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

Authors
JAVIER CARRILLO-ROSÚA1; SALVADOR MORALES-RUANO2,3, IÑAKI ESTEBAN-ARISPE2, AND PURIFICACIÓN FENOLL HACH-ALÍ2,3

Address
1 Departamento de Didáctica de las Ciencias Experimentales (Universidad de Granada), Facultad de Ciencias de la Educación, Campus de Cartuja, 18071, Granada, Spain
2 Departamento de Mineralogía y Petrología (Universidad de Granada), Facultad de Ciencias, Avd. Fuentenueva s.n., 18002, Granada, Spain
3 Instituto Andaluz de Ciencias de la Tierra (CSIC- Universidad de Granada), Facultad de Ciencias, Avd. Fuentenueva s.n., 18002, Granada, Spain.

Running title: Significance of phyllosilicate mineralogy in the epithermal environment

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.

**Keywords:**
Chlorite, epithermal, gold, mica, Spain, intermediate-sulfidation, volcanic-hosted
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 - < 100°C, 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
end of the Internal Zone of the Betic Cordillera. This neogene volcanic belt, with different series of volcanic rocks (i.e. calc-alkaline, shoshonitic, potassic calc-alkaline, ultrapotassic and basaltic series, López Ruiz and Rodriguez Badiola, 1980), formed within the context of compression, followed by an extensional event (Dewey, 1988; García Dueñas et al., 1992) and strike-slip movements in which volcanism occurs (e.g. Hernandez et al., 1987; Fernández Soler, 1996; Turner et al., 1999). Associated with this magmatism, hydrothermal systems developed, being controlled by systems of faults and fractures. The hot fluids (up to 400-450°C, Morales Ruano, 1994) reacted strongly with the host rocks and, in some districts mainly located inside calc-alkaline zone, gave rise to broad areas of alteration hosting metallic mineralization: Cabo de Gata (Pineda Velasco, 1984), Rodalquilar (e.g. Arribas et al., 1995), and Palai-Islica (Morales-Ruano et al., 2000; Carrillo-Rosúa et al., 2003a). The approximately 4 km² of Palai-Islica is one of these alteration areas (Fig. 1b) which has become a recent target of mineral exploration companies for gold and copper (Morales-Ruano et al., 2000). It appears near Carboneras town (Almería province, SE Spain) over an extensive zone of breccias and auto-breccias of andesites/dacites of ~10 Ma on age (Bellon et al., 1983; Fernandez Soler, 1996). These rocks (Fernández Soler, 1996), with a very porphyritic texture, are constituted by phenocrysts of bitownite plagioclase and hornblende (up to centimetre on size) ± clinopyroxene and orthopyroxene. In accessory amount there are quartz, Fe-Ti oxides, apatite and zircon.

SAMPLES AND METHODOLOGY
Samples were obtained from mineralization and from hydrothermally altered volcanic rocks at Palai-Islica. Two hundred and sixty-two samples selected from 21 drill cores and surface sampling campaign had been studied. Whole-rock powders, oriented aggregates of <2µm fraction (with ethylene glycol and dimethyl sulfoxide solvation and without treatment), thin sections and a selection of ion milled specimens and suspension over Cu-grids of these samples, were prepared to determine the mineralogical, chemical and textural characteristics of phyllosilicates in this deposit. Transmitted light microscopy, XRD (Phillips PW 1710, with CuKa radiation, graphite monochromator and automatic divergence slit) at the Department of Mineralogy and Petrology of the University of Granada and SEM (Zeiss DSM 950 and FESEM Leo Gemini 1530, with an EDX detector), EPMA ( Cameca SX50, with WDX detector) and TEM (Philips CM20, with an EDAX solid-state EDX detector) at the “Centro de Instrumentación Científica” of the University of Granada had been used.

A total of 461 micro-analyses of phyllosilicate were obtained with different techniques (368 EPMA, 76 SEM and 18 TEM). Natural and synthetic-certified standards were used to calibrate EPMA, SEM and TEM-AEM quantitative analyses. The operating conditions were: 20 kV (EPMA and SEM), 200 kV (TEM) accelerating potential, 30nA (EPMA) and 1-2 nA (SEM) beam current, and
acquisition time of 40-100 s (for X-ray peak and background for EPMA), 100 s (SEM, TEM). Shorter counting times was used for K and Na in TEM-AEM analyses (30 s) and EPMA (20 s at peak and 20 s at background) to minimize alkali loss (Nieto et al., 1996). AEM analysis were performed using a raster of 1000 x 200Å in scanning mode for ion-milled samples and a analytical window of 1μm x 1μm in scanning transmission mode for powders dispersed over holey C-coated formvar Cu grids. The acquired EPMA X-ray intensities were corrected for atomic number, mass-absorption and secondary fluorescence effects using the CAMECA-PAP version of the Pouchou and Pichoir (1984) procedure. The transformation of intensity ratios to concentration ratios in AEM analysis was made following the procedure of Cliff and Lorimer (1975). Structural formulas of chlorite and mica were calculated on the basis of $O_{10}(OH)_2$ and 22 and 28 negative charges, $O_{10}(OH)_8$ and $O_{10}(OH)_2$ respectively.

Four samples kaolinite (prepared as standard KBr pellets) were also analyzed by Nicolet 20SXB (“Centro de Instrumentación Científica” of the University of Granada) in order to obtain FTIR spectra and discriminate among kaolinite polytypes.

PREVIOUS DATA ABOUT THE MINERALIZATION

Two different types of mineralization, quartz veins and veinlets with sulfides and dissemination in the silicification, are recognized in the Palai-Islica deposit (Fig. 2, Carrillo-Rosúa et al., 2003a). Associated with this mineralization appears andesites/dacites which present an important hydrothermal alteration, although different in relation with both types of mineralization.

(a) Veins and veinlets of quartz with sulfides. It is the main ore of the deposit, being located at depth between +70 and –90 meter above sea level (m.a.s.l.). These veins, sometimes stockwork-like and very penetrative, are very rich in sulfides. Although these veins have a sub-vertical trend, two main sub-horizontal levels have been recognized with enrichment in Au, Ag, Zn, Pb, Cd, As and Sb, with free gold grains and with fluid inclusions showing distinct characteristics (wide variation in salinity, 20 - 30 wt. % eq. NaCl, over a narrow temperature range – 200 to 250°C) relative to the rest of the deposit (Morales-Ruano et al., 2000). Ore mineralogy consists in pyrite with occasionally high contents of chalcopyrite, sphalerite and galena. Accessory phases are very diverse, being Au-Ag alloys and different Ag-bearing sulfides and sulfosalts the most outstanding from an economic point of view (Carrillo-Rosúa et al., 2002, 2003a and b, 2008a). The main gangue minerals are quartz, white mica (“sericite”), and chlorite with minor quantities of barite, gypsum, dolomite and siderite (Carrillo-Rosúa et al., 2003a).

In relation to hydrothermal alteration, the andesites/dacites, which host the veins, are totally transformed to quartz, white mica plus chlorite, and, to a lesser extent, pyrite, dolomite, albite and epidote (Carrillo-Rosúa et al., 2003a). Hydrothermal alteration is pervasive and the only minerals which remain alteration
are quartz, zircon and apatite, although the last suffers chemical transformation (Carrillo-Rosúa et al., 2005). White mica and chlorite (=pyrite, albite and epidote) is the mineral assemblage in the proximal zones of the hydrothermal alteration. Only in distal zones, in the limit of the deposit, major phenocrysts could remain unaltered: first plagioclase, and in the less altered zones, hornblende and pyroxene. The alteration in the limit of the deposit could be defined as propylitic, with chlorite, epidote and calcite/dolomite.

(b) Dissemination in the silicification, which consists of complete replacement of the volcanic rock by quartz. Sometimes it is very porous, with holes corresponding with old volcanic phenocrysts, like vuggy silica textures. It is found at the surface of the deposit between +70 and +100 m.a.s.l. Ore minerals, mainly disseminated in holes, are very scarce being the mineralogy very flat: mainly pyrite with minor Cu-sulfides and native gold and copper (Carrillo-Rosúa et al., 2002). Apart from the typical coarse-grained quartz, the gangue minerals comprise microcrystalline quartz, white mica (“sericite”) and barite, gypsum, jarosite, natrojarosite and natroalunite in latter veins.

The silicification has halos of advanced argillic and intermediate argillic alteration characterized by quartz, pyrophyllite, kaolinite, illite and interstratified illite-smectite. In distal zones, propylitic alteration also appears.

MINERALOGICAL, TEXTURAL AND CHEMICAL CHARACTERISTICS OF THE PHYLLOSILICATES

It is noteworthy the mineralogical differences, in especial in phyllosilicates, between both types of mineralization in the Palai-Islica deposit (Table 1). The main mineralogical, textural and chemical characteristics of the phyllosilicates in relation to described mineralization types and related hydrothermally altered host rock are described.

Quartz veins with sulfides and related hydrothermal alteration

The petrographic observation and the study of X-ray diffractograms in the veins and related hydrothermal alteration have revealed that phyllosilicates are very abundant, but only chlorite and white mica have been recognized.

Chlorite textures. It appears as spherulitic aggregates (~100 μm) and rarely as inclusions in pyrite grains in the quartz veins (Fig. 3a). This spherulitic aggregates show lighter rims in respect to cores in backscattered images (Fig. 3b).

Chlorite also appears replacing amphibole, pyroxene and the groundmass in the hydrothermal alteration. Chlorite replacing maphic phenocrysts often develops bigger crystals than in replacing the groundmass and it is oriented. Thus, basal plane of chlorite is parallel to “b” and “c” axis of hornblende and pyroxene or, in other words, (001) plane of chlorite is parallel to (010) planes of amphibole and pyroxene (Fig. 3c and d). Occasionally, this maphic phenocrysts transformed to chlorite appears as “xenocrysts” inside the quartz veins (Fig. 3e). Chlorite very rarely
replaces plagioclase, being fine grained like generally in the groundmass and in some cases in mafic phenocrysts.

In the external zone characterized by propylitic alteration or even far from the deposit in zones of “regional” alteration due a widespread meteoric alteration, chlorite is also found replacing mafic phenocrysts, but generally fine grained disappearing orientated textures through outside of the veins (Fig. 3f). TEM studies of this chlorite show the existence of intercalations of 10 Å K-rich layers.

Chlorite mineral chemistry. Table 2 and Figure 4 summarize chlorite microanalyses, being notably the chemical variability. Fe/(Fe+Mg) is directly proportional to \( \text{Al}_{\text{total}} \) or \( \text{IV}_{\text{Al}} \) and Mn and inversely proportional to Si (Fig. 4a, b and c). Si is inversely proportional to \( \text{Al}_{\text{total}} \) (Fig. 4d). For the whole data, interlayer-cations (K+Na+2Ca) are proportional to octahedral vacancies although with higher slope for chlorite from the propylitic alteration than for chlorite from the hydrothermal alteration related to veins (Fig. 4e).

Chlorite from the different textural types has pronounced chemical differences in the Si, Al, Fe, Mg and Mn contents. Spherulitic aggregates of chlorite from the veins have the highest \( \text{Al}_{\text{total}} \) (2.26 - 2.85 a.p.f.u.) and Fe/(Fe+Mg) ratio (0.56 – 0.78), low Si (2.65 – 3.05 a.p.f.u.), being variable the Mn content (0.02 – 0.10 a.p.f.u.). Contrary to the whole analyses, not clear relations have been observed between different elements (Fig. 4a, b, c and d). Chemical zonation, due higher Fe/(Fe+Mg) ratio in the rims that in the cores, is revealed by backscattered images (Fig. 3b). Chlorite in “xenocrysts” from the veins presents a chemical composition between chlorite in spherulitic aggregates in the veins and chlorite in the hydrothermal alteration.

Chlorite in the hydrothermal alteration related to veins has a high content of Si (2.89 - 3.14 a.p.f.u.), low in \( \text{Al}_{\text{total}} \) (2.03 - 2.38 a.p.f.u.) and the lowest Fe/(Fe+Mg) ratio (0.05 – 0.40) of analyzed chlorites (Table 2). Chemical tendencies are the same than in the entirely analyses with the exception of Fe/(Fe+Mg) that is not related to \( \text{Al}_{\text{total}} \) (Fig. 4a).

Chlorite in the propylitic hydrothermal alteration and regional alteration has a distinctive composition characterized by intermediate and homogeneous Fe/(Fe+Mg) ratio (0.30 – 0.43) and the highest Si (3.01 – 3.61 a.p.f.u.), interlayer-cations (0.01 – 0.32 a.p.f.u.), and octahedral vacancies (0.09 – 0.87 a.p.f.u.). Chlorite from the properly propylitic alteration has intermediate Al (2.19 - 2.61 a.p.f.u.), high Mn (0.04 – 0.06 a.p.f.u.) and K (average 0.08 a.p.f.u.), while chlorite in less altered rocks (propylitic to regional alteration) has low Mn (0.01 – 0.05 a.p.f.u.) and \( \text{Al}_{\text{total}} \) (1.76 – 2.28 a.p.f.u.), and high Ca (average 0.03 a.p.f.u.).

White mica textures. White mica is the most abundant phyllosilicate. It appears in the veins as crystals and aggregate of crystals of variable size, from sub-microscopic to a hundred of microns. Mica appears disseminated, intergrowth with...
quartz, interstitial to quartz or even as inclusions in quartz, and also as micro-veins (Fig. 5a and b).

Mica is by far the most abundant phase replacing volcanic plagioclase (as phenocrysts or inclusions in amphibole and pyroxene). This mica varies from sub-microscopic to dozens of microns (typical “sericite”), occasionally with the (001) mica packet parallel to faces of the plagioclase (Fig. 5c and d) showing in TEM images a rare prismatic morphology (Fig. 5e). Mica also replaces mafic phenocrysts as sub-microscopic or microscopic disoriented crystals (Fig. 5f). Rarely mica aggregates also have a “palm” texture, but more frequent is coarse mica oriented in the mafic phenocrysts (Fig. 5g). In this last case, mica exclusively replaces the amphibole and pyroxene or it is accompanied by chlorite with the same orientation (Fig. 5h). In cases where mica and chlorite coexist, 10Å mica packets are found randomly interlayed in the chlorite stacks (Fig. 5i).

Mica also ranges from sub-microscopic to microscopic in the volcanic matrix, although fine grained crystals are much frequents.

The quartz veins are very penetrative. Thus, there is a wide range of transitional occurrences between proper veins and hydrothermally altered volcanic rock. For instance, in the veins it is frequent that mica presents characteristics of hydrothermal alteration: coarse grained that proceeds from the transformation of ferromagnesian phenocrysts and fine grained that precedes from the transformation of plagioclase (Fig. 5j).

Finally, although mica polytypism has not been systemically studied, tv1M, 2M and 3T polytypes has been deduced by XRD and TEM, the first mainly in the hydrothermal alteration and the third one only observed in the veins (Fig. 6a and b).

White mica mineral chemistry. Mica microanalyses have been summarized in Table 3, and Figure 7 and 8. The total interlayer-cations (K+Na+2Ca) range between 0.65 and 0.82, being K the dominant cation, while total octahedral cations range between 1.99 and 2.15 a.p.f.u. The Fe/(Fe+Mg) ratio range between 0.08 and 0.82, although majority of data range between 0.08 and 0.43. Al\textsubscript{total} correlate inversely to Si (m~2, Fig. 7a), and interlayer-cations content does not correlate with Al\textsubscript{total} or Si (Fig. 7b and c). But there is a negative correlation between Fe+Mg and Al\textsubscript{total}, even better with VI\textsubscript{Al} (Fig. 7d), and a roughly positive correlation between Fe+Mg and Si (Fig. 7e). The Fe content is almost always lower than Mg content (Fe/(Fe+Mg)<0.5), presenting both elements a rough positive correlation (Fig. 7f).

The mica from different locations shows also some differences in its chemical composition. Mica in the veins has relatively high content of Al (2.20 – 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 low (3.23 – 3.44 a.p.f.u.) (Fig. 7 and 8). Fe+Mg is very variable reaching relatively high values (0.08 – 0.43 a.p.f.u.). The analyses with higher Fe+Mg, move away from the linear tendency of Fe+Mg versus Al\textsubscript{total} that show the majority of analyses (Fig. 7d). Mica in the veins but originally precedent from the hydrothermal alteration shows a higher K and F content than mica directly originated in the veins (Fig. 8).
Mica in the hydrothermal alteration is characterized by a relatively high Si and low of K (0.60 – 0.77 a.p.f.u.) and total interlayer-cations (0.65 – 0.86 a.p.f.u.), and F (0.00 – 0.06 a.p.f.u.). It is also observed relatively coarse grained mica replacing plagioclase has lower Si and Fe and higher Al and K content than mica replacing ferromagnesinan phenocrysts. In respect to fine mica which replaces plagioclase, that is relatively rich in Si, K, F and Fe and poor in Al in respect to the other types of mica in the hydrothermal alteration (Fig. 7 and 8, Table 3).

Silicification and related hydrothermal alteration

Phyllosilicates in the silicification are very scarce and correspond to interstratified illite-smectite. They appear as aggregates in micro-veins in which also appear native gold crystals (Fig. 9a). These micro-veins formed after the main quartz event generation, but before the formation of sulfates (barite → Fe-Al sulfates → gypsum). Very fine grained phyllosilicates (kaolinite, pyrophyllite, discrete illite and illite-smectite interstratified) + quartz are the most abundant phases in hydrothermal alteration that encloses silicification. It is possible to recognize a mineral zonation from the silicification to the most external zones of propylitic alteration (Fig. 2).

a) Proximal area: It is constituted by quartz, pyrophyllite, kaolinite, discrete illite and illite-smectite interstratified. Zones closer to the silicification are more quartz and pyrophyllite rich, the last mineral disappearing towards peripheral zones. It is observed that pyrophyllite have a major tendency to replace plagioclase, while quartz is enriched in the matrix. Kaolinite corresponds to kaolinite (± nacrite and dickte?) polytypes according to XRD and IR spectra patterns.

b) Distal zone: It is characterized by quartz, illite and interstratified illite-smectite.

The wide presence of interstratified illite-smectite it is deduced in X-ray diffractograms with ethylene-glycol solvation, being deduced a high proportion of illite layers (~ 90% according to Reynolds (1980)). Electronic microscopy, mainly due TEM study, has confirmed interstratified illite-smectite is the only phyllosilicates found in the silicification. Backscattered images show changes in composition in several micron scale (Fig. 9b). In low magnification TEM images it is observed tabular phyllosilicates stacks up to several microns thick. Lattice-fringe images show layers always 10Å thick, and SAED patterns also show a 10Å periodicity, in a certain order pattern (Fig. 10). That is consistent with local ordered pattern in a major disorder sequence. A detailed observation of the lattice-fringe images show termination of several or individual layers in wedge (Fig. 10a and b). It is also observed splitting of 10Å layers in two 5Å layers that in hundred microns along distance fuse with its neighbour split layers (Fig. 10b). This structure could be related to screw dislocation, affecting to an interstratified illite-smectite.

Phyllosilicate mineral chemistry. Microanalysis in these phyllosilicates, except maybe TEM analyses (Tables 4 and 5), could correspond in a considerable
proportion to polycrystalline aggregates rather than individual crystal due the fine
grain character of these phyllosilicates, being, therefore, very difficult interpret these
analyses. These analyses reflect mixing between potassic illite with smectite, quartz,
kaolinite and pyrophyllite as Figure 11 suggests.

The EPMA analyses of coarse phyllosilicates in the silicification (Table 4, 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 (3.65 – 4.21 a.p.f.u.), which suggests the presence of interlayered smectite. Change in backscattered image of theses phyllosilicates is due a higher Si and lower Al content in the brighter zones than in the darker zones. That means there are domains, several microns in size, with higher proportions of smectite layers. AEM analyses of ion milled samples from the silicification have slight higher Al (2.29 – 2.40) and lower Si (3.45 – 3.55) being K similar (0.25 – 0.55 a.p.f.u.) than EPMA analyses. That is congruent with smectite layers are very penetrative, since micron size packets with illite composition have note been detected.

EPMA phyllosilicate analyses from distal alteration zone are very variable, although values up 0.79 and 2.42 a.p.f.u. of K and Al (similar to them of illite in relation to the veins and related alteration), has been found. Therefore, illite without smectite layers at micron size is presents in the distal alteration zone.

DISCUSSION

Characteristics of the transformation of volcanic rocks

It has been deduced that substrate characteristics of host rock (chemistry and crystallography) have great importance in phyllosilicate mineralogy (Table 1) and texture in hydrothermal alteration in relation to veins. The volcanic matrix, constituted by glass or fine-grained crystals, develops chlorite and mica, and a large quantity of quartz. This non-crystalline (or fine-grained) protolith conditions both its high degree of reactivity (the volcanic matrix is the “easiest” microdomain to be altered by hydrothermal fluids) and the tendency to develop fine-grained phases. In contrast, maphic phenocrysts (hornblende and pyroxenes) mainly develop phyllosilicates (chlorite and mica). Chlorite is the main phyllosilicate which transforms maphic phenocrysts in conditions of relatively “weak” hydrothermal alteration: chloritic alteration and propylitic alteration (the weakest alteration type). This phenomenon is due to the fact that chlorite transformation implies a minor chemical change (amphibole and pyroxenes are Fe-Mg-Si-(Al)-bearing in the same way as chlorite). In many cases, chlorite is oriented in the maphic phenocrysts (Fig. 3c, d). Thus, it is deduced the transformation is strongly conditioned by the crystal structure of the protolith (chain structure of Si tetrahedrons) which presents some crystallographic similitude with the layer Si tetrahedrons of chlorite. We propose, then, that hydrothermal fluids, firstly circulating through cleavage planes, produced amphibole/pyroxene dissolution: fluids were abundant, as is common in a hydrothermal system, and hot enough to enhance their reactivity. At the same time than maphic phenocrysts dissolution, epitaxial growth of (001) chlorite packets over
amphibole/pyroxene planes occurred (Fig. 12). Maybe, chlorite crystals with
others orientations also nucleate. But these less abundant and smaller crystals, due
the abundance of fluid could dissolve. The result is that crystal growth onto larger
pre-existing oriented crystals is favoured, in a way similar to an Ostwald Ripening
model (e.g. Eberl et al., 1990) but accelerated for the high reactivity due the high
fluid activity. Other types of transformation are rejected, such as the solid state
transformation for illite-smectite proposed by Altner and Ylang (1997). The
intervention of a large quantity of fluids could easily produce dissolution processes.

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

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

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

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

**Implications of chlorite chemistry**

In the Palai-Islica, chlorites have a notable chemical variety linked to texture. Firstly, it is possible to distinguish between chlorites in the quartz veins and the related chloritic and sericitic alteration, and chlorites in the propylitic alteration. The main difference is the relatively homogeneous Fe/(Fe+Mg) ratio, and higher Si (Fig. 4d) content in the latter with respect to the former. Since chlorites are widespread in the region as a regional alteration feature, chemical analyses could be useful to detect signs of ore-bearing-related hydrothermal activity.

Secondly, the variable chemical composition of chlorite related to the hydrothermal fluids themselves is very notable: chlorite from the quartz veins; chlorite from the chloritic and sericitic alteration; and the differences between them. The Fe/(Fe+Mg) ratio is extraordinarily broad, between 0.05 and 0.78. This is one of the broadest found in a range of environments, such as metamorphic or diagenetic/very low grade metamorphic, but also geothermal fields and other hydrothermal deposits (Fig. 13). The observed Fe/(Fe+Mg) variation in hydrothermal Palai-Islica chlorite is related to the characteristics of the hydrothermal fluids and the mechanism of chlorite formation. Chlorite precipitated directly from the hydrothermal fluids, like chlorite aggregates in the veins, has a high Fe/(Fe+Mg) ratio, reflecting the chemical composition and perhaps also the temperature of the hydrothermal fluids (e.g. Kranidiotis and MacLean, 1987, Saccocia and Seyfried, 1994). Nevertheless, chlorite produced by a transformation process (i.e. originating in the hydrothermal alteration) has a low Fe/(Fe+Mg) ratio, since its composition reflects the characteristics of hydrothermal fluids (i.e. composition and temperature) plus the composition of the substrate. Both maphic phenocrysts and the rock in general are relatively Mg rich, with low Fe/(Fe+Mg) ratio (Fig. 4). In addition, chlorites formed replacing phenocrysts, but subsequently incorporated within veins (Fig. 3d), have an intermediate composition. This signals that a higher interaction with the fluids increases the Fe/(Fe+Mg) ratio. In other words, hydrothermal fluids produce relatively high Fe chlorites by direct precipitation (also observable in other hydrothermal and geothermal environments, e.g. Kranidiotis and MacLean, 1987, Sanchez-Esparza et al., 2000; Hibbi and Marignac, 2001; Zaccarini et al., 2003;) and host rocks composition condition the reactant hydrothermal fluid chemistry in the host rock itself.

Si and Al, which correlate positively for ore-related hydrothermal chlorite (not in “propylitic” chlorite, Fig. 4d), are other components which clearly distinguish between chlorite from the quartz veins (higher in $A_{\text{total}}$ and $^{IV}A_{\text{I}}$, and lower in Si content), and the hydrothermal alteration (lower in $A_{\text{total}}$ and $^{IV}A_{\text{I}}$, and higher Si content). The correlation of Fe/(Fe+Mg) with Al (positive) and Si (negative) found
in the hydrothermal chlorite could be explained with Tschermack substitution
(SiMg↔IIIAlIVAl) (e.g. Walshe, 1986).

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

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

Implications of mica chemistry

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

Therefore, composition of this potassic octahedral mica could be explained by
illitic (SiIIVI\text{III}AlIV\text{IV}K\text{I}) and phengitic ((Fe+Mg)\text{IIVI}Si\text{IIVI}AlIV\text{IV}Al\text{I}) substitution vectors.
The content of F in this mica is low, although significant (up to 0.08 a.p.f.u.). There are some differences between different textural mica types. Mica from the veins usually has a lower illitic component and more F than mica from the chloritic and sericitic alteration (Fig. 7a and 8d). The differences in the illitic component could be related to “disequilibrium” and even to formation temperature. It is known that muscovite “sensu stricto” began its formation in a very low-grade metamorphic environment, in epizone conditions, around 200°C (e.g. Abad Martínez, 2002). In the Palai-Islica mica system, however, no muscovitic composition has been found at temperatures as high as 300°C (Morales-Ruano et al., 2000; Carrillo-Rosúa et al., 2003a). Similar non-muscovitic composition has been found in other Au epithermal deposits, such as Red Mountain (USA) or El Dorado (Chile). Even in these cases, more phengitic and illitic composition appears, but lower formation temperatures are also suggested (Bove et al., 2002; Carrillo-Rosúa et al., 2008b).

A complementary view could be deduced from the polytypism of Palai-Islica mica: the existence of different polytypes including 1M polytype mainly in the hydrothermal alteration domain (Fig. 6), could suggest “variable disequilibrated conditions”.

Mica in the veins could be “less disequilibrated” than mica in the hydrothermal alteration on account of a higher fluid/rock ratio in the former as compared with the latter, rather than being due to the time factor, given that they could be formed during the same time interval. A higher temperature of mica from the veins could be another factor. Higher temperatures in other environments, such as very low-grade metamorphism, led to lower and more homogeneous illitic levels (e.g. Lee et al., 1986; López Munguira and Nieto, 2000; Abad Martínez, 2002). This aspect will be discussed in the specific geothermometry section below. Ore-forming fluids are clearly responsible for the introduction of F, as is also suggested by apatite chemistry (Carrillo Rosúa et al., 2005). Therefore F in mica could be used as a “chemical vector” related to the “intensity” of hydrothermal activity in a certain zone of the Palai-Islica deposit, and by extrapolation for other similar hydrothermal areas.

There are further chemical differences linked to specific mica textural groups. “Coarse” mica, replacing volcanic plagioclase, has a higher K and Al content, along with a lower Si, and a generally lower Fe content (this suggesting a higher illitic level), than mica which replaces amphibole and pyroxene. Microcrystalline mica, replacing volcanic plagioclase, has relatively high K, but also high Si and Mg, and low Al and Fe, suggesting a contamination of the analysis with some sub-microscopic chlorite. The cause for these chemical differences could be, again, related to kinetic problems and the types of crystallization processes. Mica that replaces plagioclase crystals is finer than mica replacing maphic phenocrysts, having a higher specific surface to equilibrate with the hot hydrothermal fluids, and is therefore less “disequilibrated”, i.e. less illitic in its composition. Moreover, in mica replacing amphiboles and pyroxenes, mica really replaces chlorite by chlorite
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 – 150°C 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 quartz 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.
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 150–300°C 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 260°C ± 30°C and seems to be too high for the presence of kaolinite, but appropriate to pyrophyllite
formation (Berman, 1988; Bjorkum and Walderhaugh, 1993). In hydrothermal systems it is assumed that kaolinite occurs at temperatures not higher than 200°C (e.g. Browne, 1978; Henley and Ellis, 1983; Reyes, 1990), while in diagenetic and/or very low-grade metamorphic sequences kaolinite transforms to become dickite at temperatures of 130°C (e.g. Ehrenberg et al., 1993; Lázaro et al., 2003). This apparent inconsistency between fluid inclusion and mineralogical data could be explained by kinetic effect. Hot hydrothermal fluids interact more (more fluids + more time) with the rock in the inner zone surrounding fluid conduits (i.e. the silicification and the inner zones of the advanced argillic envelope) than in outer zones of the advanced argillic envelope, where kaolinite appears.

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

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

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

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

Outside the Palai-Isla deposit, propylitic alteration becomes a regional alteration feature, with the disappearance of epidote. This propylitic alteration represents an area with a low infiltration rate of hydrothermal fluids, a low fluid/rock ratio, and the presence of other cool meteoric regional fluids. These are responsible
for the “regional alteration” and, mixed with a certain proportion of hydrothermal fluids, they originate propylitic alteration. Thus, these rocks have suffered a minor chemical change, reflected in the chlorite chemistry, with the Fe/(Fe+Mg) ratio equal to the maphic phenocrysts.

CONCLUSIONS

Phyllosilicates are widespread phases among the mineralization and hydrothermal alteration zones in the Palai-Islica deposit. Two different phyllosilicate (alterations and/or neo-formed) assemblages have been distinguished in relation with two different kinds of ores: mica and chlorite associated with polymetallic gold and silver-rich veins; mica, interstratified illite-smectite, and kaolinite and pyrophyllite associated with gold dissemination in the silicification. The former, defined as chloritic and sericitic, is originated by near-neutral, highly metal-rich hydrothermal fluids, while the latter is produced by acidic, gold-bearing hydrothermal fluids in which a neutralization process and kinetic aspects determine a certain mineral zonation pattern (silicification → advanced argillic→ intermediate argillic). Noteworthy here is that gold precipitation occurs at temperatures ≤200ºC, which is lower than that responsible for the main hydrothermal alteration/silification formation stage. This is due to its association with interstratified illite-smectite. A propylitic halo (chlorite, epidote, calcite-bearing) encloses the other alteration zones. Therefore, two epithermal environments have been identified in the same deposit: intermediate-sulfidation and high-sulfidation.

The advanced and intermediate argillic alteration zones develop very fine grain phyllosilicates, more concentrated in volcanic phenocrysts in respect to the matrix. This is related with a rapid, enhanced dissolution process due to the low pH of the hydrothermal fluids. In the chloritic and sericitic alteration zones, coarse-grained phyllosilicates (mainly inside maphic phenocrysts due to their anisotropic structure) and epitactic crystallization features (maphic phenocrysts → chlorite → mica) appear, suggesting a weaker dissolution process due to the near-neutral conditions of the hydrothermal fluids.

Chlorite and mica show a very wide compositional range. Chlorite chemistry, mainly Fe/(Fe+Mg) ratio, and Si and Al content, distinguishes between an origin related with high- or low-temperature fluids (i.e. chlorite of propylitic/regional alteration origin). In addition, these elements strongly differ in concentrations between chlorites in the hydrothermal alteration zone and that directly precipitated in the veins, thus suggesting different genetic conditions (i.e. fluid/rock ratio, influence of substrate, temperature...). Mica also presents some chemical composition differences according to its location: veins or hydrothermal alteration, the latter being richer in illitic component and poorer in F, directly related with ore-fluids. The composition and polytypism of mica suggest that equilibrium conditions have not been reached during hydrothermal activity.
Although chlorite thermometry is said to be invalid (e.g. Jiang et al., 1994), temperatures calculated with available empirical geothermometers could be useful to estimate a range of formation temperatures, to suggest vectors of temperature variation in a hydrothermal deposit, or, when combined with other methods such as fluid inclusion, to give clues about the thermal evolution of a hydrothermal system.

ACKNOWLEDGEMENTS

This work has been supported by the Spanish projects CGL-2006-02594/BTE (Ministry of Education and Science and FEDER), and RNM-732 (Junta de Andalucía). J. Carrillo-Rosúa thanks MEC postdoctoral grant from MEC for his support. Authors are very grateful to Fernando de la Fuente Consultores S.L. for providing drill cores samples and for his help during field work and to and to technical staff of the “Centro de Instrumentación Científica” from University of Granada for his assistance with TEM, SEM and EPMA work. The manuscript was significantly improved by helpful suggestions and critiques by Dr. Saccocia and an anonymous reviewer. Editors Derek F. Bain and Crawford Elliott are sincerely thanked for his constructive comments and encouragement.

REFERENCES


Figure 1. Carrillo et al

Calc-alkaline volcanism
High K calc-alkaline and shoshonitic volcanism
Ultrapotassic volcanism
Basaltic volcanism

Paleozoic-Mesozoic basement rocks
Upper Miocene calc-alkaline rocks
Tertiary sedimentary rocks
Quaternary sediments (a) alluvial and (c) colluvial
Faults and limit of hydrothermal alteration
Outcropping Palai-Islaca deposit
Figure 2. Carrillo et al

- Carboneras fault
- Metamorphic basement
- PALAI
- Silicification
- Advanced/intermediate argillic alteration
- Quartz veins with sulphides
- Chloritic-sericitic alteration
- Propylitic alteration
Figure 3. Carrillo et al
Figure 4. Carrillo et al

- **Quartz veins**
- "Transitional" characteristics
- (veins/proximal hydrothermal alteration)
- Proximal hydrothermal alteration: related to quartz veins, and related to silicification

![Graphs and diagrams showing mineral compositions and characteristics](image-url)
Figure 5. Carrillo et al
Figure 6. Carrillo et al
Figure 7. Carrillo et al

Quartz veins:
- apparently neo-formed
- formed primary in the hydrothermal alteration

Hydrothermal alteration related to veins:
- replacing mafic phenocrysts
- coarse grained
- fine grained
- replacing plagioclase

- Phengite
- Ferrimuscovite

The figure shows various diagrams with different axes and data points indicating different types of alteration and vein formation in a hydrothermal setting.
Figure 8. Carrillo et al
Figure 9. Carrillo et al
Figure 10. Carrillo et al
Figure 11. Carrillo et al

Silicification

Advanced argillic alteration

Intermediate argillic alteration
Figure 12. Carrillo et al
Figure 13. Carrillo et al

Flu Inclusions (quartz)
Fluid Inclusions (volcanic quartz)
Quartz veins
Hydrothermal alteration

Kranidiotis & MacLean (1987)
Walshe (1986)
Cathelineau (1988)
Table 1.

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<th>Veins Sericitic alteration</th>
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X: scarce; XX: abundant; XXX: very abundant.
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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.

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<td>0.02</td>
<td>0.00 0.00</td>
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**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              |
| 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              |
| Ti     | 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              |
| 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              |
| 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              |
| Ca     | 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              |
| K      | 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              |
| Na     | 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              |
| 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              |
| 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              |
| Cl     | 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                      | 0.00                      | 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 neofomed; 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.
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<th>Intermediate argillic (n=31)</th>
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|                  | Ave                  | S.D.                     |
|                  |                      |                          |
| Si               | 3.65                 | 4.21                     |
| Al₃⁺              | 0.00                 | 0.35                     |
| Ti            | 1.78                 | 1.92                     |
| Fe            | 0.01                 | 0.01                     |
| Mg            | 0.03                 | 0.05                     |
| Mn            | 0.00                 | 0.00                     |
| Ca            | 0.02                 | 0.03                     |
| K            | 0.30                 | 0.45                     |
| Na            | 0.02                 | 0.04                     |
| Interlamina   | 0.37                 | 0.53                     |
| Cl            | 0.00                 | 0.01                     |

n: number of analyses; 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.

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<td>0.72</td>
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S.: Illite/interstratified illite-smectite from the silicification analyzed in an ion milled sample preparation; A.A.A.: mica/mica-smectite interstratified from the advanced argillic alteration analyzed in a formvar Cu grid.
FIGURE CAPTIONS

Figure 1:
(a) Cabo de Gata – Cartagena volcanic province in SE of Spain with the location of
the most important ore deposits volcanic belt (adapted from Lopez-Ruiz and
Rodriguez-Badiola, 1980): (1) Cabo de Gata. (2) Rodalquilar. (3) Carboneras (Palai-
(b) Schematic geological map showing the location of the Palai-Islica deposit and
main geological units (adapted from IGME, 1974).

Figure 2:
Schematic picture of Palai-Islica deposit which include the position of the different
kinds of mineralisations which appear on it. In the silicification, an arrow indicates a
phyllosilicate micro-vein.

Figure 3:
Transmitted light (parallel and crossed polarized) and backscattered electron (BSE)
photomicrograph of chlorites. (a and b) Spherulitic aggregates of chlorite (chl)
intergrowing with coarse quartz and sulphides in the veins. In the BSE image (b) it is
observed dark cores and bright rims in chlorite and mica (mi) interstitial and maybe
replacing chlorite. (c and d) Prismatic and basal section of hornblende (in “maximum
of illumination” and “extinction” positions) replaced by coherent orientated chlorite
in the hydrothermal alteration related to quartz veins. (e) Chlorite precedent of
hornblende replacement inside a quartz vein. (f) Incipient replacing of hornblende
(hbl) by chlorite (chl) in the propylitic alteration.

Figure 4:
Binary diagrams showing compositional variations, expressed at atoms per unit
formula, between tetrahedral and octahedral cations and interlayer cations and
vacancies in the different types of chlorites. It is showed for comparison the
Fe/(Fe+Mg) ratio of the unaltered volcanic rock and phenocrysts (data from
Fernández Soler, 1996) which hosts the Palai-Islica deposit. EPMA analyses are
plotted in black without fill, TEM-AEM analyses in dark grey fill, and SEM analyses
in grey color without fill. The influence of mica contamination and correlation line in
chlorite analyses is shown by a dotted and solid line respectively if (e).

Figure 5:
Transmitted light (plane-polarized and cross-polarized light) and TEM
photomicrographs of mica. (a) Micro-veins of mica of sub-microscopic character
inside a quartz vein. (b) Coarse mica intergrowing with quartz. Sub-microscopic (c)
and micron size (d) mica replacing a volcanic plagioclase inside hydrothermal
alteration related to quartz veins. In (d) it is observed orientated crystals parallel to
cleavage plagioclase planes, which in low magnification TEM image (e) shown a
prismatic morphology. Hornblende replaced by fine grained disorientated mica (f) and coherent orientated mica (g) in the hydrothermal alteration related to quartz veins. (h) Maphic phenocrysts prismatic section replaced by orientated chlorite and mica. (i) TEM lattice-fringe image of chlorite (14 Å) with coherent mica layers (10 Å, marked with an arrow) in a zone of mica-chlorite intergrowth similar to (h). (j) Zone of transition between a quartz vein and the related hydrothermal alteration. It is observed coarse grained mica provably originated by a transformation of a maphic phenocrysts and fined mica precedent from plagioclase transformation (inside a square in the left down corner).

Figure 6:
(a) XRD patterns of <2μm bulk sample fraction from hydrothermal alteration (down) and of mica replacing plagioclase separated by microdrilling (up) with vertical lines showing reflections of different polytypes according to Bailey (1980) and Moore and Reynolds (1997). 2.58 Å and 2.80Å peaks are marked since I_{2.80}/I_{2.58} has been related to 2M/(2M+1Md) (Maxwell and Hower, 1967). 2.42 Å, 2.45 Å (ordered) and 2.38 Å (disordered) peaks are marked in order to estimate disorder of the n60º kind (Moore and Reynolds (1997)).
(b) SAED patterns of mica showing 2M polytype (left) and 3T polytype (right) from mica replacing plagioclase in the hydrothermal alteration and disseminated mica in a vein, respectively.

Figure 7:
Binary diagrams showing compositional variations, expressed at atoms per unit formula, between major elements in the different types of mica in the quartz veins and related hydrothermal alteration. It is showed for comparison the muscovite composition (Ms) and different chemical vectors: illite substitution (Si_{1\square}Al_{IV},K_{IV}), phengite substitution ((Fe+Mg)_{1}Si_{VI}Al_{IV}Al_{III}), ferrimuscovite substitution (Fe^{3+}_{IV}Al_{III}). EPMA-WDX analyses are plotted in black without fill, TEM-AEM analyses in dark grey fill, and SEM-EDX analyses in grey color without fill.

Figure 8:
Frequency histograms for (a) K and (d) F content expressed at atoms per formula unit in the different types of analyzed mica. EPMA-WDX analyses are plotted in black columns, TEM-AEM analyses in dark grey color columns, and SEM-EDX analyses are in light grey color columns.

Figure 9:
Backscattered electron (BSE) images of illite/illite-smectite (il-sm) in the silicification. In (a), illite-smectite appears together native gold grains (au) and quartz, while in (b), it is appreciable its chemical zonation.
**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↓ Al IV↓ 1 K↓ 1) and phengite substitution ((Fe↓ Mg↓ ) Al VI↓ 1 Al IV↓ 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 1a 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
secondary type, but coetaneous with hydrothermal activity. These Th data, not in vertical scale, are from Carrillo-Rosúa (2005).
TABLE CAPTIONS

Table 1:
Summary of distribution of phyllosilicates at the Palai-Islica deposit, in relation to the primary mineralogy of the host rock.

Table 2:
Chemistry of chlorite analyzed by EPMA in the quartz veins and related hydrothermal alteration of the Palai-Islica deposit (normalized to O_{10}(OH)_8).

Table 3:
Chemistry of mica analyzed by EPMA in the quartz veins and related hydrothermal alteration of the Palai-Islica deposit (normalized to O_{10}(OH)_2).

Table 4:
Chemistry of phyllosilicates analyzed by EPMA in the silicification and related hydrothermal alteration of the Palai-Islica deposit (normalized to O_{10}(OH)_2).

Table 5:
Individual HR-TEM analyses of phyllosilicates from the silicification and advanced argillic alteration (normalized to O_{10}(OH)_2).