1	Crustal Recycling by Subduction Erosion in the central Mexican
2	Volcanic Belt
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# 35 Abstract

36 Recycling of upper plate crust in subduction zones, or 'subduction erosion', is a major 37 mechanism of crustal destruction at convergent margins. However, assessing the impact 38 of eroded crust on arc magmas is difficult owing to the compositional similarity between 39 the eroded crust, trench sediment and arc crustal basement that may all contribute to arc 40 magma formation. Here we compare Sr-Nd-Pb-Hf and trace element data of crustal 41 input material to Sr-Nd-Pb-Hf-He-O isotope chemistry of a well-characterized series of 42 olivine-phyric, high-Mg# basalts to dacites in the central Mexican Volcanic Belt (MVB). 43 Basaltic to andesitic magmas crystallize high-Ni olivines that have high mantle-like 44  $^{3}$ He/ $^{4}$ He = 7-8 R<sub>a</sub> and high crustal  $\delta^{18}$ O<sub>melt</sub> = +6.3-8.5‰ implying their host magmas to be 45 near-primary melts from a mantle infiltrated by slab-derived crustal components. 46 Remarkably, their Hf-Nd isotope and Nd/Hf trace element systematics rule out the 47 trench sediment as the recycled crust end member, and imply that the coastal and 48 offshore granodiorites are the dominant recycled crust component. Sr-Nd-Pb-Hf isotope 49 modeling shows that the granodiorites control the highly to moderately incompatible 50 elements in the calc-alkaline arc magmas, together with lesser additions of Pb- and Sr-51 rich fluids from subducted mid-oceanic ridge basalt (MORB)-type altered oceanic crust 52 (AOC). Nd-Hf mass balance suggests that the granodiorite exceeds the flux of the trench 53 sediment by at least 9-10 times, corresponding to a flux of ≥79-88 km³/km/Myr into the 54 subduction zone. At an estimated thickness of 1500-1700 m, the granodiorite may 55 buoyantly rise as bulk 'slab diapirs' into the mantle melt region and impose its trace 56 element signature (e.g. Th/La, Nb/Ta) on the prevalent calc-alkaline arc magmas. Deep 57 slab melting and local recycling of other slab components such as oceanic seamounts 58 further diversify the MVB magmas by producing rare, strongly fractionated high-La 59 magmas and a minor population of high-Nb magmas, respectively. Overall, the central 60 MVB magmas inherit their striking geochemical diversity principally from the slab, thus 61 emphasizing the importance of continental crust recycling in modern solid Earth relative 62 to its new formation in modern subduction zones.

# 63 1. INTRODUCTION

Subduction zone magmas share remarkable compositional similarities with the
continental crust. This has triggered a longstanding and controversial debate regarding
whether the continental crust was extracted from the Earth's mantle by processes similar
to those of modern convergent margins (e.g. Harrison, 2009; Plank, 2004; Stern, 2011;
Taylor, 1967). A pivotal question in this debate is the extent to which subduction

69 processing can create the typical fractionated trace element signature of the continental 70 crust, or whether this signature is mostly inherited through perpetual recycling of 71 continental crust in subduction zones (e.g. Plank, 2004; Rudnick, 1995). Continental crust 72 is recycled in subduction zones by means of the oceanic sediment subducted at the 73 trenches ('trench sediment') and by subduction erosion of the upper plate crust (Clift 74 and Vannucchi, 2004; Huene and Scholl, 1991). Trench sediment accumulates by surface 75 erosion of the continental crust and resembles average upper continental crust (Plank, 76 2004; Plank and Langmuir, 1993). Eroded crust is continental crust that is mechanically 77 removed by the subducting slab from forearc basement either by frontal or basal tectonic 78 erosion (Huene et al., 2004; Huene and Scholl, 1991).

79 Trench sediment recycling has been deduced by the strong compositional links 80 between arc magmas and conjugate trench sediments (e.g. Kay, 1980; Kelemen et al., 81 2003; Morris et al., 2002; Morris et al., 1990; Plank, 2004; Plank and Langmuir, 1993), and 82 unequivocally confirmed by the detection of cosmogenic <sup>10</sup>Be in young arc lavas (Morris 83 et al., 2002; Tera et al., 1986). In contrast, subduction erosion was first recognized from 84 geological observations. For example, uplifted igneous plutonic roots of older arcs may 85 be exposed trenchward to modern arcs which suggests a landward retreat of the trench 86 and forearc crustal removal (Huene and Scholl, 1991; Schaaf et al., 1995). Missing crust is 87 also indicated by vertical fore-arc subsidence without horizontal extension or depression 88 (Huene and Scholl, 1991; Ranero and Huene, 2000). The intensity of subduction erosion 89 may vary considerably through time and among different arc-trench systems (Clift and 90 Vannucchi, 2004; Stern, 2011). On a global scale, mass balance calculations show that 91 subduction erosion accounts for about half (~44-50%) of the crust recycled in subduction 92 zones relative to the trench sediment (~42-56%) (Clift et al., 2009; Scholl and Huene, 93 2009). Regionally, eroded crust may even exceed the mass of trench sediment by up to a 94 factor of 10 (Vannucchi et al., 2003). Clearly, in view of these numbers, the recycled 95 eroded crust must leave a chemical imprint on the arc that rivals the influence of the 96 recycled trench sediment.

97 Confirming the recycling of eroded crust in the compositions of arc magmas,

98 however, is a major challenge. The eroded crust mingles with the incoming trench

99 sediment and subducted igneous oceanic basement (AOC, altered oceanic crust), and re-

100 emerges in volcanic arcs together with material from the mantle, and possibly

101 contaminated by the arc's crustal basement. These components must then be

102 distinguished from each other in arc magmas, whereby the eroded crust is similar to

103 trench sediment and arc basement. No unique tracer exists, such as <sup>10</sup>Be for oceanic

104 trench sediment. To add complexity, basal crust from the underside of the upper plate is

- 105 not accessible, which forestalls direct comparison to arc compositions. Nevertheless,
- 106 from comprehensive Sr-Nd-Pb-B isotope and trace element studies of arc magmas,
- 107 evidence for the presence of fore-arc eroded crust has begun to accumulate (e.g. Goss
- 108 and Kay, 2006; Goss et al., 2013; Holm et al., 2014; Kay et al., 2005; Risse et al., 2013;
- 109 Tonarini et al., 2011). The common factor of these studies is that they integrate geological
- and geochemical observations that allow the detection of compositional mismatch
- 111 between arc chemistry and trench input from the subducted slab that may be reconciled
- 112 by crust removed from the fore-arc regions.

113 In the global spectrum of arc magmas, the Mexican margin is a prime setting for 114 tracing the eroded crust in volcanic arcs. First, there is strong evidence for long-term 115 crustal erosion along the Mexican Trench indicated by trench retreat and fore-arc uplift 116 (Clift and Vannucchi, 2004), and by large volumes of missing Mesozoic and Cenozoic 117 crust along the coast (Ducea et al., 2004; Keppie et al., 2012; Morán-Zenteno et al., 1996; 118 Schaaf et al., 1995). Second, the subducted crustal materials - trench sediment, AOC, 119 eroded crust – are obtainable from drill sites at the trench and offshore continental slope 120 as well as from coastal outcrops (exposed Acapulco intrusion, Hernández-Pineda et al., 121 2011; Watkins and Moore, 1981). Since these crustal materials have distinct 122 compositions, they should be traceable in the arc magmas. Here we report the results of 123 comprehensive comparison between Sr-Nd-Pb-Hf-O-He isotope and trace element data 124 of olivine-bearing arc magmas from the central Mexican Volcanic Belt (MVB) and Sr-Nd-125 Pb-Hf isotope and trace elements of relevant crustal input materials from the subducting 126 and overlying slab. Our data imply that crust recycled by subduction erosion controls 127 much of the chemistry of the arc magmas erupted in the central MVB.

128 2. GEOI

GEOLOGICAL SETTING

129 The Mexican Volcanic Belt is an active Pliocene-Quaternary volcanic arc that is related 130 to the subduction of the Cocos and Rivera plates along the Middle American Trench 131 (Figure 1) (e.g. Gómez-Tuena et al., 2007b). The trench runs oblique to the arc volcanic 132 front at an angle of ~17°, because the slab dip decreases eastward and the arc-trench gap 133 widens. In the central MVB, the slab subducts horizontally beneath the forearc and the 134 arc-trench gap measures ~360 km (Pardo and Suarez, 1995; Perez-Campos et al., 2008). 135 The study area in central Mexico comprises the monogenetic Sierra Chichinautzin 136 Volcanic Field that is flanked by the composite volcanoes Nevado de Toluca (west) and 137 Popocatepetl (east) (Figure 1, 2). The volcanoes are constructed on a ~45 km thick sialic 138 crust of Proterozoic granulites and Mesozoic metapelites, granites and limestones (e.g.

139 Ortega-Gutiérrez et al., 2012). An extensional crustal stress regime facilitates magma

- 140 ascent, and mafic and high-Mg# olivine-phyric basalts and andesites are common
- 141 (Gómez-Tuena et al., 2007b; Schaaf et al., 2005; Wallace and Carmichael, 1999).

142 Magma compositions in the central MVB range from basalt to dacites which display 143 considerable diversity in trace elements (e.g. Cai et al., 2014; LaGatta, 2003, and 144 references therein; Martinez-Serrano et al., 2004; Schaaf et al., 2005; Siebe et al., 2004a; 145 Straub et al., 2013a; Straub et al., 2014; Wallace and Carmichael, 1999). For petrogenetic 146 studies it was useful to distinguish between a 'basaltic' (olivine-normative) and 147 'andesitic' (quartz-normative) group, respectively (e.g. Straub et al., 2011b; 2013a; 2014). 148 For the discussion of recycling processes, however, we prefer a division based on the 149 source-sensitive incompatible trace elements (Figure 3). In trace element space, three 150 groups with basaltic and andesitic compositions can be distinguished (see also 151 Appendix A, Figure 1a). The first and far most abundant group (estimated >95 vol% of 152 erupted magmas) are calk-alkaline basalts to dacites (50-67 wt% SiO<sub>2</sub>) which construct 153 the voluminous (several 100 km<sup>3</sup>) composite volcanoes and most of the small-volume ( $\leq 1$ 154 km<sup>3</sup>) monogenetic cones. Calc-alkaline magmas combine low Nb = 4-14 ppm 155 abundances with arc-typical strong enrichments of large-ion lithophile elements (LILE) 156 relative to the rare earth elements (REE) and high-field-strength elements (HFSE). The 157 second group ('high-La') consists of light REE (LREE)-enriched basalts to basaltic 158 andesites that have strongly fractionated trace element patterns with strong enrichments 159 in K<sub>2</sub>O and LREE, relative depletions in Zr-Hf and steep heavy REE (HREE) patterns. 160 'High-La' magmas were first described by Gomez-Tuena et al. (2007a) in the Valle de 161 Bravo west of Nevado de Toluca. In the central MVB, only a few high-La magmas erupt 162 from small, monogenetic volcanoes but these magmas are more common in western 163 Mexico (Gomez-Tuena et al., 2011). The third group consists of Nb-rich (>17-36 ppm), 164 mildly alkaline basalts to basaltic andesites (49-57 wt% SiO<sub>2</sub>). Nb-rich magmas are 165 enriched in LILE, REE and HFSE, and their trace element pattern resemble those of 166 enriched intraplate basalts (LaGatta, 2003; Schaaf et al., 2005; Straub et al., 2013a; Wallace 167 and Carmichael, 1999). Nb-rich magmas are ubiquitous in the rear-arc region of the 168 MVB, but are rare along the arc volcanic front (e.g. Díaz-Bravo et al., 2014; Gómez-Tuena 169 et al., 2007b; Luhr, 1997).

170 In the central MVB, Nb-rich magmas erupt from a small, likely coeval group (ca. 1600-

171 1800 year ago, Siebe, 2000; Siebe et al., 2004b; Straub et al., 2013b) of monogenetic

- 172 volcanoes in the center of the Sierra Chichinautzin, located halfway between
- 173 Popocatepetl and Nevada de Toluca (Figure 2) (e.g. Straub et al., 2013b; Wallace and

174 Carmichael, 1999). These Nb-rich magmas are closely associated with the calc-alkaline

- 175 magmas, erupting from vents only a few kilometers and a few thousands year apart,
- 176 and even from the same volcano (e.g. Suchiooc, Schaaf et al., 2005; Siebe et al., 2004a;
- 177 Straub et al., 2013a; Straub et al., 2014). In our sample set, the Nb-rich magmas are over-
- 178 represented, because they were the target of a more detailed study (Straub et al., 2013a,
- 179 2013b).

# 180 3. ARC MAGMA PETROGENESIS IN THE CENTRAL MVB

181 The impact of slab contributions (such as slab fluids, slab partial melts and more 182 recently 'slab diapirs', hereafter summarily referred to as 'slab components') on arc 183 magmas and its consequences for arc petrogenesis and subduction cycling are at the core 184 of arc research (e.g. Gomez-Tuena et al., 2014; Hacker et al., 2011; Plank, 2004). This 185 question is also intensely debated in the central MVB, where much recent progress was 186 made, and for which a short summary is provided here.

187 The central MVB is constructed on thick continental basement and consequently many 188 studies propose that andesites and dacites evolve from primary basaltic mantle melt by 189 crustal processing (fractional crystallization, crustal assimilation) (e.g. Agustín-Flores et 190 al., 2011; Marquez et al., 1999; Verma, 1999a). However, in recent years evidence has 191 accumulated from several comprehensive petrologic and geochemical studies that the 192 entire range of central MVB basaltic to andesitic (and even dacitic and ryolitic) magmas 193 are near-primary melts from a subduction-modified mantle that pass the crustal 194 basement nearly unchanged (Gomez-Tuena et al., 2007a; Gómez-Tuena et al., 2008; 195 Straub et al., 2011a; Straub et al., 2013a; Straub et al., 2008). In these models high-Ni 196 olivines with up to 5400 ppm Ni play a key role (Appendix A, Figures 1b,c). These 197 olivines crystallize from basaltic and andesitic magmas and have high <sup>3</sup>He/<sup>4</sup>He ratios of 198 7-8 Ra which confirms that their host magmas originate in upper mantle. Moreover, the 199 high Ni concentrations in olivine suggests that these magmas are partial melts of 200 secondary olivine-free pyroxenite segregations in the mantle wedge (Straub et al., 201 2011b). Such segregations formed following the infiltration of silicic components from 202 slab. They melt preferentially relative to the surrounding peridotite in an upwelling 203 mantle and produce a broader range of primary basaltic to dacitic melts that mix variably during ascent to form andesites (Straub et al., 2011a; Straub et al., 2013a; Straub 204 205 et al., 2008). A major implication of this 'pyroxenite model' is that the central MVB 206 magmas are principally mixtures of slab and mantle materials that underwent little, or 207 negligible, processing in the shallow crust. Thus, the budget of their highly incompatible trace elements must be strongly controlled by recycled slab materials with littleinfluence of the subarc mantle.

210 This inference has to date been confirmed by follow-up studies which provided 211 additional insights (e.g. Straub et al., 2013a; 2014). First, the central MVB 'background 212 mantle' (mantle without subduction influence) is highly depleted through serial 213 ('repetitive') melting that is triggered by the continuous hydrous flux from slab since the 214 arc became active in Pliocene. Thus, the mantle wedge is very susceptible to be 215 chemically overprinted by slab additions (2013a; Straub et al., 2008; 2014). The effect of 216 only a few percent melt extraction on the pre-subduction mantle is illustrated in 217 Figure 3, by means of modeling the 'Old Texcal Flow'. This is a monogenetic basalt flow 218 that shows the least slab influence in central Mexico [e.g. lowest SiO2 ~49 wt%, highest 219  $TiO_2 \sim 2$  wt% and lowest Ni in olivines that are only slightly higher than the Ni of 220 olivines in mid-ocean ridge basalts (MORB)], and is considered as best proxy to a melt 221 from the original mantle wedge (Straub et al., 2013a). In incompatible trace elements, the 222 'Old Texcal Flow' resembles a ~3-4% partial melt of the average primitive mantle (or 223 'pyrolite') as given by McDonough and Sun (1995) [see Straub (2013a)]. However, the 224 'Old Texcal Flow' has no end member character in trace element space (Figure 3). While 225 the 'Old Texcal Flow' is per definition a high-Nb basalt (Nb>17 ppm), it has the lowest 226 Nb abundances of this group (Nb=17-19 ppm) and is largely intermediate to calc-227 alkaline and high-Nb series in other incompatible trace elements (Straub et al., 2014). 228 Therefore, primitive mantle cannot be the prevalent background mantle as it would 229 produce melts that are too enriched in HFSE and light REE for the calc-alkaline series. 230 However, a residual of primitive mantle, produced after only >3-10% melt loss, is highly 231 depleted incompatible elements, and can easily be modified by slab additions (Straub et 232 al., 2014). As discussed previously, in the central MVB, most of the incompatible trace 233 elements (including elements Sr, Nd, Pb and Hf which are associated with isotope 234 tracers) are either exclusively, or substantially contributed from the slab (Straub et al., 235 2013a; 2014), excepting only Ti and HREE (Ho-Lu).

Second, regardless of the extent of depletion by melting, the Ti and HREE (Ho-Lu) are
 always controlled by the mantle. In other words, calc-alkaline and high-Nb magmas

- 238 could contain larger amount of slab material without displaying a garnet signature.
- 239 Model calculations for REE that use the most recent partitioning data for fluid and/or
- 240 melt release from slab (Klimm et al., 2008; Skora and Blundy, 2010) show that absorption
- of up to 30% of slab material would not increasing Ho/Lu of the metasomatized mantle
- above MORB levels (Straub et al., 2013a; 2014). This amount agrees well with the

'pyroxenite model' that requires a minimum of 15-18% (and likely more) of a silicic slab
component in the source in order to convert peridotite to olivine-free pryoxenite (2011b;
Straub et al., 2008).

246 In summary, there is a confluence of evidence for strong slab contributions to the 247 mantle source that may make up several tens of percent of the erupted magmas (2014; 248 Gomez-Tuena et al., 2007a; Straub et al., 2011b; 2013a; 2014). At such proportions, the 249 slab components must control the highly incompatible trace element budgets of the 250 magmas. Moreover, slab components may range from strongly fractionated varieties to 251 components that equally mobilize fluid-mobile LILE, HFSE and LREE. Such diversity -252 that likely represents heterogeneous slab material rather than an extreme range of 253 fractionation - would be ideal to produce the trace element diversity of calc-alkaline, 254 high-La and Nb-rich series that are so closely associated in time and space. Thus, the 255 central MVB magmas are not only suitable for more detailed investigations of the impact 256 of the slab flux on arc chemistry, but such studies are also a vital test of the prevailing 257 petrogenetic models.

# 258

# 4. SAMPLES AND DATA FOR THIS STUDY

259 Here we present new  $\delta^{18}$ O data (n=51) for olivine phenocrysts, together with new Hf 260 and Pb isotope ratios of representative bulk rock samples (n= 37 samples). Most of these 261 samples have previously been analyzed for major and trace element abundances, Sr and 262 Nd isotope ratios, and the olivines have been analyzed for composition and <sup>3</sup>He/<sup>4</sup>He 263 (2011b; 2013a; Straub et al., 2008; 2014). In addition, 22 new volcanic rock samples were 264 analyzed for major and trace elements and Sr-Nd-Pb-Hf isotopes, as well as for major 265 element oxide and Ni concentrations of olivines of six samples (Appendix B Tables 1-5). 266 Furthermore, we analyzed up to 22 selected samples of crustal material (xenoliths, 267 basement) for major and trace elements and Sr-Nd-Pb-Hf isotope data (Appendix B 268 Tables 6-9) in order to complement the published data of crustal rocks from the 269 continental basement and offshore central Mexico (Figure 1). All new and previously 270 published data are summarized in Appendix B Table 10.

# 271 4.1. Central Mexican arc volcanic rocks

272 Sample locations for volcanic rocks are shown in Figure 2. Calc-alkaline samples are

- 273 from many monogenetic volcanoes and two composite volcanoes, Popocatepetl and
- 274 Toluca. The three high-La basalts and basaltic andesites are from monogenetic volcanoes
- 275 Yecahuazac Cone, Tuxtepec and St. Cruz. The Nb-rich series are from monogenetic
- 276 volcanoes Suchiooc, Chichinautzin and Texcal Flow.

# 277 4.2. Crustal materials

- Crustal materials used in this study include (i) continental crustal basement on which
  the MVB is constructed, (ii) coastal and offshore crustal basement, and (iii) the
  terrigenous and pelagic sediment and AOC of the Cocos and Pacific plates (Figure 1).
- 281 4.2.1. Continental crustal basement

We obtained new Hf isotope data on crustal xenoliths from Chalcatzingo and Valle de Santiago that have previously characterized for Sr-Nd-Pb isotopes and trace elements by Gómez-Tuena et al. (2008, Chalcatzingo) and Ortega-Gutiérrez et al. (2014, Valle de Santiago). Additional major and trace element data and Sr-Nd-Pb isotope ratios of

286 outcropping crust and crustal xenoliths from within and south of the Mexican Volcanic

287 Belt were compiled from Schaaf et al. (2005, Popocatepetl), Gomez-Tuena et al. (2003;

- 288 2008, Teziutlán (Puebla) and Chalcatzingo), Martinez-Serrano et al. (2004, Toluca),
- 289 Ortega-Gutiérrez et al. (2012; 2014, Puente Negro and Valle Santiago; 2011), and Pérez-
- 290 Gutiérrez et al. (2009, Xolapa terrane).
- 291 4.2.2. Coastal and offshore continental crust
- 292 We obtained coastal and offshore continental crust as proxies to crust recycled by 293 crustal erosion. The coastal samples are from the Eocene Acapulco intrusion that is now 294 exposed at the Pacific coast south of the central MVB (Hernández-Pineda et al., 2011). 295 Offshore samples are from DSDP Leg 66 drill sites that recovered biotite gneiss (Site 489) 296 and granodiorite (Site 493) basement southeast of Acapulco (Figure 1). We analyzed Hf 297 isotopes of the Acapulco intrusion [all other data are from Hernández-Pineda et al. 298 (2011)] and major and trace element abundances and Sr-Nd-Pb-Hf isotope ratios of the 299 DSDP basement samples (Appendix B Tables 7-9).
- 300 4.2.3. Cocos and Pacific Plates

301 The crustal compositions of the incoming Cocos Plate are either AOC or oceanic302 sediment.

303 4.2.3.1. Pelagic and terrigenous sediment

There are two types of sediment subducted at the trench: (i) the pelagic sediment that accumulated on the Cocos plate, and the (ii) terrigenous (hemipelagic) sediment from the North American plate which covers the continental slope, trench and the near-trench region of the Cocos plate (Watkins and Moore, 1981). The terrigenous sediment reaches a minimum thickness of 625 m on the continental slope, and is still thicker (105 m) than the pelagic sediment (65 m) at the trench Site 487 on the Cocos plate (Figure 1, Watkins et al., 1981). Both sediment types were analyzed for major and trace element abundances

- and Sr-Nd-Pb-Hf isotopes by Verma (1999b), LaGatta (2003) and Cai et al. (2014), mainly
- 312 with samples from DSDP Site 487 on the incoming Cocos plate, supplemented by
- 313 samples from DSDP Site 488 at the toe of the upper plate continental slope, and from
- 314 piston cores near the East Pacific Rise (Figure 1). A bulk trench sediment has been
- 315 calculated (Cai et al., 2014; Plank, 2014).
- 316 While not all data were obtained at each site, the two sediment types have clear
- 317 commonalities and differences. Both types have similar <sup>143</sup>Nd/<sup>144</sup>Nd ~0.5125 and <sup>87</sup>Sr/<sup>86</sup>Sr
- 318 ~ 0.7085, but the pelagic sediment has higher <sup>176</sup>Hf/<sup>177</sup>Hf (~0.28294 vs. 0.28278) and Nd/Hf
- 319 (~20 vs 8) than the terrigenous sediment, and is less radiogenic in Pb isotopes (e.g.
- 320 <sup>206</sup>Pb/<sup>204</sup>Pb 18.84 *vs* 18.52) (Cai et al., 2014; LaGatta, 2003). These differences allow these
- 321 two lithologies to be traced through the Mexican margin given the sensitivity of arcs
- 322 towards trench sediment (e.g. Carpentier et al., 2008; Elliott et al., 1997; Plank and
- 323 Langmuir, 1993).
- 324 4.2.3.2. Subducting igneous oceanic crust (AOC)
- 325 The subducted AOC has been characterized for trace elements and Sr-Nd-Pb-Hf 326 isotopes using the Miocene basalt basement drilled at DSDP Site 487 on the incoming 327 Cocos Plate (Cai et al., 2014; Verma, 1999b). These data and additional Sr-Nd-Pb-Hf 328 isotope analyses of two Site 487 basement samples (Appendix B Table 7) show that the 329 Site 487 basement resembles depleted zero-age mid-ocean ridge basalts of the East 330 Pacific Rise (PetDB, 2011). Nevertheless, the AOC now beneath the central MVB is about 331  $\sim$ 5-6 million years older than at the trench, based on the current convergence rate of 47 332 km/Ma and the arc-trench gap of 360 km (e.g. Manea and Manea, 2011). In order to 333 preclude the possibility of a significant temporal change of the AOC, we analyzed 9 334 basaltic glasses spanning 10-72 Ma from the western flank of the East Pacific Rise 335 (Pacific Plate), assuming that the crust on both flanks of the East Pacific Rise represents 336 the upwelling mantle. Sample locations are shown in Figure 1 and include DSDP Sites 337 163, 469, 470 and 472, ODP Sites 1217A, 1243B and IODP Sites 1332, 1333 and 1334. Sr-338 Nd-Pb-Hf isotope ratios for all sites, and major element oxide abundances for three sites 339 are given in Appendix Tables 8 and 9. The trace element composition of these MORB 340 glasses are from Brandl et al. (2011; 2015).
- 341 5. ANALYTICAL METHODS

The majority of the Hf isotope ratios (n=37) were obtained at the Institute for Earth
Sciences (IES), Academia Sinica, Taipei, Taiwan on a Nu Plasma using the chemical Hf
separation technique after Lee et al. (1999). Additional Sr-Nd-Pb-Hf isotope ratios of

345 MVB lavas, crustal material and MORB glasses were obtained at Lamont using chemical

- 346 separation procedures developed by Cai et al. (2014). All trace element data of bulk
- 347 rocks were obtained by solution ICP-MS methods at the Centro de Geociencias (CGEO),
- 348 Juriquilla/Qro., Universidad Nacional Autónoma de México, Mexico. Major element
- 349 oxides were obtained by solution ICP-OES at Lamont. Oxygen isotope data of olivine
- 350 were obtained at the University of Oregon at Eugene. Olivine major and trace element
- analyses and major element analyses of MORB glasses were performed at the American
- 352 Museum of Natural History in New York/USA. Details of analytical methods are given
- 353 in Appendix B together with the new data (Appendix B Tables 1-9).

# 354 6. **RESULTS**

# 355 6.1. O isotopes of the central MVB magmas

356 The  $\delta^{18}$ O of olivines range from 5.3 to 6.6‰, which corresponds to  $\delta^{18}$ O<sub>melt</sub> = 6.3=8.4‰ 357 of their basaltic and andesite equilibrium melts (Figure 4) (fractionation-correction after, 358 Bindeman, 2008). The  $\delta^{18}$ Ooliv extend to higher values than those reported by Johnson et 359 al. (2009) in young basalts from monogenetic volcanoes in the Michoacan-Guanajuato 360 Volcanic Field farther to the west ( $\delta^{18}O_{oliv}$  =5.5-6.0‰). Together with the olivines of 361 Kluchevskoy volcano, Kamchatka which have  $\delta^{18}O_{oliv}$  up to 7.6‰ (Auer et al., 2009), 362 central Mexico has the highest  $\delta^{18}$ O<sub>oliv</sub> reported in arc magmas worldwide (Martin et al., 363 2011). Notably, the Nb-rich magmas have similar values and ranges in  $\delta^{18}$ Omelt (= 364 7.2 $\pm$ 0.5‰, n=16) as the calc-alkaline ( $\delta^{18}$ Omelt = 7.4 $\pm$ 0.5‰, n=24) and high-La series 365  $(\delta^{18}O_{melt} = 6.6-7.3\%, n=2)$ . The olivines of the Old Texcal Flow ( $\delta^{18}O_{oliv} = 5.6\%$ ), which 366 best approximates the mantle prior to subduction modification, have one of the lowest 367 melt  $\delta^{18}$ Omelt = 6.4‰ of the MVB. While still slightly above the range of MORB-type 368 mantle melts ( $\delta^{18}O_{melt}$  =5.7 ± 0.2 ‰, Bindeman, 2008), the data confirm the end member 369 character of the Old Texcal Flow (Straub et al., 2013a).

# 370 6.2. Sr-Nd-Pb-Hf isotope ratios

371 The Sr-Nd-Pb-Hf isotope ratios of our samples are within the range reported from 372 previous studies (e.g. Cai et al., 2014; Martinez-Serrano et al., 2004; Meriggi et al., 2008; 373 Schaaf et al., 2005; Siebe et al., 2004a). Our data, however, illustrate for the first time the 374 systematic differences between calc-alkaline, high-La and Nb-rich magmas in all four 375 isotope systems (Figures 5-7). In Sr-Nd isotope space, the calk-alkaline and high-La 376 magmas are displaced to higher <sup>87</sup>Sr/<sup>86</sup>Sr and/or higher <sup>143</sup>Nd/<sup>144</sup>Nd relative to the Nb-377 rich series (Figure 5). The Old Texcal Flow has the most radiogenic <sup>143</sup>Nd/<sup>144</sup>Nd and least 378 radiogenic 87Sr/86Sr closest to Cenozoic MORB which agrees with its end member

379 character in trace element space (Straub et al., 2013a). In Nd-Hf isotope space, the calc-380 alkaline and high-La series, and the Nb-rich magmas, respectively, define two parallel, 381 partially overlapping trends along the terrestrial array (Vervoort et al., 2011) (Figure 6) 382 with the calc-alkaline series being displaced towards higher <sup>176</sup>Hf/<sup>177</sup>Hf at a given 383 <sup>143</sup>Nd/<sup>144</sup>Nd. Again, the Old Texcal Flow has the most radiogenic <sup>143</sup>Nd/<sup>144</sup>Nd and 384 <sup>176</sup>Hf/<sup>177</sup>Hf of the central MVB magmas, close in composition to Cenozoic MORB. In Pb 385 isotope space, all arc samples plot on a tight, linear array whereby the Nb-rich series 386 show a displacement towards more radiogenic Pb relative to the calc-alkaline magmas 387 (Figure 7) that is typical for the MVB (Díaz-Bravo et al., 2014; Gomez-Tuena et al., 388 2007a). However, the Old Texcal Flow does not form the most radiogenic end member, 389 but plots in the middle of the arc array near the transition between calc-alkaline and 390 high-Nb series with a slight, but significant displacement toward higher <sup>206</sup>Pb/<sup>204</sup>Pb.

391 The Sr-Nd-Pb isotope range of the arc magmas is much more limited than that of the 392 crustal xenoliths which represent the crustal basement (Figure 5). The arc magmas 393 generally align better with potentially recycled crustal components, such trench 394 sediment, AOC, the Acapulco/offshore granodiorites and biotite gneiss which either 395 coincide or bracket the arc array. We note that the relationships between the arc magmas 396 and the recycled components differ in all four isotope systems. For example, in Sr-Nd 397 isotope space, arc magmas are bracketed by AOC and trench sediment, and overlap 398 with the Acapulco/offshore granodiorites, whereas the biotite gneiss is far more 399 enriched than any of these components. In Nd-Hf isotope space, however, the calc-400 alkaline and high-La arc magmas are instead bracketed by the radiogenic AOC and the 401 unradiogenic granodiorites, respectively, while the trench sediments plots off the arc 402 trend. In this diagram, the Nb-rich magmas extend to slightly more unradiogenic Nd 403 and Hf isotopes than the granodiorites, and the biotite gneiss is far more unradiogenic 404 than any of these compositions. In Pb isotope space, the Cenozoic AOC and the pelagic 405 trench sediment are less radiogenic than the arc magmas, while terrigenous sediment, 406 granodiorites and biotite gneiss are more radiogenic. The granodiorite partially overlaps 407 with the high-Nb series, but not with the calc-alkaline magmas.

- 408 7. **DISCUSSION**
- 409 7.1. No evidence for crustal contamination

410 We emphasize that the new data in their entirety confirm the lack of shallow crustal

- 411 differentiation in the central MVB magmas (Straub et al., 2011b; 2013a; 2014). As
- 412 discussed earlier, and exemplified by <sup>143</sup>Nd/<sup>144</sup>Nd in Figure 8a, the systematic increase of
- 413 melt silica with radiogenic isotope ratios rules out melt evolution by fractional

414 crystallization, but links the melt silica increase to changes in source composition

- 415 (Gomez-Tuena et al., 2007a; Straub et al., 2013a; Straub et al., 2014). Crustal assimilation
- 416 (or a combination of fractional crystallization and crustal contamination), which is often
- 417 invoked for such correlations, however, fails in view of the  ${}^{3}\text{He}/{}^{4}\text{He} \delta^{18}\text{O}$  signature of
- 418 the high-Ni olivines in the basaltic to andesitic magmas (Figure 4).

419 The high-Ni, high  $^{3}$ He/ $^{4}$ He =7-8 R $_{a}$  olivines are either the only or first silicate phase in 420 all three magma series (calc-alkaline, high-La, and high-Nb magmas) (Schaaf et al., 2005; 421 Siebe et al., 2004a; Straub et al., 2008). As early-crystallizing olivines, they retain the 422 primary He-O isotopic signatures of the arc melts before possible later crustal 423 assimilation and secondary alteration (e.g. Eiler et al., 2000; Martelli et al., 2008). The 424 <sup>3</sup>He/<sup>4</sup>He is extremely sensitive towards crustal assimilation, but the high <sup>3</sup>He/<sup>4</sup>He of the 425 olivines does not correlate with melt SiO<sub>2</sub>, despite as little as 0.01% mass of assimilated 426 upper crust would be sufficient to lower the melt <sup>3</sup>He/<sup>4</sup>He below the observed range 427 (Figure 8b). This argues against crustal contamination. On the other hand, the high 428  $\delta^{18}O_{melt}$  values of the olivines are clearly above mantle values regardless of the 429 fractionation correction, and point to a crustal component in the melts (Figure 8d,e). 430 While the olivine  $\delta^{18}$ O does not correlate with the average olivine Fo<sub>78-90</sub> (corresponding 431 to Mg#=53-74 of melt) (Figure 9), it increases with increasing  $SiO_2$  of the host melts 432 (Figure 8b). The increase exceeds the  $\delta^{18}$ O increase predicted by fractional crystallization, 433 which agrees with results from high-  $\delta^{18}$ O olivine studies in the western MVB (Johnson 434 et al., 2009). This correlation cannot be attributed to crustal assimilation either, as mixing 435 of a high-Mg#, low SiO<sub>2</sub>, low  $\delta^{18}$ O component (e.g. basaltic mantle melt) with low-Mg#, 436 high SiO<sub>2</sub>, high  $\delta^{18}$ O crustal component predicts correlation of the  $\delta^{18}$ O with both melt 437 SiO<sub>2</sub> and Mg#. Moreover, several tens percent of crustal material would be required in 438 order to reproduce the increase in melt  $SiO_2$  (Figure 8d), which exceeds by far any mass 439 tolerated by the <sup>3</sup>He/<sup>4</sup>He of the olivines. Thus, if there is a crustal component in the 440 central MVB melts, it must have been added from slab. Recycled crustal material, such 441 as trench sediment or eroded crust, is initially rich in radiogenic <sup>4</sup>He and has a low 442  $^{3}$ He/ $^{4}$ He < 0.1 (e.g., Martelli et al., 2008), but this He is driven off thermally in the 443 subduction cycle. For one, the highest closure temperature for He in common rock 444 forming minerals is T<sub>c</sub> =600°C (Martelli et al., 2008). Therefore, subducted crustal <sup>4</sup>He is 445 unlikely to survive the prolonged subduction beneath the Mexican fore-arc, where the 446 slab slowly heats up >600°C before reaching ca. 700-900°C at arc front depth (e.g. Ferrari 447 et al., 2012; Manea and Manea, 2011). To the other, any remaining crustal He is unlikely 448 to survive heating to temperatures >700°C during infiltration of the slab material into the 449 hot mantle wedge prior to melt formation.

- In summary, there is no evidence of significant crustal contamination in the basalticand andesitic magmas at least in the olivine crystallization stage. Rather, the olivines
- 452 crystallize from basaltic to andesitic mantle melts that contain a crustal component from
- 453 the subducted slab. Remarkably, a correlation between melt silica and  $\delta^{18}$ O is expected
- 454 from the 'pyroxenite model' of melt-rock reaction that predicts the melt SiO<sub>2</sub> abundance
- 455 of primary melts to increase with the amount of recycled slab component (e.g.
- 456 incompatible trace elements,  $\delta^{18}$ O) in the mantle source (Straub et al., 2011b; 2014). Here,
- 457 the melting of secondary pyroxenite veins can create melt series with compositional
- 458 characteristics reminiscent of fractional crystallization and/or crustal assimilation
- 459 despite of a different genesis (Straub et al., 2014).

# 460 7.2. Identifying recycled slab components in Sr-Nd-Pb-Hf isotope space

# 461 7.2.1. Constraints from Sr-Nd-Pb-Hf systematics

- 462 The  ${}^{3}\text{He}/{}^{4}\text{He}$  -  $\delta^{18}\text{O}$  data constrain the presence of a slab-derived crustal component in 463 the arc magmas, but they do not identify this component which could be AOC, trench 464 sediment or eroded crust, or a mixture of those. This information can be obtained 465 through comparison of arc input and output in Sr-Nd-Pb-Hf isotope and trace element 466 space. To date, studies proposed that the Sr-Nd-Pb-Hf isotope range of the MVB 467 magmas was a mixture of components from the subducted AOC and trench sediment, 468 and mantle wedge (e.g. Cai et al., 2014; Gomez-Tuena et al., 2007a; Straub et al., 2013a; 469 Straub et al., 2014). If this is correct, then mixing trends calculated with these end 470 members must pass through the arc data in Sr-Nd-Pb-Hf isotope space. We tested this 471 inference by calculating first-order mixing curves shown in Figures 5-7. The shape of
- isotope mixing curves depends only on the isotope and element ratios of the end
- 473 members, but not the concentrations of the elements (Langmuir et al., 1978). Because
- 474 AOC (~MORB) and the mantle wedge have similar elemental and in first
- 475 approximation also isotopic ratios, binary mixing curves between AOC and trench
- 476 sediment are sufficient to test the validity of the AOC-trench sediment-mantle mixing
- 477 models prior to full quantification. Binary first-order mixing curves were calculated with
- 478 measured end members given in Table 2.
- 479 In Sr-Nd-Pb isotope space, the arc magmas plot on, or reasonably close to,
- 480 AOC/mantle trench sediment mixing curves (Figures 5,7). In Pb isotope space, the
- 481 Cenozoic AOC (average <sup>206</sup>Pb/<sup>204</sup>Pb ~18.1) is a better fit than the average of zero-age East
- 482 Pacific Rise MORB which is more radiogenic (<sup>206</sup>Pb/<sup>204</sup>Pb ~18.4) (PetDB, 2011) (Figure 7).
- 483 Moreover, the granodiorite and biotite gneiss emerge as possible crustal end member on
- 484 Sr-Nd-Pb mixing curves, together with the trench sediment. The Sr-Nd-Pb isotopic ratios

485 do not distinguish between trench sediment and granodiorite/biotite gneiss crustal 486 components. However, this seems possible in Nd-Hf isotope space, because of the 487 different mixing trajectories between AOC/mantle, trench sediment and 488 granodiorite/biotite gneiss. Mixing curves between AOC/mantle, and trench sediment 489 are strongly curved, because these end members have very different Nd/Hf ratios 490 (trench sediment Nd/Hf ~8-20, AOC Nd/Hf ~4, mantle Nd/Hf ~4). Therefore, these 491 curves miss the arc magmas. However, the mixing curves between AOC/mantle and 492 granodiorite are nearly linear and pass through most of the arc data, as the granodiorite 493 and biotite gneiss have a similar low Nd/Hf ~5-7 as the AOC/mantle component. This is 494 confirmed in the corresponding <sup>176</sup>Hf/<sup>177</sup>Hf vs Nd/Hf diagram, where mixing trends are 495 linear. Again, the mixing lines between AOC/mantle and trench sediment, and 496 particularly AOC/mantle - pelagic trench sediment, clearly miss the bulk of the arc data, 497 while the granodiorite emerges as ideal crustal end member for most of the calc-498 alkaline/high-La arc magmas, excepting only the Nb-rich magmas which extend to less 499 radiogenic Hf ratios than the granodiorites.

500 The shape of the AOC-sediment Nd-Hf isotope mixing curves is affected by Nd/Hf

501 fractionation, which may happen during release from slab (e.g. Kessel et al., 2005).

502 Current experimental and observational data disagree on the direction of fractionation.

503 For example, some studies suggest that Nd is preferentially released in slab fluids

504 (D<sub>Nd</sub>/D<sub>Hf</sub> <1) at pressures of 4 GPa or in a zircon-bearing slab (Kessel et al., 2005; Rubatto

- and Hermann, 2003). On the other hand, an allanite-saturated slab may preferentially
- 506 retain Nd relative to Hf at 2.5 to 3 GPa ( $D_{Nd}/D_{Hf} > 1$ ) (Klimm et al., 2008; Skora and

507 Blundy, 2010). Therefore, forward models are inconclusive, and we used an inverse

- 508 approach to test for the possible influence of Nd/Hf fractionation. This is done by
- 509 varying the Nd/Hf of trench sediment or AOC in a three component mixture (mantle,
- 510 AOC, sediment) until the Nd-Hf isotope mixing curve passed through the arc data. In
- short, partial curve fits can be achieved in Nd-Hf isotope space by decreasing the Nd/Hf
- of the trench sediment or increasing the Nd/Hf of the AOC by a factor of 7 (which is
- 513 high). However, both solutions fail in the corresponding Nd/Hf *vs* <sup>176</sup>Hf/<sup>177</sup>Hf array.
- 514 Decreasing Nd/Hf of the trench sediment causes the corresponding mixing curves to
- 515 pass below the arc data in the Nd/Hf *vs* <sup>176</sup>Hf/<sup>177</sup>Hf diagram (Figure 10a,b). Increasing
- 516 Nd/Hf of the AOC, result the corresponding mixing curve plots above the bulk of arc
- 517 data (Figure 10b,c). The only exception is the high-La group that it could be fit if one of
- 518 the slab components had a high, fractionated Nd/Hf.

In summary, the Nd-Hf trace element and isotope systematics strongly argue for the granodiorite/biotite gneiss eroded from the forearc as crustal end member in the arc magmas instead of the trench sediment. The granodiorite appears the volumetrically more important recycled lithology, as it seems prevalent in the ubiquitous calc-alkaline series. In contrast, the biotite gneiss is much farther removed from the arc array, and fits lesser well with the arc trends than the granodiorite.

## 525 7.2.2. Other slab components and processes

526 While the high-La and Nb-rich series are close to the calc-alkaline magmas in isotope 527 space, their trace element characteristics require additional processes and/or source 528 components. The calc-alkaline and high-La series likely involve the same source 529 materials, but the much higher Nd/Hf of the high-La series (by up to a factor of 3) points 530 to fractionation of these elements which most likely occurs during release from slab. The 531 few high-La magmas do not form trends in Nd-Hf isotope and trace element space and 532 thus provide no clue as which slab component - AOC or granodiorite, or a mixture of 533 both – fractionates. The fractionated nature of this slab component is consistent with 534 their other characteristics, such as the low Nb (=4-8 ppm) which is coupled with high 535 Nb/Ta (17.2-19.5) and LREE-enrichment. Arc magmas with similar signatures are 536 globally rare, but have been reported from the western MVB (Gomez-Tuena et al., 2011) 537 and the Solomon and Indonesia arcs (Goss and Kay, 2009; Koenig and Schuth, 2011; 538 Stolz et al., 1996). In either setting, these magmas have been linked to deep (≥140 km) 539 partial melting of an fairly hot (>900-1050°C) eclogitic slab that has residual rutile, but 540 lost all other REE-bearing phases like monazite and allanite (Gomez-Tuena et al., 2011; 541 Koenig and Schuth, 2011). Deep partial slab melts that escaped mingling with other slab 542 component released at shallower depths could account for the isolated eruption of high-543 La in randomly distributed small (<<1 km<sup>2</sup>) cones remote from composite and larger 544 monogenetic volcanoes.

545 The Nb-rich magmas contain isotopically different source components, as evident 546 from their systematic differences to the calc-alkaline/high-La magmas in Sr-Nd-Pb-Hf 547 space (Figures 10-12). The similarity of the Nb-rich magmas to intraplate magmas has 548 lead to suggestions that these may derive from inherently enriched mantle domains (Cai 549 et al., 2014; Gomez-Tuena et al., 2011; Wallace and Carmichael, 1999). However, their 550 high  $\delta^{18}$ O and high-Ni olivines as well as details of major and trace element systematics 551 (Straub et al., 2013a) clearly point to a slab influence that is comparable in magnitude to 552 that of calc-alkaline series in most of the Nb-rich magmas. Thus, the isotopic differences 553 imply that the mantle sources of the Nb-rich magmas were infiltrated by isotopically

554 different slab components(s). More than one factor, however, is responsible for the 555 isotopic differences. One factor is that the calc-alkaline/high-La series are more hydrou.

- isotopic differences. One factor is that the calc-alkaline/high-La series are more hydrous
  than the Nb-rich series, having several wt% melt water compared to ≤1 wt% of the Nb-
- than the Nb-rich series, having several wt% melt water compared to ≤1 wt% of the Nbrich magmas (e.g. Cervantes and Wallace, 2003a; Johnson et al., 2009; Roberge et al.,
- 558 2009). Thus, and consistent with previous models (e.g. Gomez-Tuena et al., 2007a; Straub
- et al., 2014), the source of the calc-alkaline/high-La series seems to receive more slab
- 560 fluids, such as Sr-and Pb –rich fluids (or possibly hydrous melts) from AOC. An AOC
- 561 fluid rich in the unradiogenic Pb of the Cenozoic MORB-type crust may shift the calc-
- alkaline/high-La magmas towards lesser radiogenic Pb isotope ratios relative to the
- high-Nb magmas in Pb isotope space (Figure 12). AOC fluids may also carry Sr with a
- <sup>87</sup>Sr/<sup>86</sup>Sr higher (up to~0.705, Staudigel et al., 1995) than that fresh MORB (<sup>87</sup>Sr/<sup>86</sup>Sr ~0.7023) of AOC, and shift the calc-alkaline/high-La magmas towards higher <sup>87</sup>Sr/<sup>86</sup>Sr at a given
- <sup>143</sup>Nd/<sup>144</sup>Nd (Figure 11) (e.g. Gomez-Tuena et al., 2007a; 2013a; Straub et al., 2014).

567 A fractionated fluid component that is enriched in fluid mobile LILE relative to the 568 HFSE does not account for the trace element budget of the Nb-rich magmas. Instead, the 569 slab component infiltrating the source of the Nb-rich magmas must be rich in Nb and 570 Ta, and have high Nb/Ta (16-19.4), high Nb/La (~0.9), low Th/La (0.11) and the low 571 Nd/Hf (~4). This rules out the granodiorites or similar crustal material as source as this 572 material has fractionated trace element signatures which it would transmit to the mantle 573 (Appendix Figure 2). On the other hand, intraplate basalts have the requisite isotope and 574 trace signatures (e.g. Hofmann, 2003). We tentatively suggest that the source of the high-575 Nb magmas may have been infiltrated by crust constructed by intraplate seamount 576 magmas. It is possible that such seamount crust was part of the largely inaccessible 577 continental fore-arc basement. Alternatively, it could be part of subducting Cocos plate 578 where clusters of intraplate seamounts are common (e.g. Bohrson and Reid, 1995; 579 Castillo et al., 2010; Niu and Batiza, 1997). Local recycling of seamount material, 580 mingling to some extent with granodiorite, could account for the limited distribution of 581 the Nb-rich magmas in space and time in the Sierra Chichinautzin (Straub et al., 2013b)

- as well as along the volcanic front of the entire MVB.
- 583 7.3. Magnitude and impact of the eroded crust on arc magmas

The granodiorite emerges are important component in the arc magmas. In order to quantitatively assess its influence, we used a combination of inverse methods (trace elements) and forward modeling techniques (radiogenic isotopes). This two-fold approach minimizes the inherent uncertainties of flux quantification where many variables are model-dependent.

#### 589 7.3.1. Estimating the total slab flux from trace elements

590 First, we estimated the total percentage of slab-derived Sr, Pb, Nd and Hf in the arc 591 magmas by the inverse method of Pearce et al. (1995a). The method calculates the 592 difference for each sample between the observed concentration of an element – which is 593 that of a melt from the subduction-modified mantle - and its concentration in a 594 hypothetical melt from the same mantle free from slab additions ('background mantle'). 595 These differences then scale to the percentage of the slab-derived element in the arc 596 magmas. Assuming Nb and Yb to be mantle-derived, Pearce et al. (1995a) used Nb/Yb 597 ratios to calculate the 'background magma'. In the central MVB, however, Nb is added 598 from slab, and hence TiO<sub>2</sub>/Lu is used (Straub et al., 2013a; 2014). Moreover, instead of 599 MORB-type mantle source (Pearce et al., 1995a), we used primitive mantle for 600 calculating the slab-derived percentages for the high-Nb magmas, and residual 601 primitive mantle (after 3.5% melt extraction) calculating those of the calc-alkaline and 602 high-La magmas. Only with magmas with Mg#>60 were used in order to ensure the use 603 of trace element ratios in the most primitive magmas.

604 The trace element inversion confirms a strong slab flux of Sr, Nd, Pb and Hf for all three arc magma series, with the Nb-rich magmas (>44-59% of Sr, Nd, Pb and Hf slab-605 606 derived) having about one third less slab contribution than the calc-alkaline (>69-89%) 607 and high-La series (73-96%) (Table 1). In Figure 13, the slab-derived percentages are 608 plotted against the relevant isotopic composition. The Old Texcal Flow is always the 609 least influenced by the slab flux (slab-derived Pb ~18%, Sr ~34% Nd ~16% Hf ~20%) and 610 forms a common point of origin from which the trends of calc-alkaline/high-La and 611 high-Nb magmas diverge towards different slab components. These trends agree with a 612 model of a homogenous mantle that was infiltrated by at least two isotopically distinct 613 slab components. Remarkably, there are no clear trends towards the trench sediment, 614 which confirms its negligible influence on the arc magmas. This is most evident for the 615 arc Sr that must principally originate from recycled AOC and/or granodiorite, without 616 any apparent contribution of sedimentary Sr. Another feature is that none of the arc 617 trends heads towards the same, or the same mix, of slab components in all four isotope 618 systems. This supports the concept of the slab flux being a composite of several 619 individual components that mix in variable proportions.

# 620 7.3.2. Quantifying the slab sources in isotope space

621 Forward mixing models in isotope space allow for the estimation of the individual

- 622 contributions of mantle and slab components to the arc magmas. The first step is to fit
- 623 mixing curves through the arc data with the appropriate end members (mantle, AOC,

- 624 granodiorite/seamounts). A model curve is valid if (i) it passes through the data, and (ii)
- 625 the modeled elemental ratios reasonably reproduce those of the magmas. We first used
- 626 the measured elemental ratios of the end members (Table 2). If the mixing curve did not
- 627 pass through the arc data, then the elemental ratios of the slab-derived end members
- 628 were modified based on the results from experimental studies.
- 629 Suitable mixing curves can be generated in Nd-Hf-Pb isotope space without problem
  630 (Figures 10,12). In Sr-Nd isotope space, however, the Sr/Nd of the slab component needs
- 631 to be adjusted in order to reproduce the high Sr/Nd of the arc magmas (calc-
- 632 alkaline/high-La series Sr/Nd~25±4; Nb-rich magmas Sr/Nd ~19±4). This exceeds those of
- 633 the main sources (mantle ~12-16, AOC ~12, granodiorite ~9, intraplate seamounts ~13).
- 634 Mixing curves were fitted by increasing the AOC Sr by a factor of 2.5 for the Nb-rich
- 635 magmas. For the calk-alkaline series, the Sr flux was increased by a factor of 3 for
- 636 granodiorite and 4 for AOC. While these adjustments are somewhat arbitrary, they
- 637 provide a measure of the magnitude of the required Sr excess from slab. The final
- 638 isotope and elemental ratios of the end members are given in Table 2.
- 639 For the calculation of the Sr-Nd-Pb-Hf mixing curves, compositions of idealized,
- 640 average end member are used (Figures 10-12). While mantle, AOC and granodiorite
- 641 compositions are reasonably well known (Table 2), the composition of the inferred
- 642 recycled seamount component is unknown, and therefore its quantification is tentative.
- 643 For an estimate, we used the Sr, Nd, Pb and Hf abundances of off-axis seamounts with
- Nb >13-46 ppm from Niu and Batiza (1997), and estimated the isotope ratios of end
- 645 members from the Sr-Nd-Pb-Hf isotope mixing systematics of the arc magmas.
- 646 Two different types of background mantle were chosen: a primitive mantle for the 647 Nb-rich magmas, and a residuum of primitive mantle after 3.5% melt extraction for the 648 calc-alkaline and high-La series (Table 2). The elemental abundances and ratios of the 649 slab components vary considerably depending on whether the slab material is released 650 as bulk component ('slab diapir'), or as partial fluid or melt. Forward estimates are thus 651 inherently uncertain because these depend on a multitude of often poorly known 652 variables (e.g. metamorphic history of slab, partition coefficients, mixing proportions, 653 slab residual mineralogy, thermal structure and composition, physical properties). 654 Again, we choose the simplest approach by using the measured elemental abundances 655 of the end members, with only the abundance adjustment for Sr (Table 2). This approach 656 minimizes the calculated influence of the slab flux on the arc magmas. In addition,
- 657 mixing proportions were chosen to minimize the contributions of granodiorite. In Sr-
- 658 Nd-Hf isotope space, the arc data can be reproduced with a slab component composed

- of 50% AOC and 50% granodiorites (or seamount material for the high-Nb magmas).
- 660 The same mixing ratio is valid for the AOC-seamount slab component in Pb isotope
- space. The granodiorites, however, are so enriched in Pb relative to mantle and AOC
- that only 10% in the slab component is needed to reproduce the data. A 20% of the
- 663 composite slab component was mixed with the mantle wedge, which is consistent with
- major and trace element constrained from previous studies (Straub et al., 2011b; 2013a;
- 665 2014). Modeling parameters are given in Table 2, and the results are summarized in
- 666 Table 3.
- In summary, the isotope models suggest (within model uncertainty) a slab flux similar 667 668 in magnitude to results to that produced by the trace element inversion with the 669 exception of Hf (Tables 1 and 3). Slab-derived percentages are for Sr ~78-96% (compared 670 to 49-95% from trace element inversion), for Pb ~76-86% (59-96% from inversion), for Nd 671 ~76-87% (47-93% from inversion) and for Hf ~75-87% (44-73% from inversion). The 672 significant observation is the high slab contribution relative to that of the mantle wedge, 673 and in particular that of the granodiorite. The granodiorite controls the isotope 674 chemistry of the calc-alkaline magmas/high-La, to which they supply most of the Sr 675 ~73%, Pb ~61%, Nd ~68% and Hf ~87%. Likewise, the purported seamount component 676 makes a strong, but somewhat lesser contribution to the Nb-rich magmas (Sr ~37%, Pb 677 ~54%, Nd ~51% and Hf ~46%) relative to mantle and AOC. The overall contributions of 678 the AOC fluids to the arc magmas are fairly low, with only Sr ~23-42%, Pb ~22-25%, Nd 679 ~21-25% and Hf ~27-28%. Even if contribution of the Pb AOC is likely underestimated, 680 as the model makes no allowance for Pb enrichment in AOC fluids, the moderate 681 influence of AOC-derived Pb on the arc Pb isotope ratios agrees with their lack of 682 isotopic overlap with AOC, which is unlike many other arcs where the influence of AOC 683 components is much stronger (Figures 11, 12) (e.g. Straub and Zellmer, 2012). Overall, 684 the modeling results imply a strong influence of eroded granodiorite on the calk-alkaline 685 and high-La magmas, while the Nb-rich magmas are influenced to similar extent by 686 another slab component (possibly seamounts).

# 687 7.4. Why does the trench sediment align with the MVB magmas in Sr-Nd-Pb688 isotope space?

- The Acapulco/offshore granodiorites, possibly complemented by an unknown
- 690 seamount component, provide an excellent recycled crustal component for the MVB
- 691 magmas, but the question remains why the trench sediments align so well with the arc
- 692 magmas in Sr-Nd-Pb isotope space? A simple answer may be that trench sediment and
- 693 arc magmas are essentially mixtures of the same, or similar, components from

694 continental crust and MORB. The arc magmas, however, form by mixing of these 695 components in the mantle, whereas the sediments form by mixing on the Earth' surface. 696 Marine sediment is essentially the debris of continental erosion (lithogenic dust, volcanic 697 ash, riverine and hemipelagic input) that is diluted by biogenic components in the 698 oceans (Plank, 2004; Plank and Langmuir, 1998; Vervoort et al., 2011). The sediment 699 <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd is controlled by Nd- and Sr-rich debris and dust from the North 700 American continent, and is similar in pelagic and terrigenous sediments. The continental 701 debris also controls the Pb isotope composition of the sediments, but close to mid-ocean 702 ridges the continental signal is overprinted by MORB-type Pb delivered by 703 hydrothermal fluids. Thus, only the terrigenous sediment (Pb = 21 ppm) reflects the Pb isotopes of the continental crust, whereas the Pb-rich pelagic sediment (Pb= 66 ppm 704 705 LaGatta, 2003) is displaced towards the unradiogenic Pb typical of Cenozoic MORB. In 706 Nd-Hf isotope and trace element space, however, sediment does not align with crust-707 mantle trends, because of fractionation during transport from the continent. For 708 example, early loss of Hf-rich heavy minerals in rivers (e.g. zircon) increases the Nd/Hf 709 ratio of the suspended load, and hydrothermal fluids may change the Nd and Hf isotope 710 ratios of the continental debris (e.g. Garcon et al., 2013; Garçon et al., 2014; Vervoort et 711 al., 2011). Thus, the Nd-Hf isotope and trace element signature of the continental crust is 712 different from the trench sediment, allowing their signatures to be discriminated in the 713 arc magmas.

# 714 7.5. Recycling by slab diapirism – a physical model

## 715 7.5.1. Estimating the amount of eroded recycled crust

716 A significant outcome of our study is that the trench sediment does not influence the 717 central MVB arc magmas. However, there is no evidence for sediment accumulation in 718 the trench, and all trench sediment seems to have been subducted (Manea et al., 2003). 719 Consequently, the signal of the trench sediment in the calc-alkaline arc magmas must be 720 concealed by the eroded granodiorite. We estimated the minimum amount of 721 granodiorite needed to conceal the trench sediment from the Nd and Hf fluxes. The 722 volume of the trench sediment is ~8.84 km3/km/Myr, at a convergence rate of 52 723 km/Myr, thickness of 170 m (Plank, 2014), density of 1370 kg/m<sup>3</sup> and water content of 59

- 724 wt%. Thus, it supplies Nd= 169.3 g/km/Myr and Hf= 10.6 g/km/Myr with an average
- 725 Nd/Hf =16 [based on Plank (2014)]. A similar thickness of granodiorite with a density of
- 2700 kg/m<sup>3</sup> and zero water content would supply Nd=782.9 g/km/Myr and Hf=136.0
- 727 g/km/Myr with an average Nd/Hf=5.8. Therefore, in order to generate Nd/Hf <6 of the
- total recycled crustal component, the mass of eroded crust must exceed that of the trench

sediment by at least 9-10 times. This corresponds to a minimum rate of recycledgranodiorite of ~79-88.4 km²/Myr.

731 This estimate exceeds by more than two times the estimate of Ducea et al. (2004) who 732 inferred one-dimensional exhumation rates of 0.18 km/Myr from (U-Th)/He 733 thermochronology of the south central Mexican basement, and estimated ~30 734 km<sup>3</sup>/km/Myr crustal loss by subduction during the Miocene. On the other hand, our 735 estimate compares well with the numbers derived from the reconstruction of the shape 736 of the missing Eocene to Miocene fore-arc. The unusual location of the MVB at ~360 km 737 from the trench has been interpreted as the result of a process of slab flattening between 738 middle and late Miocene (Ferrari et al., 1999). Thus, the pre-Miocene arc location is 739 inferred from the configuration of the general Rivera-Cocos subduction, where the arc is 740 ~150 km from the trench in the Jalisco-Colima region, but between 150 and 200 km from 741 the trench in Guatemala. At fore-arc crustal thickness of 20 km (Kim et al., 2010), the 742 crustal loss would be between 20x150km<sup>2</sup>=3000 km<sup>2</sup> and 20x200 km<sup>2</sup>=4000km<sup>2</sup>. Given the 743 ~50 Ma age of batholiths of the Acapulco coast (Hernández-Pineda et al., 2011), and a 744 ~17 Ma start of the MVB volcanic activity (Gómez-Tuena et al., 2007b), this yields an 745 average rate of 60-80 km3/km/Myr for the last in 50 Ma. Thus, our estimate can be 746 considered as realistic.

747 7.5.2. Granodiorite recycling by slab diapirism

748 The high rate of recycled granodiorite has consequences for the style of mass transfer 749 from slab to wedge. Assuming the subducted granodiorite to be ~9-10 times thicker than 750 trench sediment (= 170 m thick), it would reach a thickness of ~1500-1700 meters. 751 Together with the typical low density of a quartz-feldspar lithology (2700 kg/m<sup>3</sup>) and the 752 estimated slab temperatures below the arc front of ~700-900°C (Ferrari et al., 2012; 753 Manea and Manea, 2011), these are ideal conditions for buoyant detachment of the 754 granodiorite from slab as 'slab diapirs' without need for slab melting (Behn et al., 2011; 755 Gerya et al., 2004; Gómez-Tuena et al., 2014; Hacker et al., 2011). Such slab diapirs are a 756 highly efficient way to transfer large amounts of slab material into the mantle wedge. 757 Silicic diapirs can react with the peridotite in similar ways as perceived for silicic slab 758 fluids or melts, and form secondary pyroxenites. Importantly, as the granodiorite has similar low average Ho/Lu =  $2.5 \pm 0.5$  as the mantle wedge (Ho/Lu ~2.2), it will not 759 760 impose a garnet signature on the mantle either.

A recycling cartoon is shown in Figure 14. The granodiorite is depicted to rise

buoyantly in the form of diapirs without melting. It may have little intrinsic water, but

763 water could be added from the dewatering AOC, as well as from serpentinite lithologies

764 from within and below the AOC (e.g. Gómez-Tuena et al., 2014). The granodiorite 765 diapirs dominate by far the slab flux, and are complemented by deep slab melts may 766 form at >140 km and infiltrate the source of the high-La magmas. The high-Nb magmas 767 are tentatively interpreted to be recycled intraplate seamount crust that is entrained into the granodiorite diapirs. All slab components rise into the hot interior of the mantle 768 769 wedge where they react with the peridotite to form pyroxenite segregations that then 770 melt in the upwelling mantle, and mix during ascent through mantle and crust. The 771 numerous, closely spaced, but compositionally highly diverse small volume 772 monogenetic volcanoes (≤1 km<sup>3</sup>) may be the surface expressions of a heterogeneous sub-773 arc mantle interspersed with pyroxenite veins. On the other hand, a succession of 774 individual slab diapirs channelized at a preferred spot of over a longer period of time 775 (several 100 ka to 1 million years), may ultimately accumulate the eruptive volumes of 776 several 100 km<sup>3</sup> typical of the composite volcanoes (e.g. Gómez-Tuena et al., 2014).

# 777 7.6. The impact of subduction erosion on the central MVB magmas

778 Our recycling model implies that the slab flux controls the budget of the highly 779 incompatible elements in the arc magmas. We tested this inference by means of the 780 incompatible element ratios Th/La and Nb/Ta, that are difficult to fractionate during 781 subduction processing (e.g. Foley et al., 2002; Plank, 2004). Th/La ratios (=0.09 to 0.37) 782 span the global range from the low Th/La (~0.05) of the mantle to the high Th/La (~0.37) 783 of upper continental crust (e.g. Plank, 2004; Rudnick and Gao, 2002). The range of Nb/Ta 784 (=12.3-19.5) is similarly broad, and only excludes the rare, supercondritic Nb/Ta >19.9 785 reported from some arcs (Gomez-Tuena et al., 2011; Koenig and Schuth, 2011; Stolz et al., 786 1996) (Figure 15).

787 Mixing relationships with <sup>143</sup>Nd/<sup>144</sup>Nd confirm that the Th/La and Nb/Ta of the calc-788 alkaline series is inherited from the inherently heterogeneous granodiorite. The 789 granodiorites form a perfect end member that would buffers the MVB magmas at high 790 <sup>143</sup>Nd/<sup>144</sup>Nd and at a broader range of Th/La and Nb/Ta. Some granodiorites also have 791 the low Th/La and high Nb/Ta intrinsic to the high-Nb magmas. However, oceanic 792 seamounts have the same characteristics and provide a more likely end member given 793 their isotopic and trace element composition (Figure 15). 794 The strong influence of the various recycled components on MVB melt chemistry is

best evident in Nb *vs* Nb/Ta space (Figure 16). The Old Texcal Flow (proxy to melt from
mantle wedge prior to subduction modification) divides this diagram into four
quadrants. The high-La magmas all plot in the upper left quadrant which combines high
Nb/Ta >17 with low Nb concentrations typical of a signature of deep melts from eclogitic

slabs with residual rutile (Gomez-Tuena et al., 2011; Koenig and Schuth, 2011). The high-

- 800 Nb series occupy quadrant II with their combination of high Nb and Nb/Ta being
- 801 tentatively attributed to the recycling of seamount material. The calc-alkaline magmas
- 802 (quadrant III), have the low Nb and Nb/Ta (~12-16) typical of continental crust material,
- 803 here recycled by subduction erosion. Calc-alkaline magmas with these characteristics
- dominate the entire MVB volcanic front (2014; Gómez-Tuena et al., 2007b). Previous
- 805 studies linked the low arc Nb/Ta to the partial melting of an amphibole-bearing slab, as
- amphibole is the only major slab phase that can retain Nb relative to Ta, and produces
- slab melts with low Nb and Nb/Ta (Foley et al., 2002; Gomez-Tuena et al., 2007a; Gomez-
- 808Tuena et al., 2011; Koenig and Schuth, 2011). However, most of the MVB arc front is
- 809 located >80 km above the slab and thus beyond the amphibole-eclogite transition
- 810 (Tatsumi and Eggins, 1995). Here, regardless of amphibole stability, recycling of pre-
- 811 existing continental crust with intrinsically low-Nb/Ta provides a simpler cause for the
- 812 predominantly low Nb/Ta of MVB magmas.
- 813 Likewise, if the granodiorite transmits the high Th/La to the calc-alkaline series, there
- 814 is no need for additional Th/La fractionation of the magmas, either during slab
- 815 processing (e.g. Cai et al., 2014) or by shallow crustal differentiation (e.g. Plank, 2004).
- 816 Additional Th/La fractionation is only needed if all source components had lower Th/La
- 817 than the arc. While AOC, mantle wedge and average trench sediment all have low Th/La
- 818 (Cai et al., 2014), the granodiorite (Th/La=0.25±0.10) has similar high and variable Th/La
- 819 as the calc-alkaline arc magmas (=0.21±0.06). Here, our results support the crustal
- 820 recycling model of Plank (2004) who proposed that the high Th/La in global arcs is
- 821 essentially inherited from perpetual recycling of continental crust via the trench
- 822 sediment (~upper continental crust, Plank and Langmuir, 1998) and expand it to include
- 823 continental crust recycled by subduction erosion.

824 There are other compositional features that the calc-alkaline central MVB may inherit 825 from granodiorite. The low Sr/Y ~11 of the granodiorite, regardless of additional Sr from 826 AOC fluids, appears to control the low Sr/Y of the arc magmas (<50). This explains the 827 absence of 'adakitic' high Sr/Y> 50 in the central MVB that has been considered as arc 828 with a 'young and hot' slab prone to melting in previous studies (e.g. Cai et al., 2014; 829 Defant and Drummond, 1990). The granodiorites may also buffer the Ba, Rb, Ba and Pb 830 abundances on the arc to their comparatively low abundances, which are too low if the 831 arc input would be made up AOC and the trench sediment that is highly enriched in

- these elements (Gomez-Tuena et al., 2007a). Overall, the central MVB poses an excellent
- 833 example for a volcanic arc that may principally grow by recycling of pre-existing

continental crust rather than through the creation of new arc crust by subductionprocessing.

#### 836 8. CONCLUSIONS

- 837 The following are the conclusions of this study:
- 838 (1) The Nd-Hf isotope and trace element systematics of central Mexican arc magmas
  839 identify granodiorites eroded from the continental fore-arc, and not trench
  840 sediment, as the principal recycled component of continental crust.
- 841 (2) The calc-alkaline arc magmas of the central MVB (>95% of the erupted volume) are
  842 mixtures of recycled granodiorite, subducted AOC and mantle wedge. Rare,
  843 strongly fractionated high-La magmas, and a minor group of Nb-rich magmas, can
  844 be linked to deep slab melting, and the local recycled of seamount material,
  845 respectively.
- 846 (3) With an estimated mass flux of 79-88 km<sup>3</sup>/km/Myr, thickness of 1500-1700 m and
  847 density of 2700 kg/m<sup>3</sup>, the eroded granodiorite layer is conducive to the buoyant
  848 ascent from slab in form of 'slab diapirs', with no need for slab melting, at the
  849 estimated slab temperatures of 700-900°C.
- (4) Th/La, Nb/Ta and other key trace element ratios of the calc-alkaline magmas are
  inherited from the granodiorite, suggesting that the MVB arc grows by recycling of
  the continental crust rather than by formation of new continental crust.
- 853

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# 1233 11. FIGURE CAPTIONS

1234 Figure 1: Plate tectonic setting of the Trans-Mexican Volcanic Belt (MVB). a. Locations of 1235 DSDP/ODP/IODP drill sites samples on Pacific Plate (MORB glasses) and Cocos Plate (sediment, 1236 continental basement), and crust outcrops and xenoliths within and south of the MVB. Numbers 1237 in brackets next to IODP drill sites are basement ages in million years. Piston corer locations from 1238 Cai et al. (2014). Basemap from GeoMappApp (2014). b. Trans-Mexican Volcanic Belt (grey 1239 shaded) with principal Quaternary volcanoes redrawn from Blatter et al. (2001). Slab contours 1240 after Pardo and Suarez (1995). Locations of crustal materials are those of Gómez-Tuena et al. 1241 (2003, Palma Sola xenoliths), Martinez-Serrano et al. (2004, Nevado de Toluca xenoliths), Schaaf et 1242 al. (2005, Popocatepetl xenoliths), Gómez-Tuena et al. (2008, Chalcatzingo xenolith), Ortega-1243 Gutiérrez et al. (2011, Puente Negro xenoliths), Hernández-Pineda et al. (2011, Eocene Acapulco 1244 intrusion), Pérez-Gutiérrez et al. (2009, Mesozoic Xolapa migmatites) and Ortega-Gutiérrez et al. 1245 (2014, Valle Santiago xenoliths). NDT - Nevado de Toluca, POP - Popocatepetl EPR - East 1246 Pacific Rise, RFZ – Rivera Fracture Zone, MC – Mexico City, TFZ – Tamayo Fracture Zone. c. NE-1247 SW cross section of Mexican continental slope and trench with incoming Cocos plate drilled 1248 during DSDP Leg 66, redrawn from Watkins et al. (1981). Continental basement was drilled at 1249 Sites 493 (granodiorite) and 489 (B -biotite gneiss). Trench sediment was analyzed at Sites 488 and 1250 487 (Cai et al., 2014; LaGatta, 2003; Plank, 2014; Plank and Langmuir, 1998; Verma, 1999b), and 1251 oceanic basement at Site 487 (Cai et al., 2014, this study; Verma, 1999b).

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1253Figure 2: Study area in the central Mexican Volcanic Belt. Monogenetic volcanoes (small open1254circles) of the Sierra Chichinautzin Volcanic Field are flanked by Quaternary composite volcanoes1255Nevado de Toluca and Popocatepetl-Iztaccihuatl. Large symbols denote samples with olivines1256analyzed for both  ${}^{3}$ He/ ${}^{4}$ He and  $\delta^{18}$ O. Location of most mantle-like magmas ('Old Texcal Flow') is1257indicated, as well as location of high-La volcanic rocks (St. Cruz, Tuxtepec and Yecahuazac1258Cone). CV – City of Cuernavaca, TL City of Toluca

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1261 Figure 3: Multi-element diagram of incompatible trace elements of central MVB magmas 1262 normalized to primitive mantle of McDonough and Sun (1995). For clarity, only magmas with 1263 high  ${}^{3}\text{He}/{}^{4}\text{He}$  and high  $\delta^{18}\text{O}$  are shown. **a**. Thick black line denotes the 'Old Texcal Flow' which is 1264 least influenced by slab and closely resembles a ~3.5% melt from primitive mantle (Straub et al., 1265 2013a, 2013b). While per definition a high-Nb basalt (Nb=18 ppm), it has no end member 1266 character and is intermediate to calc-alkaline and high-Nb series. b. MVB magmas compared to 1267 melts from residual mantle after 3.5 to 10% melt extraction from a primitive mantle (which 1268 produced the Old Texcal Flow after minor subduction modification). Residual mantle modeled 1269 from primitive mantle McDonough and Sun (1995) and partition coefficients from Donnelly et al. 1270 (2004). Mantle depletion by melting is so efficient that the slab flux either strongly influences 1271 (MREE) or controls (LREE and more incompatible elements) the arc budgets of elements more 1272 incompatible than Ho. Only Ti and rare earth elements Ho to Lu remain mantle- controlled by 1273 mantle. See also Straub et al. (2014).

1275Figure 4:  ${}^{3}\text{He}/{}^{4}\text{He} vs \, \delta^{18}\text{O}$  of olivine phenocrysts in central MVB volcanic rocks.  $\delta^{18}\text{O}$  recalculated1276to ratios in equilibrium melt [ $\delta^{18}\text{O}_{melt} = \delta^{18}\text{O}_{oliv} + 0.088*\text{SiO}_{2}-3.57$  after Bindeman (2008)].  ${}^{3}\text{He}/{}^{4}\text{He}$  of1277olivines are from Straub et al. (2011b).  ${}^{3}\text{He}/{}^{4}\text{He}$  in MORB and continental crust from Farley et al.1278(1998) and O'Nions and Oxburgh (1988);  $\delta^{18}\text{O}$  in mantle rocks from Bindeman (2008). Host

- $1279 \qquad \text{magmas are basalts to and esites with up to 61 wt\% SiO_2.}$
- 1280

1281 Figure 5: 87Sr/86Sr vs 143Nd/144Nd of volcanic rocks and various crustal materials (Cenozoic 1282 MORB, trench sediment, continental basement). See Figure 1 for sample locations. Quaternary 1283 MORB is from the East Pacific Rise (PetDB, 2011). Large symbols denote volcanic rocks with 1284 olivines analyzed for  ${}^{3}\text{He}/{}^{4}\text{He}$  and  $\delta^{18}\text{O}$ . Thick grey lines are simple mixing curves between AOC, 1285 mantle wedge (which have similar 87Sr/86Sr and Sr/Nd) and trench sediment (see text for 1286 discussion). The biotite gneiss of DSDP Site 489 it marked with a 'B'. Inset identifies the Old 1287 Texcal Flow and illustrates differences between calc-alkaline, high-La and Nb-rich magmas. For 1288 data sources see text.

1289

1290 Figure 6: **a.** <sup>143</sup>Nd/<sup>144</sup>Nd vs. <sup>176</sup>Hf/<sup>177</sup>Hf, and **b.** <sup>176</sup>Hf/<sup>177</sup>Hf vs. Nd/Hf of central MVB magmas and 1291 crustal materials (MORB, trench sediment, continental basement). See Figure 5 for symbols. Thick 1292 grey lines are simple mixing curves between AOC and trench sediment. Note that a mantle 1293 component would not affect the curvature of the mixing line, since mantle has similar Nd/Hf ~4 1294 (as well as Nd and Hf isotopic ratios) as the AOC. Mixing models must match arc data in both 1295 diagrams to be valid. The trench sediment fails as crust end member, while the 1296 offshore/Acapulco granodiorite lie in line with the AOC and compositions. Inset identifies the 1297 Old Texcal Flow and illustrates differences between calc-alkaline, high-La and Nb-rich magmas. 1298 For data sources see text.

1299

1300 Figure 7: **a**. <sup>207</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb, and **b**. <sup>208</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb of central MVB magmas 1301 and crustal materials (MORB, trench sediment, continental basement). See Figure 5 for symbols. 1302 The thick grey line is a mixing curve (which are linear in Pb isotope space) through the central 1303 MVB magmas which are aligned with slab and mantle materials. The Cenozoic AOC (average 1304 ~18.2) fits much better as unradiogenic end member of the arc array than the more variable zero-1305 age Quaternary MORB from the East Pacific Rise. Inset identifies the Old Texcal Flow and 1306 illustrates differences between calc-alkaline, high-La and Nb-rich magmas. For data sources see 1307 text.

1308

1309Figure 8: Central MVB magmas: a. Bulk rock <sup>143</sup>Nd/<sup>144</sup>Nd vs SiO2 wt%. b. <sup>3</sup>He/<sup>4</sup>He (olivine) vs1310SiO2 wt% (bulk rock) with mixing curves from Straub et al. (2014). c.  $\delta^{18}$ O (olivine) vs SiO2 wt%1311(bulk rock), and d.  $\delta^{18}$ Omelt [calculated from olivine after Bindeman (2008):  $\delta^{18}$ Omelt =  $\delta^{18}$ Ooliv + 0.0881312\* SiO2 (wt%)-3.57] vs SiO2 wt% (bulk rock). MORB field and fractional crystallization trajectory1313after Bindeman (2008). Mixing curves calculated with a crustal component SiO2 = 69 wt% and

1314  $\delta^{18}O= 8-12$  ‰, and a mantle melt of SiO<sub>2</sub>= 49 wt% and  $\delta^{18}O= 5.8$  ‰, respectively. See text for

1315 discussion.

1317Figure 9:  $\delta^{18}O_{melt}$  vs. average fosterite of cores of olivine phenocrysts. Olivine concentrations are1318from Straub et al. (2011b; 2013a, this study; 2008). The  $\delta^{18}O$  of continental crust is after Bindeman1319(2008).

1320

1321 Figure 10: Nd-Hf isotope and trace element mixing models. Valid models require mixing curves 1322 to pass through arc data in both the 143Nd/143Nd vs 176Hf/177Hf and Nd/Hf vs 176Hf/177Hf space. The 1323 models first calculate a 'bulk slab component' (AOC and bulk trench sediment, or AOC and 1324 granodiorite) shown as thick lines with 10% increments. The bulk slab component then mixes 1325 with the mantle wedge, shown as lines with only two tick marks (1% and 10%) for clarity (dashed 1326 - denotes curve for Nb-rich magmas). for . a.-b. Mixing between AOC and bulk trench sediment 1327 with preferential release of Hf from sediment by a factor of 7. c.-d. Mixing between AOC and 1328 bulk trench sediment with preferential release of Nd from AOC by a factor of 7. Either model 1329 produces misfits in the Nd/Hf vs <sup>176</sup>Hf/<sup>177</sup>Hf space (except for the high-La basalts). e.-f. Mixing 1330 between AOC and granodiorite that have similar Nd/Hf ratios. Calc-alkaline and Nb-rich 1331 magmas require slightly different crustal and mantle end members in isotope space. Mixing 1332 model assumes primitive background mantle (Nd/Hf= 4.4) for Nb-rich magmas, and a residual 1333 mantle after by 5% melt extraction for calc-alkaline series (Nd/Hf=3.9). For details see text. 1334

Figure 11: Idealized <sup>87</sup>Sr/<sup>86</sup>Sr *vs* <sup>143</sup>Nd/<sup>144</sup>Nd mixing model for calc-alkaline/high-La and Nb-rich magmas, respectively, with AOC, granodiorite and mantle wedge as end members. The models first calculate a 'bulk slab component'(AOC and bulk trench sediment, or AOC and granodiorite) which are shown as thick lines with 10% increments. The bulk slab component then mixes with the mantle wedge, shown as lines with only two tick marks (1% and 10%) for clarity (dashed denotes curve for Nb-rich magmas). A successful model for the calc-alkaline series requires a component with increased <sup>87</sup>Sr/<sup>86</sup>Sr, depicted here to derive from subducted AOC.

1342

Figure 12: Idealized <sup>208</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb mixing model for a. calc-alkaline/high-La magmas, and b. Nb-rich magmas. The models first calculate a 'bulk slab component'(AOC and bulk trench sediment, or AOC and granodiorite) which are shown as thick lines with 10% increments (dashed - denotes curve for Nb-rich magmas in panel b). The bulk slab component then mixes with the mantle wedge, shown as lines with only two tick marks (1% and 10%) for clarity (dashed denotes curve for Nb-rich magmas).

1349

Figure 13: a. Percentage of slab-derived Pb in arc magmas vs. <sup>206</sup>Pb/<sup>208</sup>Pb. b. Percentage of slabderived Sr in arc magmas vs. <sup>87</sup>Sr/<sup>86</sup>Sr. For calculation of slab-derived percentages see text. c.
Percentage of slab-derived Nd in arc magmas vs. <sup>143</sup>Nd/<sup>143</sup>Nd. d. Percentage of slab-derived Hf in
arc magmas vs. <sup>176</sup>Hf/<sup>177</sup>Hf.

1354

1355Figure 14: Cartoon of central MVB subduction setting. Thermal structure model assumes mantle1356potential temperature of 1450°C and temperatures of ~700-800°C at about 110 km beneath the1357central MVB arc front, estimated from P-wave seismic tomography (Manea and Manea, 2011).

1358	Slab surface temperatures remains below sediment solidus (≥1050°C, Behn et al., 2011)), but are
1359	conducive to the formation of thermochemical instabilities at the slab–mantle interface.

1361 Figure 15: **a.-b.** Th/La *vs.* <sup>143</sup>Nd/<sup>144</sup>Nd, and **c.-d.** Nb/Ta *vs.* <sup>143</sup>Nd/<sup>144</sup>Nd and mixing models for

1362 MVB magmas and their source components. Stippled lines outlines the range of the

1363 Acapulco/offshore granodiorites. The mixing models first calculate a 'bulk slab component' from

AOC and eroded crust (thick lines with 10% increments). The bulk slab component then mixes

1365 with the mantle wedge, shown as lines with only two tick marks (1% and 10%) for clarity (dashed

- denotes curve for Nb-rich magmas). Averages of major Earth reservoirs (right panels) are
compiled from Plank (2004), McDonough and Sun (1995), Sun and McDonough (1989), Pfänder et

- 1368 al. (2007), and Muenker et al. (2003).
- 1369

Figure 16: Nb (ppm) *vs* Nb/Ta of central MVB arc volcanic rocks with range of MORB from Niu and Batiza (1997). Stippled lines mark average of Old Texcal Flow (proxy to subarc mantle wedge

1371 and Batiza (1997). Stippled lines mark1372 prior to subduction modification).

1373

1374

Table

	Sr	Pb	Nd	Hf
calc-alkaline magmas	87±4%	89±6%	74±8%	69±9%
from mantle	~13%	~11%	~26%	~31%
high-La series magmas	95±2%	96±2%	93±3%	73±7%
from mantle	~5%	~4%	~7%	~27%
Nb-rich magmas	49±10%	59±18%	47±16%	44±13%

~41%

~53%

~56%

~51%

from mantle

Table 1: Average percentages of slab contributions of Pb, Sr, Nd and Hf to calc-alkaline, high-La and Nb-rich magmas from trace element inversion. Table

						Pb	Sr	Nd	Hf			
	<sup>87</sup> Sr/ <sup>86</sup> Sr	<sup>143</sup> Nd/ <sup>144</sup> Nd	<sup>206</sup> Pb/ <sup>208</sup> Pb	<sup>208</sup> Pb/ <sup>208</sup> Pb	<sup>176</sup> Hf/ <sup>177</sup> Hf	ppm	ppm	ppm	ppm	Sr/Nd	Nd/Hf	Data Sources
Cenozoic MORB												
(AOC)	0.70350	0.51319	18.20	37.71	0.28321	0.62	123ª	10.28	2.57	11.9	4.00	this study
Bulk trench												
sediment	0.70825	0.51253	18.64	38.34	0.28290	38.9	208	28.5	2.48	7.3	11.5	(Cai et al., 2014; Plank, 2014)
Pelagic trench												(Cai et al., 2014; LaGatta, 2003;
sediment	0.70837	0.51253	18.51	38.19	0.28294	66.2	284	51.2	2.51	5.6	20.4	Verma, 1999b)
Terrigenous trench												(Cai et al., 2014; LaGatta, 2003;
sediment	0.70858	0.51248	18.84	38.62	0.28278	20.9	179	19.8	2.43	9.1	8.15	Verma, 1999b)
calk-alkaline/high-La												
series												
												this study; residual of primitive
												mantle from McDonough and
Background mantle												Sun (1995), after 3.5% melt
wedge	0.70307	0.51300	18.71	38.41	0.28306	0.076	7.8	0.63	0.164	12.3	3.86	extraction
Acapulco/offshore												
granodiorite	0.70460	0.51273	18.8	38.64	0.28291	13.6	294 <sup>b</sup>	32.8	5.70	9.0	5.75	this study.
Nb-rich series												
												this study; primitive mantle
Background mantle												from McDonough and Sun
wedge	0.70307	0.51300	18.71	38.41	0.28306	0.15	19.9	1.25	0.283	15.9	4.42	(1995)
												abundance data after Niu and
intraplate seamount	0.70460 <sup>c</sup>	0.51273 <sup>c</sup>	18.8°	38.64 <sup>c</sup>	0.2829 <sup>c</sup>	1.2	270	21.2	4.2	12.8	5.0	Batiza (1997), Nb>10 ppm

Table 2: Source components used for <sup>143</sup>Nd/<sup>143</sup>Nd vs. <sup>176</sup>Hf/<sup>177</sup>Hf isotope mixing models.

a Model in Figure 14, uses increased Sr abundances, by factor of 3 for calc-alkaline series (Sr= 368 ppm; Sr/Nd=36), and by a factor of 2.5 for the NEAB (Sr= 306 ppm; Sr/Nd= 30). b Model in Figure 14, uses increased Sr abundances, by factor of 4 (Sr= 1177 ppm; Sr/Nd=36) c Isotope ratios estimated from trend of Nb-rich magmas in Sr-Nd-Pb-Hf isotope space

	Sr%	Pb%	Nd%	Hf%
Calc-alkaline/high-La series				
mantle	4	14	11	14
AOC	23	25	21	27
Granodiorite	73	61	68	59
Nb-rich magmas				
mantle	22	24	24	25
AOC	42	22	25	28
Seamount	37	54	51	46

Table 3. Average percentages of Pb, Sr, Nd and Hf contributed from the mantle and the different slab reservoirs obtained from isotope modeling.

	<sup>143</sup> Nd/ <sup>144</sup> Nd	Th ppm	La ppm	Nb ppm	Ta ppm	Th/La	Nb/Ta	Data Sources
Cenozoic MORB (AOC)	0.51319	0.33	4.9	4.55	0.285	0.07	15.6	this study
Bulk trench sediment	0.51253	6.00	36.3	8.65	0.557	0.17	15.5	(Cai et al., 2014; Plank, 2014)
Pelagic trench sediment	0.51253	5.51	56.4	8.09	0.44	0.08	18.2	(Cai et al., 2014; LaGatta, 2003; Verma, 1999b)
Terrigenous trench sediment	0.51248	7.50	20.4	11.04	0.84	0.32	13.2	(Cai et al., 2014; LaGatta, 2003; Verma, 1999b)
Acapulco/offshore granodiorite	0.51270-0.51276	1.1-13.6	15.1-37.1	15.7-30.9	1.36- 1.58	0.07- 0.37	11.5- 19.6	this study.
calk-alkaline/high-La series								
Background mantle wedge	0.51300	0.0011	0.105	0.02	0.0012	0.01	16.22	this study; residual of primitive mantle from McDonough and Sun (1995), after 3.5% melt extraction
Nb-rich magmas								
Background mantle wedge	0.51300	0.0795	0.648	0.6	0.037	0.12	16.22	this study; primitive mantle from McDonough and Sun (1995)

Table 4: Source components used for Th/La vs.  $^{\rm 143}Nd/^{\rm 143}Nd$  and Nb/Ta vs.  $^{\rm 143}Nd/^{\rm 143}Nd$  mixing models.







Fig. 02 Straub et al.



Fig. 03 Straub et al.



Fig. 04 Straub et al.





Fig. 06 Straub et al.



Fig. 07 Straub et al.

208Pb/204Pb



Fig. 08 Straub et al.



Fig. 09 Straub et al.



Figure





Fig. 12 Straub et al. Figure



Fig. 13 Straub et al.







Fig. 15 Straub et al.



Fig. 16 Straub et al. Electronic Annex Click here to download Electronic Annex: Appendix\_A\_B\_rev2.pdf Electronic Annex Click here to download Electronic Annex: Appendix Table 1.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 2.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 3.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 4.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 5.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 6.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 7.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 8.xls Electronic Annex Click here to download Electronic Annex: Appendix Table 9.xls Electronic Annex Click here to download Electronic Annex: Appendix\_Table 10.xls