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

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Lithium elemental and isotopic compositions of olivines in peridotite xenoliths from Hebi in the North China Craton provide direct evidence for the highly variable δ7Li in Archean lithospheric mantle. The δ7Li 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 δ7Li 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 δ7Li characteristics of the Hebi olivines could not have been produced by recent diffusive-driven isotopic fractionation of Li and therefore the δ7Li in the cores of these olivines record the isotopic signature of the subcontinental lithospheric mantle. Our data demonstrate that abnormal δ7Li 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 because of its moderate incompatibility during mantle melting, strong fluid mobility, and the large mass fractionation, with up to 80% variation of 7Li/6Li in terrestrial samples. In contrast to the large variations in Li isotope compositions of the Earth’s surface environments, the δ7Li of mantle is more restricted, in the range of about ±14 as inferred from relatively pristine olivines and fresh MORB.

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 because of its moderate incompatibility during mantle melting, strong fluid mobility, and the large mass fractionation, with up to 80% variation of 7Li/6Li in terrestrial samples. In contrast to the large variations in Li isotope compositions of the Earth’s surface environments, the δ7Li of mantle is more restricted, in the range of about ±14 as inferred from relatively pristine olivines and fresh MORB.

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 (Fig. 1). Our data bring out the largest variation in δ7Li values among those published for olivines from peridotite xenoliths, and demonstrate the existence of abnormal δ7Li 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 craton mantle beneath the North China Craton and the low-Mg# lherzolite may represent the newly-formed or modified lithospheric mantle. The olivines in
the high-Mg# harzburgites show highly variable δ7Li. The grain cores have Li abundances of 0.9 to 2.2 ppm and δ7Li ranging from −27 to +22 and of the rims show 0.9 to 2.3 ppm and δ7Li of −38 to +20, respectively. The Li abundance and δ7Li 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-δ7Li core with lower Li abundance as compared to the low-δ7Li rim (Fig. 2).

Discussion

The δ7Li is predicted to have high diffusivity, about 3% faster than 7Li based due to a mass difference of 16.7%31. Thus, large Li isotopic fractionations can be produced by diffusion during processes of fluid/melt-rock reaction7,10,32. 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 entainment into host magmas and the transport of the mantle xenolith to the surface7,10,13,33–35, as well as during the cooling of peridotites7,10,25. The results of diffusive fractionation are reflected in the variations of δ7Li from meter to micron scale7,9,19,32,37. Thus, an important point to evaluate is whether the δ7Li 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 melt7,10, Li diffusing into country rocks from Li-rich pegmatite34, or into clinopyroxene from coexisting olivine during cooling of peridotites41. In the case of Li addition to peridotites, the mantle minerals first become enriched in 7Li because of its greater diffusion rate than δ7Li, leading to low δ7Li relative to its precursor. This mechanism can account for theobservations of isotopically heavy cores with lower Li concentrations than the light rims of minerals7,10,12,33, such as the case of 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 δ7Li 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 ppm14,39; (2) there is no apparent difference in Li abundances and δ7Li 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 δ7Li (+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 δ7Li value that is significantly higher than the normal mantle26. However, most of the samples in our study show very low δ7Li in olivines. This contradiction excludes the possibility that the δ7Li of olivines are the results of diffusive fractionation of Li isotopes during the cooling of peridotites.

We therefore conclude that the δ7Li 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 δ7Li of olivines from worldwide peridotites (Fig. 3), the δ7Li in the cores of olivines from the Hebi peridotites show extreme variation from −27 to +21, far beyond the δ7Li range (+1.6 to +5.6) of fresh MORB9. These observations suggest the existence of abnormal δ7Li in the old lithospheric mantle beneath the craton.

Another important question to be addressed relates to whether the survival of δ7Li 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 Wells40 as recommended in Zheng et al.29. 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 locality29. The partitioning experiments of Li between plagioclase and clinopyroxene showed that Li preferentially partitions into clinopyroxene as temperature decreases between 900 and 1200°C41. 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 time42. However, based on experimental studies, Dohmen et al.24 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 conditions42. 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 coefficient42. This
However, experiments have shown that $\delta^{7}\text{Li}$ of recycled components depend on the compositions of subducted materials, and concomitantly dehydration of metasomatic ocean crust, containing chloride and clinopyroxene with Li in six-fold coordination, releases fluids enriched in Li and $\text{Li}^{+}$ into the fore-arc mantle and thus introduces a low $\delta^{7}\text{Li}$ component into the deeper mantle\textsuperscript{24,25}. Therefore, the abnormal $\delta^{7}\text{Li}$ of olivines in the harzburgites indicate that the continent-oceanic 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.\textsuperscript{25}. Li isotope compositions are expressed as $\delta^{7}\text{Li} = [(\text{Li}^{7}/\text{Li}^{6})_{\text{sample}}/(\text{Li}^{7}/\text{Li}^{6})_{\text{standard}} - 1] \times 10^{3}$ relative to the National Institute of Standards and Technology standard L-SVEC with $\text{Li}^{7}/\text{Li}^{6}$ of 12.0192 and shown in Supplementary Table 1. The olivine sample BZ29\textsuperscript{25} and in-house standard of our Lab, O8334, 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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