

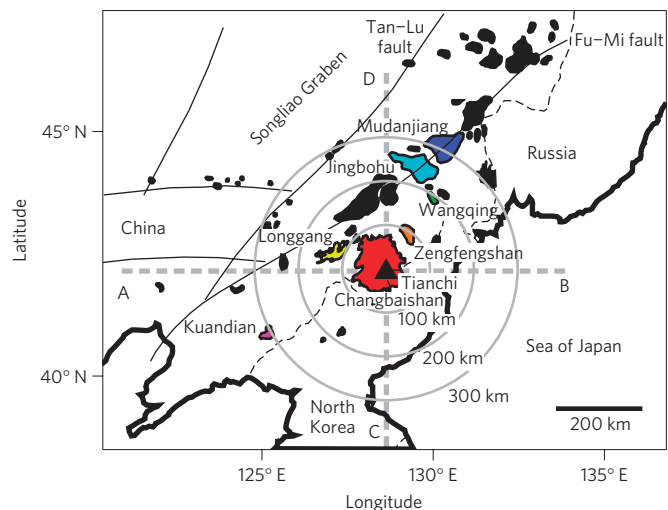
# Intensive hydration of the mantle transition zone beneath China caused by ancient slab stagnation

Takeshi Kuritani<sup>1,2\*</sup>, Eiji Ohtani<sup>1</sup> and Jun-Ichi Kimura<sup>3</sup>

**The mantle transition zone, located at depths of 410–660 km between the lower and upper mantle, is an important water reservoir in the Earth's interior<sup>1–4</sup>. However, there are regional-scale heterogeneities in the distribution of water<sup>4,5</sup>. The zone beneath northeast China, in particular, is remarkably hydrous<sup>4</sup>, but when and how it became hydrous remains uncertain. Here we combine analyses of the geochemistry of late Cenozoic basalts in northeast China with published geochemical analyses. We find a spatial correlation between basalt geochemistry and the distribution of a low-velocity zone in the underlying mantle that is interpreted as a plume upwelling from the mantle transition zone<sup>6</sup>. We therefore use the basalt geochemistry to infer the composition of the mantle transition zone. The basalts have high Ba/Th and <sup>207</sup>Pb/<sup>206</sup>Pb ratios, which we suggest record an ancient hydration event in the transition zone that occurred more than one billion years ago, probably as a result of dehydration of a subducted slab. We suggest that this ancient hydration event, combined with a more recent hydration event linked to dehydration of the subducted Pacific slab<sup>7</sup>, can account for the hydrous nature of the mantle transition zone beneath China. Our results demonstrate that the mantle transition zone can remain as a stable water reservoir in Earth's interior for timescales of more than a billion years.**

In northeast China, Cenozoic intraplate basalts are widely distributed (Fig. 1), and the underlying mantle transition zone (MTZ) contains remnants of the subducted Pacific slab<sup>8</sup>. Beneath the Changbaishan volcanic area, a prominent low-velocity anomaly with a plume-like shape was imaged in the upper mantle by P-wave tomography (Fig. 2); this is suggestive of an upwelling of wet materials from the MTZ (ref. 6). Numerical simulation also showed that the low-velocity anomaly could indicate the existence of a wet mantle plume generated by instability in the MTZ (ref. 9). The primary cause of Cenozoic magmatic activity in northeast China is interpreted as being the result of the decompression melting of upwelling asthenospheric materials above the stagnant slab<sup>10,11</sup>. Therefore, volcanic rocks around the Changbaishan area may provide useful geochemical information on the deeper part of the upper mantle that may have been affected by the MTZ-derived upwelling. Thus, we compiled geochemical data of late Cenozoic basalts from the Changbaishan area and the surrounding volcanic fields (Fig. 1).

These lavas are primarily alkaline basalts (Supplementary Fig. S1). Incompatible trace elements in the lavas have an affinity with intra-plate type characteristics, with significant positive spikes in Ba, Pb, and Sr (Supplementary Fig. S2). The lavas show systematic spatial variation in some geochemical features. The Ba/Th and Pb/U ratios of Quaternary lavas tend to decrease systematically with increasing distance from the Tianchi volcano (Fig. 3), which is

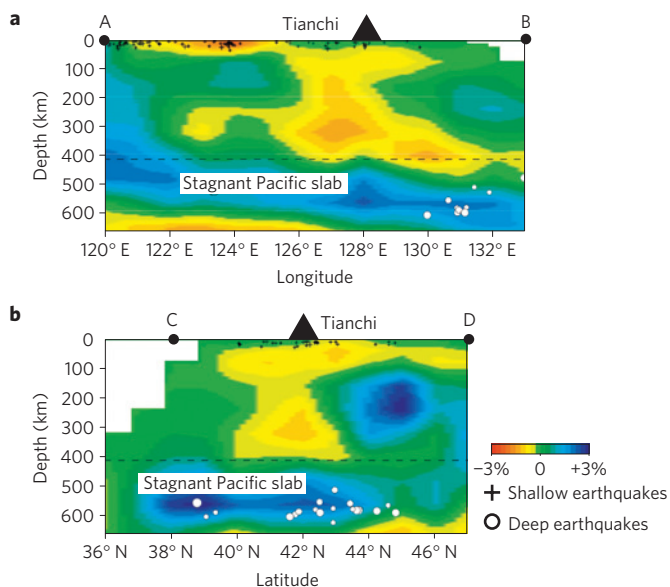


**Figure 1 | Map showing distributions of Cenozoic volcanic fields and deep faults in northeast China. The distributions are from ref. 28. The distance from Tianchi volcano, which is located in the central part of the Changbaishan area, is shown. Grey dashed lines indicate locations of cross-sections shown in Fig. 2. See Fig. 3 for colour legend.**

located in the central part of the Changbaishan area (Fig. 1). Among the basaltic lavas from the studied volcanic fields, Changbaishan lavas are found to have Sr, Nd, and Pb isotopic compositions that are close to those of the EM1 (enriched mantle-1)<sup>12</sup> (Fig. 4 and Supplementary Fig. S3)<sup>11,13</sup>. It is noteworthy that these spatial geochemical variations are not significantly affected by crustal assimilation, as suggested from the observation that the Ba/Th and <sup>87</sup>Sr/<sup>86</sup>Sr ratios of basalts are mostly independent of the SiO<sub>2</sub> content in each volcanic field (Supplementary Fig. S4).

The strong correlation between the concentric spatial variations in the geochemistry of the lavas and the plume-like shape of the low-velocity anomaly in the upper mantle beneath the Changbaishan area (Fig. 2) suggests that the geochemical variations are related to the low-velocity anomaly down to a depth of ~410 km. The volcanoes in northeast China do not have a deep-hot-spot origin because the stagnant Pacific slab prevents deep plume upwelling and the trace of such plumes is actually not detected by mantle tomography<sup>6</sup>. This is supported by low <sup>3</sup>He/<sup>4</sup>He ratios of ultramafic xenoliths<sup>10</sup>. Melting of lower crustal materials foundered in the asthenospheric mantle is also unlikely as the origin of the studied basalts, because magmas generated by this mechanism would be felsic in composition<sup>14</sup>. Therefore, considering that Ba/Th and Pb/U fractionation is not effective during the decompression melting

<sup>1</sup>Department of Earth Science, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan, <sup>2</sup>Division of Biology and Geosciences, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan, <sup>3</sup>Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology, Yokosuka 237-0061, Japan. \*e-mail: kuritani@sci.osaka-cu.ac.jp.

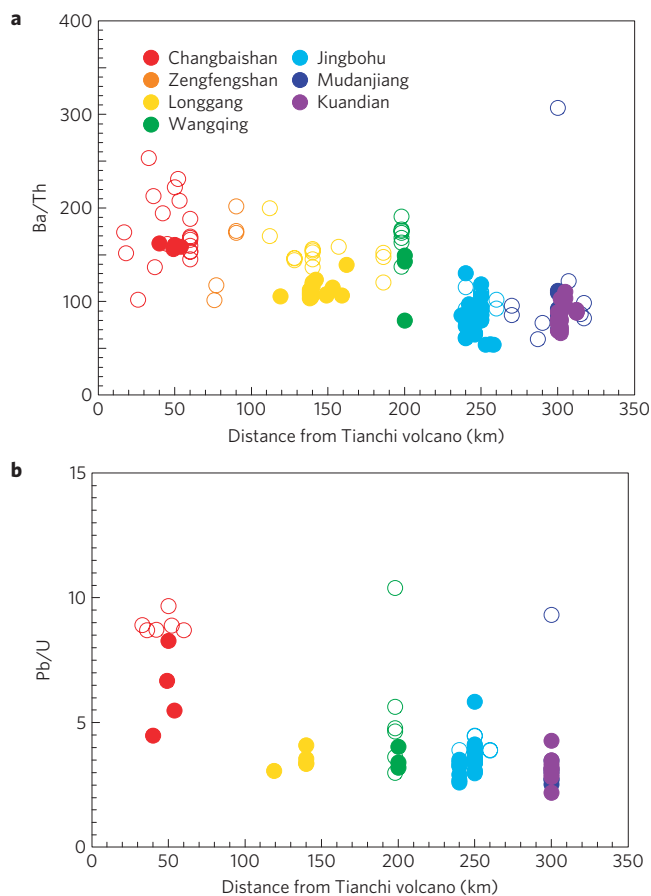


**Figure 2 | Vertical cross-sections of P-wave velocity tomography under northeast Asia.** The locations of **a**, east–west and **b**, north–south cross-sections are shown in Fig. 1. Black crosses and white circles show the shallow and deep earthquakes. The figure is slightly modified from ref. 6, © 2009 Elsevier

of the asthenospheric mantle, there are two possibilities for the origin of the geochemical signatures observed characteristically in Changbaishan lavas: (1) a component with high Ba/Th and Pb/U ratios and EM1-like characteristics resided in the lowest part of the sub-continental lithospheric mantle (SCLM), and the magmas incorporated this component through interactions between the upwelling asthenosphere and the SCLM (ref. 13); and (2) the component resided in the MTZ, and the magmas acquired the component through the melting of the upwelling asthenospheric mantle, which contained the MTZ-derived materials<sup>15</sup>. Of these hypotheses, the former is unlikely to hold true, because the lower part of the SCLM under northeast China was formed in Cenozoic times<sup>16</sup> and the formation of an EM1-like signature requires a timescale of  $> 1$  Gyr (ref. 17). From this, it is suggested that the EM1-rich materials were derived from the MTZ. Murphy *et al.*<sup>15</sup> showed that an EM1-like signature in Gausberg lamproites from Antarctica can be formed by the long-term (2–3 Gyr) isolation of subducted sediments in the MTZ.

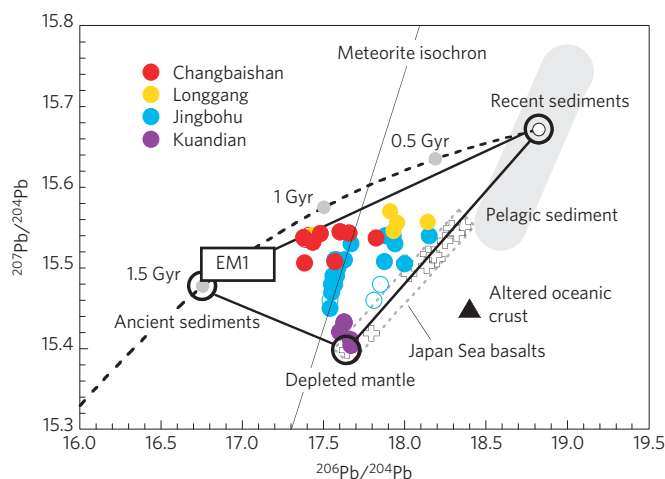
It is considered that dehydration of the stagnant Pacific slab occurs in the MTZ beneath northeast China<sup>7</sup>. However, the EM1-like signature cannot be explained by materials derived from the Pacific slab. This is because the Pacific slab has a lower  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio than the meteorite isochron<sup>18</sup>, whereas the EM1-like component has a higher  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio than the isochron (Fig. 4). In addition, although the duration of the stagnation of the Pacific slab in the MTZ is at most  $\sim 50$  Myr (ref. 19), the establishment of the EM1-like lead isotopic compositions requires the isolation of low- $\mu$  materials for periods of  $> 1$  Gyr (refs 17,20). A delaminated ancient SCLM, which might have foundered and been stagnant in the MTZ, is also unlikely to be the source material for the EM1-like signature because mantle xenoliths that represent the Archaean SCLM beneath northeast China do not have an EM1-like composition<sup>21</sup>. Therefore, the formation of the EM1-like signature must be related to an ancient ( $> 1$  Gyr ago) event in the MTZ.

One possible event resulting in the storage of low- $\mu$  ( $^{238}\text{U}/^{204}\text{Pb}$ ) materials in the MTZ is a dehydration-induced partial melting across the 410-km boundary during the ascent of the ambient mantle (that is, the transition-zone water-filter model<sup>22</sup>). However,



**Figure 3 | Spatial variations in Ba/Th and Pb/U ratios of late Cenozoic basaltic lavas from northeast China.** The horizontal axis shows the distance from the Tianchi volcano, located at the centre of the Changbaishan area. Quaternary samples are indicated by filled circles and Tertiary samples ( $< 10$  Myr) and samples of unknown ages are indicated by open circles. Samples with a significant Eu anomaly ( $\text{Eu}^* > 1.1$  or  $\text{Eu}^* < 0.9$ ), which may be significantly affected by crustal processes (that is, plagioclase fractionation or accumulation), are not plotted. See Supplementary Information for the source of the data.

this model fails to explain the formation of low- $\mu$  materials. This is because the partial melting of peridotite cannot cause a large U–Pb fractionation and, therefore, the melt cannot have a significantly different U/Pb ratio from that of the depleted ascending mantle (that is, upper mantle). Another possible event is the breakdown of mineral phases in an ancient stagnant slab in the MTZ (refs 15, 23). In subducted materials, K-hollandite in sediments is the only major phase that can release significant amounts of incompatible elements such as Ba and Pb through a breakdown in the MTZ (ref. 23). As pelagic sediments have low  $\mu$  values (as low as  $\sim 2$ ; ref. 24) and K-hollandite primarily retains the incompatible element characteristics of its host rock, the elements released by the K-hollandite breakdown could be the low- $\mu$  source materials<sup>23</sup>. Gausberg lamproites with an EM1-like signature, which may contain a considerable component of ancient subducted sediments in the MTZ, have high Pb/U and Ba/Th ratios<sup>15</sup>; these characteristics are similar to those of Changbaishan lavas. The positive spikes of Ba, Sr, and Pb are observed in the trace-element concentration patterns of northeast China basalts (Supplementary Fig. S2), and the composition of K-hollandite seems to lie on the extension of the compositional variation of the basalts in the Ba/La–Ba/Th diagram (Supplementary Fig. S5); these observations are also suggestive of the presence of a sediment component in the lava sources<sup>23</sup>.



**Figure 4 | Lead isotopic compositions of late Cenozoic basalts from northeast China.** Present-day compositions of continental crust-derived sediment that has evolved with  $\mu = 2$ , starting 1.5–0 Gyr ago, from a modified two-stage model of ref. 29 (see Supplementary Fig. S6 caption) are shown. Compositions of Japan Sea basalts (open crosses), altered oceanic crust (filled triangle), pelagic sediment (grey area), and EM1 are taken from refs 30, 18, 24, and 12, respectively. Large open circles show the present-day compositions of the three possible endmember components (Supplementary Fig. S6). The data source for lavas is given in the Supplementary Information.

K-hollandite is stable at temperatures up to  $\sim 1,700^\circ\text{C}$  under dry conditions<sup>23</sup>. Although the mantle potential temperature  $\sim 1$  Gyr ago was higher than it is today, by up to  $\sim 100^\circ\text{C}$  (ref. 25), K-hollandite could not have broken down in the MTZ under dry conditions because the geotherm of the MTZ was  $< 1,700^\circ\text{C} \sim 1$  Gyr ago. On the other hand, under wet conditions, the stability of K-hollandite is  $< 1,400^\circ\text{C} - 1,450^\circ\text{C}$  (ref. 23). Therefore, the breakdown of K-hollandite could have occurred if fluid phases were present in the ancient subducted materials. As it is possible that water was effectively transported to the MTZ by subduction processes even  $\sim 1$  Gyr ago (note that the storage capacity of water in olivine does not decrease greatly with a  $100^\circ\text{C}$  increase in temperature<sup>26</sup>), K-hollandite in the ancient stagnant slab could have been broken down by the excess water and the MTZ above this slab could thus have been metasomatized by fluids that were enriched in the elements released by the K-hollandite breakdown. It is not clear whether this ancient hydration event caused magmatism, because the location of the hydrated MTZ was not necessarily beneath China owing to the differential motion of the lithosphere relative to the underlying asthenosphere<sup>27</sup>.

The formation of the EM1-like signature requires the metasomatized MTZ to be primarily isolated for long periods of time. During these periods, neither the upper mantle nor the lower mantle interacted significantly with the metasomatized MTZ, because their lead isotopic compositions have always been lower in  $^{207}\text{Pb}/^{206}\text{Pb}$  than the meteorite isochron<sup>20</sup>. After the stagnation of the Pacific slab, it is likely that the dehydrated fluids acquired the EM1-like signature through an interaction with the metasomatized region in the MTZ. It is therefore possible that a low-density plume of hydrated peridotite ascended from the MTZ (ref. 9), as imaged by mantle tomography<sup>6</sup> (Fig. 2), and that partial melting occurred in the ascending plume at relatively shallow levels in the upper mantle, leading to the magmatism observed around the Changbaishan area. Despite the remarkable EM1-like characteristics, Changbaishan lavas do not have as high a  $\text{K}_2\text{O}$  content as Gaussberg lamproites. This can be explained by the lower contribution of the sediment component in the

source mantle for Changbaishan lavas, as suggested by the lower Ba/Th and Ba/La ratios than those of Gaussberg lamproites (Supplementary Fig. S5).

As discussed above, it is certain that subducted sediments could have been a major resource responsible for the geochemical characteristics of northeast China basalts. Therefore, incompatible elements in the source mantle for the basalts can be considered to be primarily derived from three components: the ancient subducted sediments, the recent Pacific sediments, and the recent depleted mantle. In this case, the EM1-rich Changbaishan lavas can be explained by a greater involvement of the ancient and recent sediment components among the studied lavas (Fig. 4). It is difficult to estimate the age of the above-mentioned ancient sediment component. However, if we assume that the ancient hydration was a single event that occurred  $\sim 1.5$  Gyr ago, the isotopic compositions of Changbaishan basalts can be explained by mixing  $\sim 0.5\%$  of the sediment component, consisting of a 1:2 to 1:3 mixture of the recent and ancient sediment components, with the depleted mantle (Supplementary Fig. S6). It is noteworthy that the lead isotopic compositions of northeast China basalts require involvement of both the ancient and recent sediment components in the source, because the compositions lie within the triangular field defined by the above-mentioned three components (Fig. 4). This observation is consistent with there being both ancient and recent hydration events in the MTZ.

From the above discussion, it is proposed that the remarkably hydrous nature of the MTZ beneath northeast China<sup>4</sup> is a result of at least two superimposed hydration events: an earlier ( $> 1$  Gyr ago) hydration event, which was probably caused by the stagnation of an ancient subducted slab, and a recent hydration event caused by the stagnation of the Pacific slab. Recently, it was proposed that the MTZ beneath Europe is less hydrous than that beneath East Asia, even though the subducted slab is stagnant in both regions<sup>4,5</sup>. The difference in the MTZs can be explained by the scenario in which the MTZ beneath East Asia was already hydrated because of dehydration of an ancient stagnant slab before the stagnation of the Pacific slab. This study also suggests that the MTZ that was metasomatized by ancient subduction processes could have been isolated for long periods of time ( $> 1$  Gyr). Therefore, it is proposed that the metasomatized MTZ is a long-term stable water reservoir in the Earth's interior.

Received 9 March 2011; accepted 4 August 2011; published online 4 September 2011

## References

- Smyth, J. R.  $\beta\text{-Mg}_2\text{SiO}_4$ : A potential host for water in the mantle? *Am. Mineral.* **72**, 1051–1055 (1987).
- Inoue, T., Yurimoto, H. & Kudoh, Y. Hydrous modified spinel,  $\text{Mg}_{1.75}\text{SiH}_{0.5}\text{O}_4$ : A new water reservoir in the mantle transition region. *Geophys. Res. Lett.* **22**, 117–120 (1995).
- Ohtani, E., Litasov, K., Hosoya, T., Kubo, T. & Kondo, T. Water transport into the deep mantle and formation of a hydrous transition zone. *Phys. Earth Planet. Inter.* **143–144**, 255–269 (2004).
- Karato, S. Water distribution across the mantle transition zone and its implications for global material circulation. *Earth Planet. Sci. Lett.* **301**, 413–423 (2011).
- Utada, H., Koyama, T., Obayashi, M. & Fukao, Y. A joint interpretation of electromagnetic and seismic tomography models suggests the mantle transition zone below Europe is dry. *Earth Planet. Sci. Lett.* **281**, 249–257 (2009).
- Zhao, D., Tian, Y., Lei, J., Liu, L. & Zheng, S. Seismic image and origin of the Changbai intraplate volcano in East Asia: Role of big mantle wedge above the stagnant Pacific slab. *Phys. Earth Planet. Inter.* **173**, 197–206 (2009).
- Ohtani, E. & Zhao, D. The role of water in the deep upper mantle and transition zone: Dehydration of stagnant slabs and its effects on the big mantle wedge. *Russ. Geol. Geophys.* **50**, 1073–1078 (2009).
- Fukao, Y., Obayashi, M., Inoue, H. & Nishii, M. Subducting slabs stagnant in the mantle transition zone. *J. Geophys. Res.* **97**, 4809–4822 (1992).
- Richard, G. C. & Iwamori, H. Stagnant slab, wet plumes and Cenozoic volcanism in East Asia. *Phys. Earth Planet. Inter.* **183**, 280–287 (2010).

10. Chen, Y., Zhang, Y., Graham, D., Su, S. & Deng, J. Geochemistry of Cenozoic basalts and mantle xenoliths in northeast China. *Lithos* **96**, 108–126 (2007).
11. Kuritani, T. *et al.* Intraplate magmatism related to deceleration of upwelling asthenospheric mantle: Implications from the Changbaishan shield basalts, northeast China. *Lithos* **112**, 247–258 (2009).
12. Zindler, A. & Hart, S. Chemical geodynamics. *Annu. Rev. Earth Planet. Sci.* **14**, 493–571 (1986).
13. Basu, A. R., Junwen, W., Wankang, H., Guanghong, X. & Tatsumoto, M. Major element, REE, and Pb, Nd and Sr isotopic geochemistry of Cenozoic volcanic rocks of eastern China: Implications for their origin from suboceanic-type mantle reservoirs. *Earth Planet. Sci. Lett.* **105**, 149–169 (1991).
14. Gao, S. *et al.* Recycling lower continental crust in the North China craton. *Nature* **432**, 892–897 (2004).
15. Murphy, D. T., Collerson, K. D. & Kamber, B. S. Lamproites from Gausberg, Antarctica: Possible transition zone melts of Archaean subducted sediments. *J. Petrol.* **43**, 981–1001 (2002).
16. Griffin, W. L., Andi, Z., O'Reilly, S. Y. & Ryan, C. G. in *Mantle Dynamics and Plate Interactions in East Asia* (eds Flower, M. F. G., Chung, S.-L., Lo, C.-H. & Lee, T.-Y.) 107–126 (Geodynam. Ser. Vol. 27, American Geophysical Union, 1998).
17. Rehkämper, M. & Hofmann, A. W. Recycled ocean crust and sediment in Indian Ocean MORB. *Earth Planet. Sci. Lett.* **147**, 93–106 (1997).
18. Hauff, F., Hoernle, K. & Schmidt, A. Sr–Nd–Pb composition of Mesozoic Pacific oceanic crust (Site 1149 and 801, ODP Leg 185): Implications for alteration of ocean crust and the input into the Izu–Bonin–Mariana subduction system. *Geochem. Geophys. Geosyst.* **4**, 8913 (2003).
19. Fukao, Y., Widiyantoro, S. & Obayashi, M. Stagnant slabs in the upper and lower mantle transition region. *Rev. Geophys.* **39**, 291–323 (2001).
20. Murphy, D. T., Kamber, B. S. & Collerson, K. D. A refined solution to the first terrestrial Pb-isotope paradox. *J. Petrol.* **44**, 39–53 (2003).
21. Choi, S. H., Mukasa, S. B., Zhou, X.-H., Xian, X. H. & Andronikov, A. V. Mantle dynamics beneath East Asia constrained by Sr, Nd, Pb and Hf isotopic systematics of ultramafic xenoliths and their host basalts from Hannuoba, North China. *Chem. Geol.* **248**, 40–61 (2008).
22. Bercovici, D. & Karato, S. Whole-mantle convection and the transition-zone water filter. *Nature* **425**, 39–44 (2003).
23. Rapp, R. P. *et al.* Subduction recycling of continental sediments and the origin of geochemically enriched reservoirs in the deep mantle. *Earth Planet. Sci. Lett.* **271**, 14–23 (2008).
24. Ben Othmann, D., White, W. M. & Patchett, J. The geochemistry of marine sediments, island arc magma genesis, and crust–mantle recycling. *Earth Planet. Sci. Lett.* **94**, 1–21 (1989).
25. Grove, T. L. & Parman, S. W. Thermal evolution of the Earth as recorded by komatiites. *Earth Planet. Sci. Lett.* **219**, 173–187 (2004).
26. Withers, A. C. & Hirschmann, M. M. Influence of temperature, composition, silica activity and oxygen fugacity on the H<sub>2</sub>O storage capacity of olivine at 8 GPa. *Contrib. Mineral. Petrol.* **156**, 595–605 (2008).
27. Le Pichon, X. Sea-floor spreading and continental drift. *J. Geophys. Res.* **73**, 3661–3697 (1968).
28. Liu, J., Han, J. & Fyfe, W. S. Cenozoic episodic volcanism and continental rifting in northeast China and possible link to Japan Sea development as revealed from K–Ar geochronology. *Tectonophysics* **339**, 385–401 (2001).
29. Stacey, J. S. & Kramers, J. D. Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* **26**, 207–221 (1975).
30. Cousens, B. L. & Allan, J. F. A Pb, Sr, and Nd isotopic study of basaltic rocks from the Sea of Japan, LEGS 127/128. *Proc. Ocean Drill. Program Sci. Results* **127–128**, 805–817 (1992).

### Acknowledgements

We thank D. Zhao, S. Karato, and T. Yoshida for useful discussion, and K. Putirka for constructive comments. This work was supported by the program 'Global Center of Excellence' of Tohoku University.

### Author contributions

This paper is the product of research conducted by T.K. under the support of the program 'Global Center of Excellence' of Tohoku University. All three authors contributed to the interpretation of the data and to the writing of the manuscript.

### Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on [www.nature.com/naturegeoscience](http://www.nature.com/naturegeoscience). Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to T.K.