

1 A short, sharp pulse of potassium-rich volcanism during continental collision  
2 and subduction  
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18 **ABSTRACT**

19 **Potassic volcanic rocks are characteristic of collisional tectonic zones, with recycling**  
20 **of continental crust playing an important role in their generation. Potassium-rich partial**  
21 **melts and/or fluids derived from subducted continental material initiate and/or mix with**  
22 **mantle-derived melts and then erupt at the surface with varying degrees of interaction**  
23 **with the overlying lithosphere. The details of how continental material incorporates into**  
24 **mantle melts are, however, uncertain. In particular, the depths from which the**  
25 **potassium-rich fluids/melts are released from the continental material and then reacts**

26 **with the mantle-derived melts remain a subject of debate. We have measured the boron**  
27 **isotope composition of volcanic rocks from Western Anatolia that erupted between 52–**  
28 **0.1 Ma, and span the lifetime of collisional events from initial arc-type eruptions to post-**  
29 **collisional volcanism. These data and other geochemical indices show that ultra-potassic**  
30 **volcanism was mainly confined to a narrow window between ~20–15 Ma, consistent with**  
31 **recycling of high-pressure phengite, with the timing of the potassic volcanism coincident**  
32 **with slab roll-back and break-off.**

33

## 34 INTRODUCTION

35 Subduction of the lithosphere during collisional tectonics results in the production of melt  
36 in the overlying mantle that ascends to form volcanic rocks. The petrologic, elemental and  
37 isotopic composition of these rocks reflects varying admixtures of; a) recycled components  
38 from the subducted slab, b) melts of the overlying mantle and c) assimilation of upper crustal  
39 material. In particular, subduction zone volcanic rocks are commonly enriched in fluid mobile  
40 elements, such as the alkali elements and boron (Spandler and Pirard, 2013). It is noteworthy,  
41 however, that potassium-rich rocks (>3 wt.% K<sub>2</sub>O) with high MgO concentrations >3 wt.%  
42 (e.g., lamproites and shoshonites) are largely restricted to continent-continent collision settings,  
43 where they most commonly form during the post-collisional phase of volcanism (Foley et al.,  
44 1987). Hence, continental crust recycling is commonly invoked as playing an important role in  
45 the generation of these potassic lavas (Prelević et al., 2008; Çoban et al., 2012; Ersoy and  
46 Palmer, 2013). The mechanism(s) by which potassic melts are produced is, however, subject  
47 to debate. For example, it is proposed that they are generated by; a) partial melting of sub-  
48 continental lithospheric mantle by rising asthenospheric mantle (Xu et al., 2017), b)  
49 metasomatism of harzburgite by partial melts of glimmerite (Förster et al., 2017), c) partial  
50 melting of phlogopite-harzburgite (Condamine et al., 2016), and d) partial melting of

51 phlogopite-free mixtures of phyllite and dunite (Wang et al., 2017). An important constraint on  
52 the mechanism operating in any particular setting is provided by the depth at which  
53 continentally-sourced K-rich melts/fluids mix with the mantle component of potassic lavas.

54

## 55 **WESTERN ANATOLIA VOLCANIC PROVINCE**

56 Western Anatolia (WA) forms part of the Alpine-Himalayan orogenic belt and contains  
57 a record of volcanism linked to the subduction of Tethyan oceanic crust, followed by  
58 continental collision, crustal subduction and accretion (e.g. Pourteau et al., 2016). The region  
59 has received extensive study (see Ersoy and Palmer (2013) and papers therein) and while there  
60 are subtle variations in the timing of events across the area, overall there is a progression from  
61 low-K, calc-alkaline volcanism in the Eocene and Oligocene, to a period of high-K calc-  
62 alkaline and associated shoshonitic-ultrapotassic rocks in the Miocene; ending with the  
63 eruption of Na-alkaline basalts in the Late Miocene to Holocene. This volcanic sequence  
64 reflects a progression from; arc volcanism – continental collision – post-collisional volcanism  
65 in extensional basins – final stage, OIB-like, asthenosphere-derived volcanism.

66 We have undertaken a boron isotope ( $\delta^{11}\text{B}$ ) study of samples that span the full range of  
67 Eocene-Quaternary volcanism observed in WA (Fig. 1a). Together with previously published  
68  $\delta^{11}\text{B}$  (Tonarini et al., 2005) and other geochemical data (Ersoy and Palmer, 2013) from WA,  
69 we have sought to obtain a more detailed understanding of the genesis of high-K volcanic rocks  
70 in continental collision zones.

71

## 72 **BORON ISOTOPE GEOCHEMISTRY**

73 The  $\delta^{11}\text{B}$  values and boron concentrations [B] of WA volcanic rocks range from -31.3 to  
74 +6.1 ‰ and 3.4 to 74.8  $\mu\text{g/g}$ , respectively (GSA Data Repository<sup>1</sup>). Boron is incompatible  
75 during fractional crystallization of the volcanic rock types considered here (Leeman and Sisson,

76 1996), and within the calc-alkaline suite, the rocks with the highest SiO<sub>2</sub> and lowest MgO have  
77 the highest [B]. Overall, however, there is no significant correlation between [B] or δ<sup>11</sup>B values  
78 with SiO<sub>2</sub> or MgO concentrations across the entire data set, or within any of the other volcanic  
79 groups (Fig. DR1, Table DR2). Similarly, no significant correlations exist between [B] or δ<sup>11</sup>B  
80 values with Sr, Nd or Pb isotope ratios (Fig. DR2). Additionally, [B] and δ<sup>11</sup>B values of the  
81 local continental crust, the Paleozoic-Mesozoic Menderes Massif, (4.3 to 25.8 μg/g and -14.6  
82 to -11.0 ‰, respectively; Table DR2) do not provide appropriate end-members to describe the  
83 [B]-δ<sup>11</sup>B relationships of the WA volcanic rocks by assimilation-fraction crystallization (AFC)  
84 processes (Fig. 1b).

85 Like potassium, boron is highly mobile during subduction and its isotope composition is  
86 a tracer of the processes and pathways of recycling and fluid transfer during collisional  
87 tectonics. All collisional zone volcanic rocks, regardless of provenance, have elevated boron  
88 concentrations [B] relative to the depleted mantle ([B] ~ 0.1 μg/g; δ<sup>11</sup>B -7 ‰; Marschall et al.,  
89 (2017)). Hence, the δ<sup>11</sup>B values of collisional zone volcanic rocks are dominated by  
90 contributions from the slab and the upper plate through which the lavas erupted. In island arc  
91 settings, there is a general trend from heavier δ<sup>11</sup>B values (up to +10 ‰) and lower Nb/B in  
92 volcanic rocks erupted close to the subduction front, towards more mantle-like δ<sup>11</sup>B values and  
93 higher Nb/B at greater distances behind the subduction front and greater depths to the  
94 subducted plate (De Hoog and Savov, 2017) (Fig. 2). Continental arcs (such as the Andes)  
95 show similar trends to island arcs, but with lighter δ<sup>11</sup>B values (down to -10 ‰) that reflect  
96 upper crustal assimilation. Approximately half the WA volcanic rocks fall within the range of  
97 δ<sup>11</sup>B values observed in island and continental arcs, but the remainder have lighter δ<sup>11</sup>B values,  
98 suggesting that they also contain boron from an <sup>11</sup>B-depleted source (Fig. 2).

99

## 100 TEMPORAL EVOLUTION

101           The temporal evolution of boron isotopes and other geochemical signatures yields  
102 insights into the origin of the high-K WA volcanic rocks. Overall, the period from the Lower  
103 Eocene to the present can be divided into three overlapping phases (Fig. 3). From the Lower  
104 Eocene to Lower Miocene (~52 to 23 Ma), the  $\delta^{11}\text{B}$  systematics are typical of those seen in the  
105 arc settings (De Hoog and Savov, 2017) (Fig. 3a-b). There then follows a period of more  
106 heterogeneous (post-orogenic/collisional) volcanism during the Lower to Upper Miocene (~23  
107 to 14 Ma) that contains rocks with arc-type signatures, but this also marks the period when the  
108 ultra-potassic rocks with the highest [B] and most negative  $\delta^{11}\text{B}$  values were erupted. The final  
109 period of volcanism, from the Upper Miocene to Recent (~12 to 0.1 Ma), marks the eruption  
110 of rocks with more mantle-like signatures (Fig. 3a-c).

111           We suggest here, that incorporation of boron derived from phengite is the likely source  
112 of the negative  $\delta^{11}\text{B}$  values. Phengite, with  $\delta^{11}\text{B}$  values of -29 ‰, is recorded in exhumed ultra-  
113 high pressure (UHP) rocks from the Luliang Shan terrane in NW China (Menold et al., 2016),  
114 where it is suggested that it formed in continental crust subducted to depths of ~75 km. These  
115 light values likely arise because  $^{11}\text{B}$  is progressively fractionated into the fluid phase during  
116 devolatilization as the slab is subducted into the mantle (Marschall et al., 2007), leaving the  
117 residual phengite with increasingly light  $\delta^{11}\text{B}$  values. Although this process also results in  
118 progressive depletion of boron in the slab, [B] of up to 250  $\mu\text{g/g}$  is recorded in UHP phengite  
119 (Menold et al., 2016). Thus, incorporation of boron derived from recycling of deeply subducted  
120 phengite may account for the light  $\delta^{11}\text{B}$  values observed in some WA volcanic rocks. Phengite  
121 pressure depends strongly on the water activity, but in sediment-rich systems it typically breaks  
122 down at 2.5-5.0 GPa to form a K-rich melt that rises into the overlying mantle wedge to form  
123 phlogopite or K-richterite (Schmidt and Poli, 2014). These melts are then suggested to lead to  
124 the formation of ultrapotassic volcanic rocks in collisional settings (Zheng et al., 2011).

125           The  $\delta^{11}\text{B}$  values and [B] in exhumed phengite from the Luliang Shan terrane range from  
126 -29 to -7 ‰ and 50 to 250  $\mu\text{g/g}$ , respectively (Menold et al., 2016). This range and absence of  
127 a clear correlation between [B] and  $\delta^{11}\text{B}$  values likely reflects the geochemical and  
128 mineralogical heterogeneity (in space and time) of subducted continental crust, particularly for  
129 trace elements such as boron. When this observation is coupled with the evolving P-T  
130 conditions and fluid-flow regimes during subduction, a direct correlation between  $\delta^{11}\text{B}$  values  
131 and potassium enrichment in individual volcanic rocks is not necessarily expected.  
132 Nevertheless, formation of phengite with light  $\delta^{11}\text{B}$  values is likely a common feature in  
133 continental material subducted to UHP conditions (Konrad-Schmolke and Halama, 2014;  
134 Menold et al., 2016), and the coincidence between the timing of the light  $\delta^{11}\text{B}$  values measured  
135 in the WA volcanic rocks with the period of potassic volcanism is supportive of recycling  
136 deeply subducted continental crust.

137           Further support for this hypothesis comes from the evolution of the  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio of  
138 WA volcanic rocks, which show a discrete interval of high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios (from ~2 to 6)  
139 erupted between ~20–15 Ma (Fig. 3d). This observation is important because the  $\text{K}_2\text{O}/\text{Na}_2\text{O}$   
140 ratio produced during partial melting of pelitic rocks is dependent on pressure (Schmidt, 2015),  
141 with a 10% metapelite partial melt yielding a  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio of 5 at 5 GPa, compared to a  
142  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio of 1.5 at 3 GPa. The  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio is also dependent on the water content of  
143 the metapelite, with experiments conducted with 7 wt. %  $\text{H}_2\text{O}$  yielding a  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio of  
144 <1.75 at 5 GPa compared to a ratio >5 at the same pressure with 2 wt. %  $\text{H}_2\text{O}$  (Schmidt, 2015).  
145 Comparison of the WA data and experimental studies suggests, therefore, that high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$   
146 ratio melts were generated at pressures of >3 GPa. Evidence that the K-rich rocks were derived  
147 from deep mantle processes also comes from the evolution of Tb/Yb and Ti/Yb ratios in the  
148 WA volcanic rocks (Fig. 3e-f). Both ratios increase in ultrapotassic rocks erupted between 20-

149 15 Ma, and are consistent with an increased presence of garnet in the source – i.e. an increase  
150 in the depth of mantle melting (Ersoy and Palmer, 2013).

151 Overall, the strongly negative  $\delta^{11}\text{B}$  values are most compatible with breakdown/partial  
152 melting of phengite subducted to pressures of >3 GPa to produce phlogopite/K-richterite in the  
153 overlying mantle. This hypothesis precludes a model of partial melting of phlogopite-free  
154 mixtures of phyllite and dunite (Wang et al., 2017), and the absence of negative  $\delta^{11}\text{B}$  values  
155 and high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios in the OIB-type volcanics (Fig. 3) suggests that asthenospheric melts  
156 did not play a direct role in generation of the WA ultrapotassic volcanism (cf. Xu et al., 2017).  
157 Both the phlogopite-harzburgite and glimmerite-harzburgite experimental studies yield melts  
158 with  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios similar to those observed in the WA ultrapotassic rocks (Condamine et  
159 al., 2016; Förster et al., 2017). Hence, the  $\delta^{11}\text{B}$  –  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  data support a model whereby  
160 continental material is subducted to depths of >75 km at which point phengite with strongly  
161 negative  $\delta^{11}\text{B}$  breaks down to yield potassic melts that initiate melting of the overlying  
162 lithospheric mantle to produce the ultrapotassic volcanism.

163 Mantle tomographic images of Western Anatolia have been interpreted to indicate that  
164 there was a “dramatic increase” in slab roll-back triggered by slab tearing in WA at ~15 Ma  
165 (van Hinsbergen et al., 2010) – i.e. coincident with eruption of the high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio  
166 volcanic rocks. This event may thus have accelerated descent of the subducted continental  
167 material into a P-T regime that initiated phengite breakdown and contamination of the  
168 overlying mantle. Partial melting of the contaminated mantle then led to a brief period (~5  
169 Myr) of high-potassium volcanism, with the variable  $\delta^{11}\text{B}$  and  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios reflecting the  
170 heterogeneous nature of subducted continental material (Soder and Romer, 2018). The  
171 increased slab roll-back led to inflow of uncontaminated asthenospheric mantle, which abruptly  
172 terminated the high-potassium volcanism and initiated OIB-like Na-alkaline volcanism.

173 Advances in seismic tomography have allowed for the identification of detached slabs  
174 throughout the mantle and for the correlation of mantle slabs to specific orogens (van der Meer  
175 et al., 2018). The timing of slab detachment is generally based on dating metamorphic and  
176 volcanic processes within an orogeny that may take place over a period of ~100 Myr. The age  
177 range of slab detachment and can then be used to provide upper and lower bounds for the rate  
178 of slab sinking and mantle viscosity. If, as we hypothesize, high-potassium volcanism is  
179 directly linked to slab roll-back and detachment it may be possible to provide a specific date  
180 for initiation of this process, thereby providing closer constraints on fundamental processes  
181 operating in the upper mantle.

182

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264

265 **FIGURE CAPTIONS**

266 Figure 1.

267 (a)  $K_2O$  wt.% vs  $SiO_2$  wt.%. Samples analysed for  $\delta^{11}B$  shown in bold, with other data  
268 from Ersoy and Palmer (2013) and references therein.

269 (b)  $\delta^{11}B$  ‰ vs B  $\mu g/g$ . Colours of symbols reflect classification in Figure 1a. Stars are from  
270 Menderes Massif. Data from this study and Tonarini et al. (2005).

271 Figure 2. Nb/B vs  $\delta^{11}B$  ‰. Symbols as in Figure 1. Arc data from De Hoog and Samov (2017)  
272 and references therein. WA data from Ersoy and Palmer (2013) and references therein.

273 Figure 3. Geochemical evolution of Western Anatolian volcanic rocks. Samples analysed for  
274  $\delta^{11}B$  shown in bold, with other data from Ersoy and Palmer (2013) and references  
275 therein.

276 (a)  $\delta^{11}B$ , (b) [B], (c)  $K_2O$ , (d)  $K_2O/Na_2O$ , (e) Tb/Yb, (f) Ti/Yb

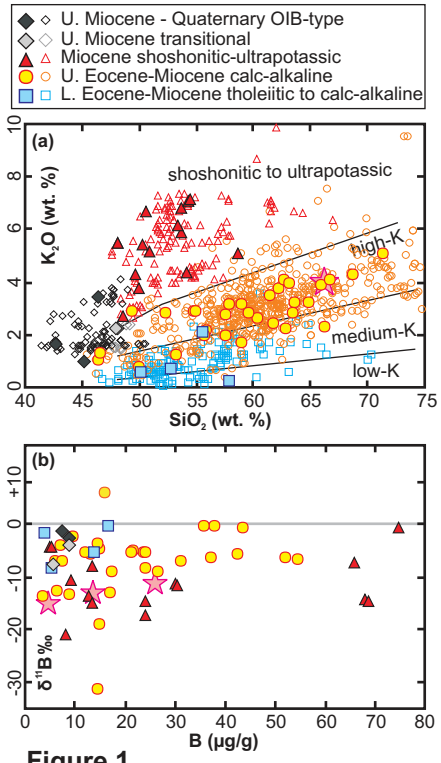


Figure 1

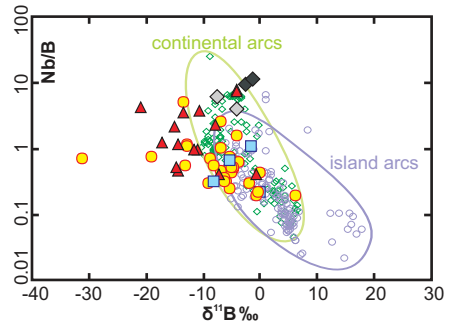


Figure 2

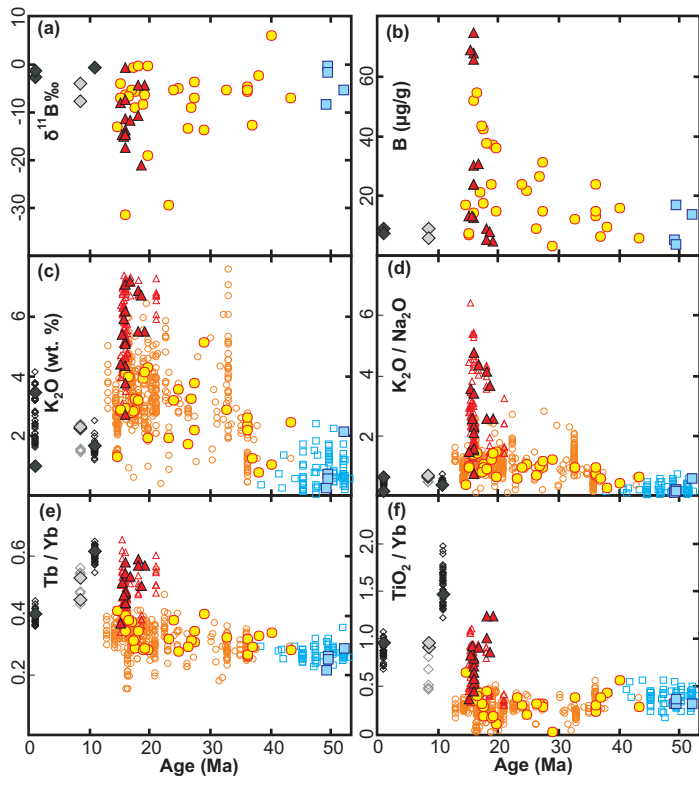


Figure 3

# A short, sharp pulse of potassium-rich volcanism during continental collision and subduction

## **SUPPLEMENTARY FILE**

### **ANALYTICAL METHODS**

The analytical method for determining the boron concentration and isotope composition of the samples has been adapted from Wei et al. (2013). All the reagents used were high purity and all the sample processing took place in clean laboratories equipped with boron-free HEPA filters at the University of Southampton.

Approximately 100 mg of rock powder was accurately weighed and transferred into a 7 ml screw top PFA vial, together with 100  $\mu$ L of 1% mannitol, 100  $\mu$ L H<sub>2</sub>O<sub>2</sub> and 1 mL 24 M HF. The vial was sealed and placed on a hot plate for 3 days at 60°C. A white precipitate, consisting largely of fluorite, was present in the sample solution after this time. Dissolution of this precipitate and analysis by inductively coupled plasma mass spectrometry (ICP-MS) revealed that it did not contain any detectable boron, in accordance with previous observations (Nakamura et al., 1992; Wei et al., 2013). After dissolution, 0.5 mL of the sample was added to 1.5 mL of water in a polypropylene centrifuge tube. After centrifuging, the supernatant was transferred to another 7 mL PFA vial and a further 2 mL of water was added to yield a 3 M HF solution.

The boron concentration was determined by taking 0.1 mL of the 3 M HF sample solution and diluting to 5 mL with 3% HNO<sub>3</sub> containing a 10 ng/g Be internal standard. The boron concentration was then determined using a Thermo Element high-resolution (HR) ICP-MS against a range of 0 to 5 ng/g boron standards (also containing 10 ng/g Be).

Boron was separated from the solution using Bio-Rad AG MP-1 anion exchange resin. The columns consisted of a polypropylene funnel fitted with a porous frit. A fresh aliquot of ~100  $\mu$ L of resin was loaded into the stem of the funnel for each separation. The overall ion



exchange chromatography procedure is summarized in Table DR1. The sample load volume was adjusted so that ~100 ng of boron was added to the column. The boron fraction was collected in a 7 mL PFA vial to which 10  $\mu$ L of 1% mannitol was added and the solution was evaporated to dryness at 55°C.

The sample was taken up in 0.5 mL of 0.5 M HNO<sub>3</sub> to yield a solution with ~200 ng/g boron. Boron isotope analyses were then carried out using a Thermo Neptune multi-collector (MC) ICP-MS following the method described in Foster (2008) that was modified with the use of a 0.3 M HF/0.5 M HNO<sub>3</sub> wash solution to speed up the wash-out time. The NIST SRM 951 boric acid standard (200 ng/g) was used during the sample-standard bracketing and to define the  $\delta^{11}\text{B}$  values of the samples. Typical in-run  $2\sigma$  precisions were <0.2 ‰.

During this study, all samples were analyzed in batches of 10. Each batch consisted of duplicates of 4 powdered rock samples, a powdered rock reference material and a blank. Thus each sample was independently analyzed for both its concentration and  $\delta^{11}\text{B}$  value at least twice, and 7 samples were analyzed in triplicate. The blank after sample dissolution was always <0.5 ng and typically <0.1 ng. The blank associated with the ion exchange chromatography was always <1 ng of boron and typically <0.3 ng (compared to a sample analyte of ~100 ng of boron). The largest difference between the highest and lowest  $\delta^{11}\text{B}$  replicate analyses of a sample was 1.0 ‰, with the average difference being 0.3 ‰ (Table DR2). The largest difference between the highest and lowest boron concentration [B] replicate analyses of a sample was 10.7 % of the absolute value, with the average difference being 3.7 %. During this study, 10 analyses of standard IAEA-B5 (basalt from Etna volcano; Gonfiantini et al., 2003) yielded an average  $\delta^{11}\text{B}$  value of  $-4.2 \pm 0.2$  ‰ ( $2\sigma$ ) and an average [B] of  $9.2 \pm 0.2$   $\mu\text{g/g}$  ( $2\sigma$ ). These values compare well with values previously obtained for this reference material (Table DR3).

In addition to the 42  $\delta^{11}\text{B}$  and [B] data listed in Table 2, Tonarini et al. (2005) report data for 16 WA volcanic rocks. They did not analyse the IAEA-B5 reference material, but they report a  $\delta^{11}\text{B}$  value of  $7.3 \pm 0.4 \text{ ‰}$  for the GSJ-JB2 basalt reference material. Four analyses of this reference material in this study yielded average  $\delta^{11}\text{B}$  and [B] values of  $7.2 \pm 0.2 \text{ ‰}$  and  $29.4 \pm 0.7 \text{ } \mu\text{g/g}$ , respectively. Hence, the  $\delta^{11}\text{B}$  values within the two data sets are directly comparable.

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## FIGURE CAPTIONS

Figure DR1.

Harker diagrams for WA volcanic rocks

(a) [B]  $\mu\text{g/g}$  vs.  $\text{SiO}_2$  wt%, (b) [B]  $\mu\text{g/g}$  vs. MgO wt%, (c)  $\delta^{11}\text{B}$  ‰ vs.  $\text{SiO}_2$  wt%, (d)  $\delta^{11}\text{B}$  vs. MgO wt%. Major element data from Ersoy and Palmer (2013), and references therein.

Figure DR2.

[B] and  $\delta^{11}\text{B}$  values versus radiogenic isotope ratios

(a) [B]  $\mu\text{g/g}$  vs  $^{87}\text{Sr}/^{86}\text{Sr}$ , (b)  $\delta^{11}\text{B}$  ‰ vs  $^{87}\text{Sr}/^{86}\text{Sr}$ , (c)  $\delta^{11}\text{B}$  ‰ vs  $^{143}\text{Nd}/^{144}\text{Nd}$ , (d)  $\delta^{11}\text{B}$  ‰ vs  $^{208}\text{Pb}/^{204}\text{Pb}$ . Radiogenic isotope data from Ersoy and Palmer (2013), and references therein.

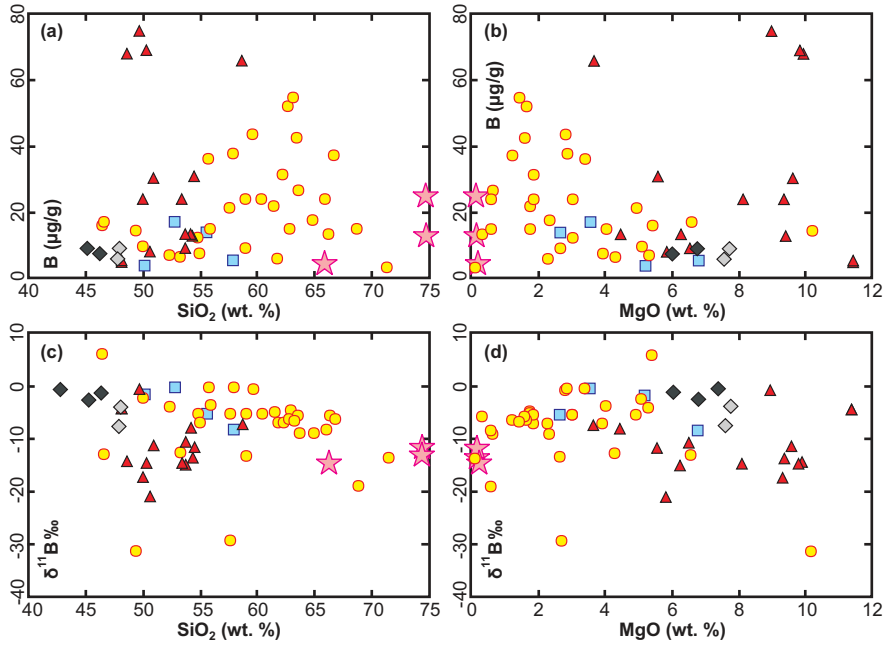


Figure DR1

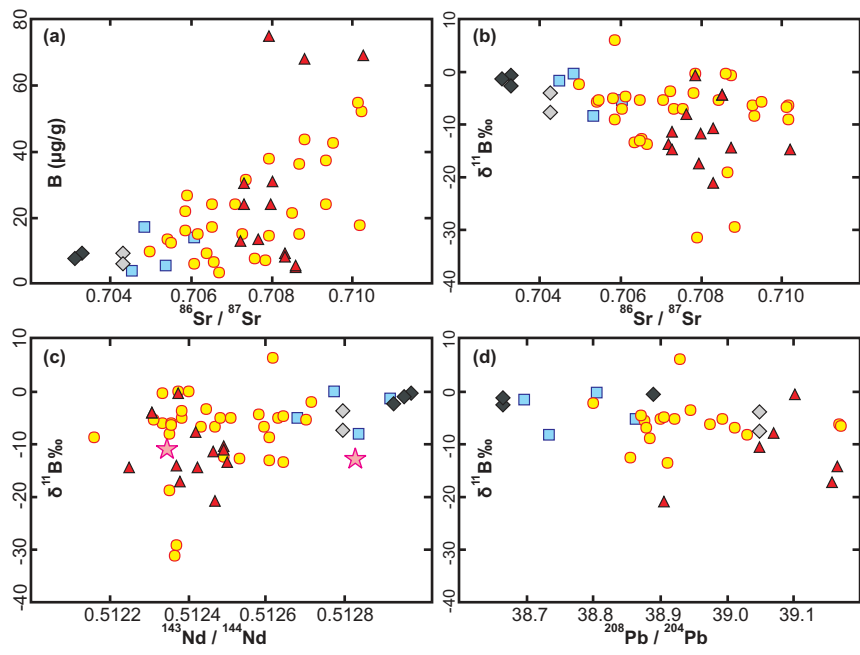


Figure DR2

Table DR1  
Ion exchange chromatography procedure

<b>Step</b>	<b>Operation</b>
Step 1	Resin washing and conditioning 2.5 mL H <sub>2</sub> O 0.5 mL 24 M HF 1.5 mL H <sub>2</sub> O
Step 2	Sample loading 3 M HF (volume adjusted according to sample)
Step 3	Matrix elution 2 x 0.5 mL H <sub>2</sub> O 8.5 mL 0.1 M HCl
Step 4	Boron collection 1.2 mL 24 N HF

Table DR2.

Boron concentration and isotope data for samples analysed in this study (UTM coordinates give sample location)

Sample (UTM)	B concentration ( $\mu\text{g/g}$ )				$\delta^{11}\text{B}$ (‰)			
	1 <sup>st</sup> run	2 <sup>nd</sup> run	3 <sup>rd</sup> run	mean	1 <sup>st</sup> run	2 <sup>nd</sup> run	3 <sup>rd</sup> run	mean
<i>Early Eocene orogenic</i> (Kizderbent volcanics)								
G5 (0651592/4488750)	5.2	5.1		<b>5.2</b>	-8.3	-8.3		<b>-8.3</b>
G28 (0651592/4488750)	16.9	16.8	16.6	<b>16.8</b>	-0.6	-0.5	0.2	<b>-0.3</b>
G45 (0749558/4499472)	3.8	3.7		<b>3.8</b>	-1.7	-1.6		<b>-1.6</b>
G48 (0737486/4502470)	14.2	13.6	13.9	<b>13.9</b>	-5.2	-5.3	-5.7	<b>-5.4</b>
<i>Middle Eocene – Miocene orogenic</i> (Late Eocene Balıklıçeşme volcanics)								
B5 (0492827/4448313)	16.1	16.3	16.0	<b>16.1</b>	6.3	6.2	5.8	<b>6.1</b>
B11 (0500469/4459685)	12.9	13.3		<b>13.1</b>	-5.5	-5.8		<b>-5.7</b>
B12 (0486130/4466913)	14.6	14.9		<b>14.7</b>	-4.6	-4.7		<b>-4.7</b>
B17 (0473433/4454350)	23.1	24.0	23.7	<b>23.6</b>	-5.7	-5.3	-4.8	<b>-5.3</b>
B35 (0485295/4455090)	9.9	9.3		<b>9.6</b>	-2.2	-2.2		<b>-2.2</b>
C15 (0481003/4413380)	6.4	6.0		<b>6.2</b>	-12.6	-13.1		<b>-12.8</b>
C42 (0466010/4432014)	6.2	5.6		<b>5.9</b>	-7.0	-7.3		<b>-7.1</b>
(Oligocene Kirazlı volcanics)								
B21 (0477628/4444050)	3.4	3.4		<b>3.4</b>	-13.7	-13.5		<b>-13.6</b>
C7 (0480017/4430858)	11.9	12.0		<b>12.0</b>	-5.2	-5.2		<b>-5.2</b>
C9 (0477916/4420541)	14.6	14.4	14.7	<b>14.6</b>	-3.8	-3.7	-4.1	<b>-3.8</b>
C31 (0497168/4425055)	26.5	26.7		<b>26.6</b>	-8.9	-9.4		<b>-9.1</b>
C36 (0474152/4433482)	21.0	21.9		<b>21.5</b>	-5.1	-4.8		<b>-5.0</b>
(Oligocene Hallaçlar volcanics)								
HG2 (0530735/4407610)	31.0	31.1		<b>31.1</b>	-6.8	-7.0		<b>-6.9</b>
HG9 (0536865/4436733)	24.0	24.3	23.9	<b>24.1</b>	-5.0	-5.4	-5.1	<b>-5.2</b>
(Oligocene Keşan volcanics)								
K20 (0469494/4521168)	8.5	9.4		<b>9.0</b>	-13.2	-13.2		<b>-13.2</b>
(Miocene Yuntdağı volcanics)								



129 (0540981/4353496)	15	14.3		<b>14.7</b>	-19.1	-19.1	5.8	<b>-19.1</b>
(Miocene Yağcıdağ volcanics)								
510 (0657381/4302983)	49.7	54.6		<b>52.1</b>	-6.1	-6.3		<b>-6.2</b>
YF2 (0657381/4302983)	53.5	55.4	54.1	<b>54.3</b>	-6.6	-6.5	-6.3	<b>-6.5</b>
(Miocene Eğreltidağ volcanics)								
521 (0657795/4308366)	25.1	23.1		<b>24.1</b>	-8.6	-8.1		<b>-8.4</b>
(Miocene Sevinçler volcanics)								
718 (0652561/4322172)	36.7	37.4		<b>37.1</b>	-6.4	-6.4		<b>-6.4</b>
(Miocene Miocene Asitepe volcanics)								
754 (0636380/4309275)	42.8	42.1		<b>42.5</b>	-5.7	-5.3		<b>-5.5</b>
(Miocene Yaylaköy volcanics)								
L36 (0453515/4270500)	21.7	20.5		<b>21.1</b>	-5.6	-5.8		<b>-5.4</b>
(Miocene Armağandağ volcanics)								
L47 (0451794/4236840)	43.7	43.2		<b>43.5</b>	-0.8	-0.8		<b>-0.8</b>
(Miocene Kuzayır lamproite)								
518 (0660886/4311660)	9.1	9.3		<b>9.2</b>	-11.2	-10.2		<b>-10.7</b>
528 (0660886/4311660)	8.2	7.8		<b>8.0</b>	-20.8	-21.2		<b>-21.0</b>
(Miocene Doğanca lamproite)								
K17 (0475167/4528879)	4.8	5.1		<b>5.0</b>	-4.0	-4.4		<b>-4.2</b>
K17B (0475167/4528879)	4.9	5.4		<b>5.2</b>	-4.3	-4.1		<b>-4.2</b>
(Miocene Kayacık volcanics)								
756 (0601705/4305141)	16.7	18.0		<b>17.4</b>	-9.1	-8.8		<b>-8.9</b>
(Miocene Güre lamproite)								
822 (0679728/4281490)	66.2	71.2		<b>68.7</b>	-14.7	-14.8		<b>-14.7</b>
(Miocene Karaburun volcanics)								
L30 (0458200/4275780)	14.1	14.7		<b>14.4</b>	-31.4	-31.3		<b>-31.3</b>
(Miocene Orhanlar basalt)								
536 (0680006/4311835)	24.5	23.7		<b>24.1</b>	-17.2	-17.4		<b>-17.3</b>
541 (0679810/4310909)	67.3	68.5		<b>67.9</b>	-14.7	-14.2		<b>-14.4</b>
543 (0679836/4310901)	72.8	76.7		<b>74.8</b>	-0.5	-1.0		<b>-0.8</b>
(Miocene Naşa basalt)								

746 (0671372/4333717)	13.4	13.6	<b>13.5</b>	-8.0	-8.2	<b>-8.1</b>
<i>Transitional – Miocene</i>						
(Late Miocene Kabaklar basalt)						
520-1 (0671542/4298101)	5.9	5.7	<b>5.8</b>	-7.4	-7.6	<b>-7.5</b>
<i>Basement Rocks</i>						
(Menderes Massif - gneiss)						
G01 (0673572/4300943)	13.4	13.1	<b>13.3</b>	-13.3	-12.9	<b>-13.1</b>
G02 (0673572/4300943)	24.9	26.7	<b>25.8</b>	-11.3	-10.8	<b>-11.0</b>
(Menderes Massif - Rahmanlar granite)						
Y23-2 (0674406/4302063)	4.1	4.4	<b>4.3</b>	-14.1	-15.1	<b>-14.6</b>

Table DR3.

Boron concentration and isotope data for IAEA-B5 reference material

<b>Source</b>	<b>[B] (<math>\mu\text{g/g}</math>) <math>\pm 2\sigma</math></b>	<b><math>\delta^{11}\text{B}</math> (<math>\text{‰}</math>) <math>\pm 2\sigma</math></b>
This study	$9.2 \pm 0.2$	$-4.2 \pm 0.2$
Gonfiantini et al., 2003	$10.0 \pm 1.2$	$-4.1 \pm 2.7$
Pi et al., 2014	$9.3 \pm 0.1$	$-3.9 \pm 0.2$
Romer et al., 2014	$10.0 \pm 1.0$	$-3.7 \pm 0.7$
Hansen et al., 2017		$-4.3 \pm 0.2$
Berryman et al., 2017	$9.3 \pm 0.4$	$-4.3 \pm 0.2$