

1 Article

2 Implications of Hf isotopes for the evolution of the 3 mantle source of magmas associated with the giant El 4 Teniente Cu-Mo megabreccia deposit, central Chile

5 Charles R. Stern^{1*}, Kwan-Nang Pang², Hao-Yang Lee², M. Alexandra Skewes¹, Alejandra Arévalo³

6 ¹ Department of Geological Sciences, University of Colorado, Boulder, Colorado, 80309-0399 USA;
7 Charles.Stern@colorado.edu

8 ² Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan; knpang@earth.sinica.edu.tw

9 ³ Escuela de Ingeniería, Universidad de O'Higgins, VI Región, Chile; aarevalot@gmail.com

10 * Correspondence: Charles.Stern@colorado.edu; Tel. +1-303-492-7170

11

12 **Abstract:** We have determined Hf isotopic compositions of 12 samples associated with the giant El
13 Teniente Cu-Mo deposit, Chile. The samples range in age from ≥ 8.9 to 2.3 Ma and provide
14 information about the temporal evolution of their magmatic sources from the Late Miocene to
15 Pliocene. Together with previously published data, the new analysis indicate a temporal decrease
16 of 10 $\epsilon_{\text{Hf}(t)}$ units, from +11.6 down to +1.6, in the 12.7 m.y. from 15 to 2.3 Ma. These variations imply
17 increasing incorporation of continental crust through time in the magmas that formed these rocks.
18 The fact that the samples include mantle-derived olivine basalts and olivine lamprophyres suggests
19 that these continental components were incorporated into their mantle source, and not by intra-
20 crustal contamination (MASH). We attribute the increase, between the Middle Miocene and
21 Pliocene, of crustal components in the subarc mantle source below El Teniente to be due to increased
22 subduction erosion and transport of crust into the mantle. The deposit formed above a large, long-
23 lived, vertically zoned magma chamber that developed due to compressive deformation and
24 persisted between the period ~ 7 to 4.6 Ma. Progressively more hydrous mantle-derived mafic
25 magmas feed this chamber from below, providing heat, H₂O, S and metals, but no unique "fertile"
26 Cu-rich magma was involved in the formation of the deposit. As the volume of these mantle-derived
27 magmas decreased from the Late Miocene into the Pliocene, the chamber crystallized and solidified,
28 producing felsic plutons and large metal-rich magmatic-hydrothermal breccias that emplaced Cu
29 and S into the older (≥ 8.9 Ma) mafic host rocks of this megabreccia deposit.

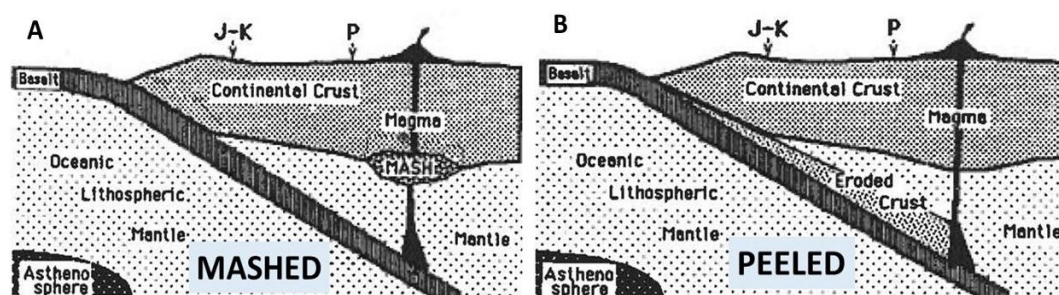
30 **Keywords:** El Teniente Cu-Mo deposit, Andean magmatism, subduction erosion, mantle source
31 region contamination, Hafnium isotopes

32

33 1. Introduction

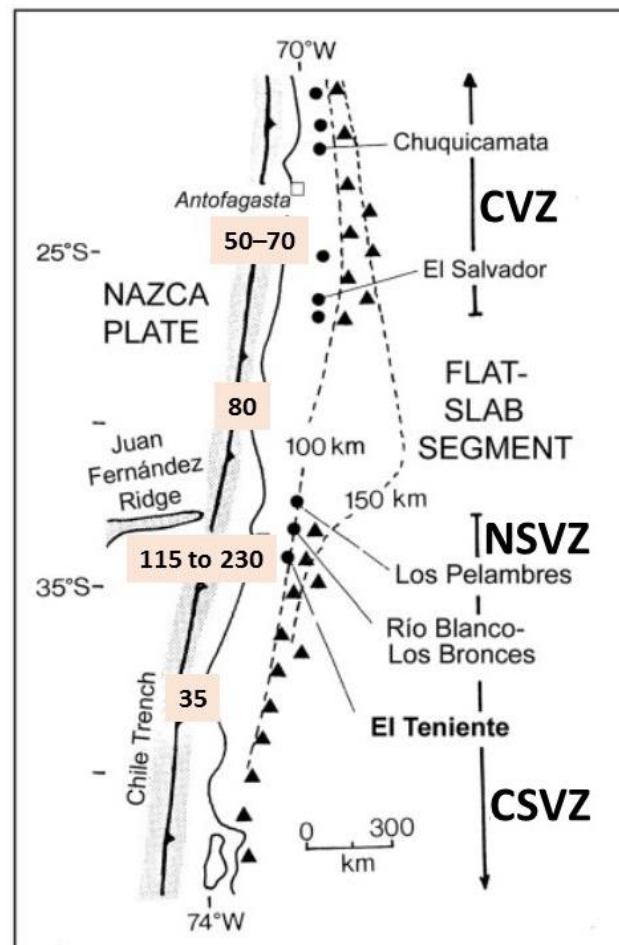
34 The isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7050$; $\epsilon_{\text{Nd}} \leq -2$; $\epsilon_{\text{Hf}} \leq +2$) of some recently erupted Andean
35 volcanic rocks indicate that they have incorporated continental crust. Two very different processes
36 for the incorporation of crust into Andean magmas have been proposed (Figure 1) [1]. One, MASH
37 (Mixing, Assimilation, Storage and Homogenization) involves intra-crustal assimilation of crust as
38 mantle-derived magmas rise from their source through the crust to the surface [2]. Another (PEELED)
39 involves mantle source region contamination by crustal components subducted below the mantle
40 wedge and released into the wedge by either melting or dehydration and volatile transport [3,4].
41 These two different models have very different implications for geochemical cycling associated with
42 subduction zones, and for the growth and evolution of both the continental crust and mantle [5].

43 The amount of crustal components incorporated into recently erupted Andean volcanic rocks
 44 varies along strike from south-to-north, as do various geologic and tectonic features such as crustal
 45 thickness and age, subduction angle, trench depth and sediment fill, and the localized presence of
 46 bouyant features such as oceanic seamount chains and spreading ridges being subducted below the
 47 South American continental margin (Figure 2) [4]. For instance, in the Central Volcanic Zone (CVZ)
 48 of northern Chile, the crust is much thicker (≥ 70 km) than below the central part of the Southern
 49 Volcanic Zone (≤ 35 km; CSVZ; Figure 2) and the isotopic compositions of the recently erupted
 50 volcanic rocks suggests more crustal components have been incorporated in CVZ than CSVZ
 51 magmas [3-5]. This could reflect greater amounts of crustal assimilation by mantle-derived magmas
 52 as they rose through the thicker CVZ crust, but in this same region the trench is devoid of sediment
 53 due to the arid conditions in northern Chile, and compared to the CSVZ, much more significant
 54 amounts of subduction erosion, at rates estimated to be 50–70 km³/km/my since ~150 Ma (Figure 2)
 55 [5], have truncated the continental margin [6] and caused the arc to migrate eastward ~250 km since
 56 the Jurassic (Figure 1). The subduction of tectonically eroded crust has been invoked not only to
 57 explain the crustal components in CVZ magmas [3-5,7,8], but also the uplift and crustal thickening
 58 observed in this part of the Andes [9].
 59



60
 61 **Figure 1.** Two alternative explanations for the incorporation of continental crust into Andean magmas
 62 [1]. (A) MASHED on the left involves Mixing, Assimilation, Storage and Homogenization (MASH) at
 63 either the lower crust/mantle boundary or in the crust [2]. (B) PEELED on the right involves recycling
 64 of subduction eroded crust into the mantle wedge source [3-5]. J-K and P indicate the position of the
 65 Jurassic-Cretaceous and Pliocene plutonic belts, respectively, in the Andes of northern Chile. The
 66 recently active volcanic arc is ~250 km east of the Jurassic arc as a result of subduction erosion [6].
 67

68 In the same way, at the northern end of the Andean SVZ (NSVZ; Figures 2 and 3), where the
 69 MASH model was first presented [2], the crust thickens to ≥ 60 km compared to ≤ 35 km below the
 70 CSVZ, and the isotopic compositions of recently erupted volcanic rocks indicate that they contain
 71 greater amount of crustal components [3-5,10,11]. However, the subduction of the Juan Fernández
 72 Ridge has caused the subduction angle to flatten, increasing the rate of subduction erosion west of
 73 the NSVZ to between 115 to 230 km³/km/my over the last 10 m.y., during which time the active
 74 volcanic arc between 33–34°S migrated ~50 km to the east (Figure 3). Stern [3-5] therefore proposed
 75 that crustal components were preferentially incorporated in NSVZ compared to CSVZ magmas by
 76 increased rates of subduction erosion and mantle source region contamination by subducted
 77 components, and not by intra-crustal MASH processes.

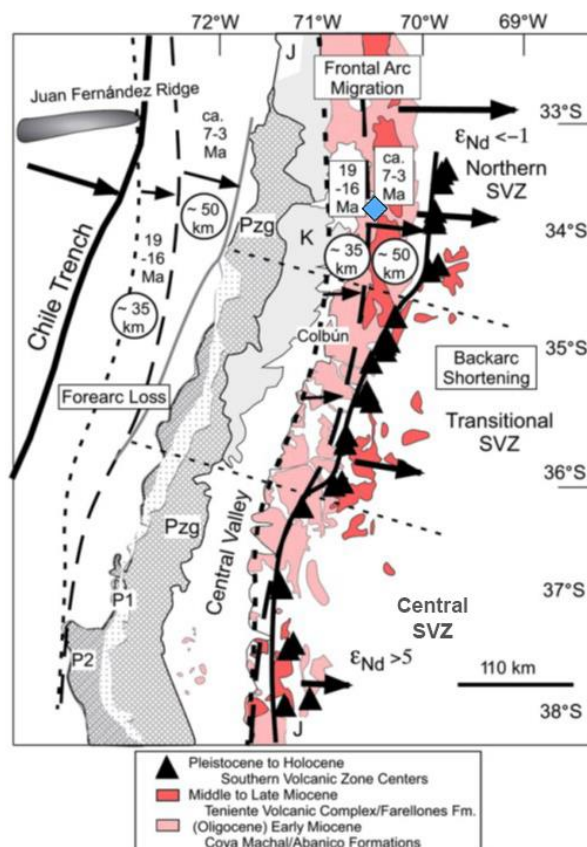


78
79
80
81
82
83
84
85
86
87
88
89
90

Figure 2. Location of El Teniente and two other giant Late Miocene Cu-Mo deposits, Los Pelambres and Río Blanco-Los Bronces, in the Andes of central Chile. Map also shows tectonic features such as the Chile Trench, which is the boundary between the Nazca and South American plates, the depth in kilometers (100 and 150 km dashed lines) to the Benioff Zone below South America, and the locus of subduction of the Juan Fernández Ridge. This also marks the boundary between the Andean Flat-Slab segment, below which the subduction angle is very low, as indicated by the depths to the upper boundary of the subducted slab, and the northern and central parts of the Andean Southern Volcanic Zone (NSVZ and CSVZ) of active volcanoes, below which subduction angle is steeper. The numbers in the boxes are the estimated rates of subduction erosion in $\text{km}^3/\text{km}/\text{my}$ in each region [5]. The map also shows the location of the Central Volcanic Zone (CVZ) and some of the other giant Late Eocene and Early Oligocene Cu-Mo deposits in northern Chile.

91
92
93
94
95
96
97
98
99

Temporal variations in Andean igneous rocks also are not unambiguously related to either changes in crustal thickness or rates of subduction erosion. Below the NSVZ, in the region where the El Teniente deposit formed in the Late Miocene, the crust has thickened and been uplifted since the Middle Miocene [12-20], and Sr, Nd and Pb isotopic data indicate increased proportions of continental crust in the igneous rocks emplaced through time (Figures 4 and 5) [10,21-24]. However, as described above, the southward migration of the locus of subduction of the Juan Fernández Ridge has also caused, during this same time period, flattening of the angle of subduction, >50 km of eastward migration of the volcanic arc, and increased rates of subduction erosion (Figure 3) [3-5,10,25-27].



100

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

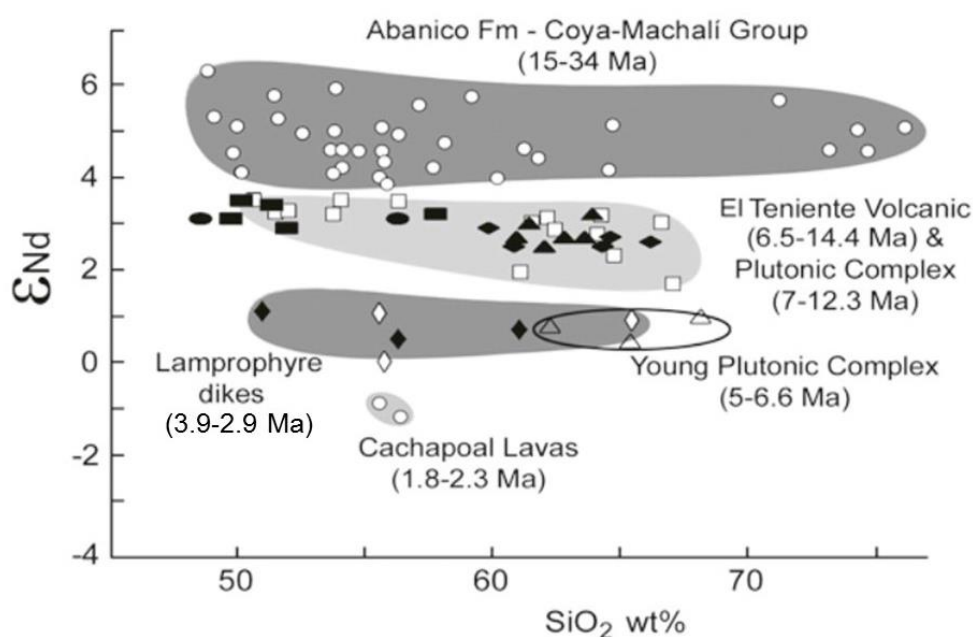
120

121

122

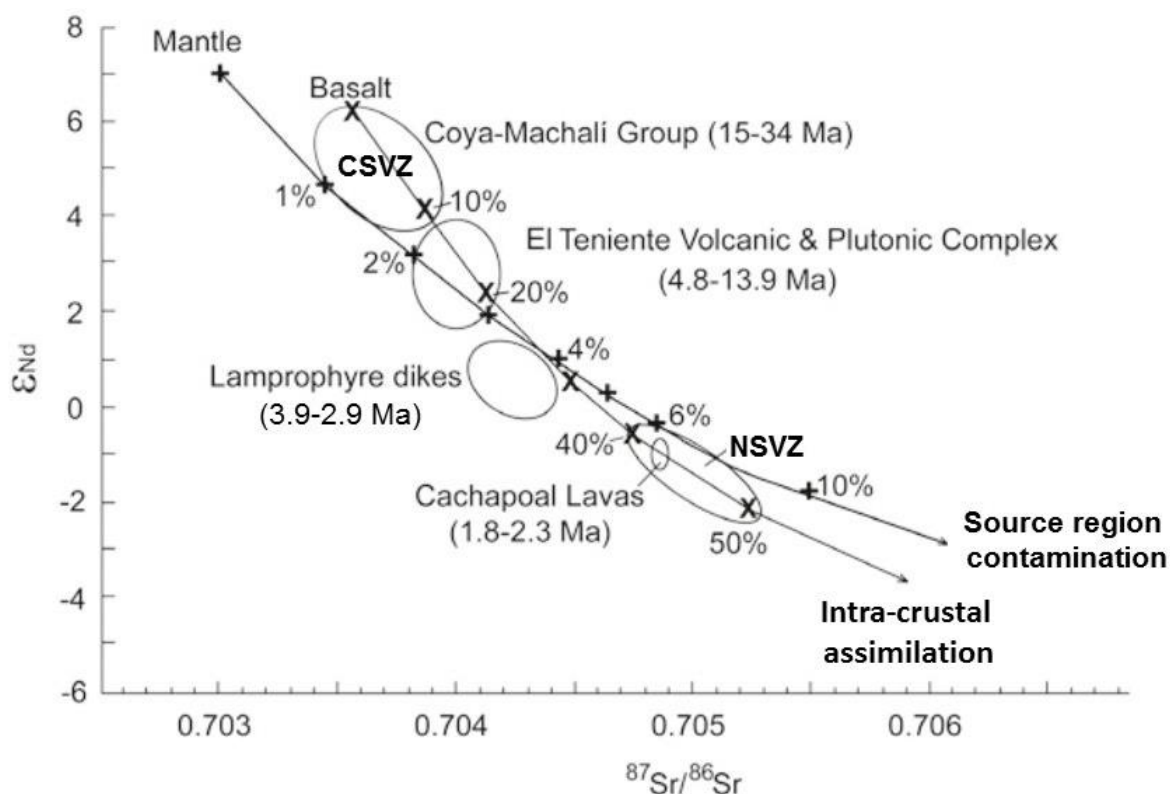
Figure 3. Regional map of central Chile between $\sim 32^{\circ}\text{S}$ and 38°S , with lines showing correlations of early Miocene to Holocene arc fronts on land and inferred position of corresponding coastlines offshore [10]. Arrows show relative amounts of frontal-arc migration, forearc loss, and backarc shortening. Northwest–southeast trending dashed lines show offsets in the modern volcanic front that separate the Southern Volcanic Zone (SVZ) into the northern, transitional, and central segments [4]. In the active arc region, lines connect outcrop patterns marking early Miocene (pink), middle to late Miocene (red), and SVZ (undashed, connecting Pleistocene to Holocene volcanic centers (triangles)) magmatic fronts. Arrows between the lines indicate inferred distance (given in circles) of frontal-arc migration from 19 to 16 Ma and from 7 to 3 Ma. In the forearc, lines between the trench and the coast show inferred early Miocene (short dashed) and middle to late Miocene (long dashed) coastlines under the assumption that the distance of frontal-arc migration equals the width of missing coast. Arrows between the lines indicate distance (shown in circles) of inferred loss from ca. 19 to 16 Ma. And 7 to 3 Ma. In the backarc, the length and position of arrows show the location and proportional amounts of crustal shortening over the past 20 my inferred from structural profiles. Also shown are other outcrop patterns that have long been used as evidence for forearc subduction erosion along this margin [6]. The first is the northward narrowing and disappearance of the Paleozoic high pressure (P1) and low pressure (P2) paired metamorphic and granitoid (Pzg) belts along the coast. The second is the presence of Jurassic arc rocks (marked by J) along the coast north of 33°S , but inland near the SVZ at $\sim 38^{\circ}\text{S}$. K indicates Cretaceous magmatic rocks. ϵ_{Nd} is +5 for active SVZ volcanoes south of 36°S , and ≤ -1 for those in the northern SVZ north of 34°S , as a result of increased mantle source region contamination by subducted crust due to the northward increase in the rate of subduction erosion associated with the subduction of the Juan Fernández Ridge at 33°S [3-5]. El Teniente occurs at the blue diamond

123 In summary, spatial and temporal variations in geologic factors such as crustal thickness and
 124 rates of subduction erosion rates do not unambiguously favor MASH versus source region
 125 contamination (Figure 1) in producing the spatial and temporal isotopic variations that indicate
 126 increased incorporation of continental crust in some Andean magmas. An alternative approach to
 127 distinguish these two processes is geochemical modelling focused specifically on mafic olivine-
 128 bearing basaltic rocks clearly derived from the mantle without significant evidence for or possibility
 129 of intra-crustal contamination. For instance, to produce the northward increase of $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7039
 130 to 0.7050 and decrease in ϵ_{Nd} from $>+5$ to <-1 (Figures 3-5) observed in olivine basalts erupted from
 131 CSVZ compared to NSVZ volcanoes, would require, because of the relative high Sr = >450 ppm and
 132 Nd = 9 ppm of Andean basalts, intra-crustal assimilation (MASH) of >40 wt % of Andean crust (Figure
 133 5) [3,10,21,22]. For NSVZ basalts, with no macro or microscopic evidence of crustal xenoliths or
 134 xenocrysts, this is considered to be an unacceptably large amount of crustal assimilation. In contrast,
 135 because of the relatively low Sr = 36 ppm and Nd = 1.8 ppm of Andean subarc mantle, these variations
 136 could be produced by incorporation in the mantle source region of only 5 wt % more subducted crust
 137 and sediment below the NSVZ (Figure 5), where current subduction erosion rates are estimated as
 138 between 115 to 230 $\text{km}^3/\text{km}/\text{my}$ (Figure 2), than the 1 wt % estimated to have been incorporated in
 139 the mantle below the CSVZ, where subduction erosion rates are estimated as only ~ 35 $\text{km}^3/\text{km}/\text{my}$
 140 (Figures 2).



141

142 **Figure 4.** Published values of ϵ_{Nd} vs SiO_2 (wt %) for igneous rocks of different ages from the transect
 143 across the Andes at the latitude of El Teniente (34°S ; open symbols [10,14, 17,21-24]), compared with
 144 values for samples of the host-rocks in the deposit (filled symbols including the Teniente Mafic
 145 Complex (■), Sewell Tonalite (▲), felsic porphyries (◆), and Porphyry A granitoid (●); [23]). Although
 146 the youngest felsic plutons in the deposit are the same age (7.1 to 4.6 Ma) as rocks from the regionally
 147 defined Younger Plutonic Complex (6.6 to 5 Ma; [10]) they are isotopically similar to the older host-
 148 rocks of the deposit as well as to Teniente Volcanic and Plutonic Complex rocks.



149

150

151

152

153

154

155

156

157

158

159

160

161

162

163

164

165

166

167

168

169

170

171

172

173

Figure 5. Sr versus Nd isotopic values of the various groups of igneous rocks of different ages across a transect of the Andes at the latitude of El Teniente (34°S; fields and data sources from Figure 4). The figure illustrates both a source region contamination model of primitive mantle ($Sr=36$ ppm with $^{87}Sr/^{86}Sr=0.703$ and $Nd=1.8$ ppm with $\epsilon_{Nd}=+7$; [21]) mixed with various proportion of subducted crust and sediment ($Sr=380$ ppm with $^{87}Sr/^{86}Sr=0.70763$ and $Nd=42.3$ ppm with $\epsilon_{Nd}=-5.1$), and also a MASH model for a Coya-Machali basalt ($Sr=450$ ppm with $^{87}Sr/^{86}Sr=0.7035$ and $Nd=9$ ppm with $\epsilon_{Nd}=+6$) assimilating various proportion of Paleozoic-Triassic Andean granite basement ($Sr=350$ ppm with $^{87}Sr/^{86}Sr=0.7075$ and $Nd=20$ ppm with $\epsilon_{Nd}=-6$; [10]) Both models reproduce the isotopic compositions of the progressively younger rocks in the transect, but the latter model requires assimilation of unacceptably high proportions of granite crust and is inconsistent with generation of primitive low SiO_2 olivine-bearing mafic rocks in each age group, as well as the increasingly higher Sr content of the progressively younger rocks, which is due instead to decreasing degrees of partial mantle melting [3-5,10], consistent with decreasing volume of magmas erupted through time at this latitude in the Andes.

Exactly similar temporal isotopic changes as those observed between recently erupted CSVZ and NSVZ basalts occurred between the Miocene and Pliocene in igneous rocks associated with the giant El Teniente Cu-Mo deposit (Figures 2-5) [21-23]. As a contribution to the understanding of Andean magmagenesis its implications for the formation of the El Teniente ore deposit, we have determined Hf isotopes in igneous rocks ranging in age from ≥ 8.9 to 2.3 Ma from the area of the deposit. These samples (Table 1) include an olivine basalts (8.9 Ma), an olivine lamprophyre (3.1 Ma), and an olivine-bearing basaltic andesites (2.3 Ma), as well as other mafic and felsic plutons associated with the deposit. The data obtained provide information about the temporal evolution of their magmatic sources from the Late Miocene to Pliocene, and constrain the relative role of MASH and mantle source region contamination processes in the generation of Andean magmas.

Table 1. Samples analyzed [21-23,37].

sample #	rock type	age Ma	SiO ₂	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	ε _{Nd}	ε _{Hf} [37]
Late Miocene (≥8.9 Ma) mafic host rocks							
EX-2004-04	ol basalt	8.9	51.9	0.70405	0.512782	2.9	
1411-1630	gabbro	≥8.9	51.1	0.70396	0.512818	3.5	
540-2082	basalt	≥8.9	51.3	0.70404	0.512813	3.4	
QT-4	basalt	≥8.9	49.7	0.70421	0.512798	3.1	
Late Miocene to Early Pliocene (7.1 to 4.8 Ma) felsic plutonic rocks							
Ttc5	Sewell tonalite	7.1	63.7	0.70386	0.512770	2.7	7.9
1473-970	Porphyry A	5.7	48.5	0.70409	0.512799	3.1	
1446-266	Porphyry A	5.7	56.3	0.70406	0.512795	3.1	7.7
1300-403	Teniente dacite	5.3	66.3	0.70402	0.512762	2.6	7.2
1394-92	latite dike	4.8	60.9	0.70405	0.512785	2.5	6.9
Pliocene (3.8 to 2.3) lamprophyres and basaltic andesites							
Ttc1	hbl lamprophyre	3.8	56.3	0.70425	0.512660	0.7	
AS-2003-1	ol lamprophyre	3.1	51.3	0.70425	0.512700	1.2	
PVF1	ol basaltic andesite	2.3	55.6	0.70485	0.512580	-1.1	

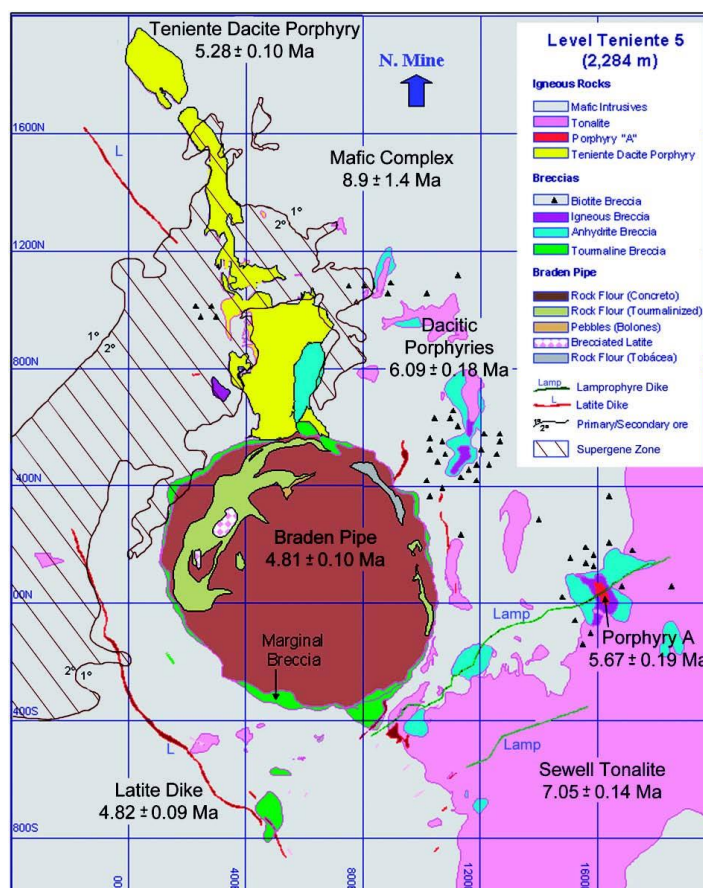
174

175 2. Geologic Background

176 2.1. El Teniente Cu-Mo deposit

177 The giant El Teniente Cu-Mo deposit, located in central Chile (34°05'S, 70°21'W; Figures 2 and 3)
 178 is one of the largest such deposits in the world [28-38]. It is the southernmost in a belt of Late Miocene
 179 giant Cu-Mo deposits which also include Los Pelambres and Río Blanco-Los Bronces [39,40]. El
 180 Teniente has been described as a porphyry deposit formed around the central Teniente Dacite
 181 Porphyry dike (Figure 6) [30], or alternatively as a magmatic-hydrothermal breccia deposit formed
 182 either in association with the intrusion of dacite to diorite dikes [36] or by the generation of multiple
 183 large mineralized breccias, including the central Braden breccia pipe, by exsolution of high-
 184 temperature mineral-rich magmatic-hydrothermal fluids from the roof of an underlying large, long-
 185 lived and vertically stratified magma chamber recharged from below by mantle-derived magmas
 186 [23,32,33,38]. The two other Miocene deposits in this belt are also characterized by the presence of
 187 multiple large mineralized magmatic-hydrothermal breccias [38-42].

188 Pb, S, O and H isotopic studies of the igneous rocks and ore minerals in the deposit indicate that
 189 El Teniente is clearly an orthomagmatic deposit, with Cu, Mo and S being derived from the associated
 190 igneous rocks [32,33,39,43-45]. Igneous rocks spatially related with the deposit range in age from mid
 191 Tertiary to Pliocene. Over this time period the volume of magmatic rocks decreased progressively
 192 [22,23,38,39], and in the Pliocene the locus of Andean arc magmatism at the latitude of El Teniente
 193 (34°S), near the current northern end of the Andean Southern Volcanic Zone (NSVZ; Figures 2 and
 194 3), migrated ~50 km to the east as subduction angle flattened [25]. This, we suggest, was due to the
 195 southward migration of the locus of subduction of the Juan Fernández Ridge (21,25-27,38,39).



196

197

198

199

200

201

202

203

204

205

206

207

208

209

210

211

212

213

214

215

216

217

Figure 6. Geological map of level Teniente 5 (2284 m above sea level) in the mine [32,33]. The Dacitic Porphyries north of the Sewell Tonalite, are mapped as a distal portion of this pluton, although they are younger [34] and have an independent origin [36]. The spatial extent of biotite breccias is projected onto this level from where they have been mapped between levels Teniente 4 and 8.

The igneous rock in the vicinity of El Teniente include continental volcanic rocks, up to 3300 m thick, of the Oligocene to Early Miocene (≥ 15 Ma) Coya-Machali (or Abanico; Figure 3) Fm. [15,46,47], erupted above thin (< 30 km) crust, or in a transtensional intra-arc basin [48]. These formed by relatively high degrees of partial melting of subarc mantle modified to a small degree by the influx from below of slab-derived components [10,17,46]. This is indicated by their low La/Yb ratios (2-6), as well as their low initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7033-0.7039) and high ϵ_{Nd} (+6.5 to +4; Figures 4 and 5). Although the Coya-Machali Formation volcanic rocks do not crop out either within or in the immediate vicinity of the El Teniente deposit (Figures 3 and 6), these rocks occur both to the west and the east of the deposit, and they almost certainly also occur at depth below the deposit.

Extrusive rocks of the Miocene Farellones Formation, locally referred to as the Teniente Volcanic Complex [10], are the oldest rocks exposed in the immediate area surrounding the deposit (Figure 3). The Farellones Formation, a sequence of > 2500 m of lavas, volcanoclastic rocks, dikes, sills and stocks of basaltic to rhyolitic composition, was erupted after an Early Miocene (19-16 Ma) episode of crustal deformation, thickening and uplift [10,14]. The Teniente Volcanic Complex near the deposit has been correlated with the upper part of this formation and dated between 14.4 and 6.5 Ma [10,31]. No extrusive rocks with ages less than 6.5 Ma have been found within the El Teniente deposit.

218 The Teniente Volcanic Complex consists of tholeiitic to calc-alkaline extrusive rocks, which
219 plot in the medium to high-K group of convergent plate boundary arc magmas [10]. Mafic rocks of
220 the Teniente Volcanic Complex generally have higher La/Yb (4-9) compared with rocks of the older
221 Coya-Machali Formation, and mafic, intermediate and silicic rocks also have higher initial $^{87}\text{Sr}/^{86}\text{Sr}$
222 (0.7039-0.7041; Figure 5) and lower initial ϵ_{Nd} (+2.7 to +3.6; Figures 4 and 5). These differences are
223 interpreted to represent a change from magma genesis below relatively thin continental crust during
224 the mid-Tertiary, when the Coya-Machali Formation was generated, to conditions of thickened
225 continental crust when the Teniente Volcanic Complex formed in the Middle to Late Miocene.

226 The extrusive rocks of the Teniente Volcanic Complex were intruded during a Late Miocene
227 (9-5 Ma) episode of further crustal deformation, thickening and uplift, between ~8.9 and 4.6 Ma
228 [10,14,31,34,48], by gabbro, diabase, diorite, tonalite, latite, and dacite porphyry plutons of the
229 Teniente Plutonic Complex. Within the immediate area of the deposit (Figure 6) these include 1)
230 the >50 km³ Teniente Mafic Complex (8.9 ± 2.4 Ma) of mafic intrusives with the form of a laccolith
231 2000 m thick in the center of the deposit; 2) the equigranular holocrystalline Sewell Tonalite complex
232 (7.05 ± 0.14 Ma), with an estimated volume of ~30 km³ [23]; and 3) a series of much smaller volume
233 (<1 km each) dacite and diorite porphyries (6.09 ± 0.18 Ma), the unusual Cu- and S-rich anhydrite-
234 bearing Porphyry A stock (5.67 ± 0.19 Ma) [49], the Teniente Dacite Porphyry dike (5.28 ± 0.10 Ma), a
235 few latite dikes (4.82 ± 0.09 Ma), and finally a small dacite porphyry (4.58 ± 0.10 Ma). These intrusive
236 rocks have isotopic compositions similar to Teniente Volcanic Complex extrusives (Figures 4 and 5).

237 Multiple Cu-mineralized magmatic-hydrothermal breccia pipes were emplaced into these
238 plutonic rocks during the same time period as the felsic porphyry intrusions, between at least 6.3 and
239 4.4 Ma (Figure 6). Post-mineralization phases include high-MgO (≥7.50 wt %) olivine (Fo88) and
240 hornblende lamprophyres (3.8 to 2.9 Ma) [10,22,31,34] and olivine (Fo64) basaltic andesite (MgO ≥ 4.5
241 wt %) lavas in the valley of the Cachapoal river just west of the El Teniente deposit (2.3 Ma) [21].
242 After this the locus of Andean arc magmatism migrated eastwards ~50 km (Figure 3).

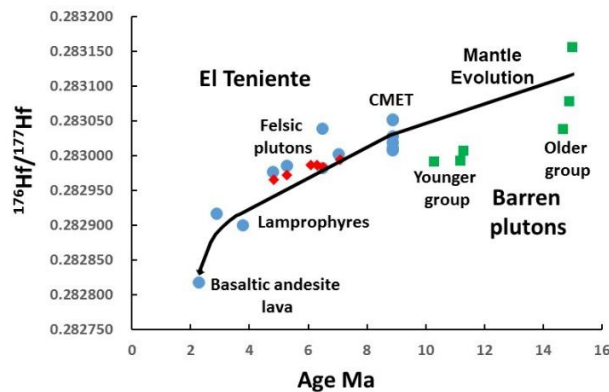
243

244 2.2. Previous Hf isotopic studies

245 Hf isotopes have previously been determined in zircons from felsic plutons both within [37]
246 and in the near vicinity [50] of the El Teniente deposit (Figure 7). The Hf isotopic composition of
247 zircons in six samples of felsic plutons within the deposit, that range in age from 7.1 to 4.8 Ma, have
248 overall high initial average of $\epsilon_{\text{Hf}} = +7.4 \pm 1.2$ and range from +6 to +10 (Table 1), which rules out
249 significant crustal contamination [37]. There was little change in these compositions during this time,
250 but the older four plutons (7.1 to 6.1 Ma) average $\epsilon_{\text{Hf}} = +7.8$, while the younger Teniente Dacite
251 Porphyry (5.3 Ma) has $\epsilon_{\text{Hf}} = +7.2$ and the youngest latite dike (4.8 Ma) has $\epsilon_{\text{Hf}} = +6.9$ (Table 1), so some
252 small but significant temporal change, with decreasing ϵ_{Hf} through time, is apparent.

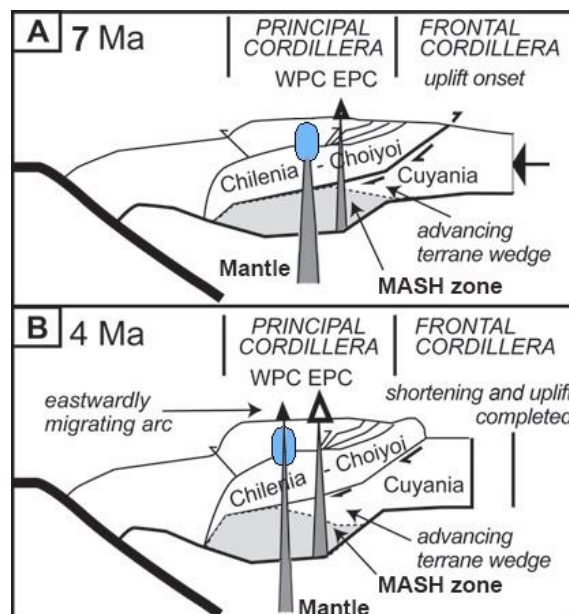
253 Hf isotopic compositions were also determined in four barren Middle and Late Miocene
254 plutonic complexes in the vicinity of El Teniente [50]. These can be divided into an older group (~15
255 Ma) and a younger group (10 to 12 Ma), both groups being older than the felsic plutons within the El
256 Teniente deposit (Figure 7). The older group is characterized by quartz monzogabbroic compositions
257 with 54.0 to 57.5 wt % SiO₂, while the younger group are quartz monzodioritic with higher SiO₂ from
258 61.6 to 66.8 wt %. ϵ_{Hf} for the older group ranges from +9.8 to +13.7 and averages +11.6 (Figure 7),
259 while ϵ_{Hf} for the younger group has a lower range of +7.6 to +8.5 and lower average of +8.0. These
260 differences are also associated with increasing ϵ_{Os} from +32 to +160 for the older compared to the

261 younger group. Both the Hf and Os isotopic data suggests increasing incorporation of crustal
 262 components with time, and the younger plutons, which have higher SiO₂, are noteworthy for the
 263 presence of abundant mafic enclaves indicating intra-crustal (MASH) assimilation on a macroscopic
 264 scale. These are absent from the older plutonic group which have more primitive isotopic
 265 compositions and lower SiO₂.
 266



267
 268 **Figure 7.** $^{176}\text{Hf}/^{177}\text{Hf}$ versus age (Ma) for samples from El Teniente (blue circles from Table 2; red
 269 diamonds from [37]) and Middle Miocene barren plutons in the same general area (green squares from
 270 [50]). Mantle isotopic evolution line is draw from average of older group of Middle Miocene barren
 271 plutons through Late Miocene Teniente Mafic Complex (CMET) olivine basalts and gabbros, to olivine
 272 lamprophyres and olivine-bearing basaltic andesites, ignoring the younger group of barren plutons
 273 because these have macroscopic evidence for intra-crustal assimilation [50]. The amount of subducted
 274 crust plus sediment added to the mantle to generate this line is indicated in Figure 9.

275
 276 Hf and Nd isotopic compositions have also been determined for five Late Miocene to Pliocene
 277 (8.3 to ~3 Ma) plutons from the Eastern Principal Cordillera ~40 km east of El Teniente (Figure 8) [24].
 278 These have lower more radiogenic ϵ_{Hf} (+4 to -4) and ϵ_{Nd} (+3 to 0) than the felsic plutons in El Teniente.
 279 Crustal-contamination (MASH) processes involving assimilation of Paleozoic and Mesozoic
 280 basement rocks are evidently involved in the genesis of the igneous rocks from the Eastern Cordillera
 281 (Figure 8), both because some contain zircon crystal with older (Paleozoic) inherited cores and others
 282 have wide ranges (+1 to -4) of zircon ϵ_{Hf} values [24]. We agree with this interpretation. However, it
 283 has also been suggested[24], based on the low ϵ_{Nd} values of the Pliocene olivine lamprophyres (+1.2
 284 to +0.7) and olivine-bearing basaltic andesites (-1.1; Figures 4 and 5; Table 1; [21-23]) emplaced in the
 285 Western Cordillera in the vicinity of El Teniente, which are similar to those in the Pliocene plutons of
 286 the Eastern Cordillera, that these low ϵ_{Nd} values reflects a westward propagation of the Eastern
 287 Cordillera magmatic isotopic signatures, caused by westward thrusting and material transport of the
 288 Eastern Cordillera basement under the Western Cordillera in the Pliocene (Figure 8). We disagree
 289 with this interpretation as it fails to take into account the fact that the Pliocene high-Mg olivine
 290 lamprophyres, as well as the olivine-bearing basaltic andesite lavas, are likely to be mantle-derived,
 291 without significant crustal contamination. For high-Mg olivine lamprophyres in general, an origin by
 292 hydrous (6-16 wt % H₂O) melting of mantle has been suggested [51-55]. As discussed in more detail
 293 below, we therefore interpret these temporal change in both ϵ_{Hf} and ϵ_{Nd} to lower more radiogenic
 294 values as reflecting a progressive change in mantle composition due to subduction of increased
 295 proportions of continental crust, and not to intra-crustal (MASH) contamination processes.



296

297

298

299

300

301

302

303

304

305

306

307

308

309

310

311

312

313

314

315

316

317

318

319

320

321

322

323

324

Figure 8. Schematic profiles [18-20,24] of crustal evolution of the Andes of central Chile and Argentina at 7 Ma (A) and 4 Ma (B). Evolution is characterized by increased shortening rates along the eastern flank of the orogenic belt after 7 Ma, where the Chilenia-Choioyoi block overrides the Cuyania terrane, producing uplift of the Frontal Cordillera. This also produced increasing crustal thickness which led to uplift of the entire belt. Deformation amounts suggest that the Cuyania block descended immediately below the eastern part of the magmatic arc, changing composition of the base of the crust and thus changing the crustal magmatic source (MASH zone) below the Eastern Principle Cordillera (EPC). However, below the Western Principle Cordillera, magmas continued to rise from the mantle without intra-crustal assimilation in a MASH zone. After 7 Ma, these magmas did not reach the surface, but were mixed, stored and homogenized in a large magma chamber (blue) below El Teniente. Within this chamber the felsic plutons of the deposit developed without crustal assimilation and above it the mineralized breccias in the deposit were emplaced (see Figure 10). As subduction angle flattened and magma supply from the mantle decreased this chamber solidified. After 4 Ma, high-MgO olivine lamprophyres and olivine-bearing basaltic andesites, derived from a mantle hydrated and isotopically modified by increased proportions of subducted crust and sediment (Figure 7), rose through the now crystallized magma chamber, without any intra-crustal assimilation, to form dikes and lavas.

Finally, ϵ_{HF} values between +6.9 to +9.6 were determined for 8 plutonic rocks between the ages of 28.1 and 11.5 Ma from the region north of El Teniente between 32-33°S [47]. The oldest sample, a dacite sill (sample Ab-143; 28.1 Ma), which has $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.70661$ and is likely to have assimilated crustal material, has lower ϵ_{HF} of +7.8 than younger (22.2-17.7 Ma) gabbro, microgabbro and granodiorite samples which average ϵ_{HF} of +8.9. All the still younger plutons have lower ϵ_{HF} and the youngest (11.5 Ma; sample Z-132) has an ϵ_{HF} of +7.0. This suggest decreasing ϵ_{HF} with time beginning after ~17 Ma, and possibly before this time. Since these samples are all north of the current locus of subduction of the Juan Fernández Ridge, in an area where ridge subduction, decreasing subduction angle, eastward arc migration and increased rates of subduction erosion all happened earlier than at the latitude of El Teniente, we do not consider them appropriate for evaluating the temporal evolution of the mantle source of El Teniente magmatic rocks.

325 3. Samples and Methods

326 Twelve samples were selected for Hf-isotopic analysis (Table 1). These range in age from ≥ 8.9
327 to 2.3 Ma and include 1) four samples from the Teniente Mafic Complex, including one olivine (Fo74)
328 basalt, one gabbro and two other olivine-free basalts; 2) five syn-mineralization felsic intrusions that
329 range in age from 7.1 to 4.8 Ma, including four samples previously analyzed for Hf-isotopes in zircon
330 [37]; and 3) three post-mineralization samples that range in age from 3.8 to 2.3 Ma, including one
331 high-MgO (7.9 wt %; Ni ~ 190 and Cr ~ 390 ppm) olivine (Fo88) lamprophyre [22] and one olivine-
332 bearing (Fo64) basaltic andesite. All the samples have been previously analyzed for major and trace
333 element contents and Sr and Nd isotopic compositions (Table 1) [21-23].

334 Ground sample weighing ~ 200 mg was decomposed in 15 ml screw-top Savillex Teflon®
335 vials with a 1:1 mixture of 27 N HF and 16 N HNO₃ at $\sim 150^\circ\text{C}$ for 5 days. The sample solution was
336 evaporated to incipient dryness and redissolved first by 2 ml 4 N HCl and then by 1 N HCl. The dried
337 sample was then taken into solution by 1 ml 2N HCl and 8 ml 6 N HCl-0.2 N HF prior to chemical
338 separation. Hafnium was separated from the matrix elements by two columns packed with Ln-spec
339 resin (50–100 μm) from Eichrom Industries. Major elements and REE were eluted by 3 N HCl and 6
340 N HCl, and then Ti and Zr were eluted using a 2 N HCl-0.1 N HF mixture. Hafnium was collected
341 from the column with 2 N HCl and 0.2 N HF, and was then evaporated to incipient dryness and taken
342 up by 2 N HCl-0.2 N HF. The chromatographic procedures are repeated again on the same column
343 for further purification. Hafnium isotopes were measured on Nu Plasma II multi-collector ICP-MS
344 connected to a Aridus II desolvator and an enhanced sensitivity system with Ni 325-294 skimmer
345 cone and Ni 319-646 sampler cone. The measured $^{176}\text{Hf}/^{177}\text{Hf}$ values were normalized for mass
346 fractionation based on $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$. Long-term mean value for the Hf standard JMC475 in the
347 laboratory is $^{176}\text{Hf}/^{177}\text{Hf} = 0.282164 \pm 8$ ($n = 55$). The $^{176}\text{Lu}/^{177}\text{Hf}$ ratio was calculated from the Lu and
348 Hf contents determined by ICP-MS techniques by Activations Laboratories (Canada).

349

350 4. Results

351 The ϵ_{Hf} determined on the bulk-rock samples of the 7.1 to 4.8 Ma felsic plutons are similar
352 within analytical error to those determined previously on zircons for the same plutons [37]. Although
353 Muñoz et al. [37] concluded that there was no change in ϵ_{Hf} among these plutons, the new data for
354 samples formed over the larger ~ 6.6 m.y. interval from ≥ 8.9 to 2.3 Ma indicates that there was a clear
355 progressive decrease in ϵ_{Hf} with decreasing age (Figure 7). The ϵ_{Hf} for the twelve samples ranges from
356 an average of +9.1 for the four samples of ≥ 8.9 Ma Teniente Mafic Complex basalts and gabbros down
357 to +1.6 for the 2.3 Ma olivine-bearing basaltic andesite lava flow which is the last manifestation of
358 magmatic activity in the region of El Teniente prior to the eastward migration of the volcanic arc
359 (Table 2). This implies a drop of 7.5 ϵ_{Hf} units over this 6.6 m.y. interval.

360 Muñoz et al. [37] also suggested that the full ϵ_{Hf} range of +6 to +10 of the 7.1 to 4.8 Ma felsic
361 plutons is “identical to preceding Cenozoic barren magmatic activity in Central Chile.” However,
362 although their average ϵ_{Hf} values of +6.9 to +7.9 (Table 1) are in fact somewhat lower than the younger
363 group (10-12 Ma) of barren plutons, for which macroscopic and Os isotopic evidence of upper crustal
364 assimilation has been documented, they are significantly lower than the older group (~ 15 Ma; Figure
365 7). When the ϵ_{Hf} of the older ~ 15 Ma barren plutons in the region, which average +11.6 [50], are taken
366 into account, it is clear that ϵ_{Hf} values have not remained constant through time (Figure 7). In fact,

367 there has been an overall decrease of 10 ϵ_{Hf} units for igneous rocks emplaced in the vicinity of El
 368 Teniente in the 12.7 m.y. period from the Middle Miocene to the Pliocene.
 369

Table 2. Hf isotopes of the El Teniente samples.

Sample	Lu (ppm)	Hf (ppm)	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$2\sigma \times 10^{-6}$	$(^{176}\text{Hf}/^{177}\text{Hf})_i$	$\epsilon_{\text{Hf}(t)}$
Late Miocene (≥ 8.9 Ma) pre-mineralization mafic host rocks							
EX-2004-04	0.25	2.7	0.0131	0.2830107	3.3	0.283009	8.6
1411-1630	0.21	1.7	0.0175	0.2830506	6.1	0.283048	9.9
1411-1630 dup	0.21	1.7	0.0175	0.2830512	3.6	0.283048	10.0
540-2082	0.24	1.9	0.0179	0.2830072	3.9	0.283004	8.4
540-2082 dup	0.24	1.9	0.0179	0.2830272	4.2	0.283024	9.1
QT-4	0.25	2.5	0.0142	0.2830179	3.4	0.283016	8.8
Late Miocene to Early Pliocene (7.1 to 4.8 Ma) syn-mineralization felsic plutonic rocks							
Ttc-5	0.11	3.2	0.0049	0.2830014	11	0.283001	8.2
1473-970	0.16	2.8	0.0081	0.2830385	6.0	0.283038	9.5
1446-266	0.11	3.9	0.0040	0.2829811	7.5	0.282981	7.5
1300-403	0.06	2.4	0.0036	0.2829843	3.7	0.282984	7.6
1394-92	0.07	2.9	0.0034	0.2829762	2.8	0.282976	7.3
Pliocene (3.8 to 2.3) post-mineralization olivine lamprophyres and basaltic andesites							
Ttc1	0.12	3.5	0.0049	0.2828997	3.8	0.282899	4.6
AS-2003-1	0.18	3.1	0.0082	0.2829158	3.1	0.282915	5.1
PVF1	0.30	5.0	0.0085	0.2828165	2.3	0.282816	1.6

370

371 5. Discussion

372 5.1. Andean magmagenesis

373 The observed 10 ϵ_{Hf} unit decrease for igneous rocks emplaced in the vicinity of El Teniente
 374 in the 12.7 m.y. period from the Middle Miocene to the Pliocene is consistent with decreasing $\epsilon_{\text{Nd}(t)}$
 375 from +5 to -1.1, increasing $^{87}\text{Sr}/^{86}\text{Sr}(i)$ from 0.70376 to 0.70485, and increasing $^{206}\text{Pb}/^{204}\text{Pb}$ from 18.55 to
 376 18.68 determined for these same samples (Figures 4 and 5) [21-23]. These variations imply increasing
 377 incorporation of continental crust through time in the magmas that formed these rocks.

378 The fact that the samples include mantle-derived olivine basalts and high-Mg olivine
 379 lamprophyres suggests that these continental components were incorporated into their mantle source,
 380 and not by intra-crustal contamination (MASH). This suggestion is supported by two other lines of
 381 evidence. One is that for all the rocks of variable SiO_2 content within the igneous associations of
 382 specific ages identified in the area of El Teniente, the isotopic compositions do not vary as SiO_2
 383 increases (Figure 4). The isotopic compositions of the different associations vary through time, but
 384 not as a function of SiO_2 . This implies that crystal fractionation processes are not combined with intra-
 385 crustal assimilation in the generation of the range of rocks from basalts through rhyolites formed
 386 during each of these successive magmatic events. Second, models of intra-crustal assimilation
 387 (MASH) for Sr and Nd isotopes (Figure 5; [21-23]) indicate that relatively large proportions (>40 wt %)
 388 of crust must be assimilated to produce the Sr and Nd isotopic changes observed between mid
 389 Tertiary basalts and Pliocene olivine lamprophyres and olivine-bearing basaltic andesites. This is

390 considered to be an unacceptably large amount of crust to be assimilated in olivine-bearing mafic
391 magmas.

392 In contrast, models of mantle source region contamination by subducted crustal components
393 indicates that the Sr and Nd isotopic evolution of the subarc mantle source of the mafic magmas
394 erupted in the vicinity of El Teniente between the mid Tertiary and Pliocene can be produced by the
395 incorporation of increased, but still relatively small proportions of subducted crust and sediment
396 (Figure 5; 3, 10,21-23). Mid Tertiary Coya-Machali group mafic volcanic rocks require the addition to
397 a primitive subarc mantle of only 1 wt % subducted crust and sediment, while Pliocene olivine
398 lamprophyres and basaltic andesites require the addition of between 4-6 wt % subducted crust to
399 produce an appropriately isotopically modified mantle source.

400 The difference between these intra-crustal assimilation and mantle source region
401 contamination models reflects the relatively high Sr (450 ppm) and Nd (9 ppm) contents of a basalt
402 relative to the crust being assimilated, thus requiring a relatively large proportion of crust to produce
403 the appropriate isotopic leverage. In contrast the low Sr (36 ppm) and Nd (1.8 ppm) contents of the
404 mantle allows a much smaller proportion of subducted crust and sediment to produce the
405 appropriate isotopic leverage (Figure 5; [3-5,10,21-23]. For the Hf isotopic system, the same logic
406 applies. The olivine basalts and gabbros of the Teniente Mafic Complex contain an average of 2 ppm
407 Hf (Table 2), while average upper continental crust contains 5.3 ppm (Table 3) and bulk continental
408 crust 3.7 ppm Hf [56]. In contrast, primitive mantle contains only 0.28 ppm Hf [57], so the proportion
409 of crust needed to modify the Hf isotopic composition of the mantle is small compared to that needed
410 to be assimilated by a basalt.

411 Since the mantle source region contamination model better explains the Sr and Nd isotopic
412 evolution through time of the same olivine-bearing mafic rocks that we have analyzed for Hf isotopes,
413 we also interpret the temporal change in their Hf isotopic compositions to reflect the isotopic
414 evolution of their mantle source affected by increased incorporation of subducted crust and sediment.
415 To quantitatively evaluate the amount of source region contamination to produce these Hf isotopic
416 variations is complicated for two reasons. The first is the inherent complexities involved in
417 subduction zone magmatism, such as the amounts of pelagic, terrigenous and tectonically eroded
418 continental crust being subducted, and the uncertainty in the processes of transfer of these
419 components into the overlying mantle wedge by either dehydration and volatile transport, melting
420 or diapiric uprising of these low density materials. The second is that information is not available for
421 the Hf contents and isotopic compositions of all these different components relevant to
422 magmagenesis in the vicinity of El Teniente, in particular for the coastal and off shore Paleozoic and
423 early Mesozoic crustal rocks being tectonically eroded and subducted.

424 In the central Mexican magmatic belt, west of where subduction erosion rates are estimated
425 as 79-88 km³/km/my, and where Hf concentration and isotopic data are available for both pelagic and
426 terrigenous sediment, as well as coastal continental rocks, Straub et al. [58] concluded that tectonically
427 eroded continental crust, consisting of coastal and off-shore granodiorite plutons, was the dominant
428 control on the isotopic composition of the calc-alkaline arc magmas, and that neither intra-crustal
429 assimilation nor subducted trench sediment played a significant role in the genesis of these magmas.
430 For the El Teniente rocks, we calculated a model assuming for Hf contents the average estimated
431 values for primitive mantle and the average upper crust for the subducted crust and sediment, as
432 well as a low crustal ¹⁷⁶Hf/¹⁷⁷Hf isotopic ratio similar to that determined by Straub et al. [58] for

433 Mexican basement biotite gneisses (Table 3). This model can generate results (Figures 7 and 9)
 434 consistent with those previously determined for the Sr and Nd isotopic systems for which more
 435 published values for the materials involved in Andean magmagenesis are available [10,21-23]. These
 436 models indicate that the addition of 1 wt % subducted crust and sediment can produce an isotopically
 437 modified mantle appropriate for the generation of the mid Tertiary Coya-Machali basalts. Addition
 438 of progressively greater amounts of 2, 4 and 6 wt % subducted crust and sediment is required to
 439 further modify the mantle to produce the Late Miocene Teniente Mafic Complex olivine basalts and
 440 gabbros, the Pliocene olivine lamprophyres and younger Pliocene basaltic andesites, respectively.
 441

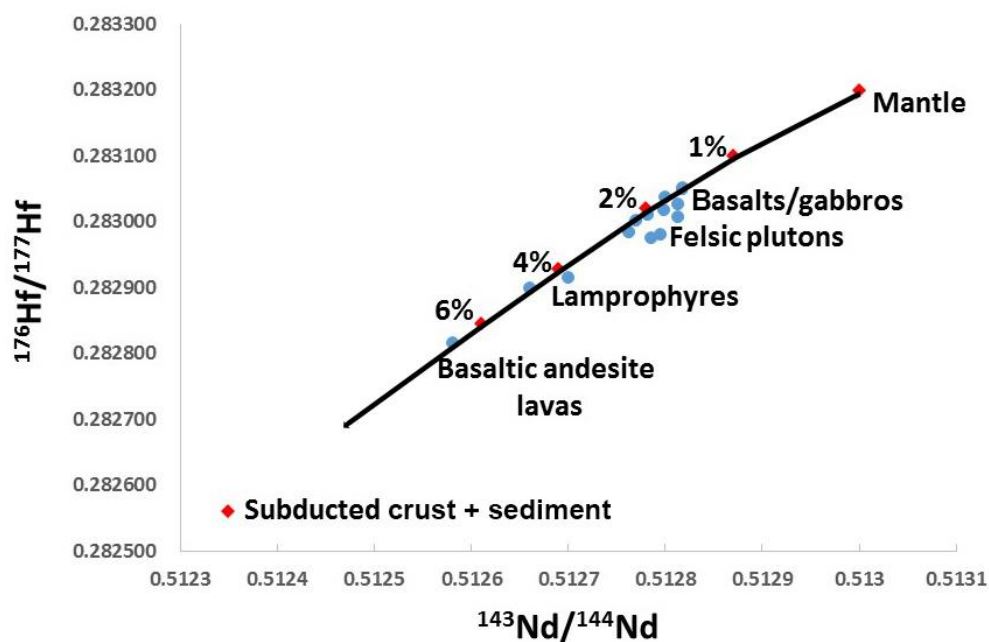
Table 3. Parameters used for the mantle modified by subducted crust+sediment model [22].

	Mantle	Crust + Sediment
Sr ppm	36	380
$^{87}\text{Sr}/^{86}\text{Sr}$	0.7030	0.70763
Nd ppm	1.8	42.3
$^{143}\text{Nd}/^{144}\text{Nd}$	0.51300	0.51235
Hf ppm	0.28	5.3
$^{176}\text{Hf}/^{177}\text{Hf}$	0.28320	0.28256

442 What can be said unequivocally in support of this model of the isotopic evolution of the subarc
 443 mantle underlying El Teniente is that the rate of subduction erosion and amount of Paleozoic and
 444 early Mesozoic crust being subducted did increase as the locus of subduction of the Juan Fernández
 445 Ridge migrated southward. Prior to impingement of the ridge on the northern end of the SVZ,
 446 subduction erosion rates may have been similar to those estimated presently for the central SVZ of
 447 $35 \text{ km}^3/\text{km}/\text{my}$ (Figure 2; [5]). Over the last ~10 m.y., as the ridge approached its current position at
 448 the northern end of the SVZ (Figures 2 and 3; [26,27]), rates of subduction erosion west of El Teniente
 449 increased to possibly as high as between 115 to $230 \text{ km}^3/\text{km}/\text{my}$ [5]. This increased rate of subduction
 450 erosion must be considered as the most probable cause for the increased crustal Hf, Sr, Nd and Pb
 451 isotopic signatures in the igneous rocks associated with the El Teniente deposit through time.

452 A second important factor that changed over the same time period, was that the angle of
 453 subduction decreased, thus contributing, along with subduction erosion, to the ~50 km eastward
 454 migration of the Andean arc in the Pliocene (Figure 3; [10,25]). Decreasing subduction angle reduced
 455 the volume of the subarc mantle wedge and resulted in a progressive decrease in the volume of
 456 magmas being produced prior to arc migration. Even if the amount of crustal components transferred
 457 from the subducted slab into the mantle wedge remained the same through time, which it didn't
 458 since subduction erosion rates increased, the decreasing volume of the wedge would result in these
 459 components becoming progressively more significant within the wedge. Stern [3-5] and Kay et al. [10]
 460 have shown that the decreasing volume of magma erupted in the vicinity of El Teniente through time
 461 from the mid Tertiary to Pliocene is consistent with decreasing percent of mantle partial melting as
 462 the angle of subduction decreased. This resulted in increasing Sr contents, from 450 to 700-900 ppm
 463 in association with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the sequence of mid Tertiary basalts to Pliocene olivine
 464 bearing mantle-derived lamprophyres [22]. Decreased degrees of mantle partial melting may also
 465 explain the somewhat higher Hf contents of the small volume of Pliocene olivine lamprophyres (>3
 466 ppm) and basaltic andesite lavas (5 ppm) compared to the older Teniente Mafic Complex olivine

467 basalts and gabbros (2 ppm; Table 2). Lamprophyres in general have been attributed to small degrees,
 468 relative to basalts, of partial melting of hydrated (6 to 16 wt % H₂O) mantle [51-55], H₂O being one of
 469 the subducted components likely to increase in significance in the mantle wedge as mantle volume
 470 decreases.



471
 472 Figure 9. $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ for samples from El Teniente (Table 2; blue circles) compared
 473 to isotopic values of a primitive mantle (Table 3) modified by the addition of various proportions (red
 474 diamonds) of subducted crust and sediment.

475
 476 In summary, the Hf isotopic data are consistent with Sr, Nd and Pb isotopic data, and suggest
 477 the incorporation of small but progressively increasing proportions of continental crust in the mantle
 478 source of the mafic magmas erupted in the vicinity of El Teniente between 15 and 2.3 Ma. Trench
 479 sediment recycling has been confirmed by the detection of cosmogenic ^{10}Be in many, including
 480 Andean arc, lavas [59-61], and comprehensive trace-element and isotopic studies have also provided
 481 evidence for the incorporation of fore-arc eroded crust in the subarc mantle source of both Andean
 482 [3-5,7,8,10,11] and arc volcanoes along other convergent plate boundaries [58,62-64]. The model
 483 developed for the El Teniente area suggests that increasing rates of subduction erosion through time
 484 has resulted in variable, but nevertheless relatively small (1 to ≤ 6 %) amounts of subducted crust
 485 having significantly affecting the isotopic composition of the mantle source of the mafic magmas
 486 through time. Models for magmagenesis in other arcs, for instance the central Mexican volcanic belt,
 487 have suggested much larger amounts of recycled crust involved in the generation of both mafic and
 488 intermediate arc magmas; from $>60\%$ in conjunction with diapiric uprise and melting of subducted
 489 crust [58] to 100% resulting in the generation of andesites by bulk melting of subducted crust
 490 "relaminated" below the mantle wedge [63].

491 492 5.2. El Teniente deposit

493 The giant El Teniente Cu-Mo deposit originally contained ≥ 100 million metric tonnes (Mt) of
 494 Cu [32,33]. Pb, S and Os isotopic data [43-45,65] indicate that Cu, Mo and S were derived from the
 495 associated igneous rocks. O and H isotopic and fluid inclusion data suggest that these metals were

496 transported and deposited by high-temperature magmatic fluids [38,39,66], and a significant
497 proportion of the Cu ore is contained with magmatic-hydrothermal breccia pipes [32-36]. Important
498 questions concerning the genesis of El Teniente, and any other giant orthomagmatic ore deposit, are:
499 1) Was the large amount of metal in the deposit derived from a large amount of magma or a unique
500 metal-rich magma?; and 2) How were the metals transferred from the magma into the host rocks?

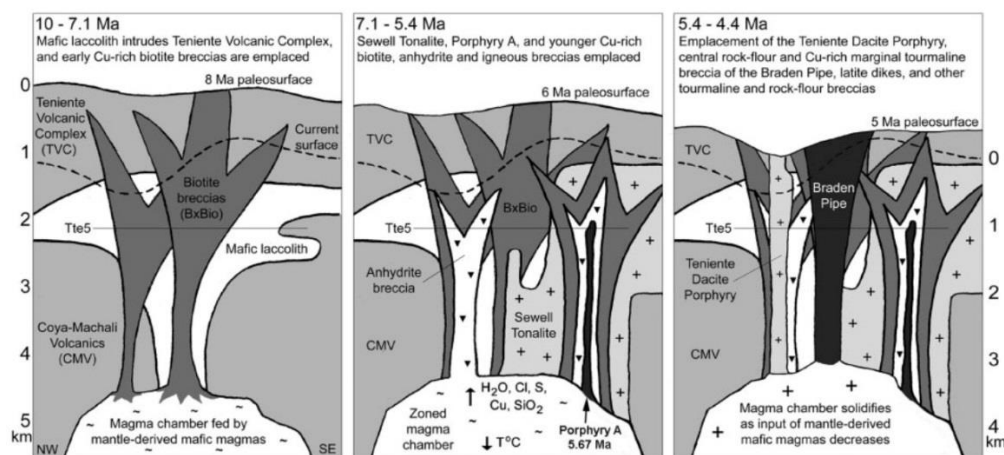
501 Muñoz et al. [37] conclude that the high initial ϵ_{Hf} values (total average of +7.4) of the syn-
502 mineralization felsic plutons “rules out involvement of any significant crustal contamination in the
503 genesis of the El Teniente magmas.” We agree, at least with regard to intra-crustal assimilation
504 (MASH). However, they then go on to suggest, based “entirely on the near constant Hf isotopic
505 composition shown by the Cenozoic igneous of the region” that they also “envision that Cenozoic
506 magmatism in central Chile originates from a MASH reservoir.” We disagree, given the clear
507 evidence that the ϵ_{Hf} values of Cenozoic magma, in particular mantle-derived mafic magmas erupted
508 in the region, were not at all constant, but progressively decreased significantly with time.

509 We suggest instead that the near constancy of the Hf isotopic composition of the 7.1 to 4.8
510 Ma felsic plutons in the El Teniente deposit is a result of mixing, storage and homogenization (but
511 not crustal assimilation) of mantle-derived magmas in a large vertically zoned upper crustal magma
512 chamber (Figure 10) which developed as a result of compressive deformation after 7 Ma (Figure 8).
513 These mafic mantle-derived magmas provided heat, water, S and metals into the base of this magma
514 chamber [67], which became vertically stratified with more hydrous and more silica-rich magmas
515 closer to the surface. As the input of mantle-derived magmas decreased during the Late Miocene,
516 and uplift and erosion brought the roof of the chamber closer to the surface [12,13], the upper part of
517 the chamber crystallized and differentiated into the magmas that formed the felsic plutons. Although
518 the Hf isotopic composition of the mantle-derived magmas may have been evolving over this same
519 time period (Figure 7), the large volume of the magma chamber into which these magmas mixed
520 limited the variations observed within the progressively younger felsic plutons, although some
521 decrease in their ϵ_{Hf} values is apparent. Once this large magma chamber fully crystallized, mantle-
522 derived olivine lamprophyre dikes were able to penetrate up to the surface, and these clearly exhibit
523 lower ϵ_{Hf} resulting from increased source region contamination of the mantle by subducted
524 components.

525 Muñoz et al. [37] further suggest that, as a result of crustal thickening, dehydration melting in
526 the deep crustal hot zone [68] within which the MASH reservoir was located “probably influenced
527 the fertility of the magmas by increasing the melt component derived from this process relative to
528 the component derived from primary” mantle melts. They do not detail what specific characteristics
529 make a magma more “fertile”, but they note that dehydration melting leads to the development of
530 water undersaturated magmas, which are less, not more likely to be able to exsolve mineral-rich
531 magmatic fluids.

532 In contrast, we do conclude that the mantle-derived olivine basalts emplaced in the Teniente
533 Mafic Complex prior to the development of the large magms chamber below the deposit, and the
534 mantle-derived olivine lamprophyres which cut through the deposit after this magma chamber fully
535 solidified, have changed their isotopic compositions due to increased contamination of the mantle
536 source region with subducted components, but we do not observe [22,23] any significant change in
537 the Cu contents between the pre-mineralization olivine basalts (100 ppm) and the post-mineralization
538 olivine lamprophyres (100 ppm). Therefore we do not believe that source region contamination

539 generated a uniquely “fertile” magma with respect to Cu content. We have suggested instead that
 540 the large amount of Cu in the deposit reflects a large amount of magma in the chamber above which
 541 the deposit developed [38,39,69,70]. To produce the $\geq 100 \times 10^6$ tonnes of Cu in the deposit requires a
 542 batholith-size ($\geq 600 \text{ km}^3$) amount of magma with ~ 100 ppm Cu. What made the deposit giant was
 543 that over the ~ 3 m.y. period that a magma chamber existed below the developing deposit, Cu, S heat
 544 and water from mantle derived magmas were added continuously to the base of the chamber and
 545 subsequently concentrated near the roof of the chamber by volatile transport. Clearly, because of
 546 increased source region contamination by subducted materials the mantle wedge did become
 547 progressively more hydrated, ultimately leading to the generation of lamprophyric magmas, which
 548 require 6-16 wt % H_2O , instead of olivine basalts, which require only 2 wt % H_2O [52-55]. Increasing
 549 H_2O content of the mantle-derived magmas through the time that they were mixed into the overlying
 550 magmas chamber may have resulted in more oxidizing conditions within the chamber, enhancing
 551 the process of volatile transfer of S and metals towards the roof of the chamber (Figure 10; [49,51,71].



552
 553 Figure 10. Model for the multistage development of the El Teniente deposit [23,32,33,39]. The main
 554 features of the model include (1) a large, long-lived (≥ 3 Myr) open-system magma chamber,
 555 crystallizing at ≥ 4 km depth, fed from below by mantle-derived mafic magmas and exsolving mineral-
 556 rich high-temperature magmatic fluids through its roof to produce the large breccia pipes that are
 557 prominent features this deposit; (2) decreasing magma supply in the Late Miocene and Pliocene as
 558 subduction angle decreases, leading to crystallization and solidification of this chamber; (3) progressive
 559 uplift and erosion that enhances this crystallization and solidification process and results in telescoping
 560 of different types of breccia and igneous rocks [12,13]; (4) progressive igneous differentiation of the
 561 magma chamber associated with crystallization and volatile loss, generating felsic porphyries that
 562 intrude previously mineralized rocks above the chamber. No coeval volcanism is known to have
 563 occurred during mineralization, but once the chamber solidified, post-mineralization mantle-derived
 564 olivine lamprophyre dikes were emplaced.

565
 566 Older studies of El Teniente suggested that Cu was transferred into the host rocks in
 567 association with the intrusion of the Teniente Dacite Porphyry, but new age dates indicate that much
 568 of the mineralization preceds this event, and that this essentially barren porphyry, where it intrudes
 569 outside the deposit, creates alteration but not mineralization. Instead we have suggested that the Cu
 570 and S were transferred into the host rocks of the deposit from the roof of the large magma chamber
 571 by exsolution of high-temperature metal-rich fluids generating multiple large magmatic-

572 hydrothermal mineralized breccia complexes such as the central Braden Pipe, and El Teniente is thus
573 better classified as a megabreccia deposit (Figure 10; [23,32,33,38,39]. Vry et al. [36] suggested that
574 such breccias formed in association with the intrusion of the small dacite and diorite dikes to the
575 northeast of the Braden pipe (Figure 6). However, we suggest instead that the breccias formed first
576 and the porphyries intruded into the zone of weakness created by the breccias, since some of these
577 porphyry bodies, such as Porphyry A (Figure 6) contain clasts of the breccias they intrude, and others
578 of these small porphyries have no associated breccias surrounding them.

579 6. Conclusions

- 580 1. The Hf isotopic data are consistent with the Sr, Nd and Pb data, and imply the incorporation
581 of small, but progressively increasing proportions of continental crust into the mantle source
582 of the mafic magmas erupted in the vicinity of El Teniente between ≥ 15 and 2.3 Ma.
- 583 2. The felsic plutons in the deposit formed by mixing, storage and homogenization, combined
584 with crystal-liquid differentiation, but not crustal assimilation (not MASH), in a large, long-
585 lived, vertically zoned magma chamber that developed due to compressive deformation and
586 persisted between the period ~ 7 to 4.6 Ma.
- 587 3. Progressively more hydrous and radiogenic mantle-derived mafic magmas feed this
588 chamber from below, providing heat, H₂O, S and metals, but no unique “fertile” Cu-rich
589 magma was involved in the formation of the deposit.
- 590 4. As the volume of these mantle-derived magmas decreased from the Late Miocene into the
591 Pliocene, the chamber crystallized and solidified, producing both felsic plutons and large
592 magmatic-hydrothermal breccias that emplaced Cu and S into the older (≥ 8.9 Ma) mafic
593 Teniente Mafic Complex host rocks of the deposit. The deposit is therefore best classified as
594 a megabreccia deposit.

595

596 **Author Contributions:** Conceptualization, Charles R Stern, M Alexandra Skewes and Alejandra Arévalo; Data
597 curation, Kwan-Nang Pang and Hao-Yang Lee; Project administration, Charles R Stern, M Alexandra Skewes
598 and Alejandra Arévalo; Writing – original draft, Charles R Stern; Writing – review & editing, Kwan-Nang
599 Pang, Hao-Yang Lee, M Alexandra Skewes and Alejandra Arévalo.

600

601 **Funding:** The analytical work was supported by Ministry of Science and Technology, Republic of China
602 (Taiwan) grant MOST 105-2628-M-001-002-MY4 to K.-N.P.

603

604 **Acknowledgments:** We thank Patricio Zuñiga, Ricardo Floody, Domingo Espiñeira and René Padilla for
605 collaboration in the collection and characterization of the samples from El Teniente.

606

607 **Conflicts of Interest:** We have no conflicts of interests.

608 References

- 609 1. Hickey-Vargas, R. Peeled or MASHed? *Nature* **1991**, *350*, 381-382.
- 610 2. Hildreth, W.; Moorbath, S. Crustal contributions to arc magmatism in the Andes of central Chile. *Contrib.*
611 *Mineral. Petrol.* **1988**, *103*, 361-386.
- 612 3. Stern, C.R. Role of subduction erosion in the generation of Andean magmas. *Geology* **1991**, *19*, 78-81.
- 613 4. Stern, C.R. Active Andean volcanism: its geologic and tectonic setting. *Rev. Geol. Chile* **2004**, *31*, 161-208.

- 614 5. Stern, C.R. Subduction erosion: rates, mechanisms, and its role in arc magmatism and the evolution of the
615 continental crust and mantle. *Gondwana Res.* **2011**, *20*, 284–308.
- 616 6. Rutland, R.W.R. Andean orogeny and ocean floor spreading. *Nature* **1971**, *233*, 252-255.
- 617 7. Goss, A.R.; Mahlburg Kay, S.; Mpodozis, C. Andean adakite-like high-Mg andesites on the Northern
618 margin of the Chilean-Pampean flat-slab (27–28.5°S) associated with frontal arc migration and fore-arc
619 subduction erosion. *J. Petrol.* **2013**, *54*, 2193–2234.
- 620 8. Risse, A.; Trumbull, R.B.; Kay, S.M.; Coira, B.; Romer, R.L. Multi-stage evolution of Late Neogene mantle-
621 derived Magmas from the Central Andes Back-arc in the Southern Puna Plateau of Argentina. *J. Petrol.*
622 **2013**, *10*, 1963–1995.
- 623 9. Lamb, S.; Davis, P. Cenozoic climate change as a possible cause for the rise of the Andes. *Nature* **2003**, *425*,
624 792-797.
- 625 10. Kay, S.M.; Godoy, E.; Kurtz, A. Episodic arc migration, crustal thickening, subduction erosion, and
626 magmatism in the south-central Andes. *Geol. Soc. Amer. Bull.* **2005**, *117*, 67-88.
- 627 11. Holm, P.M.; Søger, N.; Thorup-Dyhr, C.; Rohde-Nielsen, M. Enrichments of the mantle sources beneath
628 the Southern Volcanic Zone (Andes) by fluids and melts derived from abraded upper continental crust.
629 *Contrib. Mineral. Petrol.* **2014**, *167*, 1004.
- 630 12. Skewes, M.A.; Holmgren, C. Solevantamiento Andino, erosión y emplazamiento de brechas mineralizadas
631 en el depósito de cobre porfídico Los Bronces, Chile Central (33°S): aplicación de termometría de
632 inclusiones fluidas. *Rev. Geol. Chile* **1993**, *20*, 71-84.
- 633 13. Skewes, M.A.; Stern, C.R. Tectonic trigger for the formation of late Miocene Cu-rich breccia pipes in the
634 Andes of central Chile. *Geology* **1994**, *22*, 551-554.
- 635 14. Kurtz, A.C.; Kay, S.M.; Charrier, R.; Farrar, E. Geochronology of Miocene plutons and exhumation history
636 of the El Teniente region, Central Chile (34-35°S). *Rev. Geol. Chile* **1997**, *16*, 145-162.
- 637 15. Charrier, R.; Baeza, O.; Elgueta, S.; Flynn, J.J.; Gans, P.; Kay, S.M.; Muñoz, N.; Wyss, A.R.; Zurita, E.
638 Evidence for Cenozoic extensional basin development and tectonic inversion south of the flat-slab segment,
639 southern Central Andes, Chile (33°-36°S.L.). *J. S. Amer. Earth Sci.* **2002**, *15*, 117-139.
- 640 16. Giambiagi, L.B.; Ramos, V.A. Structural evolution of the Andes in a transitional zone between flat and
641 normal subduction (33°30'-33°45'S), Argentina and Chile. *J. S. Amer. Earth Sci.* **2002**, *15*, 101-116.
- 642 17. Nyström, J.; Vergara, M.; Morata, D.; Levi, B. Tertiary volcanism during extension in the Andean foothills
643 of central Chile (33°15'-33°45'S). *Geol. Soc. Amer. Bull.* **2003**, *115*, 1523-1537.
- 644 18. Farías, M.; Charrier, R.; Carretier, S.; Martinod, J.; Fock, A.; Campbell, D.; Cáceres, J.; Comte, D. Late
645 Miocene high and rapid surface uplift and its erosional response in the Andes of central Chile (33°-35°S).
646 *Tectonics* **2008**, *27*, TC1005.
- 647 19. Farías, M.; Comte, D.; Charrier, R.; Martinod, J.; Tassara, A.; Fock, A. Crustal-scale structural architecture
648 of the central Chile Andes based on 3D seismic tomography, seismicity, and surface geology: implications
649 for mountain building in subduction zones. *Tectonics* **2010**, *29*, TC3006.
- 650 20. Giambiagi, L.B.; Mescua, J.; Bechis, F.; Tassara, A.; Hoke, G. Thrust belts of the southern Central Andes:
651 Along-strike variations in shortening, topography, crustal geometry, and denudation. *Geol. Soc. Amer. Bull.*
652 **2012**, *124*, 1339–1351.
- 653 21. Stern, C.R.; Skewes, M.A. Miocene to present magmatic evolution at the northern end of the Andean
654 Southern Volcanic Zone, central Chile. *Rev. Geol. Chile* **1995**, *22*, 261-272.
- 655 22. Stern, C.R.; Floody, R.; Espiñeira, D. Pliocene olivine-hornblende-lamprophyre dikes from Quebrada de
656 los Sapos, El Teniente, Central Chile (34°S): Implications for the subarc mantle. *Andean Geol.* **2011**, *38*, 1-22.

- 657 23. Stern, C.R.; Skewes, M.A.; Arévalo, A. Magmatic evolution of the giant El Teniente Cu-Mo deposit, Central
658 Chile. *J. Petrol.* **2012**, *52*, 1591-1617.
- 659 24. Muñoz, M.; Farías, M.; Charrier, R.; Fanning, C.M.; Polvé, M.; Deckart, K. Isotopic shifts in the Cenozoic
660 Andean arc of central Chile: records of an evolving basement throughout cordilleran arc mountain
661 building. *Geology* **2013**, *41*, 931-934.
- 662 25. Stern, C.R. Pliocene to present migration of the volcanic front, Andean Southern Volcanic Zone. *Rev. Geol.*
663 *Chile* **1989**, *16*, 145-162.
- 664 26. Yáñez, G.; Ranero, C.; von Huene, R.; Díaz, J. Magnetic anomaly interpretation across the southern Central
665 Andes (32°-33.5°S): the role of the Juan Fernández ridge in the late Tertiary evolution of the margin. *J.*
666 *Geophys. Res.* **2001**, *106*, 6325-6345.
- 667 27. Yáñez, G.; Cembrano, J.; Pardo, M.; Ranero, C.; Selles, D. The Challenger-Juan Fernández-Maipo major
668 tectonic transition of the Nazca-Andean subduction system at 33-34°S: geodynamic evidence and
669 implications. *J. S. Amer. Earth Sci.* **2002**, *15*, 23-38.
- 670 28. Lindgren, W.; Bastin, E.S. Geology of the Braden mine, Rancagua, Chile. *Econ. Geol.* **1922**, *17*, 75-99.
- 671 29. Howell, F.H.; Molloy, S. Geology of the Braden orebody, Chile, South America. *Econ. Geol.* **1960**, *70*, 863-
672 905.
- 673 30. Camus, F. Geology of the El Teniente orebody with emphasis on wall-rock alteration. *Econ. Geol.* **1975**, *70*,
674 1341-1372.
- 675 31. Cuadra, P. Geocronología K-Ar del yacimiento El Teniente y áreas adyacentes. *Rev. Geol. Chile* **1986**, *27*, 3-
676 26.
- 677 32. Skewes, M.A.; Arévalo, A.; Floody, R.; Zuñiga, P.; Stern, C.R. The giant El Teniente breccia deposit:
678 hypogene copper distribution and emplacement. In *Global Exploration 2002: Integrated Methods of Discovery*,
679 Goldfarb, R.J., Nielson, R.L. Eds.; Society of Economic Geologists: USA, 2002; Special Publications 9, pp.
680 299-332.
- 681 33. Skewes, M.A.; Arévalo, A.; Floody, R.; Zuñiga, P.; Stern, C.R. The El Teniente megabreccia deposit, the
682 world's largest copper deposit. In *Super Porphyry Copper and Gold Deposits: A Global Perspective*, Porter, T.M.,
683 Ed.; PGC Publishing: Adelaide, Australia, 2005; Volume 1, pp. 83-114.
- 684 34. Makshev, V.; Munizaga, F.; McWilliams, M.; Fanning, M.; Marther, R.; Ruiz, J.; Zentilli, M. Chronology for
685 El Teniente, Chilean Andes, from U-Pb, ⁴⁰Ar/³⁹Ar, Re-Os, and fission track dating: implications for the
686 formation of a supergiant porphyry Cu-Mo deposit. In *Andean Metallogeny: New Discoveries, Concepts and*
687 *Updates*, Sillitoe, R.H., Perelló, J., Vidal, C.E. Eds.; Society of Economic Geologists: USA, 2004; Special
688 Publications 11, pp. 15-54.
- 689 35. Cannell, J.; Cooke, D.; Walshe, J.L.; Stein, H. Geology, mineralization, alteration, and structural evolution
690 of El Teniente porphyry Cu-Mo deposit. *Econ. Geol.* **2005**, *100*, 979-1004.
- 691 36. Vry, V.H.; Wilkinson, J.J.; Seguel, J.; Millán, J. Multistage intrusion brecciation and veining at El Teniente,
692 Chile: evolution of a nested porphyry system. *Econ. Geol.* **2010**, *105*, 119-153.
- 693 37. Muñoz, M.; Charrier, R.; Fanning, C.M.; Makshev, V.; and Deckart, K. Zircon trace element and O-Hf
694 isotope analyses of mineralized intrusions from El Teniente ore deposit, Chilean Andes: Constraints on the
695 source and magmatic evolution of porphyry Cu-Mo related magmas. *J. Petrol.* **2012**, *53*, 1091-1122.
- 696 38. Skewes, M.A.; Stern, C.R. Genesis of the giant Late Miocene to Pliocene copper deposits of central Chile in
697 the context of Andean magmatic and tectonic evolution. *Internat. Geol. Rev.* **1995**, *37*, 71-84.
- 698 39. Stern, C.R.; Skewes, M.A. Origin of giant Miocene and Pliocene Cu-Mo deposits in Central Chile: Role of
699 ridge subduction, decreased subduction angle, subduction erosion, crustal thickening and long-lived,

- 700 batholiths-size, open system magma chambers. In *Super Porphyry Copper and Gold Deposits: A Global*
701 *Perspective*, Porter, T.M., Ed.; PGC Publishing: Adelaide, Australia, 2005; Volume 1, pp. 65-82.
- 702 40. Warnaaars, F.W.; Holmgren, C.; Barassi, S. Porphyry copper and Tourmaline breccias at Los Bronces-Río
703 Blanco, Chile. *Econ. Geol.* **1985**, *80*, 1544-1565.
- 704 41. Skewes, M.A.; Stern, C.R. Late Miocene mineralized breccias in the Andes of central Chile: Sr- and Nd-
705 isotopic evidence for multiple magmatic sources. In *Andean Copper Deposits*, Camus, F., Sillitoe, R.H.,
706 Petersen, R., Eds.; Society of Economic Geologists: USA, 1996; Special Publications 5, pp. 119-130.
- 707 42. Skewes, M.A.; Holmgren, C.; Stern, C.R. The Donoso copper-rich, tourmaline-bearing breccia pipe in
708 central Chile: petrologic, fluid inclusion and stable isotope evidence for an origin from magmatic fluids.
709 *Mineral. Deposita* **2003**, *38*, 2-21.
- 710 43. Kusakabe, M.; Hori, M.; Nakagawa, S.; Matsuhisa, Y.; Ojeda, J.M.; Serrano, L.M. Oxygen and sulfur isotopic
711 compositions of quartz, anhydrite and sulfide minerals from the El Teniente and Río Blanco porphyry
712 copper deposits, Chile. *Bull. Geol. Survey Japan* **1984**, *35*, 583-614.
- 713 44. Kusakabe, M., Hori, M. & Matsuhisa, Y. Primary mineralization-alteration of the El Teniente and Río
714 Blanco porphyry copper deposits, Chile; stable isotope, fluid inclusion and Mg²⁺/Fe²⁺/Fe³⁺ ratios of
715 hydrothermal fluids. In *Stable Isotopes and Fluid Processes in Mineralization*, Herbert, H.K., Ho, S.E., Eds.;
716 University of Western Australia Press, Perth, Australia, 1990; pp. 244-259.
- 717 45. Puig, A. Geologic and metallogenic significance of the isotopic composition of lead in galenas of the
718 Chilean Andes. *Econ. Geol.* **1988**, *83*, 843-858.
- 719 46. Muñoz, M.; Fuentes, F.; Vergara, M.; Aguirre, L.; Nyström, J.O. Abanico East Formation: petrology and
720 geochemistry of volcanic rocks behind the Cenozoic arc front in the Andean Cordillera, central Chile
721 (33°50'S). *Rev. Geol. Chile* **2006**, *33*, 109-140.
- 722 47. Montecinos, P.; Schärer, U.; Vergara, M.; Aguirre, L. Lithospheric origin of Oligocene--Miocene
723 magmatism in Central Chile: U-Pb ages and Sr-Pb-Hf isotope composition of minerals. *J. Petrol.* **2008**, *49*,
724 555-580.
- 725 48. Godoy, E.; Yáñez, G.; Vera, E. Inversion of an Oligocene volcanic tectonic basin and uplifting of its
726 superimposed Miocene magmatic arc in the Chilean Central Andes: first seismic and gravity evidences.
727 *Tectonophys.* **1999**, *306*, 217-236.
- 728 49. Stern, C.R.; Funk, J.A.; Skewes, M.A.; Arévalo, A. Magmatic anhydrite in plutonic rocks at the El Teniente
729 Cu-Mo deposit, Chile, and the role of sulfur- and copper-rich magmas in its formation. *Econ. Geol.* **2007**, *102*,
730 1335-1344.
- 731 50. Deckart, K.; Godoy, E.; Bertens, A.; Saeed, A.; Jeréz, D. Barren Miocene granitoids in the central Andean
732 metallogenic belt, Chile: Geochemistry and Nd-Hf and U-Pb isotope systematics. *Andean Geol.* **2010**, *37*, 1-
733 31.
- 734 51. Blatter, D.K.; Carmichael, I.S.E. Hornblende peridotite xenoliths from central Mexico reveal the highly
735 oxidized nature of subarc upper mantle. *Geology* **1998**, *26*, 1035-1038.
- 736 52. Blatter, D.K.; Carmichael, I.S.E. Hydrous phase equilibria of a Mexican high-silica andesite: a candidate for
737 mantle origin? *Geochim. Cosmochim. Acta* **2001**, *65*, 4043-4065.
- 738 53. Moore, G.M.; Carmichael, I.S.E. The hydrous phase equilibria (to 3kbar) of an andesite and basaltic andesite
739 from Western Mexico: constraints on water content and conditions of phenocrysts growth. *Contrib. Mineral.*
740 *Petrol.* **1998**, *130*, 304-319.
- 741 54. Carmichael, I.S.E. The andesite aqueduct: perspectives in the evolution of intermediate magmas in west-
742 central Mexico. *Contrib. Mineral. Petrol.* **2002**, *143*, 641-663.

- 743 55. Barclay, J.; Carmichael, I.S.E. A Hornblende Basalt from Western Mexico: Water-saturated Phase Relations
744 Constrain a Pressure-Temperature Window of Eruptibility. *J. Petrol.* **2004**, *45*, 485-506.
- 745 56. Rudnick R.; Gao S. Composition of the continental crust. In *The Crust*, R. L. Rudnick, R.L., Ed.; Elsevier-
746 Pergamon, Oxford, England, 2002; pp. 1-64.
- 747 57. McDonough W.F.; Sun S.S. The composition of the Earth. *Chem. Geol.* **1995**, *120*, 223-253.
- 748 58. Straub, S.M.; Gómez-Tuena, A.; Bindeman, I.N.; Bolge, L.L.; Brandl, P.A.; Espinasa-Perena, R.; Solari, L.;
749 Stuart, F.M.; Vannucchi, P.; Zellmer, G.F. Crustal recycling by subduction erosion in the central Mexican
750 Volcanic Belt. *Geochim. Cosmochim. Acta* **2015**, *166*, 29-52.
- 751 59. Tera F.; Brown L.; Morris J.; Sacks I.S. Sediment incorporation in island-arc magmas: Inferences from ¹⁰Be.
752 *Geochim. Cosmochim. Acta* **1986**, *50*, 535-550.
- 753 60. Morris J.D.; Leeman W.P.; Tera F. The subducted component in island arc lavas: constraints from Be
754 isotopes and B-Be systematics. *Nature* **1990**, *344*, 31-36.
- 755 61. Morris J.D.; Gosse J.; Brachfeld, S.; Tera F. Cosmogenic ¹⁰Be and the solid earth: studies in geomagnetism,
756 subduction zone processes, and active tectonics. In *Reviews in Mineralogy*, Grew, E., Ed.; Mineralogical
757 Society of America, Washington, DC, USA, 2002; pp. 207-270.
- 758 62. Tonarini S.; Leeman W.P.; Leat P.T. Subduction erosion of forearc mantle wedge implicated in the genesis
759 of the South Sandwich Island (SSI) arc: evidence from boron isotope systematics. *Earth Planet. Sci. Lett.* **2011**,
760 *301*, 275-284.
- 761 63. Gómez-Tuena, A.; Cavazos-Tovar, J.G.; Parolari, M.; Straub, S.M.; Espinasa-Pereña, R. Geochronological
762 and geochemical evidence of continental crust 'reamination' in the origin of intermediate arc magmas.
763 *Lithos* **2018**, *322*, 52-66.
- 764 64. Goss, A.R.; Kay, S.M. Steep REE patterns and enriched Pb isotopes in southern Central American arc
765 magmas: evidence for forearc subduction erosion? *Geochem. Geophys. Geosyst.* **2006**, *7*, 1-20.
- 766 65. Freydier, C.; Ruiz, J.; Chesley, J.; Candless, T.; Munizaga, F. Re-Os isotope systematics of sulfides from
767 felsic igneous rocks: application to base metal porphyry mineralization in Chile. *Geology* **1997**, *25*, 775-778.
- 768 66. Klemm, L.M.; Pettke, T.; Heinrich, C.L.; Campos, E. Hydrothermal evolution of the El Teniente deposit,
769 Chile: porphyry Cu-Mo ore deposition from low-salinity magmatic fluids. *Econ. Geol.* **2007**, *102*, 1021-1045.
- 770 67. Hattori, K.H.; Keith, J.D. Contributions of mafic melt for porphyry deposits: evidence from Pinatubo and
771 Bingham. *Mineral. Deposita* **2001**, *36*, 799-806.
- 772 68. Annen, C.; Blundy, J.D.; Sparks, R.S.J. The genesis of intermediate and silica magmas in deep crustal hot
773 zones. *J. Petrol.* **2006**, *47*, 505-539.
- 774 69. Cloos, M. Bubbling magma chambers, cupulas and porphyry copper deposits. *Internat. Geol. Revs.* **2001**, *43*,
775 285-311.
- 776 70. Richards, J.P. Cumulative factors in the generation of giant calc-alkaline porphyry Cu deposits. In *Super*
777 *Porphyry Copper and Gold Deposits: A Global Perspective*, Porter, T.M., Ed.; PGC Publishing, Adelaide,
778 Australia, 2005; Volume 1, pp. 7-26.
- 779 71. Garrido, I.; Cembrano, J.; Siña, A.; Stedman, P.; Yáñez, G.A. High magma oxidation state and bulk crustal
780 shortening: key factors in the genesis of Andean porphyry copper deposits, central Chile (31-34°S). *Rev.*
781 *Geol. Chile* **2002**, *29*, 43-54.