1   **Revision 2**

2   **The relationship of destinezite to the acid sulfate alteration at the El Laco**

3   **magnetite deposit, Chile**

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5   Francisco Velasco

6   Departamento de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, E-48080

7   Bilbao, Spain francisco.velasco@ehu.es

8   Noelia De la Pinta

9   Departamentos de Física de la Materia Condensada y Física Aplicada, Facultad de

10   Ciencia y Tecnología, E-48080 Bilbao, Spain

11   Fernando Tornos

12   Instituto de Geociencias (IGEO, CSIC-UCM) – Doctor Severo Ochoa, 7, E-28040

13   Madrid, Spain

14   Thomas Briezewski

15   Departamentos de Física de la Materia Condensada y Física Aplicada, Facultad de

16   Ciencia y Tecnología, E-48080 Bilbao, Spain

17   Aitor Larrañaga

18   Sgiker Servicios Científicos, Universidad del País Vasco, Barrio Sarriena, s/n, E-48940

19   Leioa, Vizcaya,Spain

20

21   Corresponding author, e-mail: francisco.velasco@ehu.es

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22   **Abstract**

23   Destinezite, ideally $Fe^{3+}_2(PO_4)(SO_4)(OH) \cdot 6(H_2O)$, is found as nodular lumps in hematite-

24   rich epiclastic sediments accumulated in small crater lakes on the slopes of El Laco

25   volcano. These lumps are almost entirely dominated by fine-grained destinezite

26   replacing earlier lipscombite, and associated with gray hematite. The crystal structure of

27   destinezite has been re-examined in order to test for possible differences with respect

28   to the earthy and poorly crystalline destinezite that forms by weathering in cave soils and

29   mine waste dumps. The structural refinements confirm that the differences found are

30   rather minor. The El Laco destinezite was refined in space group $P\overline{1}$ with a = 9.5828(2),

31   b = 9.7440(3), c =7.3302(3) Å, and α = 98.796(3)°, β = 107.985(3)°, γ = 63.898(2)°, V =

32   584.50(4) Å^3 and Z= 1. We measured by calorimetry the enthalpy and derived the

33   entropy and the Gibbs free energy of formation of destinezite (-4051.7 ± 4.3 kJ.mol^{-1}, $-$

34   1518.5 ± 20.0 kJ.mol^{-1}, -3598.9 ± 7.1 kJ.mol^{-1}, respectively). This has allowed us to

35   estimate the equilibrium constant in the temperature range 0–300°C (log K = $-27.97\pm$

36   1.1). We can predict that destinezite coexists with hematite over the range of conditions

37   that typically encompass the steam-heated hydrothermal environments recognized at El

38   Laco. The presence of destinezite along with hematite and the occurrence of alunite,

39   jarosite and variscite in the system provide evidence of intense hydrothermal alteration

40   during the extrusion of Fe-rich melts at El Laco volcano. The mineral assemblage and

41   the available geochemical data suggest that destinezite formed in hydrothermal

42   conditions by "maturation" of an immiscible Fe–P-rich melt. An unknown Fe–P–O phase

43   produced by this melt was first replaced by lipscombite and later, owing to intense

44   sulfidation, by destinezite. This replacement took place in the vadose zone above the

45   paleowater table by relatively cool (<150ºC) groundwaters acidified by oxidation of

46   magmatic SO_2 to aqueous sulfate in a steam-heated system. Our model precludes other

47   modes of formation, such as devitrification of hypothetical Fe–P–S–O-rich melts ejected

48   from the volcano and supergene crystallization.

49

50   Keywords: destinezite, acid-sulfate alteration, magnetite–apatite deposit, El Laco

51   volcano, Chile

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Introduction

Destinezite and its partially amorphous equivalent, diadochite, both ideally hydrated hydroxyphosphate-sulfates of ferric Fe, are rare minerals of the general formula $Fe^{3+}_2(PO_4)(SO_4)(OH) \cdot 6H_2O$ (Matsubara et al., 1999; Peacor et al., 1999; Naslund et al., 2002; Lledó, 2005). Generally, diadochite is partially amorphous, whereas its polymorph destinezite is crystalline. They occur in cave soils, weathered gossans and mine-waste dumps as poorly crystalline phases (Peacor et al., 1999; Anthony et al., 2005). Destinezite is the more common of the two owing to its clay-like nature and its tendency to occur mixed in with other earthy minerals, such as delvauxite, melanterite, rockbridgeite, phosphosiderite and "limonite" (names and formula of all mentioned minerals in this text are in Table 1), which make its identification difficult.

Lumps of destinezite were first reported from El Laco by Naslund et al. (2002) as clasts intermingled with unconsolidated "tephra", part of the eruptive products of the volcano. Some authors have suggested that they are pyroclastic fragments of an immiscible Fe-P-S-rich magma erupted by the volcano (Henríquez and Nyström, 1998; Lledó, 2005; Naslund et al., 2009). With this interpretation, these authors provided support for the hypothesis that magnetite ores from El Laco represent crystallized Fe-oxide melts (Nystrom and Henríquez, 1994; Naslund et al., 2002; Lledó, 2005; Mungall et al., 2018). As an alternative view, the supergene origin traditionally attributed to destinezite–diadochite implies that they formed in direct contact with the atmosphere and at room temperature (Moiseeva, 1967, 1970; Peacor et al., 1999).

In this article, we describe the occurrence of destinezite and propose that it formed

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76 during the advanced argillic alteration at the El Laco hydrothermal system. Whatever the

77 ultimate origin of the destinezite, it must have had an Fe-bearing phosphate precursor

78 that was transformed by sulfidation and hydration during a late low-temperature event.

79 The lack of thermodynamic properties necessary to test this interpretation prevents us

80 from determining whether the stability field of destinezite is compatible with that of the

81 assemblage of associated minerals and with the geochemical conditions of alteration.

82 We wish to acquire the thermodynamic data considered essential to discuss the origin of

83 the El Laco destinezite, chiefly enthalpy, entropy, and its Gibbs free energy of formation.

84 This research provides new information on destinezite, in particular its chemical

85 composition, its degree of crystallinity, and some aspects of crystal structure. The study

86 also provides insights about the process of transformation of the identified phosphate

87 precursor, based on the stability fields of the mineral phases involved.

88 **Geological background**

89 The El Laco Fe deposit is located in the active Cenozoic volcanic arc of the Andes

90 near the Chile–Argentina border, at 4800–5200 meters above sea level (Fig. 1). Four

91 volcanic units dominated by flows have been recognized in the area (Velasco et al.,

92 2016). Perhaps the most intriguing feature is the presence of stratabound bodies of

93 magnetite at or near the contact between the Lower and Upper Andesite units. A

94 younger generation of later andesite flows, volumetrically less important, is found near

95 the principal vent. Andesite belonging to the Upper and Lower units have high content of

96 magnetite, mainly occurring as small microphenocrysts in the volcanic groundmass. It

97 also contains small crystals of apatite, both disseminated in the groundmass and

98 included in the pyroxene phenocrysts (Velasco et al., 2016; Tornos et al., 2017).

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99   The deposit comprises seven ore bodies of massive magnetite within a 8 x 4 km^2

100   area, with estimated resources of about 750 Mt of ore grading about 60% Fe (Naslund et

101   al., 2002; Tornos et al., 2016, 2017). Magnetite ore bodies form a semicircle around an

102   andesitic plug; their location may be controlled by a caldera collapse structure (Fig. 1)

103   (Keller et al., 2018). They occur either as subvertical dikes or as related larger strata

104   bound bodies, linked invariably to a recognizable feeder structure. These magnetite ore

105   bodies resemble edifices typical of basaltic shield volcanoes and include dome- or cone-

106   like morphologies, having associated lava-lake infillings and volcanoclastic deposits

107   (Nystrom and Henríquez, 1994; Tornos et al., 2017). Crosscutting the whole magnetite

108   lenses are abundant but discontinuous tubes coated with skeletal clinopyroxene and

109   euhedral magnetite with unidirectional growth structures. Tubes and, to a lesser extent,

110   abundant vesicles, are irregularly coated by products of hydrothermal activity such as

111   quartz, sanidine, alunite, hematite, Fe-bearing phosphates, and fluorite.

112   Magnetite is the dominant mineral in the large stratabound orebodies, but it has

113   been widely replaced by maghemite, and this transformed to hematite in zones that

114   underwent pervasive hydrothermal alteration. Most of the magnetite is characteristically

115   Ti-poor, with TiO$_2$ contents lower than 0.1 wt%, and trace amounts of Cr, V, and Ni

116   (Dare et al., 2015; Velasco et al., 2016; Broughm et al., 2017). Apatite, largely

117   fluorapatite, is locally abundant and may reach up to 10 vol.% in the feeder structures.In

118   the stratabound bodies, it is fairly common to find it lining cavities or nucleating along

119   intrusive contacts (Henriquez and Martin, 1978).

120   Regional mapping, geochemistry, and petrography show that there are several

121   superimposed stages of hydrothermal activity (Rhodes et al., 1999; Naranjo et al., 2010;

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122   Velasco and Tornos, 2012; Tornos et al., 2016, 2017). In deep areas beneath the

123   stratabound ores, the andesite has undergone pervasive high-temperature alkali-calcic

124   alteration. Both phenocrysts and groundmass are replaced by diopside, adularia, a

125   scapolite-group mineral, magnetite and anhydrite. At shallow depth, the alteration

126   resulted in strong bleaching of the andesite owing to pervasive replacement by alunite

127   and to the leaching of Fe associated with the advanced argillic alteration of the rocks

128   (Fig. 1A, 1B). This alteration was mainly controlled by northwest-southeast faults. The

129   resulting assemblages consist of fine-grained alunite exhibiting a pseudocubic habit

130   (rhombohedral crystals with nearly cubic angles), kaolinite, smectite, gypsum, tridymite,

131   jarosite, variscite, fluorite and, more rarely, pyrite and chalcopyrite. Most of the hematite

132   occurs as a pseudomorph after magnetite but locally appears as coarse-grained

133   euhedral to subhedral crystals replacing magnetite and disseminated in the altered

134   andesite.

135   The ore bodies, especially at Laco Sur, are commonly brecciated, with fragments

136   of the altered host andesite supported by massive magnetite (Henriquez and Martin,

137   1978; Nystrom and Henríquez, 1994; Naslund et al., 2002; Henriquez et al., 2003;

138   Nystrom et al., 2016; Ovalle et al., 2018). These exposures have been recently

139   interpreted as being part of small diatreme–maar complexes (Tornos et al., 2016, 2017).

140   These complexes end up in crater lakes that are infilled by alluvial fan and fluvioglacial

141   sediments made up almost exclusively of hematite. In some instances, they are covered

142   by later structureless eluvial gravel and silt. The hematite shows a well-defined parallel

143   but discontinuous layering, with poorly sorted grain-size distribution and local erosional

144   bottoms, all of them indicative of traction in a subaqueous environment. These hematite-

145 rich deposits have been interpreted as variably reworked and altered pyroclastic ejecta

146 coeval with the steam-rich extrusion of the Fe-rich melts (Tornos et al., 2017).

147   Within the hematite-rich sediments (Fig. 2), abundant angular clasts or irregular

148 compact lumps (nodules) up to 15 cm in diameter are composed mainly of destinezite.

149 Its characteristic orange color contrasts with the dark gray groundmass (Naslund et al.,

150 2003; Lledó, 2005; Naslund et al., 2009; Nystrom et al., 2016; Tornos et al., 2017).

151 These lumps are found along some certain horizons (Fig. 2A, 2B). Interpretation of their

152 original morphology can be difficult because the nodules usually are broken and

153 scattered. In some cases, they preserve a bread crust structure and an unclear internal

154 lamination, and fractures similar to those found in juvenile pyroclastic fragments.

155 According to Lledó (2005) and Naslund et al. (2009), these lumps represent ejected

156 fragments of devitrified magma (bombs), which would explain why they usually present

157 a flat bottom, indicative of ductility when they impacted the ground. Most of the

158 destinezite aggregates have inclusions of hematite, mainly filling microfissures and, less

159 commonly, oxidized magnetite, grouped in nooks and crannies, and showing secondary

160 alteration.The intimate association of destinezite with hematite suggests that both

161 originated during the same process, prior to glacial erosion, transport, and

162 sedimentation, to form the overlying alluvial Holocene Fe-rich deposits.

163 **Materials and methods**

164   Twenty samples of destinezite were prepared and polished as standard thin

165 sections ready to be observed under the petrographic microscope in transmitted and

166 reflected light. After inspection to check for the presence of inclusions and

167 inhomogeneous zones, the cleanest samples were selected for the thermal study and

168 Rietveld refinement of X-ray diffraction data; those showing inclusions of magnetite or

169 hematite at the edge of grains or remnants of other minerals were rejected.

170 **X-ray diffraction analysis.** No single crystals of destinezite could be isolated for a

171 single-crystal study. Hence, several almost pure samples were powdered in an agate

172 mortar under ambient conditions to acquire powder X-ray diffraction patterns (XRD). The

173 scans were obtained using a Philips X-Pert PRO automated diffractometer with Cu$K\alpha$

174 radiation (λ=1.5418 Å) and a PIXcel solid-state detector (active length in 2θ 3.347°) at

175 the General Research Services (SGIker) of the University of Basque Country, Leioa,

176 Spain), operated at 40 kV and 40 mA in theta–theta configuration, and fitted with a

177 diffracted-beam monochrometer to filter out fluorescent X-rays. The samples were

178 mounted on a zero-background silicon wafer fixed in a generic sample holder. Data were

179 collected from 5 to 80° 2θ (step size = 0.026° and time per step = 4600 s) at room

180 temperature. A fixed divergence and antiscatter slit provided a constant volume of

181 sample illumination.

182 Removal of instrumental broadening was done by collecting a pattern for the LaB_6

183 standard at the same conditions and settings. The data obtained were fitted using the

184 Rietveld approach and the FullProf software (Rodríguez-Carvajal, 2001). For the

185 identification of phases in the powder mounts, we made use of the Powder Diffraction

186 File (PDF) database. We used the PANalytical X´Pert High Score program to index all

187 observed maxima. Run products from heating experiments were mounted on silicon

188 plates and analyzed with the same diffractometer (at room temperature), operated at 40

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189 kV and 40 mA, using a continuous scan at increments of 0.026º 2θ and counting times

190 of 600 second per step.

191   The refinement of the structure of the representative sample (DiadoX-1A) was

192 performed in the space group P$\overline{1}$ using the parameters for destinezite described by

193 Peacor et al. (1999). To check the validity and to establish confidence in the results, we

194 collected five replicate patterns in order to minimize instrumental drift as well as short-

195 period fluctuations of the samples. The procedure did not require the removal of regions

196 shared by other foreign peak positions because of the absence of potential

197 contaminants. Consequently, we assumed that all the reflections are compatible with the

198 destinezite, and that no others reflections are present.

199   **Scanning Electron Microscopy (SEM).** The samples used for experiments were

200 characterized by scanning electron microscopy after coating with carbon using the

201 Schottky field emission (JEOL JSM-7000F) microscope at the SGIker Labs (University of

202 Basque Country). This unit ran at an accelerating voltage of 20 keV at a beam current in

203 the range 10–20 nA. The SEM images, results of energy-dispersive x-ray spectroscopy

204 analyses (EDS), and element-distribution patterns were used to characterize the

205 products.

206   **Electron-microprobe (EMP) analyses.** The chemical composition of selected

207 samples was investigated using the CAMEBAX electron microprobe (SGIker Labs) at an

208 accelerating voltage of 15 kV, with a current of 10 nA, a beam diameter of 2–3 μm, and

209 the following standards supplied by Spi Structure Probe Inc.: jadeite (Na), sanidine (K),

210 diopside (Ca), spodumene (Al, Si), hematite (Fe), olivine (Mg), apatite (P), alunite (S),

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211 and pure metals (Mn, Cr, V, Ni, and Ti); the X-ray lines measured are *K*α in all cases.

212 Interferences between elements were minimized, and concentrations were corrected for

213 major-element matrix effects using the PAPmatrix correction procedure ([Pouchou and

214 Pichoir, 1984](#)). Detection limits were calculated with an accuracy of 2σ at the 95%

215 confidence level. At these conditions, the detection limits of all oxides was 0.01 wt.%,

216 and for minor and trace elements, it was better than 200-500 μg/g depending on the

217 elements and settings.

218 **Calorimetric and thermogravimetric experiments**. Thermogravimetric measurements

219 (thermogravimetric and differential thermogravimetric analysis, TGA and DTG,

220 respectively) were performed on dry samples of "pure" destinezite (weight of samples

221 approx. 5–15 mg) on a TA Discovery series instrument over the temperature range 50–

222 900ºC with a constant heating rate of 5ºC/min, under a nitrogen atmosphere with a flow

223 rate of 20mL/min. Temperature calibration was performed under the same experimental

224 conditions using the Curie temperatures of nickel and aluminum as standards.

225 Differential scanning calorimetry (DSC) measurements were performed on the same

226 samples on SDT Q600 and DSC Q2000 TA calorimeter instruments, using heating rate

227 of 10ºC/min under helium atmosphere (these equipment and lab facilities belong to the

228 Department of Applied Physic II, University of Basque Country, Leioa Spain). The DSC

229 samples were cut as small pieces with an approximate mass between 15-35 mg, and

230 then hermetically sealed in aluminum pans. For proper calibration of temperature and

231 heat flux was employed indium and sapphire as reference materials. Quantitative

232 DSC/DTG data obtained with the above instruments have allowed to calculate the ΔH

233 associated with each one of the seven stages of decomposition of the destinezite that

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234   have been distinguished during the entire heating experiment (see Table 3). The

235   procedure assumes that the change in enthalpy per degree is equivalent to the heat

236   capacity of the material, at constant pressure, and may be measured by estimating the

237   area under the DSC curve between the temperature limits of each discriminated reaction

238   step. All the measures of DSC and TGA were coupled with other techniques, such as X-

239   ray diffraction and SEM-EDX, to provide an understanding of phase transitions, mainly

240   the characterization of the intermediate and final products formed at each heating stage.

241   After the identification of intermediate and final species in each one of the reaction steps

242   (see Table 3 and description of 'Thermogravimetric analysis and thermodynamic data for

243   destinezite' section) it is concluded that the final products, upon reaching the

244   temperature of 900ºC, are rodolicoite, grattarolaite and hematite. This find justify the

245   selection of the previous temperature interval because the obtained final products have

246   been well identified and their enthalpy of formation ΔH^o_f are known. Therefore, from the

247   thermodynamic data of these products and using the Hess´s Law, it may be obtained the

248   enthalpy change ΔH of the balanced reaction representing the overall process for the

249   selected temperature range (50–900ºC), and then it possible to determinate the enthalpy

250   of formation ΔH^o_f of the destinezite**.** Applying a similar procedure, may be evaluated the

251   entropy change from DSC measurements, by dividing the corresponding enthalpy

252   change for each reaction step by the temperature. The standard entropy change (ΔS^o)

253   for the overall process, using again the Hess's Law may be computed (Anderson, 2005).

254   Therefore, it can be also estimated the standard entropy of formation ΔS^o_f of the

255   destinezite by application of Hess' Law. Finally, these values were used to calculate the

256   standard Gibbs free energy of formation with $\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f$, where ΔH^o_f and ΔS^o_f

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257   are, respectively, the standard enthalpy and entropy of formation determined from the

258   above calorimetric measurements, and T the standard temperature (298.15 K).

259   The values obtained of enthalpy, entropy, and Gibbs free energy of formation for the

260   destinezite have been compared with data estimated by non-experimental methods.

261   These crude estimates are mainly based on a) the ideal mixing model adopted by

262   Nriagu and Dell (1974), Hemingway et al. (2002) and Gas'kova et al. (2008), and b) the

263   theoretical approach adapted by La Iglesia (2009), based on the model of the

264   contribution of polyhedral units of Hazen (1985) and Chermak and Rimstidt (1989). The

265   latter method allows us to predict the values of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ with an uncertainty of less

266   than 1.5% compared to those calculated from the experimental values. These estimates

267   show a good fit with the experimental results and led us to determine the solubility

268   product of other Fe-bearing phosphate minerals in order to discuss phase relationship

269   among minerals in the system Fe–P–S–O–H.

270   **Results**

271   **Mineralogical features of destinezite lumps**

272   Although the destinezite is invariably the main component (>95vol.%) of the lumps,

273   they usually enclose variable amounts of platy pseudohexagonal crystals of hematite of

274   several millimeters across, a few relics of partially oxidized subhedral magnetite and,

275   more rarely, small inclusions of monazite and quartz. In rare cases, the lumps retain

276   relics of a poorly characterized Fe phosphate mineral, whose variable composition

277   deviates from the ideal stoichiometry of common high-temperature anhydrous Fe

278   phosphate minerals (e.g., heterosite). Individual crystals of destinezite are not visible to

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279   the naked eye, but are visible under the microscope. Texturally, they largely consist of

280   an aggregate of equigranular, interlocking, and randomly oriented anhedral to subhedral

281   grains (*de-1* in Fig. 3A). Locally, these aggregates seem to have recrystallized to

282   medium-grained polygonal aggregates, preferentially aligned along the wall of sealed

283   microfractures that crosscut the lumps. This second generation of destinezite (*de-2* in

284   Fig. 3A, 3B), with a platy shape and a pseudohexagonal outline (Fig. 3B, 4B), may attain

285   dimensions up to 50 μm across. The relative large size and the habit of the faceted

286   crystals of destinezite, in addition of their association with idiomorphic hematite (Fig.

287   4A), suggest that they grew as a result of the circulation of late hot solutions along the

288   fractures and pores in the lumps.

289   The determination of the optical properties of this destinezite is difficult, particularly

290   because of the small size of the crystals, their strong absorption, dispersion, and

291   anomalous extinction. Observed in thin section under transmitted plane-polarized light,

292   they show a continuous change in color, from yellow to deep brown to black, causing

293   irregular variations in birefringence, even at the scale of individual crystals. Rare

294   destinezite aggregates show an incipient replacement to a suite of secondary Fe

295   phosphate and sulfate minerals intermingled with supergene "limonite". These

296   secondary minerals may coat the aggregates, forming a layer up to 0.5 mm thick with a

297   rusty edge and an earthy brittle structure. They may also fill some crisscrossing

298   fractures, as thin films of submicroscopic aggregates exhibiting spherulitic micro-textures

299   (Fig. 3C).The X-ray diffraction and results of semi-quantitative EMP analyses of these

300   products indicate that they consist of variable proportions of diverse minerals, chiefly

301   cacoxenite, tinticite, rockbridgeite, and an uncommon Sr-rich jarosite (up to 5 wt% SrO)

302   (Fig. 3C).

303   The 'crystalline' hematite in the lumps presents similar characteristics to those of

304   the hematite that dominates in the sediments; the subhedral tabular to platy crystals

305   display a bright grey color. These grains are faceted (pinacoid, rhombohedron,

306   hexagonal prism), may exhibit skeletal textures, and locally attain several centimeters

307   across, which suggests growth under hydrothermal conditions (Vorobyeva and Melnik,

308   1977; Catling and Moore, 2003; Demianets et al., 2003). In some cases, the largest

309   grains host rare minute inclusions of chalcopyrite and euhedral pyrite, which indicates

310   that hematite and sulphides formed during the same hydrothermal event. In the more

311   oxidized samples, the edge of the hematite crystals is replaced by colloform goethite,

312   whereas the magnetite grains show evidences of supergene transformation to hematite.

313   However, this process did not reach completion, preserving abundant remnants of

314   magnetite within the secondary hematite.

315   **Chemical and isotopic composition of destinezite**

316   The average result of 40 selected EMP analyses (Table 2) reveals that the

317   composition of the destinezite is relatively uniform, in comparison with data reported in

318   the literature (Matsubara et al., 1999; Lledó, 2005). With respect to the ideal formula, our

319   results indicate a slight excess of Fe and P and a deficiency in S. An indirect estimate of

320   the H_2O content by subtraction of the analytical total from 100% suggests ca. 5.5

321   molecules per cell. This figure is in accordance with the values estimated by Matsubara

322   et al. (1999), and previously reported by Fleischer and Mandarino (1995) and Moiseeva

323   (1967). However, these results disagree with the six molecules of H_2O in the ideal

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324 formula proposed by Peacor et al. (1999), and the value obtained with the Penfield

325 method by Anthony et al. (2005) using samples of natural destinezite collected at Haut-

326 le-Bastia, Belgium. This apparent deficiency in H_2O could be presumably caused by the

327 damage or partial dehydration of the crystals under the EMP beam during the analysis,

328 even using defocused beams and short-duration counts. Although this explanation does

329 not satisfy the disagreement generated about the number of H_2O molecules in

330 destinezite, it indicates the ability to lose H_2O during the analyses in conditions close to

331 the ambient temperature (Fig. 4B). In fact, the color of this mineral easily changes when

332 it is observed in the field (reddish orange to brownish) compared to the laboratory

333 (yellowish orange), where it is in a dry atmosphere.

334   With respect to major elements, the results of the EMP analyses suggest a limited

335 substitution of SO_4 for PO_4, and minor or no substitution of Al for Fe^{3+} at the octahedral

336 sites of the structure. However, most of the analyses yield considerable amounts of SiO_2

337 (up to 4wt%; ca. 0.5 wt% on average), which probably reflects contamination by nano-

338 inclusions of quartz rather than substitution by SiO_4 at the tetrahedral sites. The

339 abundance of Ca in a large number of samples (up to 0.5 wt% CaO) could also reflect

340 contamination by admixtures of minerals resulting from the alteration of plagioclase in

341 the andesite, or the presence of traces of calcium-rich minerals (invisible nanoparticles

342 of anhydrite or gypsum?) derived from the destabilization of apatite. It is noteworthy that

343 apatite was not found in the nodules, nor in the horizons in which the destinezite occur.

344 However, it has been found in some pyroclastic or epiclastic horizons (Nystrom and

345 Henríquez, 1994; Nystrom et al., 2016) far from areas affected by hydrothermal

346 alteration. As part of an ongoing investigation, values of $\delta^{34}S$ and $\delta^{18}O_{(SO4)}$ values and

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347   the Sr-isotope composition were determined for a few samples of pure destinezite, in

348   order to provide information on the source of S and the history of the fluids that have

349   participated in the formation of this mineral. Preliminary results have yielded δ^{34}S values

350   of 1.5 and 2.8 ‰ and $\delta^{18}O_{(SO4)}$ values of 0.1 and 1.9 ‰ (two samples), and a range of

351    $^{87}Sr/^{86}Sr$ values between 0.7077 to 0.7081 (four samples; mean of 0.7080).

352   In addition to destinezite, we have also analyzed the rare remnants of Fe

353   phosphate grains found in the core of some lumps. Under the microscope, these relics

354   occur as nearly opaque inclusions less than 5–10 μm across. In thin section they show

355   a variable color, from deep reddish brown to dark green. They show irregular intricate

356   intergrowths with the host destinezite. Their distribution within the lumps is independent

357   of the open fractures that formed later. Analysis of these remnants indicates variable

358   and nonstoichiometric compositions, ranging from a SO_4-free end-member with a

359   relatively high Fe_2O_3 content and anhydrous character to a SO_3-rich and relatively

360   Fe_2O_3-poor composition, close to the ideal stoichiometry of the destinezite. This

361   continuum clearly indicates that the majority of the compositions obtained indeed

362   represent admixtures of the two minerals. Most of our S-free results approach the

363   general formula $Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2$, which corresponds to lipscombite (see Table 2

364   for the average result of 14 selected analyses). This formula was obtained assuming

365   that the FeO_{total} from the EMP analyses is recalculated to FeO and Fe_2O_3 according to

366   the ideal Fe^{2+}/Fe^{3+} value of 1:2 proposed by Yakubovich et al. (2006) for minerals with

367   composition similar to the lipscombite–barbosalite family.

368   **Rietveld refinement of the destinezite structure**

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369   Peacor et al. (1999) showed that destinezite from soils at Alum Cave Bluff, in

370   Tennessee, is triclinic. Its structure consists of infinite chains of Fe-$(O,OH,H_2O)_6$

371   octahedra attached to sulfate and phosphate tetrahedra. These structural characteristics

372   should not change with minor variations in composition, which could include minor P-for-

373   S substitution, relatively high Fe contents, or a deficit in H_2O molecules as suggested by

374   our analyses. Neither should they vary with the apparent higher crystallinity shown by

375   our samples, as the grains show well-defined shapes and well-formed crystals (Fig. 3B,

376   4B). Accordingly, it seems appropriate to verify if the variations in grain size cited above

377   provide detectable modifications in the structure, especially considering that destinezite

378   used to solve the structure by Peacor et al. (1999) has a supergene origin.

379   The structure of the El Laco destinezite was refined using the FullProf code, in the

380   space group $P\bar{1}$ starting with the structure parameters refined by Peacor et al. (1999).

381   The bond lengths, bond angles and bond-valence summations are in good agreement

382   with the expected ones, which demonstrates conformity between the experimental and

383   calculated data. The final reliability factors are as follows: Rp= 5.64, Rwp = 7.76, Bragg

384   R-factor = 11.7, and Chi2 = 1.89. As found by Peacor et al. (1999), our data indicate a

385   structure consisting of chains of octahedra containing Fe and O linked to sulfate and

386   phosphate tetrahedral forming layers parallel to (010). Interlayers of H_2O molecules

387   provide the hydrogen bonds that link the layers. The resulting structure resembles the

388   layers seen in clay minerals, which explains the platiness of the pseudohexagonal

389   crystals and cleavage observed under electron microscopy (Fig. 4B). The differences

390   between the cell parameter refined in our study [a = 9.5828(2) Å, b = 9.7440(3) Å, c =

391   7.3302(3) Å, α = 98.796(3)°, β = 107.985(3)°, and γ = 63.898(2)°] and the parameters

18

392 found by Peacor et al. (1999) and Lledó (2005) are very small or negligible, and within

393 the expected margins of the experimental error. These results confirm the relative

394 stability and tolerance of the crystal structure in spite of variations in composition,

395 degree of cohesion of the samples, and different environments of formation.
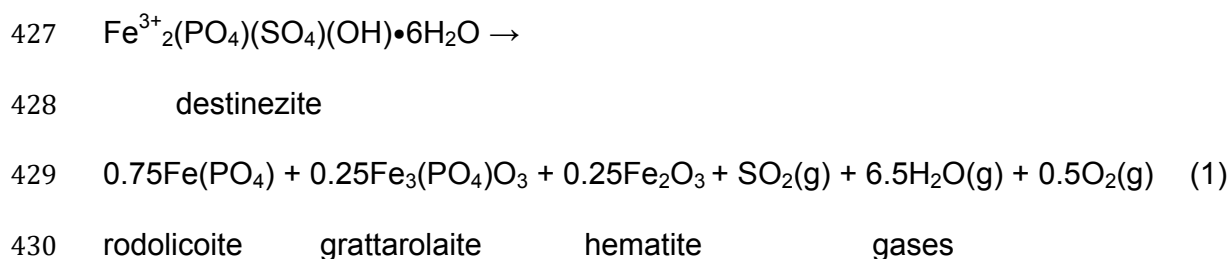
396 Although we do not have data to compare the degree of crystallinity between

397 subhedral destinezite and partially amorphous diadochite, our estimate of crystallite size,

398 ca. 250(50) nm, indicates that it is well above the limiting size typical of poorly crystalline

399 or partially amorphous materials. Usually, the size of particles in poorly crystalline

400 samples (i.e., crystalline polymers) is below 50 nm, and even less than 10–20 nm. The

401 average size of the crystalline domains (coherently diffracting domains) of the sample

402 can be estimated from the broadening of the signals using the Scherrer equation. From

403 the FullProf analysis, we also obtained the average apparent size of the crystals, ca.

404 230(5) nm, and the average maximum strain, ca. 0.17(3)%. These results are in good

405 accordance with the previously calculated crystalline size of the crystallites and confirm

406 the relatively coarse grain-size of the destinezite crystals.

407 **Thermogravimetric analysis and thermodynamic data for destinezite**

408 The results of TG/DTG experiments and the DSC calorimetric studies of the

409 destinezite (Fig. 5A, 5B) reveal several steps of mass loss with an increase of

410 temperature in the range between 50 and 900ºC, which correspond to various

411 processes of decomposition. The DSC measurements shed light on the enthalpy change

412 (ΔH) associated with each of the thermogravimetric events encountered (Table 3). The

413 overall process could be described as follows: (i) The first two losses in weight upon

414   heating, observed at 50–110ºC and 110–165ºC, are attributed to the dehydration of the

415   mineral, whereas (ii) the third and fourth changes (at 165–350ºC and 350–594ºC,

416   respectively), could be related to the completion of dehydration and formation of an

417   intermediate complex consisting of lipscombite and an Fe-phosphate-rich product

418   (glass). The fifth step (iii) (594–648ºC) could indicate the onset of dehydroxylation of the

419   lipscombite with the formation of mikasaite, followed by the progressive degradation by

420   thermal stress of the previously formed products. During this stage, one can expect the

421   formation of grattarolaite and the complete devolatilization of mikasaite. The last two

422   stages (iv) (at 648–725ºC and 725–900ºC, respectively) correspond to the complete

423   decomposition of lipscombite and mikasaite, concurrently with the final formation of

424   crystalline rodolicoite, grattarolaite, and hematite.

425   The overall thermal process of decomposition of destinezite may be summarized

426   by the following chemical equation:

427    $Fe^{3+}_2(PO_4)(SO_4)(OH) \bullet 6H_2O \rightarrow$

428   destinezite

429    $0.75Fe(PO_4) + 0.25Fe_3(PO_4)O_3 + 0.25Fe_2O_3 + SO_2(g) + 6.5H_2O(g) + 0.5O_2(g)$ (1)

430   rodolicoite   grattarolaite   hematite   gases

431   These reaction products are in good accordance with the results found by Pieczara

432   et al. (2017) in experiments using synthetic P-doped ferrihydrite and with the behavior of

433   the Fe–P–O system at high temperatures (Wentrup, 1935; Zhang et al., 2011). The

434   same mineral assemblage was found at the Santa Barbara lignite mine, probably

435   derived from natural thermal alteration of vivianite in sediments (Cipriani et al., 1997).

436   Taking into account the reaction (1) and Hess's Law (2),

437    $\Delta H°rxn = \Sigma \Delta H°_f$ (products)$-\Sigma \Delta H°_f$ (reactants)   (2)

438   it is possible to calculate the standard enthalpy of formation of destinezite, taking into

439   account that $\Delta H°rxn$ is the measured $\Delta H°DSC$ at 900 ºC (480 kJ/mol), and the

440    $\Delta H°_f$(reactants) is equivalent to $\Delta H°_f$(destinezite). From the enthalpy values

441   corresponding to $\Delta H°_f$(products) that appear tabulated in the thermodynamic tables (i.e.

442   Roine, 2002), we have obtained the enthalpy value corresponding to destinezite: ($\Delta H°_f$ =

443   –4051.7(4.3) kJ/mol) (Table 4). For the calculation of the standard entropy, we used the

444   same procedure as outlined in reaction (2), resulting in a value of $\Delta S°_f$(destinezite) = –

445   1518.5(20.0) kJ/mol (Table 4). Accordingly, applying the relationship $\Delta G° = \Delta H°- T\Delta S°$,

446   we obtained a value of the Gibbs free energy of destinezite: –3598.9(7.1) kJ/mol.

447   The above properties allow us to extend the default thermodynamic dataset LLNL

448   (compiled at the Lawrence Livermore National Laboratory) that makes use of the

449   Geochemist's Workbench (GWB) applications (Bethke, 1996) by adding destinezite to

450   the list of mineral phases. To calculate the solubility product, we have used the following

451   basic reaction of destinezite dissolution that involves only as basis the aqueous species

452   appropriate for the code:

453   Destinezite = 2 Fe^{2+} + SO_4^{2-} + HPO_4^{2-} + 0.5 O_2(aq) + 6 H_2O (3)
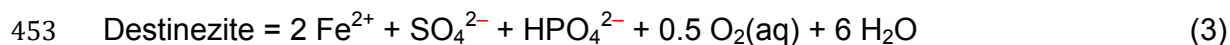
454   From the standard-state free energies of formation of species in the reaction, the

455   calculated solubility product, expressed in logarithmic form, is log K(298) = –27.97(1.1).

456   According to Anderson (2005), both $\Delta H°r$ and $\Delta S°r$ are constants at the low

457   temperatures being considered (i.e., in the range typical of epithermal steam-heated

21

458   alteration, usually about 60–250ºC). As a result, it is possible write, as an approximation,

459    $\Delta G°r(T) = \Delta H°r(298) - T\Delta S°r(298)$, where T is temperature in Kelvin. It is then possible

460   calculate the equilibrium constant for the above hydrothermal low-temperature range

461   with $\Delta G°r(T) = -RTlnK$, using the data available from the literature for the species

462   mentioned in the dissolution reaction (3).

463   **Discussion**

464   The presence of anhydrous Fe phosphate minerals preserved as remnants in the

465   lumps, in addition of the size, morphology and location of these rocks, strongly support

466   the hypothesis that they track the existence of a Fe–P melt ejected by the volcano. Most

467   investigators of these rocks (Haggerty, 1970a; 1976; Lledó, 2005; Mungall and Naslund,

468   2009; Naslund et al., 2009; Mungall et al., 2011, 2018) have interpreted these minerals

469   as the product of the crystallization of a phosphate-rich melt that was immiscible in the

470   Fe-rich melt forming the El Laco magnetite deposit. Phosphate minerals like those

471   described here have been found as secondary phases in some granitic pegmatites

472   (Baijot et al., 2014) and meteorites (Buseck and Holdsworth, 1977), suggesting a

473   magmatic affiliation.

474   At El Laco, textures considered indicative of phosphate minerals crystallized from a

475   melt, such as the presence of meniscus, rounded aggregates and spherical inclusions,

476   were probably destroyed during their replacement by destinezite. However, Mungall et

477   al. (2018) have described evidences of the existence of such a liquid in the hematite-rich

478   sediments, in the form of complex fine-grained Fe phosphate minerals enclosed within

479   euhedral hematite crystals or armored by hematite aggregates. An Fe phosphate phase

480 similar to that found in the core of the destinezite lumps has also been found in material

481 cementing ash-sized hematite. Its composition approaches an unidentified anhydrous Fe

482 phosphate of formula $Fe^{2+}_3Fe^{3+}(PO_4)_3$ and is possibly related to vivianite, phosphoferrite,

483 or lipscombite according to the description of Haggerty (1970b,1991). Analyses of the

484 same material provided by Mungall and Naslund (2009) and Mungall et al., (2018) also

485 indicate the presence of similar minerals with the general formula $Fe_5(PO_4)_4(OH)_3•2H_2O$,

486 which are comparable to beraunite, dufrénite, or ferrian giniite. In addition to these

487 variable results in the composition of the interstitial phosphates, Lledó (2005) reported

488 on diadochite from El Laco, with an unusually high Fe content, up to 58.4 wt.% Fe_2O_3.

489 As a whole, these analytical results point to a mixture of minerals, with prevalence of

490 lipscombite over destinezite. We believe that lipscombite probably is the main product of

491 the hydrothermal recrystallization of an unknown high-temperature phosphate precursor

492 that solidified from a residual melt near the Fe_2O_3–$FePO_4$ eutectic (Mungall et al., 2018).

493 Thus we assume that the lipscombite, found as a relict secondary mineral, formed at the

494 expense of a magmatic mineral.

The hydrothermal formation of destinezite

496   The intergrowth of the destinezite with gray hematite, as well as the presence of

497 relics of lipscombite, which is devoid of S, the relative large grain-size of the destinezite

498 crystals, and the presence of jarosite replacing the edge of the grains, all suggest that

499 the destinezite formed by reaction of a phosphate precursor with late fluids. Reaction of

500 a SO_2-rich gas exsolved during the crystallization of the Fe-rich melts with vadose water

501 (Sillitoe and Burrows, 2002; Tornos et al., 2017) could have promoted the transformation

502 of lipscombite and related phases to destinezite. The inferred hydrothermal

503   decomposition requires a chemical environment with variable activities of phosphate and

504   sulfate, at temperatures below 300ºC, and high fluid pressures. These conditions

505   typically occur in low-sulfide oxidized systems (SO_4^{2-}>H_2S) characterized by an

506   abundance of sulfate of steam-heated origin, as proposed by Sillitoe and Burrows

507   (2002). The presence of lipscombite and the described scenario preclude other

508   mechanisms for the formation of destinezite, such as its direct precipitation from fluids

509   generated from the remobilization of the apatite–magnetite ores. In this scenario, a large

510   part of the magnetite was replaced by maghemite as a metastable intermediate

511   transformation phase, and ultimately to hematite as the end product (up to 40%

512   according to Tornos et al. 2017), with most of the apatite being completely destroyed.

513   Our preferred model for the formation of destinezite involves a complex

514   polyphase evolution with two distinct steps: (i) an early stage of crystallization of a

515   hypothetical Fe phosphate precursor, followed by (ii) a second stage of intense

516   sulfidation of the former phosphate mineral and oxidation of the magnetite. Finally, both

517   processes were followed by an incipient stage of supergene alteration observed only at

518   the edges of some broken lumps.

519   *1 Early stage*

520   The conditions of formation of the hypothetical phosphate precursors are difficult

521   to estimate. However, the formation of lipscombite has been obtained under

522   hydrothermal conditions by transformation of ferric phosphate phases over the

523   temperature range between 110ºC and 560ºC (Gheith, 1953; Song et al., 2005;

524   Yakubovich et al., 2006). These experiments have yielded hydroxylated Fe phosphate

24

525   compounds of variable composition whose stability and structural organization are

526   determined by the ratio of Fe^{2+} to Fe^{3+}, which depends on the oxygen fugacity of the

527   system; in the case of lipscombite, that ratio is 1:2 according to Yakubovich et al.,

528   (2006). According to Gheith (1953), lipscombite containing a high proportion of trivalent

529   Fe can form from heterosite or rodolicoite in the presence of Fe oxide below 560ºC, if

530   the ferric ions are partially reduced. This temperature limit agrees with our calorimetric

531   experiments, in which the lipscombite remains stable up to its final destabilization

532   (dehydroxylation) at about ca. 600ºC. Lipscombite is more likely to form at high to

533   moderate temperatures by hydrothermal processes in volcanic environments

534   characterized by high values of oxygen fugacity. Also, the redox conditions suggested

535   seem to be consistent with those at El Laco, which is characterized by an unusually high

536   fO_2 that allows anhydrite to be stable from magmatic to hydrothermal conditions (Tornos

537   et al., 2017). In any case, and despite the complex thermal behaviour of this mineral in

538   an oxygenated environment (Song et al., 2005), the above studies support a magmatic-

539   hydrothermal derivation for the iron phosphate precursor preserved in the core of some

540   lumps.

541   Replacement of the presumed primary (magmatic?) phosphate minerals by

542   lipscombite requires high P and low sulfate contents in the system. The precipitation of

543   lipscombite most likely arises by a chemical reaction involving an aqueous phosphate

544   derived from the consolidated Fe–P melt and hematite from the tephra:

545   "Fe–P melt" + H_2O + 0.25 Hematite = 0.5 Lipscombite + 0.125 O_2(aq)   (4)
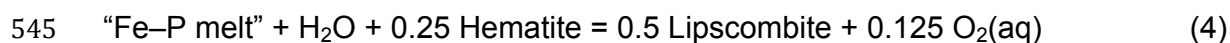
546   In the formulation of this reaction, we have taken rodolicoite as a proxy for the solidified

25

547   Fe–P-rich melt. The alteration of the pristine magmatic phosphate (i.e., fluorapatite)

548   present in the host rocks and ores could proceed in the presence of magnetite under

549   acidic conditions:

550   Fluorapatite + 1.5 Magnetite + 10H$^+$= 1.5 Lipscombite + HF(aq) + 5 Ca^{2+} + 1.5 H$_2$O   (5)
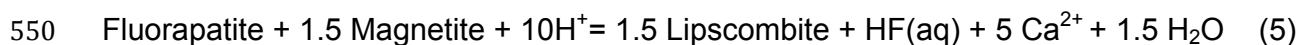
551   At an early hydrothermal stage of alteration, large amounts of phosphate could be

552   released to the fluids, facilitating the replacement of the precursor Fe phosphate

553   minerals. If this hypothesis holds, the lipscombite remnants in the lumps would have

554   formed early, likely at conditions of high or moderate temperature. We do not know the

555   requirement under which these reactions take place, but it is possible to discuss the

556   conditions of thermodynamic stability of these minerals in light of the estimate of the

557   Gibbs free energy of formation using the predictive method proposed by Nriagu (1976)

558   and data from Nriagu and Dell (1974). The dissociation constant for lipscombite, log

559   K(298) = –22.87, was calculated from the following dissolution reaction through the

560   GWB program (Bethke, 1996):

561   Lipscombite + 2H$^+$ = 3 Fe^{2+} + 2 HPO$_4^{2-}$ + 0.5 O$_2$(aq) + 2 H$_2$O   (6)
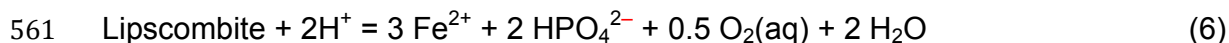
562   According to the activity–activity diagrams (Fig. 6), lipscombite is prevalent at

563   relatively high temperatures, where high concentrations of phosphate are present in the

564   fluid. To favor the stabilization of lipscombite, we have assumed geologically reasonable

565   hydrothermal conditions, with a temperature of ~300–200ºC, a moderately acidic fluid,

566   and realistic activities of Ca^{2+} and K$^+$ (10^{-2}), keeping low the activity of SO$_4^{2-}$.

567   Interestingly, the diagrams in Figure 6 reveal a significant reduction in the stability field

568   of lipscombite if temperature or pH decreases. Significantly, the above conditions

26

569   preclude the occurrence of jarosite and destinezite. The diagrams also show that the

570   apatite saturation-line is clearly pH-dependent (Fig. 6A). The formation of fluorite is

571   favored by the destabilization of fluorapatite if the concentration of F reaches high levels

572   at the assumed conditions, which probably explain the occurrence of fluorite crystals

573   coating euhedral magnetite in some ore bodies (Tornos et al., 2017).

574   ***2 Sulfidation stage***

575   The replacement of lipscombite by destinezite involves a dramatic increase of the

576   activity of sulfate (Fig. 6B) and a strong decrease in the activity of P. Conditions inferred

577   for this reaction entail a highly oxidizing and acidic (pH < 3) environment that is

578   compatible with the formation of steam-heated systems, as a result of condensation of

579   magmatic vapor in groundwater at temperatures that seldom exceed 200ºC (Sillitoe,

580   1993; Hedenquist and Taran, 2013; Sillitoe, 2015). Under these circumstances,

581   lipscombite can almost be destabilized to destinezite:

582   Lipscombite + 0.25 O_2(aq) + 2.5H^++ 7H_2O + 1.5 SO_4^{2-}= 1.5Destinezite + 0.5 $H_2PO_4^-$
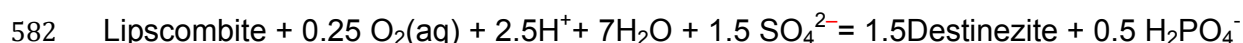
583   (R-7)

584   A comparison of the stability fields of the minerals involved indicates that at

585   temperatures below ca. 150ºC, lipscombite is no longer stable (Fig. 6C), whereas the

586   stability field of the destinezite + hematite assemblage is favored (hatched areas in Fig.

587   6).

588   The $\delta^{34}S$ values of two samples of destinezite ($\delta^{34}S_{SO4}$ = 1.5, 2.8‰) are

589   significantly lower than the magmatic-hydrothermal signature of sulfate minerals that

590   typically record sulfate coexisting with reduced S derived from the disproportionation of

27

591   magmatic SO_2, between 20 and 25‰, according to Rye (2005). The above values

592   suggest that the system likely was strongly oxidized, and that all the S was in the form of

593   sulfate, The precipitate, destinezite, inherited the original signature of the melt, as can

594   be expected in a steam-heated system (Rye, 2005). These values are consistent with

595   the reaction of lipscombite with fluids within a steam-heated system. The oxygen isotope

596   data of the same samples of destinezite plot away from those of magmatic fluids. They

597   are close to 0‰ ($\delta^{18}O_{(SO4)}$ values of 0.1 and 1.9‰), indicating that the oxygen was not of

598   magmatic origin but dominantly meteoric (Rye, 2005), perhaps with a minor contribution

599   from an ^{18}O-enriched source that could either be the magmatic gas or the replaced

600   andesite at a high fluid:rock ratio. Preliminary Sr isotope data for four samples

601   ($^{87}Sr/^{86}Sr_{avg}$ = 0.7080) reveal values that are higher than most of the reported values for

602   the El Laco andesite (between 0.7066 and 0.7074 according to Tornos et al., (2017), but

603   are lower than the values of the magnetite–apatite rocks ($^{87}Sr/^{86}Sr$ ≈ 0.7083; Tornos et

604   al., 2017). These values are also consistent with a mixture of Sr inherited from the

605   magmatic fluids and the host andesite rocks. Alternatively, the Sr could be derived from

606   andesite equilibrated with fluids exsolved from the Fe-rich melt. In brief, the isotopic data

607   suggest that the S and oxygen of the destinezite are inherited from the superimposed

608   steam-heated alteration.

609   Interestingly, we have not detected Al phosphate–sulfate minerals (APS, i.e.,

610   woodhouseite, crandallite, svanbergite) in the lumps. These minerals can coexist with

611   alunite or kaolinite in zones of advanced argillic alteration (Stoffregen and Alpers, 1987).

612   The lack of APS minerals in steam-heated alteration zones at El Laco is interpreted as

613   being indicative of a shortage of P in later fluids or, alternatively, a paucity of primary

614 apatite in the host rocks. Thus, the lack of these minerals in altered areas from El Laco

615 proves that the activity of phosphate during most of the stages of the steam-heated

616 alteration process was low; the major source of P in forming destinezite was the

617 immiscible phosphate melts ejected by the volcano.

618 Contrary to a previous report concerning the APS, variscite has been found in

619 zones at El Laco in that have undergone intense steam-heated alteration (e.g., Cristales

620 Grandes, Fig.1). According to our model, variscite extends its stability field into the

621 region of low and moderate pH, even at very low phosphate concentrations (Fig. 6D).

622 Interestingly, this diagram shows that the variscite–alunite boundary roughly overlies the

623 position of the destinezite–hematite boundary. Thus, mineral assemblages with variscite

624 and alunite or hematite or both (Dill, 2001) are compatible with the formation of

625 destinezite during the waning stage of steam-heated alteration. Variscite probably

626 formed coevally with destinezite and alunite at a stage when the dissolved Al, mainly

627 from the breakdown of plagioclase, was incorporated into the fluids. The virtual absence

628 of pyrite and the ubiquitous presence of alunite and gypsum everywhere are in good

629 agreement with the proposed scenario.

630 *3 Final supergene stage*

631 The rare replacement of destinezite by Sr-rich jarosite indicates that the surface

632 runoff waters at El Laco had a rather abundant concentration of K, Sr, and sulfate,

633 sufficient to promote the supergene replacement of destinezite by jarosite. Similarly,

634 some lumps exposed to acidic meteoric solutions show an alteration along rims

635 consisting of a mixture of cacoxenite, tinticite, and strengite mixed with earthy goethite.

29

636   In these surficial environments, the field of stability of tinticite coincides with that of

637   cacoxenite, both being stable under oxidizing and acidic conditions (Nriagu and Dell,

638   1974). All these products derived from the alteration of destinezite, are unequivocally of

639   supergene origin, and prove the early and hypogene character of this mineral.

640   **Implications**

641   Our research demonstrates that the rare lumps of destinezite (e.g., Fe–P–S-rich

642   tephra) found in the hematite-rich sediments that infill crater lakes at El Laco volcano are

643   the result of a complex evolution of an immiscible phosphate-rich melts erupted by the

644   volcano. This transformation of the pyroclasts to destinezite happened during the

645   hydrothermal alteration of the volcanic rocks to alunite, mainly provoked by the cooling

646   and the active circulation of oxidizing waters after eruption. During this process, the Fe–

647   P-rich immiscible fraction of the melt separated from the parent silicate magma and was

648   almost entirely destabilized to lipscombite and later, to destinezite. Concurrently, a large

649   part of the magnetite ores and Fe oxide ashs underwent oxidation.

650   This finding can provide key constraints on the long-standing controversy about

651   whether the Fe oxide–apatite deposits are magmatic or hydrothermal in origin. Until this

652   point, most studies on the origin of the magnetite–apatite deposits as a result of

653   magmatic immiscibility have been confined to the study and interpretation of melt

654   inclusions hosted within pyroxene and plagioclase phenocrysts, the geochemistry of the

655   volcanic rocks, and interpretations of magma sources on the basis of isotopic indicators.

656   However, the occurrence of Fe–P-rich pyroclasts transformed to destinezite provides a

657   striking direct confirmation that such magmas exist and should be considered an

30

658   additional source of information.

659   The hydrothermal transformation of the above Fe–P-rich melt to almost

660   monomineralic destinezite took place in a steam-heated environment fed by deeper

661   boiling fluids near the surface (acid sulfate waters). This hypogenic interpretation for the

662   El Laco destinezite has two major implications: (1) this mineral represents the final

663   product of the replacement of a pristine immiscible Fe–P-rich melt ejected by the

664   volcano, and (2) destinezite may form over a range of geological environments that is

665   much broader than is currently assumed. It has heretofore invariably been viewed as

666   having a supergene derivation.

667   In order to fill the gap of thermodynamic data necessary to discuss the stability

668   domains of assemblages of hydrated Fe phosphate–sulfate and Fe oxide minerals, and

669   to be able to predict the conditions favorable for the formation of destinezite, we

670   measured the thermal decomposition of this mineral by the classical TGA and DSC

671   techniques. With those results, we have derived its enthalpy, entropy, free energy of

672   formation, and the equilibrium constant for its dissolution reaction. These new

673   thermodynamic values have been used to calculate mineral-stability diagrams in

674   activity–activity coordinates. These are then used to identify environmental conditions

675   under which the destinezite + hematite association is thermodynamically stable. From

676   these thermodynamic properties, it follows that the destinezite behaves as a stable

677   mineral over a wide range of hydrothermal conditions, provided that the hydrothermal

678   environment is acidic, the temperature is low (<150°C), and the sulfate contents are high

679   to very high, keeping the P concentrations low in the fluids. These thermodynamic

680   constraints agree well with the physicochemical characteristics of the El Laco

31

681   hydrothermal area, which has been subjected to pervasive steam-heated alteration.

682

683   **Acknowledgments**

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846   **Figure captions and Tables**

847   Figure 1 Schematic geological map of the El Laco volcano, northern Chile (A) showing

848   the major magnetite-apatite deposits (black areas) and zones of hydrothermal alteration

849   (red areas) hosted in the Pliocene andesitic rocks (modified from Tornos et al., 2016).

850   Star symbol indicates the main location of the destinezite-rich rocks near the Laco Sur

851   ore body. (B) General view of El Laco volcano from south. Note the zone of intense

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852 alunitization of the volcanics at the south slope of the mountain (light colour is the Pasos

853 Blancos area).

854 Figure 2 (A) Unconsolidated hematite-rich epiclastic deposits beneath the Laco Sur

855 orebody showing a crude layering and poor grain sorting. The horizon containing

856 destinezite lumps displays intense orange color. (B) Cluster of destinezite fragments

857 with size between 2 and 10 cm in diameter belonging to the same chaotic layer. The

858 layer is mainly composed of rubble and fine-grained debris of hematite and is interpreted

859 as representing surge deposits deposited into a crater lake. Note the intense

860 fragmentation and the angled character of the destinezite clasts.

861 Figure 3 Photomicrographs of El Laco destinezite. (A) Massive fine-grained destinezite

862 (de-1) criss-crossed by multiple fractures rimmed by coarse grained destinezite (de-2);

863 hematite crystals (hm) usually occur near these microfractures. (B) Large coarse-

864 grained subhedral destinezite crystals (de-2) overgrowing primary massive aggregates

865 close to the microveins; lighter edges and dark core sectors (brown colors) in some

866 crystals indicate incipient transformation to supergene iron-phosphate products

867 (tinticite?). (C) Porous incrustations of supergene Sr-rich jarosite (Sr-jar) associated with

868 spherulitic cacoxenite (radiate fibrous growth) that occasionally occur coating some

869 destinezite lumps. Images taken in transmitted light microscopy mode with crossed

870 polarizers.

871 Figure 4 Backscattered electron (BSE) images for the destinezite. (A) Equigranular

872 aggregate of destinezite (de-1) with thick hematite crystals displaying the typical

873 tabular/platy habit; both are affected by a fracture filled of supergene goethite. (B)

874   Aggregate of individual crystals of destinezite (de-2) exhibiting the pseudohexagonal

875   habit and the presence of abundant cleavage cracks along (100) as result of a

876   significant loss of water. Bleached zones (light gray) along the cleavage and fractures of

877   some crystals reveal variable transformation to secondary Fe-phosphate products. Black

878   zones are pore and cracks.

879   Figure 5 Thermal decomposition analysis of the El Laco destinezite under N_2-gas

880   atmosphere at a heating rate of 5ºC/min. (A) Thermogravimetric curve TG (in blue) and

881   differential thermogravimetric curve DTG (in red); mass loss in percent and mass

882   derivative in %/ºC, respectively. (B) Thermal decomposition for the destinezite (TG in

883   %), heat capacity (Cp, J/gºC), and associated enthalpy change (ΔH, J/g) in the

884   temperature range of 50 to 900ºC.

885   Figure 6 Phase stability diagrams for the Fe-P-S-O system calculated using the Act2

886   application with GWB (Bethke, 2005) to illustrate the transformation of lipscombite to

887   destinezite in low-temperature hydrothermal conditions. The restrictions imposed are

888   those typical of the steam-heated environment, assuming geochemically reasonable

889   ranges of concentrations of dissolved species: activities of Fe^{2+}, K^+, and Ca^{2+} are set at

890   10^{-2}, while for SO_4^{2-} and HPO_4^{2-} the activity value vary according the model. Red solid

891   and dashed lines define the boundary separating the domains of the stable phases. The

892   open and cross-hatched circular areas represent the proposed initial (1) and final (2)

893   conditions for the transformation of lipscombite to destinezite. (A) Plot of stability fields of

894   iron phosphate, sulphate, and oxide in terms of variable dissolved total phosphate and

895   pH. The above imposed constraints to define the field boundaries include a SO_4^{2-} activity

896   of 10^{-2}, and oxidizing conditions. The upper half of the diagram illustrates the significant

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897   reduction of the stability field of lipscombite with decreasing temperature. Dashed-lines

898   correspond to boundaries of stability field at 200 and 100ºC. The plot of lower part of the

899   diagram shows the stable destinezite-hematite equilibrium at low temperature (100ºC).

900   Blue dashed line is for the apatite-fluorite boundary at 300ºC. Arrows indicate the

901   presumable trend followed by the fluids for the transformation of lipscombite to

902   destinezite and for fluorite precipitation. (B) Stability relationship between the three

903   identified phases (destinezite, lipscombite, and hematite) in aqueous solutions at

904   temperature of 100ºC and variable pH (2, 3, and 4). Note the enlargement of the

905   destinezite field as the pH decreases in conformity with environments dominated by

906   acid-sulfate hydrothermal alteration. (C) Temperature-pH diagram for the main minerals

907   found in the destinezite lumps. Activities of iron and sulfur are the same as in (A). Note

908   the significant reduction of the stability field of lipscombite when the activity of HPO_4^{2-}

909   decreases from 10^{-3} to 10^{-5}. (D) Activity-pH diagram for the $K_2O-Al_2O_3-SiO_2-P_2O_5-H_2O$

910   system calculated at 100ºC showing the stability of variscite relative to alunite, kaolinite,

911   muscovite, and K-feldspar; the dashed line correspond to the destinezite-hematite

912   boundary showed in lower half of the (A) diagram.

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914   **TABLES**

915   **Table 1** Mineral chemical groups, names, and formulae for minerals cited in this study

916   **Table 2** Average microprobe analysis (wt %) of the El Laco destinezite and lipscombite

917   remnants from different lumps. For comparison, some published results of

918   destinezite/diadochite are included.

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919   *(text to place at the bottom of this table2)*

920   Columns: (1) destinezite (this study; average of 40 analyses); (2) theoretical composition

921   of destinezite; (3) "diadochite" from El Laco (Lledó, 2005); average of 4 analyses by wet-

922   chemical method; (4) destinezite from Alum Cave Bluff, Tennessee USA (Peacor et al.,

923   1995); (5) destinezite from the Hinomaru-Nako mine, Japan (Matsubara et al., (1999); (6)

924   destinezite from Haut-le-Bastia, Belgium (Anthony et al., 2005); (7) diadochite from

925   Kurama Ridge, Urbekistan (Moiseeva, 1967); (8) lipscombite from remnants within the

926   lumps (this study, average of 14 analyses); (9) theoretical composition of lipscombite; the

927   amounts of FeO and Fe_2O_3 were calculated according the Fe^{2+}/Fe^{3+} ratio of 1:2

928   (Yakubovich et al., 2006). The H_2O content of destinezite and lipscombite were

929   determined by difference, and apfu on the basis of 15 and 10 oxygens, respectively; (*)

930   water loss during wet chemical analysis; (#) water calculated by the Penfield method.

931   Rem. Amount of contaminants (mainly MgO, MnO, SrO, Na_2O, K_2O, usually below

932   detection limits). n.d. Not detected.

933   **Table 3** Variation of the enthalpy (ΔH in J/g) of the different stages of decomposition of

934   El Laco destinezite during the heating. DSC values determined in atmosphere of

935   nitrogen.

936   **Table 4** Thermodynamic properties for the products and reactants involved in the

937   calorimetric assays and calculated values for the El Laco destinezite.

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Table 1

Group	Mineral name	Mineral formula
Oxides anion $-O^{2-}$	Goethite	$Fe^{3+}O(OH)$
	Hematite	αFe_2O_3
	Maghemite	γFe_2O_3
	Magnetite	Fe_3O_4
Phosphates anion $-PO_4^{3-}$	Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$
	Barbosalite	$Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2$
	Beraunite	$Fe^{2+}Fe^{3+}_5(PO_4)_4(OH)_5 \cdot 4H_2O$
	Cacoxenite	$(Fe^{3+}Al)_{25}(PO_4)_{17}O_6(OH)_{12} \cdot 75H_2O$
	Crandallite	$CaAl_3(PO_4)_2(OH)_5 \cdot H2O$
	Delvauxite	$CaFe^{3+}_4(PO_4,SO_4)_2(OH)_8 \cdot 4\text{-}6(H_2O)$
	Dufrénite	$Fe^{2+}Fe^{3+}_4(PO_4)_3(OH)_5 \cdot 2H_2O$
	Giniite	$Fe^{2+}Fe^{3+}_4(PO_4)_4(OH)_2 \cdot 2H_2O$
	Grattarolaite	$Fe^{3+}_3PO_4O_3$
	Heterosite	$Fe^{3+}PO4$
	Lipscombite	$Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2$
	Monazite	$(La,Ce,Nd)PO_4$
	Phosphoferrite	$(Fe^{2+},Mn)_3(PO_4)_2 \cdot 3H_2O$
	Phosphosiderite	$Fe^{3+}PO_4 \cdot 2H_2O$
	Rockbridgeite	$Fe^{3+}_5(PO_4)_3(OH)_5$
	Rodolicoite	$Fe^{3+}PO_4$
	Strengite	$Fe^{3+}PO_4 \cdot 2H_2O$
	Tinticite	$Fe^{3+}_5(PO_4,VO_4)_4 \cdot 7H_2O$
	Variscite	$AlPO_4 \cdot 2H_2O$
	Vivianite	$Fe^{2+}_3(PO4)_2 \cdot 8H_2O$
Sulfate-phosphates anions $-SO_4^{2-}$, $-PO_4^{3-}$	Destinezite	$Fe^{3+}_2(PO_4)(SO_4)(OH) \cdot 6H_2O$
	Diadochite	$Fe^{3+}_2(PO_4)(SO_4)(OH) \cdot 6H_2O$
	Svanbergite	$SrAl_3(PO_4)(SO_4)(OH)_6$
	Woodhouseite	$CaAl_3(PO_4)(SO_4)(OH)_6$
Sulfates anion $-SO_4^{2-}$	Alunite	$KAl_3(SO_4)_2(OH)_6$
	Anhydrite	$CaSO_4$
	Gypsum	$CaSO_4 \cdot 2H_2O$
	Jarosite	$KFe^{3+}_3(SO_4)_2(OH)_6$
	Melanterite	$Fe^{3+}SO_4 \cdot 7H_2O$
	Mikasaite	$Fe^{3+}_2(SO_4)_3$
Sulfides	Chalcopyrite	$CuFeS$

anion -S^{2-}	Pyrite	FeS_2
Silicates anion -Si_xO_y	Kaolinite	$Al_2Si_2O_5(OH)_4$
	K-feldspar	$(K,Na)(Si,Al)_4O_8$
	Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$
	Plagioclase	$(Na,Ca)(Si,Al)_4O_8$
	Quartz	SiO_2
	Smectite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$
	Tridymite	SiO_2
Halides anion -F^{1-}	Fluorite	CaF_2

Table 2

	Destinezite			Destinezite/diadochite from the literature				
	1		2	3		4	5	6
	wt%	StdDev	wt%	wt%	StdDev	wt%	wt%	wt%
P2O5	18.35	0.96	16.59	22.15	0.19	17.10	17.06	16.83
SO3	17.41	1.58	18.71	15.94	0.58	20.70	19.78	17.21
FeO(t)	34.89	1.90	35.59			32.57	34.61	34.01
Fe2O3*	38.77		37.33	47.70	1.19	36.20	38.46	37.80
FeO*				0.86	0.02			
CaO	0.44	0.17	n.d.	0.57	0.40	n.d.	n.d.	n.d.
SiO2	0.50	0.18	n.d.	0.28	0.12	n.d.	n.d.	n.d.
Al2O3	0.22	0.30	n.d.	n.d.		2.70	0.33	n.d.
MgO	0.04	0.06	n.d.	0.04	0.02	0.30	n.d.	n.d.
MnO	0.01	0.01	n.d.	n.d.		n.d.	n.d.	n.d.
Rem.				1.00				0.89
H2O	24.26		27.37	10.21(*)	0.74	23.00	24.37	26.8(#)
Total	100.00		100.00	97.89		100.00	100.00	72.73
			Number of ions on the basis of 15 oxygens					
P	1.14	0.15	1.00	1.64	0.01	1.06		1.04
S	0.96	0.11	1.00	1.05	1.04	1.14		0.94
Fe^{3+}	2.14	0.26	2.00	3.08	0.10	1.99		2.07
Fe^{2+}				0.06	0.00	0.08		
Ca	0.03	0.02		0.05	0.04			
Al	0.01	0.04				0.17		
Mg	0.00	0.00		0.00	0.00			
Mn	0.00	0.00						
OH	1.00		1.00	1.00		1.00		1.00
H2O	5.43		6.00	2.48		5.11		6.00

7	Lipscombite 8		9
wt%	wt%	StdDev	wt%
15.92	36.26	1.15	36.26
19.16	0.20	0.21	n.d.
34.84	53.60	1.14	55.05
38.72	39.91		40.79
	17.69		18.35
n.d.	0.64	0.50	0.00
n.d.	0.63	0.19	0.00
0.72	0.25	0.19	0.00
n.d.	0.06	0.40	n.d.
n.d.	0.33	0.90	n.d.
0.69			n.d.
24.68	4.66		4.60
99.89	100.00		100.00
	Ions on the basis of 10 oxygens		
0.99	1.99	0.29	2.00
1.06	0.01	0.00	
2.14	1.94	0.26	2.00
	0.97	0.13	1.00
	0.04	0.07	
0.05	0.01	0.00	
	0.00	0.00	
	0.01	0.00	
1.00	2.02		2.00
5.55			

Table 3

Step	T_i(ºC)	T_f(ºC)	%mass loss	$\Delta H_{associated}$ (J/g)	Assignation
1	50	115	9.4	210	1rst partial dehydration: $2 \cdot H_2O$
2	115	166	9.1		2nd partial dehydration: $2 \cdot H_2O$
3	165	350	12.0	315	Complete' dehydration and formation of lipscombite, $Fe^{2+}Fe^{3+}2(PO4)2(OH)2$; begin the formation of mikasaite and amorph iron phosphate hydroxide
4	350	594		58	
5	594	648	1.7	539	Partial dehydration of lipscombite and formation of mikasaite plus iron phosphate
6	648	725	9.9		Partial dehydration and desulfurization with formation of grattarolaite Fe3(PO4)O3 and iron phosphate Fe4(P4O12)3; decomposition of mikasaite
7	725	900	3.0		Complete decomposition of limpscombite and mikasaite (desulfuration) and formation of hematite, grattarolaite, and rodolicoite

Table 4

Formula	Min. Name	DfH°	DfS°	DfG°
		(KJ/mol)	(J/mol.K)	(KJ/mol)
Fe^{2+}		-92.257	-2.456	-91.525
SO_4^{2-}		-909.602	-554.219	-774.362
HPO_4^{2-}		-1292.082	-680.884	-1089.076
$SO_{2(g)}$		-296.81	11.00	-300.09
$H_2O(g)$		-241.83	-44.42	-228.58
$Fe3(PO_4)_3$	Grattarolaite	-2097.92	-1024.63	-1930.04
$Fe(PO_4)$	Rodolicoite	-1297.00	-384.95	-1182.23
Fe_2O_3	Hematite	-823.00	-274.88	-741.04

Formula	Min. Name	DfH°	DfS°	DfG°
$Fe_2(SO4)(PO_4)(OH).6H_2O$	Destinezite	-4051.70	-1518.47	-3598.98
$Fe_2(SO4)(PO_4)(OH).6H_2O$	Destinezite	-3928.16		-3570.00
$Fe_2(SO4)(PO_4)(OH).6H_2O$	Destinezite	-3999.45		-3425.27

Source
HSC database (Roine, 2002)
HSC database (Roine, 2002)
HSC database (Roine, 2002)
HSC database (Roine, 2002)
HSC database (Roine, 2002)
Values estimated by applying the method of addition of oxide units (Fe as trivalent) (La Iglesia,2009)
HSC database (Roine, 2002)
HSC database (Roine, 2002)

This study: experimental
Values obtained according the method of La Iglesia (2009)
Values obtained following the ideal mixing method (Nriagu & Dell 1974; Gaskova, 2008)

A

Map labels	
Cristales Grandes	
San Vicente Bajo	
Rodados Negros	
San Vicente Alto	
Laco Norte	
Laco Sur	

652000E
656000E
7368000N
7364000N
7360000N
5325

N

QUATERNARY RECENT
- Alluvial and nival deposits
- Glacial and fluvioglacial drifts

PLEISTOCENE - HOLOCENE
- Andesites & Riolites

PLIOCENE VOLCANISM
- Andesites with piroxenes
- Andesites and local levels of massive iron
- Andesites with advanced argillic alteration
- Massive magnetite flows (domes and dikes)
- Andesites containing massive magnetite bedded deposits

MIOCENE VOLCANISM
- Old ignimbrite flows, rhyolites & horblend-rich andesites.

0   1   2 Km

B

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6