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Ancient mantle plume components constrained by tungsten isotope variability in arc lavas

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Abstract





Tungsten isotope anomalies in modern rocks are exclusively associated with plumerelated basalts and may provide a unique tool to identify recycled plume material in subduction zone magmatism. In Central America, the Cocos and Coiba Ridges are subducting with the Cocos plate. These ridges may introduce material into the arc magma source that was derived from the Galápagos plume, which has been shown to carry anomalous ¹⁸²W signatures. Here, we report negative μ^{182} W values together with trace element data for <5 Ma old adakites and back-arc basanites, as well as accreted basalt terranes that formed as a result of Galápagos plume activity in the last 70 Myr. In adakites and basanites, these μ^{182} W deficits derive from a slab melt component that dominates the W budget of their source. In addition, negative

 μ^{182} W in accreted mafic terranes attest to the longevity of the primordial W isotope signature in the Galápagos plume and the involvement of a Galápagos-related magma source in the Central American arc system over time.

Received 16 February 2023 | Accepted 6 June 2023 | Published 23 June 2023

Introduction

Mass transfer from variable components of the subducting oceanic lithosphere into the arc mantle and subsequent incorporation into arc magmas represents a major paradigm in Earth Sciences. While there is strong evidence for the involvement of fluids and subducted sediments in the mantle source of many arc magmas (Tera et al., 1986), the nature of direct contributions of subducted basaltic crust remains debated. However, slab melting under certain conditions has become central to many models of subduction zone processes (e.g., Yogodzinski et al., 2015). Here, we use isotope and concentration data for W in arc-related rocks to trace slab- and plume-derived source components in arc magmas. Variations in the distribution of ¹⁸²W in terrestrial rocks must have been established within the first 50 Myr of Earth's history due to the short half-life of its extinct parent isotope ¹⁸²Hf (e.g., Willbold et al., 2011). The only known modern setting exhibiting negative ¹⁸²W variability is ocean islands associated with deep-seated mantle plumes, such as Galápagos (e.g., Mundl-Petermeier et al., 2020). In this context, the Central American arc system is a prime location for using W isotopes as a tracer for oceanic crust and plume-mantle components in arc magmas. Here, the 13 to 15 Ma old Cocos and Coiba Ridge (CCR), and other hotspot traces related to the Galápagos plume, are being subducted along the Panama-Costa Rica section of the Central American arc system (Hauff et al., 2000; Abratis and Wörner, 2001; Gazel et al., 2009, 2011). About 1.5 to 5 Ma old adakitic lavas from Panama and Costa Rica are of particular interest, since involvement of a slab melt component in their petrogenesis has previously been proposed (e.g., Defant et al., 1991; Abratis and Wörner, 2001; Gazel et al., 2009).

Identification of negative W isotope anomalies in these adakites would thus provide a strong, first-hand indication for the involvement of plume-derived subducted oceanic crust in arc melts from the Central American arc system. Further, a suite of alkaline mafic lavas (basanites) in the back-arc in Costa Rica dated at 4 to 6 Ma possibly record a mantle contribution from the Galápagos plume (Abratis and Wörner, 2001). Here, radiogenic W isotope systematics provide a powerful tracer to identify different source components that may be derived from the Galápagos plume.

Samples and Methods

We selected 14 well-characterised adakites from the Costa Rica and Panama arc front and five basanites from behind the volcanic arc of southern Costa Rica for W isotope and trace element analysis. To constrain the isotopic composition of subducted material we also analysed ocean island basalt (OIB) terranes that were accreted to the forearc of Costa Rica and Panama. The latter were interpreted to represent 18 to 71 Ma old hotspot tracks of the Galápagos plume (e.g., Appel et al., 1994; Hauff et al., 2000; Wegner et al., 2011; Gazel et al., 2018). Further details on the samples as well as Sr, Pb and Nd isotope compositions can be found in Appel et al. (1994), Abratis and Wörner (2001) and Wegner et al. (2011). The W isotopic compositions are reported as $\mu^{182}W$, representing the part per million deviation of the ¹⁸²W/¹⁸⁴W ratio of a sample from W standard NIST 3163. Detailed descriptions of methods and analytical results are provided in the Supplementary Information.

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Results and Discussion

The adakites range in SiO₂ content between 53 to 69 wt. % and show high Sr/Y ratios from 100 to 200 at low Y concentrations of 7 to 14 µg/g. They feature prominent depletions in high field strength elements (HFSE) and are low in heavy rare earth elements (HREE) due to melting of hydrous meta-basalt with residual rutile and garnet (Figure S-1; Martin et al., 2005). Their W isotopic compositions range from $\mu^{182}W = -6.89 \pm 2.95$ to $+0.87 \pm 2.95$ (external reproducibility, 2 s.d.). There are no observable correlations between µ¹⁸²W and either major or trace element concentrations, their ratios or with any radiogenic isotope ratios. Basanites have SiO2 concentrations from 43 to 47 wt. % with high MgO of 6.3 to 9.3 wt. %. They show trace element patterns that are strongly enriched in incompatible elements with notable depletions in HFSE comparable to the adakites. Although their Sr/Y ratios are elevated compared to normal arc lava and range between 42 and 120, they also have high Y concentrations (17.5 to 30 µg/g) and are silica-undersaturated, which places them outside the compositional range expected for adakitic rocks (Martin *et al.*, 2005). Values for μ^{182} W range from -9.04 ± 4.32 to $+1.74 \pm 4.32$. Similar to the adakites, no correlations with other chemical or radiogenic isotope tracers can be observed. Accreted OIB have MgO concentrations ranging from 6 to 21 wt. %. Trace element patterns show typical intraplate affinities, similar to the modern Galápagos archipelago with enriched incompatible elements and a relative depletion in Pb. Their μ^{182} W ranges from -9.72 ± 4.8 to $+0.98 \pm 2.95$. Thus, as a first-order observation, all three rock types related to the Costa Rica-Panama subduction zone show resolvable W isotope deficits. In the following, we will address likely scenarios that can reconcile this observation.

Previous results for modern basalts from the Galápagos archipelago, together with our own data for the accreted OIB terranes, provide an approximation of the isotopic composition of the basalts from the CCR, that are currently subducted below Central America. A chemical and isotopic zonation within the Galápagos plume (Hoernle et al., 2000) is mirrored by contrasting negative W isotopic compositions of basalts from the central and eastern domains of the Galápagos islands ($\mu^{182}W = -22$ and -5, respectively; Mundl-Petermeier et al., 2020). This chemical zonation is also reflected in the CCR, as well as in the basaltic rocks accreted in the Central American forearc (Gazel et al., 2018 and references therein). We find that the W isotopic compositions of the accreted CCR rocks analysed here do not fully reflect the entire range observed in the modern Galápagos archipelago. However, μ^{182} W deficits of up to -9.72 ± 4.80 confirm that the Galápagos plume is isotopically variable and, more importantly, show that the incorporated primordial W isotopic signature has existed for at least the past 70 Myr. This implies that the unusual W isotopic signature is a long-lived, persistent characteristic of the plume. If equivalents of such basaltic rocks from the CCR are also subducted to the depth where magmas are formed, these arc magmas would also be expected to show similar µ¹⁸²W deficits.

This is, in fact, supported by our observations: the μ^{182} W deficits of up to -6.89 ± 2.95 in the adakites cover almost the entire range of μ^{182} W variations measured in the accreted CCR basalts, providing a clear indication for involvement of a Galápagos plume component in their source. We will now test whether partial melts of the subducted basalts from the CCR contributed to the μ^{182} W deficits or, alternatively, the mantle wedge below Costa Rica and Panama contained material from the Galápagos plume, as was proposed for the origin of the basanites (Abratis and Wörner, 2001). The geochemical behaviour of W in subduction zones is best studied using W/Th ratios

(König et al., 2008). Bulk partition coefficients of W and Th are very similar during mantle melting (Arevalo and McDonough, 2008), resulting in only small variations of W/Th ratios in oceanic basalts (MORB = 0.09 to 0.24, OIB = 0.08 to 0.19; König et al., 2011; Kurzweil et al., 2019). During differentiation of mafic magmas, this ratio should remain constant. However, W is mobile in subduction zone fluids (Bali et al., 2012), resulting in elevated W/Th ratios in arc magmas compared to MORB and OIB (Fig. 1; König et al., 2008; Stubbs et al., 2022). Indeed, W/Th ratios for "normal" arc lavas from Central America, with W/Th ranging from 0.05 to 0.43, fall into the global arc magma range (Fig. 1). In contrast, adakites and basanites show surprisingly low W/Th ratios between 0.02 and 0.06, substantially lower than MORB, OIB and most arc front lava previously measured. Only five of the 19 adakites and basanite samples have elevated W/Th (>0.09). These also record high Ba/Th ratios of >280 or high ⁸⁷Sr/⁸⁶Sr ratios of >0.704, in line with additional fluid or sedimentary components in their source (Fig. 1, Table S-1; Stubbs et al., 2022). Neither involvement of slab fluids, nor the addition of an enriched mantle source, can explain the exceptionally low average W/Th ratios in the remaining adakites and basanites, because such components would result in higher, not lower, W/Th ratios. On the other hand, such low W/Th ratios could be due to melting of subducted basalts with residual rutile, where rutile preferentially retains W and other HFSE (Rudnick et al., 2000; Zack et al., 2002; Bali et al., 2012). Strong depletions of Nb, Ta and Ti in adakites and basanites also make a strong case for the involvement of rutile (Fig. S-1). Moreover, elevated Nb/Ta ratios in both adakites (18.01 ± 1.86) and basanites (20.1 ± 1.85) compared to typical values found in oceanic basalts (Nb/Ta = 14.5 to 16.5; Gale et al., 2013; Tang et al., 2019) are complementary to low Nb/Ta ratios in rutile (Green and Pearson, 1987). Combined, the unusual W isotope deficits and low W/Th ratios make a strong case that the petrogenesis of adakites and basanites is linked to partial melting of a subducted metabasaltic source derived from the Galápagos plume. This either involves the slab melt directly or a mantle source modified by slab melts derived from CCR basalts.



Figure 1 Fluid mobile element systematics for Panama and Costa Rica arc rocks and compiled arc data from König *et al.* (2011), Kurzweil *et al.* (2019), Mazza *et al.* (2020), and Stubbs *et al.* (2022). MORB and OIB fields defined after König *et al.* (2011) and Kurzweil *et al.* (2019). Adakitic rocks from Laeger *et al.* (2013) and Straub *et al.* (2015).

Based on the large range of silica content, it was argued that the adakites in Costa Rica and Panama do not represent pure slab melts, but rather derive from a mantle wedge metasomatised by slab melts (Gazel et al., 2009, 2011; Martin et al., 2005). To test this model with our data, we performed simple mixing calculations between a slab-derived melt and a subduction-modified mantle wedge (Fig. 2; see Supplementary Information for model parameters). The source of adakites is best represented by a mantle wedge metasomatised by 3 to 20 wt. % of a slab melt with low W/Th of 0.018. This is in good agreement with previous models using radiogenic isotopes (Gazel et al., 2009). The variability of $\mu^{182} \breve{W}$ in the adakites and the lack of correlation with other geochemical parameters require that the slab was heterogeneous in μ^{182} W. Therefore, this model constrains the maximum W isotope deficit of a slab melt necessary to explain the range observed in the adakites. As shown in Figure 3a, assuming μ^{182} W values varying between -12 to 0 for the subducted CCR basalts can reconcile the isotopic compositions of most adakites. Three samples with high Ba/Th and Ŵ/Th, however, plot outside of this plausible mixing field, which is likely due to an additional component in their source.

To account for the enriched trace element signature observed in the basanites, we included an enriched source model component in our calculations. Following slab window formation below Costa Rica and Panama, previous models have argued for the ascent and decompression melting of a mantle component that was derived from the Galápagos plume as the source for the basanites (Abratis and Wörner, 2001; Gazel et al., 2011). However, similar to the case of the adakites, the low W/Th ratios of the basanites require an additional slab melt component. In our model, the enriched mantle composition was estimated from the average Galápagos basalt. Melting of this enriched mantle modified by 2 to 10 wt. % slab melt formed from CCR basalts can explain the observed incompatible element enrichment in basanites while maintaining their low W/Th ratios (Figs. 2, S-2). Finally, we can test how this enriched Galápagos mantle influences the W isotopic composition of the basanites. Model A in Figure 3b uses the enriched mantle composition assuming $\mu^{182}W = 0$, while model B involves a Galápagos mantle with $\mu^{182}\dot{W}$ as low as -6. Each model encompasses the observed



Figure 2 Two component mixing models for melts derived from a depleted mantle or an enriched mantle modified by Cocos and Coiba Ridge (CCR) melts. Endmember compositions and model parameters can be found in the Supplementary Information. Samples with W/Th > 0.2 not shown.



Figure 3 Two component mixing models between modelled slab melt and three different mantle compositions: (a) mixing with depleted mantle to model the W isotope composition of adakites and (b) mixing with two types of enriched mantle (models A and B) to produce the source composition of basanites. Grey dashed lines represent the error of the W isotopic composition of the upper mantle. Model parameters can be found in the Supplementary Information.

basanite compositions including the most anomalous basanite ($\mu^{182}W = -9.04 \pm 4.32$). Model A, however, shows that contributions of isotopically anomalous W from the enriched mantle source are not required to explain the variability observed in the basanites. If this mantle source is characterised by depletions in $\mu^{182}W$, values cannot be significantly lower than -6, as it is shown in model B. It is therefore unlikely that this component reflects the composition of the modern central Galápagos domain (Bekaert *et al.*, 2021). In any case, the negative W isotope signal observed in adakties and basanites from Costa Rica and Panama requires a slab melt component that carries the anomalous $\mu^{182}W$ from the Galápagos plume.

Conclusions

The tungsten isotope systematics of the adakites verify melting of subducted oceanic crust at mantle depth in the Central American arc system. Melts derived from a hybridised mantle wedge with negative μ^{182} W signatures provide strong evidence that this contribution is related to Cocos and Coiba Ridges

(CCR). In the case of the back-arc basanites, this signature is possibly modified by mantle components derived from the Galápagos plume, although their contribution is not strictly required to explain their isotopic budget. Unusually low W/Th in both adakites and basanites imply control by residual rutile on the W budget of their sources. These observations further strengthen previous proposals for magma genesis for these adakites and basanites related to the evolution of a slab window below Costa Rica and Panama as a consequence of CCR collision with the Central American subduction zone. Finally, we document that the anomalous low μ^{182} W signal is a long-lived (>70 Myr) geochemical signature of the Galápagos plume.

Acknowledgements

This study was funded through the Priority Programme 1833 "Building a Habitable Earth" of the German Science Foundation (DFG grant No. WI 3579/3-1 to MW). GW acknowledges DFG grants No. WO 362/10 and WO 362/27-2 for providing funds for sampling in the field. We thank Caroline Soderman and Jonas Tusch for their constructive review of the manuscript and Helen Williams for editorial handling. M. Abratis, W. Wegner, S. Rausch, and R. Harmon are thanked for their efforts during strenuous fieldwork in Central America. We acknowledge Rachel Bezard for helpful discussions and Dirk Hoffmann for support with mass spectrometry and clean lab maintenance.

Editor: Helen Williams

Additional Information

Supplementary Information accompanies this letter at https:// www.geochemicalperspectivesletters.org/article2321.



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Cite this letter as: Messling, N., Wörner, G., Willbold, M. (2023) Ancient mantle plume components constrained by tungsten isotope variability in arc lavas. *Geochem. Persp. Let.* 26, 31–35. https://doi.org/10.7185/geochemlet.2321

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Supplementary Information

The Supplementary Information includes:

- > Methods
- Binary Mixing Models
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- Supplementary Figures S-1 to S-5
- Supplementary Information References

Methods

Analytical techniques utilised in this study are based on W separation procedures described in earlier work (Willbold *et al.*, 2011; Mei *et al.*, 2018; Tusch *et al.*, 2019). We further optimised the W separation procedure for larger sample sizes while maintaining measurement precision and accuracy. Therefore, we devised a new W separation procedure to process up to 6 g of sample material on a three-step ion exchange chromatography. We utilised the precipitation of a W-free fluoride phase during sample digestion, which removed the majority of matrix elements, while quantitatively retaining W. Sample preparation was carried out under metal-free clean laboratory conditions at the University of Göttingen.

1. Sample preparation and trace element measurement

All adakites and basanites were available as powders that were initially used by Abratis and Wörner (2001) and Wegner *et al.* (2011). These powders were prepared using an agate ball mill after crushing in the field and washing with distilled water. Additional samples from accreted fore-arc terranes (QUE-020, PAR-023 and PAV-030) were crushed into 1–2 cm large chips in a steel jaw crusher. To avoid metal contamination the samples were then washed with Milli-Q water (Merck Millipore). After drying, the chips were packed into plastic bags and crushed with a hydraulic press into pieces smaller than 5 mm. The crushed samples were ground in agate ball mills and used for trace element and isotopic analysis. The new trace element measurements were conducted as described in Hegner *et al.* (2022) on a ThermoFisher Scientific iCap Q-ICPMS. Sample powders were digested in a picotrace DAS high-pressure digestion system at 220 °C in 1.2 mL concentrated HF and 0.3 mL concentrated HNO₃ to ensure complete digestion of refractory minerals. In addition, reference materials ranging from basalts to rhyolites were equally prepared in order to accurately represent the compositional range of samples measured in this study.



2. Tungsten sample digestion and separation

All steps were carried out using double distilled acids (Savillex DST-1000) or ultra-pure reagents, which were diluted to appropriate concentrations using 18.2 M Ω cm water (Merck Millipore Milli-Q). Between 2 and 6 g of sample powder were weighed out in 60 or 90 mL Savillex beakers. For every 2 g of sample powder, 10 mL 6 M HCl and 10 mL 24 M HF were added. In the closed beaker the samples were digested at 150 °C for 3 days, ultrasonicating the samples at the beginning and end of the digestion. After completely drying down the sample at 130 °C, 10 mL 0.5 M HCl-1 M HF were added and heated for 1-2 h. The samples were transferred into a 50 mL centrifuge tube and centrifuged for 15 min. The acid supernatant was decanted and stored in another centrifuge tube. To the fluoride residue, another 10 mL 0.5 M HCl-1 M HF were added, which was then placed into a heated ultrasonic bath at 60 °C for 15 min. After centrifuging and decanting this step was repeated once more. W was quantitively transferred into the supernatant at this point (Fig. S-3a). The fluoride residue, containing a significant fraction of matrix elements was therefore discarded. The 30 mL of the combined supernatant were used for the ion exchange procedure. The full elution scheme of all ion exchange procedures used is described in Table S-2. After the first anion (10 mL AG1x8) chemistry the sample solution was directly passed through an Eichrom prefilter column to remove dissolved organic compounds. After this step and every following ion exchange chromatography samples were treated with HNO₃-H₂O₂ as described in Tusch et al. (2019). On the following 1 mL TEVA column, W was separated from the remaining HFSE as described in Mei et al. (2018). Lastly, a 1 mL anion clean-up chemistry was used to separate remaining matrix elements. For several samples, an aliquot was taken after the digestion of the samples to show no W is lost during the fluoride precipitation procedure. Typically, 60–90 % of the W budget of the samples is recovered using this chemical separation procedure (Fig. S-3b). Further, we compared digestion yields of the reference material JB-2 for complete digestion and fluoride precipitation digestion. All results are provided in Figure S-3a. Procedural blanks for the entire chemical separation procedure ranged from 96 to 841 pg for every 6 g of digested material, with an average of 346 pg (n = 9) corresponding to an average blank contribution of 0.6 %. Elution patterns for the first anion and the TEVA exchange chromatography for some matrix elements and the HFSE is provided in Figure S-4.

3. Tungsten isotope measurement

The W isotopic compositions of samples and reference materials were determined on a Thermo Fisher Scientific Neptune Plus MC-ICP-MS at the University of Göttingen. A Teledyne Cetac Aridus III desolvating nebuliser equipped with the Teledyne Cetac QuickWash3 accessory was used as the sample introduction system. Similar to Tusch et al. (2019), a cyclonic quartz spray chamber was interconnected between the desolvating nebuliser and the torch to improve the signal stability by increasing the expansion volume of the inlet system. Faraday cups were connected to a series of 10^{11} , 10^{12} and $10^{13} \Omega$ amplifier boards to measure ion currents of the W isotopes, as well as those of ¹⁷⁷Hf, ¹⁷⁸Hf, ¹⁸¹Ta and ¹⁸⁸Os, which were monitored for the correction of isobaric interferences on W. $10^{11} \Omega$ amplifiers were used for 177 Hf, 182 W, 183 W, 184 W and 186 W, whereas ¹⁸⁸Os was monitored using a $10^{12} \Omega$ amplifier and ¹⁷⁸Hf and ¹⁸⁰W using a $10^{13} \Omega$ amplifier. Typical sensitivities with a Ni standard sample cone and X skimmer cone and a 60 µL/min nebuliser were 300-350 V/ppm of total W. Triplet analyses were conducted for each sample, with 60 cycles and an integration time of 8.39 seconds per analysis. For samples with high W concentrations 6 individual measurements were conducted. Each sample was bracketed with a 240 ng/g W NIST SRM 3163 solution. Data reduction was carried out offline using a Python script using exponential law to correct for mass bias, normalising to ${}^{186}W/{}^{184}W =$ 0.92767 (Völkening et al., 1991). For a high-precision triplet measurement, ~650 ng of W were required. The external reproducibility was calculated by repeated measurements of in-house reference materials 'Granite 232' (described in Haack, 1969) and 'Basalt Me21', collected from the 'Hoher Meißner' basalt quarry, that were measured at the beginning and the end of every measurement sequence (Fig. S-5). Data is expressed as μ^{182} W which is defined as ($^{182}W/^{184}W_{sample}$ / $^{182}W/^{184}W_{NIST 3163}$ - 1) × 1,000,000. The external μ^{182} W



reproducibility (2 s.d.) for Granite 232 is 3.61 ppm (n = 13) and 4.36 ppm for Me21 (n = 24) for triplet measurements. For sextuplet analysis, the reproducibility was improved to 2.95 ppm for Me21 (n = 8), in good agreement with the external reproducibility reported in recent literature (2.9-4.5 ppm, Jansen et al., 2022; 1.45–2.73 ppm, Tusch et al., 2022). The W isotope data for single measurements is provided in Figure S-4 together with μ^{183} W data and values normalised to 186 W/ 183 W. This also includes μ^{182} W values (normalised to ¹⁸⁶W/¹⁸³W), corrected for mass-independent fractionation with the equation from Budde et al. (2022). We observe mass-independent W isotope variations resulting in deficits in μ^{182} W as low as -20 ppm, similar to previous studies (Kruijer and Kleine, 2018; Archer et al., 2019; Tusch et al., 2019; Tappe et al., 2020; Budde et al., 2022). This effect likely occurs during the dry-down procedure between ion exchange chromatography steps and often coincides with significant losses of W (Willbold et al., 2011; Tusch et al., 2019; Budde et al., 2022). We applied the dry-down procedure described by Tusch et al. (2019), adding several steps of HNO₃-H₂O₂ to the W cuts following the dry-down after each chromatography step. However, this procedure does not result in a decrease in the ¹⁸³W effect in our samples. The precipitation of fluorides likely has no influence on the analytical ¹⁸³W effect, since the magnitude of this effect is in line with previous methods that applied a complete digestion procedure (Tusch et al., 2019). In this study, we used ¹⁸⁶W/¹⁸⁴W for the mass bias correction to avoid any analytical effects of ¹⁸³W. When corrected for mass-independent fractionation (Budde et al., 2022), μ^{182} W values normalised to 186 W/ 183 W are in good agreement with those normalised to 186 W/ 184 W within 3 ppm (Table S-4).

Binary Mixing Models

The models shown in Figures 2 and 3 are based on simple binary mixing calculations between a mantle wedge with a depleted mantle or enriched mantle composition. All parameters relevant for modelling are summarised in Table S-3. In the model, we assume a slab melt composition that was produced by partially melting a protolith with a composition of the average CCR basalts and a residual eclogitic mineral assemblage from Gazel et al. (2009). We calculated the HFSE abundances in the slab melt using partition coefficients from Kessel et al. (2005). We did not use Nb/La ratios reported in Gazel et al. (2009), since these were higher than the Nb/La ratios measured in the adakites. Partition coefficients for W between melt and rutile during slab melting are poorly constrained. The W/Th ratio was therefore estimated based on the lowest W/Th ratio of the adakites (W/Th = 0.023) as well as their major element chemistry (SiO₂ = 53 to 69 wt. %). For instance, assuming a slab melt W/Th ratio >0.019 would require a 35 % contribution from the slab melt, resulting in an unrealistically high SiO₂ (>57 wt. %) content in the hybridised bulk mantle composition. On the other end of the spectrum, assuming a W/Th ratio <0.014 for the slab melt, a W isotope deficit exceeding the composition of basalts from the modern central Galápagos domain ($\mu^{182}W > -22$) would be necessary to achieve the measured W isotopic composition of the adakites with this model. The currently subducting Cocos and Coiba ridges fully reflect the chemical zonation of the Galápagos Archipelago (e.g., Werner et al., 2003). It is therefore unlikely that the W isotopic composition of the subducted ridges only represent the central Galápagos domain. As such, we assume an intermediary W/Th ratio of 0.018 in our model, yielding slab melt contributions of 3 to 20 % that are in good agreement with radiogenic isotope modelling from Gazel et al. (2009). As a result, the slab melt components in the central American arc system only require a μ^{182} W isotope composition of 0 to -12. This range is in line with the isotopic composition of accreted OIB terranes measured in this study as well as basalts from the Galápagos Archipelago. The μ^{182} W value of the upper mantle is assumed to be 0 (e.g., Willbold et al., 2011; Jansen et al., 2022). To estimate an error for this value we used the reproducibility of our standard (95 % confidence interval: $\mu^{182}W = 0.98$) in our model calculations. Addition of sediment can potentially provide significant contributions to the W budget in arc melts. Trace element systematics in Central American arc rock generally show decreasing sediment addition towards the



southeast (Leeman et al., 1994; Patino et al., 2000). In southern Costa Rica and Panama, sediment contribution to arc rocks is considered small (Bekaert et al., 2021). Previous models assumed a contribution of 0.1 to 0.6 % sediment-derived melts for arc rocks in this region (Gazel et al., 2009). The 'global subducted sediment' (GLOSS) composite by Plank and Langmuir (1998) does not report concentration data for W. We therefore used a W/Th ratio of 0.21 based on global W sediment data (Kirchenbaur and Münker, 2015; Kurzweil et al., 2019; Stubbs et al., 2022) to calculate the W concentration in the sediment melt. This likely overestimates the W contribution of sediments, as residual rutile in the sediments during subduction would result in lower W/Th ratios in the melt. However, using the maximum W/Th ratios calculated here for sediment melts and the sediment proportions estimated in Gazel et al. (2009), the maximum contribution of sediment melt to the average W budget of adakites is less than 4 % (<13.5 ng/g). We used the lower bound of 0.1 % sediment proportion for our calculations. Based on the model of influx and arc parallel mantle flow beneath Costa Rica and Panama (Abratis and Wörner, 2001; Hoernle et al., 2008) it is reasonable to assume that the mantle wedge has been modified by subduction zone processes. To account for this, we used upper mantle W concentration of 10 ng/g for the mantle source with slightly elevated W/Th ratios of 0.19 similar to the average arc basalt (König et al., 2008, 2011; Mazza et al., 2020; Stubbs et al., 2022). The trace element budget of the enriched Galápagos mantle source was back-calculated using the average Galápagos basalt composition compiled from the GEOROC database, while assuming 11 % batch melting of the Galápagos mantle (White *et al.*, 1993). We assumed a constant W/Th of 0.11 in agreement with W/Th ratios measured in accreted Galápagos OIB terranes as well as global OIB data (König et al., 2011; Kurzweil et al., 2019).

Supplementary Tables

Table S-1W isotope and long-lived radiogenic isotope data and trace element data for reanalysed samples.

Tables S-1 (.xlsx) is available for download from the online version of this article at <u>https://doi.org/10.7185/geochemlet.2321</u>.

Step	Reagent	Acid volume (mL)			
I. BioRad AG1x8 100–200 mesh, 10 mL resin (20 mL Bio-Rad Econo-Pac [®] columns)					
Clean	1 mM DTPA-1 M HCl	4×10			
	3 M HNO3-0.2 M HF	4×10			
	6 M HNO3-0.2 M HF	4×10			
	H ₂ O	4×10			
Condition	0.5 M HCl–1 M HF	4×10			
Load	0.5 M HCl–1 M HF	3 × 10			
Elute Matrix	0.005 M HCl-1 M HF	4×10			
Elute HFSE and Ti	0.5 M HCl-1 % H ₂ O ₂	10 × 10			
	0.005 M HCl-1 M HF	1×10			
Collect Mo, W, Sn	3 M HNO3-0.2 M HF	5.5×10			

Table S-2Tungsten ion exchange matrix separation procedure.



Table S-2 continued.

Step	Reagent	Acid volume (mL)				
II. Eichrom prefilter resin 100–150 mesh, 1 mL resin (2 mL Biorad Poly-Prep® columns)						
Clean	3 M HC1–0.2 M HF	2 × 10				
	6 M HNO ₃ -0.2 M HF	2×10				
	H ₂ O	1×10				
Condition	3 M HNO ₃ -0.2 M HF	2×2				
Load & Collect	3 M HNO ₃ -0.2 M HF	55				
Collect	3 M HNO ₃ -0.2 M HF	2 × 1				
III. Eichrom TEVA 100–150 mesh, 1 mL resin (2 mL Biorad Poly-Prep® columns) on 0.4						
mL Eichrom prefilter resin						
Clean	6 M HNO ₃ 0.2 M HF	2×10				
	H ₂ O	1×10				
	3 M HCl-0.02 M HF	2×10				
Condition	9 M HCl-0.02 M HF	4×1				
Load	9 M HCl-0.02 M HF	2				
Rinse	9 M HCl-0.02 M HF	5 imes 0.5				
Collect W	3 M HCl-0.02 M HF	4×2				
Collect Mo	3 M HNO ₃ -0.2 M HF	3 × 2				
IV. BioRad AG1x8 100–200 mesh, 1 mL resin (2 mL Biorad Poly-Prep® columns) on 0.4						
mL Eichrom prefilter resin						
Clean	0.5 M HCl–1 M HF	1×10				
	3 M HNO ₃ -0.2 M HF	1×10				
	6 M HNO ₃ -0.2 M HF	1×10				
	H ₂ O	2×2				
Condition	0.5 M HCl–1 M HF	4×1				
Load	0.5 M HCl–1 M HF	3				
Elute Matrix	0.005 M HCl–1 M HF	3 × 1				
Collect W	3 M HNO ₃ –0.2 M HF	3×2				



Parameter	CCR slab melt	Sediment melt	Mantle wedge	Enriched mantle	Galápagos mantle
W (ng/g)	112	2250	10	14	14 ^e
W/Th	0.018	0.21 ^{c,d}	0.19	0.11 ^{b,c}	0.11
Nb/La	0.16	0.16 ^a	0.9 ^f	1.3°	1.4 ^e
$\mu^{182}W$	0 to -12	0	0	0	0 to -6

Table S-3Parameters used for the binary mixing models.

^a Gazel *et al.* (2009).

b K = a + a + a + (2009).

^b König *et al.* (2011). ^c Kurzweil *et al.* (2019).

 $\operatorname{Kurzwell} et ut. (2019).$

^d Kirchenbaur and Münker (2015); Stubbs *et al.* (2022). ^e Calculated from baselt data compiled from https://georga.eu.op.22.N

^e Calculated from basalt data compiled from https://georoc.eu on 22 November 2022 (Geist *et al.*, 2002, 2005, 2006; Gibson and Geist, 2010; Gibson *et al.*, 2012, 2016; Handley *et al.*, 2011; Harpp and Weis, 2020; Harpp *et al.*, 2003; Peterson *et al.*, 2017, 2014). ^f Salters and Stracke (2004).

Table S-4W isotope data for single measurements of samples and in-house reference materials, including valuesnormalised to $^{186}W/^{184}W$ and $^{186}W/^{183}W$.

 Table S-5
 Trace element concentrations of the acid supernatant from reference material JB-2 after the fluoride leaching procedure.

Tables S-4 and S-5 (.xlsx) are available for download from the online version of this article at <u>https://doi.org/10.7185/geochemlet.2321</u>.



Supplementary Figures



Figure S-1 Primitive mantle-normalised trace element patterns for average concentrations of adakites and basanites analysed for W isotopes. Shaded areas represent the entire trace element variability of each group. Primitive mantle values from Palme and O'Neill (2014).



Figure S-2 Primitive mantle-normalised trace element patterns of average measured basanites plotted together with the modelled basanite melt composition. The model calculation assumes low degree melting of an enriched mantle source modified by 5 % slab melt as constrained by the modelled Nb/La and W/Th ratios shown in Figure 2. Also shown is the modelled composition of the Galápagos mantle assuming that the average Galápagos basalt was derived by 11 % batch melting of the mantle source. See text for further explanation. Primitive mantle values from Palme and O'Neill (2014).





Figure S-3 (a) Chemistry yield of different digestion methods for selected trace elements. The fluorideprecipitation digestion was prepared under the same conditions as samples analysed for W isotopes. Normalisation values are the compiled values from for GSJ basaltic reference material JB-2 from Jochum *et al.* (2016). Trace element concentration data provided in Table S-5. (b) Chemistry yield from W separation procedure determined from 1 ‰ aliquots taken after sample digestion and after the separation procedure on selected samples.





Figure S-4 Elution curves of selected elements for matrix separation procedures described in Table S-2. (a) I. Anion exchange chemistry (BioRad AG1x8 100–200 mesh, 10 mL resin). (b) III. TEVA chemistry (Eichrom TEVA 100–150 mesh, 1 mL resin).



Figure S-5 μ^{182} W values of in-house reference materials Granite 232 and Me21 basalt measured over the course of two years. Coloured lines show average values of the samples. Lightly coloured areas mark the 2 s.d. calculated for each sample or method.



Supplementary Information References

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