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Potassium isotope evidence for sediment recycling into the orogenic lithospheric mantle

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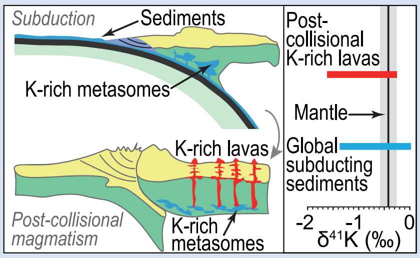
Abstract



Post-collisional highly potassic magmatism in large orogenic belts has been taken as evidence for recycling of continent-derived K-rich sediments within the orogenic lithospheric mantle. Potassium isotopes may provide important insights into the origins of K in these magmas, since subducting sediments exhibit much more variable K isotopic compositions relative to the mantle. Here we report high precision K isotope data for 41 representative potassic and ultra-potassic volcanic rocks from the whole Alpine-Himalayan orogenic belt. $\delta^{41}K_{NIST\ SRM3141a}$ of these samples vary from −1.55 ‰ to −0.32 ‰, comparable to the range of global subducting sediments but significantly exceeding the range of pristine mantle defined by oceanic basalts (−0.42 ± 0.08 ‰). Monte Carlo simulation suggests this large K isotopic range can be reproduced by recycling of up to 5 % isotopically heterogeneous sediments into the depleted mantle. Our results highlight K isotopes as a potential tracer of recycled sediments in the mantle.

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Introduction

Post-collisional potassic and ultra-potassic volcanic and plutonic rocks contain up to ~10 wt. % K_2O and are one of the most distinctive magmatic types that frequently occurred in global orogenic belts at least since the late Archean (*e.g.*, Couzinié *et al.*, 2016). Their derivation from the mantle is evident from their high MgO contents (>6 wt. %) and Mg# (>0.6), highly forsteritic (Fo_{85-95}) olivine phenocrysts, and the occurrence of mantle xenoliths or xenocrysts entrained by these lavas (*e.g.*, Foley *et al.*, 1987; Prelević *et al.*, 2013). Despite this, direct partial melting of mantle peridotite is unlikely to generate melts with >2 wt. % K_2O (*e.g.*, Walter, 1998). These highly potassic lavas are usually enriched in incompatible trace elements, with extreme radiogenic isotopic compositions and trace element patterns resembling those of subducting sediments (*e.g.*, Foley *et al.*, 1987; Williams *et al.*, 2004; Prelević *et al.*, 2008; Avanzinelli *et al.*, 2009; Conticelli *et al.*, 2009; Zhao *et al.*, 2009; Couzinié *et al.*, 2016). These features indicate that the recycling of continent-derived sediments into their mantle sources contributes to the peculiar K enrichment in these lavas. However, correlated relationships between K enrichment and common indices of sediment contribution in highly potassic lavas such as Th/La, Sm/La, Th/Nb, Hf/Sm and radiogenic isotopes (*e.g.*, Sr, Nd, Pb, and Os) are rarely observed (Tommasini *et al.*, 2011; Prelević *et al.*, 2013). This decoupled behaviour might reflect that (1) the budget of Th, Nb, Hf and REE in sediments is dominated by accessory minerals (*e.g.*, epidote, rutile and zircon) barely accommodating K, and (2) radiogenic isotopic compositions depend on age and time-integrated parent/daughter ratio, unrelated to K abundance in sediments.

Recent developments in high precision K isotopic analysis (≤0.06 ‰) revealed large K isotopic variation (~1.3 ‰) in sediments, which has been ascribed to low temperature processes such as chemical weathering or diagenesis (Li *et al.*, 2019; Chen *et al.*, 2020; Hu *et al.*, 2020; Huang *et al.*, 2020; Santiago Ramos *et al.*, 2020; Teng *et al.*, 2020). By contrast, high temperature magmatic processes do not significantly fractionate K isotopes (Tuller-Ross *et al.*, 2019a,b; Hu *et al.*, 2021a). Hence, potassium isotopes can potentially be used to trace sedimentary K in mantle-derived melts, which has been recently applied to explain the K isotopic variations in intracontinental basalts from northeast China (Sun *et al.*, 2020) and arc lavas from Lesser Antilles (Hu *et al.*, 2021b).

Here we report the first comprehensive K isotope dataset for representative post-collisional K-rich lavas from eight regions within the Cenozoic Alpine-Himalayan orogenic belt (AHOB; Fig. 1a). These samples are well characterised for their petrology, mineralogy, major, trace element, and radiogenic isotope geochemistry (Prelević *et al.*, 2005, 2008, 2012, 2015; Zhao *et al.*, 2009; S.-A. Liu *et al.*, 2020). They cover major types of K-rich volcanic rocks, ranging from lamproite, shoshonite, high-K calc-alkaline basalt-andesite to leucite-bearing silica undersaturated rock (leucitite, melilite, and ugandite), and span a wide range of K_2O contents from 3.6 to 11.2 wt. % and K_2O/Na_2O from 1.1 to 10.4, of which the majority are ultra-potassic (Fig. 1b,c). All samples have trace element patterns

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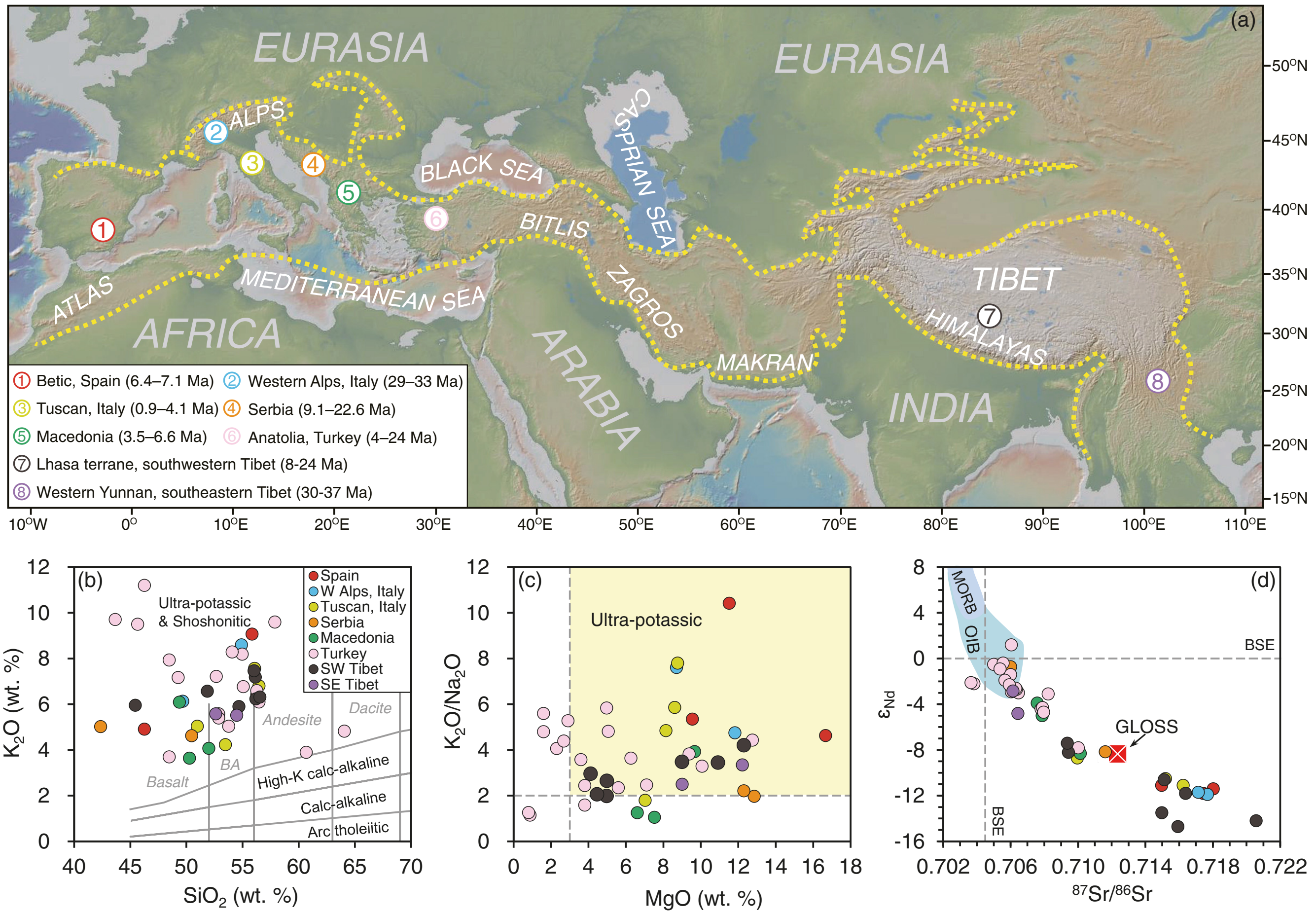

Figure 1 **(a)** Topographic map (http://www.geomapapp.org / CC BY) showing the region of Alpine-Himalayan orogenic belt (bounded by yellow dashed curves). Numbers in circles refer to the locations of K-rich volcanic rocks investigated in this study. **(b)** K_2O *vs.* SiO_2 diagram for classification of volcanic rocks (Peccerillo and Taylor, 1976). **(c)** K_2O/Na_2O *vs.* MgO. The ultra-potassic field is from Foley *et al.* (1987). **(d)** ε_{Nd} *vs.* $^{87}Sr/^{86}Sr$. ε_{Nd} and $^{87}Sr/^{86}Sr$ were calculated at the eruption age. The average global subducting sediments (GLOSS) is from Plank (2014). Major element and Sr-Nd isotope data as well as corresponding references are provided in Table S-1.

resembling upper crustal materials (Fig. S-1) and display a range of Sr and Nd isotopic ratios from OIB-like to continental crust-like (Fig. 1d). Our study finds large K isotopic variation in these K-rich rocks, comparable to subducting sediments, supporting recycling of sediments into the mantle wedge beneath accretionary orogens.

Potassium Isotope Systematics of K-rich Volcanic Rocks

$\delta^{41}K$ of all samples vary from −1.55 ‰ to −0.32 ‰, mimicking the range of global subducting sediments ($\delta^{41}K = -1.30$ ‰ to −0.02 ‰; Hu *et al.*, 2020) (Fig. 2). Two lamproites from Macedonia and Turkey have the lowest $\delta^{41}K$ (−1.55 ± 0.05 ‰ and −0.80 ± 0.05 ‰) reported for mantle-derived lavas. $\delta^{41}K$ of the other 39 samples range from −0.62 ± 0.05 ‰ to −0.32 ± 0.05 ‰, which greatly exceeds our analytical precision (≤0.06 ‰). To date, high precision $\delta^{41}K$ value of the mantle is not well constrained due to the large analytical uncertainties of previous studies (Tuller-Ross *et al.*, 2019a). Nonetheless, the most recent study suggested an average mantle $\delta^{41}K$ of −0.42 ± 0.08 ‰ (2 s.d.; Hu *et al.*, 2021a) and significant numbers of lamproites and shoshonites investigated in this study have resolvably lower $\delta^{41}K$ compared to this mantle value.

Post-eruption alteration processes cannot account for the large K isotopic variation in our samples since correlation

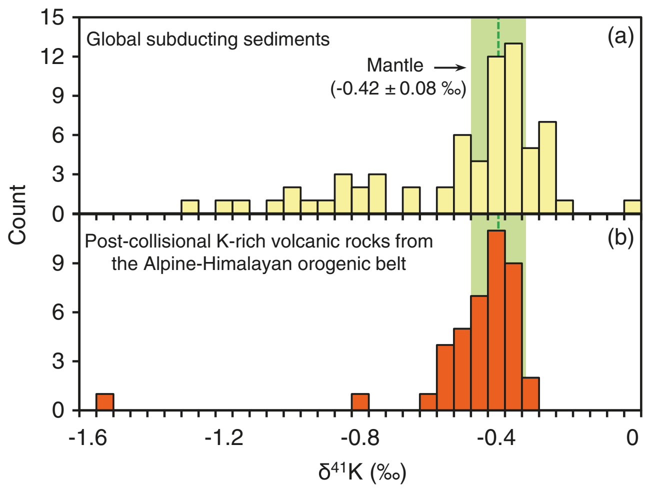

Figure 2 Comparison of $\delta^{41}K$ between global subducting sediments (Hu *et al.*, 2020) and K-rich volcanic rocks from the AHOB (this study). The mantle $\delta^{41}K$ value (−0.42 ± 0.08 ‰) is from Hu *et al.* (2021a).

between $\delta^{41}K$ and loss on ignition (LOI) is lacking and the isotopically lightest samples have very low LOI (Fig. S-2). Potassium isotope fractionation during partial melting of the

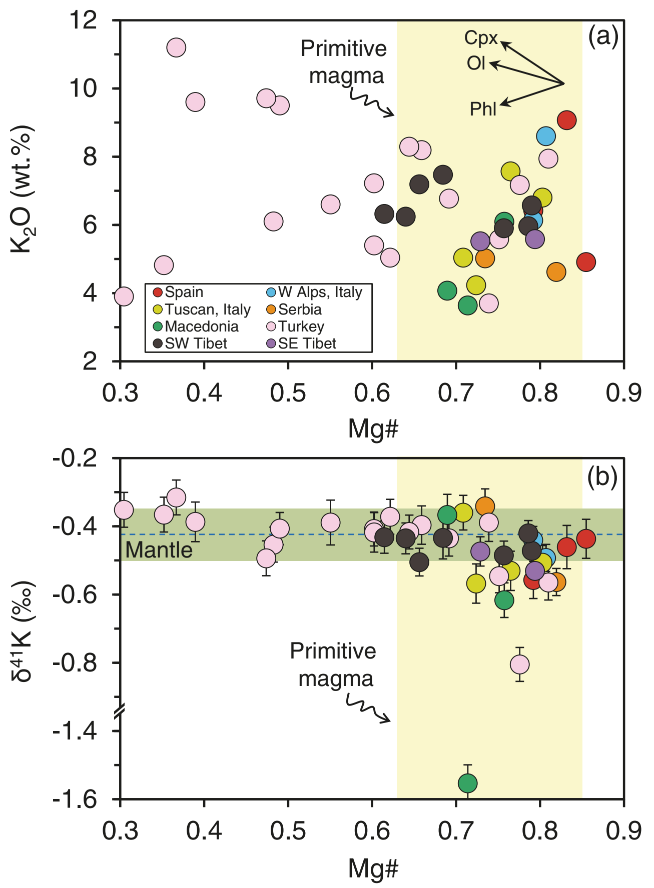

Figure 3 **(a)** K_2O *vs.* Mg#. The vectors qualitatively indicate evolution of melts during fractional crystallisation of olivine (Ol), clinopyroxene (Cpx) and phlogopite (Phl). The yellow bar refers to the putative Mg# range (0.63–0.85) of primitive magmas, which was calculated based on the forsterite contents (85–95 %) of olivine phenocrysts in K-rich volcanic rocks from the AHOB (Prelević *et al.*, 2013) and the experimentally determined olivine-liquid Fe-Mg exchange coefficient ($K_{D,Fe-Mg}^{Ol/liquid} = 0.3$; Roeder and Emslie, 1970). **(b)** $\delta^{41}K$ *vs.* Mg#. The mantle $\delta^{41}K$ (−0.42 ± 0.08 ‰) is from Hu *et al.* (2021a).

mantle and differentiation of mafic magmas is limited and only highly differentiated, Mg-depleted melts have slightly lower $\delta^{41}K$ than primitive melts (Tuller-Ross *et al.*, 2019b; Hu *et al.*, 2021a). The absence of correlation between $\delta^{41}K$ and indices of differentiation such as Mg#, SiO_2 and K_2O in our samples further confirms this (Figs. 3b, S-3). More importantly, low $\delta^{41}K$ values are only observed in samples with Mg# > 0.7 (Fig. 3b), which have been commonly considered as primary or near-primary melts that suffered limited differentiation and crustal contamination (Prelević *et al.*, 2013). Therefore, K isotopic variation in these K-rich lavas most likely reflects source heterogeneity.

Potassium Isotope Heterogeneity in Mantle Sources

Altered oceanic crust (AOC) and sediments dominate the K budget in subducting slabs, which may lead to K isotope heterogeneity in the mantle (Hu *et al.*, 2020). $\delta^{41}K$ of the AOC range from −1.07 ‰ to +0.01 ‰, and hence incorporation of recycled AOC in the mantle can potentially explain the heterogeneous $\delta^{41}K$ in our samples (Hu *et al.*, 2020; Santiago Ramos *et al.*, 2020). However, the AOC is characterised by MORB-like positive ε_{Nd} (Staudigel *et al.*, 1995), inconsistent with the negative ε_{Nd} of the K-rich volcanic rocks (Fig. 1d). Fluids released from subducting oceanic mafic crust were inferred to have higher $\delta^{41}K$ (0.13 ‰ to 1.37 ‰) than the mantle (H. Liu *et al.*, 2020), and hence cannot result in the low $\delta^{41}K$ in our samples. Subducting sediments characterised by variable and negative ε_{Nd} are most likely to be the K source (Fig. 4). Limited K isotope fractionation in subducting sediments occurs during prograde metamorphic dehydration (Wang *et al.*, 2021). Therefore, K isotopic signatures of subducting sediments could be transferred to the mantle source of K-rich lavas.

Heavy K isotopes were preferentially released into hydrosphere during continental weathering, leaving the residues enriched in light K isotopes (Li *et al.*, 2019; Chen *et al.*, 2020; Teng *et al.*, 2020). Terrigenous sediments that underwent moderate to intensive weathering display a range of $\delta^{41}K$ from −0.70 ‰ to −0.35 ‰ (Hu *et al.*, 2020), covering $\delta^{41}K$ of all but two of our samples. Incorporation of K into authigenic clay minerals during diagenesis strongly favours light K isotopes, producing sediments with $\delta^{41}K$ down to −1.31 ‰ (Hu *et al.*, 2020), which approaches the lowest value of our samples. Therefore, recycled authigenic clay-rich sediments, which are difficult to identify by trace elements and radiogenic isotopes, likely contribute to K in the two lamproites with extremely low $\delta^{41}K$. The scarcity of such samples is also consistent with the low fractions of isotopically light clay-rich sediments in global subducting sediments (Fig. 2). In addition, these low $\delta^{41}K$ lamproites mainly occur in the eastern Mediterranean provinces (Serbia, Macedonia, and Turkey) and are characterised by less radiogenic Sr and unradiogenic Nd isotopic signatures compared to the western Mediterranean counterparts (Spain and Italy), which reflects involvement of sediments with different age and provenance in their sources (Prelević *et al.*, 2008). The distinct K isotopic feature between samples from these two provinces further indicates regional heterogeneity in $\delta^{41}K$ of recycled sediments.

A Monte Carlo mixing model between the DMM (depleted MORB mantle) and subducted sediments shows that the addition of up to 5 % sediment in the mantle can almost reproduce the full range of $\delta^{41}K$ in these K-rich volcanic rocks

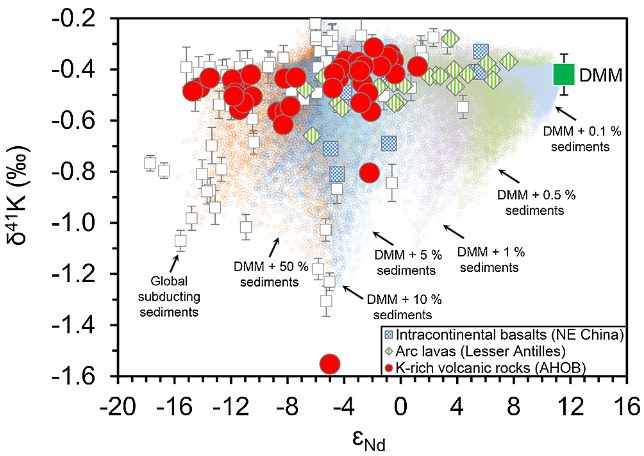

Figure 4 $\delta^{41}K$ *vs.* ε_{Nd} (calculated back at the eruption or depositional age). The $\delta^{41}K$ and ε_{Nd} of global subducting sediments are from Hu *et al.* (2020) and Plank (2014). $\delta^{41}K$ of the DMM is assumed to be the average mantle value and ε_{Nd} of the DMM is from Workman and Hart (2005). Small circles with different colours represent random mixing of subducted sediments with the DMM at variable proportions from a Monte Carlo simulation, of which the details are provided in the Supplementary Information.

because of the much higher K content in sediments than in the mantle (Fig. 4). The actual amount of sediment may be much lower considering that sediment melts, which are more enriched in incompatible elements than bulk sediments, were most likely added into the mantle. The sediment fraction derived above is significantly lower than that used in partial melting experiments on a mixture of peridotite and sediment or sediment-derived melt to generate ultra-potassic melts (≥25 %; Mallik *et al.*, 2015; Förster *et al.*, 2020). Therefore, if the experimental amount of sediment is employed in our model, δ^{41}K of ultra-potassic melts will completely inherit those of recycled sediments. Overall, recycling of a small amount of isotopically anomalous sediments into the mantle can significantly modify δ^{41}K of the mantle. This process can adequately explain the large variations of δ^{41}K and especially low δ^{41}K that are often observed in isotopically "enriched" (*i.e.* low ε_{Nd}) mantle-derived melts erupted in various tectonic settings (Fig. 4). Therefore, K isotopes may become one of the most sensitive indicators for the presence of sediments in the mantle.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2123.

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References

Avanzinelli, R., Lustrino, M., Mattei, M., Melluso, L., Conticelli, S. (2009) Potassic and ultrapotassic magmatism in the circum-Tyrrhenian region: significance of carbonated pelitic vs. pelitic sediment recycling at destructive plate margins. *Lithos* 113, 213–227.

Chen, H., Liu, X.-M., Wang, K. (2020) Potassium isotope fractionation during chemical weathering of basalts. *Earth and Planetary Science Letters* 539, 116192.

Conticelli, S., Guarnieri, L., Farinelli, A., Mattei, M., Avanzinelli, R., Bianchini, G., Boari, E., Tommasini, S., Tiepolo, M., Prelević, D. (2009) Trace elements and Sr–Nd–Pb isotopes of K-rich, shoshonitic, and calc-alkaline magmatism of the Western Mediterranean Region: genesis of ultrapotassic to calc-alkaline magmatic associations in a post-collisional geodynamic setting. *Lithos* 107, 68–92.

Couzinié, S., Laurent, O., Moyen, J.-F., Zeh, A., Bouilhol, P., Villaros, A. (2016) Post-collisional magmatism: crustal growth not identified by zircon Hf–O isotopes. *Earth and Planetary Science Letters* 456, 182–195.

Foley, S., Venturelli, G., Green, D., Toscani, L. (1987) The ultrapotassic rocks: characteristics, classification, and constraints for petrogenetic models. *Earth-Science Reviews* 24, 81–134.

Förster, M.W., Buhre, S., Xu, B., Prelević, D., Mertz-Kraus, R., Foley, S.F. (2020) Two-stage origin of K-enrichment in ultrapotassic magmatism simulated by melting of experimentally metasomatized mantle. *Minerals* 10, 41.

Hu, Y., Teng, F.-Z., Plank, T., Chauvel, C. (2020) Potassium isotopic heterogeneity in subducting oceanic plates. *Science Advances* 6, eabb2472.

Hu, Y., Teng, F.Z., Helz, R.T., Chauvel, C. (2021a) Potassium isotope fractionation during magmatic differentiation and the composition of the mantle. *Journal of Geophysical Research: Solid Earth* 126, e2020JB021543.

Hu, Y., Teng, F.-Z., Chauvel, C. (2021b) Potassium isotopic evidence for sedimentary input to the mantle source of Lesser Antilles lavas. *Geochimica et Cosmochimica Acta* 295, 98–111.

Huang, T.-Y., Teng, F.-Z., Rudnick, R.L., Chen, X.-Y., Hu, Y., Liu, Y.-S., Wu, F.-Y. (2020) Heterogeneous potassium isotopic composition of the upper continental crust. *Geochimica et Cosmochimica Acta* 278, 122–136.

Li, S., Li, W., Beard, B.L., Raymo, M.E., Wang, X., Chen, Y., Chen, J. (2019) K isotopes as a tracer for continental weathering and geological K cycling. *Proceedings of the National Academy of Sciences* 116, 8740–8745.

Liu, H., Wang, K., Sun, W.-D., Xiao, Y., Xue, Y.-Y., Tuller-Ross, B. (2020) Extremely light K in subducted low-T altered oceanic crust: Implications for K recycling in subduction zone. *Geochimica et Cosmochimica Acta* 277, 206–223.

Liu, S.A., Wang, Z.Z., Yang, C., Li, S.G., Ke, S. (2020) Mg and Zn isotope evidence for two types of mantle metasomatism and deep recycling of magnesium carbonates. *Journal of Geophysical Research: Solid Earth,* e2020JB020684.

Mallik, A., Nelson, J., Dasgupta, R. (2015) Partial melting of fertile peridotite fluxed by hydrous rhyolitic melt at 2–3 GPa: implications for mantle wedge hybridization by sediment melt and generation of ultrapotassic magmas in convergent margins. *Contributions to Mineralogy and Petrology* 169, 48.

Peccerillo, A., Taylor, S. (1976) Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu area, northern Turkey. *Contributions to Mineralogy and Petrology* 58, 63–81.

Plank, T. (2014) 4.17 – The chemical composition of subducting sediments. In: Holland, H.D., Turekian, K.K. (Eds.) *Treatise on Geochemistry*. Second Edition, Elsevier, Oxford, 607–629.

Prelević, D., Foley, S.F., Romer, R.L., Cvetković, V., Downes, H. (2005) Tertiary ultrapotassic volcanism in Serbia: constraints on petrogenesis and mantle source characteristics. *Journal of Petrology* 46, 1443–1487.

Prelević, D., Foley, S.F., Romer, R., Conticelli, S. (2008) Mediterranean Tertiary lamproites derived from multiple source components in postcollisional geodynamics. *Geochimica et Cosmochimica Acta* 72, 2125–2156.

Prelević, D., Akal, C., Foley, S.F., Romer, R.L., Stracke, A., Van Den Bogaard, P. (2012) Ultrapotassic mafic rocks as geochemical proxies for post-collisional dynamics of orogenic lithospheric mantle: the case of southwestern Anatolia, Turkey. *Journal of Petrology* 53, 1019–1055.

Prelević, D., Jacob, D.E., Foley, S.F. (2013) Recycling plus: a new recipe for the formation of Alpine–Himalayan orogenic mantle lithosphere. *Earth and Planetary Science Letters* 362, 187–197.

Prelević, D., Akal, C., Romer, R.L., Mertz-Kraus, R., Helvaci, C. (2015) Magmatic response to slab tearing: constraints from the Afyon Alkaline Volcanic Complex, Western Turkey. *Journal of Petrology* 56, 527–562.

Roeder, P.L., Emslie, R. (1970) Olivine-liquid equilibrium. *Contributions to Mineralogy and Petrology* 29, 275–289.

Santiago Ramos, D.P., Coogan, L.A., Murphy, J.G., Higgins, J.A. (2020) Low-temperature oceanic crust alteration and the isotopic budgets of potassium and magnesium in seawater. *Earth and Planetary Science Letters* 541, 116290.

Staudigel, H., Davies, G.R., Hart, S.R., Marchant, K.M., Smith, B.M. (1995) Large scale isotopic Sr, Nd and O isotopic anatomy of altered oceanic crust: DSDP/ODP sites 417/418. *Earth and Planetary Science Letters* 130, 169–185.

Sun, Y., Teng, F.-Z., Hu, Y., Chen, X.-Y., Pang, K.-N. (2020) Tracing subducted oceanic slabs in the mantle by using potassium isotopes. *Geochimica et Cosmochimica Acta* 278, 353–360.

Teng, F.-Z., Hu, Y., Ma, J.-L., Wei, G.-J., Rudnick, R.L. (2020) Potassium isotope fractionation during continental weathering and implications for global K isotopic balance. *Geochimica et Cosmochimica Acta* 278, 261–271.

Tommasini, S., Avanzinelli, R., Conticelli, S. (2011) The Th/La and Sm/La conundrum of the Tethyan realm lamproites. *Earth and Planetary Science Letters* 301, 469–478.

Tuller-Ross, B., Marty, B., Chen, H., Kelley, K.A., Lee, H., Wang, K. (2019a) Potassium isotope systematics of oceanic basalts. *Geochimica et Cosmochimica Acta* 259, 144–154.

Tuller-Ross, B., Savage, P.S., Chen, H., Wang, K. (2019b) Potassium isotope fractionation during magmatic differentiation of basalt to rhyolite. *Chemical Geology* 525, 37–45.

Walter, M.J. (1998) Melting of garnet peridotite and the origin of komatiite and depleted lithosphere. *Journal of Petrology* 39, 29–60.

Wang, Z.-Z, Teng, F.-Z., Busigny, V., Liu, S.-A. (2021) Evidence from HP/UHP metasediments for subduction of isotopically heterogeneous potassium into the mantle. *American Mineralogist* in press. doi: 10.2138/am-2021-7923.

Williams, H.M., Turner, S.P., Pearce, J.A., Kelley, S., Harris, N. (2004) Nature of the source regions for post-collisional, potassic magmatism in southern and northern Tibet from geochemical variations and inverse trace element modelling. *Journal of Petrology* 45, 555–607.

Workman, R.K., Hart, S.R. (2005) Major and trace element composition of the depleted MORB mantle (DMM). *Earth and Planetary Science Letters* 231, 53–72.

Zhao, Z., Mo, X., Dilek, Y., Niu, Y., DePaolo, D.J., Robinson, P., Zhu, D., Sun, C., Dong, G., Zhou, S. (2009) Geochemical and Sr–Nd–Pb–O isotopic compositions of the post-collisional ultrapotassic magmatism in SW Tibet: petrogenesis and implications for India intra-continental subduction beneath southern Tibet. *Lithos* 113, 190–212.