

Water storage in cratonic mantle

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Abstract

Knowledge of the water capacity of the deep lithosphere is crucial for validating models of craton growth and for constraining solid earth volatile cycles over geologic time. However, experimental constraints on water solubility and partitioning often disagree with natural rock data. We present a bulk compositionally dependent model of water storage capacity in pyrolite over a range of lithospheric mantle pressures and temperatures. Models are compared against published xenolith nominally anhydrous mineral (NAM) water contents, which have been recalculated to reflect the last water content of the mantle lithosphere by using coexisting pyroxene water contents in the same samples. Our main findings are that (1) regardless of tectonic setting, olivine records similar recalculated water contents, suggesting a common level of water undersaturation in the lithospheric mantle, and (2) equilibrium water partitioning between clinopyroxene and orthopyroxene (D_{cpx/opx}) increases down-temperature. We propose these trends may be explained by re-hydration/re-fertilization of cratonic mantle early during coalescence, followed by cooling-induced water exsolution from orthopyroxene and garnet formation as cratons thicken and stabilize.

1 | INTRODUCTION

Mantle water content is an important parameter that controls its petro-physical properties and, as a consequence, evolution of the mantle lithosphere over Earth's history. On the present-day Earth, the distribution of water in the mantle varies across tectonic setting, with a depleted upper mantle containing 50–200 parts per million (ppm) H₂O by weight (Demouchy & Bolfan-Casanova, 2016; Hirschmann, 2006), but up to 1500 ppm H₂O occurring above subducted, devolatilized oceanic slabs (e.g. Ulmer, 2001). These variations largely reflect processes that have shaped the Earth's mantle during the Phanerozoic, since 'cold, steep and deep' subduction became the dominant mechanism of volatile input into the deep Earth (Bodnar et al., 2013; Palin et al., 2020).

In contrast to Phanerozoic Earth, the geodynamics of early Earth are more enigmatic, but likely differed significantly from the style of plate tectonics that operates today (e.g. Piccolo et al., 2020). Higher initial mantle potential temperatures (e.g. Ganne & Feng, 2017; Herzberg, Condie, & Korenaga, 2010) led to unique styles and compositions of magmatism, which infer that different mechanisms of

lithospheric evolution governed the Archean and Proterozoic compared to the Phanerozoic (Condie, 2021). The influence of volatiles on the mantle and crustal deformation and geodynamics may also have evolved during these regime shifts, as distributions of melt inclusions in high-grade rocks through geologic time show peaks correlating with major plate tectonic transitions (Nicoli & Ferrero, 2021). In addition, the water carrying capacity of altered oceanic crust is also thought to have been higher in the geological past than today, owing to an evolution in its maficity (e.g. Palin & White, 2016).

The most significant tectonic development in early Earth history was the fusion of lithospheric nuclei into cratons, setting the stage for formation of the continents. However, the mechanisms by which cratons coalesced remains open to debate (Pearson et al., 2021). On one hand, cratons must have remained cold, thick and buoyant for long periods of time to satisfy current seismic imaging, xenolith constraints and heatflow data. On the other hand, at some point in the cratons' evolution, they must have been deformable enough to suture into large blocks, perhaps facilitated by hydrated mantle shear zones (Lee et al., 2008). Trace amounts of water in olivine enhance the creep rate via hydrolytic weakening (Brodholt & Refson, 2000)

and water also lowers mantle viscosity (Hirth & Kohlstedt, 1996), with both factors enhancing deformation. Present-day constraints of water content in the cratonic mantle from xenoliths show spatial heterogeneity at both vertical and lateral scales (Peslier et al., 2017). However, the origins of such water heterogeneity are not agreed upon—either it was inherited, that is ‘frozen in’ after the cratons formed, like fossil seismic anisotropy that somehow persists over billions of years (Silver and Chan, 1988), or, post-cratonization metasomatism modified the original hydration state of the cratonic mantle.

While metasomatized mantle may contain hydrous minerals, the vast majority of cratonic mantle is highly depleted (Lee, Luffi, & Chin, 2011), which confers the long-lived chemical buoyancy needed to counteract the negative buoyancy associated with a cold, thick thermal boundary layer (Jordan, 1981). The largest mantle water reservoir is incorporated within nominally anhydrous minerals (NAMs) (Bell & Rossman, 1992) where water is substituted as various species in crystal lattice defects. Water solubility in NAMs increases with increasing pressure, and experimental mineral/melt partition coefficients are highest for clinopyroxene and orthopyroxene followed by garnet, then olivine (Aubaud, Hauri, & Hirschmann, 2004; Hauri, Gaetani, & Green, 2006; Tenner et al., 2009). Here, the partition coefficient is defined as the ratio of the concentration of a trace element (in this case, water) in the mineral to that in the melt at equilibrium: $D_{\text{mineral}}^{\text{H}_2\text{O}} = \frac{C_{\text{mineral}}^{\text{H}_2\text{O}}}{C_{\text{melt}}^{\text{H}_2\text{O}}}$.

Pyroxenes, in particular, are an important NAM water reservoir owing to them having higher D values compared to olivine and garnet. Hauri et al. (2006) found that D positively correlates with Al in orthopyroxene, owing to the coupled substitutions $\text{H}^+ + \text{Al}^{3+} \leftrightarrow 2 \text{Mg}^{2+}$ and $\text{H}^+ + \text{Al}^{3+} \leftrightarrow \text{Si}^{4+}$ (Keppler & Bolfan-Casanova, 2006). Aluminium-free enstatite has comparable H-solubility to clinopyroxene at <4.5 GPa, but Al-bearing enstatite may contain up to three times as much H_2O at these conditions (Mierdel et al., 2007). Importantly, $D_{\text{Cpx/Opx}}$ converges to values ~1 for melt-present, high-T conditions (>1000°C) (Hauri et al., 2006), though subsolidus values are higher at ~2 (Demouchy et al., 2017). This suggests that water partitions equally between clinopyroxene and orthopyroxene in the presence of partial melt, but water is preferentially partitioned into clinopyroxene as the mantle cools.

Despite extensive experimental and observational data on water partitioning between mantle NAMs, straightforward interpretation of measured NAM water contents in exhumed mantle rocks remains challenging. This is largely due to (1) a lack of synergistic information reported from xenoliths (e.g. the absence of calculated final equilibration P - T conditions that constrain the sample's thermal history); (2) H^+ only measured in one NAM, but not in coexisting minerals, thus prohibiting effective determination of partitioning relationships and (3) the lack of a thermodynamically based framework for predicting the maximum solubility of H^+ in different NAMs as a function of P , T and mineral composition. While individual parameterizations exist for certain NAMs, as derived from high- P /high- T laboratory experiments, an integrated approach is needed that considers all coexisting NAMs within mantle rocks to quantitatively compare water storage model predictions as a function of geodynamic environment

Statement of significance

Using new thermodynamic models of water capacity in mantle minerals combined with a global xenolith compilation, we show that non-negligible water may be released as a result of lowered solubility with decreasing temperature and/or increasing pressure in mantle lithosphere, and that such a mechanism could potentially explain enigmatic mid-lithospheric discontinuities as hydrated horizons.

to measured data obtained from natural peridotites. Here, we directly address this issue, and combine a survey of global xenolith NAM water data with the results of petrological forward modelling at upper mantle P - T conditions, which allows us to determine mineral equilibria and storage capacities in canonical pyrolite mantle (Ringwood, 1975) (Figure 1a). We then compare these predictions to H_2O contents from mantle xenoliths erupted within cratonic and non-cratonic regions worldwide, and propose that cooling-induced hydrogen loss (or ‘sweating’) during craton formation is a common geological phenomenon, which may be necessary for cratons’ long-term preservation.

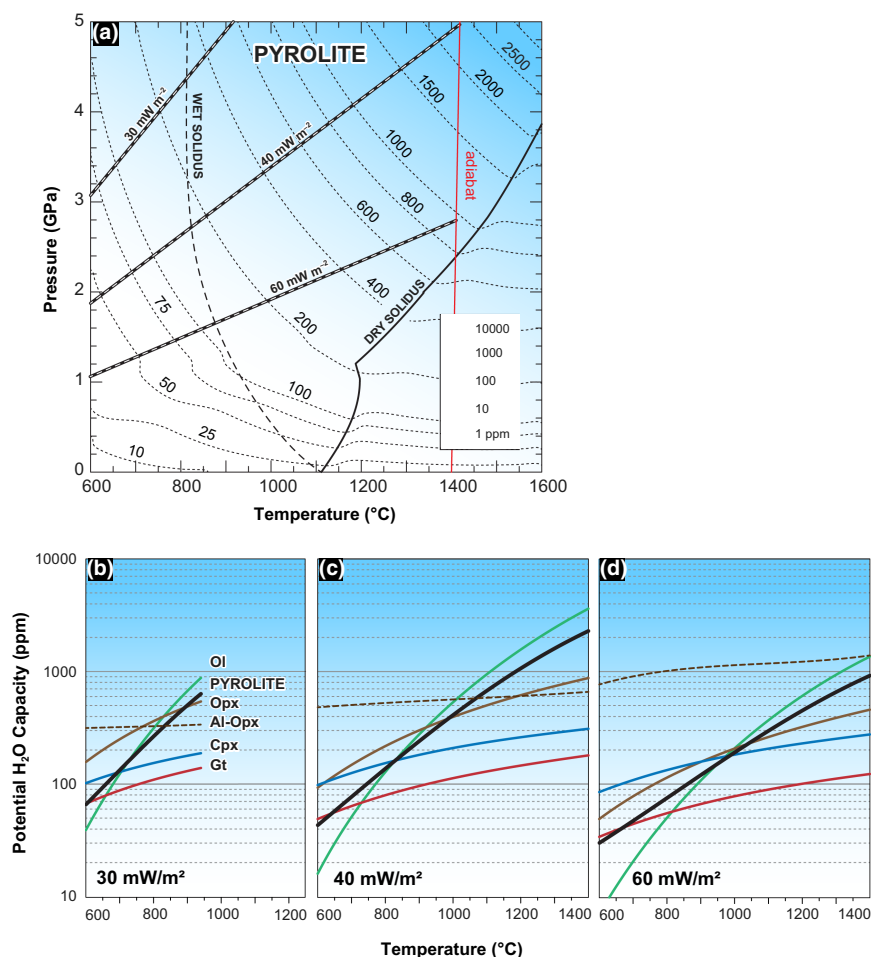
2 | H_2O CAPACITY OF MANTLE NAMs

2.1 | Models

Stable phase equilibria for anhydrous pyrolite (Ringwood, 1975) and an average garnet harzburgite from the Slave craton (Kopylova & Russell, 2000) (Figure S1) were calculated in the Na_2O - CaO - FeO - MgO - Al_2O_3 - SiO_2 - Cr_2O_3 (NCFMASCr) chemical system using the Gibbs-free energy minimization modelling program Theriak-Domino (de Capitani & Petrakakis, 2010), internally consistent thermodynamic dataset ds-622 (Holland & Powell, 2011), and activity-composition relations for olivine, garnet, clinopyroxene, orthopyroxene, spinel, plagioclase and ultramafic silicate melt (Jennings & Holland, 2015). The pyrolite and Slave compositions were selected as representative end-members of typical cratonic mantle lithosphere. The Slave sample's lower Al_2O_3 content and slightly higher XMg (Table S1) expands the orthopyroxene stability field compared to pyrolite and suppresses garnet stability, but other phase relations are similar. Calculated phase relations for pyrolite (Figure S1a-b) resemble those for typical peridotite (cf. KLB-1; Jennings & Holland, 2015).

The potential H_2O contents (ppm) of diopside, pyrope, Al-free enstatite and olivine ($\text{Fo} = 0.9$) (Figure S3) were individually calculated within the pressure-temperature (P - T) range 0-5 GPa and 600-1600°C using parameterizations experimentally determined by Bromiley et al. (2004), Lu and Keppler (1997), Mierdel and Keppler (2004) and Zhao et al. (2004), respectively, alongside the Pitzer and Sterner (1994) equation of state for H_2O . For both considered bulk compositions, the total potential bulk H_2O content hosted within

FIGURE 1 Modelled H₂O storage. (a) Potential H₂O capacity for pyrolite at *P*-*T* conditions of the cratonic mantle. (b-d) H₂O capacity in NAMs and bulk pyrolite along typical mantle geotherms



NAMs at any given *P*-*T* condition (Figure S3) was determined using a two-step mass-balance procedure: (1) calculated volume proportions of each NAM were converted to weight percentages using their densities, and then individually combined with their maximum H₂O content at that *P*-*T* point; and (2) bulk rock H₂O content was calculated by summing the H₂O contents of each mineral constituent with respect to their individual mass fraction. Contributions from olivine in the bulk pyrolite model considered variations in the calculated equilibrium Fo content [atomic Mg/(Mg+Fe)] over the modelled *P*-*T* range.

The calculated potential H₂O content of individual NAMs is shown in Figure 1b-d, and that for bulk pyrolite was determined from a weighted calculation involving the proportions of each phase and their individual H solubilities at *P*-*T* conditions relevant to the continental lithospheric mantle. The potential H₂O carrying capacity increases with *P* and *T*, ranging from ~30–60 ppm at 600 °C and 1–3 GPa, and up to ~2,400 ppm at 5 GPa at ~1,400 °C (Figure 1a). H₂O carrying capacities in individual NAMs along model geotherms for cold, moderate and warm cratonic lithosphere are shown in Figure 1b–d and are compared to xenolith data in Figure 2 and Figure 3. Modelled mineral composition and phase proportion data within this *P*-*T* space and along specific geotherms are detailed in Figures S1–S6.

2.2 | Xenolith data

Given the strong thermobarometric dependence of hydrogen solubility in NAMs, the tectonic and thermal evolution of a xenolith should be considered when interpreting lithospheric water content. Literature data (see SI for references) have been compiled for mantle xenoliths that report H₂O concentrations in coexisting olivine, orthopyroxene and clinopyroxene and a previously published final *P*-*T* condition of equilibration (Table S3). As we discuss further in the following section, our filtering of published xenolith NAM H₂O values yields an internally consistent dataset, as we recalculate olivine H₂O contents using both orthopyroxene and clinopyroxene present in the same xenolith (discussed below). While this approach results in fewer plotted data points (Figures 2, 3) compared to previous literature surveys of NAM H₂O in mantle minerals (Demouchy & Bolfan-Casanova, 2016; Peslier, 2010; Peslier et al., 2017) it allows a direct comparison to experimentally derived H₂O partitioning studies as well as our phase equilibria models.

Calculated final *P*-*T* conditions for xenoliths from Siberia, Kaapvaal and Wyoming Cratons plot close to geotherms corresponding to low heat flow (30–40 mW m^{−2}), which is characteristic of present-day Archean shields (e.g. Pollack & Chapman, 1977)

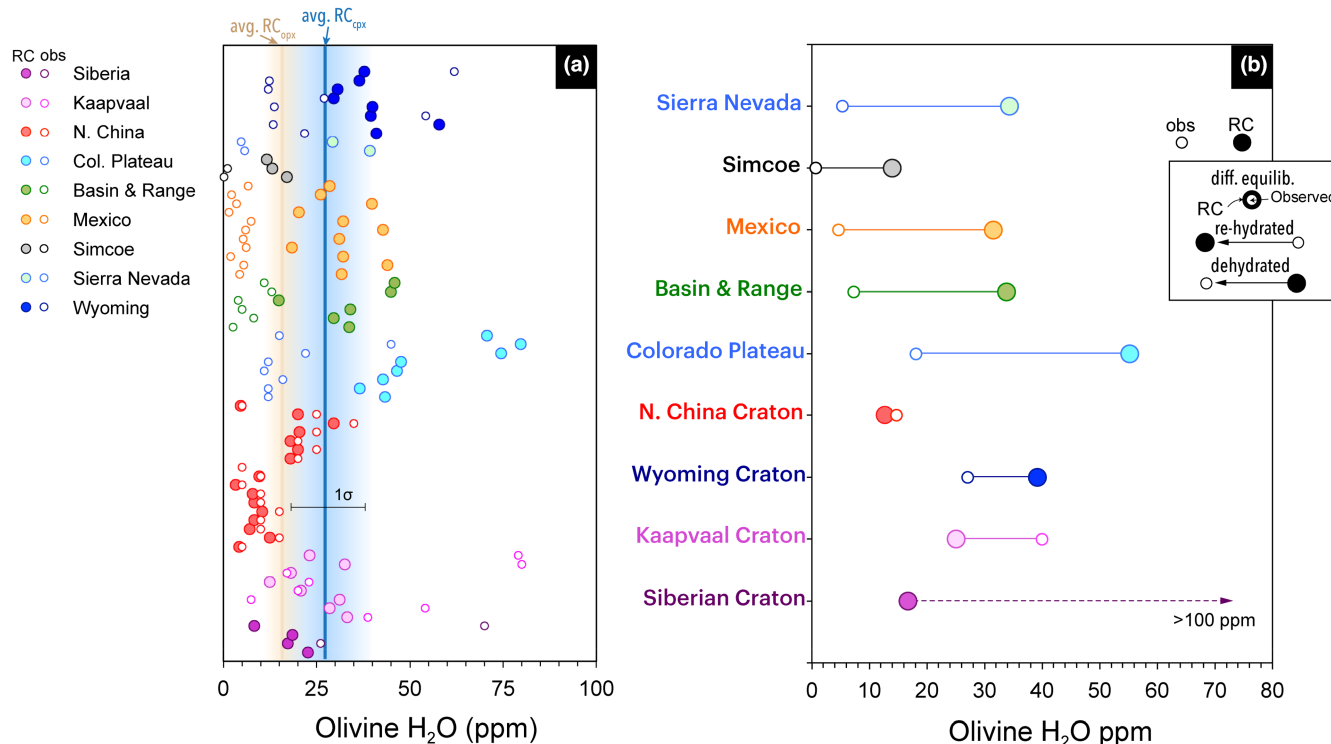


FIGURE 2 Literature xenolith data. (a) Individual xenoliths with previously published coexisting olivine, clinopyroxene and orthopyroxene water contents (see SI for references). All data plotted are olivine water contents. Open symbols = observed (i.e. measured) olivine water content. Filled symbols = olivine water contents recalculated to clinopyroxene water content (RC). Vertical bold lines represent average recalculated olivine water contents (all xenolith data). (b) Comparison between RC and observed olivine water contents. Symbols represent averages for each locality. Inset shows that positive or negative differences in RC versus observed values could indicate dehydration and rehydration respectively

(Figure 3a). A notable exception in this dataset is the North China Craton, with xenoliths plotting along a hotter geotherm (Figure 3a), consistent with proposed recent magmatic rejuvenation and lithospheric thinning (Xu & Zhao, 2009). Off-craton xenoliths from the Basin and Range, USA, which fall close to or above the 60mWm^{-2} geotherm (Figure 3), also reflect actively extending lithosphere. Off-craton xenoliths from Mexico and Simcoe plot near to the 60mWm^{-2} geotherm, which is typical of active arcs (e.g. Ziagos, Blackwell, & Mooser, 1985). In contrast, xenoliths sampling the extinct Sierra Nevada arc (subduction ended at $\sim 80\text{Ma}$; garnet-bearing xenoliths were erupted at $\sim 8\text{Ma}$) plot along a 40mWm^{-2} geotherm, similar to cratons, and indicative of the cold and thick final conditions of the Sierran arc root (Chin, Lee, & Blichert-Toft, 2015).

2.2.1 | Seeing through the 'veil' of diffusive loss of water in NAMs

A major concern when studying volatiles in NAMs is the extent to which post-formation processes affect the water content of the mineral (i.e. determining whether the measured concentration is primary or secondary). For xenoliths, rapid diffusive water loss from olivine during ascent to the Earth's surface is common (Mackwell & Kohlstedt, 1990). Importantly, the activation energy for H^+ diffusivity

in olivine is higher than that for pyroxenes (Xu et al., 2019). Thus, at high T ($>1,000^\circ\text{C}$), diffusive water loss may be significant in olivine, but negligible in pyroxene, despite similar diffusivities at lower temperatures in both minerals.

Given the large difference in diffusivity at $>1,000^\circ\text{C}$ (Xu et al., 2019), clinopyroxene water contents in erupted xenoliths may be less susceptible to water loss compared to orthopyroxene and olivine (Chin et al., 2021; Warren & Hauri, 2014). However, limited xenolith evidence also suggests that orthopyroxene may be more susceptible to diffusive water loss compared to clinopyroxene (Tian et al., 2017). Thus, we use the water contents of clinopyroxene, where available in the same xenoliths, to recalculate olivine water contents to concentrations that were last in equilibrium with the pyroxene, assuming that present-day water contents reflect some post-formation water loss. We refer to these recalculated values, abbreviated as 'RC' henceforth, as 'last' values, denoting the water content that was presumably reflective of last equilibration in the lithosphere. We also recalculated olivine water contents based on water contents of orthopyroxenes coexisting with olivine (see Table S1), but for the purposes of this paper, focus on clinopyroxene-recalculated olivine water contents based on the diffusivity arguments above.

To obtain RC olivine water contents from our compilation of observed olivine water contents, we used an averaged experimental

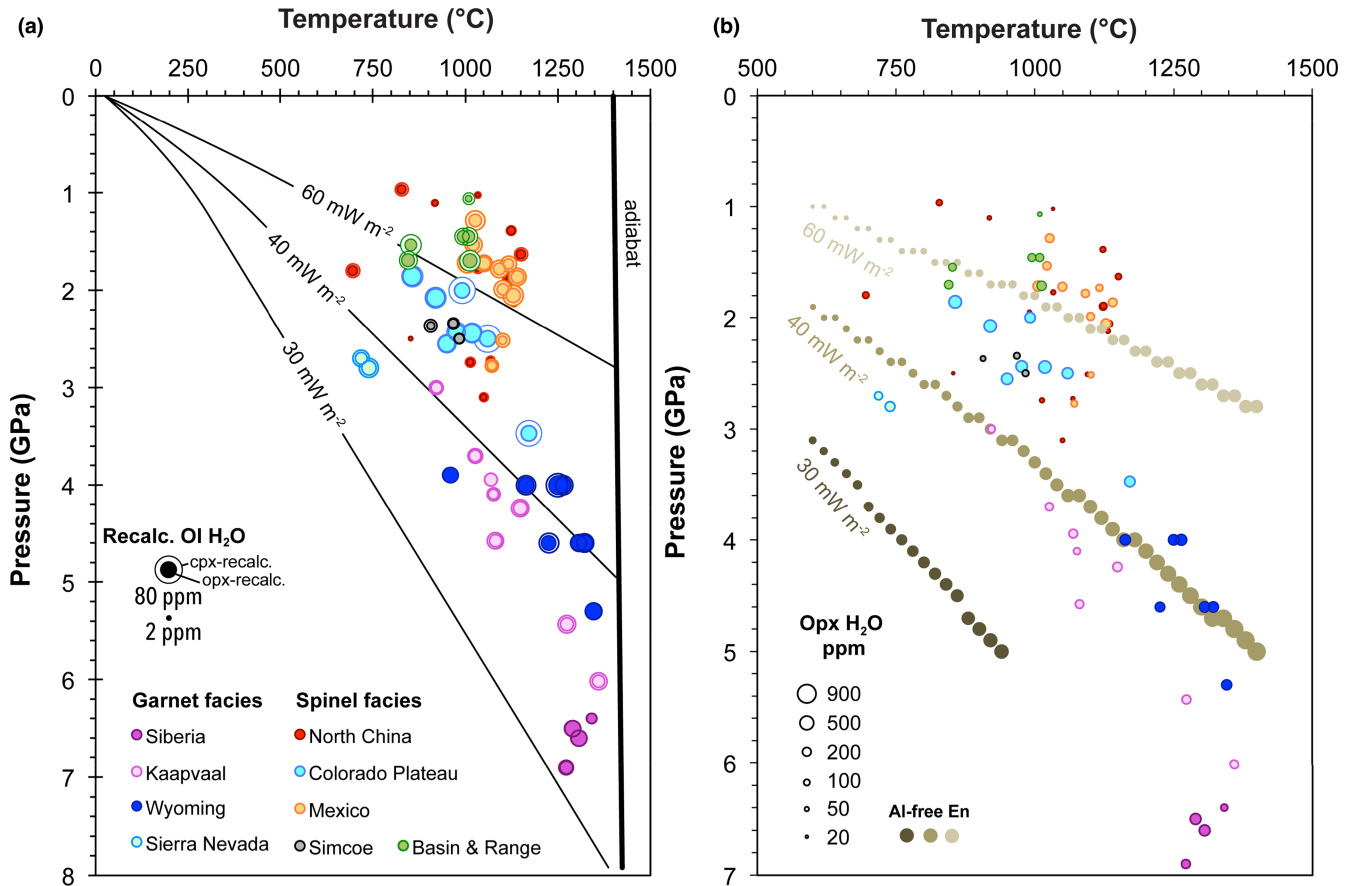


FIGURE 3 (a) RC olivine H₂O in P-T space. (b) Measured orthopyroxene H₂O in P-T space. Brown circles are modelled orthopyroxene H₂O storage capacities along different model geotherms (from Figure 1)

partition coefficient of $D_{\text{cpx/ol}} = 12$ from Hauri et al. (2006). In other words, RC $C_{\text{H}_2\text{O}}$ olivine = (measured $C_{\text{H}_2\text{O}}$ cpx)/12. While $D_{\text{pyroxene/H}_2\text{O}}$ varies as a function of the Al³⁺ content in pyroxene (Hauri et al., 2006), this effect is most pronounced at high Al₂O₃ (>4 wt.%). Most cratonic pyroxenes, particularly those that have equilibrated with garnet, have <4 wt.% Al₂O₃ (Pearson, Canil, & Shirey, 2003). Unfortunately, there is a lack of experimental data on the variation of $D_{\text{Pyroxene/H}_2\text{O}}$ for such low-Al³⁺ pyroxenes, and so we use a fixed ($D_{\text{cpx/ol}} = 12$) partition coefficient in all olivine water re-calculation. Figure 2 compares observed olivine water content with recalculated-to-clinopyroxene olivine (RC) water content.

In their comprehensive survey of mantle peridotites, Warren and Hauri (2014) found that both clino- and orthopyroxene water contents may be better archives of primary mantle hydration state than olivine or either pyroxene alone. In particular, the ratio of water contents in coexisting pyroxene pairs ($R_{\text{cpx/opx}}$) is often compared to experimentally determined $D_{\text{mineral/melt}}$ values—from which an effective $D_{\text{cpx/opx}}$ can be calculated—to assess the degree of equilibrium. For $R_{\text{cpx/opx}}$, Warren and Hauri (2014) compiled literature xenolith data and report an equilibrium value of 2.6 ± 0.9 ($n = 141$). By contrast, the average experimental $D_{\text{cpx/opx}}$ is 1.3 ± 0.3 ($n = 10$) (Aubaud et al., 2004; Hauri et al., 2006; O'Leary, Gaetani, & Hauri, 2010; Tenner et al., 2009). For all localities investigated in this study,

$R_{\text{cpx/opx}}$ fall within these established ranges, indicating equilibrium (Figure 4).

2.2.2 | Xenolith NAM water contents

Although Siberian xenoliths report very high measured olivine water contents (>300 ppm at 7 GPa, 1250°C), RC values for these olivines are much lower than measured values (Figure 2, Table S3). Such a large negative difference in RC versus measured olivine H₂O content could indicate re-hydration of olivine during eruption or during emplacement, or anomalously high olivine water content due to metasomatism shortly before eruption. However, $R_{\text{cpx/opx}}$ for Siberian xenoliths (0.91 ± 0.32) is close to experimental D values (1.3 ± 0.3) (Figure 4), indicating that the pyroxenes retained an equilibrium state. Kaapvaal xenoliths have an average RC olivine H₂O content of 25 ppm and show a smaller dispersion of $\Delta\text{H}_2\text{O}$ (Figure 2) compared to those from Siberia; Kaapvaal xenoliths also have $R_{\text{cpx/opx}}$ within the range of experimental D values (1.72 ± 0.4) (Figure 4). The Wyoming Craton has the highest RC olivine H₂O out of all cratons (39 ppm), $R_{\text{cpx/opx}}$ is within the experimental range (1.6 ± 0.35), and generally shows a positive $\Delta\text{H}_2\text{O}$. Finally, the craton-like Proterozoic Colorado Plateau is characterized by unusually high RC olivine water

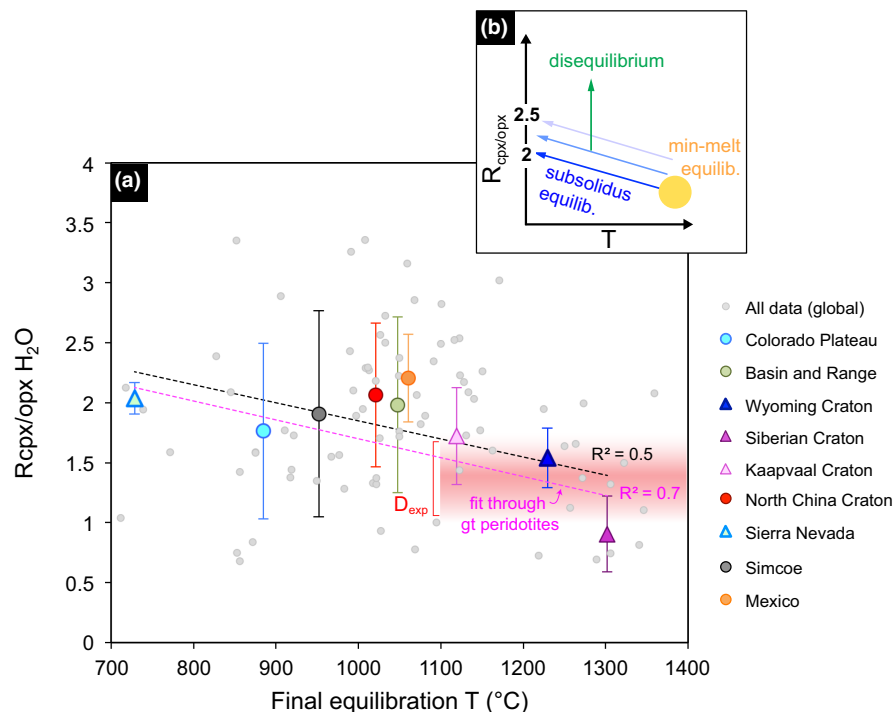


FIGURE 4 (a) Ratio of measured H₂O in clinopyroxene/orthopyroxene vs. final equilibration T in mantle xenoliths. Error bars 1 σ . Dashed lines show regressions through global data (black) and garnet peridotites only (magenta). (b) Potential mechanisms responsible for shifts in R

contents attributed to Cenozoic flat slab subduction and metasomatism (Li et al., 2008) (Figure 2).

Measured orthopyroxene water contents are shown in Figure 3b for the same xenoliths for which RC olivine water contents are reported. As clinopyroxene water contents show a similar distribution to values for orthopyroxene in Figure 3a, we only show orthopyroxene for simplicity. In general, orthopyroxene water content does not show a marked increase with increasing depth.

In contrast to cratons, non-cratonic mantle xenoliths show RC olivine water contents that are higher than measured values (Figure 2). Notably, neither olivine nor orthopyroxene in xenoliths from lithospheric mantle above subduction zones (Simcoe, Mexico and Sierra Nevada) is particularly more hydrous than those in xenoliths from the Basin and Range and cratons.

3 | DISCUSSION

3.1 | A consistent level of olivine water undersaturation in the lithospheric mantle?

Although our method of pyroxene-anchored recalculation of olivine water contents usually yields a higher value than the observed water content (Figure 2b), it is possible that even these values may be a minimum bound on the last water content representative of the lithospheric mantle. Recent work comparing spectroscopic versus bulk methods of analysing water in NAMs shows higher values using bulk methods, suggesting there may be 'missing' water stored in minerals, perhaps as molecular H₂ (Moine et al., 2020). In addition, water freed during metamorphic reactions in the deep lithosphere could also form hydro-garnet, which is undetectable during

routine petrographic study (Lamadrid et al., 2014). Despite these uncertainties, the RC values we report are internally consistent with coexisting pyroxenes, and thus reflect the last water content of the lithospheric mantle prior to eruption.

When the RC olivine water contents are plotted as a function of depth (Figure 3), we find a relatively constant value around 30 ppm (Figure 2). This holds across cratonic versus off-cratonic boundaries—the average RC olivine is 28 ± 18 ppm for cratonic xenoliths (Siberia, Kaapvaal, Wyoming, North China, Colorado Plateau) and 26 ± 12 ppm for off-cratonic xenoliths (Simcoe, Mexico, Sierra Nevada, Basin and Range). Such a consistent RC olivine water content may reflect a universal equilibrated state of water undersaturation in the background lithospheric mantle. Interestingly, the observation that global olivine has recalculated water contents around 30–40 ppm could also reconcile why a large number of mantle xenoliths with 'dry' A-type fabric often contain large populations of 'wet' E-type intragranular microstructures (Bernard et al., 2019; Chin et al., 2021), since this water content is at the boundary between the two olivine fabric types (Karato et al., 2008).

3.2 | Implications for cratonization processes

3.2.1 | P–T paths and water 'sweating'

Various aspects of mineral-based thermobarometry should be considered when interpreting thermal histories of xenoliths with respect to the hydration state of the lithosphere, because the solubility of volatiles is strongly pressure and temperature dependent. Most P–T conditions of equilibration of peridotites are constrained simultaneously using Al-in-orthopyroxene barometry coupled with

Mg, Fe or Ca-based cation exchange thermometry between garnet and orthopyroxene or clinopyroxene. However, because Al^{3+} diffusivity is much slower than that of divalent cations at temperatures of the cool lithospheric mantle (Cherniak & Dimanov, 2010), transient thermal events may shift previously equilibrated xenoliths off the geotherm, leading to spurious calculated P - T arrays (Lee, 1998). Large temperature shifts will thus significantly affect the potential water capacity of a NAM, allowing it to release and redistribute previously incorporated water into the surrounding matrix or consume more in post-formation hydration events (Figure 1).

This issue may be particularly important for Al solubility in mantle minerals, especially for metamorphic reactions involving pyroxenes and garnet. Owing to the positive dP/dT slope of the spinel-garnet transition, garnet inevitably forms during isobaric cooling (Figure 5a) at high-pressure subsolidus conditions of the cratonic lithospheric mantle. H^+ participates in a coupled substitution with Al^{3+} in orthopyroxene (Keppler & Bolfan-Casanova, 2006), and so the behaviour of Al^{3+} in the lithospheric mantle should also impact its water content and distribution. Studies of cratonic peridotites show that garnet and clinopyroxene are often spatially associated with orthopyroxene (Cox et al., 1987; Saltzer et al., 2001; Tomlinson et al., 2018), with the former occurring as lamellae within the latter. This led to the idea that garnet and clinopyroxene may have exsolved as a result of cooling from originally homogenous high- T , low- P and high-Al orthopyroxene (Cox et al., 1987). Exsolution-induced water release could therefore be significant for Al-enstatite, which can theoretically hold similar concentrations of H^+ as olivine at high temperatures (Figure 1), and which participates in the metamorphic garnet-forming reaction during cooling and/or increasing pressure (Figure 5a). Because garnet has much lower $D_{\text{H}_2\text{O}}$ compared to pyroxene (Hauri et al., 2006; Tenner et al., 2009), garnet formation from orthopyroxene should thus release water into the host peridotite, which may then be taken up by clinopyroxene, which has a higher $D_{\text{H}_2\text{O}}$, or react to form amphibole. We propose that the down-temperature increase in $R_{\text{cpx/opx}}$ (Figure 4) may partially reflect closed-system re-partitioning of water into clinopyroxene as orthopyroxene exsolves garnet.

3.2.2 | The Sierra Nevada mantle as an analog for cratonic lithosphere formation

One example of potential cooling-induced water exsolution due to garnet formation from orthopyroxene is recorded by peridotite xenoliths from the Sierra Nevada, California (Chin et al., 2012). Although the Sierra Nevada formed as a Mesozoic arc, several aspects of its lithospheric evolution are reminiscent of the cratonic lithosphere (Gibson, 2017; Lee et al., 2011). These include equilibration of Sierran peridotite xenoliths along an anomalously cold geotherm similar to cratonic conditions, and recording final pressures up to ~4 GPa (Ducea & Saleeby, 1996), similar to cratonic xenoliths. The inferred P - T path (Figure 5a) of the Sierran peridotites is interpreted to represent significant tectonic thickening in a compressional

subduction zone (Chin et al., 2012). Following melt depletion and subsequently during deformation and thickening, the Sierran mantle was melt-infiltrated and hydrated (Lee, 2005; Chin et al., 2014). The final equilibration at low temperatures (<800°C) and high pressures (3–4 GPa), together with rapid cooling to 'lock' in chemical and textural evidence, preserved garnet exsolution lamellae in orthopyroxene grains (Chin et al., 2014). Furthermore, rapid thickening and cooling may have promoted minor exsolution of water from olivine to form amphibole replacing clinopyroxene (Chin et al., 2016). In fact, Chin et al. (2016) found that the observed discrepancy between measured olivine water content versus clinopyroxene-recalculated (i.e. RC) olivine water content could actually account for the 'missing water' needed to form the observed amphibole, further bolstering an exsolution hypothesis. In Figure 4a, the Sierran xenoliths plot at the lowest temperatures and have the highest $R_{\text{cpx/opx}}$, consistent with subsolidus re-equilibration and re-distribution of water between pyroxenes.

3.2.3 | The need for an early re-hydration process during cratonization

Exsolution-induced garnet formation and associated water release from orthopyroxene in melt-depleted peridotites, alone, is unlikely to account for the puzzling occurrence of garnet harzburgite in the cratonic lithosphere. Metasomatism is usually required to explain the observed proportions of garnet and clinopyroxene compared to the volumes expected for melt-depleted peridotite, as well as the mineralogical heterogeneity observed in xenoliths sampled at different depths. Yet, a balance must be struck between 'ad hoc' metasomatism, which re-introduces major elements, volatiles, heat-producing incompatible elements and thus will reheat and redensify the mantle, and the apparent long-term preservation of stable, thick, cold cratonic mantle lithosphere (Rudnick et al., 1998). We propose that metasomatism occurring early in the cratonization process—for example, while initially melt-depleted residues undergo thickening, deformation and stabilization, as discussed above in the Sierra Nevada case—could re-introduce volatiles into a rock matrix during retrograde metamorphism, after which exsolution-induced garnet formation and water release due to decreased temperatures and increased pressures results in water re-distribution.

Our argument stems from the geophysical imaging showing that many cratons contain complex internal structure, such as dipping layers reminiscent of subducted slabs (Mercier et al., 2008) or suture zones formed via continent–continent collision (Figure 5b). This indicates that these cratons likely formed due to mobile lid tectonics, which have operated at an increasingly global scale since at least the Mesoarchean (Palin & Santosh, 2020). Owing to their cold, highly viscous states, it is unlikely that significant deformation occurred in most cratons after their initial formation, although, the disturbed Wyoming and North China Cratons are notable exceptions (Liu et al., 2018). Thus, the presence of intra-cratonic layering and/or past plate boundaries suggests that

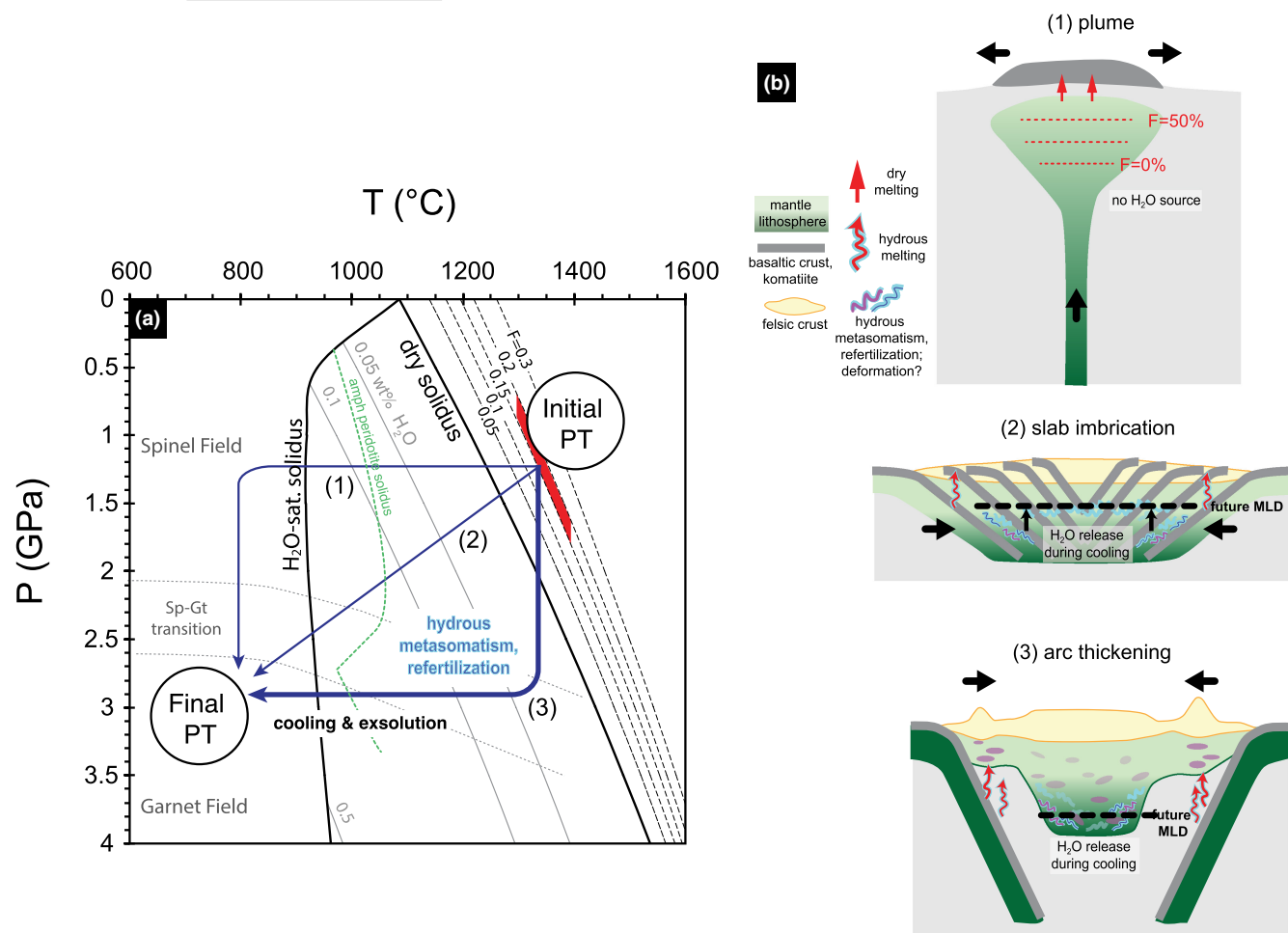


FIGURE 5 (a) *P*-*T* diagram after Chin et al. (2012) and Lee and Chin (2014) showing paths of mantle lithosphere starting from shallow, high-*T* melt depletion and subsequent cooling and thickening. (b) Cratonization models based on Lee et al. (2011). Cooling-induced hydration to form lithospheric discontinuities is shown

cratonic nuclei were initially mobile and deformed during coalescence in the Archean-Proterozoic to generate such structures (Capitanio et al., 2020).

One way to enhance deformation in mantle rock is to add water, which has a weakening effect and lowers viscosity (Hirth & Kohlstedt, 1996) and enhances creep rate (Karato, 1986). Rehydration may therefore allow previously melt-depleted cratonic nuclei to deform while forming thick roots. Too much hydration, however, would impede preservation, owing to the low viscosity conferred by hydration. By contrast, mantle lithosphere that is too dry will have difficulty in localizing shear zones and promoting ongoing deformation to form cratonic nuclei. One potential scenario is heterogeneous distribution of water in the mantle lithosphere, perhaps localized in fossil shear zones (Speciale et al., 2020), which we discuss further below.

Syn-cratonization scenarios that could rehydrate proto-cratonic roots as they deform and thicken into keels include serpentinitization and refertilization. If cratons form by imbrication of oceanic slabs (Figure 5b), (re)hydration could occur by serpentinitization. In fact, serpentinitization has been called upon to explain Si-enrichment observed beneath the Kaapvaal Craton (Canil &

Lee, 2009). Refertilization during thickening, via melt infiltration and hydration (cf., Chin et al., 2012), may be another way to reintroduce volatiles. We propose that syn-cratonization rehydration/refertilization, akin to the process described earlier in this paper for the Sierra Nevada, could have also been favourable for the development of deep lithospheric shear zones (e.g. Dijkstra, et al., 2002). In experiments on an H₂O-saturated, olivine-rich shear zone (1.2 GPa, 900°C), Precigout et al. (2019) found high H₂O content in olivine in areas where the shear strain was localized. The observed H₂O amounts exceeded the predicted amount for grain boundary saturation; instead, cavitation rate may increase with strain rate, resulting in progressive H₂O transfer from low to high strain zones.

Initially, small grain size and high water contents could facilitate early strain localization and craton mobility, perhaps aiding the several 100's of Ma time-scales needed for craton coalescence. Grain size in shear zones and mylonites tends to be reduced because dynamic recrystallization promotes weakening; but, grain growth (static recrystallization) counteracts this process (Montési & Hirth, 2003). In fact, olivine grain growth takes far longer if the grains are 'damp' as opposed to being water-saturated (Speciale et al., 2020). Damp,

rather than water-saturated or completely dry, olivine and pyroxene could be prevalent shortly following syn-cratonization rehydration, boosting the originally depleted mantle lithosphere's water content. Following the final cooling and stabilization of the craton, this re-introduced water would exsolve from orthopyroxene during garnet formation. Olivine would also exsolve water due to the reduced solubility at a decreased temperature, increasing mantle viscosity and ending this initial window of craton deformation. The slowing of grain growth with decreased water content and this inherited heterogeneity of water distribution in the lithosphere could also explain why, despite average coarse (~1 cm) grain sizes, cratonic peridotites of various grain sizes and textures are still sampled in geologically recent kimberlites.

In summary, we propose that 'sweating' of lithospheric water during cratonization could explain the roughly constant 30ppm last water content observed in mantle olivines. In addition, the increase in $R_{\text{cpx/opx}}$ with decreasing temperature, particularly for cratonic regions (Figure 4), is consistent with the subsolidus re-distribution of water into clinopyroxene compared to orthopyroxene. This may occur as orthopyroxene exsolves garnet, releasing water which would favour to enter clinopyroxene due to its higher D relative to garnet, olivine and orthopyroxene.

3.2.4 | Speculations on the origin of the mid-lithospheric discontinuity

Finally, our data compilation and forward modelling may shed new light on the origin of the so-called 'mid-lithospheric discontinuity' (MLD), which has been identified through seismic shear wave receiver function studies performed on all major continents on Earth (e.g. Selway, Ford, & Kelemen, 2015). Vertical seismic velocity profiles consistently observe a significant decrease in P - and S -wave velocities at depths of ~60–160km, although this is most pronounced at ~80–100km. In regions that are tectonically active, this is often interpreted as representing the lithosphere–asthenosphere boundary (LAB: Ford et al., 2010); however, in stable continental and cratonic regions, the LAB may be as deep as 300km (Artemieva & Mooney, 2001; Kind, Yuan, & Kumar, 2012), and the continuity of this low-velocity band through the lithosphere is more difficult to explain. Some previous studies have invoked the presence of concentrated partial melt at MLD depths (Thybo & Perchuc, 1997), an up-temperature transition in olivine deformation behaviour from elastic to anelastic that promotes grain boundary sliding and bulk-rock weakening (Karato, 1986), or compositional gradients that produce different mineral assemblages above and below the MLD, such as bulk-peridotite Mg\# (Yuan & Romanowicz, 2010).

An intriguing extension of the latter hypothesis is that the MLD may be caused by a hydrated layer within the lithosphere, either caused by small concentrations of hydrous minerals (phlogopite, amphibole) or wetter olivine compared to ambient lithospheric mantle (Liu et al., 2018). Geochemical calculations performed by Selway et al. (2015) showed that infiltration of water into pyrolite at various

depths across the MLD produced sufficient volumes of amphibole and phlogopite to reduce the bulk-rock seismic velocity and replicate the MLD. In addition, Eeken et al. (2018) calculated that even 0.25 wt.% H_2O added to peridotite already produces ~13% of a hydrous mineral assemblage in the host peridotite, which is on the high end for generally 'depleted' cratonic mantle.

However, to date, most or all such studies invoke post-cratonization metasomatism to explain a hydration origin for the MLD. Instead, we argue that our mechanism of early, syn-cratonization rehydration/refertilization followed by cooling-induced water exsolution from NAMs may release, at minimum, 100's of ppm of water *per mineral*. This may be further facilitated along favourable P - T paths such as (3) in Figure 5a, wherein mantle is thickened isothermally (i.e. during rapid tectonic or magmatic thickening) and then cooled isobarically into the garnet stability field. In fact, the sharpest decreases in water solubility in olivine and orthopyroxene along the three geotherms discussed above are predicted at pressures of 2.5–3.5 GPa just below the solidus (Figure S1), which is equivalent to 90–120 km depth below the Earth's surface. We propose that 'sweating' of water in the deep lithosphere due to changing P - T conditions and hence solubility during cratonization may have been a ubiquitous phenomenon in the early Earth, and circumvents the issue of different cratons having different geological histories. Our hypothesis provides a self-consistent cratonization model that does not necessitate ad hoc metasomatism post-dating craton formation to explain intra-cratonic layering.

4 | CONCLUSIONS

New thermodynamically constrained models of NAM water storage capacities for pyrolite and garnet harzburgite at 0–5 GPa and 600–1600°C show that cratonic mantle can potentially hold up to ~2000ppm H_2O along typical geotherms. When comparing these predicted capacities with published data, we show that: (1) recalculated olivine water contents to be in equilibrium with clinopyroxene are consistent regardless of tectonic setting, implying that global lithospheric mantle reflects an equilibrium level of undersaturation (~10-times lower than its potential storage capacity), (2) pyroxene-measured water contents reflect undersaturation (about ~2 times relative to maximum storage capacity) and (3) the ratio of water that can be incorporated in clinopyroxene/orthopyroxene increases with decreasing temperature. These models provide a quantitative framework onto which future investigations of NAM research can build. In particular, knowledge of xenolith P - T history may be used to quantify the potential magnitude of fluid release, and our calculated values may allow for predictive modelling of subsolidus (re-) partitioning of water in different tectonic settings throughout geological time. Cooling may thus dynamically drive devolatilization and self-catalyse mineralogical transformation, eliminating the need for invoking ad hoc hydration events driven by externally derived aqueous fluids, which are often suggested to explain the trace element and volatile characteristics of many cratonic xenoliths.

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CONFLICT OF INTEREST

The authors declare no competing interests.

AUTHORS' CONTRIBUTIONS

EJC devised the study and compiled data from natural samples, and RMP performed petrological calculations. Both authors interpreted the results and wrote the manuscript.

DATA AVAILABILITY STATEMENT

All data used in this work are provided in Table S3 or can be found in articles referenced in the main text.

REFERENCES

- Artemieva, I. M., & Mooney, W. D. (2001). Thermal thickness and evolution of Precambrian lithosphere: A global study. *Journal of Geophysical Research: Solid Earth*, 106(B8), 16387–16414.
- Aubaud, C., Hauri, E. H., & Hirschmann, M. M. (2004). Hydrogen partition coefficients between nominally anhydrous minerals and basaltic melts. *Geophysical Research Letters*, 31(20), L20611.
- Bell, D. R., & Rossman, G. R. (1992). Water in Earth's mantle: The role of nominally anhydrous minerals. *Science*, 255(5050), 1391–1397.
- Bernard, R. E., Behr, W. M., Becker, T. W., & Young, D. J. (2019). Relationships between olivine CPO and deformation parameters in naturally deformed rocks and implications for mantle seismic anisotropy. *Geochemistry, Geophysics, Geosystems*, 20, 3469–3494.
- Bodnar, R. J., Azbej, T., Becker, S. P., Cannatelli, C., Fall, A., & Severs, M. J. (2013). Whole earth geohydrologic cycle, from the clouds to the core: The distribution of water in the dynamic earth system. *The Geological Society of America Special Paper*, 500, 431–461.
- Brodholt, J. P., & Refson, K. (2000). An ab initio study of hydrogen in forsterite and a possible mechanism for hydrolytic weakening. *Journal of Geophysical Research: Solid Earth*, 105, 18977–18982.
- Bromiley, G. D., Keppler, H., McCammon, C., Bromiley, F. A., & Jacobsen, S. D. (2004). Hydrogen solubility and speciation in natural, gem-quality chromian diopside. *American Mineralogist*, 89, 941–949.
- Canil, D., & Lee, C.-T. A. (2009). Were deep cratonic mantle roots hydrated in Archean oceans? *Geology*, 37(7), 667–670.
- Capitanio, F. A., Nebel, O., & Cawood, P. A. (2020). Thermochemical lithosphere differentiation and the origin of cratonic mantle. *Nature*, 588(7836), 89–94.
- Cherniak, D. J., & Dimanov, A. (2010). Diffusion in pyroxene, mica and amphibole. *Reviews in Mineralogy and Geochemistry*, 72(1), 641–690.
- Chin, E. J., Lee, C.-T. A., & Barnes, J. D. (2014). Thickening, refertilization, and the deep lithosphere filter in continental arcs: Constraints from major and trace elements and oxygen isotopes. *Earth and Planetary Science Letters*, 397, 184–200.
- Chin, E. J., Lee, C.-T. A., Luffi, P., & Tice, M. (2012). Deep lithospheric thickening and Refertilization beneath continental arcs: Case study of the P, T and compositional evolution of peridotite xenoliths from the Sierra Nevada, California. *Journal of Petrology*, 53(3), 477–511.
- Chin, E. J., Lee, C. T. A., & Blichert-Toft, J. (2015). Growth of upper plate lithosphere controls tempo of arc magmatism: Constraints from Al-diffusion kinetics and coupled Lu-Hf and Sm-Nd chronology. *Geochemical Perspectives Letters*, 1, 20–32.
- Chin, E. J., Soustelle, V., Hirth, G., Saal, A., Kruckenberg, S. C., & Eiler, J. (2016). Microstructural and geochemical constraints on the evolution of deep arc lithosphere. *Geochemistry, Geophysics, Geosystems*, 17(7), 2497–2521.
- Chin, E. J., Chilson-Parks, B., Boneh, Y., Hirth, G., Saal, A., Hearn, B. C., & Hauri, E. (2021). The peridotite deformation cycle in cratons and the deep impact of subduction. *Tectonophysics*, 817, 229029.
- Condie, K. C. (2021). Two major transitions in earth history: Evidence of two lithospheric strength thresholds. *The Journal of Geology*, 129, 455–473.
- Cox, K. G., Smith, M. R., & Beswetherick, S. (1987). Textural studies of garnet lherzolites: Evidence of exsolution origin from high-temperature harzburgites. In P. H. Nixon (Ed.), *Mantle xenoliths*. John Wiley and Sons Ltd.
- de Capitani, C., & Petrakakis, K. (2010). The computation of equilibrium assemblage diagrams with Theriak/domino software. *American Mineralogist*, 95(7), 1006–1016.
- Demouchy, S., & Bolfan-Casanova, N. (2016). Distribution and transport of hydrogen in the lithospheric mantle: A review. *Lithos*, 240, 402–425.
- Demouchy, S., Shcheka, S., Denis, C. M., & Thoraval, C. (2017). Subsolidus hydrogen partitioning between nominally anhydrous minerals in garnet-bearing peridotite. *American Mineralogist*, 102(9), 1822–1831.
- Dijkstra, A. H., Drury, M. R., Vissers, R. L., & Newman, J. (2002). On the role of melt-rock reaction in mantle shear zone formation in the Othris peridotite massif (Greece). *Journal of Structural Geology*, 24(9), 1431–1450.
- Ducea, M. N., & Saleeby, J. B. (1996). Buoyancy sources for a large, unrooted mountain range, the Sierra Nevada, California: Evidence from xenolith thermobarometry. *Journal of Geophysical Research*, 101, 8229–8244.
- Eeken, T., Goes, S., Pedersen, H. A., Arndt, N. T., & Bouilhol, P. (2018). Seismic evidence for depth-dependent metasomatism in cratons. *Earth and Planetary Science Letters*, 491, 148–159.
- Ford, H. A., Fischer, K. M., Abt, D. L., Rychert, C. A., & Elkins-Tanton, L. T. (2010). The lithosphere–asthenosphere boundary and cratonic lithospheric layering beneath Australia from Sp wave imaging. *Earth and Planetary Science Letters*, 300(3–4), 299–310.
- Ganne, J., & Feng, X. (2017). Primary magmas and mantle temperatures through time. *Geochemistry, Geophysics, Geosystems*, 18, 872–888.
- Gibson, S. A. (2017). On the nature and origin of garnet in highly-refractory Archean lithospheric mantle: Constraints from garnet exsolved in Kaapvaal craton orthopyroxenes. *Mineralogical Magazine*, 81(4), 781–809.
- Hauri, E. H., Gaetani, G. A., & Green, T. H. (2006). Partitioning of water during melting of the Earth's upper mantle at H₂O-undersaturated conditions. *Earth and Planetary Science Letters*, 248(3), 715–734.
- Herzberg, C., Condie, K., & Korenaga, J. (2010). Thermal history of the earth and its petrological expression. *Earth and Planetary Science Letters*, 292(1–2), 79–88.
- Hirth, G., & Kohlstedt, D. L. (1996). Water in the oceanic upper mantle: Implications for rheology, melt extraction and the evolution of the lithosphere. *Earth and Planetary Science Letters*, 144(1–2), 93–108.
- Hirschmann, M. M. (2006). Water, melting, and the deep earth H₂O cycle. *Annual Review of Earth and Planetary Sciences*, 34(1), 629–653.
- Holland, T. J. B., & Powell, R. (2011). An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. *Journal of Metamorphic Geology*, 29(3), 333–383.

- Jennings, E. S., & Holland, T. J. (2015). A simple thermodynamic model for melting of peridotite in the system NCFMASOcr. *Journal of Petrology*, 56(5), 869–892.
- Jordan, T. H. (1981). Continents as a chemical boundary layer. Philosophical transactions of the Royal Society of London. *Series A, Mathematical and Physical Sciences*, 301(1461), 359–373.
- Karato, S. (1986). Does partial melting reduce the creep strength of the upper mantle? *Nature*, 319, 309–310.
- Karato, S.-i., Jung, H., Katayama, I., & Skemer, P. (2008). Geodynamic significance of seismic anisotropy of the upper mantle: New insights from laboratory studies: *Annu. Review of Earth and Planetary Sciences*, 36, 59–95.
- Keppler, H., & Bolfan-Casanova, N. (2006). Thermodynamics of water solubility and partitioning. *Reviews in Mineralogy and Geochemistry*, 62(1), 193–230.
- Kind, R., Yuan, X., & Kumar, P. (2012). Seismic receiver functions and the lithosphere–asthenosphere boundary. *Tectonophysics*, 536, 25–43.
- Kopylova, M. G., & Russell, J. K. (2000). Chemical stratification of cratonic lithosphere: Constraints from the northern slave craton, Canada. *Earth and Planetary Science Letters*, 181(1), 71–87.
- Lamadrid, H., Lamb, W., Santosh, M., & Bodnar, R. (2014). Raman spectroscopic characterization of H₂O in CO₂-rich fluid inclusions in granulite facies metamorphic rocks. *Gondwana Research*, 26, 301–310.
- Lee, C. (1998). Are inflected geotherms real? International kimberlite conference (pp. 489–491). International Kimberlite Conference. Extended abstracts.
- Lee, C. T. A. (2005). Trace element evidence for hydrous metasomatism at the base of the north American lithosphere and possible association with Laramide low-angle subduction. *The Journal of Geology*, 113(6), 673–685.
- Lee, C.-T. A., Luffi, P., Höink, T., Li, Z.-X. A., & Lenardic, A. (2008). The role of serpentine in preferential craton formation in the late Archean by lithosphere underthrusting. *Earth and Planetary Science Letters*, 269, 96–104.
- Lee, C.-T. A., & Chin, E. J. (2014). Calculating melting temperatures and pressures of peridotite protoliths: Implications for the origin of cratonic mantle. *Earth and Planetary Science Letters*, 403, 273–286.
- Lee, C.-T. A., Luffi, P., & Chin, E. J. (2011). Building and destroying continental mantle. *Annual Review of Earth and Planetary Sciences*, 39(1), 59–90.
- Li, Z.-X. A., Lee, C.-T. A., Peslier, A. H., Lenardic, A., & Mackwell, S. J. (2008). Water contents in mantle xenoliths from the Colorado plateau and vicinity: Implications for the mantle rheology and hydration-induced thinning of continental lithosphere. *Journal of Geophysical Research: Solid Earth*, 113(B9), 1–22.
- Liu, L., Morgan, J. P., Xu, Y., & Menzies, M. (2018). Craton destruction 1: Cratonic keel delamination along a weak midlithospheric discontinuity layer. *Journal of geophysical research: Solid Earth*, 123, 10040–10068.
- Lu, R., & Keppler, H. (1997). Water solubility in pyrope to 100 kbar. *Contributions to Mineralogy and Petrology*, 129, 35–42.
- Mackwell, S. J., & Kohlstedt, D. L. (1990). Diffusion of hydrogen in olivine: Implications for water in the mantle. *Journal of Geophysical Research: Solid Earth*, 95(B4), 5079–5088.
- Mercier, J. P., Bostock, M., Audet, P., Gaherty, J., Garnero, E., & Revenaugh, J. (2008). The teleseismic signature of fossil subduction: Northwestern Canada. *Journal of Geophysical Research: Solid Earth*, 113(B4), 1–16.
- Mierdel, K., & Keppler, H. (2004). The temperature dependence of water solubility in enstatite. *Contributions to Mineralogy and Petrology*, 148, 305–311.
- Mierdel, K., Keppler, H., Smyth, J. R., & Langenhorst, F. (2007). Water solubility in aluminous orthopyroxene and the origin of Earth's asthenosphere. *Science*, 315(5810), 364–368.
- Moine, B., Bolfan-Casanova, N., Radu, I., Ionov, D., Costin, G., Korsakov, A., Golovin, A., Oleinikov, O., Deloule, E., & Cottin, J. (2020). Molecular hydrogen in minerals as a clue to interpreted D variations in the mantle. *Nature Communications*, 11, 1–10.
- Montési, L. G., & Hirth, G. (2003). Grain size evolution and the rheology of ductile shear zones: From laboratory experiments to postseismic creep. *Earth and Planetary Science Letters*, 211(1–2), 97–110.
- Nicoli, G., & Ferrero, S. (2021). Nanorocks, volatiles and plate tectonics. *Geoscience Frontiers*, 12, 101188.
- O'Leary, J. A., Gaetani, G. A., & Hauri, E. H. (2010). The effect of tetrahedral Al³⁺ on the partitioning of water between clinopyroxene and silicate melt. *Earth and Planetary Science Letters*, 297(1–2), 111–120.
- Palin, R. M., & Santosh, M. (2020). Plate tectonics: What, where, why, and when? *Gondwana Research*, 100, 3–24.
- Palin, R. M., Santosh, M., Cao, W., Li, S. S., Hernández-Urbe, D., & Parsons, A. (2020). Secular change and the onset of plate tectonics on earth. *Earth-Science Reviews*, 207, 103172.
- Palin, R. M., & White, R. W. (2016). Emergence of blueschists on earth linked to secular changes in oceanic crust composition. *Nature Geoscience*, 9(1), 60–64.
- Pearson, D. G., Scott, J. M., Liu, J., Schaeffer, A., Wang, L. H., van Hunen, J., Szilas, K., Chacko, T., & Kelemen, P. B. (2021). Deep continental roots and cratons. *Nature*, 596(7871), 199–210.
- Peslier, A. H. (2010). A review of water contents of nominally anhydrous natural minerals in the mantles of earth, Mars and the moon. *Journal of Volcanology and Geothermal Research*, 197, 239–258.
- Peslier, A. H., Schönbächler, M., Busemann, H., & Karato, S. I. (2017). Water in the Earth's interior: Distribution and origin. *Space Science Reviews*, 212(1), 743–810.
- Pearson, D., Canil, D., & Shirey, S. (2003). Mantle samples included in volcanic rocks: Xenoliths and diamonds. *Treatise on Geochemistry*, 2, 171–275.
- Piccolo, A., Kaus, B. J., White, R. W., Palin, R. M., & Reuber, G. S. (2020). Plume–Lid interactions during the Archean and implications for the generation of early continental terranes. *Gondwana Research*, 88, 150–168.
- Pitzer, K. S., & Sterner, S. M. (1994). Equations of state valid continuously from zero to extreme pressures for H₂O and CO₂. *The Journal of Chemical Physics*, 101, 3111–3116.
- Pollack, H. N., & Chapman, D. S. (1977). On the regional variation of heat flow, geotherms, and lithospheric thickness. *Tectonophysics*, 38, 279–296.
- Précigout, J., Stünitz, H., & Villeneuve, J. (2019). Excess water storage induced by viscous strain localization during high-pressure shear experiment. *Scientific Reports*, 9(1), 1–9.
- Ringwood, A. E., 1975. *Composition and petrology of the Earth's mantle*. MacGraw-hill, v. 618.
- Rudnick, R. L., McDonough, W. F., & O'Connell, R. J. (1998). Thermal structure, thickness and composition of continental lithosphere. *Chemical Geology*, 145(3–4), 395–411.
- Saltzer, R. L., Chatterjee, N., & Grove, T. L. (2001). The spatial distribution of garnets and pyroxenes in mantle peridotites: Pressure-temperature history of peridotites from the Kaapvaal craton. *Journal of Petrology*, 42(12), 2215–2229.
- Selway, K., Ford, H., & Kelemen, P. (2015). The seismic mid-lithosphere discontinuity. *Earth and Planetary Science Letters*, 414, 45–57.
- Silver, P. G., & Chan, W. W. (1988). Implications for continental structure and evolution from seismic anisotropy. *Nature*, 335, 34–39.
- Speciale, P. A., Behr, W. M., Hirth, G., & Tople, L. (2020). Rates of olivine grain growth during dynamic recrystallization and postdeformation annealing. *Journal of geophysical research: Solid Earth*, 125(11), e2020JB020415.
- Tenner, T. J., Hirschmann, M. M., Withers, A. C., & Hervig, R. L. (2009). Hydrogen partitioning between nominally anhydrous upper mantle minerals and melt between 3 and 5 GPa and applications to hydrous peridotite partial melting. *Chemical Geology*, 262(1), 42–56.

- Tomlinson, E. L., Kamber, B. S., Hoare, B. C., Stead, C. V., & Ildefonse, B. (2018). An exsolution origin for Archean mantle garnet. *Geology*, 46(2), 123–126.
- Thybo, H., & Perchuc, E. (1997). The seismic 8 discontinuity and partial melting in continental mantle. *Science*, 275(5306), 1626–1629.
- Tian, Z. Z., Liu, J., Xia, Q. K., Ingrin, J., Hao, Y. T., & Christophe, D. (2017). Water concentration profiles in natural mantle orthopyroxenes: A geochronometer for long annealing of xenoliths within magma. *Geology*, 45(1), 87–90.
- Ulmer, P. (2001). Partial melting in the mantle wedge – The role of H₂O in the genesis of mantle-derived 'arc-related' magmas. *Physics of the Earth and Planetary Interiors*, 127(1–4), 215–232.
- Warren, J. M., & Hauri, E. H. (2014). Pyroxenes as tracers of mantle water variations. *Journal of geophysical research: Solid Earth*, 119(3), 1851–1881.
- Xu, P., & Zhao, D. (2009). Upper-mantle velocity structure beneath the North China craton: Implications for lithospheric thinning. *Geophysical Journal International*, 177, 1279–1283.
- Xu, Y., Tang, W., Hui, H., Rudnick, R. L., Shang, S., & Zhang, Z. (2019). Reconciling the discrepancy between the dehydration rates in mantle olivine and pyroxene during xenolith emplacement. *Geochimica et Cosmochimica Acta*, 267, 179–195.
- Yuan, H., & Romanowicz, B. (2010). Lithospheric layering in the north American craton. *Nature*, 466(7310), 1063–1068.
- Zhao, Y.-H., Ginsberg, S., & Kohlstedt, D. (2004). Solubility of hydrogen in olivine: Dependence on temperature and iron content. *Contributions to Mineralogy and Petrology*, 147, 155–161.
- Ziagos, J. P., Blackwell, D. D., & Mooser, F. (1985). Heat flow in southern Mexico and the thermal effects of subduction. *Journal of Geophysical Research: Solid Earth*, 90, 5410–5420.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

Data S1. Supporting Information

Table S3. Compiled literature data of water content in NAMs and P–T conditions

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