1 Title

SIGNIFICANCE OF PHYLLOSILICATE MINERALOGY AND MINERAL CHEMISTRY IN THE EPITHERMAL ENVIRONMENT. INSIGHTS FROM THE PALAI-ISLICA AU-CU DEPOSIT (ALMERÍA, SE SPAIN)

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Running title:

Significance of phyllosilicate mineralogy in the epithermal environment

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Abstract:

X-ray diffraction, optical and electronic microscopy (scanning and transmitted), electron microprobe and Fourier transform infra red spectroscopy has been used to study phyllosilicates in the Palai-Islica Au-Cu epithermal, volcanic-hosted deposit, in order to link phyllosilicate mineralogy and mineral chemistry to ore genesis. Thus, different phyllosilicate assemblages characterize two types of mineralization, and related hydrothermal alteration. Chlorite and mica appear in polymetallic quartz veins with sulfides, and in the related chloritic and sericitic hydrothermal alteration. These minerals have notable textural and chemical differences (*i.e.* Fe/(Fe+Mg), Si and Al in chlorite and illitic and phengitic components in mica) amongst veins and altered rocks, revealing different genetic conditions. These chemical features also distinguish propylitic and regional, non ore-

related, low-temperature alteration. Hot hydrothermal fluids of near-neutral pH are responsible for vein mineralization and alteration. Illite, interstratified illite-smectite, kaolinite and pyrophyllite are characteristic, with a distribution pattern by zones, for the intermediate argillic and advanced argillic alteration around areas of silicification. In the latter, native gold appears associated to interstratified illite-smectite, suggesting a relatively low temperature formation. Hot, low-pH fluids are responsible for this mineralization and alteration assemblage. The present study contributes to epithermal models showing the co-existence of two different alteration styles in the same hydrothermal system.

INTRODUCTION

Hydrothermal ore deposits containing gold, silver and different base metals, have been extracted in the Cabo de Gata-Cartagena volcanic belt, in southeastern Spain, since 2000 BC. More than 3000 mining sites have been identified in the area and in the last century the region became one of the most important base-metal producers in Europe. In recent years the area has been the target of different mineral exploration companies looking for Au and Cu and mining activity has also taken place (*i.e.* Rodalquilar and Herrerias since 1992; Arribas *et al.*, 1995; Carrillo-Rosúa *et al.*, 2003c). These hydrothermal deposits range from epithermal to mesothermal, and vary enormously in their host rocks (rhyolites to andesites, schists or sedimentary rocks), ore mineral textures, associations, paragenetic sequences and proportions of precious metals (*e.g.* Morales-Ruano, 1994; Arribas and Tosdal, 1994; Arribas *et al.*, 1995; Morales-Ruano *et al.*, 2000). In the area there are also bentonitic-type clay deposits (formed at low temperature - < 100ºC, Leone *et al.*, 1983; Caballero *et al.*, 1985; Caballero *et al.*, 2005), extracted for industrial purposes.

Therefore a great variety of phyllosilicates and alteration assemblages could be expected in the Cabo de Gata-Cartagena volcanic belt, interesting for two reasons: firstly as an indicator of potential metalliferous deposits, and secondly as an industrial mineral in itself. Detailed mineralogical studies of phyllosilicates have been performed in the bentonitic low-temperature assemblage deposits (*e.g.* Caballero *et al.*, 2005 and references therein) whereas studies for the high-temperature group of deposits have been more partial/preliminary in nature (Arribas *et al.*, 1995; Morales-Ruano *et al.*, 2000).

Our research focuses on the Palai-Islica deposit, where recent exploration activity has demonstrated the presence of Au-Cu mineralization, related with the outcropping of an area of pervasive hydrothermal alteration (Morales-Ruano *et al.*, 2000). A study using X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), electron microprobe (EPMA) and transmission electron microscopy (TEM), Fourier transform infra red spectroscopy (FTIR) was performed. The main object of this research is to characterize the mineralogy and mineral chemistry of phyllosilicates related with ore-mineralization, and to discuss hydrothermal alteration typology and its implication in ore genesis. This argument falls within the classification and discussion of epithermal deposits (*e.g.* Simmons *et al.*, 2005). This paper is noteworthy because it shows the co-existence of two different alteration styles in the same hydrothermal system. Special mention should also be made of the mineralogical transformation from volcanic rocks to phyllosilicates during hydrothermal activity, as well as the chemistry of phyllosilicates, and their relation to the conditions of the hydrothermal fluids.

GEOLOGICAL BACKGROUND

The Palai-Islica is an Au-Cu epithermal deposit hosted by calc-alkaline rocks of the Cabo de Gata-Cartagena volcanic belt (Fig. 1a), which comprises part of the eastern

95 end of the Internal Zone of the Betic Cordillera. This neogene volcanic belt, with
96 different series of volcanic rocks (*i.e.* calc-alkaline, shoshonitic, potassic calc-
97 alkaline, ultrapotassic and basaltic series, López Ruiz and Rodriguez Badiola, 1980),
98 formed within the context of compression, followed by an extensional event (Dewey,
99 1988; García Dueñas *et al*., 1992) and strike-slip movements in which volcanism
100 occurs (*e.g.* Hernandez *et al*., 1987; Fernández Soler, 1996; Turner *et al*., 1999).
101 Associated with this magmatism, hydrothermal systems developed, being controlled
102 by systems of faults and fractures. The hot fluids (up to 400-450°C, Morales Ruano,
103 1994) reacted strongly with the host rocks and, in some districts mainly located
104 inside calc-alkaline zone, gave rise to broad areas of alteration hosting metallic
105 mineralization: Cabo de Gata (Pineda Velasco, 1984), Rodalquilar (*e.g.* Arribas *et*
106 *al*., 1995), and Palai-Islica (Morales-Ruano *et al*., 2000; Carrillo-Rosúa *et al*.,
107 2003a). The approximately 4 km^2 of Palai-Islica is one of these alteration areas (Fig.
108 1b) which has become a recent target of mineral exploration companies for gold and
109 copper (Morales-Ruano *et al*., 2000). It appears near Carboneras town (Almería
110 province, SE Spain) over an extensive zone of breccias and auto-breccias of
111 andesites/dacites of ~10 Ma on age (Bellon *et al*., 1983; Fernandez Soler, 1996).
112 These rocks (Fernández Soler, 1996), with a very porphyritic texture, are constituted
113 by phenocrysts of bitownite plagioclase and hornblende (up to centimetre on size) ±
114 clinopyroxene and orthopyroxene. In accessory amount there are quartz, Fe-Ti
115 oxides, apatite and zircon.
116
117   SAMPLES AND METHODOLOGY
118 Samples were obtained from mineralization and from hydrothermally altered
119 volcanic rocks at Palai-Islica. Two hundred and sixty-two samples selected from 21
120 drill cores and surface sampling campaign had been studied. Whole-rock powders,
121 oriented aggregates of <2μm fraction (with ethylene glycol and dimethyl sulfoxide
122 solvation and without treatment), thin sections and a selection of ion milled
123 specimens and suspension over Cu-grids of these samples, were prepared to
124 determine the mineralogical, chemical and textural characteristics of phyllosilicates
125 in this deposit. Transmitted light microscopy, XRD (Phillips PW 1710, with CuKα
126 radiation, graphite monochromator and automatic divergence slit) at the Department
127 of Mineralogy and Petrology of the University of Granada and SEM (Zeiss DSM
128 950 and FESEM Leo Gemini 1530, with an EDX detector), EPMA (Cameca SX50,
129 with WDX detector) and TEM (Philips CM20, with an EDAX solid-state EDX
130 detector) at the "Centro de Instrumentación Científica" of the University of Granada
131 had been used.
132   A total of 461 micro-analyses of phyllosilicate were obtained with different
133 techniques (368 EPMA, 76 SEM and 18 TEM). Natural and synthetic-certified
134 standards were used to calibrate EPMA, SEM and TEM-AEM quantitative analyses.
135 The operating conditions were: 20 kV (EPMA and SEM), 200 kV (TEM)
136 accelerating potential, 30nA (EPMA) and 1-2 nA (SEM) beam current, and

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137 acquisition time of 40-100 s (for X-ray peak and background for EPMA), 100 s
138 (SEM, TEM). Shorter counting times was used for K and Na in TEM-AEM analyses
139 (30 s) and EPMA (20 s at peak and 20 s at background) to minimize alkali loss
140 (Nieto *et al*., 1996). AEM analysis were performed using a raster of 1000 x 200Å in
141 scanning mode for ion-milled samples and a analytical window of 1µm x 1µm in
142 scanning transmission mode for powders dispersed over holey C-coated formvar Cu
143 grids. The acquired EPMA X-ray intensities were corrected for atomic number,
144 mass-absorption and secondary fluorescence effects using the CAMECA-PAP
145 version of the Pouchou and Pichoir (1984) procedure. The transformation of
146 intensity ratios to concentration ratios in AEM analysis was made following the
147 procedure of Cliff and Lorimer (1975). Structural formulas of chlorite and mica were
148 calculated on the basis of $O_{10}(OH)_2$ and 22 and 28 negative charges, $O_{10}(OH)_8$ and
149 $O_{10}(OH)_2$ respectively.
150 Four samples kaolinite (prepared as standard KBr pellets) were also analyzed by
151 Nicolet 20SXB ("Centro de Instrumentación Científica" of the University of
152 Granada) in order to obtain FTIR spectra and discriminate among kaolinite
153 polytypes.
154
155 PREVIOUS DATA ABOUT THE MINERALIZATION
156 Two different types of mineralization, quartz veins and veinlets with sulfides and
157 dissemination in the silicification, are recognized in the Palai-Islica deposit (Fig. 2,
158 Carrillo-Rosúa *et al*., 2003a). Associated with this mineralization appears
159 andesites/dacites which present an important hydrothermal alteration, although
160 different in relation with both types of mineralization.
161　　　(a) *Veins and veinlets of quartz with sulfides*. It is the main ore of the deposit,
162 being located at depth between +70 and –90 meter above sea level (m.a.s.l.). These
163 veins, sometimes stockwork-like and very penetrative, are very rich in sulfides.
164 Although these veins have a sub-vertical trend, two main sub-horizontal levels have
165 been recognized with enrichment in Au, Ag, Zn, Pb, Cd, As and Sb, with free gold
166 grains and with fluid inclusions showing distinct characteristics (wide variation in
167 salinity, 20 - 30 wt. % eq. NaCl, over a narrow temperature range – 200 to 250ºC)
168 relative to the rest of the deposit (Morales-Ruano *et al*., 2000). Ore mineralogy
169 consists in pyrite with occasionally high contents of chalcopyrite, sphalerite and
170 galena. Accessory phases are very diverse, being Au-Ag alloys and different Ag-
171 bearing sulfides and sulfosalts the most outstanding from an economic point of view
172 (Carrillo-Rosúa *et al*., 2002, 2003a and b, 2008a). The main gangue minerals are
173 quartz, white mica ("sericite"), and chlorite with minor quantities of barite, gypsum,
174 dolomite and siderite (Carrillo-Rosúa *et al*., 2003a).
175　　　In relation to hydrothermal alteration, the andesites/dacites, which host the
176 veins, are totally transformed to quartz, white mica plus chlorite, and, to a lesser
177 extent, pyrite, dolomite, albite and epidote (Carrillo-Rosúa *et al*., 2003a).
178 Hydrothermal alteration is pervasive and the only minerals which remain alteration

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179 are quartz, zircon and apatite, although the last suffers chemical transformation
180 (Carrillo-Rosúa *et al*., 2005). White mica and chlorite (±pyrite, albite and epidote) is
181 the mineral assemblage in the proximal zones of the hydrothermal alteration. Only in
182 distal zones, in the limit of the deposit, major phenocrysts could remain unaltered:
183 first plagioclase, and in the less altered zones, hornblende and pyroxene. The
184 alteration in the limit of the deposit could be defined as propylitic, with chlorite,
185 epidote and calcite/dolomite.
186   (b) *Dissemination in the silicification*, which consists of complete
187 replacement of the volcanic rock by quartz. Sometimes it is very porous, with holes
188 corresponding with old volcanic phenocrysts, like *vuggy silica* textures. It is found at
189 the surface of the deposit between +70 and +100 m.a.s.l. Ore minerals, mainly
190 disseminated in holes, are very scarce being the mineralogy very flat: mainly pyrite
191 with minor Cu-sulfides and native gold and copper (Carrillo-Rosúa *et al*., 2002).
192 Apart from the typical coarse-grained quartz, the gangue minerals comprise
193 microcrystalline quartz, white mica ("sericite") and barite, gypsum, jarosite,
194 natrojarosite and natroalunite in latter veins.
195   The silicification has halos of advanced argillic and intermediate argillic
196 alteration characterized by quartz, pyrophyllite, kaolinite, illite and interstratified
197 illite-smectite. In distal zones, propylitic alteration also appears.
198
199   MINERALOGICAL, TEXTURAL AND CHEMICAL CHARACTERISTICS OF
200   THE PHYLLOSILICATES
201 It is noteworthy the mineralogical differences, in especial in phyllosilicates, between
202 both types of mineralization in the Palai-Islica deposit (Table 1). The main
203 mineralogical, textural and chemical characteristics of the phyllosilicates in relation
204 to described mineralization types and related hydrothermally altered host rock are
205 described.
206
207 *Quartz veins with sulfides and related hydrothermal alteration*
208 The petrographic observation and the study of X-ray difractograms in the veins and
209 related hydrothermal alteration have revealed that phyllosilicates are very abundant,
210 but only chlorite and white mica have been recognized.
211   *Chlorite textures*. It appears as spherulitic aggregates (~100 μm) and rarely as
212 inclusions in pyrite grains in the quartz veins (Fig. 3a). This spherulitic aggregates
213 show lighter rims in respect to cores in backscattered images (Fig. 3b).
214   Chlorite also appears replacing amphibole, pyroxene and the groundmass in
215 the hydrothermal alteration. Chlorite replacing maphic phenocrysts often develops
216 bigger crystals than in replacing the groundmass and it is oriented. Thus, basal plane
217 of chlorite is parallel to "b" and "c" axis of hornblende and pyroxene or, in other
218 words, (001) plane of chlorite is parallel to (010) planes of amphibole and pyroxene
219 (Fig. 3c and d). Occasionally, this maphic phenocrysts transformed to chlorite
220 appears as "xenocrysts" inside the quartz veins (Fig. 3e). Chlorite very rarely

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221 replaces plagioclase, being fine grained like generally in the groundmass and in
222 some cases in maphic phenocrysts.
223   In the external zone characterized by propylitic alteration or even far from the
224 deposit in zones of "regional" alteration due a widespread meteoric alteration,
225 chlorite is also found replacing maphic phenocrysts, but generally fine grained
226 disappearing orientated textures through outside of the veins (Fig. 3f). TEM studies
227 of this chlorite show the existence of intercalations of 10 Å K-rich layers.
228
229   *Chlorite mineral chemistry*. Table 2 and Figure 4 summarize chlorite
230 microanalyses, being notably the chemical variability. Fe/(Fe+Mg) is directly
231 proportional to Al_{total} or ^{IV}Al and Mn and inversely proportional to Si (Fig. 4a, b and
232 c). Si is inversely proportional to Al_{total} (Fig. 4d). For the whole data, interlayer-
233 cations (K+Na+2Ca) are proportional to octahedral vacancies although with higher
234 slope for chlorite from the propylitic alteration than for chlorite from the
235 hydrothermal alteration related to veins (Fig. 4e).
236   Chlorite from the different textural types has pronounced chemical
237 differences in the Si, Al, Fe, Mg and Mn contents. Spherulitic aggregates of chlorite
238 from the veins have the highest Al_{total} (2.26 - 2.85 a.p.f.u.) and Fe/(Fe+Mg) ratio
239 (0.56 – 0.78), low Si (2.65 – 3.05 a.p.f.u.), being variable the Mn content (0.02 –
240 0.10 a.p.f.u.). Contrary to the whole analyses, not clear relations have been observed
241 between different elements (Fig. 4a, b, c and d). Chemical zonation, due higher
242 Fe/(Fe+Mg) ratio in the rimes that in the cores, is revealed by backscattered images
243 (Fig. 3b). Chlorite in "xenocrysts" from the veins presents a chemical composition
244 between chlorite in spherulitic aggregates in the veins and chlorite in the
245 hydrothermal alteration.
246   Chlorite in the hydrothermal alteration related to veins has a high content of
247 Si (2.89 - 3.14 a.p.f.u.), low in Al_{total} (2.03 - 2.38 a.p.f.u.) and the lowest Fe/(Fe+Mg)
248 ratio (0.05 – 0.40) of analyzed chlorites (Table 2). Chemical tendencies are the same
249 than in the entirely analyses with the exception of Fe/(Fe+Mg) that is not related to
250 Al_{total} (Fig. 4a).
251   Chlorite in the propylitic hydrothermal alteration and regional alteration has a
252 distinctive composition characterized by intermediate and homogeneous Fe/(Fe+Mg)
253 ratio (0.30 – 0.43) and the highest Si (3.01 – 3.61 a.p.f.u.), interlayer-cations (0.01 –
254 0.32 a.p.f.u.), and octahedral vacancies (0.09 – 0.87 a.p.f.u.). Chlorite from the
255 properly propylitic alteration has intermediate Al (2.19 - 2.61 a.p.f.u.), high Mn (0.04
256 – 0.06 a.p.f.u.) and K (average 0.08 a.p.f.u.), while chlorite in less altered rocks
257 (propylitic to regional alteration) has low Mn (0.01 – 0.05 a.p.f.u.) and Al_{total} (1.76 –
258 2.28 a.p.f.u.), and high Ca (average 0.03 a.p.f.u.).
259   *White mica textures*. White mica is the most abundant phyllosilicate. It
260 appears in the veins as crystals and aggregate of crystals of variable size, from sub-
261 microscopic to a hundred of microns. Mica appears disseminated, intergrowth with

262 quartz, interstitial to quartz or even as inclusions in quartz, and also as micro-veins
263 (Fig. 5a and b).
264   Mica is by far the most abundant phase replacing volcanic plagioclase (as
265 phenocrysts or inclusions in amphibole and pyroxene). This mica varies from sub-
266 microscopic to dozens of microns (typical "sericite"), occasionally with the (001)
267 mica packet parallel to faces of the plagioclase (Fig. 5c and d) showing in TEM
268 images a rare prismatic morphology (Fig. 5e). Mica also replaces maphic
269 phenocrysts as sub-microscopic or microscopic disorientated crystals (Fig. 5f).
270 Rarely mica aggregates also have a "palm" texture, but more frequent is coarse mica
271 orientated in the maphic phenocrysts (Fig. 5g). In this last case, mica exclusively
272 replaces the amphibole and pyroxene or it is accompanied by chlorite with the same
273 orientation (Fig. 5h). In cases where mica and chlorite coexist, 10Å mica packets are
274 found randomly interlayed in the chlorite stacks (Fig. 5i).
275   Mica also ranges from sub-microscopic to microscopic in the volcanic
276 matrix, although fine grained crystals are much frequents.
277   The quartz veins are very penetrative. Thus, there is a wide range of
278 transitional occurrences between proper veins and hydrothermally altered volcanic
279 rock. For instance, in the veins it is frequent that mica presents characteristics of
280 hydrothermal alteration: coarse grained that proceeds from the transformation of
281 ferromagnesian phenocrysts and fine grained that precedes from the transformation
282 of plagioclase (Fig. 5j).
283   Finally, although mica polytypism has not been systemically studied, *tv1M,*
284 *2M* and *3T* polytypes has been deduced by XRD and TEM, the first mainly in the
285 hydrothermal alteration and the third one only observed in the veins (Fig. 6a and b).
286   *White mica mineral chemistry*. Mica microanalyses have been summarized in
287 Table 3, and Figure 7 and 8. The total interlayer-cations (K+Na+2Ca) range between
288 0.65 and 0.82, being K the dominant cation, while total octahedral cations range
289 between 1.99 and 2.15 a.p.f.u. The Fe/(Fe+Mg) ratio range between 0.08 and 0.82,
290 although majority of data range between 0.08 and 0.43. Al_{total} correlate inversely to
291 Si (m~2, Fig. 7a), and interlayer-cations content does not correlate with Al_{total} or Si
292 (Fig. 7b and c). But there is a negative correlation between Fe+Mg and Al_{total}, even
293 better with ^{VI}Al (Fig. 7d), and a roughly positive correlation between Fe+Mg and Si
294 (Fig. 7e). The Fe content is almost always lower than Mg content (Fe/(Fe+Mg)>0.5),
295 presenting both elements a rough positive correlation (Fig. 7f).
296   The mica from different locations shows also some differences in its
297 chemical composition. Mica in the veins has relatively high content of Al (2.20 –
298 2.65 a.p.f.u.), K (0.60 – 0.82 a.p.f.u.) and F (0.00 – 0.08 a.p.f.u.), while Si content is
299 low (3.23 – 3.44 a.p.f.u.) (Fig. 7 and 8). Fe+Mg is very variable reaching relatively
300 high values (0.08 – 0.43 a.p.f.u.). The analyses with higher Fe+Mg, move away from
301 the linear tendency of Fe+Mg *versus* Al_{total} that show the majority of analyses (Fig.
302 7d). Mica in the veins but originally precedent from the hydrothermal alteration
303 shows a higher K and F content than mica directly originated in the veins (Fig. 8).

304   Mica in the hydrothermal alteration is characterized by a relatively high Si
305   and low of K (0.60 – 0.77 a.p.f.u.) and total interlayer-cations (0.65 – 0.86 a.p.f.u.),
306   and F (0.00 – 0.06 a.p.f.u.). It is also observed relatively coarse grained mica
307   replacing plagioclase has lower Si and Fe and higher Al and K content than mica
308   replacing ferromagnesian phenocrysts. In respect to fine mica which replaces
309   plagioclase, that is relatively rich in Si, K, F and Fe and poor in Al in respect to the
310   other types of mica in the hydrothermal alteration (Fig. 7 and 8, Table 3).

311

312   *Silicification and related hydrothermal alteration*
313   Phyllosilicates in the silicification are very scarce and correspond to interstratified
314   illite-smectite. They appear as aggregates in micro-veins in which also appear native
315   gold crystals (Fig. 9a). These micro-veins formed after the main quartz event
316   generation, but before the formation of sulfates (barite ➔ Fe-Al sulfates ➔
317   gypsum). Very fine grained phyllosilicates (kaolinite, pyrophyllite, discrete illite and
318   illite-smectite interstratified) + quartz are the most abundant phases in hydrothermal
319   alteration that encloses silicification. It is possible to recognize a mineral zonation
320   from the silicification to the most external zones of propylitic alteration (Fig. 2).
321   a) Proximal area: It is constituted by quartz, pyrophyllite, kaolinite, discrete
322   illite and illite-smectite interstratified. Zones closer to the silicification are more
323   quartz and pyrophyllite rich, the last mineral disappearing towards peripheral zones.
324   It is observed that pyrophyllite have a major tendency to replace plagioclase, while
325   quartz is enriched in the matrix. Kaolinite corresponds to kaolinite (± nacrite and
326   dickte?) polytypes according to XRD and IR spectra patterns.
327   b) Distal zone: It is characterized by quartz, illite and interstratified illite-
328   smectite.
329   The wide presence of interstratified illite-smectite it is deduced in X-ray
330   difractograms with ethylene-glycol solvation, being deduced a high proportion of
331   illite layers (~ 90% according to Reynolds (1980)).
332   Electronic microscopy, mainly due TEM study, has confirmed interstratified
333   illite-smectite is the only phyllosilicates found in the silicification. Backscattered
334   images show changes in composition in several micron scale (Fig. 9b). In low
335   magnification TEM images it is observed tabular phyllosilicates stacks up to several
336   microns thick. Lattice-fringe images show layers always 10Å thick, and SAED
337   patterns also show a 10Å periodicity, in a certain order pattern (Fig. 10). That is
338   consistent with local ordered pattern in a major disorder sequence. A detailed
339   observation of the lattice-fringe images show termination of several or individual
340   layers in wedge (Fig. 10a and b). It is also observed splitting of 10Å layers in two 5Å
341   layers that in hundred microns along distance fuse with its neighbour split layers
342   (Fig. 10b). This structure could be related to screw dislocation, affecting to an
343   interstratified illite-smectite.
344   *Phyllosilicate mineral chemistry*. Microanalysis in these phyllosilicates,
345   except maybe TEM analyses (Tables 4 and 5), could correspond in a considerable

346 proportion to polycrystalline aggregates rather than individual crystal due the fine
347 grain character of these phyllosilicates, being, therefore, very difficult interpret these
348 analyses. These analyses reflect mixing between potassic illite with smectite, quartz,
349 kaolinite and pyrophyllite as Figure 11 suggests.
350   The EPMA analyses of coarse phyllosilicates in the silicification (Table 4,
351 Fig. 11) have low K (0.30 – 0.45 a.p.f.u.) and Al (1.57 - 2.27 a.p.f.u.) and high Si
352 (3.65 – 4.21 a.p.f.u.), which suggests the presence of interlayered smectite. Change
353 in backscattered image of theses phyllosilicates is due a higher Si and lower Al
354 content in the brighter zones than in the darker zones. That means there are domains,
355 several microns in size, with higher proportions of smectite layers. AEM analyses of
356 ion milled samples from the silicification have slight higher Al (2.29 – 2.40) and
357 lower Si (3.45 – 3.55) being K similar (0.25 – 0.55 a.p.f.u.) than EPMA analyses.
358 That is congruent with smectite layers are very penetrative, since micron size packets
359 with illite composition have note been detected.
360   EPMA phyllosilicate analyses from distal alteration zone are very variable,
361 although values up 0.79 and 2.42 a.p.f.u. of K and Al (similar to them of illite in
362 relation to the veins and related alteration), has been found. Therefore, illite without
363 smectite layers at micron size is presents in the distal alteration zone.
364
365   DISCUSSION
366 *Characteristics of the transformation of volcanic rocks*
367 It has been deduced that substrate characteristics of host rock (chemistry and
368 crystallography) have great importance in phyllosilicate mineralogy (Table 1) and
369 texture in hydrothermal alteration in relation to veins. The volcanic matrix,
370 constituted by glass or fine-grained crystals, develops chlorite and mica, and a large
371 quantity of quartz. This non-crystalline (or fine-grained) protolith conditions both its
372 high degree of reactivity (the volcanic matrix is the "easiest" microdomain to be
373 altered by hydrothermal fluids) and the tendency to develop fine-grained phases. In
374 contrast, maphic phenocrysts (hornblende and pyroxenes) mainly develop
375 phyllosilicates (chlorite and mica). Chlorite is the main phyllosilicate which
376 transforms maphic phenocrysts in conditions of relatively "weak" hydrothermal
377 alteration: chloritic alteration and propylitic alteration (the weakest alteration type).
378 This phenomenon is due to the fact that chlorite transformation implies a minor
379 chemical change (amphibole and pyroxenes are Fe-Mg-Si-(Al)-bearing in the same
380 way as chlorite). In many cases, chlorite is oriented in the maphic phenocrysts (Fig.
381 3c, d). Thus, it is deduced the transformation is strongly conditioned by the crystal
382 structure of the protolith (chain structure of Si tetrahedrons) which presents some
383 crystallographic similitude with the layer Si tetrahedrons of chlorite. We propose,
384 then, that hydrothermal fluids, firstly circulating through cleavage planes, produced
385 amphibole/pyroxene dissolution: fluids were abundant, as is common in a
386 hydrothermal system, and hot enough to enhance their reactivity. At the same time
387 than maphic phenocrysts dissolution, epitaxial growth of (001) chlorite packets over

388 (100) amphibole/pyroxene planes occurred (Fig. 12). Maybe, chlorite crystals with
389 others orientations also nucleate. But these less abundant and smaller crystals, due
390 the abundance of fluid could dissolve. The result is that crystal growth onto larger
391 pre-existing oriented crystals is favoured, in a way similar to an Ostwald Ripening
392 model (*e.g.* Eberl *et al.*, 1990) but accelerated for the high reactivity due the high
393 fluid activity. Other types of transformation are rejected, such as the solid state
394 transformation for illite-smectite proposed by Altner and Ylang (1997). The
395 intervention of a large quantity of fluids could easily produce dissolution processes.

396 Only in propylitic alteration do we find relicts of hornblende, while further
397 hydrothermal alteration produces total replacement of amphiboles/pyroxenes by
398 chlorite.

399 Mica also replaces maphic phenocrysts, either as phyllosilicate alone, or
400 intergrown with chlorite, mainly in zones of sericitic alteration. This mica or mica-
401 chlorite intergrowth is also usually orientated with the (001) mica planes parallel to
402 (100) amphibole/pyroxene planes. Our interpretation is that mica replaces chlorite,
403 with an epitaxial mica growth over chlorite, and simultaneous chlorite dissolution.
404 This occurs in a further hydrothermal alteration stage, with Mg-Fe loss and K
405 incorporation in the rock. It is also possible mica and chlorite intergrowth, mainly in
406 the chloritic-sericitic alteration zones, as suggest the presence of coherent mica –one
407 layer- in chlorite stacks (Fig. 5i), maybe more difficult to explain with a dissolution
408 (chlorite) -precipitation (mica) process.

409 Plagioclase phenocrysts are mainly replaced by mica, due to their lack of Fe
410 and Mg, necessary for chlorite formation. This mica is finer-grained than the mica
411 which replaces amphibole and pyroxene, reflecting a different crystallization
412 process. Plagioclase tectosilicate structure does not normally condition a specific
413 mica orientation, favouring nucleation rather than crystal growth. Only occasionally
414 could (001) and (010) plagioclase cleavage planes constitute preferential places for
415 growth of (001) packets of mica, sometimes with rare prismatic habit (Fig. 5d and e),
416 these being the main channel of hydrothermal fluids during the alteration processes.
417 The size of mica crystals in plagioclase, from sub-microscopic, to "sericite" size,
418 could be related to the changes in the saturation state of hydrothermal fluids. Highly
419 saturated fluids, usually linked only to sericitic alteration, could lead to sub-
420 microscopic crystals formed in volcanic plagioclase (Fig. 5c), and sometimes also
421 simultaneously formed in maphic phenocrysts.

422 In the hydrothermal alteration related to the silicification, the formation of
423 phyllosilicates implies a lesser control of rock substrate than that seen in vein-related
424 hydrothermal alteration. In this case, a lower pH in hydrothermal fluids enhances
425 rapid dissolution processes, avoiding significant control of volcanic substrate
426 chemistry in the crystallization of phyllosilicates, and also avoiding epitactic
427 phyllosilicate growth. Therefore, very fine, usually sub-microscopic phyllosilicate
428 crystals (interstratified illite-smectite, illite, kaolinite and pyrophyllite), are formed
429 indistinctly over the volcanic matrix, maphic phenocrysts and plagioclase.

10

430   Nevertheless as compared with phenocrysts, the matrix still favours quartz rather
431   than phyllosilicate formation.
432

433   *Implications of chlorite chemistry*
434   In the Palai-Islica, chlorites have a notable chemical variety linked to texture. Firstly,
435   it is possible to distinguish between chlorites in the quartz veins and the related
436   chloritic and sericitic alteration, and chlorites in the propylitic alteration. The main
437   difference is the relatively homogeneous Fe/(Fe+Mg) ratio, and higher Si (Fig. 4d)
438   content in the latter with respect to the former. Since chlorites are widespread in the
439   region as a regional alteration feature, chemical analyses could be useful to detect
440   signs of ore-bearing-related hydrothermal activity.
441   Secondly, the variable chemical composition of chlorite related to the
442   hydrothermal fluids themselves is very notable: chlorite from the quartz veins;
443   chlorite from the chloritic and sericitic alteration; and the differences between them.
444   The Fe/(Fe+Mg) ratio is extraordinarily broad, between 0.05 and 0.78. This is one of
445   the broadest found in a range of environments, such as metamorphic or
446   diagenetic/very low grade metamorphic, but also geothermal fields and other
447   hydrothermal deposits (Fig. 13). The observed Fe/(Fe+Mg) variation in
448   hydrothermal Palai-Islica chlorite is related to the characteristics of the hydrothermal
449   fluids and the mechanism of chlorite formation. Chlorite precipitated directly from
450   the hydrothermal fluids, like chlorite aggregates in the veins, has a high Fe/(Fe+Mg)
451   ratio, reflecting the chemical composition and perhaps also the temperature of the
452   hydrothermal fluids (*e.g.* Kranidiotis and MacLean, 1987, Saccocia and Seyfried,
453   1994). Nevertheless, chlorite produced by a transformation process (*i.e.* originating
454   in the hydrothermal alteration) has a low Fe/(Fe+Mg) ratio, since its composition
455   reflects the characteristics of hydrothermal fluids (*i.e.* composition and temperature)
456   plus the composition of the substrate. Both maphic phenocrysts and the rock in
457   general are relatively Mg rich, with low Fe/(Fe+Mg) ratio (Fig. 4).. In addition,
458   chlorites formed replacing phenocrysts, but subsequently incorporated within veins
459   (Fig. 3d), have an intermediate composition. This signals that a higher interaction
460   with the fluids increases the Fe/(Fe+Mg) ratio. In other words, hydrothermal fluids
461   produce relatively high Fe chlorites by direct precipitation (also observable in other
462   hydrothermal and geothermal environments, *e.g.* Kranidiotis and MacLean, 1987,
463   Sanchez-España *et al.*, 2000; Hibti and Marignac, 2001; Zaccarini *et al.*, 2003;) and
464   host rocks composition condition the reactant hydrothermal fluid chemistry in the
465   host rock itself.
466   Si and Al, which correlate positively for ore-related hydrothermal chlorite (not
467   in "propylitic" chlorite, Fig. 4d), are other components which clearly distinguish
468   between chlorite from the quartz veins (higher in Al_{total} and ^{IV}Al, and lower in Si
469   content), and the hydrothermal alteration (lower in Al_{total} and ^{IV}Al, and higher Si
470   content). The correlation of Fe/(Fe+Mg) with Al (positive) and Si (negative) found

471 in the hydrothermal chlorite could be explained with Tschermack substitution
472 $(SiMg \leftrightarrow {}^{IV}Al\,{}^{VI}Al)$ (*e.g.* Walshe, 1986).

473 Octahedral vacancies are significant (0.04 – 0.29 a.p.f.u.) in chlorites from the
474 veins and chloritic/sericitic alteration, and very abundant (0.09 – 0.87 a.p.f.u.) in
475 chlorites from the propylitic alteration. Different studies have shown hydrothermal
476 chlorite to have appreciable octahedral vacancies (*e.g.* McDowell and Elders, 1980:
477 0.01 –0.22; Cathelineau and Nieva, 1985: 0.02 – 0.42; Kranidiotis and MacLean:
478 0.00 – 0.12; Fulignati *et al.*, 1997: 0.15 – 0.25 a.p.f.u.) in comparison with
479 metamorphic chlorite, especially high-grade (Laird, 1988). Shau *et al.* (1990) and
480 Jiang *et al.* (1994) associate these vacancies to the existence of mica or smectite
481 layers or inclusions. In our study, this is the case for propylitic chlorite according to
482 K+Na+2Ca contents (Fig. 4e) and TEM observations. But in in chlorite from the
483 veins and from chloritic/sericitic hydrothermal alteration, apparent vacancies are
484 only partially related to a contamination effect of mica grains (Fig. 4e): they could
485 also correspond with true vacancies, which existence have been demonstrate by
486 Schmidt and Livi (1999).

487 Finally, Mn is a relatively abundant element in the chlorite studied (up to 0.10
488 a.p.f.u.), more abundant than in chlorites from a sedimentary-metamorphic
489 environment (*e.g.* Abad Martínez, 2002; Albee, 1962). It is even relatively high in
490 comparison with other hydrothermal occurrences (*e.g.* Albee, 1962; Zaccarini *et al.*,
491 2003). Mn in chlorite from Palai-Islica is roughly proportional to the Fe/(Fe+Mg)
492 ratio (Fig. 4b), reaching higher values in chlorites from the veins. Therefore its
493 concentration has much to do with ore-fluids. Association of Mn-bearing minerals
494 with hydrothermal ore-bearing activity has been also highlighted in carbonate phases
495 (Carrillo-Rosúa *et al.*, 2005).

496

497 *Implications of mica chemistry*

498 Microprobe analyses of mica of different textural kinds show interlayer-charge
499 between 0.65 a.p.f.u. and 0.86 a.p.f.u. Therefore a large number of analyses
500 correspond to an illite-smectite composition (charge below 0.75 according to
501 Newman and Brown (1987)). Nevertheless the numerous difractograms never show
502 modifications of (001) peaks after ethylene glycol solvation. The interlayer
503 composition is dominantly potassic, while the paragonitic and margaritic component
504 is very low (generally lower than 0.05 and 0.02 a.p.f.u. of Na and Ca respectively).
505 In the octahedral layer, meanwhile, Fe+Mg (0.08 - 0.42 a.p.f.u.) content is
506 considerably high, the octahedral charge usually being between 2 and 2.05. Fe
507 content is almost always lower than Mg content, and usually very similar for each
508 textural mica type, Mg content being the most variable (Fig. 7f). Therefore the
509 Fe/(Fe+Mg) ratio is variable although in a lower range than in chlorite (mainly
510 between 0.1 and 0.4).

511 Therefore, composition of this potassic octahedral mica could be explained by
512 illitic $(Si_1 \square_1 Al^{IV}{}_{-1}K_{-1})$ and phengitic $((Fe+Mg)_1 Si_1\,{}^{VI}Al_{-1}\,{}^{IV}Al_{-1})$ substitution vectors.

513   The content of F in this mica is low, although significant (up to 0.08 a.p.f.u.). There
514 are some differences between different textural mica types. Mica from the veins
515 usually has a lower illitic component and more F than mica from the chloritic and
516 sericitic alteration (Fig. 7a and 8d). The differences in the illitic component could be
517 related to "disequilibrium" and even to formation temperature. It is known that
518 muscovite "*sensu stricto*" began its formation in a very low-grade metamorphic
519 environment, in epizone conditions, around 200ºC (*e.g.* Abad Martínez, 2002). In the
520 Palai-Islica mica system, however, no muscovitic composition has been found at
521 temperatures as high as 300ºC (Morales-Ruano *et al.*, 2000; Carrillo-Rosúa *et al.*,
522 2003a). Similar non-muscovitic composition has been found in other Au epithermal
523 deposits, such as Red Mountain (USA) or El Dorado (Chile). Even in these cases,
524 more phengitic and illitic composition appears, but lower formation temperatures are
525 also suggested (Bove *et al.*, 2002; Carrillo-Rosúa *et al.*, 2008b).
526   A complementary view could be deduced from the polytypism of Palai-Islica
527 mica: the existence of different polytypes including *1M* polytype mainly in the
528 hydrothermal alteration domain (Fig. 6), could suggest "variable disequilibrated
529 conditions".
530   Mica in the veins could be "less disequilibrated" than mica in the hydrothermal
531 alteration on account of a higher fluid/rock ratio in the former as compared with the
532 latter, rather than being due to the time factor, given that they could be formed
533 during the same time interval. A higher temperature of mica from the veins could be
534 another factor. Higher temperatures in other environments, such as very low-grade
535 metamorphism, led to lower and more homogeneous illitic levels (*e.g.* Lee *et al.*,
536 1986; López Munguira and Nieto, 2000; Abad Martínez, 2002). This aspect will be
537 discussed in the specific geothermometry section below. Ore-forming fluids are
538 clearly responsible for the introduction of F, as is also suggested by apatite chemistry
539 (Carrillo Rosua *et al.*, 2005). Therefore F in mica could be used as a "chemical
540 vector" related to the "intensity" of hydrothermal activity in a certain zone of the
541 Palai-Islica deposit, and by extrapolation for other similar hydrothermal areas.
542   There are further chemical differences linked to specific mica textural groups.
543 "Coarse" mica, replacing volcanic plagioclase, has a higher K and Al content, along
544 with a lower Si, and a generally lower Fe content (this suggesting a higher illitic
545 level), than mica which replaces amphibole and pyroxene. Microcrystalline mica,
546 replacing volcanic plagioclase, has relatively high K, but also high Si and Mg, and
547 low Al and Fe, suggesting a contamination of the analysis with some sub-
548 microscopic chlorite. The cause for these chemical differences could be, again,
549 related to kinetic problems and the types of crystallization processes. Mica that
550 replaces plagioclase crystals is finer than mica replacing maphic phenocrysts, having
551 a higher specific surface to equilibrate with the hot hydrothermal fluids, and is
552 therefore less "disequilibrated", *i.e.* less illitic in its composition. Moreover, in mica
553 replacing amphiboles and pyroxenes, mica really replaces chlorite by chlorite

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dissolution, epitactic mica crystallization favouring a Fe/(Fe+Mg) ratio similar to that of the chlorite which it replaces.

Finally, mica crystals in the veins which represent "xenocrysts" from the hydrothermal alteration have a relatively high F content compared with mica directly crystallized in the vein, reflecting a longer "history" of interaction with the F-bearing hydrothermal fluids.

Geothermometry

Despite the questionable validity of chlorite thermometry (*e.g.* Shau *et al*., 1990; Jiang *et al*., 1994), Walshe (1986), Kranidiotis and MacLean (1987) and Cathelineau (1988), equations have been tentatively applied and the results plotted in Figure 13. It is significant that the temperatures obtained by chlorite geothermometry for the veins are 75 – 150ºC higher than in the hydrothermal alteration. Nevertheless, fluid inclusion data do not show higher temperatures of homogenization (Th) in the veins than in the hydrothermal alteration. In fact, they even show the opposite: the same mode value, but a higher range reaching lower Th (Carrillo-Rosúa, 2005). We could conclude the empirical chlorite geothermometers does not work at all in the case of Palai-Islica deposit. Or try to do further considerations if we consider it could works at least qualitatively (not quantitatively) within a certain system, as it could be the Palai-Islica deposit. Empirical observations (*e.g.* Kranidiotis and MacLean, 1987; Cathelineau, 1988) and thermodynamic calculations for high-variance assemblages (Vidal *et al*., 2005) could support the second alternative.

We can do the following consideration. The measured fluid inclusions in the hydrothermal alteration are secondary in respect to the volcanic quartz phenocrysts, and are probably representative of "peak" conditions of the hydrothermal system. In this "peak" conditions fluids have enough energy to crack quartz phenocrysts and cause the fluid inclusions, while at lower temperatures hydrothermal fluids have not enough energy, and do not produce fluid inclusions. In the quartz veins, however, fluid inclusion better represents the full range of hydrothermal fluid activity since quart is crystallizing and fluid inclusion are primary. Therefore it is possible that in the hydrothermal alteration the average temperature during the activity of the hydrothermal system could be lower than in the veins, although the peak (or peaks) would be the same. This would be in accordance with the chlorite geothermometry, but also with the illitic component of mica (related in some way with temperature, Cathelineau (1988)). Lower average temperature in the volcanic hydrothermally altered rocks than in the veins seems reasonable, and could be related to a drop in temperature of the hydrothermal fluids after leaving the main conduct channels (veins) and circulating through the host rocks (hydrothermal alteration). Alternative, could be related to a cooling of the fluids in the pores and cracks of the host rock in contact with neoformed minerals (and therefore with interaction mineral-fluid and possibility to modify mineral-chlorite…- composition) while the veins are sealed by mineralization processes.

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Alteration typology and genetic implications in ore deposition

It is noteworthy that the two different gold-bearing mineralizations develop pervasive halos of hydrothermal alteration, but with significant mineral differences, especially in relation to phyllosilicate phases (Fig. 2).

The quartz veins with sulfides (the most important form of mineralization) are polymetallic (Cu, Zn, Pb, Au, Ag…) and sulphur-rich. Veins and their related hydrothermal alteration are characterised by dioctahedral mica and chlorite as phyllosilicate phases. This alteration could be defined as sericitic in zones where mica is the dominant mineral phase, and chloritic when chlorite is abundant (with possible presence of albite). The former represents a higher intensity of hydrothermal alteration. This means that the mineralization type and associated alteration are related to hydrothermal fluids, which are base and precious metal-bearing and of near-neutral pH. Furthermore, they have temperatures of 150–300ºC according to fluid inclusion studies (Morales-Ruano *et al*., 2000). These features coincide with an intermediate-sulfidation hydrothermal system (Hedenquist *et al*., 2000).

The silicification is a type of mineralization which is poor in sulfide sulphur and base metals, although it contains high grades of gold. It develops a very different hydrothermal alteration. The core is constituted by the silicification containing ore gold-bearing mineralization. The silicification is surrounded by an advanced argillic envelope, mainly formed by pyrophyllite, kaolinite (with low disorder), illite and quartz. An outer-intermediate argillic envelope is constituted by illite and interstratified illite-smectite and quartz.

This silicification + advanced argillic alteration represents an intense leaching of the volcanic rock with lixiviation of the different cations present in the rock with the exception of Si + Al (argillic alteration), and only Si (silicification) in more extreme conditions. Very low pH fluids are deduced compatible with the formation of advanced argillic phyllosilicate assemblage (*e.g.* Reyes, 1990; Fialips *et al*., 1998), and are responsible for this extreme lixiviation process, coherent with a high-sulfidation hydrothermal environment (*e.g.* Hedenquist *et al*., 2000). The transition of silicification to advanced argillic envelopes is explained by progressive fluid modification due to rock interaction in the movement of hydrothermal fluids from their feeder conduits, situated in silicification zones, to external areas. This progressive fluid modification would imply a rise in pH level and a fall in temperature, according to the mineralogical zonation: kaolinite located in outer zones, as compared with pyrophyllite, is of a lower temperature phase (*e.g.* Browne, 1978; Henley and Ellis, 1983; Reyes, 1990). However, available fluid inclusion data (Carrillo-Rosúa, 2005) suggest the inexistence of appreciable changes in temperature of homogenization between silicification, advanced argillic alteration with pyrophyllite, and advanced argillic alteration with kaolinite. This Th, measured in secondary fluid inclusions in quartz volcanic phenocrysts, is mainly 260ºC ± 30ºC and seems to be too high for the presence of kaolinite, but appropriate to pyrophyllite

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638 formation (Berman, 1988; Bjorkum and Walderhaugh, 1993). In hydrothermal
639 systems it is assumed that kaolinite occurs at temperatures not higher than 200ºC
640 (*e.g.* Browne, 1978; Henley and Ellis, 1983; Reyes, 1990), while in diagenetic and/or
641 very low-grade metamorphic sequences kaolinite transforms to become dickite at
642 temperatures of 130ºC (*e.g.* Ehrenberg *et al*., 1993; Lázaro *et al*., 2003). This
643 apparent inconsistency between fluid inclusion and mineralogical data could be
644 explained by kinetic effect. Hot hydrothermal fluids interact more (more fluids +
645 more time) with the rock in the inner zone surrounding fluid conduits (*i.e.* the
646 silicification and the inner zones of the advanced argillic envelope) than in outer
647 zones of the advanced argillic envelope, where kaolinite appears.

648   The intermediate argillic alteration area characterized by illite and
649 interstratified illite-smectite represents a less intense alteration and lixiviation area
650 originated by higher pH fluids, in comparison to silicification and advanced argillic
651 alteration zones. Its origin is related to the same hydrothermal fluids which produce
652 silicification + advanced argillic envelope, although they are neutralized due to rock
653 interaction and there may also be a lower fluid/rock ratio.

654   Seeing as its presence is not consistent with temperatures higher than 200ºC
655 (*e.g.* Merriman and Peacor, 1991), interstratified illite-smectite in the silicification
656 and in the advanced argillic envelope could be related to a second stage in the
657 formation of the silicification + argillic envelope. This second stage would be of
658 lower temperature (<200ºC) and higher pH in respect to the first stage, and, very
659 significantly, is responsible for the gold mineralization. This is deduced from the
660 association of native gold and direct precipitated interstratified illite-smectite
661 aggregates (no illites without smectite interstratification have been found). This
662 illite-smectite is very illite-rich, which could suggest a lower formation temperature,
663 although still close to 200ºC (*e.g.* Merriman and Peacor, 1991).

664   The interstratified illite-smectite in the intermediate argillic alteration zone
665 could have been precipitated in the first hydrothermal stage due to a higher pH and
666 lower temperature and fluid/rock ratio conditions in this more external area, but also
667 in the second stage hydrothermal event.

668   Surrounding the chloritic and sericitic alteration zones (related to the quartz
669 veins) as well as argillic and silicification areas, there is a zone of weak alteration
670 that could be defined as propylitic. In this area, plagioclase phenocrysts could remain
671 unaltered or with only some phyllosilicate crystals (*i.e.* illite and interstratified illite-
672 smectite), while maphic phenocrysts are usually totally or partially altered to
673 chlorite. The presence of epidote and calcite (rather than dolomite - which could
674 appear occasionally in chloritic and sericitic alteration, Carrillo-Rosúa *et al*., 2005) is
675 also usually a characteristic feature.

676   Outside the Palai-Islica deposit, propylitic alteration becomes a regional
677 alteration feature, with the disappearance of epidote. This propylitic alteration
678 represents an area with a low infiltration rate of hydrothermal fluids, a low fluid/rock
679 ratio, and the presence of other cool meteoric regional fluids. These are responsible

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680 for the "regional alteration" and, mixed with a certain proportion of hydrothermal
681 fluids, they originate propylitic alteration. Thus, these rocks have suffered a minor
682 chemical change, reflected in the chlorite chemistry, with the Fe/(Fe+Mg) ratio equal
683 to the maphic phenocrysts.
684
685   CONCLUSIONS
686 Phyllosilicates are widespread phases among the mineralization and hydrothermal
687 alteration zones in the Palai-Islica deposit. Two different phyllosilicate (alterations
688 and/or neo-formed) assemblages have been distinguished in relation with two
689 different kinds of ores: mica and chlorite associated with polymetallic gold and
690 silver-rich veins; mica, interstratified illite-smectite, and kaolinite and pyrophyllite
691 associated with gold dissemination in the silicification. The former, defined as
692 chloritic and sericitic, is originated by near-neutral, highly metal-rich hydrothermal
693 fluids, while the latter is produced by acidic, gold-bearing hydrothermal fluids in
694 which a neutralization process and kinetic aspects determine a certain mineral
695 zonation pattern (silicification ➔ advanced argillic➔ intermediate argillic).
696 Noteworthy here is that gold precipitation occurs at temperatures ≤ 200ºC, which is
697 lower than that responsible for the main hydrothermal alteration/silification
698 formation stage. This is due to its association with interstratified illite-smectite. A
699 propylitic halo (chlorite, epidote, calcite- bearing) encloses the other alteration
700 zones. Therefore, two epithermal environments have been identified in the same
701 deposit: intermediate-sulfidation and high-sulfidation.
702   The advanced and intermediate argillic alteration zones develop very fine
703 grain phyllosilicates, more concentrated in volcanic phenocrysts in respect to the
704 matrix. This is related with a rapid, enhanced dissolution process due to the low pH
705 of the hydrothermal fluids. In the chloritic and sericitic alteration zones, coarse-
706 grained phyllosilicates (mainly inside maphic phenocrysts due to their anisotropic
707 structure) and epitactic crystallization features (maphic phenocrysts ➔ chlorite ➔
708 mica) appear, suggesting a weaker dissolution process due to the near-neutral
709 conditions of the hydrothermal fluids.
710   Chlorite and mica show a very wide compositional range. Chlorite chemistry,
711 mainly Fe/(Fe+Mg) ratio, and Si and Al content, distinguishes between an origin
712 related with high- or low- temperature fluids (*i.e.* chlorite of propylitic/regional
713 alteration origin). In addition, these elements strongly differ in concentrations
714 between chlorites in the hydrothermal alteration zone and that directly precipitated in
715 the veins, thus suggesting different genetic conditions (*i.e.* fluid/rock ratio, influence
716 of substrate, temperature…). Mica also presents some chemical composition
717 differences according to its location: veins or hydrothermal alteration, the latter
718 being richer in illitic component and poorer in F, directly related with ore-fluids. The
719 composition and polytypism of mica suggest that equilibrium conditions have not
720 been reached during hydrothermal activity.

721　　　　Although chlorite thermometry is said to be invalid (*e.g.* Jiang *et al*., 1994),
722 temperatures calculated with available empirical geothermometers could be useful to
723 estimate a range of formation temperatures, to suggest vectors of temperature
724 variation in a hydrothermal deposit, or, when combined with other methods such as
725 fluid inclusion, to give clues about the thermal evolution of a hydrothermal system.
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982

Figure 1. Carrillo et al

Map (a):
France
Spain
Africa

6
7
Mazarrón
Cartagena
5
Vera
Aguilas
4
N

Carboneras
3
2
ALMERIA
1
Cabo de Gata
0 10 20 30 40 50km.

||||| Calc-alkaline volcanism

High K calc-alkaline and shoshonitic volcanism

Ultrapotassic volcanism

Basaltic volcanism

Map (b):
755º   762º
b

PALAI
ISLICA
MEDITERRANEAN SEA
Carboneras

Paleozoic-Mesozoic basement rocks

Upper Miocene calc-alkaline rocks

Tertiary sedimentary rocks

A   C   Quaternary sediments
(a) alluvial and (c) colluvial

Faults and
limit of hydrothermal alteration

Outcropping
Palai-Islica deposit

Figure 2. Carrillo et al

Figure 3. Carrillo et al
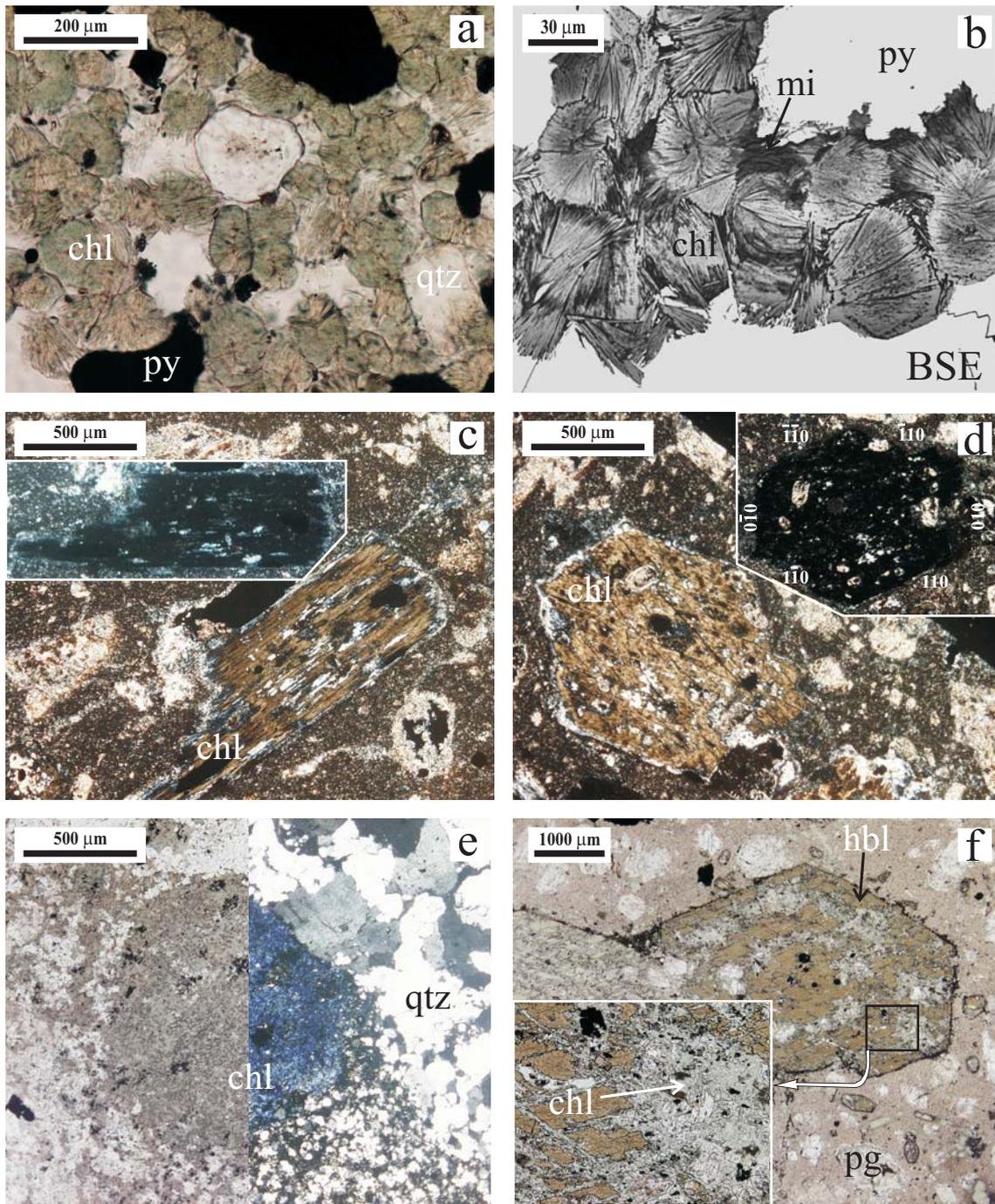
Figure 4. Carrillo et al
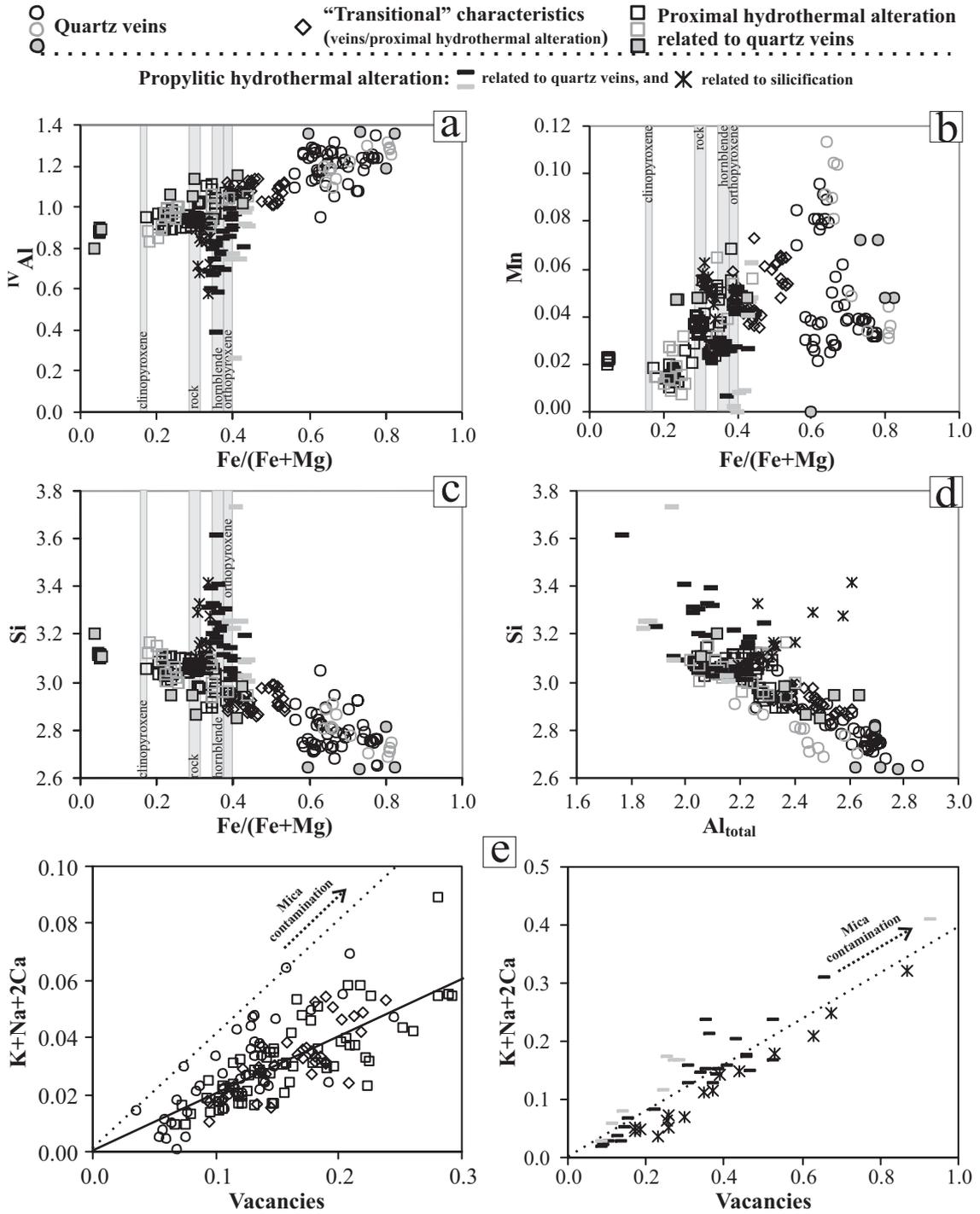
Figure 5. Carrillo et al
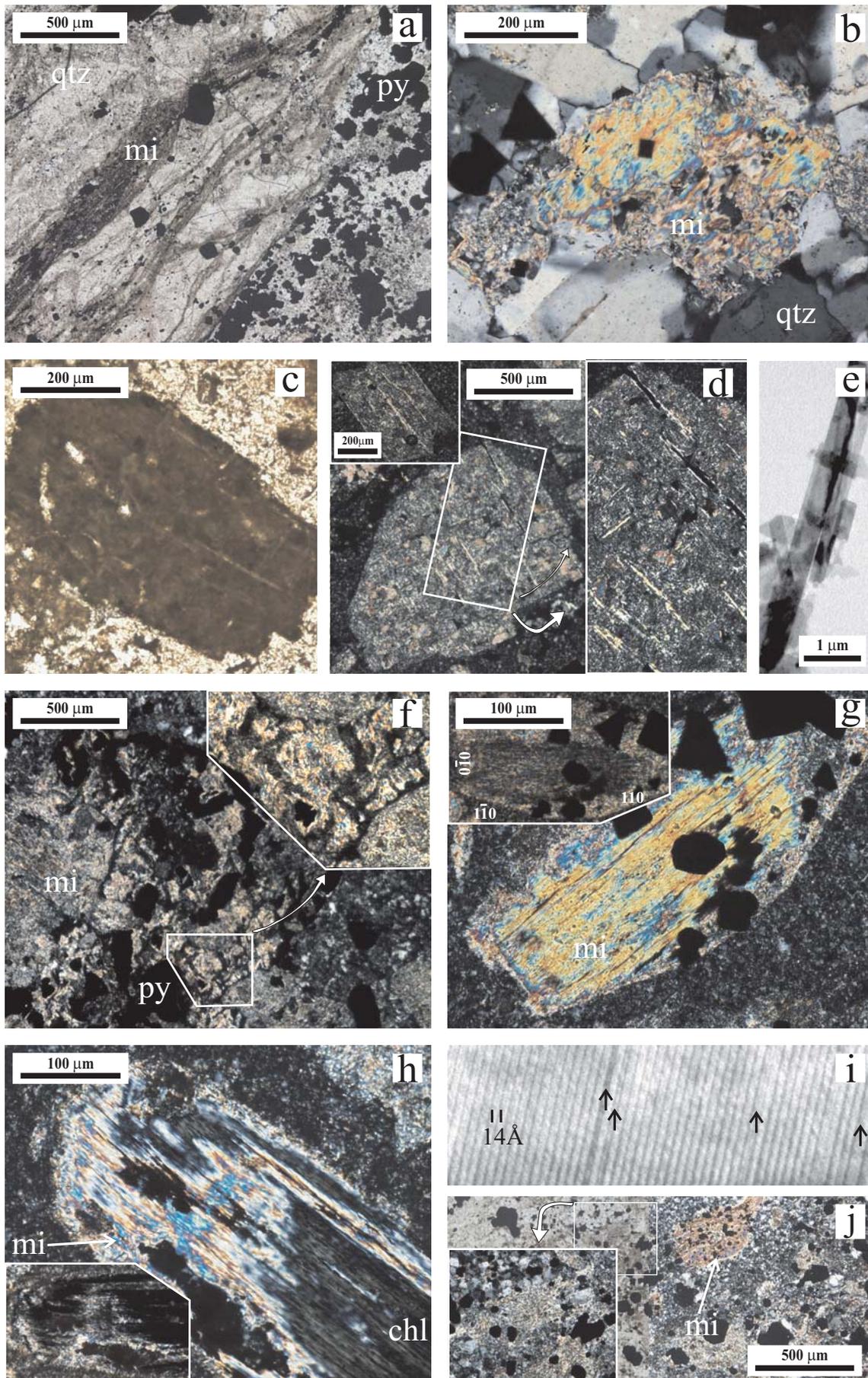
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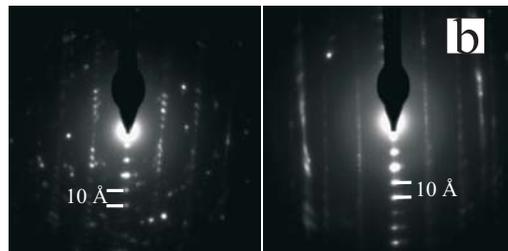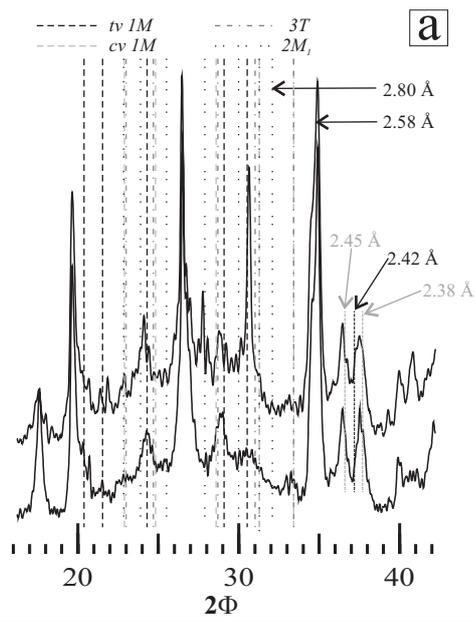
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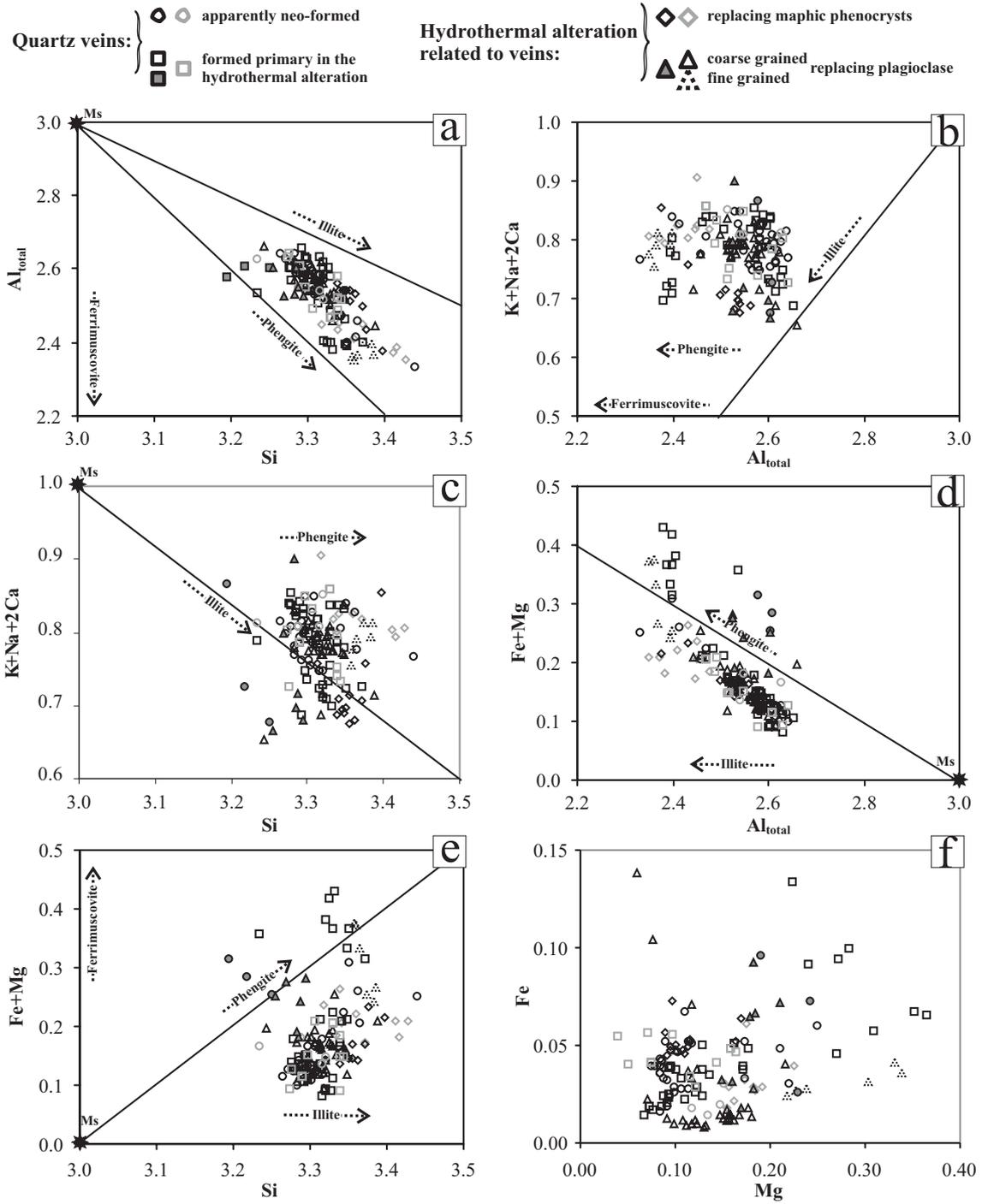
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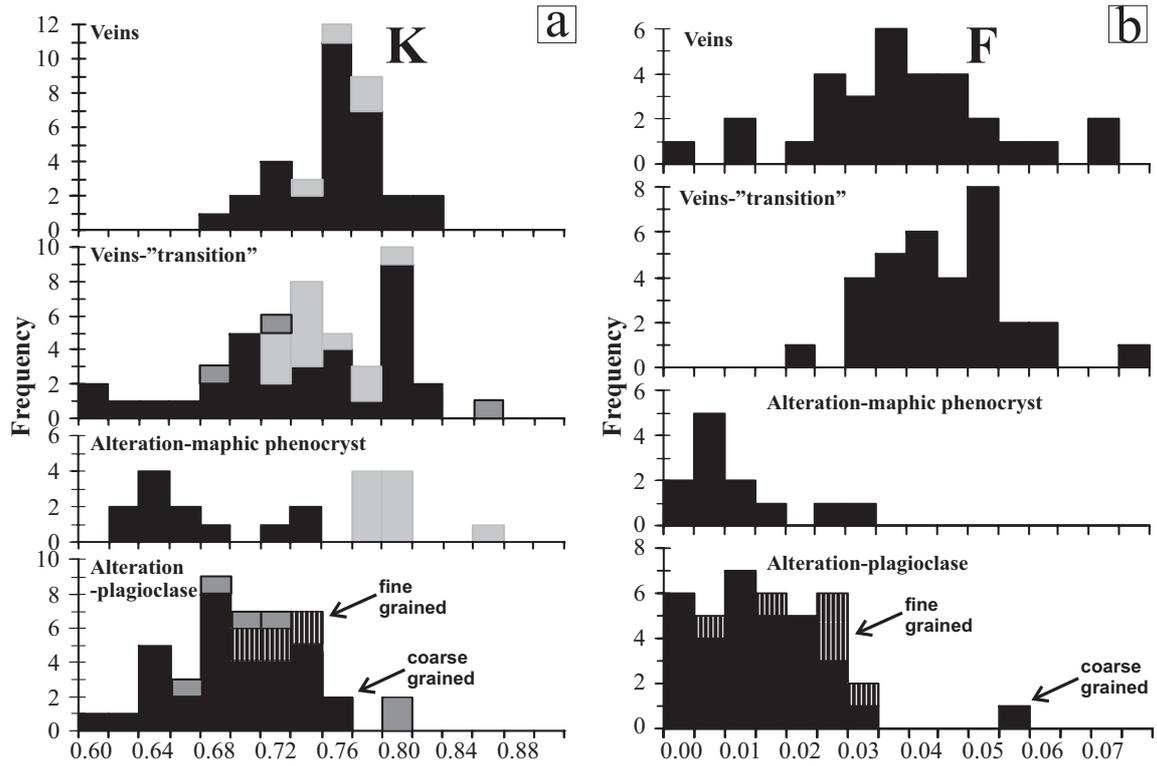
Figure 9. Carrillo et al
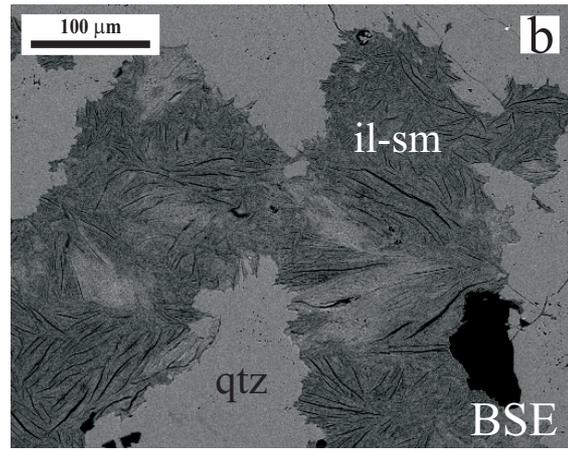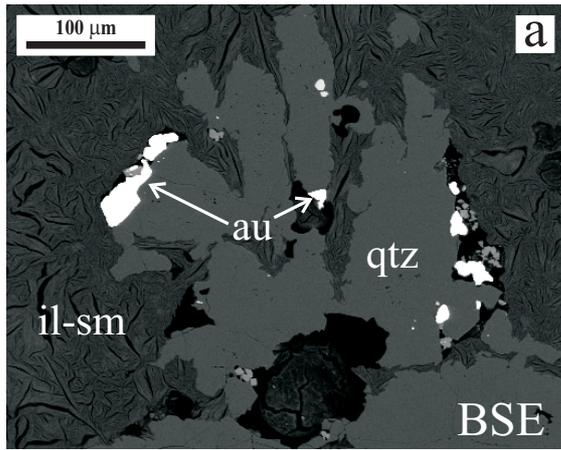
Figure 10. Carrillo et al
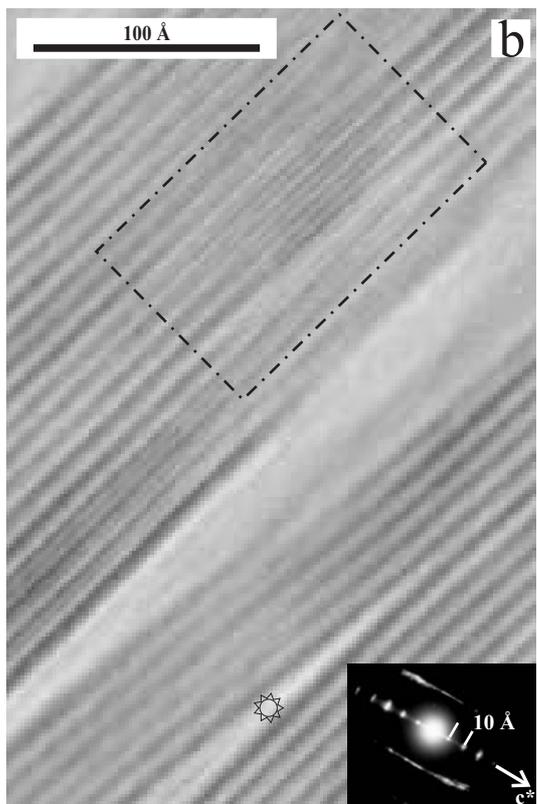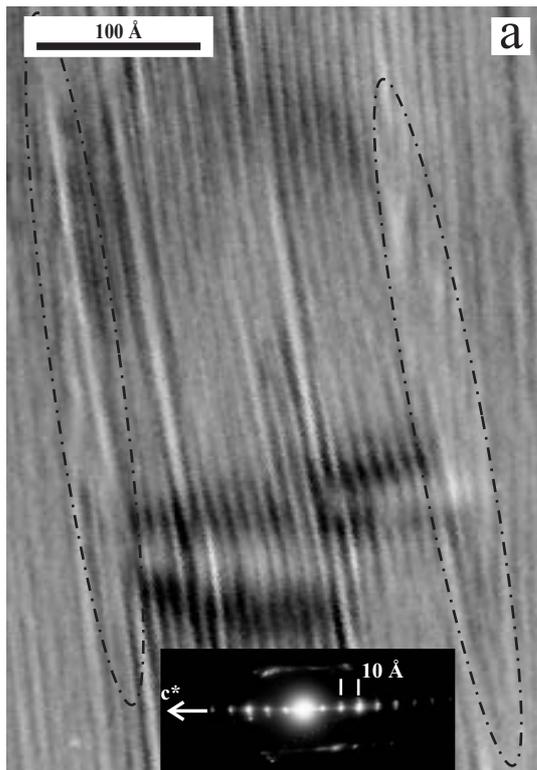
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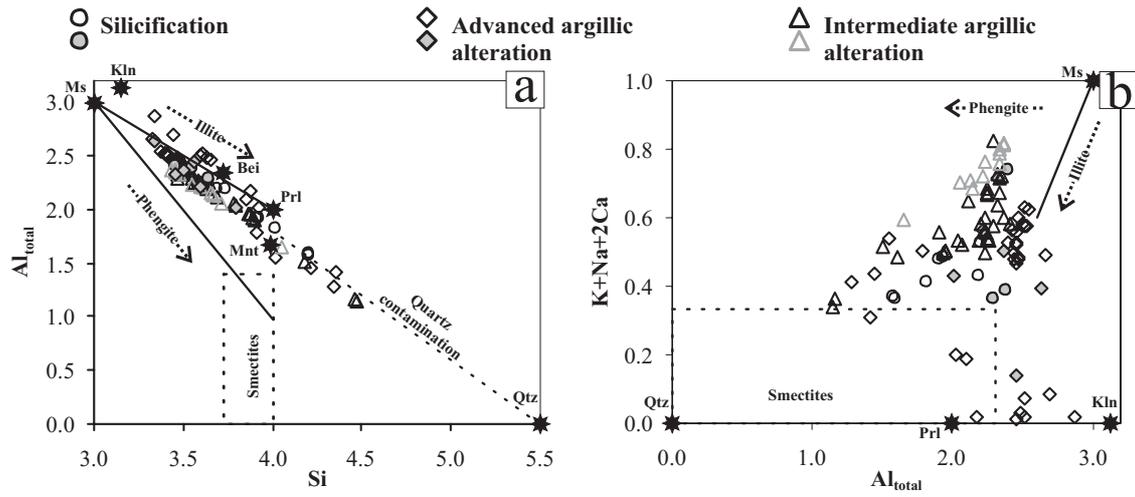
Figure 12. Carrillo et al

Fe/(Fe+Mg)
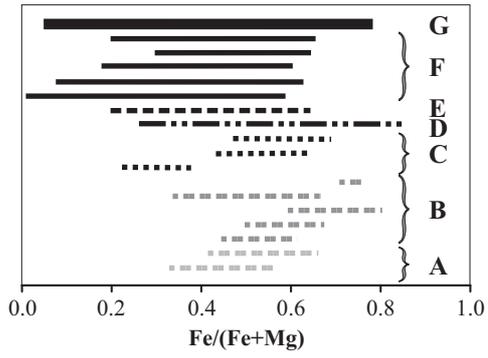
Figure 13. Carrillo et al
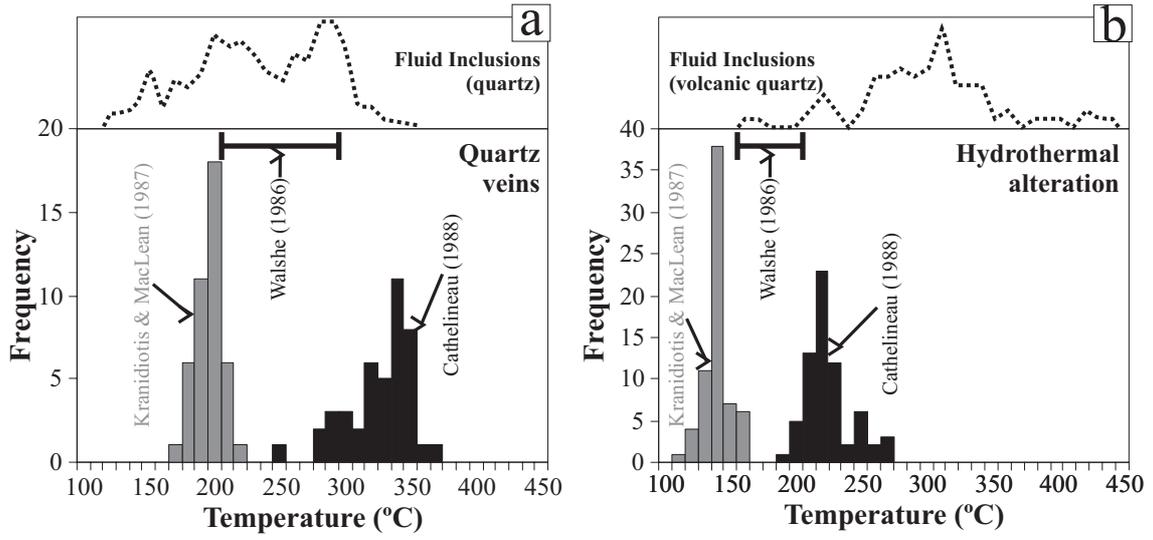
Table 1.

	Veins	Sericitic alteration	Chloritic alteration	Silicification	Advanced argillic alteration	Intermediate argillic alteration
Chlorite	XX	X (maphic phenocrysts)	XXX (matrix and maphic phenocrysts)			
Mica	XX	XXX (matrix, plagioclase and maphic phenocrysts)	X (matrix and plagioclase)		XX	XX
Interstratified illite-smectite				X	X	X
Kaolinite					XX	
Pyrophyllite					XX	

X: scarce; XX: abundant; XXX: very abundant

Table 2.

% weight	Veins (n=43)				Alteration (n=67)				Transitional (n=36)				Propylitic (n=41)			
	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.
SiO_2	20.05	26.84	24.60	1.20	26.73	33.48	30.35	1.19	23.94	28.87	27.22	1.23	29.18	34.99	31.45	1.50
TiO_2	0.01	0.06	0.03	0.01	0.00	0.54	0.03	0.07	0.00	0.07	0.02	0.01	0.00	23.00	4.34	8.20
Al_2O_3	13.91	21.65	19.53	1.73	16.41	20.55	18.43	1.02	16.20	20.94	19.30	1.17	0.00	21.13	13.98	7.52
FeO	24.67	35.83	30.94	2.82	2.68	21.73	14.71	4.39	18.97	27.30	22.50	2.40	12.38	22.17	17.53	2.46
MgO	5.71	11.68	8.81	1.84	18.32	30.77	22.36	2.85	11.38	18.09	15.09	1.90	13.82	20.53	18.12	1.31
MnO	0.22	1.05	0.50	0.23	0.12	0.80	0.35	0.15	0.39	0.77	0.55	0.10	0.07	0.72	0.46	0.16
CaO	0.00	0.12	0.05	0.03	0.03	0.15	0.08	0.03	0.03	0.14	0.07	0.03	0.03	0.63	0.23	0.16
K_2O	0.00	0.26	0.05	0.05	0.00	0.47	0.07	0.09	0.01	0.16	0.07	0.04	0.03	2.34	0.48	0.46
Na_2O	0.00	0.09	0.04	0.03	0.00	0.09	0.03	0.02	0.00	0.08	0.03	0.02	0.01	0.39	0.08	0.07
a.p.u.f.																
Si	2.65	3.05	2.79	0.08	2.89	3.14	3.05	0.05	2.86	2.99	2.92	0.04	3.01	3.61	3.19	0.13
Ti	0.00	0.01	0.00	0.00	0.00	0.04	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
^{IV}Al	0.95	1.35	1.21	0.08	0.86	1.11	0.95	0.05	1.01	1.14	1.08	0.04	0.39	0.99	0.81	0.13
^{VI}Al	1.15	1.52	1.40	0.07	1.09	1.41	1.23	0.08	1.23	1.50	1.36	0.07	1.06	2.03	1.38	0.19
Fe	2.41	3.40	2.94	0.27	0.21	1.86	1.24	0.38	1.70	2.43	2.02	0.23	1.02	1.92	1.49	0.22
Mg	0.98	1.91	1.49	0.28	2.79	4.26	3.34	0.34	2.10	2.80	2.41	0.22	2.03	3.07	2.74	0.20
Mn	0.02	0.10	0.05	0.02	0.01	0.07	0.03	0.01	0.04	0.07	0.05	0.01	0.01	0.06	0.04	0.01
Vacancies	0.04	0.25	0.12	0.04	0.07	0.29	0.16	0.05	0.09	0.24	0.16	0.04	0.09	0.87	0.35	0.17
Ca	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.02	0.01	0.00	0.00	0.07	0.03	0.02
K	0.00	0.04	0.01	0.01	0.00	0.06	0.01	0.01	0.00	0.02	0.01	0.01	0.00	0.29	0.06	0.06
Na	0.00	0.02	0.01	0.01	0.00	0.02	0.01	0.00	0.00	0.02	0.01	0.00	0.00	0.08	0.02	0.01
K+Na+2Ca	0.00	0.07	0.03	0.02	0.01	0.09	0.03	0.01	0.01	0.05	0.03	0.01	0.01	0.31	0.10	0.07

n: number of analysis; Min: minimum.; Max: maximum.; Ave: average; S.D.: (standard deviation). Veins: chlorite from the quartz veins with sulphides; Alteration: Chlorite from the hydrothermal alteration related to quartz veins with sulphides; Transitional: chlorite from the quartz veins but originated in the hydrothermal alteration ("xenocrysts"). Propylitic: chlorite from the most marginal zones of the Palai-Islica deposit, in areas of propylitic/regional low temperature alteration.

Table 3.

% weight	Veins-neo. (n=28)				Veins-tran (n=33)				Alteration - c.P. (n=32)				Alteration - f..P. (n=6)				Alteration - Map. (n=12)			
	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.
SiO_2	49.12	53.75	50.92	1.02	47.99	52.57	50.57	1.11	49.78	52.98	51.22	0.84	50.32	52.66	51.35	0.85	50.10	52.55	51.80	0.74
Al_2O_3	26.93	35.37	32.93	1.89	29.99	35.37	32.83	1.44	31.70	35.16	33.42	0.93	29.86	31.62	30.67	0.60	30.26	33.81	32.93	1.08
TiO_2	0.04	0.22	0.08	0.04	0.02	0.09	0.06	0.02	0.00	0.07	0.03	0.02	0.04	0.07	0.05	0.01	0.02	0.05	0.03	0.01
FeO	0.30	5.89	1.15	1.32	0.28	2.37	0.78	0.48	0.18	2.58	0.76	0.67	0.45	0.74	0.57	0.10	0.84	1.35	0.97	0.14
MgO	0.74	2.57	1.14	0.47	0.71	3.81	1.58	0.86	0.62	2.21	1.18	0.40	2.28	3.52	2.83	0.52	0.94	1.71	1.16	0.25
MnO	0.00	0.05	0.01	0.01	0.00	0.07	0.02	0.02	0.00	0.08	0.03	0.02	0.04	0.08	0.06	0.02	0.00	0.02	0.00	0.01
CaO	0.02	0.45	0.11	0.10	0.04	0.26	0.12	0.05	0.05	0.51	0.13	0.12	0.33	0.40	0.35	0.03	0.06	0.26	0.20	0.06
K_2O	7.94	9.95	9.10	0.44	7.41	9.73	8.81	0.68	7.35	9.17	8.47	0.63	8.34	8.86	8.62	0.20	7.30	8.77	8.05	0.43
Na_2O	0.04	0.30	0.16	0.07	0.08	0.78	0.23	0.16	0.07	1.11	0.34	0.30	0.12	0.18	0.15	0.03	0.08	0.82	0.21	0.19
F	0.00	0.33	0.18	0.08	0.10	0.37	0.21	0.05	0.00	0.28	0.06	0.08	0.03	0.15	0.10	0.04	0.00	0.14	0.05	0.05
Cl	0.00	0.09	0.01	0.02	0.00	0.05	0.02	0.01	0.00	0.05	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.06	0.02	0.01
Total	92.14	98.97	95.80	1.67	92.14	97.62	95.23	1.49	92.07	97.62	95.66	1.22	92.99	96.52	94.73	1.53	91.86	96.59	95.41	1.37
O=F	0.00	0.14	0.08	0.03	0.04	0.15	0.09	0.02	0.00	0.12	0.03	0.03	0.01	0.06	0.04	0.02	0.00	0.06	0.02	0.02
O=Cl	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
a.p.u.f.																				
Si	3.26	3.44	3.32	0.05	3.23	3.37	3.31	0.03	3.24	3.39	3.32	0.03	3.36	3.39	3.37	0.01	3.31	3.40	3.35	0.02
^{IV}Al	0.56	0.74	0.69	0.05	0.63	0.77	0.69	0.03	0.61	0.76	0.68	0.02	0.61	0.64	0.63	0.01	0.60	0.69	0.65	0.02
^{VI}Al	1.75	1.93	1.87	0.05	1.71	1.95	1.85	0.06	1.79	1.94	1.86	0.03	1.71	1.87	1.74	0.03	1.77	1.90	1.87	0.04
Ti	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.02	0.34	0.06	0.08	0.01	0.13	0.04	0.03	0.01	0.14	0.04	0.04	0.02	0.04	0.03	0.01	0.04	0.07	0.05	0.01
Mg	0.07	0.25	0.11	0.04	0.07	0.36	0.15	0.08	0.06	0.22	0.11	0.04	0.22	0.34	0.28	0.05	0.09	0.17	0.11	0.03
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$^{VI}\Sigma$	1.97	2.02	2.00	0.01	2.01	2.15	2.05	0.04	1.99	2.10	2.03	0.02	2.02	2.10	2.06	0.03	2.01	2.07	2.03	0.01
Ca	0.00	0.03	0.01	0.01	0.00	0.02	0.01	0.00	0.00	0.03	0.01	0.01	0.02	0.03	0.02	0.00	0.00	0.02	0.01	0.00
K	0.68	0.82	0.76	0.03	0.60	0.82	0.74	0.06	0.60	0.77	0.70	0.05	0.69	0.74	0.72	0.02	0.62	0.74	0.67	0.04
Na	0.01	0.04	0.02	0.01	0.01	0.10	0.03	0.02	0.01	0.15	0.04	0.04	0.02	0.02	0.02	0.00	0.01	0.11	0.03	0.02
K+Na+2Ca	0.75	0.85	0.79	0.03	0.69	0.86	0.78	0.05	0.65	0.84	0.76	0.05	0.75	0.81	0.79	0.02	0.68	0.86	0.72	0.05
F	0.00	0.07	0.04	0.02	0.02	0.08	0.04	0.01	0.00	0.06	0.01	0.02	0.01	0.03	0.02	0.01	0.00	0.03	0.01	0.01
Cl	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00

n: number of analysis; Min: minimum.; Max: maximum.; Ave: average; S.D.: (standard deviation). Veins-neo: mica from the quartz veins apparently neoformed; Veins-tran: mica from the quartz veins formed primary in hydrothermal alteration; Alteration-c.P.: relatively "coarse" mica replacing plagioclase from the hydrothermal alteration related to quartz veins; Alteration-f.P.: "fine" mica replacing plagioclase from the hydrothermal alteration related to quartz veins; Alteration-Map.: mica replacing maphic phenocrysts from the hydrothermal alteration related to quartz veins.

Table 4.

% weight	Silicification (n=8)				Advanced argillic (n=31)				Intermediate argillic (n=31)			
	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.	Min	Max	Ave	S.D.
SiO_2	49.45	64.40	59.12	5.24	41.64	62.63	50.97	4.68	47.36	66.55	53.61	4.55
Al_2O_3	19.27	28.37	24.68	3.00	14.30	35.29	27.84	6.05	10.30	30.78	25.91	4.85
TiO_2	0.00	0.02	0.01	0.01	0.00	0.20	0.03	0.06	0.01	0.38	0.06	0.06
FeO	0.11	0.19	0.15	0.02	0.02	4.16	0.56	0.81	0.17	0.97	0.44	0.18
MgO	0.31	0.51	0.41	0.06	0.04	1.57	0.81	0.48	0.33	1.84	1.11	0.49
MnO	0.00	0.02	0.01	0.01	0.00	0.03	0.01	0.01	0.00	0.07	0.02	0.02
CaO	0.24	0.48	0.33	0.08	0.03	0.82	0.24	0.21	0.03	0.85	0.26	0.21
K_2O	3.39	5.29	4.41	0.66	0.05	7.19	3.78	2.43	2.67	9.05	6.13	1.43
Na_2O	0.16	0.30	0.22	0.05	0.03	0.81	0.16	0.15	0.05	0.23	0.15	0.05
Cl	0.01	0.08	0.05	0.02	0.00	0.21	0.06	0.05	0.02	0.26	0.10	0.07
F	0.01	0.12	0.06	0.04	0.00	0.20	0.08	0.06	0.04	0.28	0.14	0.07
total	81.55	97.12	89.44	5.21	69.01	98.04	84.54	9.24	62.36	96.37	87.95	7.90
O=F	0.01	0.05	0.02	0.02	0.00	0.09	0.03	0.03	0.02	0.12	0.06	0.03
O=Cl	0.00	0.02	0.01	0.00	0.00	0.05	0.01	0.01	0.00	0.06	0.02	0.02
a.p.u.f.												
Si	3.65	4.21	3.92	0.20	3.32	4.36	3.62	0.29	3.47	4.47	3.72	0.27
^{IV}Al	0.00	0.35	0.08	0.20	0.00	0.68	0.38	0.29	0.00	0.53	0.28	0.27
^{VI}Al	1.78	1.92	1.85	0.05	1.57	2.21	1.93	0.15	1.61	1.92	1.81	0.07
Ti	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.00	0.00
Fe	0.01	0.01	0.01	0.00	0.00	0.27	0.03	0.05	0.01	0.06	0.03	0.01
Mg	0.03	0.05	0.04	0.01	0.01	0.15	0.08	0.05	0.03	0.20	0.12	0.05
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$^{VI}\Sigma$	1.61	1.97	1.85	0.13	1.80	2.23	2.04	0.09	1.80	2.06	1.96	0.07
Ca	0.02	0.03	0.02	0.01	0.00	0.06	0.02	0.02	0.00	0.06	0.02	0.02
K	0.30	0.45	0.37	0.06	0.00	0.57	0.33	0.20	0.32	0.79	0.54	0.11
Na	0.02	0.04	0.03	0.00	0.00	0.13	0.02	0.02	0.01	0.03	0.02	0.01
Interlámina	0.37	0.53	0.45	0.06	0.01	0.63	0.39	0.21	0.34	0.83	0.58	0.10
F	0.00	0.03	0.01	0.01	0.00	0.05	0.02	0.02	0.01	0.06	0.03	0.01
Cl	0.00	0.01	0.01	0.00	0.00	0.03	0.01	0.01	0.00	0.03	0.01	0.01

n: number of analysis; Min: minimum.; Max: maximum.; Ave: average; S.D.: (standard deviation). Silicification: illite/ interstratified illite-smectite from the silicification; Advanced argillic: Phyllosilicates from the advanced argillic alteration; Intermediate argillic: Phyllosilicates from the intermediate argillic alteration.

Table 5.

	S.	S.	S.	A.A.A.	A.A.A.	A.A.A.	A.A.A.	A.A.A.	A.A.A.
Si	3.45	3.55	3.64	3.33	3.56	3.46	3.80	3.50	3.60
^{IV}Al	0.55	0.45	0.36	2.63	2.45	2.32	2.01	2.37	2.22
^{VI}Al	1.85	1.93	1.93	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.01	0.01	0.01	0.00	0.00	0.01	0.03	0.00	0.00
Mg	0.12	0.13	0.10	0.19	0.14	0.24	0.14	0.19	0.19
$^{VI}\Sigma$	1.98	2.07	2.04	2.15	2.15	2.02	1.98	2.06	2.01
Ca				0.00	0.00	0.00	0.00	0.00	0.09
K	0.55	0.39	0.25	0.39	0.14	0.60	0.38	0.50	0.39
Na	0.19	0.00	0.11	0.00	0.00	0.11	0.05	0.00	0.00
K+Na+2Ca	0.74	0.39	0.36	0.39	0.14	0.72	0.43	0.50	0.57

S.: Illite/ interstratified illite-smectite from the silicification analyzed in an ion milled sample preparation; A.A.A.: mica/mica-smectite intestratified from the advanced argillic alteration analyzed in a formvar Cu grid.

FIGURE CAPTIONS
Figure 1:
1003 (a) Cabo de Gata – Cartagena volcanic province in SE of Spain with the location of
1004 the most important ore deposits volcanic belt (adapted from Lopez-Ruiz and
1005 Rodriguez-Badiola, 1980): (1) Cabo de Gata. (2) Rodalquilar. (3) Carboneras (Palai-
1006 Islica). (4) Herrerías and Sierra Almagrera. (5) Aguilas. (6) Mazarrón. (7) Cartagena.
1007 (b) Schematic geological map showing the location of the Palai-Islica deposit and
1008 main geological units (adapted from IGME, 1974).
1009
1010 **Figure 2:**
1011 Schematic picture of Palai-Islica deposit which include the position of the different
1012 kinds of mineralisations which appear on it. In the silicification, an arrow indicates a
1013 phyllosilicate micro-vein.
1014
1015 **Figure 3:**
1016 Transmitted light (parallel and crossed polarized) and backscattered electron (BSE)
1017 photomicrograph of chlorites. (a and b) Spherulitic aggregates of chlorite (chl)
1018 intergrowing with coarse quartz and sulphides in the veins. In the BSE image (b) it is
1019 observed dark cores and bright rims in chlorite and mica (mi) interstitial and maybe
1020 replacing chlorite. (c and d) Prismatic and basal section of hornblende (in "maximum
1021 of illumination" and "extinction" positions) replaced by coherent orientated chlorite
1022 in the hydrothermal alteration related to quartz veins. (e) Chlorite precedent of
1023 hornblende replacement inside a quartz vein. (f) Incipient replacing of hornblende
1024 (hbl) by chlorite (chl) in the propylitic alteration.
1025
1026 **Figure 4:**
1027 Binary diagrams showing compositional variations, expressed at atoms per unit
1028 formula, between tetrahedral and octahedral cations and interlayer cations and
1029 vacancies in the different types of chlorites. It is showed for comparison the
1030 Fe/(Fe+Mg) ratio of the unaltered volcanic rock and phenocrysts (data from
1031 Fernández Soler, 1996) which hosts the Palai-Islica deposit. EPMA analyses are
1032 plotted in black without fill, TEM-AEM analyses in dark grey fill, and SEM analyses
1033 in grey color without fill. The influence of mica contamination and correlation line in
1034 chlorite analyses is shown by a dotted and solid line respectively if (e).
1035
1036 **Figure 5:**
1037 Transmitted light (plane-polarized and cross-polarized light) and TEM
1038 photomicrographs of mica. (a) Micro-veins of mica of sub-microscopic character
1039 inside a quartz vein. (b) Coarse mica intergrowing with quartz. Sub-microscopic (c)
1040 and micron size (d) mica replacing a volcanic plagioclase inside hydrothermal
1041 alteration related to quartz veins. In (d) it is observed orientated crystals parallel to
1042 cleavage plagioclase planes, which in low magnification TEM image (e) shown a

1043 prismatic morphology. Hornblende replaced by fine grained disorientated mica (f)
1044 and coherent orientated mica (g) in the hydrothermal alteration related to quartz
1045 veins. (h) Maphic phenocrysts prismatic section replaced by orientated chlorite and
1046 mica. (i) TEM lattice-fringe image of chlorite (14 Å) with coherent mica layers (10
1047 Å, marked with an arrow) in a zone of mica-chlorite intergrowth similar to (h). (j)
1048 Zone of transition between a quartz vein and the related hydrothermal alteration. It is
1049 observed coarse grained mica provably originated by a transformation of a maphic
1050 phenocrysts and fined mica precedent from plagioclase transformation (inside a
1051 square in the left down corner).
1052
1053 **Figure 6:**
1054 (a) XRD patterns of <2μm bulk sample fraction from hydrothermal alteration (down)
1055 and of mica replacing plagioclase separated by microdrilling (up) with vertical lines
1056 showing reflections of different polytypes according to Bailey (1980) and Moore and
1057 Reynolds (1997). 2.58 Å and 2.80Å peaks are marked since $I_{2.80}/I_{2.58}$ has been related
1058 to $2M/(2M+1Md)$ (Maxwell and Hower, 1967). 2.42 Å, 2.45 Å (ordered) and 2.38 Å
1059 (disordef) peaks are marked in order to estimate disorder of the n60º kind (Moore
1060 and Reynolds (1997).
1061 (b) SAED patterns of mica showing $2M$ polytype (left) and $3T$ polytype (right) from
1062 mica replacing plagioclase in the hydrothermal alteration and disseminated mica in a
1063 vein, respectively.
1064
1065 **Figure 7:**
1066 Binary diagrams showing compositional variations, expressed at atoms per unit
1067 formula, between major elements in the different types of mica in the quartz veins
1068 and related hydrothermal alteration. It is showed for comparison the muscovite
1069 composition (Ms) and different chemical vectors: illite substitution ($Si_1\square_1Al^{IV}_{-1}K_{-1}$),
1070 phengite substitution ($(Fe+Mg)_1Si_1^{VI}Al_{-1}^{IV}Al_{-1}$), ferrimuscovite substitution
1071 ($Fe^{3+}_1{}^{IV}Al_{-1}$). EPMA-WDX analyses are plotted in black without fill, TEM-AEM
1072 analyses in dark grey fill, and SEM-EDX analyses in grey color without fill.
1073
1074 **Figure 8:**
1075 Frequency histograms for (a) K and (d) F content expressed at atoms per formula
1076 unit in the different types of analyzed mica. EPMA-WDX analyses are plotted in
1077 black columns, TEM-AEM analyses in dark grey color columns, and SEM-EDX
1078 analyses are in light grey color columns.
1079
1080 **Figure 9:**
1081 Backscattered electron (BSE) images of illite/illite-smectite (il-sm) in the
1082 silicification. In (a), illite-smectite appears together native gold grains (au) and
1083 quartz, while in (b), it is appreciable its chemical zonation.
1084

Figure 10:

HR-TEM (BSE) images of illite/interstratified illite-smectite with 10Å periodicity in the silicification and relatively disorder SAED pattern. In (a) it is observed termination of several layers in wedge (inside oval). In (b) individual layer termination wedge is showed (noted by a start) and also splitting 10Å layers into 5Å layers (noted by a dotted square), maybe related with screw dislocation affecting interstratified illite-smectite.

Figure 11:

Binary diagrams showing compositional variations, expressed at atoms per unit formula, between Si, Al and K+Na+2Ca of phyllosilicates from the silicification and related hydrothermal alteration. It is showed for comparison the muscovite (Ms), kaolinite (Kln), pyrophyllite (Prl), beidellite (Bei), montmorillonite (Mnt) and quartz (Qtz) composition, and: illite substitution ($Si_1\square_1Al^{IV}_{-1}K_{-1}$) and phengite substitution ($(Fe+Mg)_1Si_1{}^{VI}Al_1{}^{IV}Al_1$) chemical vectors. EPMA-WDX analyses are plotted in black, while SEM-EDX analyses are plotted in grey color and TEM-AEM analysis in grey filled symbol.

Figure 12:

Variation of the la relation of Fe/(Fe+Mg) in chlorites from Palai-Islica and from different geological settings: (A) metabasites from New Zeland (Copper, 1972); metapelites from New Caledonia (Black, 1975); (B) sedimentary rocks and metasedimentary rocks from the SE, NW of Spain and Kazahastan (Abad *et al.*, 2001; 2003a; 2003b); sandstones from Texas (Boles and Franks, 1979), sediments from the Gulf Cost (Ahn and Peacor, 1985); (C) Geothermal field in Los Azufres- Mexico- (Cathelineau and Nieva, 1985), and Salton Sea-USA- (McDowell and Elders, 1980), Pantelleria-Italy- (Fulignati *et al.*, 1997); (D) Hydrothermal vents in Atlantic and Pacific mid-ocean ridge (Saccacocia and Gillis, 1995) (E) Altered granites (Hecht *et al.*, 1999); (F) Cu veins and stratabound Cu deposits associated to basic rocks in the north of Italy −*v.d.*: various deposits- (Zaccarini *et al.*, 2003); VHMS deposits from Canada (Kranidiotis and MacLean, 1987), from Iberian Pyrite Belt (Sánchez España *et al.*, 2000), and from Morocco (Hibti and Marignac, 2001); (G) Palai-Islica Au-Cu epithermal deposit.

Figure 13:

Frequency histograms of temperature obtained with Kranidiotis and MacLean (1987) (grey) and Cathelineau (1988) chlorite geothermometers in (a) quartz veins with sulphides and (b) hydrothermal alteration related to quartz veins. A horizontal line show the interval of temperatures calculated by Walshe (1986) geothermometer for selected analyses which reflect chlorite chemical composition variability. It is also showed for comparison Th data of fluid inclusions in quartz from the veins and in volcanic quartz phenocrysts in the hydrothermal alteration. The last fluid inclusions

1127   secondary type, but coetaneous with hydrothermal activity. These Th data, not in
1128   vertical scale, are from Carrillo-Rosúa (2005).
1129

TABLE CAPTIONS

1131 **Table 1:**

1132 Summary of distribution of phyllosilicates at the Palai-Islica deposit, in relation to
1133 the primary mineralogy of the host rock.

1134

1135 **Table 2:**

1136 Chemistry of chlorite analyzed by EPMA in the quartz veins and related
1137 hydrothermal alteration of the Palai-Islica deposit (normalized to $O_{10}(OH)_8$).

1138

1139 **Table 3:**

1140 Chemistry of mica analyzed by EPMA in the quartz veins and related hydrothermal
1141 alteration of the Palai-Islica deposit (normalized to $O_{10}(OH)_2$).

1142

1143 **Table 4:**

1144 Chemistry of phyllosilicates analyzed by EPMA in the silicification and related
1145 hydrothermal alteration of the Palai-Islica deposit (normalized to $O_{10}(OH)_2$).

1146

1147 **Table 5:**

1148 Individual HR-TEM analyses of phyllosilicates from the silicification and advanced
1149 argillic alteration (normalized to $O_{10}(OH)_2$).

1150