 2.8 Ga and 2.0 Ga (Doucet et al., 2015; Ionov
et al., 2015a; Ionov et al., 2015b).

The Aldan shield is the largest area of exposed Archean and Paleoproterozoic (3.6–1.9 Ga) crustal rocks
on the Siberian craton (Frost et al., 1998; Jahn et al., 1998; Nutman et al., 1992). The shield is made up of two
blocks, the Aldan in the north and the Stanovoy in the south. An area in the eastern Stanovoy Range is called
Tokinsky Stanovik and is made of Quaternary alkali basaltic rocks with Ar-Ar ages of 0.59–0.28 Ma (Rasskazov
et al., 2000). Mantle xenoliths in this area are hosted by the basaltic lavas, by contrast with those from the central craton, where they occur in kimberlites.

**SAMPLE OVERVIEW**

The peridotite xenoliths from Tok are spinel harzburgites, lherzolites, and wehrlites (Fig. 2 and Table 1). Detailed petrographic and geochemical studies of these xenoliths (Ionov et al., 2005a; Ionov et al., 2005b) indicate that the lithospheric mantle beneath Tok first experienced high degrees of melt extraction (up to 25–40%) and then large-scale metasomatic re-working, erasing the geochemical signatures of initial melting events and imparting signatures of enriched melts/fluids in the majority of the samples (Ionov et al., 2006a). Upward migration of mafic silicate melts mainly produced this extensive reworking, followed by the percolation of low-temperature, alkali-rich melts and fluids (Ionov et al., 2006a). Chromatographic fractionation and fractional crystallization of the melts strongly enriched the host peridotite in light (L) rare earth elements (REE) close to the percolation front and dramatically changed the chemical composition of the initial liquids, which progressively evolved from high-T basaltic melts to low-T, alkali-rich silicate and then CO$_2$- and P$_2$O$_5$-rich derivatives (Ionov et al., 2006a). During thermal relaxation of the metasomatic system to ambient geotherm (“retrograde” metasomatism), the percolation front migrated downwards. Small-volume residual fluids were trapped, and crystallized volatile-rich accessory minerals such as apatite (F, Cl-rich; up to 1000 ppm H$_2$O), amphibole (up to 2 to 4 wt.% H$_2$O) and phlogopite (up to 5 wt.% H$_2$O) (Ionov et al., 2006a). Shortly before the entrainment of the xenoliths into Quaternary basaltic magma, fluids with low water activity (e.g., due to low H$_2$O/CO$_2$) migrated through the lithospheric mantle section triggering the breakdown of hydrous amphibole and phlogopite into anhydrous assemblages and the formation of whitlockite (an anhydrous, halogen-poor and Ca–Mg-rich phosphate) (Ionov et al., 2006b).

Tok peridotites are subdivided in two rock series based on their petrography, modal abundances, Mg# [Mg/(Mg+Fe)$_{at}$] and trace element signatures (Ionov et al., 2005a; Ionov et al., 2005b) (Table 1 and supplementary data 1):
(1) The lherzolite-harzburgite (LH) series groups “normal” (in terms of Mg# and modal composition) fertile to refractory rocks, which are melt extraction residues with relatively low FeO (7.4–9.0 wt.%) and a Mg# ≥ 0.89 (Fig. 3 and 4). The LH series rocks in this study include seven harzburgites, one cpx-poor lherzolite (9510-16) and one fertile lherzolite (9506-2) (Table 1 and Fig. 2). The majority of the LH rocks are variably metasomatized refractory melting residues that have low heavy (H) REE abundances and show consistent gradual enrichments from HREE to LREE. Their LREE patterns are commonly La-enriched in particular for phosphate-bearing samples.

(2) The lherzolite-wehrlite (LW) series is composed of rocks with low Mg# (<0.89), high modal olivine (72–84 wt.%), cpx (7–22 wt.%), and cpx/opx ratios. This series was produced by the reaction of refractory residual peridotites with evolved, Fe-rich (Mg# = 0.6–0.7), silica-undersaturated melts at high melt/rock ratios. This metasomatic process caused replacement of opx by cpx (Fig. 3) and Fe (±Ca, ± trace element) enrichments (Fig. 4c) (Ionov et al., 2005a; Ionov et al., 2005b). The LW series peridotites have lower Mg# than the LH series rocks: 0.829–0.889 for the opx-poor lherzolites and 0.839–0.868 for the wehrlites (Table 1 and Fig. 4a). They have HREE and middle (M) REE abundances five times higher than the refractory LH series rocks (Fig. 5a). Light REE abundances in the LH and LW rock series partly overlap (Fig. 5a).

Both LH and LW series rocks have higher HREE (e.g., Yb in Fig. 5) than refractory peridotites from orogenic (e.g., Horoman Massif, Takazawa et al., 2000) and cratonic settings (e.g., spinel and garnet peridotites from Udachnaya, Ionov et al., 2010) and generally plot above the melting trend in Al₂O₃ vs. Yb plots (Fig. 5b), defined using trace element modelling for non-modal fractional melting of a spinel peridotite with the primitive mantle composition (Doucet et al., 2013). We modelled the partition coefficient between opx and cpx (D\text{cpx/opx}) following the method of Liang et al. (2013). The measured and predicted D\text{cpx/opx} are in good agreement, indicating that REE are in equilibrium between opx and cpx (Fig. 6) in the LH and LW series peridotites. Therefore, opx and cpx are chemically equilibrated and unaffected by host basaltic magma.

The Os-Hf-Sr-Nd isotope study on the spinel peridotites from Tok suggests that, before being highly metasomatized, the lithospheric mantle beneath the SE margin of the Siberian craton formed between 2.8 and
2.0 Ga, i.e., at about the same time as the central and the north-eastern parts of the craton (Doucet et al., 2015; Ionov et al., 2015a; Ionov et al., 2015b).

To sum up, the petrographic and geochemical data of the Tok xenoliths indicate extensive metasomatic reworking of their original residual “protoliths” in two stages: (1) iron enrichments and replacement of opx by cpx in the LW series rocks, produced by the interaction of the protolith with evolved silicate melts; (2) precipitation of fine-grained interstitial materials containing phosphates and alkali feldspar, both in the LH and LW suites, by the migration of water-poor, CO$_2$-rich fluids through the host peridotite (Ionov et al., 2006a; Ionov et al., 2006b). Overall, the uppermost mantle beneath the SE margin of the Siberian craton may be one of the most strongly metasomatized continental mantle domains worldwide.

METHODS

Sample preparation

Fresh material from xenolith cores (0.1–1 kg) was crushed to <1–2 mm between two hydraulically driven wear-resistant tungsten carbide plates. Gem-quality (i.e., the purest crystals without cracks and inclusions) olivine, opx and cpx, preferably unbroken crystals, were handpicked from sieved >1 mm size fraction for olivine (15–67 per mineral) and 0.6–1 mm for pyroxene (20–40 grains per mineral) under a binocular microscope. The mineral grains were set in epoxy before being polished on two parallel surfaces at the Département de Géologie de l’Université Jean Monnet in Saint-Etienne (France) and at the State Key Laboratory for Mineral Deposits Research of Nanjing University (China). The thickness of the double-polished mineral grains determined with a Mitutoyo digimatic micrometer ranges from 90 to 916 µm (±1 µm). The polished sections were placed in a desiccator before FTIR analyses to eliminate potential surface water.

Fourier Transform Infrared spectroscopy (FTIR)

A continuum infrared microscope in combination with a Nicolet iS50 FTIR at Nanjing University (China) was used to analyze water in olivine and pyroxene. The crystallographic orientation of each polished mineral grain was determined using interference figures under a petrographic microscope. Areas of 30 × 30 to 80 × 80
µm² were measured under transmission mode in the wavenumber range of 7000–650 cm⁻¹ with a resolution of 4 cm⁻¹ and 256 scans. A wire-grid Zn-Se infrared polarizer rotated parallel to each principal axis of the oriented mineral grain was used during FTIR analyses. Each analysis was performed in a pre-dried air environment to minimize interference from ambient atmospheric water vapor. Cross-sections were measured to assess the homogeneity of hydrogen distribution within the grain. Typically, at least one new background spectrum was collected every two hours.

The spectra were normalized to a thickness of 1 cm to be compared with each other and with literature data. The baseline was manually corrected using the Omnic© software. The total integrated absorbance (Aₜₒₜ), corresponding to the sum of areas integrated beneath the O-H bands with the vector of the incident infrared light parallel to three principal axes (E//α, E//β, and E//γ), was used to calculate water concentration in each mineral according to the following expression of the Beer-Lambert law:

\[ C_{H_2O} = \frac{A_{tot}}{I'}, \]

where \( C_{H_2O} \) is water concentration (in ppm by weight H₂O), and \( I' \) is the integral specific absorption coefficient, which is characteristic of the mineral composition (in ppm⁻¹ cm²). The absorption coefficient used for olivine was \( I' = 5.32 \pm 0.34 \) ppm⁻¹ cm² between 3800 and 3400 cm⁻¹ (Group 1) and \( 2.22 \pm 0.1 \) ppm⁻¹ cm² between 3400 and 3100 cm⁻¹ (Group 2) (Bell et al., 2003), for opx was \( I' = 15.6 \pm 0.94 \) ppm⁻¹ cm² between 3650 and 2600 cm⁻¹ (Bell et al., 1995), and for cpx was \( I' = 7.09 \pm 0.32 \) ppm⁻¹ cm² between 3650 and 3000 cm⁻¹ (Bell et al., 1995). For each mineral of one sample, at least two grains were analyzed to obtain the total integrated absorbance (\( A_{tot} \)).

**FTIR SPECTRA AND OH ABSORBANCE**

Absorption bands due to O–H vibrations in olivine and pyroxene of the 14 Tok peridotite xenoliths are located between 3650 and 3100 cm⁻¹ and 3650 and 2600 cm⁻¹ respectively (supplementary data 2). These spectra are similar to the published OH spectra for olivine and pyroxene in kimberlite-hosted mantle xenoliths from the Siberian craton (Doucet et al., 2014; Matsyuk and Langer, 2004), the Kaapvaal craton (Bell et al., 2003; Peslier, 2005).
et al., 2010; Peslier et al., 2008), the Ontong Java Plateau (Demouchy et al., 2015), and the Tanzanian craton (Hui et al., 2015). Olivine in the majority of the Tok samples has barely detectable OH bands at 3572 and 3525 cm$^{-1}$, and 3707 and 3683 cm$^{-1}$, and could correspond to nano-inclusions of Ti-clinohumite and serpentine respectively (Khisina and Wirth, 2008; Khisina et al., 2008; Kitamura et al., 1987; Koch-Müller et al., 2006; Matsyuk and Langer, 2004; Miller et al., 1987; Mosenfelder et al., 2006). However, such nano-inclusions are undetectable under an optical microscope. The OH absorbance at 3525 cm$^{-1}$ could also be related to intrinsic Ti-defects in olivine (Tollan et al., 2018). In olivine, Ti$^{3+}$ or Ti$^{4+}$ can substitute Mg$^{2+}$ in the octahedral site, and the charge can be balanced by H$^+$ replacing Si$^{4+}$, creating the Ti-clinohumite point defect (Jollands et al., 2016). Titanium being highly incompatible in olivine ($D^{\text{ol/melt}}<0.01$, McKenzie and O’Nions, 1991), the incorporation of Ti in olivine from refractory peridotite can only occur during metasomatism. The contribution of the nano-inclusions remains controversial, but the low alteration of samples (loss on ignition <0.05 wt.%) suggests that these inclusions might have been formed in a mantle environment (Khisina and Wirth, 2008).

The opx have OH bands at 3600, 3565, 3525, and 3440 cm$^{-1}$ (Fig. 7d-f). The cpx have OH bands at 3630, 3525 and 3440 cm$^{-1}$ (Fig. 7g-i). The OH band located at ~3525 cm$^{-1}$ is similar to natural samples from various tectonic settings (Bonadiman et al., 2009; Demouchy et al., 2015; Denis et al., 2018; Peslier et al., 2002). The available experimental work suggests that substitution mechanisms can explain OH bands above 3400 cm$^{-1}$. In that case, the structural hydroxyl is linked to trivalent cations in the pyroxene structure (Stalder, 2004; Stalder and Skogby, 2002) such as aluminum, sodium and chromium (Aubaud et al., 2004; Bromiley and Keppler, 2004; Hauri et al., 2006; Mierdel and Keppler, 2004; Rauch and Keppler, 2002; Stalder, 2004; Stalder and Skogby, 2002; Tenner et al., 2009). However, the absence of correlation between Al$^{IV}$, Al$^{VI}$, Na, Cr and water content in the pyroxene (supplementary data 1) makes any band attribution to specific lattice defect difficult (Peslier et al., 2012). On the other hand, the absence of OH bands at ~3675–3695 cm$^{-1}$, generally attributed to nano-inclusions of amphibole (Della Ventura et al., 2007; Kovács et al., 2012), suggests that all water has been detected as hydroxyl in intrinsic defects.
The majority of opx has homogenous flat core profiles, excluding the lower absorbance at rims (Fig. 8), and cpx (except cpx from 9510-19) have uniform water content. The cpx from sample 9519-19 has lower abundance at the rim (Fig. 8d), but the difference between the core and rim is limited and close to the uncertainties. The opx with diffusion profiles exhibits much more significant variations between the core and rim (Fig 8a–c). In order to convert the total integrated absorption into H$_2$O concentrations, we used absorption coefficients from Bell et al. (2003) for olivine and Bell et al. (1995) for pyroxene. We do, however, acknowledge that there remains uncertainty as to the correct choice of absorption coefficient, particularly for olivine (for discussions, see Kovacs et al. (2010); Withers et al. (2012); Demouchy and Bolfan-Casanova (2016); Tollan et al. (2018)), and therefore also provide the total integrated absorbances in Table 1.

The concentrations in the mineral cores are 0–3 ppm H$_2$O for olivine, 49–106 ppm H$_2$O for opx, and 97–300 ppm H$_2$O for cpx (Table 1). The olivine and pyroxene data show that olivine is not in equilibrium with opx and cpx (Fig.9a,b) with D$_{opx/ol}$ and D$_{cpx/ol}$ ranges of 33–374 and 16–822 respectively while the experimental equilibrium range is 3.5–12.2 (D$_{opx/ol}$) (Demouchy et al., 2017; Hauri et al., 2006) and 3.3–33 (D$_{cpx/ol}$) (Novella et al., 2014; Tenner et al., 2009). On the other hand, opx and cpx appear to be in equilibrium (Fig.9c) with D$_{cpx/opx}$ from 1 to 3 with an average of 2, in line with experimental values ranging from 1.2 to 3.5 (D$_{cpx/opx}$) (Hauri et al., 2006; Kovács et al., 2012).

DISCUSSION

Preservation of mantle water content in olivine and pyroxenes

Water content in NAMs is often disturbed during magmatic ascent because hydrogen diffuses rapidly through NAMs at magmatic temperatures (T > 800°C) (Demouchy, 2010; Demouchy and Mackwell, 2003; Kohlstedt and Mackwell, 1998; Mackwell and Kohlstedt, 1990). Host magma, such as continental alkali basalts, may contain up to ~4 wt.% H$_2$O (Dixon et al., 2002; Dixon et al., 1988; Hochstaedter et al., 1990; Simons et al., 2002; Sisson and Layne, 1993; Stolper and Newman, 1994; Wallace, 2005; Xia et al., 2016) and could
potentially add water to the xenolith. Alternatively, the xenoliths could lose hydrogen via dehydration during decompression and a decrease of water activity (Demouchy et al., 2006; Demouchy and Mackwell, 2006b; Marshall et al., 2018; Patkó et al., 2019) (Demouchy et al., 2006; Demouchy and Mackwell, 2006a; Ingrin and Blanchard, 2006; Peslier and Luhr, 2006; Peslier et al., 2008). This phenomenon may even cause partial or complete dehydration of the grains resulting in no detectable water (Denis et al., 2018; Tian et al., 2017). Therefore, it is essential to establish to what extent measured water concentrations in olivine and pyroxenes may reflect equilibrium mantle concentrations, and this can be done using two approaches. The first is to measure H in profiles across individual grains to determine whether concentration gradients are present and whether they are induced by diffusive loss (or gain) of H. The second is to compare inter-mineral water distribution coefficients with experimental equilibrium water partitioning studies.

The olivine absorbance in thick double-polished grain mounts (>500 µm) is barely above FTIR detection limits, and olivine is not in equilibrium with coexisting pyroxenes, whereas the cores of opx and cpx are equilibrated with each other which indicates water loss in olivine. By contrast, the majority of opx and cpx from xenolith 9510-19 shows water loss at grain edges, but flat absorbance profiles in cores and uniform absorbance values in the cores of different grains. Our data suggest that water had time to diffuse out of olivine and opx but not (or very limited) in cpx, which is in line with recent studies (Tian et al., 2017). Therefore, it is crucial to investigate the effects of diffusion in mineral grains to explore the distribution of water. We model the water loss in olivine and opx using the 1D-diffusion modeling of Peslier et al. (2008), using the equation of Shewmon (1983) (supplementary data 3) and parameters of (Demouchy and Mackwell, 2006a; Stalder and Skogby, 2003; Tian et al., 2017). We assumed a chemical diffusion of H by mobility of metal vacancies, the only mechanism for which diffusion in olivine and opx is significantly faster than cpx and probably the dominant process that controls water diffusion in mantle minerals (Tian et al., 2017; Tollan et al., 2018) (Table 2 and 3 of supplementary data 2). The best fit to the opx data is obtained using the water concentrations measured in the cores as initial water concentrations and diffusion time during 19 days at 900°C, two days at 1000°C and 6h at 1100°C (Fig. 8a). Water diffusion at temperatures above 1200°C is not well constrained by experimental studies.
(Tian et al., 2017). The water profiles cannot be reproduced by assuming 25% higher initial water content. We also modelled the water dehydration in olivine at temperatures ranging from 900°C to 1100°C for the same diffusion time (19 days, two days, and 6h) (Fig. 8c,d). The initial (pre-dehydration) water concentration in olivine was estimated following the method of Warren and Hauri (2014) using theoretical pyroxene/olivine partition coefficients ($D_{\text{cpx/ol}}^{\text{opx}}$ and $D_{\text{opx/ol}}^{\text{cpx}}$) (Table 2). The average estimated water concentration in olivine is 24 ± 13(1σ) ppm. The olivine is degassed to <1 ppm after 19 days at 900°C, two days at 1000°C and 6h at 1100°C (Fig. 8c,d), which suggests that dehydration of olivine and opx may occur between 900°C (similar to equilibrium temperatures of the xenoliths) and >1100°C, but also relatively by rapidly to not to affect water in the cpx. At high temperatures (>1100°C), water diffuses 1-2 orders of magnitude faster in olivine than in opx and up to 10 orders of magnitude faster in olivine than in cpx (Demouchy and Bolfan-Casanova, 2016; Ferriss et al., 2016; Ingrin and Blanchard, 2006; Stalder and Behrens, 2006; Stalder et al., 2007; Stalder and Skogby, 2007; Tian et al., 2017; Woods et al., 2000; Xu et al., 2019), and two orders of magnitude faster in opx than in cpx (Tian et al., 2017). On the other hand, water diffusion in cpx is still too fast to avoid partial loss if dehydration occurs at mantle depths (Ferriss et al., 2016; Tian et al., 2017; Xu et al., 2019). Therefore, water diffusion should occur at a sufficiently high temperature to dehydrate olivine and opx edges, but slow enough to preserve the water in the cores of opx and the cpx. Moreover, the shape of the majority of the cpx FTIR spectra in this study (Fig. 7) shows the predominance of OH absorbance at 3630 cm$^{-1}$ defined by Patkó et al. (2019) as “type 1 spectra”. The cpx generally have two intense bands at ~3630 and 3525 cm$^{-1}$ and type 1 spectra is defined when absorption intensity values at ~3630 cm$^{-1}$ dominate. Patkó et al. (2019) show that cpx with type 1 spectra have higher maximum and average water content, and concluded that cpx with type 1 spectra are likely to represent the original conditions, presumably under high water activity. The type 1 spectra of cpx from Tok t suggests that the water content in pyroxenes has been preserved from eruptive processes. In addition, the presence of dry olivine suggests a slow rate of high-temperature annealing (Patkó et al., 2019).

The Tok xenoliths were collected in thick alkali basalt lava flows away from eruption centers, which cover 210 km$^2$ in the region; the presence of hawaiites among the volcanic rocks suggests large amounts of hot
(>1000˚C, probably >1200˚C) magma produced (Ionov et al., 2005b). Altogether, the water diffusion profiles in minerals, the water equilibrium between the opx and cpx cores, and field evidence indicate that the transport of the Tok xenoliths in hot host magmas followed by rapid cooling is consistent with dehydration of the xenoliths during the eruption and emplacement of the lava. The effect of the eruption, emplacement, and cooling on the water content of the minerals is in agreement with Li abundances and δ7Li disequilibria between olivine and pyroxenes attributed to the cooling in thick lava flow (Ionov and Seitz, 2008). Hence, we posit that cpx is the most robust recorder of water content in mantle xenoliths hosted in lava flows.

**Water in orthopyroxene and clinopyroxene – melting vs. metasomatism**

**Partial melting and water content.** The tectonic settings responsible for the formation of cratons are still debated, but it is generally accepted that the cratonic mantle lithosphere under ancient continental cores underwent at least 30–40% of melt extraction (Bernstein et al., 1998; Boyd, 1989; Boyd et al., 1997; Doucet et al., 2012; Ionov et al., 2010; Kopylova et al., 1999; Lee, 2006; Pearson and Wittig, 2008; Simon et al., 2007). These melting events occurred during the Archean or early in the Proterozoic (Carlson et al., 1999; Doucet et al., 2015; Ionov et al., 2015a; Ionov et al., 2015b; Pearson et al., 1995a; Wiggers de Vries et al., 2013; Wittig et al., 2010) and must have left behind dry, water-depleted residues (Aubaud et al., 2004; Aubaud et al., 2008; Grant et al., 2006; Grant et al., 2007; Hauri et al., 2006; Tenner et al., 2009). To investigate the links between the distribution of water in the lithospheric mantle of Tok and the melting processes, we modeled the water content of melting residues assuming that water behaves as an incompatible element (Hellebrand et al., 2002; Johnson et al., 1990; Shaw, 1970) (Table 4 of supplementary data 1). We simulated two types of melting: non-modal fractional melting and batch melting (Shaw, 1970) using the partition coefficients of Tenner et al. (2009) for melting at 3GPa (supplementary data 3 and 4). In the first series of modelling, we use the water estimate for the primitive mantle (1100 ppm H2O) as the initial water content of the melting source (Bell and Rossman, 1992; Palme and O'Neill, 2003). The non-modal fractional melting model produces "dry" bulk-rock residues and pyroxenes (both < 0.1 ppm H2O) after only 6–7% of melt extraction at 3 GPa. By contrast, in the batch melting
model, the residue still contains about 20 ppm H$_2$O in bulk rock, 30 ppm H$_2$O in opx, and 30 ppm H$_2$O in cpx even after 25% melting.

In the second series of modeling, the water content estimate for a water-depleted source (180 ppm H$_2$O), similar to the source region of mid-ocean ridge basalts (MORB), is used as the initial water content of the fertile peridotite source (Danyushevsky et al., 2000; Dixon et al., 1988; Michael, 1995; Michael, 1988; Sobolev and Chaussidon, 1996). After 4–5% of fractional melting, the bulk residue becomes “dry” (< 0.1 ppm of water). Even if the partition coefficient of Sokol et al. (2013) between olivine and melt is applied ($D_{\text{H}_2\text{O}}^{\text{ol/melt}} \approx 0.003$, which is 5 times higher than the partition coefficient of Tenner et al. (2009), $D_{\text{H}_2\text{O}}^{\text{ol/melt}} \approx 0.0006$), the water content in opx and cpx of <0.1 ppm H$_2$O is obtained. The residue contains <10 ppm H$_2$O in opx and cpx after 25% of batch melting, which is lower than the degrees of melting commonly inferred for cratonic peridotites, i.e. 30 to 40% (Lee et al., 2011). This value is lower than the water content in Tok pyroxenes as well.

The opx from the Tok xenoliths in this study contain up to 106 ppm H$_2$O and the cpx up to 300 ppm. Our modelling shows that such water concentrations cannot be residual after partial melting, especially at high melting degrees (30–40%) and thus was added to the xenoliths after melt extraction. This inference agrees with the absence of a correlation between water content in the pyroxenes and melts depletion indices in this study. Metasomatism generally erases the record of partial melting for incompatible elements in residues and may control the distribution of water in the cratonic mantle (Doucet et al., 2014; Hui et al., 2015; Peslier and Bizimis, 2015; Peslier et al., 2012; Selway et al., 2014).

**Metasomatism and water content.** Recent studies on water distribution in cratonic mantle reveal positive correlations between water in minerals and metasomatism indices (see review by Peslier et al., 2017). For example, the water content in garnets correlates with TiO$_2$ concentration in garnet from the in Kaapvaal (South Africa) and Udachnaya (central Siberia) xenoliths (Doucet et al., 2014; Peslier et al., 2012). Water content in cpx from Kaapvaal peridotites correlate with its trace element compositions. The water content in olivine from Udachnaya peridotites is generally higher with xenoliths with high olivine Mg# (Fig. 10a), high...
modal cpx (Fig. 10b) (Doucet et al., 2014). These correlations indicate that the water has been added to the lithospheric mantle by melts or fluids derived from the asthenosphere (Bell and Rossman, 1992; Doucet et al., 2014; Peslier et al., 2012).

The mantle beneath Tok experienced a pervasive and complex metasomatic transformation, first by evolved mafic melts to form the LW series rocks containing accessory hydrous phases, then by “dry” fluids that affected refractory peridotites of both the LH and LW series. The first metasomatic event encompassed the whole lithospheric mantle section “sampled” by the xenoliths (likely in the depth range of 40–60 km) (Ionov et al., 2005a; Ionov et al., 2005b), and locally erased the geochemical record of previous melting events. It was not directly related to the late Cenozoic basaltic volcanism, but could probably be associated with an earlier magmatic event. The melts/fluids of this first major metasomatic event, which enriched some Tok peridotites in Fe and massively crystallized new cpx, may be similar to metasomatic agents responsible for modal metasomatism of Udachnaya garnet peridotites (Doucet et al., 2013). This similarity and the presence of accessory water-bearing minerals in the LW Tok series suggest significant water content in the mantle beneath Tok during this event and are in apparent contradiction with the “normal” water content measured in Tok pyroxenes. The first metasomatic episode could be related to a significant tectono-magmatic event at the SE margin of the Siberian craton in the late-Mesozoic to early-Cenozoic (Zonenshain et al., 1990), that involved alkali magmatism and graben formation and possibly associated with subduction in the adjacent paleo-Pacific oceanic basin. The combination of these two events may have resulted in the delamination of the lower lithospheric mantle beneath Tok, and supplied the heat and melts/fluids for the main metasomatic event in the shallow lithospheric mantle (Ionov et al., 2005a; Ionov et al., 2005b).

Following this first major metasomatism event, small-scale late-stage metasomatic episodes continued in the lithospheric mantle beneath Tok until the eruption of the basaltic magmas that host the xenoliths. Melts and/or fluids with a low water activity (e.g., due to low H₂O/CO₂) migrated through the lithospheric mantle shortly before the entrainment of the xenoliths into the host magma and their ascent to the surface. Evidence for this migration of CO₂-rich, water-poor melts/fluids is recorded in the peridotite xenoliths as follows (Ionov et
(Ivanov et al., 2006a; Ivanov et al., 2006b): (i) the presence of quenched cryptocrystalline materials with empty vesicles and of fine-grained aggregates (alkali feldspar, Ti-rich oxides, micro-phenocrystals of olivine, cpx, spinel and phosphates); (ii) the breakdown of “hydrous” amphibole and phlogopite into “anhydrous” assemblages (e.g., Ba-Ti-rich silicates); and (iii) the formation of whitlockite group minerals (anhydrous, halogen-poor and Ca–Mg-rich phosphates, mainly the Na-rich merrillite). These “dry” melts/fluids affected almost every xenolith from Tok, both from the LW and from the LH series. They were chemically different from the fluids that previously crystallized volatile-rich minerals and probably came from a genetically distinct source, possibly related to the Quaternary alkali basaltic magmatism (Ivanov et al., 2006a; Ivanov et al., 2006b).

The absence of correlations (i.e., decoupling) between the water content in opx and cpx with modal cpx and FeO (Fig. 10c–f), and other indices of melt metasomatism in Tok peridotites, suggest that the water abundances are either (i) not related to the first metasomatic episode that produced iron and cpx enrichments, or (ii) were modified by later metasomatic events. The water abundances in opx and cpx are similar to those in the cratonic mantle, and opx–cpx equilibrium indicates no significant water loss. These observations suggest that either (i) the opx and cpx were not (or little) affected by the dry metasomatism or (ii) they were dehydrated by the dry metasomatism and have been enriched by later events.

In comparison, strongly metasomatized xenoliths with low water content in NAMs (1–39 ppm H$_2$O in olivine with an average of 10 ppm H$_2$O) also occur on the Tanzanian craton (Hui et al., 2015). The Tanzanian craton has been affected by a mantle plume, which has significantly reworked the cratonic lithospheric mantle (Lee and Rudnick, 1999). The Tanzanian peridotites experienced Fe-enrichments (bulk FeO up to 10 wt.%; olivine Mg# down to 89) and precipitation of cpx (up to 14% with an average of 4–5%), probably caused by relatively water-poor (<1 wt.% H$_2$O), yet LREE- and Fe-enriched plume-derived melts (Hui et al., 2015).

The potential metasomatic agents responsible for water addition to the Tok peridotites have an estimated average water content between 0.6 ± 0.4 and 1.0 ± 0.9 wt.% H$_2$O (O'Leary et al., 2010) (Table 2), using the temperature of equilibration and the potential temperature of the metasomatic agent in the mantle (i.e., 1200°C; Ivanov et al. (2005b)) (Table 1). Such water content is similar to those in mid-ocean ridge basalts (~0.1-0.5 wt.%
H₂O) and ocean island basalts (~0.1-1 wt.% H₂O), but generally lower than for other mantle-derived melts i.e.,
back-arc basalts (~0.5-2.1 wt.% H₂O), island arc basalts (~2-8 wt.% H₂O) and continental flood basalts (~3-7
wt.% H₂O) (Xia et al., 2016 and reference therein). Overall, the decoupling between water and iron suggests that
(i) the iron enrichments that likely caused the thermo-mechanical erosion of the southeastern margin of the
Siberian craton were not accompanied by water enrichment; or (ii) the Fe enrichment event was accompanied by
water enrichment, but overprinted by subsequent processes, such as “dry” metasomatism by water-poor
melts/fluids.

**Water controls on the stability of the cratonic lithospheric mantle**

To investigate the role of water and iron in the stability of cratonic lithosphere, we modeled the viscosity
(Fig. 11) in the Tok peridotite mantle as a function of depth, water content in olivine and whole-rock major
element compositions following the methods of Li et al. (2008) and Peslier et al. (2010)- (Table 5 of
supplementary data 1). We used the average estimated water concentration in Tok olivine, i.e., 24 ± 13 (1σ) ppm
(see above). Viscosity estimates for our Tok samples are compared here to those for the lithospheric mantle
beneath Udachnaya in the central Siberian craton (η_eff=8.4 x 10^{16} to 1.9 x 10^{28} Pa·s⁻¹) (Doucet et al., 2014), the
Kaapvaal craton (η_eff=4.8 x 10^{17} to 1.7 x 10^{24} Pa·s⁻¹) (Peslier et al., 2010), the Tanzanian craton (η_eff=4.8 x 10^{17}
to 1.7 x 10^{24} Pa·s⁻¹) (Hui et al., 2015) and a range of viscosity estimates for the asthenosphere (η_eff=5.4 x 10^{17} to
2.7 x 10^{25} Pa·s⁻¹ and d=3.33 g·cm⁻³) (Fleming et al., 2007; Larsen et al., 2005; Pollitz et al., 1998; Sjöberg et al.,
2000). On the one hand, the estimated viscosity range of Tok peridotites (LH and LW series) of 1.7 x 10^{28} to 1.9
x 10^{31} Pa·s⁻¹ tends to be significantly higher than the average viscosity estimated for the asthenosphere of 3.7 x
10^{18} Pa·s⁻¹ (Fig. 11). On the other, the viscosity range of the Tok peridotites is narrower than that calculated for
Udachnaya peridotites. The latter, however, is so significant that it may indicate the superposition of multiple
processes. The viscosity range for the Tanzanian craton is narrower than that for the central Siberian craton, with
less extreme high values. At depths <100 km, the Tanzanian peridotite xenoliths yield a viscosity range (η_eff=4.8
x 10^{17} to 1.7 x 10^{24} Pa·s⁻¹) lower than for the Tok peridotites because the former contain more water (1 to 39
ppm H₂O in olivine with an average of 10 ppm H₂O). However, Hui et al. (2015) showed that the low viscosities calculated for the Tanzanian peridotites result from the combination of low water content with higher equilibration temperatures (930-1410 °C) and a hotter geotherm (50 MW/m² vs. 41 MW/m² for most other cratons (Lee and Rudnick, 1999)), consistent with the presence of a mantle plume beneath the Tanzanian craton (Aulbach et al., 2008; Lee and Rudnick, 1999; Pik et al., 2006; Selway et al., 2014), and indicate that the most significant influence on viscosity estimates is exerted by mantle temperature (e.g., Karato, 2010). Regarding the viscosities of the Tok peridotites, the relatively low temperature of equilibrium (800-1000°C with an average of 950°C) and the low water content in olivine (24 ± 13(1σ) ppm) make the lithospheric mantle beneath the SE margin of the Siberian craton viscous and therefore resistant.

**IMPLICATIONS**

This work reports the water content in the nominally anhydrous minerals of the peridotite xenoliths from Tok, representative of the lithospheric mantle beneath the SE Siberian craton. Olivine is mostly “dry” due to dehydration; the opx rims are also affected by the dehydration, but their cores preserve their mantle water concentrations. The cpx are not affected by dehydration and are in equilibrium with water in the opx cores. Altogether, our data indicate that the dehydration occurred at high temperature (900 to >1000°C) in a short time (several days) during emplacement and cooling, and demonstrate that cpx is the most robust recorder of water abundances in mantle xenoliths hosted in lava flows.

The lithospheric mantle beneath the SE margin of the Siberian craton has lost its cratonic keel, supposedly by thermo-magmatic erosion triggered by large-scale Fe enrichment metasomatic events involving mafic melts, which simultaneously heated up and metasomatized the lithospheric mantle. The initial (pre-dehydration) olivine (24 ± 13(1σ) ppm), opx (74 ± 34(1σ) ppm) and cpx (146 ± 75(1σ) ppm) water content of the peridotite xenoliths from Tok are similar to those in olivine in diamond inclusions (Jean et al., 2016) and minerals from refractory spinel peridotites from the central Siberian craton (Doucet et al., 2014), and similar to
un-metasomatized cratonic minerals (Peslier et al., 2017). All of this suggests that the SE margin of the Siberian

craton lithospheric mantle is relatively “dry” with an average bulk water content of 41 ± 13(1σ) ppm.

The decoupling between the water abundances in mantle minerals and metasomatic indices suggests that

the large-scale metasomatism responsible for the Fe enrichments was asynchronous with water enrichments or

has been overprinted by later processes. Our findings question the notion of “wet” metasomatism by large scale

water-rich asthenospheric melts, proposed in previous studies (Doucet et al., 2014; Li et al., 2018; Peslier et al.,

2012), as a valid explanation for cratonic mantle delamination (Li et al., 2015; Xia et al., 2017). Instead, we infer

that water abundance variations are spatially localized and limited in time and probably result from local,

spatially restricted melting and metasomatism events in the mantle (Peslier et al., 2017).

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REFERENCES


Grant, K., Kohn, S., and Brooker, R. (2006) Solubility and partitioning of water in synthetic forsterite and enstatite in the system MgO-SiO$_2$-H$_2$O±Al$_2$O$_3$. Contributions to Mineralogy and Petrology, 151(6), 651-664.


Streckeisen, A. (1976) To each plutonic rock its proper name. Earth Science Reviews, 12, 1-33.


**FIGURE CAPTIONS**

**Fig. 1.** (a) Location map of the Tok volcanic field (red star) and the Udachnaya kimberlite pipe (blue circle) in the Siberian craton, adapted from Ashchepkov et al. (2010); the insert in the upper right corner shows the
position of the craton in the Russian Federation. Also shown are the Anabar and Aldan shields and main
kimberlite fields. (b) A sketch map of Tok basaltic field, eruption center, and mantle xenoliths occurrences
alongside the upper river Tok, after Ionov et al. (2005b).

Fig. 2. Modal proportions of olivine and pyroxenes in Tok peridotites in this study (filled symbols) and other
available data (empty symbols) (Ionov et al., 2005a; Ionov et al., 2005b). The peridotite types are after
Streckeisen (1976): (1) lherzolite, (2) harzburgite, (3) dunite, and (4) wehrlite. Tok peridotite xenoliths are
subdivided into two groups, the lherzolite-harzburgite series (LH, green circles) and the lherzolite-wehrlite
series (LW, red squares). Dashed contours delimit LH (green) and LW (red) series.

Fig. 3. Co-variation plots of modal olivine vs. clinopyroxene (a) and orthopyroxene (b) for Tok peridotites
(Ionov et al., 2005a; Ionov et al., 2005b) [see Fig. 2. for symbols]. Also shown are Udachnaya spinel (black
circles) and garnet peridotites (blue squares) (Doucet et al., 2013; Doucet et al., 2012; Ionov et al., 2010),
Horoman peridotites (grey zone; Takazawa et al. (2000)) and primitive mantle (PM) estimates (Johnson, 1998).
Red and green arrows show metasomatism trends.

Fig. 4. Co-variation plots of major elements in whole-rock (WR) Tok spinel peridotites (Ionov et al., 2005a;
Ionov et al., 2005b): Al₂O₃ vs. Mg# = [Mg/(Mg+Fe)₉₅] (a) and FeO_T (total iron) (b); CaO vs. FeO_T (c) [see Fig.
2 and 3 for symbols]. Also shown are Udachnaya spinel and garnet peridotites (Doucet et al., 2013; Doucet et
al., 2012; Ionov et al., 2010), Horoman peridotites (grey zone; Takazawa et al. (2000)) and primitive mantle
estimates (Johnson, 1998). Arrows show melting (bold black curve in a) and metasomatism trends.

Fig. 5. (a) Primitive mantle-normalized (McDonough and Sun, 1995) REE patterns of whole-rock LH (green
field) and LW (red field) series refractory peridotites from Tok (Ionov et al., 2005a; Ionov et al., 2005b). Also
shown are the harzburgites (dot-dashed grey field) and the lherzolites (hatched grey field) from the Horoman
massif (Takazawa et al., 2000). (b) Co-variation plot of Al₂O₃ vs. Yb (in ppm) for whole-rock (WR) Tok peridotites (Ionov et al., 2005a; Ionov et al., 2005b) in comparison with trace element modelling for non-modal fractional melting of a spinel peridotite with the primitive mantle composition (Doucet et al., 2013). Also shown are Udachnaya spinel and garnet peridotites (Doucet et al., 2013; Doucet et al., 2012; Ionov et al., 2010), Horoman peridotites (grey zone; Takazawa et al. (2000)) and primitive mantle estimates (Johnson, 1998) [see Fig. 2 and 3 for symbols]. The bold black curve shows the melting trend.

**Fig. 6.** REE partitioning between orthopyroxene and clinopyroxene (D⁰px/opx) for Tok peridotites from the LH series (green curves) and LW series (red curves) (a) in this study compared to off-craton peridotite from Vitim (blue curves; (Ionov, 2004)) and predicted D⁰px/opx (Liang et al., 2013) (b). The comparison between measured D⁰px/opx and predicted D⁰px/opx for Y, Dy, Sm, and Ce for Tok xenoliths in this study indicates that opx and cpx are in equilibrium (c).

**Fig. 7.** Representative FTIR spectra along E//α, E//β and E//γ crystallographic axis of olivine (a,b,c), opx (d,e,f) and cpx (g,h,i) for each sample (LH series in green and LW series in red) in the O-H vibration region from 3800 to 2800 cm⁻¹ for olivine and 3800 to 2600 cm⁻¹ for pyroxenes. Absorbance plotted for a sample thickness of 1 cm.

**Fig. 8.** Absorbance area in cm⁻² the opx from sample 9510-4 (a), 9510-11 (b), 9503-2 (c), and cpx from sample 9508-50 and 9810-19 (d), i.e. area integrated beneath OH bands, vs. distance across minerals grains in μm. The diffusion modelling of H loss uses Eq. (5) from Peslier et al. (2008): hydrogen diffusion models are based on 2-dimension diffusion equations for a sample of finite size surrounded by an infinite medium containing no H (Shewmon, 1983). The H diffusion coefficients (Diff, in m²s⁻¹) is assumed to be similar for each axis with 10⁻¹⁴ m²/s at 900°C, 10⁻¹³ m²/s at 1000°C and 10⁻¹² m²/s at 11000°C (isotropic)(Tian et al., 2017). For each opx in (a), three models are achieved at 900°C with two different initial concentrations: the two first models uses the water...
content measured in the core of olivine (~2-3 ppm H$_2$O) (solid curves), and the second one, a water content of 25% higher (dashed curves). The two first models are the best fit for the FTIR data revealing that the mantle water content of Tok opx has been preserved in their cores.

Fig. 9. Assessment of equilibrium for water between minerals by comparing ratios of water content measured with partition coefficient measured experimentally. H06, (Hauri et al., 2006); T09, (Tenner et al., 2009); N14, (Novella et al., 2014); D17, (Demouchy et al., 2017).

Fig. 10. Covariation plots of water content in opx and cpx (H$_2$O in ppm) vs. Mg# in olivine (a-b), modal clinopyroxene (c-d) and FeO$_T$ (e-f) for Tok (Ionov et al., 2005a; Ionov et al., 2005b) [see Fig. 2 and 3 for symbols]. Also shown are the data for Udachnaya garnet peridotites (Doucet et al., 2013; Doucet et al., 2012; Ionov et al., 2010), primitive mantle estimates (Johnson, 1998), the peridotite xenoliths from the Kaapvaal (yellow field or dot) (Peslier et al., 2010) the Tanzanian cratons (white ellipses or dot) (Hui et al., 2015) and the North China Craton (data compiled by Peslier et al., 2017). For comparison, we also plot the estimated value for the sub-cratonic lithospheric mantle Peslier et al. (2017).

Fig. 11. Effective viscosity (in Pa s) vs. depth (in km and GPa) of peridotite xenoliths from Tok (red field), Udachnaya (blue field) (Doucet et al., 2014), the Kaapvaal (yellow field) (Peslier et al., 2010) and the Tanzanian cratons (empty field) (Hui et al., 2015). The viscosity was calculated for olivine aggregates in dislocation creep with the estimated olivine water content assuming equilibrium with the cpx (Table 2), and using the equation of Li et al. (2008). The grey curve represents the viscosity of the cratonic mantle estimated with a constant water content of 300 ppm. The cratonic geotherm was calculated assuming a heat flow of 40 mW/m$^2$ following the equation $T = 360.73 + 9.0612P - 0.0206P^2 + (2.0 \times 10^{-5})P^3$, with T in K and P in km. Are also shown the range of the viscosities of the asthenosphere (grey field) (Fleming et al., 2007; Larsen et al., 2005; Pollitz et al., 1998;
Sjöberg et al., 2000), the spinel stability field (brown field) and the depth of the lithosphere-asthenosphere boundary (LAB) beneath the central part of the Siberian craton.
Table 1: Summary of petrological data, and water content in olivine and pyroxenes for Tok xenoliths in this study

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Rock</th>
<th>T (°C)</th>
<th>Mg#</th>
<th>Modal abundances (wt.%)</th>
<th>d</th>
<th>Viscosity</th>
<th>Total integrated absorbance (A\textsubscript{1632})</th>
<th>Water contents in minerals and whole-rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>9501-2</td>
<td>Hzb</td>
<td>910</td>
<td>0.908</td>
<td>78.6 17.2 3.1 0.3 0.7* 0.12</td>
<td>3.34</td>
<td>4.2E+30</td>
<td>0.56 2.6 927 854 0.3 0.2 20 33 59 27 120** 48 30</td>
<td></td>
</tr>
<tr>
<td>9506-2</td>
<td>Lhz</td>
<td>1001</td>
<td>0.889</td>
<td>53.9 26.3 17.3 2.5</td>
<td>3.35</td>
<td>1.7E+28</td>
<td>3.3 0 933 688 0.6 0.2 16 26 60 24 97 20 41</td>
<td></td>
</tr>
<tr>
<td>9508-31</td>
<td>Hzb</td>
<td>887</td>
<td>0.911</td>
<td>76.5 16.6 4.8 0.4 1.7* 0.06</td>
<td>tr.</td>
<td>1.9E+31</td>
<td>1.0 0 870 0.2 0.1 22 0 56 22 /132/ 129 32</td>
<td></td>
</tr>
<tr>
<td>9509-50</td>
<td>Hzb</td>
<td>992</td>
<td>0.907</td>
<td>77.1 17.6 3.6 0.7 0.9* 0.07</td>
<td>3.34</td>
<td>2.1E+28</td>
<td>1.2 0 1340 883 0.2 0.1 21 34 86 23 125 30 36</td>
<td></td>
</tr>
<tr>
<td>9510-2</td>
<td>Hzb</td>
<td>914</td>
<td>0.912</td>
<td>77.2 16.6 4.3 0.4 1.3* 0.12</td>
<td>3.34</td>
<td>9.2E+29</td>
<td>7.5 1.6 1656 2125 1.5 0.3 50 82 106 33 300** 57 69</td>
<td></td>
</tr>
<tr>
<td>9510-4</td>
<td>Hzb</td>
<td>926</td>
<td>0.909</td>
<td>79.9 16.0 2.7 0.4 1.0* 0.11</td>
<td>3.34</td>
<td>5.6E+29</td>
<td>4.6 1.1 1631 1688 1.0 0.9 40 65 105 17 238 53 55</td>
<td></td>
</tr>
<tr>
<td>9510-8</td>
<td>Hzb</td>
<td>950</td>
<td>0.904</td>
<td>79.2 14.9 4.9 0.4 0.6* 0.08</td>
<td>3.35</td>
<td>2.1E+29</td>
<td>4.6 3.0 1160 1086 1.1 0.7 26 42 75 25 153 42 39</td>
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</tr>
<tr>
<td>9510-16</td>
<td>Lhz</td>
<td>957</td>
<td>0.894</td>
<td>78.2 17.4 4.0 0.4</td>
<td>3.35</td>
<td>2.0E+29</td>
<td>3.1 1.3 1283 1607 0.7 0.3 19 40 29 18 114 46 36</td>
<td></td>
</tr>
<tr>
<td>9510-19</td>
<td>Hzb</td>
<td>951</td>
<td>0.907</td>
<td>72.7 22.8 3.4 0.7</td>
<td>0.30</td>
<td>3.5E+29</td>
<td>0.90 1.1 1091 701 0.3 0.1 17 27 70 13 99 28 31</td>
<td></td>
</tr>
</tbody>
</table>

Hzb, harzburgite; Lhz, lherzolite; Wh, wehrlite; Ol, olivine; OpX, orthopyroxene; Cpx, clinopyroxene; Spl, spinel; Felds, feldspath; Ap, apatite; Wh, whitlockite; Am, amphibole; Phl, phlogopite. Mg#, Mg/(Mg+Fe). Petrographic, modal abundances and temperature estimates are after Ionov et al. (2005b, d); *feldspaths host Fe-Ti oxides; density (in g.cm\textsuperscript{-3}) estimated using the method of Lange and Carmichael (1990) for T=940°C at 1.5 GPa; viscosity (Pa.s\textsuperscript{-1}) estimated using methods of Li et al. (2008) and Peslier et al. (2010) assuming P=2.0 GPa. A\textsubscript{1632}, total integrated absorbance for olivine, opx and cpx; G1, absorbance for Group 1 OH Band between 3800-3400 cm\textsuperscript{-1}; G2, absorbance for Group 1 OH Band between 3400-3100 cm\textsuperscript{-1}; n.a., not analyzed. [1], measured olivine water contents estimated using Bell et al. (2003) absorption coefficient; [2], estimated olivine water contents calculated assuming equilibrium with cpx, see Table 2; /, estimated cpx and opx water contents calculated assuming equilibrium between cpx and opx, see Table 2; ± (2σ), two sigma error on water estimates; ** water estimates in cpx assuming E/β and E/α are equal.
Table 2: Partition coefficients, olivine and pyroxenes water content estimates, and melt in equilibrium with pyroxene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>$D_{\text{opx}}^{\text{ol}}$</th>
<th>$D_{\text{cpx}}^{\text{ol}}$</th>
<th>$D_{\text{opx}}^{\text{melt}}$</th>
<th>$D_{\text{cpx}}^{\text{melt}}$</th>
<th>$D_{\text{opx}}^{\text{melt}}$</th>
<th>$D_{\text{cpx}}^{\text{melt}}$</th>
<th>$O_{\text{eq}}$</th>
<th>$O_{\text{eq}}$</th>
<th>$O_{\text{eq}}$ ± (2σ)</th>
<th>$O_{\text{eq}}$ ± (2σ)</th>
<th>$O_{\text{eq}}$ ± (2σ)</th>
<th>$O_{\text{eq}}$ ± (2σ)</th>
<th>$H_{2}O_{\text{MELT}}$</th>
<th>$H_{2}O_{\text{MELT}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9501-2</td>
<td>HzB</td>
<td>190</td>
<td>387</td>
<td>2</td>
<td>0.005</td>
<td>0.021</td>
<td>0.014</td>
<td>4</td>
<td>3</td>
<td>36</td>
<td>3.6</td>
<td>20</td>
<td>33</td>
<td>67</td>
<td>66</td>
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<tr>
<td>9502-2</td>
<td>HzB</td>
<td>95</td>
<td>154</td>
<td>2</td>
<td>0.014</td>
<td>0.029</td>
<td>0.022</td>
<td>2</td>
<td>2</td>
<td>29</td>
<td>2.9</td>
<td>16</td>
<td>26</td>
<td>54</td>
<td>53</td>
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<tr>
<td>9508-31</td>
<td>HzB</td>
<td>295</td>
<td>693</td>
<td>2</td>
<td>0.006</td>
<td>0.025</td>
<td>0.016</td>
<td>4</td>
<td>3</td>
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<td>36</td>
<td>74</td>
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<tr>
<td>9508-50</td>
<td>HzB</td>
<td>374</td>
<td>543</td>
<td>1</td>
<td>0.009</td>
<td>0.022</td>
<td>0.017</td>
<td>3</td>
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<td>3.8</td>
<td>21</td>
<td>34</td>
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<td>68</td>
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<td>9510-2</td>
<td>HzB</td>
<td>70</td>
<td>197</td>
<td>3</td>
<td>0.006</td>
<td>0.026</td>
<td>0.017</td>
<td>5</td>
<td>3</td>
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<td>9.1</td>
<td>50</td>
<td>82</td>
<td>168</td>
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<td>9510-4</td>
<td>HzB</td>
<td>109</td>
<td>248</td>
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<td>0.006</td>
<td>0.022</td>
<td>0.015</td>
<td>4</td>
<td>2</td>
<td>72</td>
<td>7.2</td>
<td>40</td>
<td>65</td>
<td>133</td>
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<td>9510-8</td>
<td>HzB</td>
<td>68</td>
<td>139</td>
<td>2</td>
<td>0.007</td>
<td>0.024</td>
<td>0.017</td>
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<td>2</td>
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<td>0.023</td>
<td>0.016</td>
<td>3</td>
<td>2</td>
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<td>9510-19</td>
<td>HzB</td>
<td>269</td>
<td>381</td>
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<td>0.008</td>
<td>0.019</td>
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<td></td>
<td>0.008</td>
<td>0.023</td>
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<td>26</td>
<td></td>
<td></td>
<td></td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

$L_h$ - olivine, $O_{\text{eq}}$, $O_{\text{eq}}$, $O_{\text{eq}}$, $O_{\text{eq}}$, average of olivine, opx and cpx water contents estimates using partition coefficients. $H_{2}O_{\text{MELT}}$, water contents estimate of potential metasomatic agent with the cpx using $D_{\text{opx}}^{\text{ol}}$ of O'Leary et al (2010).

$D_{\text{opx}}^{\text{ol}}$ partition coefficient between opx or cpx with melt; $D_{\text{opx}}^{\text{ol}} = \exp(-5.66+8.4[\text{IVAI}]\text{opx} + 10[\text{Ca}]\text{opx})$; $D_{\text{cpx}}^{\text{ol}} = \exp(-5+6.3[\text{IVAI}]\text{cpx} -1.2[\text{Ca}]\text{cpx} +1600/T)$; $T_1$, Temperature of equilibration; $T_2$, 1200°C; meas, partition coefficient calculated using measured water contents in minerals; O10, partition coefficient between opx and cpx with melt using method of O'Leary et al (2010). $O_{\text{eq}}$, $O_{\text{eq}}$, $O_{\text{eq}}$ olivine, opx and cpx water contents calculated using partition coefficients. N14, partition coefficient of Novella et al (2014); T09, partition coefficient of Tenner et al (2009), av., average of olivine, opx and cpx water content estimates using partition coefficients. $H_{2}O_{\text{MELT}}$, water contents estimate of potential metasomatic agent with the cpx using $D_{\text{opx}}^{\text{ol}}$ of O'Leary et al (2010).
Exposed AR-PR1 crustal rocks
Craton boundary
Kimberlite field
Tok basaltic field
Udachnaya

(a) (b)

Tok basaltic field
Rivers
Eruption centers
Lava flows
Mantle xenoliths

River Tok
Nakit

Fig. 1
Fig. 2

LH series
this study

LW series
this study

other samples

other samples
Fig. 3

(a) Modal clinopyroxene (wt.%) vs. Modal olivine (wt.%) for the LW series.

(b) Modal orthopyroxene (wt.%) vs. Modal olivine (wt.%) for the LW series and LH series.

Legend:
- LW series
- LH series
- Horoman massif
- Udachnaya (Central Siberian Craton)
- Spinel harzburgites
- Garnet peridotites
Fig. 4

(a) Mg\# in WR vs. Al_2O_3 in WR, wt. %

(b) FeO_T in WR vs. Al_2O_3 in WR, wt. %

(c) FeO_T in WR vs. CaO in WR, wt. %

LH series
LW series
PM
Melting trend
Fig. 5

(a) 

WR/PM

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

LW series
LH series
Horoman, hz
Horoman, lh
Fertile LH

(b) 

Yb in WR, ppm

Al₂O₃ in WR, wt. %

LW series
LH series
Melting trend

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Fig. 6

(a) DCpx/Opx measured

(b) DCpx/Opx predicted

(c) $D_{\text{DCpx/Opx}}$ predicted vs $D_{\text{DCpx/Opx}}$ measured

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Vitim
Fig. 8

Orthopyroxene

9510-4

Absorbance (cm$^{-1}$)

0  200  400  600  800  1000  1200  1400

distance in μm

Δ=215

Core + 25%

T°C=900°C, t= 19 days
T°C=1000°C, t= 2 days
T°C=1100°C, t= 6 hrs

Orthopyroxene

9510-11

Absorbance (cm$^{-1}$)

0  100  200  300  400  500  600  700  800  900

distance in μm

Orthopyroxene

9508-50

Absorbance (cm$^{-1}$)

0  100  200  300  400  500  600  700  800  900

distance in μm

Δ=50

Clinopyroxene

9510-19

Absorbance (cm$^{-1}$)

0  100  200  300  400  500  600  700  800  900

distance in μm

Δ=50

T°C=900°C, t= 19 days
T°C=1000°C, t= 2 days
T°C=1100°C, t= 6 hrs
Fig. 9

(a) 

(b) 

(c) 

H$_2$O in orthopyroxene (ppm)

H$_2$O in olivine (ppm)

H$_2$O in clinopyroxene (ppm)

D$_{Opx/Ol}$ = 3.5 (D17)

D$_{Opx/Ol}$ = 12.2 (H06)

D$_{Cpx/Ol}$ = 3.3 (N14)

D$_{Cpx/Opx}$ = 1.2 (H06)

Cpx - Opx equilibrium

Ol - Cpx equilibrium

Ol - Opx equilibrium

H$_2$O in orthopyroxene (ppm)

H$_2$O in clinopyroxene (ppm)

H$_2$O in olivine (ppm)
Fig. 11

- Asthenosphere
- 300 ppm H₂O
- Udachnaya
- LAB - Central Siberia
- Tanzania
- Kaapvaal
- Mantle viscosity - 40 mW/m² - 300 ppm H₂O

(a) Depth (km)
(b) 10^{16} 10^{18} 10^{20} 10^{22} 10^{24} 10^{26} 10^{28} 10^{30} \eta_{\text{eff}} (\text{Pa.s})