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# Abnormal lithium isotope composition from the ancient lithospheric mantle beneath the North China Craton

Yan-Jie Tang<sup>1</sup>, Hong-Fu Zhang<sup>1,2</sup>, Etienne Deloule<sup>3</sup>, Ben-Xun Su<sup>1</sup>, Ji-Feng Ying<sup>1</sup>, M. Santosh<sup>4</sup> & Yan Xiao<sup>1</sup>Received  
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requests for materials  
should be addressed to  
Y.-J.T. (jtangyanjie@  
mail.igcas.ac.cn)

<sup>1</sup>State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, P.O. Box 9825, Beijing 100029, China, <sup>2</sup>State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, China, <sup>3</sup>Centre National de la Recherche Scientifique, CRPG, BP20, 54501 Vandoeuvre-Les-Nancy Cedex, France, <sup>4</sup>School of Earth Science and Resources, China University of Geosciences, Beijing 100083, China.

Lithium elemental and isotopic compositions of olivines in peridotite xenoliths from Hebi in the North China Craton provide direct evidence for the highly variable  $\delta^7\text{Li}$  in Archean lithospheric mantle. The  $\delta^7\text{Li}$  in the cores of olivines from the Hebi high-Mg# peridotites (Fo > 91) show extreme variation from  $-27$  to  $+21$ , in marked deviation from the  $\delta^7\text{Li}$  range of fresh MORB ( $+1.6$  to  $+5.6$ ) although the Li abundances of the olivines are within the range of normal mantle (1–2 ppm). The Li abundances and  $\delta^7\text{Li}$  characteristics of the Hebi olivines could not have been produced by recent diffusive-driven isotopic fractionation of Li and therefore the  $\delta^7\text{Li}$  in the cores of these olivines record the isotopic signature of the subcontinental lithospheric mantle. Our data demonstrate that abnormal  $\delta^7\text{Li}$  may be preserved in the ancient lithospheric mantle as observed in our study from the central North China Craton, which suggest that the subcontinental lithospheric mantle has experienced modification of fluid/melt derived from recycled oceanic crust.

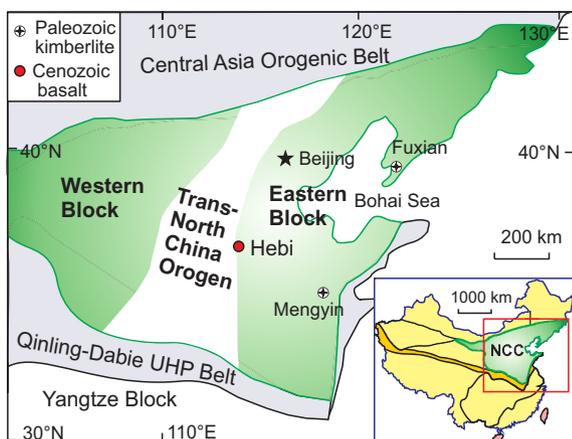
Lithium has proven to be an important geochemical tracer for fluid-related processes in the Earth's surface as well as crust-mantle recycling<sup>1,2</sup> because of its moderate incompatibility during mantle melting<sup>3</sup>, strong fluid mobility<sup>4</sup>, and the large mass fractionation, with up to 80% variation of  $^7\text{Li}/^6\text{Li}$  in terrestrial samples<sup>1</sup>. In contrast to the large variations in Li isotope compositions of the Earth's surface environments, the  $\delta^7\text{Li}$  of mantle is more restricted, in the range of about  $+4 \pm 2$  as inferred from relatively pristine olivines and fresh MORB<sup>5–8</sup>.

The Li isotopic heterogeneity in the mantle caused by fluid/melt-rock interaction can be rehomogenized by diffusion over geologically short time periods due to the fast diffusion of Li<sup>7,9–14</sup>, and thus the mantle is broadly characterized by homogeneous Li isotope composition. However, several studies have suggested the existence of abnormal  $\delta^7\text{Li}$  in the mantle, such as high  $\delta^7\text{Li}$  (up to  $+7.9$ ) of HIMU lavas<sup>15,16</sup>, and low  $\delta^7\text{Li}$  (lower than  $-7.0$ ) of mantle-derived minerals<sup>17–20</sup> and lavas<sup>21</sup>, which are considered to result from isotope fractionation during the dehydration of subducted oceanic crust<sup>22,23</sup>. To date, the data on abnormal  $\delta^7\text{Li}$  are mainly recorded from indirect samples of the mantle or directly on clinopyroxene separates in peridotites, although the latter are susceptible to recent diffusive fractionation of Li isotopes during the entrainment and transportation of the xenoliths by host magma due to the much faster diffusion of Li in pyroxene than in olivine<sup>9,24,25</sup>. In contrast, the Li isotope compositions in the cores of large olivine grains from peridotite xenoliths, which represent direct samples of the upper mantle, provide more robust signature of the lithospheric mantle.

In this study, we report the anomalous Li isotope compositions of olivines in a suite of peridotite xenoliths from the Hebi locality in the central North China Craton, one of the world's oldest continental nuclei<sup>26</sup> (Fig. 1). Our data bring out the largest variation in  $\delta^7\text{Li}$  values among those published for olivines from peridotite xenoliths<sup>7,27,28</sup>, and demonstrate the existence of abnormal  $\delta^7\text{Li}$  in the ancient subcontinental lithospheric mantle.

## Results

The peridotite xenoliths in the Hebi Cenozoic basalts (about 4 Ma) of present study are remarkably fresh and about 5 cm in diameter. They are coarse-grained with olivine grains typically ranging in size from 3 to 6 mm in diameter, with a maximum up to 10 mm. Compositionally, the rocks are dominantly high-Mg# (Fo > 91) harzburgites with one low-Mg# (Fo < 91) lherzolite (HB29; Supplementary Table 1). The high-Mg# harzburgite xenoliths have been interpreted as shallow relics of the Archean cratonic mantle beneath the North China Craton and the low-Mg# lherzolite may represent the newly-formed<sup>29</sup> or modified lithospheric mantle<sup>30</sup>. The olivines in

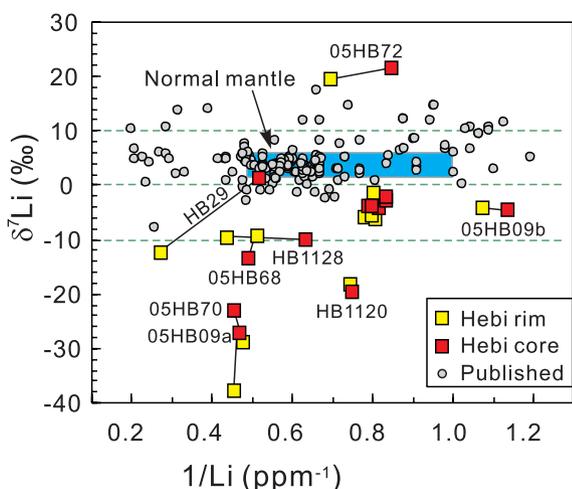


**Figure 1** | Sketch map showing the major tectonic units of the North China Craton and the localities of Hebi xenolith and Paleozoic kimberlites (tectonic units revised after Zhao et al.<sup>48</sup>). The inset shows location of the North China Craton (NCC).

the high-Mg# harzburgites show highly variable  $\delta^7\text{Li}$ . The grain cores have Li abundances of 0.9 to 2.2 ppm and  $\delta^7\text{Li}$  ranging from  $-27$  to  $+22$  and of the rims show 0.9 to 2.3 ppm and  $\delta^7\text{Li}$  of  $-38$  to  $+20$ , respectively. The Li abundance and  $\delta^7\text{Li}$  of olivine in the low-Mg# lherzolite are 1.9 ppm and  $+1.2$  in the core and 3.6 ppm and  $-13$  in the rim, showing high- $\delta^7\text{Li}$  core with lower Li abundance as compared to the low- $\delta^7\text{Li}$  rim (Fig. 2).

## Discussion

The  $^6\text{Li}$  is predicted to have high diffusivity, about 3% faster than  $^7\text{Li}$  based due to a mass difference of 16.7%<sup>31</sup>. Thus, large Li isotopic fractionations can be produced by diffusion during processes of fluid/melt-rock reaction<sup>7,10,32</sup>. Hence, diffusion-driven fractionation of Li isotopes has been invoked to explain the Li isotopic variations in peridotites, a process that could occur during rock-melt/fluid reaction prior to or coincident with the entrainment into host magmas and the transport of the mantle xenolith to the surface<sup>10,13,33–35</sup>, as well as during the cooling of peridotites<sup>12,14,36</sup>. The results of diffusive



**Figure 2** | Variation of  $\delta^7\text{Li}$  with Li abundances of olivines in the Hebi xenoliths compared to the published data for olivines from worldwide peridotites. Data sources: Seitz et al.<sup>5</sup>, Magna et al.<sup>6</sup>, Jeffcoate et al.<sup>7</sup>, Rudnick and Ionov<sup>10</sup>, Halama et al.<sup>34</sup>, Tang et al.<sup>18–20</sup>, Wagner and Deloule<sup>49</sup>, Ionov and Seitz<sup>12</sup>, Aulbach and Rudnick<sup>13</sup>, Zhang et al.<sup>46</sup>, Gao et al.<sup>36</sup>. The field for normal mantle is based on the compositions of relatively pristine olivines and fresh MORB<sup>5–8</sup>. The dashed lines link the core and rim of each olivine.

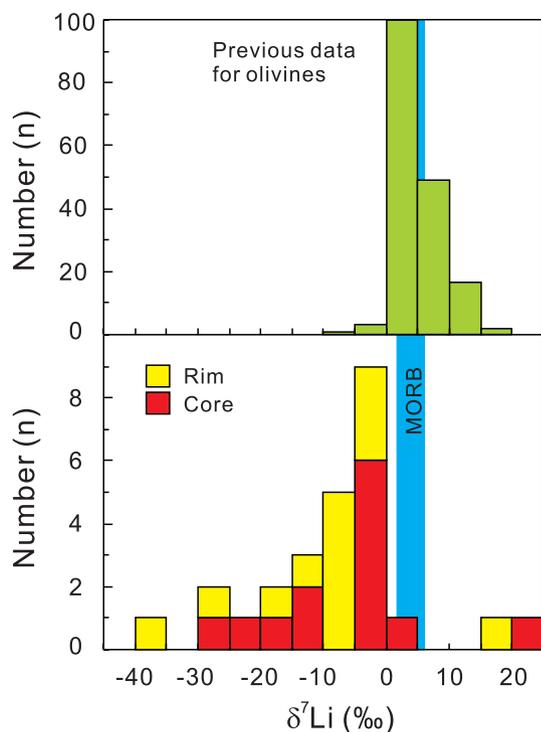
fractionation are reflected in the variations of  $\delta^7\text{Li}$  from meter to micron scale<sup>7,9,19,32,37</sup>. Thus, an important point to evaluate is whether the  $\delta^7\text{Li}$  values obtained from the olivines provide robust signature of the lithospheric mantle.

Modeling of diffusive fractionation of Li isotopes generally assumes ingress of Li into rocks or minerals from a source of Li, such as Li diffusing into peridotite from melt<sup>32</sup>, Li diffusing into country rocks from Li-rich pegmatite<sup>37</sup>, or into clinopyroxene from coexisting olivine during cooling of peridotites<sup>14</sup>. In the case of Li addition to peridotites, the mantle minerals first become enriched in  $^6\text{Li}$  because of its greater diffusion rate than  $^7\text{Li}$ , leading to low  $\delta^7\text{Li}$  relative to its precursor. This mechanism can account for the observations of isotopically heavy cores with lower Li concentrations than the light rims of minerals<sup>7,10,25</sup>, such as the low-Mg# sample HB29 in our present study (Fig. 2), and suggest recent diffusive ingress of Li into the rim of olivine. However, the model of diffusive ingress of Li does not adequately explain the characteristics of Li abundances and  $\delta^7\text{Li}$  of olivines in the high-Mg# peridotites because (1) the Li content does not show enrichment, and the values are close to that of the normal mantle of 1–2 ppm<sup>38,39</sup>; (2) there is no apparent difference in Li abundances and  $\delta^7\text{Li}$  between the rims and the cores of most olivines from the high-Mg# samples; and (3) olivine from the sample 05HB72 has a Li abundance of 1 ppm and much higher  $\delta^7\text{Li}$  ( $+20$ ) than the normal mantle, further excluding the possibility of recent diffusive ingress of Li.

In the case of Li diffusion into clinopyroxene from coexisting olivine during the cooling of peridotites, the olivine should have a  $\delta^7\text{Li}$  value that is significantly higher than the normal mantle<sup>36</sup>. However, most of the samples in our study show very low  $\delta^7\text{Li}$  in olivines. This contradiction excludes the possibility that the  $\delta^7\text{Li}$  of olivines are the results of diffusive fractionation of Li isotopes during the cooling of peridotites.

We therefore conclude that the  $\delta^7\text{Li}$  in the cores of large olivine grains from the Hebi peridotites reflect the signatures of the lithospheric mantle beneath the North China Craton. Compared to the published  $\delta^7\text{Li}$  of olivines from worldwide peridotites (Fig. 3), the  $\delta^7\text{Li}$  in the cores of olivines from the Hebi peridotites show extreme variation from  $-27$  to  $+21$ , far beyond the  $\delta^7\text{Li}$  range ( $+1.6$  to  $+5.6$ ) of fresh MORB<sup>8</sup>. These observations suggest the existence of abnormal  $\delta^7\text{Li}$  in the old lithospheric mantle beneath the craton.

Another important question to be addressed relates to whether the survival of  $\delta^7\text{Li}$  anomaly in the mantle over a long time scale is theoretically possible. Equilibration temperatures for the Hebi peridotites have been estimated using two-pyroxene thermometer of Wells<sup>40</sup> as recommended in Zheng et al.<sup>29</sup>. The estimated equilibrium temperatures of the harzburgites vary from about 900 to 1150°C and that of the lherzolite is 1020°C, which are consistent with those estimated previously for the peridotites from the same locality<sup>29</sup>. The partitioning experiments of Li between plagioclase and clinopyroxene showed that Li preferentially partitions into clinopyroxene as temperature decreases between 900 and 1200°C<sup>41</sup>. As a result, we infer that the estimated equilibrium temperatures exceed the closure temperatures for Li in clinopyroxene and the system of Li in the peridotite remains open although the closure temperature for Li in olivine is unknown. At the estimated mantle temperatures, Li heterogeneities are likely to be rehomogenized through time<sup>11</sup>. However, based on experimental studies, Dohmen et al.<sup>24</sup> proposed two mechanisms of Li diffusion, a fast (interstitial site) mechanism and a slow (vacancy, octahedral site) mechanism, and suggested that the former is unlikely to be dominant in most natural systems. The diffusion of Li in the slow mechanism is about an order of magnitude faster than that of Fe, Mg and most other divalent cations in olivine; such diffusion of Li in olivine will be much slower than that in clinopyroxene at the same conditions<sup>24</sup>. Another study of an olivine xenocryst suggested that the diffusion coefficients of Li in olivine fell within a factor of three of the Mg-Fe interdiffusion coefficient<sup>42</sup>. This



**Figure 3** | Histograms of  $\delta^7\text{Li}$  for olivines in the Hebi xenoliths and those from worldwide peridotites. Data sources as in Fig. 2.

is generally in agreement with the experimental observations that the diffusion of Li into olivine is similar to that of divalent cations<sup>9,24,43</sup>. Calculations based on the diffusion coefficient of Li in clinopyroxene suggested that a kilometer-thick altered oceanic crust could lose most of the excess Li in a few tens of millions years<sup>11</sup>. On the other hand, the rocks can preserve  $^7\text{Li}/^6\text{Li}$  distinctive from the ambient mantle over a time period over 1,500 Ma<sup>16</sup> regardless of the model based on the fast mechanism of diffusion<sup>41</sup>. A recent experimental study shows that very large Li isotopic fractionations persisted after the Li concentration had become effectively homogenized, which suggests that it takes much longer for the isotopic composition to become uniform compared to the time it takes for diffusion to homogenize the Li concentration<sup>25</sup>. Therefore, the survival of  $\delta^7\text{Li}$  anomaly in the mantle over a relatively long time scale is possible, as also evidenced from Li isotopic variations in the Trinity Ophiolite<sup>32</sup> and peridotite xenoliths from the northeastern North China Craton<sup>20</sup>.

It has been proposed that abnormal  $\delta^7\text{Li}$  in lithospheric mantle could be produced by infiltration of mantle peridotites by isotopically normal fluid/melt derived from the asthenosphere<sup>10,13,32</sup> and  $\delta^7\text{Li}$ -anomaly melt/fluid related to subducted slab<sup>16–18,20,21</sup>. For the first possibility, the normal mantle-derived fluid/melt could produce the  $\delta^7\text{Li}$  of olivines higher than  $-10$  (published data in Figs. 2 and 3), which cannot account for the low  $\delta^7\text{Li}$  of  $-30$  in the cores of olivines. Furthermore, olivines in the peridotites/pyroxenites metasomatized by the normal mantle-derived fluid/melt should have higher Li contents than that of the normal mantle<sup>20</sup>, which is contrast to our observations. Therefore, the  $\delta^7\text{Li}$ -anomaly can be related to the subducted slab because the fluids released by the dehydration of subducted slab are rich in  $^7\text{Li}$ , whereas the slab tends to be depleted in  $^7\text{Li}$ . The low- $\delta^7\text{Li}$  component is subducted into the deeper mantle to form a low- $\delta^7\text{Li}$  reservoir, which could be the potential source of low  $\delta^7\text{Li}$ <sup>22,23</sup>. However, it has been proposed that dehydration can only produce  $\delta^7\text{Li}$  decrease of up to 3‰, and that the deeply subducted eclogites possess higher  $\delta^7\text{Li}$  than the mantle<sup>44</sup>. Thus, the isotopic composition of the upper mantle with contributions of recycled components by subduction remains speculative and the mechanism of origin of abnormal  $\delta^7\text{Li}$  in the lithospheric mantle is equivocal.

However, experiments have shown that  $\delta^7\text{Li}$  of recycled components depend on the compositions of subducted materials, and concomitant dehydration of metabasic oceanic crust, containing chlorite and clinopyroxene with Li in six-fold coordination, releases fluids enriched in Li and  $^7\text{Li}$  into the fore-arc mantle and thus introduces a low  $\delta^7\text{Li}$  component into the deeper mantle<sup>23,45</sup>. Therefore, the abnormal  $\delta^7\text{Li}$  of olivines in the harzburgites indicate that the subcontinental lithospheric mantle experienced the modification of fluid/melt derived from recycled oceanic crust.

## Methods

Li concentrations and isotopic ratios were measured on gold-coated thin sections using Cameca IMS-1280 ion microprobe at the Institute of Geology and Geophysics, Chinese Academy of Sciences, following the procedures described in Zhang et al.<sup>46</sup>. Li isotope compositions are expressed as  $\delta^7\text{Li}$  ( $= [(^7\text{Li}/^6\text{Li})_{\text{sample}} / (^7\text{Li}/^6\text{Li})_{\text{standard}} - 1] \times 1000$ ) relative to the National Institute of Standards and Technology standard L-SVEC with  $^7\text{Li}/^6\text{Li}$  of 12.0192 and shown in Supplementary Table 1. The olivine sample BZ29<sup>47</sup> and in-house standard of our Lab, Ol334, were used as standards to correct the measured data. For the two standards our  $\delta^7\text{Li}$  are  $+4.9 \pm 0.9$  and  $-3.1 \pm 0.9$ , respectively, well consistent with the recommended values ( $+4.4$  and  $-3.2$ ) within analytical error. The external  $2\sigma$  errors of the isotope compositions for both the standards and the samples are less than 2.7‰, with the majority less than 2.0‰. The measured olivine grains in our samples are homogeneous in major elemental compositions at a mineral scale and show Fo values similar to that of the standards. Thus, matrix effect can be excluded in our measurements and the obtained data are reliable.

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## Author contributions

Y.J.T., H.F.Z. and E.D. contributed equally to idea development. Y.J.T. wrote the main text. B.X.S., J.F.Y., M.S. and Y.X. contributed equally to the intellectual growth of this paper.

## Additional information

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