

Revision 1

Origin and Petrogenetic Implications of Anomalous Olivine From a Cascade Forearc Basalt

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ABSTRACT

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Erupted absarokitic-shoshonitic volcanics in subduction zones make up a relatively small proportion of the total erupted volcanic material. However, they are a critical component for quantifying subduction metasomatism and mantle source heterogeneity. This study examines the geochemistry of anomalous olivine within a forearc absarokite lava and associated tephra, a compositional end-member of the Cascadia subduction zone magmatism, to infer mantle heterogeneity and magma petrogenesis. Ni concentrations from the young (42 ka) Quartzville absarokitic basalt lava flow and tephra in the Cascade forearc are up to ~6400 ppm Ni with correspondingly low Ca, averaging ~850 ppm Ca in Fo₉₁ olivine cores. Decreasing of Ni and Ca toward the olivine rims cannot be accounted for by simple fractional crystallization and instead necessitates magma mixing ± diffusive re-equilibration between the high-Ni, low-Ca olivine cores and low-Ni, high-Ca rims. δ¹⁸O of olivine phenocrysts (5.64 ‰) are elevated compared to other Cascade compositional components and outside of range typically associated with peridotitic olivine, or olivine crystallizing from peridotite-derived basaltic magmas. Trace element contents of whole rock, melt inclusions, and scoria glass have high Sr, high Dy/Yb and low Y, characteristic of adakitic slab melts, however major element compositions are of an alkali-rich basalt. In addition, similar trace element compositions between all analyzed glasses, indicates a related petrogenesis between all components. We propose that a slab partial melt has reacted with depleted harzburgite in the mantle wedge, underlying the older Western Cascades (~40-10 Ma). Reaction of the siliceous slab-derived melt with depleted harzburgite could produce a metasomatized, zoned pyroxenite-harzburgite mantle source. High-Ni, low-Ca olivine crystallize from melts of the subarc mantle reaction-pyroxenite. Later melting of the metasomatized harzburgite produces the absarokitic bulk composition, with olivine compositions

65 recording diffusive re-equilibration following incorporation of pyroxenite-derived olivine in a
66 peridotitic magma. Importantly, then, the observed olivine chemistry reflects mineralogical
67 variations in the subarc mantle while melt trace element variations record melts/fluids derived
68 from the subducting plate. High-Fo olivine rims (up to $\sim\text{Fo}_{94}$) appear to be the result of late stage
69 oxidation in the lava flow resulting from SO_2 degassing and are unrelated to the otherwise
70 complex magma petrogenesis.

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INTRODUCTION

73 Shoshonitic magmas, including the more primitive absarokites, are found in volcanic arcs
74 around the world, typically associated with low degree partial melts of highly fluid-
75 metasomatized mantle (e.g., Kamenetsky et al., 1995; Luhr, 1997; Hesse and Gove, 2003; Rowe
76 et al., 2009). Given their normally small erupted volumes, and formation as low degree partial
77 melts, shoshonites may preserve evidence of small-scale heterogeneity lost during
78 homogenization of larger melt fractions. In the Cascade volcanic arc, a global endmember for
79 “hot” subduction (Syracuse et al., 2010), absarokites and shoshonites are rare. However,
80 shoshonitic magmas comprise one of a number of distinct magmatic compositions, each
81 providing insight into subduction zone magma genesis in the Cascadia system (Borg et al., 1997;
82 Conrey et al., 1997; Reiners et al., 2000; Leeman et al., 2005; Schmidt et al., 2008; Rowe et al.,
83 2009; Schmidt et al., 2013). This study focuses on the petrogenesis of the most primitive
84 absarokite identified to date in the Cascade arc. In particular, prior research has identified the
85 presence of anomalous olivine compositions, characterized by high Ni (>6000 ppm Ni) and low
86 Ca (<900 ppm Ca) contents in olivine ranging from $\sim\text{Fo}_{88-94}$ (Conrey et al., 1997; Rowe et al.,
87 2006; 2009). Prior petrogenic models have not taken into account the significance of these

88 anomalous olivine grains. Here we utilize the unique mineral chemistry to create a holistic
89 petrogenic model related to subduction zone processes in this global endmember of “hot”
90 subduction.

91 **SAMPLES AND ANALYTICAL METHODS**

92 **Samples**

93 The herein named Quartzville basalt is located in the Quartzville mining district in the
94 western forearc margin of the Oregon Cascades (Lat. 44° 36.047’N, Long, 122° 20.146’W)(Fig.
95 1; Rowe et al., 2006, 2009). Field relations of the scoria cone and lava flow indicate the
96 Quartzville volcanism is much younger than the surrounding Western Cascades (~40-10 Ma),
97 with the cinder cone preserved on a peak and lava filling the incised valley below (Fig. 1). Field
98 observations are consistent with a young Ar-Ar age of 42 ka (Supplemental Table S1). The flow
99 and cone represent a relatively small volume and isolated eruptive event. The flow thickness
100 averages ~10m, thinning to 2m near the southern tip, with a total estimated eruptive volume of
101 $\sim 4.5 \times 10^{-3} \text{ km}^3$. Bulk samples were collected both from the lava flow interior (exposed at an old
102 quarry site) and from the scoria cone. Whole rock characterization results in classification of the
103 Quartzville basalt as an absarokite (Supplemental Table S2; Conrey et al., 1997) with high K₂O
104 (3.11 wt. %) and Na₂O (2.88 wt. %) (Rowe et al., 2006; 2009). Although recent convention is to
105 generalize the classification of these alkali rich mafic magmas as shoshonites, here we maintain
106 the more formal definition based on whole rock geochemistry and mineralogy. Despite
107 differences in major element composition between the scoria glass and lava whole rock, identical
108 trace element signatures indicate the two share a common petrogenesis (Rowe et al., 2006).
109 Whole rock Sr, Nd, Pb, Re, and Os isotopes are reported by Schmidt et al. (2008, 2013). Of
110 particular note, Re concentrations from the Quartzville absarokite are relatively low compared to

111 other Cascade arc basalts with a concentration of 0.007 ppb (Schmidt et al., 2013) and a $^{87}\text{Sr}/^{86}\text{Sr}$
112 of 0.70382 that is more radiogenic than other Cascade basalts and basaltic andesites (Schmidt et
113 al., 2008).

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115 **Analytical Methods**

116 **Mineral analyses.** Mineral major and minor element compositions were determined by
117 electron microprobe analysis (EMPA) on a Cameca SX 100 at Oregon State University, using a
118 15 KV, 30 nA electron beam focused to a 1 μm spot. Transects were carried out from core to rim
119 on 6 olivine grains from the lava flow and an additional 4 grains from the scoria. Olivine core-
120 rim analyses compliment olivine spot analyses taken adjacent to melt inclusions from the lava
121 (Rowe et al., 2006) and scoria (Rowe et al., 2009). Multiple analyses of San Carlos olivine (Fo_{90})
122 analyzed as a secondary standard indicate Ni and Mn analyses have a precision of 10 % while Ca
123 analyses have a precision of 14 %. Olivine X-ray maps were produced on a JEOL 8500F
124 Hyperprobe at Washington State University and on the Oregon State University CAMECA SX-
125 100. Clinopyroxene transects were made on several grains using the same beam conditions
126 utilized for olivine analyses.

127 **Oxygen isotopes.** Olivine oxygen isotope ($\delta^{18}\text{O}$) compositions were determined for a
128 suite of primitive Cascade arc, forearc, and backarc basalts, including the forearc Quartzville
129 basalt. Whole rock compositions corresponding to sample names/numbers are reported by Rowe
130 et al. (2009). Following picking, olivine grains for oxygen isotope analysis were rinsed in a sonic
131 bath of ethanol. Olivine grains selected for analysis were free from alteration as well as obvious
132 melt inclusions and/or abundant spinel (oxide) inclusions. Oxygen isotopes of olivine grains
133 were measured by CO_2 laser fluorination at California Institute of Technology on four

134 consecutive days following the method described by Eiler et al. (2000). San Carlos olivine grains
135 were analyzed repeatedly over the four analytical sessions with a reproducibility of $\pm 0.11\%$
136 (1σ). Oxygen isotope measurements were corrected based on daily analysis of GMG-2 garnet
137 standard (5.8‰ accepted lab value), analyzed 3-4 times a day (Supplemental Table S3).
138 Unknown samples were analyzed 2-3 times, with sample weights from 1.8-3 mg. Several
139 samples have isotopic ranges greater than that predicted by reproducibility of the olivine
140 standards with up to 0.45‰ variation.

141 **RESULTS**

142 **Petrography**

143 Within the lava, olivine is the major phenocryst phase with microphenocrysts of
144 clinopyroxene (grading into groundmass). Olivine are predominantly euhedral to subhedral,
145 however many of the largest grains (up to $\sim 500 \mu\text{m}$) are also broken, with only a portion of the
146 grain preserved in the thin section (Fig. 2). Jagged and embayed edges, and crystallized melt
147 inclusions are also associated with euhedral grains. X-ray mapping indicates an increase in Mg
148 toward the rim of olivine grains, consistent with mineral transects (Fig. 3). Abundant oxide
149 mineral inclusions (Cr-spinel and magnetite) occur in olivine-hosted melt inclusions and within
150 olivine grains (Cr-spinel). The abundance of magnetite and spinel inclusions in olivine is highly
151 variable, although olivine crystals absent of inclusions are rare. Oxide inclusions are often
152 concentrated within particular zones in olivine crystals (Fig. 2). In addition, a small proportion of
153 olivine have an unusual symplectitic texture, with magnetite apparently exsolving out of the
154 olivine, roughly perpendicular to crystal margins. This texture becomes increasingly developed
155 towards the interior of the olivine and is absent at grain boundaries (Fig. 2).

156 Clinopyroxene microphenocrysts have a maximum grain size of $\sim 400 \mu\text{m}$, however,

157 crystals are predominantly smaller than 200 μm . Clinopyroxene are euhedral with distinctive
158 zoning evident petrographically and in back-scatter imaging (Fig. 4).

159 The lava groundmass is composed predominantly of plagioclase and clinopyroxene with
160 lesser magnetite and apatite. Groundmass X-ray mapping indicates abundant sulfur-bearing
161 apatite with decreasing sulfur towards the rims.

162 Olivine is the only phenocryst phase observed in the Quartzville scoria with grain sizes
163 comparable to those observed in the lava. Scoria groundmass phases proportionally are
164 dominated by olivine > clinopyroxene > micro-apatite (Fig. 5). Notable differences of the scoria
165 petrography to the petrography of the lava are the absence of magnetite inclusions in the olivine,
166 and the absence of magnetite and plagioclase as groundmass phases. Petrographic characteristics
167 of the lava and scoria are summarized in Table 1 along with the characteristic mineral
168 geochemical variations.

169 **Mineral chemistry**

170 **Olivine.** Olivine from within the lava, ranging from $\text{Fo}_{93.8-88.6}$ (average $\text{Fo}_{90.7}$), have
171 significantly more variability than olivine observed within the scoria which have relatively
172 restricted compositions ($\text{Fo}_{90.6-88.2}$; average $\text{Fo}_{89.4}$) (Fig. 4; Table 1, 2). Groundmass olivine in the
173 scoria sample has an average composition of Fo_{89} . Table 2 reports average and representative
174 olivine analyses while the complete dataset is available as Supplemental Table S4.

175 Nickel concentrations in olivine phenocrysts are exceptionally high, varying from 6400-
176 800 ppm Ni in the lava to 5500-1100 ppm Ni in the scoria (Fig. 6). Nickel concentrations do not
177 vary linearly with olivine major element composition. Instead, the maximum Ni concentration
178 coincides with a $\sim\text{Fo}_{91}$ olivine (Fig. 6). Nickel concentrations decrease significantly from Fo_{91} to
179 $\text{Fo}_{88.4}$. However, while more variable, above Fo_{91} olivine Ni concentrations also decrease with

180 increasing forsterite content up to Fo_{93.8}.

181 Below Fo₉₁, olivine Ca concentrations are inversely correlated to Ni in olivine, with a
182 minimum concentration of ~860 ppm Ca at Fo₉₁, increasing to 1785 ppm toward both lower and
183 high Fo content (Fig. 6, 7). However, although correlated the relationship is non-linear. As Ni
184 decreases from a maximum of 6380 to ~4500 ppm Ni, Ca contents in olivine have no consistent
185 co-variation and remain relatively constant at 930 +/- 110 ppm Ca (Fig. 7). Below ~4500 ppm
186 Ni, Ca concentrations linearly increase. Manganese concentrations decrease from 2320 to 680
187 ppm Mn as olivine Fo content decreases from Fo_{93.8} to Fo₉₁. Below Fo₉₁, Mn is significantly
188 more variable but generally increases toward 1500 ppm as Fo content decreases. Olivine Mn and
189 Ca contents are broadly correlated, and Mn shares the same relationship as Ca with decreasing
190 Ni contents.

191 Although groundmass olivine are less common, analysis of a
192 groundmass/microphenocryst olivine from the scoria sample indicates the olivine is more
193 evolved with an average composition of Fo₈₉ (Fig. 5). The groundmass olivine core to rim has
194 decreasing Ni, from 1860 to 1310 ppm, and increasing Ca, from 1605 to 1940 ppm, respectively,
195 similar to olivine phenocryst rim compositions from both the lava and the scoria.

196 **Olivine transects.** Olivine from the lava have both normal and reverse grading toward
197 grain rims (Table 1). Reverse Fe-Mg grading is generally only observed in the outermost 50 µm
198 of the olivine, with Fo content increasing to ~Fo₉₄. Prior to the increase in Fo content at the rim,
199 there is a decrease to ~Fo_{89.5}. Normally zoned olivine have rim compositions that match the
200 minimum (Fo_{89.5}) observed in reversely zoned crystals (Fig. 8). Transects of olivine from the
201 scoria sample are all normally zoned and show no evidence for the increase in Fo content in the
202 grain boundaries with a rim composition varying from Fo_{88.7} to Fo_{89.4} (Fig. 8). Regardless of

203 olivine rim composition (Fo content), Ni concentrations systematically and significantly decrease
204 over the outer 100-200 μm of the grains, from ~6000-5000 ppm Ni in the core to 2000-1000 ppm
205 Ni in the rims (Fig. 8). The same pattern is observed in olivine from the scoria although
206 maximum Ni concentrations in the grain cores are substantially lower, generally < 4000 ppm Ni
207 (Fig. 8). Ca concentrations in olivine are again independent of olivine rim variation (Fo content)
208 and vary from 800-1000 ppm Ca throughout most of the olivine but increase to as high as 1750
209 ppm Ca at the grain margin, the mirror image of Ni variation in olivine in the outer 100-200 μm
210 of the olivine. Manganese variations in olivine transects are less discernable (Fig. 3).

211 **Clinopyroxene.** Clinopyroxene phenocryst transects all have irregular Fe-Mg oscillatory
212 zoning. The same Fe-Mg zoning is evident both in larger microphenocrysts and in groundmass
213 clinopyroxene, with high-Fe rims indicated from X-ray mapping. The full chemical analysis of
214 clinopyroxene is available in Supplemental Table S5. The Mg# of clinopyroxene phenocrysts
215 ranges from 82 to 89. Groundmass clinopyroxene have an average core Mg# of 86.2 ± 1.5 ,
216 compositionally similar to larger phenocrysts. Despite the elevated Ni concentrations in olivine,
217 Ni in clinopyroxene is below detection limit (~450 ppm). Fe_2O_3 in clinopyroxene is calculated
218 stoichiometrically. Although clinopyroxene compositions are variable, nearly all transects
219 indicate an increase in $\text{Fe}_2\text{O}_3/\text{FeO}$ at the grain rims (Fig. 4).

220 **Olivine oxygen isotopes.** Duplicate analyses of oxygen isotopes from olivine crystals
221 recovered from the Quartzville lava flow give identical $\delta^{18}\text{O}$ values of 5.64‰. Other basalt types
222 identified by Rowe et al. (2009), including calc-alkaline, low-K tholeiite, and enriched-intraplate
223 basalts (or OIB-like), have $\delta^{18}\text{O}$ ranging from 5.5 to 5.2‰ in Central Oregon with an average of
224 5.34‰, significantly lower than the Quartzville basalt (Fig. 9). The variability observed within
225 the other Central Oregon basalts is dominantly within the range for upper mantle olivine ($5.2 \pm$

226 0.2; Matthey et al., 1994; Eiler et al., 2000), and does not correlate to basalt major element
227 composition (Fig. 9). Oxygen isotope analyses of Central Oregon Cascade forearc, arc, and
228 backarc basalts are available in Supplemental Table S3.

229 **Melt compositions.** Supplemental Table S2 summarizes the whole rock/melt
230 compositions from melt inclusions, scoria glass, and lava samples including new analyses of
231 scoria glass and compositions reported by Rowe et al. (2006, 2009). Scoria glass is
232 compositionally variable, with MgO and CaO decreasing with increasing SiO₂, as a result of
233 varying amounts of fractional crystallization of clinopyroxene ± olivine during eruption. Scoria
234 glass MgO wt. % ranges from 4.3 to 4.8 wt. % compared to 6.7 wt. % in olivine-hosted
235 inclusions calculated to be in equilibrium with their host olivine (Rowe et al., 2009) and 9.86 wt.
236 % MgO in the whole rock lava (Rowe et al., 2006). Olivine compositions adjacent to melt
237 inclusions in olivine from the lava range from Fo_{89.4-92.2} and from Fo_{86.1-90.2} from the scoria
238 (Rowe et al., 2006). No groundmass glass was evident in the lava sample. High MgO in the
239 whole rock has previously been ascribed to olivine accumulation (Rowe et al., 2006). FeO* (total
240 Fe) from the lava whole rock and scoria glass is uniformly low, with a limited range in
241 concentrations from 6.3 to 6.5 wt. % FeO* and olivine-hosted melt inclusions from the scoria
242 with 6.7 wt. % FeO*. Importantly, all four materials (lava, scoria, and olivine-hosted melt
243 inclusions in the lava and scoria), have the same relative trace element variability (Fig. 10). All
244 samples are extremely enriched in large ion lithophile elements (LILE's) and light rare earth
245 elements (LREE's) and comparably depleted in high field strength elements (HFSE; especially
246 Nb and Ta) and heavy rare earth elements (HREE's). The whole rock Ni concentration is 256
247 ppm compared to 13.9 ppm in the scoria glass. Trace element characteristics of the lava are
248 adakite-like (Defant and Drummond, 1990), with normalized Dy/Yb and La/Yb of 3 and 53.5,

249 respectively, and a Sr/Nd of 31.2 with a Sr/Y of 151.

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DISCUSSION

252 **Mantle Xenocrystic Olivine?**

253 The anomalous olivine compositions in the Quartzville basalt and scoria have the
254 potential to provide important constraints on the origin and petrogenesis of the magma. First,
255 however, non-magmatic origins (i.e. mantle xenocrysts) for the olivine must be ruled out.

256 Although most of the olivine grains have euhedral textures (Fig. 2), this does not
257 necessitate a magmatic origin, as euhedral rims can mantle xenocrystic olivine (e.g. Kamenetsky
258 et al., 2008; Arndt et al., 2010; Pilbeam et al., 2013). The unique magnetite exsolution texture
259 identified in a small proportion of grains may suggest a xenocrystic origin for this population of
260 grains- note that the grain margin is free from magnetite exsolution and may reflect olivine rim
261 crystallization (Fig. 2). However, the mineral composition is identical between these particular
262 grains with exsolution textures and cores of other olivine grains, which lack this texture, and
263 would suggest a common origin for the cores of most of the olivine grains despite the presence
264 or absence of this texture. The observed exsolution texture could result from a change to more
265 oxidizing magmatic conditions, resulting in a reduction of the olivine stability field (Muan and
266 Osborn, 1956), and a subsolidus exsolution of magnetite. This interpretation is consistent with
267 the high oxidation state ($> \text{FMQ} + 1.5$) of the erupted magma (Rowe et al., 2009). In contrast, the
268 presence of melt embayments and silicate melt inclusions supports a magmatic origin for these
269 olivine. Olivine-hosted melt inclusion trace element compositions from both the lava and scoria
270 match that of their respective host rocks that not only suggests a magmatic origin but that the
271 melts are related (Rowe et al., 2006; 2009). As stated above, melt inclusions are found in up to

272 Fo₉₂ olivine from the lava, implying a magmatic origin for most olivine grains.

273 Although mantle xenoliths are rare in the Cascades, Ni contents from harzburgite and
274 websterite xenoliths from Simcoe Volcano, in the Washington Cascades, range from ~1885 –
275 3380 ppm Ni (Brandon & Draper, 1996). Olivine Ni contents from Quartzville are significantly
276 greater than observed in peridotitic olivine, with cores typically ranging from 4500 – 6380 ppm
277 Ni. These concentrations are well above typical mantle-derived olivine (generally below 3800
278 ppm Ni), also strongly favoring a magmatic origin for these olivine (Fig. 7; e.g. Kamenetsky et
279 al., 2006; Elburg et al., 2006; Sobolev et al., 2007; Straub et al., 2008).

280 Early studies of low-Ca olivine suggested that many of these olivine were derived from
281 mantle peridotites (e.g., Simkin and Smith, 1970). However, more recent examination into low-
282 Ca olivine has identified numerous occurrences of magmatic low-Ca olivine (e.g., Kamenetsky
283 et al., 2006). When compared to mantle peridotite olivine, where Ca contents are generally below
284 700 ppm, Ca concentrations in Quartzville olivine are enriched (Fig. 7). In these examples of
285 magmatic occurrences, low-Ca (< 1070 ppm Ca) olivine are often associated with high-Ni (up to
286 3930 ppm Ni) contents in high-Fo olivine.

287 Consistent with an inferred magmatic origin of olivine from textural and trace element
288 data, $\delta^{18}\text{O}$ of the high-Ni olivine ($5.64 \pm 0.1\%$) are greater than the values attributed to mantle
289 peridotite which range from 4.8 – 5.5‰ (average of $5.18 \pm 0.28\%$; Matthey et al., 1994). It could
290 be argued that if the olivine cores are of mantle origin (xenocrystic), with magmatic rims, bulk
291 olivine isotopic analysis would reflect a mixture of the two components. Oxygen isotopic
292 analysis of other primitive basalts in the Oregon Cascades, however, are all within error of
293 “mantle olivine” (Matthey et al., 1994). If rim olivine growth was altering the isotopic
294 composition of the Quartzville olivine, we would predict that the measured $\delta^{18}\text{O}$ would be a

295 minimum value and thus the original olivine core isotopic value would be even further removed
296 from the previously defined mantle olivine compositional range.

297 Overall, multiple lines of evidence, textural and compositional, support the conclusion
298 that high-Fo, high-Ni, low-Ca olivine are not simply transported mantle xenocrysts. Therefore,
299 understanding the origin of these anomalous olivine will provide constraints on the magma
300 petrogenesis for this unusual forearc magmatism.

301 **Olivine-melt equilibrium and partitioning**

302 **Fe-Mg olivine-melt equilibrium.** Major element compositions of re-homogenized
303 olivine-hosted melt inclusions for the Quartzville lava were previously deemed to be unreliable
304 (Rowe et al., 2006). However, from melt inclusion trace elements (Rowe et al., 2006; Rowe et
305 al., 2009) and field relations, we can conclude that scoria and lava samples are genetically
306 related. From this relationship, we can reassess the olivine-melt Fe-Mg equilibrium. A ferrous-
307 ferric ratio ($\text{Fe}^{3+}/\Sigma\text{Fe}$ of ~ 0.32) is calculated using the algorithm of Sack et al. (1980) from the
308 calculated $f\text{O}_2$ ($f\text{O}_2$ of $\sim \Delta\text{FMQ} + 1.5\text{-}1.9$; Rowe et al., 2009; Jugo et al., 2010), the scoria glass
309 composition, and an assumed temperature of 1115°C (Rowe et al., 2006). With an olivine-melt
310 $K_d^{\text{Fe-Mg}}$ of 0.30 ± 0.03 after Roedder and Emslie (1970) and the same $\text{Fe}^{3+}/\Sigma\text{Fe}$ between the
311 scoria and lava, we can make the assumption that the average melt inclusion composition from
312 the scoria, trapped in olivine with an average $\text{Fo}_{89.4}$ olivine composition, is equivalent to the melt
313 composition that is in equilibrium with $\text{Fo}_{89.4}$ olivine from the lava. This olivine composition
314 matches the minimum Fo content in the olivine profiles prior to the spike in Fo content to $\text{Fo}_{93.8}$
315 at the olivine rims (Fig. 8).

316 This new assessment of Fe-Mg equilibrium suggests that the high MgO wt. % of the lava
317 (9.8 wt. % MgO) is the result of approximately ~ 7.8 wt. % olivine accumulation, consistent with

318 prior estimates of olivine accumulation (Rowe et al., 2006). Two important conclusions come
319 from these observations. First, if the olivine core to near-rim variation in olivine forsterite
320 content is the result of fractional crystallization, this would imply a minimal amount of
321 fractionation to get from $\sim\text{Fo}_{91}$ to $\sim\text{Fo}_{89}$. Second, the presence of accumulated olivine must be
322 taken into account for any petrogenetic model. The question must then become what is the
323 origin for the accumulated olivine. This question, and the high Fo content olivine rims ($> \text{Fo}_{91}$)
324 are discussed further below.

325 **Ni and Ca olivine-melt partitioning.** Nickel and Ca partitioning in olivine provides an
326 opportunity to assess the evolution of olivine crystals in the melt on the basis of a fractional
327 crystallization model. Assuming a final melt composition similar to that of the scoria olivine-
328 hosted melt inclusions with equilibrium $\text{Fo}_{89.4}$ olivine and an $\text{Fe}^{3+}/\text{Fe}_{\text{Total}}$ of 0.32, only 3 wt. % of
329 equilibrium olivine needs to be added back to the melt for an Fo_{91} olivine to be the equilibrium
330 olivine composition. Note we do not use the scoria glass composition here because of the slight
331 disequilibria between scoria glass and rim olivine discussed above. Overall, this model suggests
332 a minimal amount of olivine fractionation is recorded in the Fe-Mg variation of the crystals and
333 forms the basis for the following discussion.

334 Prior studies have documented that the abundance of Ca in olivine is a function of olivine
335 Fo content, pressure, and melt composition (e.g., Stormer, 1973; Libourel, 1999; Jurewicz and
336 Watson, 1988). Experimental absarokitic run products suggest a slight decrease in Ca in olivine
337 partitioning with increasing magmatic water content, from ~ 0.029 to 0.024 (Hesse and Grove,
338 2003). However, partition coefficients calculated from experimental run products are higher than
339 used in our modeling. Calculated olivine trace element compositions using these partition
340 coefficients would be even further removed from observed low-Ca variations. Using average

341 inclusion and olivine compositions for the scoria we can define a partition coefficient $D_{Ca}^{ol-melt}$ of
342 0.017. Given the minimal olivine fractionation and thus little change to a theoretical melt
343 composition, we can assume a nearly constant partition coefficient for Ca in olivine. This
344 calculated value is similar to that predicted by Jurewicz and Watson (1988) for high-Fo basalts
345 (e.g., 0.016). In an olivine-dominated crystallizing assemblage, CaO in the melt will remain
346 nearly unchanged (< 0.5 wt. % CaO increase) for the small amount of olivine crystallization we
347 predict. The effect is even more pronounced with the addition of clinopyroxene fractionation
348 which will reduce the abundance of CaO available in the melt with continued crystallization.
349 Given the incompatible behavior of Ca in olivine and its dependence on CaO in the melt (e.g.
350 Jurewicz and Watson, 1988), we cannot explain the ~ 1000 ppm increase in Ca in olivine from
351 core to rim with a simple fractionation model (Fig. 7a).

352 Experimental studies have long identified that Ni olivine-melt partition coefficients are
353 strongly dependent on melt composition (both as a function of MgO content and melt
354 polymerization) and temperature (e.g., Hart and Davis, 1978; Leeman and Lindstrom, 1978;
355 Kinzler et al., 1990; Beattie et al., 1991; Wang and Gaetani, 2008; Li and Ripley, 2010).
356 However, these two parameters have proven difficult to deconvolve, given the interdependence
357 of temperature and melt composition (Hart and Davis, 1978; Li and Ripley, 2010). For the scoria
358 melt, with a Ni melt concentration of ~14 ppm, and olivine rim compositions we obtain
359 reasonably good agreement between MgO-dependent algorithms ($D_{Ni}^{ol-melt}$ of 25.6-30.6; Hart and
360 Davis, 1978; Kinzler et al., 1990) and more compositional and temperature dependent algorithms
361 ($D_{Ni}^{ol-melt}$ of 26.3; Li and Ripley, 2010) for Ni in olivine partitioning. Since this represents the
362 most evolved melt composition, following the MgO-dependent partitioning behavior, these
363 calculated D's are maximum values. Unlike Ca, the highly compatible nature of Ni in olivine

364 means that fractionation of olivine will have a significant effect on Ni melt contents and
365 subsequent olivine crystallization.

366 Using the same methodology described for Ca above, Ni contents in olivine can drop by
367 ~2500 ppm, even with the minimal anticipated olivine fractionation. As stated, this would
368 represent a maximum change in Ni since the more primitive (by ~1 wt. % MgO) theoretical
369 starting melt composition would result in a lower Ni in olivine partition coefficient (e.g. Hart and
370 Davis, 1978; Leeman and Lindstrom 1978). However, while this model can explain much of the
371 variation in Ni in olivine, it does not account for Ni concentrations as low as 1000 ppm observed
372 near grain boundaries (Fig. 6, 7). From this modeling, it is apparent that the co-variation in
373 olivine Ni and Ca concentrations cannot be reasonably explained using a fractional
374 crystallization model with olivine evolving from ~Fo₉₁ to ~Fo₈₉ compositions (Fig. 7).

375 **Paradoxical compositions**

376 Modeling of olivine compositions, particularly for Ni and Ca in olivine, indicates olivine
377 core compositions cannot be generated from the melt in which they are transported by simple
378 fractional crystallization. The variations we observe in olivine profiles are instead more
379 consistent with diffusive re-equilibration following incorporation of olivine grains into a more
380 Ca-rich, Ni-poor melt, as similarly observed by Kamenetsky et al. (2006). The presence of low-
381 Ca magmatic olivine are typically attributed to crystallization from a low-Ca melt (e.g.,
382 Kamenetsky et al., 2006; Elburg et al., 2006). Although the re-homogenized major element
383 compositions of olivine-hosted melt inclusions from the lava are compromised due to Fe-
384 dilution, elements not strongly controlled by olivine crystallization/dissolution have far greater
385 variability than predicted from heating experiments (Rowe et al., 2006). This is especially true
386 of CaO, with 5 wt. % variation (from ~ 8 – 13 wt. % CaO) reported in inclusions minimally

387 effected by Fe-dilution (rehomogenized between 1125-1150°C; Rowe et al., 2006). Taken
388 qualitatively, re-homogenized olivine-hosted melt inclusion compositions from the lava may, in
389 fact, provide evidence of a low-CaO, high-SiO₂ (up to 54 wt. % SiO₂) melt component not
390 observed in either scoria glass or olivine-hosted inclusions from the scoria.

391 Melt inclusion, groundmass scoria glass, and lava whole rock trace elements all have the
392 same overall distribution patterns (Rowe et al, 2006; 2009), and indicate a related petrogenesis.
393 This is inconsistent with the inferred disequilibrium and melt heterogeneity indicated by mineral
394 chemistry and re-homogenized melt inclusion major element compositions. Hesse and Grove
395 (2003), propose that for Mexican volcanic belt absarokites, trace elements record a deeper,
396 “original” source, while major elements instead record later re-equilibration between the original
397 melt and shallower hot mantle. In order to explain two melts with different major element
398 characteristics but similar trace element signatures, we propose a similar model whereby
399 incompatible trace elements record the original slab-derived fluid-rich melt but subsequent
400 metasomatism and re-equilibration impart this trace element signature on a mineralogically
401 variable (veined?) subarc mantle.

402 **Nature of sources**

403 The origin or cause of enriched Ni concentrations in olivine is variably ascribed to
404 different mantle sources (including eclogitic and pyroxenitic domains) and/or magmatic
405 compositions and oxidation states and therefore is of great interest as a potential constraint on
406 intrinsic magma properties and/or mantle source domains (e.g., Davis and Smith, 1993; Sobolev
407 et al., 2007; Straub et al., 2008; Wang and Gaetani, 2008). High-Ni olivine have been identified
408 in several volcanic arcs in addition to the Cascades, including Japan, Kamchatka, and the
409 Mexican volcanic belt (Straub et al., 2008; Tatsumi et al., 2006; Ishimaru and Arai, 2008).

410 However, to date no single model readily explains all of the observed occurrences of high-Ni
411 magmatic olivine. Given the compositional variability of the host lavas and the widespread and
412 diverse localities at which anomalous olivine are observed it is perhaps not surprising that the
413 origins of these olivine are debated.

414 Prior efforts at understanding the genesis of high-Ni magmatic olivine have focused on two
415 main processes altering Ni partitioning behavior. All models require modification of the mantle
416 peridotite source or primitive basalts through addition of a silicic component (e.g. an eclogitic
417 melt or siliceous subduction component). It is proposed that addition of a siliceous component to
418 the mantle source results in the conversion of olivine to pyroxene (e.g., $\text{SiO}_2 + \text{Mg}_2\text{SiO}_4 =$
419 $\text{Mg}_2\text{Si}_2\text{O}_6$; Sobolev et al., 2005, 2007; Straub et al., 2008). Sobolev et al. (2005, 2007) argue that
420 conversion to a pyroxene-dominant source lithology changes the buffering of trace elements (e.g.
421 the bulk partition coefficient for Ni in pyroxene is lower than for Ni in olivine), allowing primary
422 basaltic melts to have higher Ni contents, reflected then in subsequent olivine crystallization.
423 However, the partition coefficient of Ni in olivine has been demonstrated to strongly increase
424 with melt polymerization and decreasing MgO content (Leeman and Scheidegger, 1977; Hart
425 and Davis, 1978; Leeman and Lindstrom, 1978; Kinzler et al., 1990; Li and Ripley, 2010).
426 Although starting from a similar reacted mantle source, Straub et al. (2008) argues that a melt
427 generated from a pyroxenite source, with higher SiO_2 and lower MgO, will therefore result in
428 higher Ni in the crystallizing olivine because of the increase in Ni in olivine partitioning (i.e.
429 without a significant change to the primary melt Ni content). Alternatively, Wang and Gaetani
430 (2008) suggest that because of the effect of melt polymerization on Ni in olivine partitioning,
431 you do not need a reaction-pyroxene dominant lithology and that simply adding eclogitic partial
432 melts to tholeiitic basalts promotes crystallization of relatively high-Ni olivine. Despite

433 variations, all models require fundamental changes to either primitive basalt compositions or
434 mantle source lithologies and thus the origin of these chemically anomalous high-Ni olivine can
435 provide significant constraints on magma petrogenesis and evolution.

436 A mineralogically distinctive source (i.e. non-peridotitic) is consistent with olivine $\delta^{18}\text{O}$
437 ($5.64 \pm 0.1 \text{ ‰}$), greater than that typically observed in mantle peridotite olivine or peridotite-
438 derived magmatic olivine. Given the primitive nature of the olivine phenocrysts, it is unlikely
439 that these isotopically heavy $\delta^{18}\text{O}$ values are the result of crystallization or crustal contamination,
440 both of which may slightly increase $\delta^{18}\text{O}$ in basalts (Bindeman et al., 2004; Harmon and Hoefs,
441 1995). In the following discussion we propose two possible sources of pyroxene-dominated
442 lithologies.

443 Glass trace element signatures with very low Yb (1.2 ppm) and Y (20 ppm), and high
444 $[\text{Dy}/\text{Yb}]_{\text{N}}$ (3), are consistent with a residual garnet phase in the source region (Fig. 10). One
445 obvious potential source for garnet is in eclogitized subducted oceanic crust at depths greater
446 than 45 km in the down-going Juan de Fuca Plate (Bostock et al., 2002). Given the young (~8
447 Ma) and hot nature of the subducting plate (Stein and Stein, 1996; Syracuse et al., 2010), a low
448 degree partial melt of eclogitic crust is not unreasonable. Heavy $\delta^{18}\text{O}$ isotopic signatures in
449 olivine, similar to the Quartzville olivine, are found in many arc settings worldwide, and are
450 often attributed to a number of different processes including melting of de-serpentinized mantle
451 and slab melting (e.g., Bindeman et al., 2005; Eiler et al., 2005; Johnson et al., 2009; Auer et al.,
452 2009). Quartzville olivine oxygen isotopic signatures are also similar to high-Mg andesites from
453 the Cascades ($\delta^{18}\text{O}$ 5.49 – 5.78‰), suspected of containing a slab melt component (Bindeman et
454 al. 2005). If the high $\delta^{18}\text{O}$ isotopic signature of the olivine were inherited from the subducting
455 plate, this may indicate that the fluid came from the upper part of the oceanic crust, altered by

456 seawater at low temperature (Muehlenbachs, 1986; Auer et al., 2009). However, Bindeman et al.
457 (2005) compiled oxygen isotopic analyses from world-wide adakites thought to be related to slab
458 melting, and this study suggests that isotopic exchange between slab melts and the mantle wedge
459 may buffer the variability observed in olivine such that the location within the subducting plate
460 where melting is taking place is more difficult to reconcile.

461 High-Mg dacitic magmas, thought to be derived from partial melting of the subducting
462 plate (adakites), have characteristic trace element signatures with high Sr concentrations and
463 La/Yb ratios (e.g., Kay, 1978). Despite melt trace element similarities, the major element
464 composition of the lava, glasses and melt inclusions, including the qualitative higher SiO₂, lower
465 CaO re-homogenized inclusions, are not evolved enough to resemble a typical adakitic slab melt.
466 However, similar to the two-stage model of Hesse and Grove (2003), the subducting plate could
467 represent the original source of the trace element signature.

468 Following the generation of a siliceous subduction component, ascent and metasomatism
469 of the overlying peridotitic mantle could result in a pyroxene-dominated lithology as olivine is
470 converted to orthopyroxene (e.g., Straub et al., 2008). As previously introduced, from various
471 models it has been proposed that melts generated from this reaction-pyroxene dominant source
472 lithology could produce melts with fundamentally higher Ni contents (Sobolev et al., 2005,
473 2007) or have higher SiO₂ and lower MgO (Straub et al., 2008). The resultant olivine
474 crystallization from reaction-pyroxene dominant source lithologies in either case would be
475 relatively high in Ni compared to those crystallizing from peridotite-derived magmas. This
476 change in Ni behavior could occur because of both lower Ni partition coefficients in pyroxene
477 compared to olivine (Sobolev et al., 2005, 2007) and increasing Ni in olivine partitioning with
478 melt polymerization and decreasing MgO (Straub et al., 2008). While our results cannot

479 necessarily distinguish between these two mechanisms of Ni enrichment, both may be impacting
480 observed olivine compositions. The correlation between high-Ni and low-Ca in olivine is
481 consistent with a change in source mineral buffering, while the qualitatively higher melt SiO₂ at
482 low MgO contents in rehomogenized inclusions favors a melt polymerization control on Ni
483 partitioning.

484 Sobolev et al. (2007) further investigated the mineralogical response to pyroxenite versus
485 peridotite melting, indicating that pyroxenite melts characteristically have high Ni/Mg
486 ($100 \times \text{Ni/Mg}$ of $\sim 1.5\text{-}2.5$) and low Ca/Fe ($100 \times \text{Ca/Fe}$ of $\sim 2\text{-}2.5$) at low Mn/Fe ($100 \times \text{Mn/Fe}$ of
487 $\sim 1.1\text{-}1.3$). While Mn/Fe ratios are not as well constrained in the present study, for the range of
488 Fo_{91-89.5} (excluding high-Fo and low-Fo rim growth), we observe olivine compositions near the
489 pyroxenite-melt field with average $100 \times \text{Ni/Mg}$, $100 \times \text{Ca/Fe}$, and $100 \times \text{Mn/Fe}$ of 1.39, 1.39 and
490 1.34, respectively (Fig. 7b).

491 Although olivine cores are thought to record crystallization from a melt of a pyroxenite-
492 dominated source lithology, diffusive re-equilibration on the olivine rims (higher Ca and lower
493 Ni), coupled with a change in major element melt composition recorded by the host lava and
494 glasses, suggests olivine grains record a mixing event. Prior trace element modeling has
495 suggested the Quartzville basalt could be generated by high significant fluid fluxing (up to 6 wt.
496 % of a hydrous subduction component) of a highly depleted mantle peridotite which had
497 previously undergone ~ 25 % melting (Rowe et al., 2009). A mixing based model to explain the
498 core-rim variation in olivine is also consistent with observations of magma production from the
499 Mexican Volcanic Belt (Straub et al., 2008, 2011).

500 The change in source mineralogy, from a pyroxenite-dominated to a depleted harzburgitic
501 peridotite, can be produced following the model of Straub et al. (2008) whereby the addition of a

502 SiO₂-rich subduction component to the mantle wedge will result in vertical zones of pyroxenite,
503 surrounded by depleted mantle. However, as discussed above, trace elements derived from the
504 subducted plate would reflect the original garnet-bearing source and may rapidly re-equilibrate
505 as a result of their high abundances relative to the surrounding mantle (Hesse and Grove, 2003;
506 Straub et al., 2008; Straub et al., 2014). The result would be a mantle source containing both
507 reaction-pyroxenite and highly fluid-fluxed, depleted peridotitic mantle (Fig. 11). Initial melt
508 production in the pyroxenite zone, and subsequent olivine crystallization, would result in olivine
509 with high Ni and low Ca. Later melts of the fluid-fluxed, depleted mantle incorporating early
510 pyroxenite-derived olivine would explain the similarity in incompatible trace element
511 abundances in the melt inclusions as well as host lava and scoria, despite the disequilibrium in
512 olivine composition resulting from olivine overgrowth and diffusive re-equilibration with the
513 peridotite-derived melt.

514 The magma mixing scenario of Wang and Gaetani (2008) could be proposed as an
515 alternative model to that proposed above. However, a magma mixing model with no fundamental
516 change to the source lithology could explain the olivine compositional variations, but not the
517 nearly identical melt trace element compositions between melt inclusions, lava, and scoria. For
518 all of our observations to be true, we need to have a mineralogically variable source that has been
519 overprinted with the same incompatible trace element signature. Importantly, this implies that
520 the source of the unique olivine chemistry is in the subarc mantle wedge, while the origin of the
521 enriched trace element signature is the subducting plate.

522 **Olivine rim growth**

523 The last aspect of the anomalous olivine compositions to be explained are the very high
524 forsterite rim compositions (F_{O91-94}). Two main mechanisms may provide an explanation for the

525 very high forsterite ($>Fo_{91}$) olivine near the rims of the olivine grains in the lava. First, the
526 mixing event discussed above may result in equilibrium crystallization of the very high Fo
527 olivine rims. However, Fe-Mg equilibrium calculations suggest Fo_{86} olivine should be in
528 equilibrium with the host melt (consistent with the lowest recorded Fo content prior to the high
529 Fo olivine rim). In addition, despite the similar glass/whole rock trace element signatures and
530 identical Ni-Ca in olivine rim co-variation, high Fo rims are not observed on olivine from the
531 scoria. The highest Ni concentrations are not observed in the high-Fo olivine, and Ni
532 concentrations systematically, and nearly linearly, decrease toward the olivine rim regardless of
533 the switch from normal to reverse Fe-Mg zoning in olivine from the lava. Olivine grains from the
534 scoria, where no reverse zoning is observed, display the same trend in Ni decreasing steadily
535 toward the rim (Fig. 3). Similarly, Ca concentrations increase towards the rim in olivine crystals
536 of both the lava and scoria, irrespective of the normal or reverse Fe-Mg zoning. The high olivine
537 Fo contents ($> Fo_{91}$), therefore, are unique to the lava flow, despite a similar petrogenic history
538 between the lava and scoria. This suggests the high-Fo rims may be related to eruptive processes.

539 A second potential mechanism for causing the high Fo contents and reversed Fe-Mg
540 zoning in the outer 25-50 μm is an increase in the oxidation state during slow cooling of the lava.
541 Assuming melt composition remains unchanged, in order to crystallize an $Fo_{93.8}$ olivine from the
542 average scoria MI composition (Supplemental Table S2), $Fe^{3+}/Fe_{\text{Total}}$ would need to increase to
543 0.62, corresponding to an oxidation state of approximately $+4.6 \log fO_2$ (ΔFMQ). While this
544 oxidation state is high relative to other basalts in the Cascades which are generally at or below
545 FMQ (Rowe et al., 2009), it corresponds well with estimated oxidation states for minettes from
546 the western Mexico Volcanic Belt which vary from $+3.4$ to $+7 \log fO_2$ (ΔFMQ ; Wallace and
547 Carmichael, 1989).

548 As previously mentioned, spinel composition in the lava ranges from a high-Cr to high-
549 Fe end member (compositional data presented by Rowe et al. (2006) are provided in
550 Supplemental Table S6). As calculated temperature and Mg# decreases, the Fe component, and
551 calculated oxidation state also increase (Ballhaus et al., 1991). Calculated oxidation states in the
552 lowest temperature spinels are up to +4.1 log fO_2 (ΔFMQ), similar to the predicted +4.6 log fO_2
553 (ΔFMQ) from olivine compositions required to produce the high Fo olivine rims. The low-T,
554 high-Fe spinels likely reflect low-T re-equilibration (Kamenetsky et al., 2001). However, this re-
555 equilibration may also be a function of increasing oxidation state of the lava upon cooling and
556 degassing.

557 Interestingly, Wallace and Carmichael (1989) also argue that oxidation of the western
558 Mexico Volcanic Belt minettes is a rapid, late process and that pre-eruptive fO_2 was
559 approximately +3.2-3.7 log fO_2 (ΔFMQ). A late oxidation model fits well with our mineralogical
560 observation of high Fo olivine rims only observed on olivine in the dense, more crystalline lava
561 but not on olivine from the rapidly quenched scoria. Additionally, the observed increase in
562 Fe^{3+}/Fe^{2+} calculated for clinopyroxene rims compositions from the lava is consistent with a late
563 oxidation event (Fig. 4). Wallace and Carmichael (1989) propose that oxidation is related to
564 volatile degassing, specifically the loss of H_2 derived from H_2O , based on observations and
565 similar arguments from pillow lavas where pillow interiors have a higher Fe^{3+}/Fe_{Total} versus
566 exterior glassy rinds (Christie et al., 1986). Alternatively, Metrich et al. (2009) argue that the
567 reduction of sulfur in initially oxidized systems will result in further oxidation of the melt during
568 degassing. In this case SO_4^{2-} (melt) (S^{6+}) reduces to SO_2 (gas) (S^{4+}) such that 1 mol of sulfate may
569 oxidize 2 mol Fe^{2+} .

570 Using the variably degassed melt inclusions from the scoria as a proxy for degassing

571 behavior in the lava we can evaluate the effect of degassing on the oxidation state of the magma
572 (note that Rowe et al., 2006 report similarly high S melt contents for melt inclusions). Melt
573 inclusions from the scoria have a maximum concentration of ~0.6 wt. % S (~87 % S^{6+}/S_{Total})
574 while the scoria has a minimum concentration of 0.26 wt. % S (Rowe et al., 2009). Rowe et al.
575 (2007) demonstrated that for this scoria composition as degassing progresses (decreasing sulfur
576 concentration) the proportion of sulfate decreases linearly and the amount of sulfur, as sulfide in
577 the melt, stays relatively constant. This reduction of sulfate equates to a loss of 0.011 mol S^{6+} for
578 every 100 g of magma, allowing for the oxidation of ~0.022 mol Fe^{2+} per 100 g of melt. Based
579 on the average inclusion composition described above, for every 100 g of magma there is
580 approximately 0.064 mol Fe^{2+} (assuming the same $Fe^{3+}/Fe_{\text{Total}}$ of 0.32). In order to generate the
581 highest Fo rim olivine from the same melt composition, we require $Fe^{3+}/Fe_{\text{Total}}$ of 0.62 or the
582 oxidation of an additional 0.028 mol Fe^{2+} per 100 g of magma. Therefore nearly all of the
583 oxidation of the Fe needed to explain the dramatic increase in olivine rim compositions can be
584 accommodated by reduction and degassing of oxidized sulfur (S^{6+}) and subsequent Fe oxidation
585 ($Fe^{2+} \rightarrow Fe^{3+}$). If we assume that melt inclusions from the scoria represent an initial sulfur
586 content for the scoria and lava melt compositions, then we can explain the lacking of high-Fo
587 rims on olivine from the scoria simply reflecting faster cooling of the scoria upon eruption
588 compared to the slowly cooled lava. This would imply, based on observations at Quartzville, that
589 degassing of extremely high concentrations of oxidized sulfur must be coupled with slow cooling
590 of the mafic magma to produce the high-Fo olivine rims.

591 **IMPLICATIONS**

592 Understanding the petrogenesis of the compositionally anomalous olivine from the
593 Quartzville absarokite has significant implications for Cascade arc magma genesis, and more

594 broadly, subduction zone processes. Our results imply that an end-member of Cascade arc
595 magmatism is derived from slab melting and the re-equilibration of that melt with the mantle
596 wedge. Significant to subduction zone processes in general, our results suggest that siliceous slab
597 melts may re-equilibrate with the sub-arc mantle, resulting in a mineralogical change while
598 imprinting a more widespread trace element signature to the mantle wedge. Important to magma
599 genesis, these results suggest that the mineralogical reactions (i.e. conversion of olivine to
600 pyroxene) occurring in the mantle wedge may be decoupled from more classical trace element
601 subduction signatures derived from the subducting plate. A similar process has been suggested in
602 other volcanic arcs (e.g., Hesse and Grove, 2003; Straub et al., 2008; 2011; 2014) and may
603 therefore imply a more widespread subduction zone process, often over-looked because of the
604 relatively small volume of this magmatic composition.

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840

841 **Figure Captions**

842

843 **Figure 1.** Location map for the Quartzville basalt within the Oregon Cascades. The older
844 Western Cascades (dark grey; ~ 40-10 Ma) are distinguished from the younger High Cascades
845 (light grey; ~10 Ma – present). Major volcanic centers in the High Cascades are indicated with
846 triangles. The position of the Quartzville basalt (QV; 42 ka) is indicated within the older Western

847 Cascades.

848

849 **Figure 2.** Olivine thin section petrographic images indicating the range of textures and
850 morphologies observed. Predominantly euhedral grains (a; c) are most common, however,
851 skeletal or partial grains are sometimes observed (b). Magnetite and/or spinel inclusions in
852 olivine may be zoned (a), or randomly distributed. Chains of oxide phases (+/- a silicate phase),
853 increase in size into the grain, perpendicular to grain boundary (c, d).

854

855 **Figure 3.** X-ray mapping of Mg (a, c), Mn (b), and Ni (d), variations in an olivine grain from the
856 lava flow. Note that Mg intensity increases (indicated by warm colors) around the olivine rim,
857 characteristic of the high-Fo rim compositions. Additionally, Mn X-ray intensities increase
858 towards the rim while Ni decreases, consistent with quantitative transect measurements.

859

860 **Figure 4.** Representative backscatter electron images (BSE) of clinopyroxene sector (a) and
861 oscillatory (b) zonation and textures and corresponding calculated $\text{Fe}_2\text{O}_3/\text{FeO}$ along analytical
862 transects (c, d). Oscillatory zoning is evident in some grains (b), with grain rims having high Fe
863 concentrations.

864

865 **Figure 5.** Backscatter electron image (BSE) of the scoria glass in contact with an olivine
866 phenocryst. Groundmass is dominated by clinopyroxene and olivine with microapatite. Olivine
867 compositions are indicated for the phenocryst and groundmass grains.

868

869 **Figure 6.** (a) Ni and (b) Ca concentrations (ppm) versus olivine Fo# for Quartzville olivine

870 grains from both the scoria (open) and lava (closed).

871

872 **Figure 7.** Ca versus Ni variations in olivine. (a) Quartzville Ca and Ni olivine concentrations
873 overlain on a 2D smoothed histogram of a compilation of mantle olivine (Fo₈₉₋₉₃; N= 4444)
874 from the georoc database (<http://georem.mpch-mainz.gwdg.de/>). Also indicated are the starting
875 (green square) and ending (red star) compositions assuming Ni and Ca partitioning and olivine
876 fractionation (from Fo₉₁ to Fo₈₉) as described in the text. The black line is a linear regression of
877 olivine chemical variation based on olivine with less than 4500 ppm Ni, showing the offset at
878 higher Ni concentrations. (b) Normalized Ca and Ni variations after Sobolev et al. (2007),
879 compared to olivine compositions from other Cascade arc end-member magmas which generally
880 are higher Ca and lower Ni (data from Rowe et al., 2009). Also plotted (dashed ellipses) are the
881 fields olivine derived from pyroxenite and peridotite sources from Sobolev et al. (2007). Same
882 symbols as in figure 6.

883

884 **Figure 8.** Representative core-rim transects across olivine grains from the lava (a-d) and scoria
885 (e-h) for Fo# (a, e), Ni (b, f), Ca (c, g), and Mn (d, h).

886

887 **Figure 9.** Oxygen isotope ($\delta^{18}\text{O}$) variation of olivine phenocrysts from Cascades basalts, versus
888 whole rock MgO wt. %. Upper mantle olivine field from Matthey et al. (1994). Quartzville is
889 indicated as the black square. Arc lavas and backarc lavas (shoshonite, calc-alkaline basalts,
890 enriched intraplate basalt, and low-K tholeiites) are classified after Rowe et al. (2009).

891

892 **Figure 10.** Lava, scoria and melt inclusion trace element compositions normalized to primitive

893 mantle (McDonough and Sun, 1995). Note significant heavy rare earth element depletion and
894 consistency between lava, scoria, and average melt inclusions. Modified from Rowe et al. (2006,
895 2009).

896

897 **Figure 11.** Schematic model of mantle processes in the generation of the Quartzville basalt.

898 Depth of eclogitized crust from Bostock et al. (2002). (1) Slab partial melting of eclogitic crust
899 resulting in a siliceous melt with an adakite-like trace signature (e.g., high Sr/Y, La/Yb). Box
900 shows enlargement of proposed re-equilibration model where the high-SiO₂ melt reacts with the
901 olivine in the depleted harzburgite to generate reaction-pyroxenite (red). Trace element re-
902 equilibration extends (grey) beyond the silica + olivine = orthopyroxene reaction such that
903 melting of both zones will have a similar trace element signature. High Ni, low Ca olivine
904 crystallizes from a melt of reaction-pyroxenite, while lower Ni, high Ca olivine rims crystalize
905 from melt derived from slab fluid-fluxed depleted harzburgite at (2).

906

Table 1. Summary of the petrography for scoria and lava, and olivine compositional details.

	<i>Phases</i>	<i>Characteristics</i>	<i>Compositions</i>	<i>Transect details</i>
Scoria				
<i>Phenocrysts</i>	olivine	euhedral, up to 500 μm ; no magnetite inclusions in olivine	Fo _{90.6-88.4} Ni 1100-5500 ppm Ca 658-1746 ppm Mn 730-1617 ppm	normally zoned rim compositions Fo _{88.7-89.4} Ni decreases from 5000-6000 ppm in cores to 1000-2000 ppm in rims Ca varies inversely with Ni
<i>Groundmass</i>	olivine > clinopyroxene > apatite		Fo ₈₉ Ni 1310-1860 ppm Ca 1605-1940 ppm	
Lava				
<i>Phenocrysts</i>	olivine	euhedral-subhedral, some broken, some embayed edges, up to 500 μm abundant magnetite-spinel inclusions	Fo _{93.8-88.6} , Ave. Fo _{90.7} Ni 800-6400 ppm Ca 860-1785 ppm Mn 680-2320 ppm	both normal (predominant; rim composition \sim Fo ₈₉) and reverse (minor; only in outer 50 μm ; up to \sim Fo ₉₄) zoning Ni does not vary linearly with Fo content; Max Ni at \sim Fo ₉₁ ; Ni decreases to higher and lower Ca varies inversely with Ni Mn varies inversely with Ni
	clinopyroxene microphenocrysts	euhedral, up to 400 μm , most <200 μm	Mg# 82-89	increase in Fe ₂ O ₃ /FeO toward rim
<i>Groundmass</i>	Plagioclase-clinopyroxene > magnetite > apatite	decreasing S at rims of apatite	Cpx Mg# \sim 86	

Table 2: Representative and average olivine compositions from the lava and scoria samples.

Oxide (wt%)	SiO ₂	Al ₂ O ₃	MnO	FeO	NiO	MgO	CaO	TiO ₂	Cr ₂ O ₃	Total	Fo#
Scoria											
Average	40.17	0.03	0.14	10.24	0.40	48.49	0.17	0.01	0.04	99.68	89.4
s.d.	0.56	0.05	0.03	0.63	0.13	0.49	0.03	0.01	0.02	0.58	0.6
04-053-5.1	40.37	0.02	0.14	11.00	0.22	48.51	0.24	0.00	0.03	100.54	88.7
04-036_4.12	40.76	0.01	0.12	10.09	0.42	48.40	0.15	0.01	0.06	100.02	89.5
04-036_1.1	40.90	0.01	0.13	9.25	0.64	48.80	0.13	0.01	0.08	99.96	90.4
g.m. rim	40.47	0.04	0.17	10.59	0.14	47.49	0.28	0.04	0.02	99.26	88.9
g.m. core	40.24	0.05	0.18	10.32	0.26	47.76	0.23	0.01	0.04	99.10	89.2
Lava											
Average	40.42	0.03	0.13	8.97	0.55	49.06	0.15	0.01	0.05	99.37	90.7
s.d.	0.34	0.07	0.04	0.84	0.14	0.82	0.04	0.01	0.03	0.57	0.9
04-044-5.1	39.54	0.00	0.14	10.79	0.31	48.35	0.16	0.01	0.01	99.30	88.9
03-050-7.1	40.14	0.03	0.12	9.53	0.51	48.36	0.13	0.00	0.03	98.85	90.0
04-047-22.1	40.40	0.01	0.09	8.62	0.76	48.76	0.12	0.00	0.07	98.83	91.0
03-1_1.1	40.81	0.02	0.17	7.65	0.49	49.89	0.14	0.01	0.03	99.25	92.1
03-1_3.26	41.01	0.00	0.30	6.06	0.10	51.64	0.23	0.02	0.02	99.39	93.8

Note: "g.m." denotes groundmass olivine.

Ni, ppm	Ca, ppm	Mn, ppm
3011	1212	1091
949	242	206
1723	1723	1107
3306	1107	896
5003	926	1025
1093	1995	1280
2031	1612	1399
4284	1038	992
1065	268	274
2431	1126	1056
4031	933	918
5963	861	681
3879	1015	1322
789	1647	2320

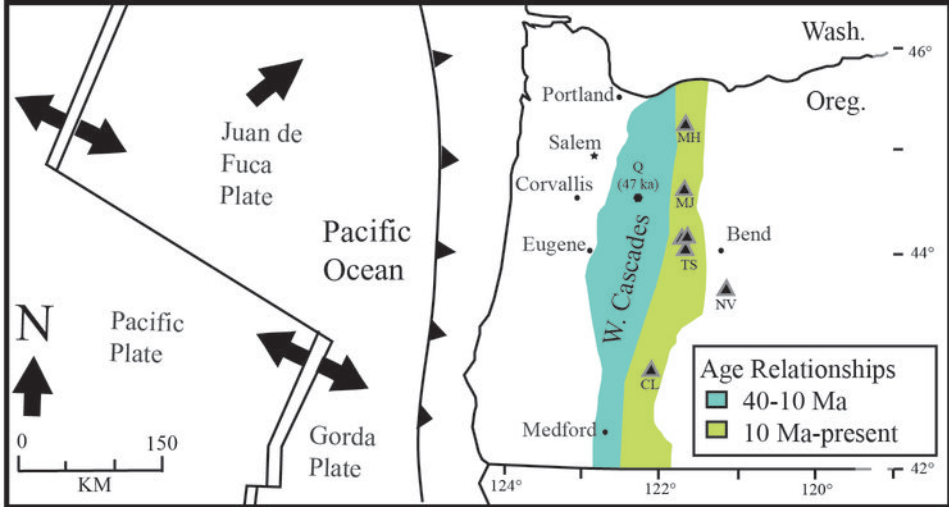


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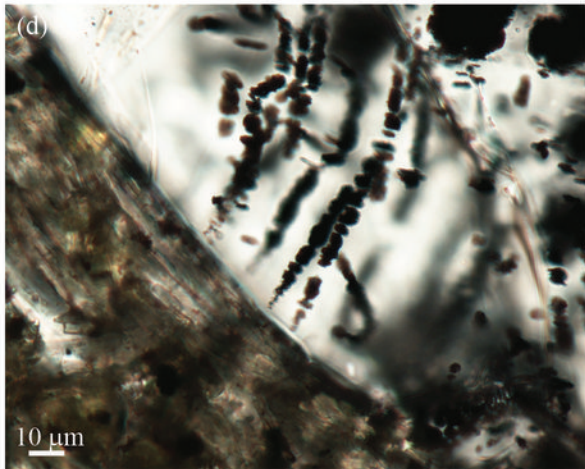
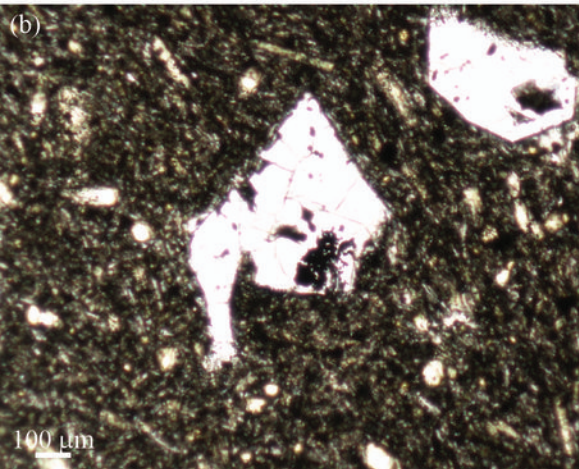
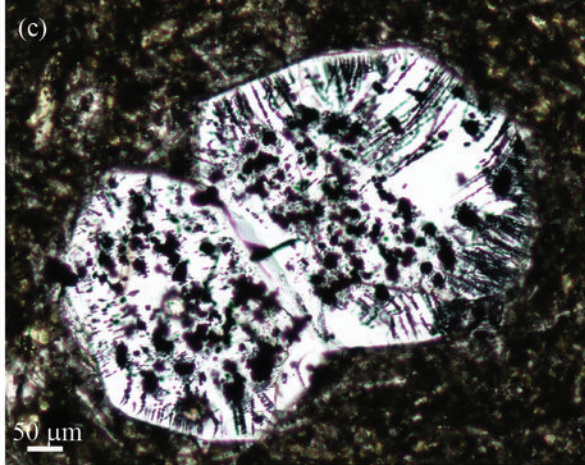
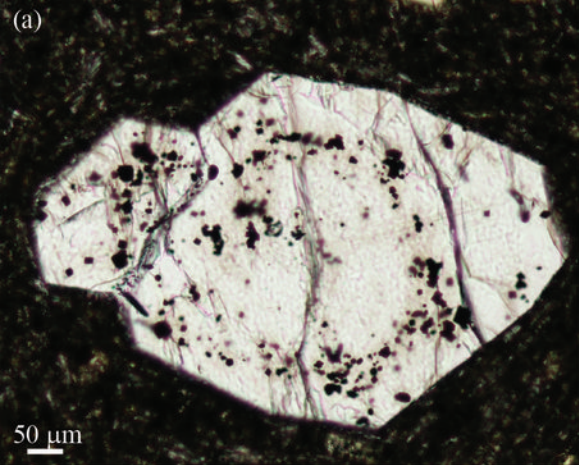


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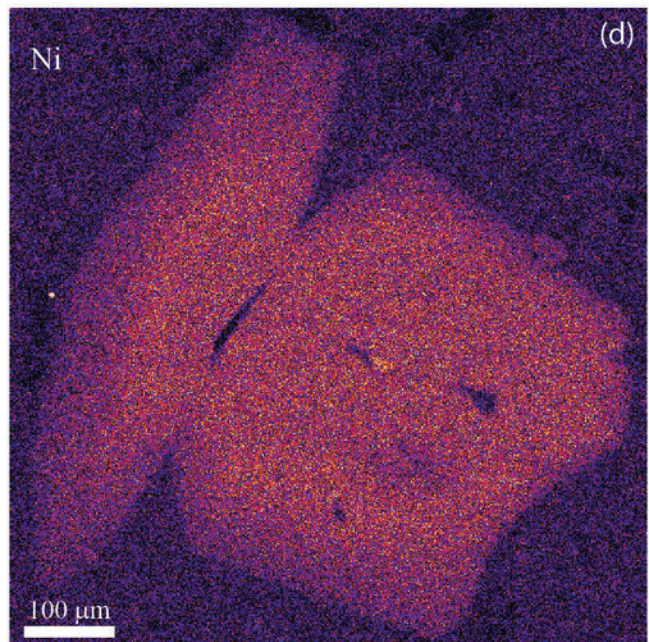
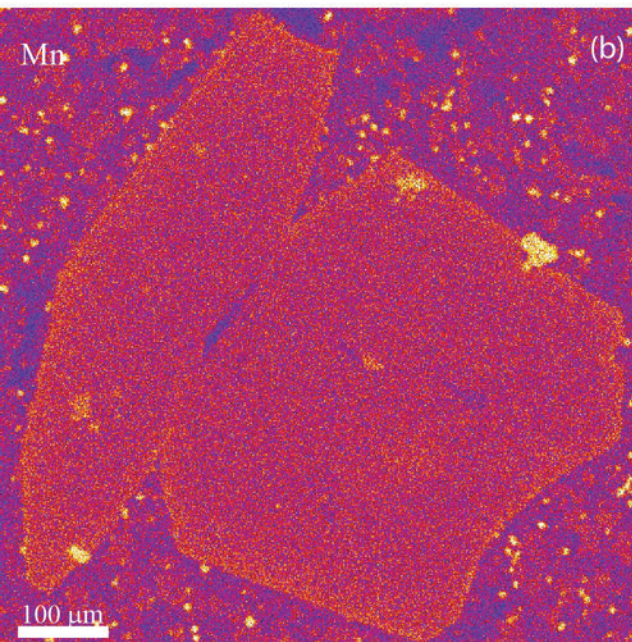
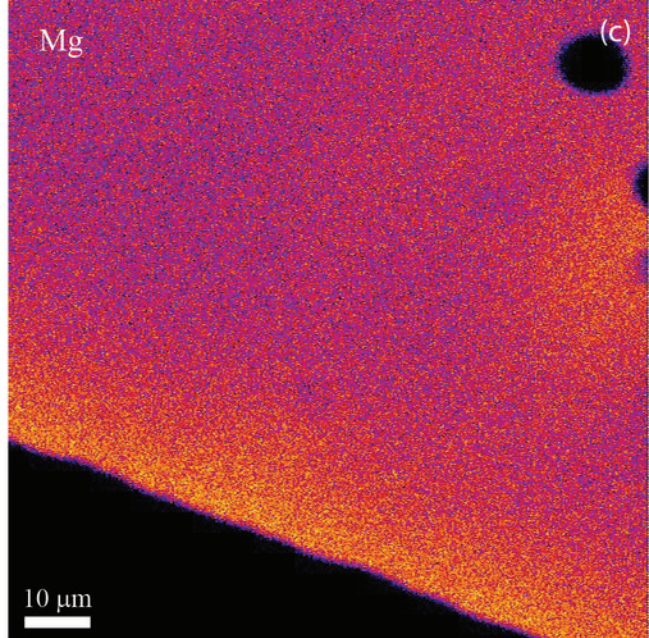
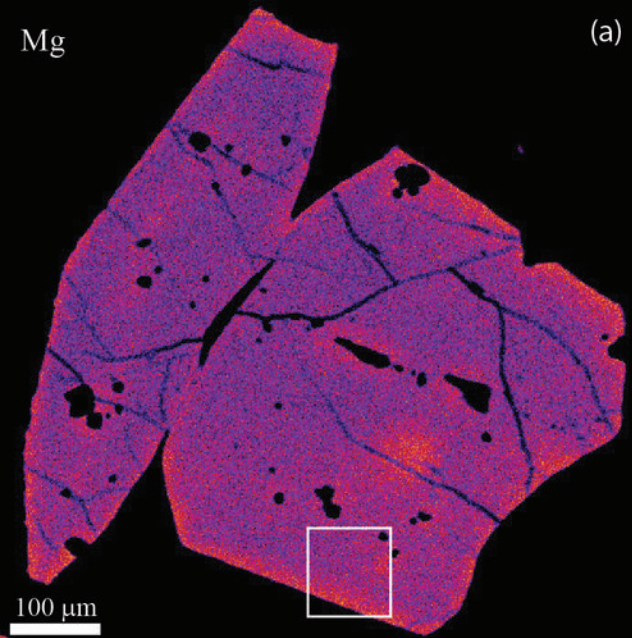


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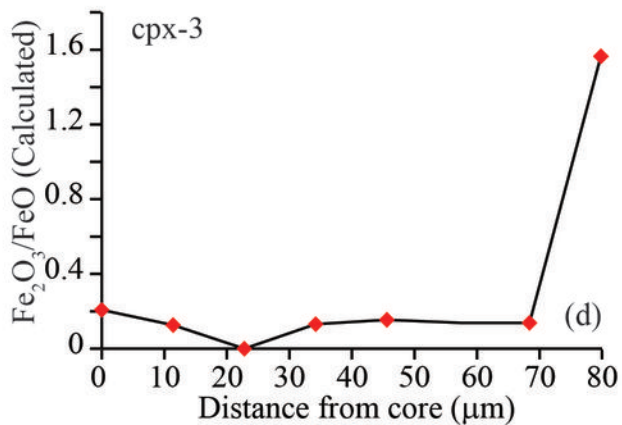
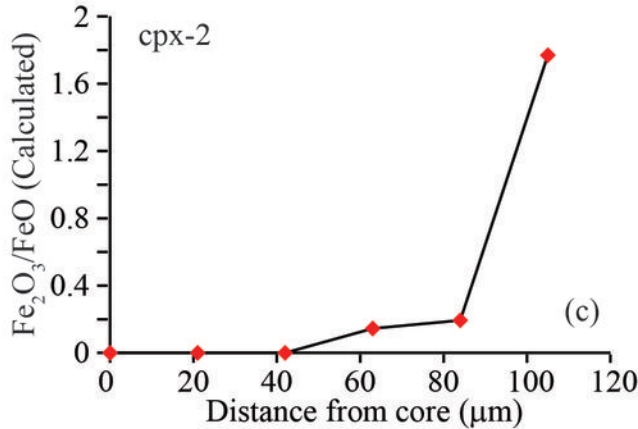
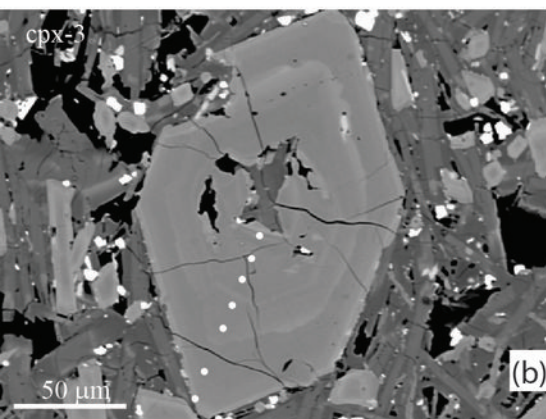
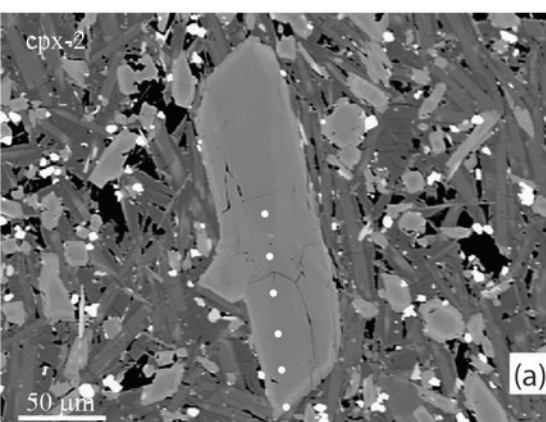


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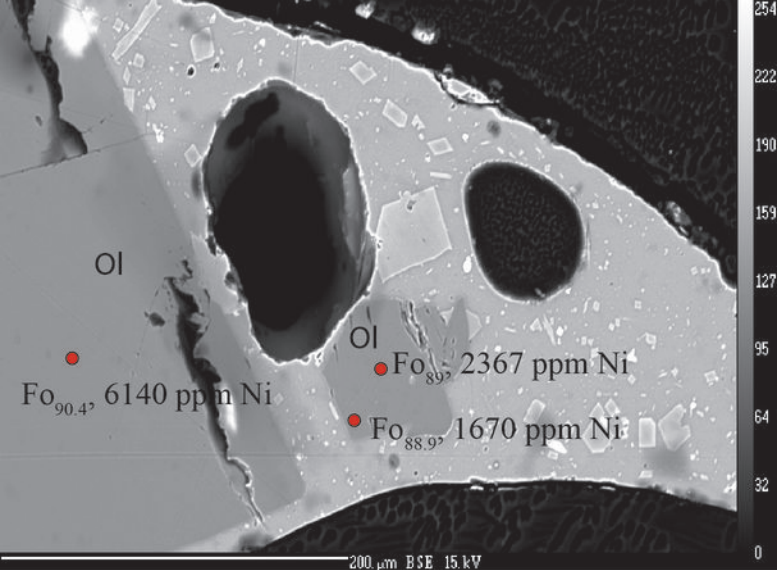


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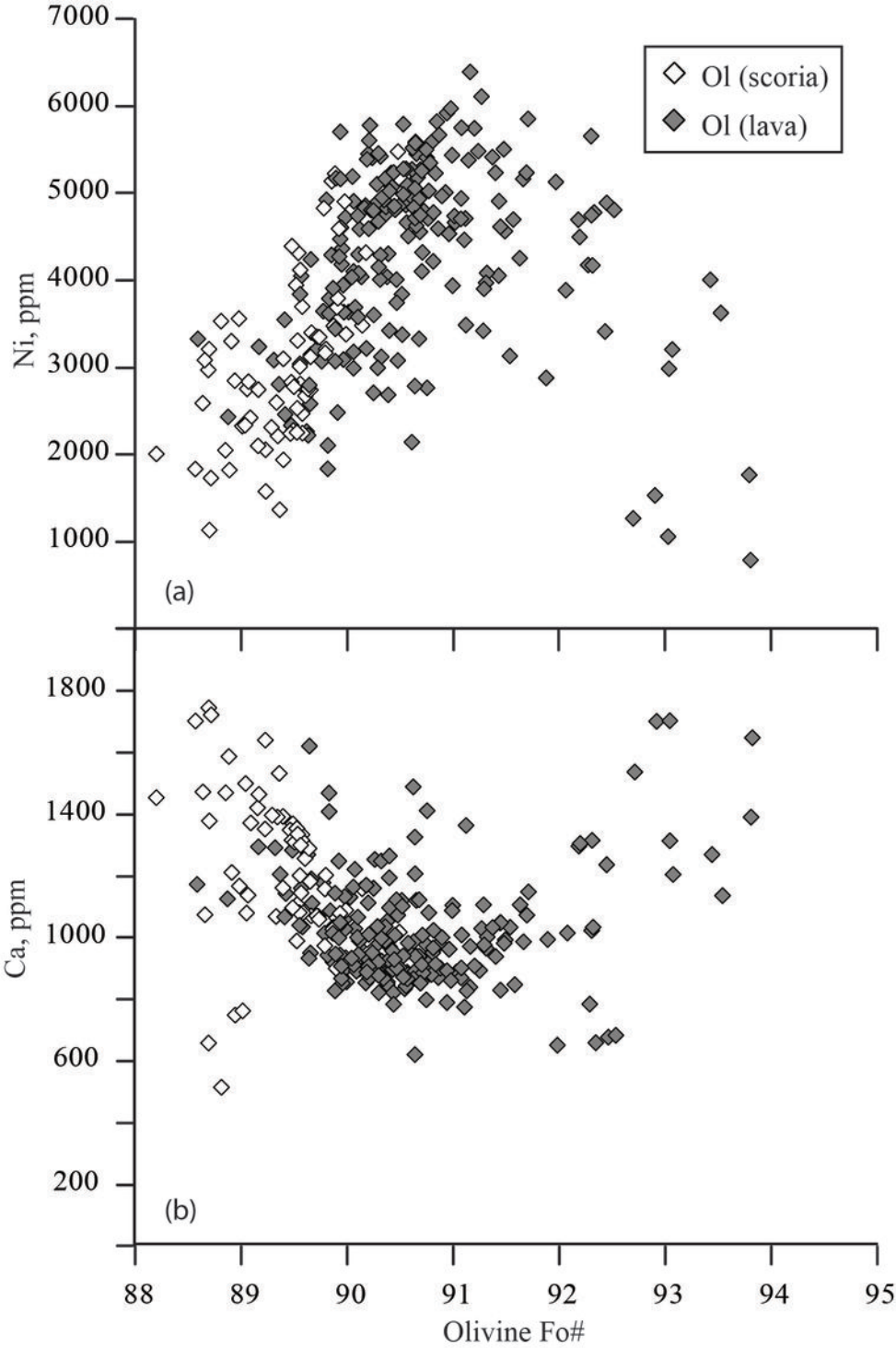


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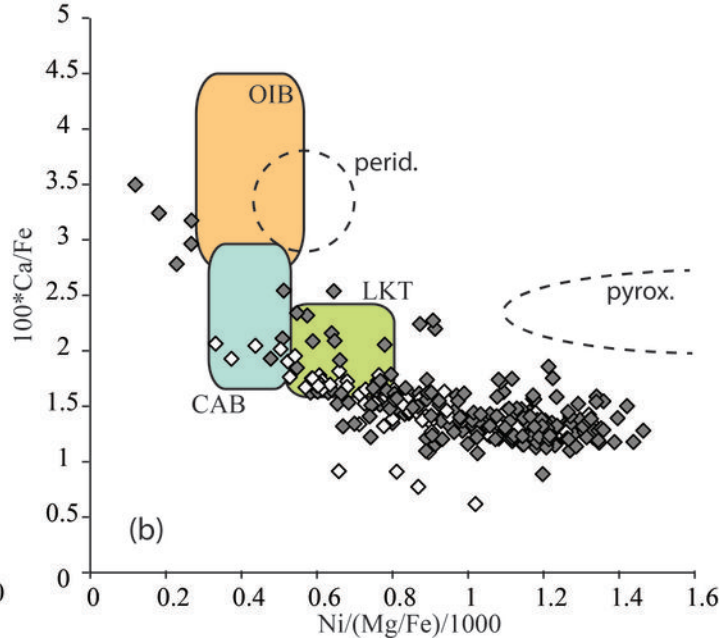
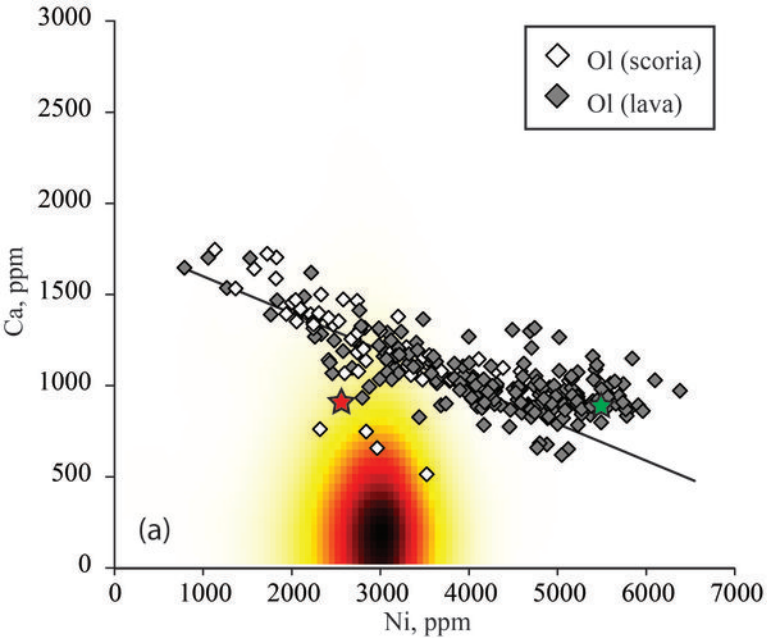


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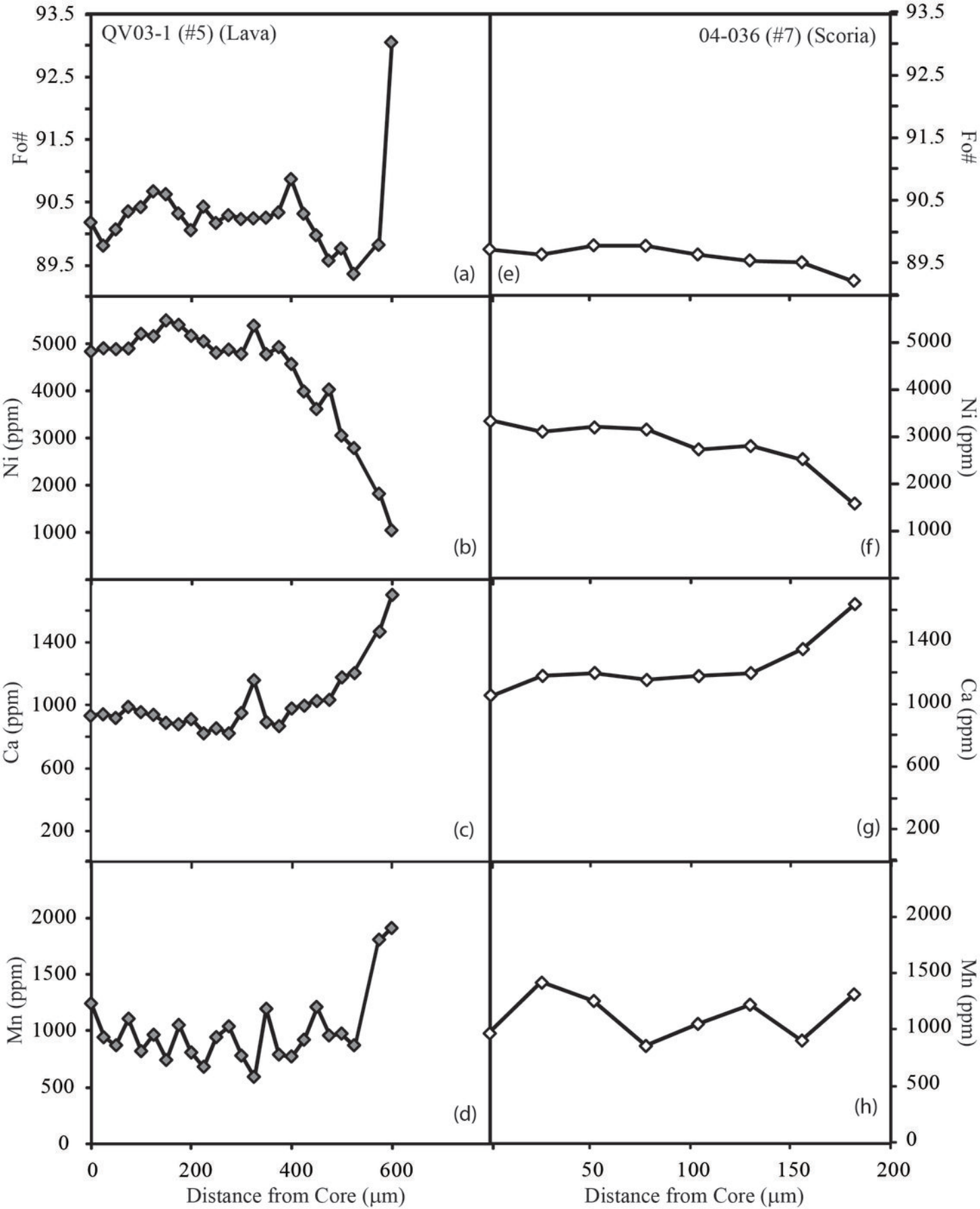


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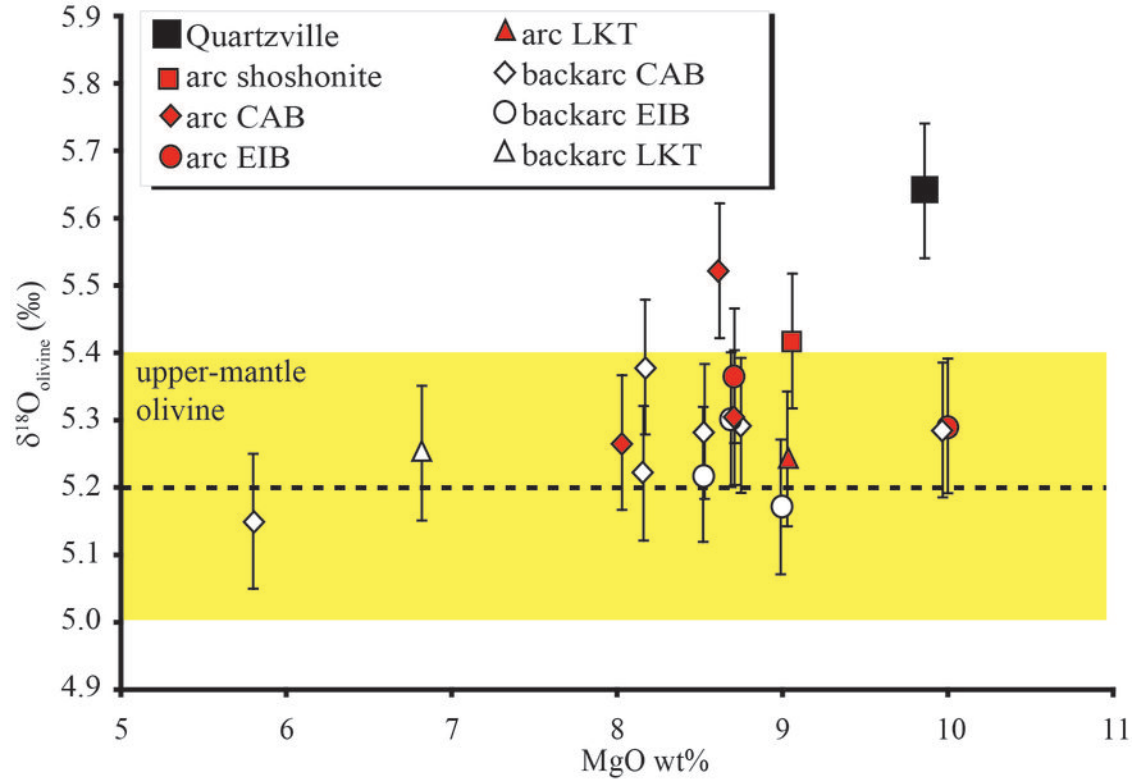


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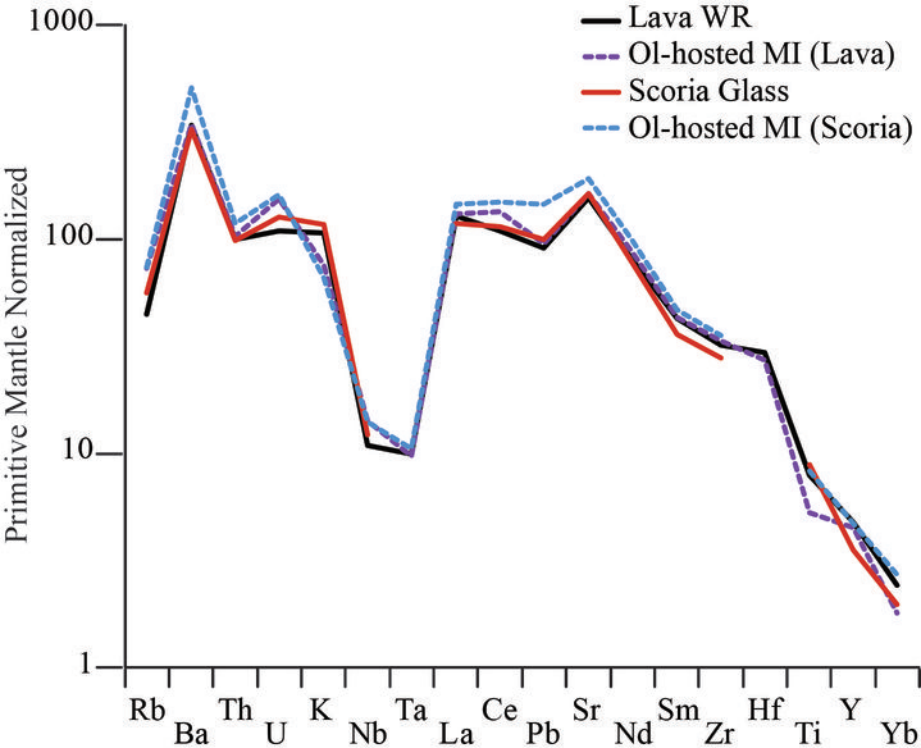


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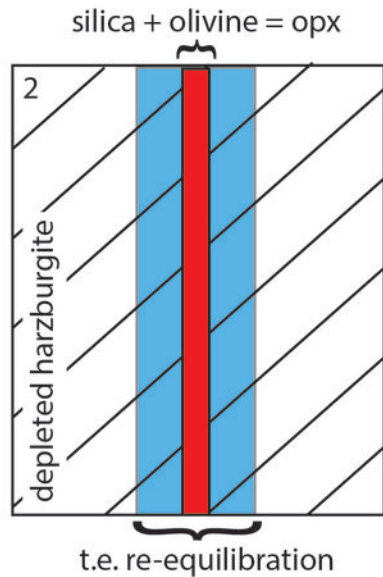
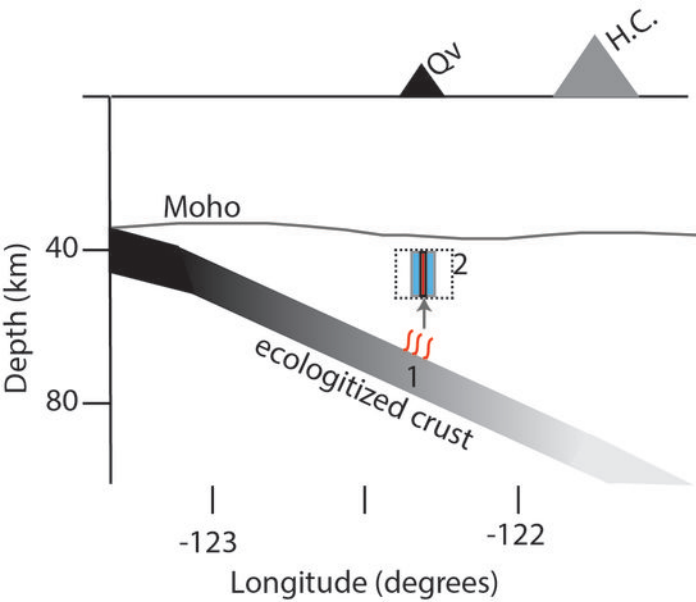


Figure 11