TEXT S2: PETROGRAPHY.

LAS MONTAÑETAS FACIES.

Perovskite-bearing amphibole pyroxenites.

The overall rock microstructure of alkali pyroxenites is that of a prismatic pyroxene cumulate with brown interstitial Mg-hastingsite/pargasite in variable amounts. Pyroxene crystals are subidiomorphic and frequently zoned showing a pink core (titanian diopside) full of rutile needles and pale green or uncoloured rims (diopside). Minor brown phlogopite also occurs in some samples growing around pyroxenes.

Apatite is ubiquitous and commonly forms interstitial aggregates of subidiomorphic to allotriomorphic crystals between pyroxenes. They are full of fluid inclusions. Allotriomorphic perovskite includes crystals of apatite and titanomagnetite. Titanomagnetite has also an interstitial position among pyroxenes. Some samples contain allotriomorphic titanite crystals growing around perovskite and interstitial nepheline. In this case pyroxene in the contact with interstitial nepheline shows a low greenish pleochroism (diopside).

Pegmatite ijolites.

Pegmatite ijolites are coarse to very coarse grained rocks frequently with comb texture defined by the orientation of large (2-10 cms) pyroxene crystals. They vary compositionally from ijolitic terms to feldspathic ijolites or even malignites grading to nepheline syenites. In the less evolved rocks the occurrence of perovskite, sometimes surrounded by titanite, is common. Pyroxene forms subidiomorphic green crystals with abundant inclusions of apatite and calcite. It is a calcic pyroxene (Ti-poor diopside) in the less evolved varieties or calc-sodic (aegirine augite) in feldspathic ijolites or malignites. Subidiomorphic brown mica grows over pyroxene.

Nepheline is usually interstitial to all other phases, except alkali feldspar, and is heavily altered to zeolites and carbonates. Feldspathic ijolites and malignites contain interstitial alkali feldspar. Calcite, very common in the most feldspar-rich terms, is included in pyroxenes or fills interstices between other minerals.

Apatite is subidiomorphic and occurs as inclusions in pyroxene, perovskite, biotite, nepheline and alkali feldspar. It frequently contains many fluid inclusions and forms radiate aggregates. When it is included in nepheline or alkali feldspar it appears corroded. Titanite is allotriomorphic and grows interstitially between pyroxenes or around perovskite. In some samples melanite occurs growing over titanite.

Nepheline syenites.

They form dykes or masses that grade from pegmatite ijolite to silicocarbonatites or carbonatites. They are medium to coarse grained rocks with a general texture defined by large idiomorphic alkali feldspar crystals. This mineral is very perthitic and frequently shows Karsbald twins. It includes pyroxene, apatite and zircon crystals.

Pyroxenes are idiomorphic aegirine augites forming short prisms with calcite and apatite inclusions. They are commonly corroded by interstitial carbonates and show oxidized rims. Biotite forms subidiomorphic crystals with rims transformed to Fe-Ti oxide minerals. Nepheline, heavily transformed into calcite and zeolites, forms subidiomorphic crystals included in alkali feldspar. Calcite can form subidiomorphic inclusions in pyroxene or fill interstices between alkali feldspars (Figure S4a). Occasionally the abundance of calcite is outstanding reaching up to 15 % total volume

of the nepheline syenites. In contact with alkali feldspar reaction rims composed of colourless garnet, analcime and prehnite can be observed.

Apatite, pyrochlore, zircon and titanite are common accessory phases. Subidiomorphic prismatic apatite occurs as corroded inclusions in pyroxene, nepheline and alkali feldspar. Pyrochlore occurs as metamictic subidiomorphic inclusions in alkali feldspar. Subidiomorphic zircon crystals are frequently fractured. Titanite is scarce and forms idiomorphic crystals with oxide-rich rims.

The disequilibrium textures shown by pyroxene and alkali feldspar crystals in contact with calcite could be attributed to the thermal effect produced by the intrusion of gabbros, pyroxenites and wehrlites from Montaña Blanca-Milocho (as designated by [33]).

Carbonatites and silicocarbonatites.

Carbonatites are very heterogeneous rocks both texturally and compositionally. Coarse-grained sövites are dominant with variable content of silicate minerals. Occasionally silicates reach 50 % of the rock and then they can be classified as silicocarbonatites. Dykes with lower thickness and magnitude are usually fine to medium grained alvikites.

Calcite forms large platy subidiomorphic crystals commonly with consertal texture and occasionally with small inclusions of barite and strontianite. Aegirine augite/aegirine form subidiomorphic crystals with many apatite and calcite inclusions. They occasionally occur intergrown with calcite.

Biotite occurs as large primary idiomorphic crystals, frequently zoned. In the carbonatites affected by the shear zones these minerals form granoblastic aggregates with common kink-bands. Rims are frequently transformed to magnetite.

Subidiomophic, very perthitic alkali feldspar crystals (sanidine) are always strongly transformed to aggregates consisting of albite, hyalophane, prehnite, pumpellyite, carbonates and analcime. Nepheline occurs as idiomorphic pseudomorphs composed of aggregates of phrehnite-pumpellyite, epidote, magnetite, garnet, albite, chlorite and analcime.

Prismatic subidiomorphic or subrounded apatite inclusions are seen in sanidine, aegirine augite, biotite-phlogopite and calcite. In calcite, apatite forms aggregates of radiate acicular crystals inside or around the crystal margins. In this case crystals carry frequent fluid inclusions. This observation is consistent with the experimental results in the system CaO-CO_2-H_2O-P_2O_5, which showed that P_2O_5-bearing systems precipitate apatite before calcite [62].

Magnetite and Mn-rich ilmenite form discrete subidiomorphic crystals. Magnetite also appears as inclusions in sanidine and calcite. Titanite is scarce and forms idiomorphic crystals frequently included in calcite and overgrown by oxide minerals. Zircon forms idiomorphic fractured crystals included in calcite and alkali feldspar. It is often transformed to baddeleyite [55]. Pyrochlore forms zoned subidiomorphic crystals included in calcite (Figure S4b and Figure S4c) and alkali feldspar. Monazite is included in apatite crystals or around it. Minor crystals of chalcopyrite, sphalerite and pyrite can be found.

Some of the carbonatites frequently show a pinkish or purple colour with calcite full of hematite microexsolutions. This feature and also the reaction coronas composed of magnetite, epidote, chlorite, titanite and calcite found around aegirine augite/aegirine in contact with calcite or the growth of britholite around apatite crystals could be attributed to the thermal effect produced by the intrusion of gabbros, pyroxenites and wehrlites from Montaña Blanca-Milocho (as designated by [33]).

LOS JABLITOS FACIES.

Nepheline syenite.

Los Jablitos nepheline syenites are composed by alkali feldspar and nepheline, together with aegirine augite/aegirine. Apatite and titanite are common accessory phases. They can show both agpaitic or miaskitic textures.

In the agpaitic types, nepheline (partially transformed into zeolites) appears as subidiomorphic crystals that host aegirine augite epitaxic inclusions. These early nepheline crystals are set in a groundmass composed of subidiomorphic aegirine augite and alkali feldspar crystals. In other samples with miaskitic textures aegirine augite crystallizes first and nepheline does so a later stage.

Apatite forms subidiomorphic crystals included in pyroxene, titanite, nepheline and alkali feldspar. It is frequently corroded and contains many fluid inclusions. Biotite only appears in some rocks as subidiomorphic crystals with oxidized rims. Minor amounts of titanite form small subidiomorphic crystals included in nepheline and alkali feldspar.

Carbonatite.

Los Jablitos nepheline syenites are cut by thin medium- to fine-grained alvikite dykes. They are dark pink or purple in colour with calcite crystals full of hematite microexsolutions. This could be attributed to the thermal effect produced by the intrusion of gabbros, pyroxenites and wehrlites from Montaña Blanca-Milocho (as designated by [33]).

Apatite forms subrounded discrete grains or aggregates included or placed around calcite margins.

MONTAÑA DE LOS FRAILES FACIES.

Melteigites-ijolites-urtites.

In Montaña de Los Frailes biotite melteigites are dominant and grade locally to ijolites-urtites. The overall rock microstructure of these rocks is that of a prismatic pyroxene cumulate. Pyroxene crystals are subidiomorphic and frequently zoned showing a pink core (titanian diopside) and pale green or uncoloured rims (diopside). Minor brown biotite also occurs in some samples growing around pyroxenes.

Apatite is ubiquitous and commonly forms interstitial aggregates of subidiomorphic to allotriomorphic crystals between pyroxenes. Titanomagnetite has also an interstitial position among pyroxenes. Some samples contain allotriomorphic titanite between the pyroxene crystals and interstitial nepheline and calcite. In this case pyroxene in contact with interstitial nepheline has a low greenish pleochroism (diopside).

Some bands inside the dominant melteigite are nepheline-rich and can be classified as ijolites or even urtites. In urtite samples, fresh idiomorphic nepheline crystals can be observed. Green subidiomorphic pyroxene crystals and idiomorphic apatite and titanite can be observed among idiomorphic nepheline crystals. Biotite with a dark to light green pleochroism grows over pyroxene. In some areas interstitial calcite crystals occur. Andradite garnet grows around pyroxene in these calcite-filled areas (Figure 4d).

Nepheline syenite network.

Late nepheline syenites form a network of pinkish dykes and veins that cut the melteigites-ijolites-urtites. They are heterogranular rocks with coarse to very coarse

grain-size and frequently showing comb textures due to the orientation of alkali-feldspar and pyroxene aggregates. The occurrence of radiate aggregates of prismatic aegirine augite crystals, frequently transformed to oxide minerals, is quite common. They are included in subidiomorphic alkali feldspar and heavily altered nepheline. Allotriomorphic fractured zircon grains commonly occur.

Carbonatite.

In Montaña de Los Frailes carbonatite dykes show two trends N 8 E- 40º E (around 20 cm thickness) and N 160º E-70º E (around 1 m thickness).

Carbonatites oriented following a N 160º E trend usually show zonation parallel to the dyke margins. In the margins idiomorphic calcite crystals are concentrated. Calcite crystals include prismatic alkali feldspar, idiomorphic titanite (ore-rich rims) (Figure S4e), red pleochroic idiomorphic biotite plates and prismatic apatite crystals both isolated or as aggregates. In the inner areas silicate minerals are more abundant: idiomorphic green pyroxene crystals, prismatic alkali feldspar crystals (Karsbald twinned) sometimes partially albitized, red idiomorphic biotite (occasionally growing around pyroxene) and large idiomorphic titanite crystals (Figure S4e). Apatite is also very common and shows prismatic shapes, that form fibrous-radiate aggregates. Calcite fills interstices between other minerals.

Carbonatites following a N 8º E 40º E trend are calcite-rich and contains minor amounts of red biotite plates, prismatic apatite and allotriomorphic alkaline feldspar among large calcite crystals.

BARRANCO DEL AGUA SALADA FACIES.

Alkali pyroxenites.

Alkali pyroxenites grading to melteigites are predominantly medium to coarse grained rocks containing usually phlogopite and perovskite (Playa de Esquinzo) or amphibole (Playa de Tebeto). In the area around Barranco del Agua Salada these rocks are scarce or absent. They are commonly adcumulates to mesocumulates with clinopyroxene (titanian diopside and diopside), kaersutitic amphibole, subidiomorphic perovskite and idiomorphic apatite as cumulus phases while phlogopite, titanomagnetite, titanite, nepheline and calcite are intercumulus minerals.

Phlogopite grows around pyroxene and amphibole as subidiomorphic crystals. Titanite occurs as allotriomorphic crystals growing around titanomagnetite or perovskite or also as idiomorphic crystal inclusions in nepheline. Perovskite forms subrounded grains always surrounded by Fe-Ti oxide minerals and titanite (Figure S4f) with some apatite inclusions. Nepheline occurs always interstitially and totally transformed to zeolites and carbonates. In some samples calcite grains occur interstitially or in veins.

Perovskite-bearing ijolites s.l.

Perovskite-bearing ijolites s.l. are meso- to orthocumulates, with the nepheline/clinopyroxene ratio increasing from melteigite to ijolite (Figure S4g and S5a**)**. This is the dominant rock type in Barranco del Agua Salada Facies but it is also common in the coastal outcrops associated with alkali pyroxenites.

In perovskite-bearing melteigites the cumulus phase is a prismatic to subidiomorphic yellow clinopyroxene (Figure S4g and S5a). Nepheline is an intercumulus mineral representing variable amount of trapped liquid. Minor brown phlogopite and kaersutite are additional intercumulus mineral phases in the melteigites found in Playa de Tebeto outcrops. Abundant apatite and perovskite are present as early

crystallization phases. In some samples allotriomorphic titanite is seen in place of perovskite.

In perovskite-bearing ijolites, heavily altered nepheline (muscovite + cancrinite + natrolite pseudomorphs) constitutes the cumulus phase while pyroxene, magnetite, apatite and perovskite occur interstitially. These ijolites have idiomorphic, square to hexagonal-sectioned crystals of nepheline set in compact aggregates of prismatic subidiomorphic diopside. In finer-grained samples, the clinopyroxene aggregates form continuous rims around the nepheline and define a "web-like" texture. Apatite grains are commonly enclosed in nepheline and pyroxene. Titanite grows as allotriomorphic crystals around titanomagnetite or perovskite or as idiomorphic inclusions in nepheline. Perovskite forms subrounded grains always surrounded by titanite with some apatite inclusions. In urtitic ijolites the occurrence of interstitial melanite crystals is common.

Biotitic malignites (Feldspathic ijolite - biotitic malignites - nepheline syenites).

This group includes a set of rocks with very variable grain size and contents of alkali feldspar, nepheline and mafic minerals found in the coastal area south of Playa del Águila. The resulting rocks can be classified as feldspathic ijolites, malignites or nepheline syenites.

In fine-grained types, the rock texture is characterized by the presence of poikilitic crystals both idiomorphic (titanite and zoned biotite) and allotriomorphic (nepheline, alkali feldspar and calcite) containing small idiomorphic zoned pyroxene crystals (titanian diopside, diopside and aegirine augite), apatite and titanomagnetite. Inside the biotite crystals colourless cores and outer rims with strong red-brown pleochroism are observed.

In coarse- to very coarse-grained varieties, textures are equigranular with large idiomorphic zoned pyroxene (titanian diopside, diopside and aegirine augite), apatite, titanite, perovskite and biotite (Figure S5b). Nepheline, alkali feldspar (Figure S5c) and calcite occur interstitially. Biotite forms large crystals growing over or as aggregates around pyroxenes. Nepheline is subidiomorphic and occurs interstitially or as inclusions in alkali feldspar.

It is interesting to point out that pyroxene crystals show a strong and frequently discontinous zoning. Cores are usually colourless or with a light pink pleochroism. Towards the outer zones a colourless zone appears, and, in some crystals, in contact with alkali feldspar/calcite rich areas, pyroxene rims show a light or even dark green colour. This zoning can be continuous although in some crystals it changes directly from the pink inner zone to outer dark green rims.

Feldspathic ijolite veins.

These rocks occur locally as veins cutting and brecciating perovskite-bearing melteigites-ijolites in the ravines around Barranco del Agua Salada (Montaña de la Morriña, Barranco del Agua Salada) or in the Playa de Esquinzo. Feldspathic ijolites contain aegirine augite and short hexagonal or square crystals of zoned nepheline, which is invariably highly altered (to cancrinite and white mica) and pinkish or almost red in colour. Pyroxene and nepheline are enclosed by clear "pools" of interstitial or poikilitic alkali feldspar. Orange-brown phlogopite is also common. Accessory minerals include titanite, apatite and magnetite.

This feldspathic ijolite contains numerous fragments of variable size of biotitic micromelteigite and the adjacent perovskite-bearing melteigites-ijolites.

Intrusive breccias with medium- to fine-grained ijolite-nephelinite matrix.

These are very heterogeneous porphyritic rocks containing abundant fragments of xenocrysts and different rock types. This breccia can be observed south of Playa del Águila.

The most common phenocrysts are subidiomorphic (diopside and titanian diopside) pyroxenes and heavily altered nepheline (zeolites + carbonates). Biotite phenocrysts also occur occasionally. The groundmass contains small nepheline and calcite crystals interstitially or as ocelli.

The xenocrysts are fragments of fractured apatite, perovskite, titanite and ore minerals (surrounded by biotite), aegirine augite and mixed crystals with green core (aegirine augite) and pink rim (titanian diopside). Fragments of pyroxenites, perovskite-bearing melteigites-ijolites, biotite malignites, pegmatite ijolites and nephelinites are outstanding.

Late nepheline syenite network.

Late nepheline syenite forms a network of pinkish dykes and veins that cut all the lithologies found either in the coastal outcrops or in the ravines around Barranco del Agua Salada, some of them associated to feldspathic ijolites. They are heterogranular rocks with coarse to very coarse grain size frequently with comb texture due to the orientation of alkali-feldspar and pyroxene aggregates. The occurrence of radiate aggregates of prismatic aegirine augite crystals, frequently transformed to oxide minerals, is common (Figure S5d). They are included in subidiomorphic alkali feldspar and heavily altered nepheline.

Allotriomorphic fractured zircon grains and idiomorphic pyrochlore crystals are common inclusions in alkali-feldspar. In some samples biotite crystals with rims transformed to ore minerals can be observed.

Nephelinite and phonolitic nephelinites.

Nephelinite and phonolitic nephelinite dykes constitute the latest intrusions found in the southwestern area of the Esquinzo ultra-alkaline complex. They clearly cut all the plutonic rocks described above.

Nephelinites are strongly porphyritic with predominant pyroxene and nepheline phenocrysts and minor amounts of Fe-Ti oxide minerals. Pyroxenes are yellow in colour, prismatic and full of fractures. Nepheline forms short hexagonal or square crystals, which are invariably highly altered. The groundmass consists mainly of fine-grained pyroxene, nepheline and titaniferous magnetite. Accessory minerals include apatite, titanite and perovskite.

Phonolitic nephelinites are also strongly porphyritic with a fine-grained groundmass. They consist mainly of hexagonal nepheline and strongly zoned green pyroxene phenocrysts with minor amounts of red-brown garnet, alkali feldspar and titanite set in a groundmass of nepheline, alkali feldspar and pyroxene. Large alkali feldspar phenocrysts contain abundant inclusions of acicular and prismatic green pyroxene and also nepheline. Accessory minerals include apatite and oxide minerals.