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PRELIMINARY STUDY OF THE ORE DEPOSITS AND HYDROTHERMAL  
ALTERATION IN THE RODALQUILAR CALDERA COMPLEX, SOUTHEASTERN SPAIN

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# PRELIMINARY STUDY OF THE ORE DEPOSITS AND HYDROTHERMAL ALTERATION IN THE RODALQUILAR CALDERA COMPLEX, SOUTHEASTERN SPAIN

## SUMMARY

The Rodalquilar gold-alunite deposits are the first documented example of caldera-related epithermal gold mineralization in Europe. Mineralization occurs in rhyolitic tuffs and domes of the Rodalquilar caldera complex in the Miocene Cabo de Gata volcanic field. Geologic constraints indicate a close temporal relationship between the mineralization and a late magmatic phase of the caldera cycle. A zone of extensive advanced argillically altered rocks trends from east to west through the caldera and is well delineated by Landsat Thematic Mapper data. Aeromagnetic and gravity data show that an east-west trending gravity and aeromagnetic high coincides with the distribution of the altered rock. The source of this geophysical anomaly is considered to be andesitic magma that intruded into the base of the volcanic pile and is regarded as the heat source responsible for hydrothermal circulation. Illite and alunite K-Ar data indicate an age for the mineralization of 10.8 Ma. Recent drilling in the core of the system shows that hydrothermally altered rocks continue to depths of over 900 m and are characterized by assemblages typical of acid-sulfate epithermal systems. A deep sericitic zone, with chlorite present below about 500 m, grades upward into argillic, advanced argillic and silicic (vuggy silica) zones. Zonation of the alteration assemblages also occurs laterally; the advanced argillic alteration mineral assemblage is replaced by chlorite within the argillic zone at or near the ground surface.

Ore deposits within the Rodalquilar complex consist of alunite, gold-alunite, and lead-zinc-silver-gold veins. The gold-alunite deposits are the most important economically. They are preferentially localized in ring and radial fractures of the Lomilla caldera nested within the Rodalquilar caldera. Gold extends over a vertical interval of about 200 m below the original paleosurface and changes at depth to a complex sulfide assemblage. Most gold was deposited in the highest part of the center of upwelling fluid following the peak of acidic alteration. Highest gold values, with a median near 8 g/t, occur in black, pyritic, banded chalcidony that fills preexisting open spaces and fractures within advanced argillically altered rocks. Hypogene alunite in the central core assemblage reaches depths of more than 300 m, is characterized by high sodium content, and is accompanied, below the zone of supergene oxidation, by kaolinite, zunyite, diaspore, pyrite and aluminum phosphate-sulfates. Stable isotope data indicate that this alunite formed in a magmatic-hydrothermal environment (Rye et al., 1988) from the disproportionation of  $\text{SO}_2$  derived from a magma. The  $\delta^{34}\text{S}$  data of coeval pyrite indicate the  $\delta^{34}\text{S}$  of bulk sulfur in the system was  $\sim 7$  per mil. Barren alunite-jarosite veins are extensive throughout the district to a depth of about 50 m. Stable isotope data from these alunites indicate that they were derived by the oxidation of  $\text{H}_2\text{S}$  in a steam-heated environment that in some places was superimposed on the advanced argillic assemblage as the hydrothermal system collapsed.  $\delta\text{D}$  data from alunite indicate that seawater was probably an important component of the water in the ore forming fluids.

## INTRODUCTION AND PREVIOUS WORK

The Rodalquilar base- and precious-metal deposits are the first documented example of caldera-related epithermal gold mineralization in Europe. Mineralization occurs in

rhyolitic tuffs and domes of the Rodalquilar caldera complex in the Miocene Cabo de Gata volcanic field (Fig. 1). The geological setting of the Cabo de Gata volcanic field and the evolution of the Los Frailes, Rodalquilar and Lomilla calderas have been discussed in two related papers (Cunningham et al., 1989; Rytuba et al., 1989). This report builds upon those studies and concentrates on the origin of ore deposits and associated hydrothermal alteration within the Rodalquilar caldera and the nested Lomilla caldera.

Epithermal deposits within the Rodalquilar caldera are closely associated with an east-west trending zone of extensive, advanced argillically altered rocks. All the volcanic and volcanoclastic units exposed over an area of more than 25 km<sup>2</sup> were subject to intense alteration produced by hot, acidic, hydrothermal fluids. By contrast, in the area of the Los Frailes caldera, a few kms to the south, the only evidence of hydrothermal alteration is the presence of small bentonite deposits. Some of these bentonite deposits probably originated from the alteration of hot airfall tuffs that fell into the ocean, whereas others, as suggested by Martín Vivaldi (1963) and Leone et al. (1983), were derived from the reaction of the host rock with low temperature, slightly alkaline, meteoric waters that ascended through post-caldera structures. Thus, the magnitude and nature of hydrothermal activity in both calderas contrasted significantly. Several features that occur in the Rodalquilar caldera may have contributed to the existence of ore deposits within it. These include, the predominance of rhyolitic magmatism and pyroclastic eruptions, the abundance of permeable zones along fractures related to caldera collapse and resurgence, the emplacement of a heat source at depth, and the possible invasion of seawater into the hydrothermal system. Conversely, the Los Frailes caldera volcanism was predominantly dacitic, pyroclastic eruptions were not as common, and, most importantly, favorable permeable zones may have been sealed by massive dacite domes that filled the lower part of the caldera (Cunningham et al., 1989).

Mining in the Cabo de Gata volcanic field started in the early 1800's exploiting lead-zinc-silver veins of the Cabo de Gata center, 4 km west of the village of San José (Fig. 1). Gold was found in the same veins around 1880 and soon after in veins near the town of Rodalquilar, 10 km northeast of San José, where small alunite pits already existed. Mining in the Cabo de Gata center ended at the beginning of the 20th century, but in the Rodalquilar area mining continued intermittently until 1966 when the ore grade fell considerably. Total production from Rodalquilar is about 6 tonnes of gold and minor amounts of lead and zinc. Average gold grades for underground and open-pit mining for the period 1943-1966, when ADARO operated the deposit, were 8 grams per tonne and 2 grams per tonne, respectively (Sierra and Leal, 1968). During the 1980's, following the development of epithermal gold models, the peak in the price of gold, and the technical advances in the recovery of low grade ores, the Rodalquilar deposits became attractive to several exploration companies. Today, St. Joe Transacción, owned by Cluff Resources and Antofagasta Holdings, is starting a three-year mining project for the recovery of about 650,000 tonnes of ore at an average grade of 2.5 grams of gold per tonne (Skillings Mining Review, 1988). The Spanish government, through its mineral exploration company, ADARO, holds most of the metal reserves. ADARO has drilled and evaluated several small ore bodies, but no tonnage or grade information has been released.

Earlier studies on gold mineralization at Rodalquilar include those by Friedrich (1960), Lodder (1966), Sierra and Leal (1968), Martín Vivaldi et al., (1971) and, more recently, Pineda Velasco (1984) and Friedrich et al., (1984). This preliminary report is an extended version of an oral presentation given at the annual meeting of the Geological Society of America in Denver, Colorado, November 3, 1988 (Arribas et al., 1988). A series of presentations on the Rodalquilar deposits were given at the symposium "Gold 89", held in Toulouse, France, May 1989 (Arribas et al., 1989, Rytuba et al., 1989).

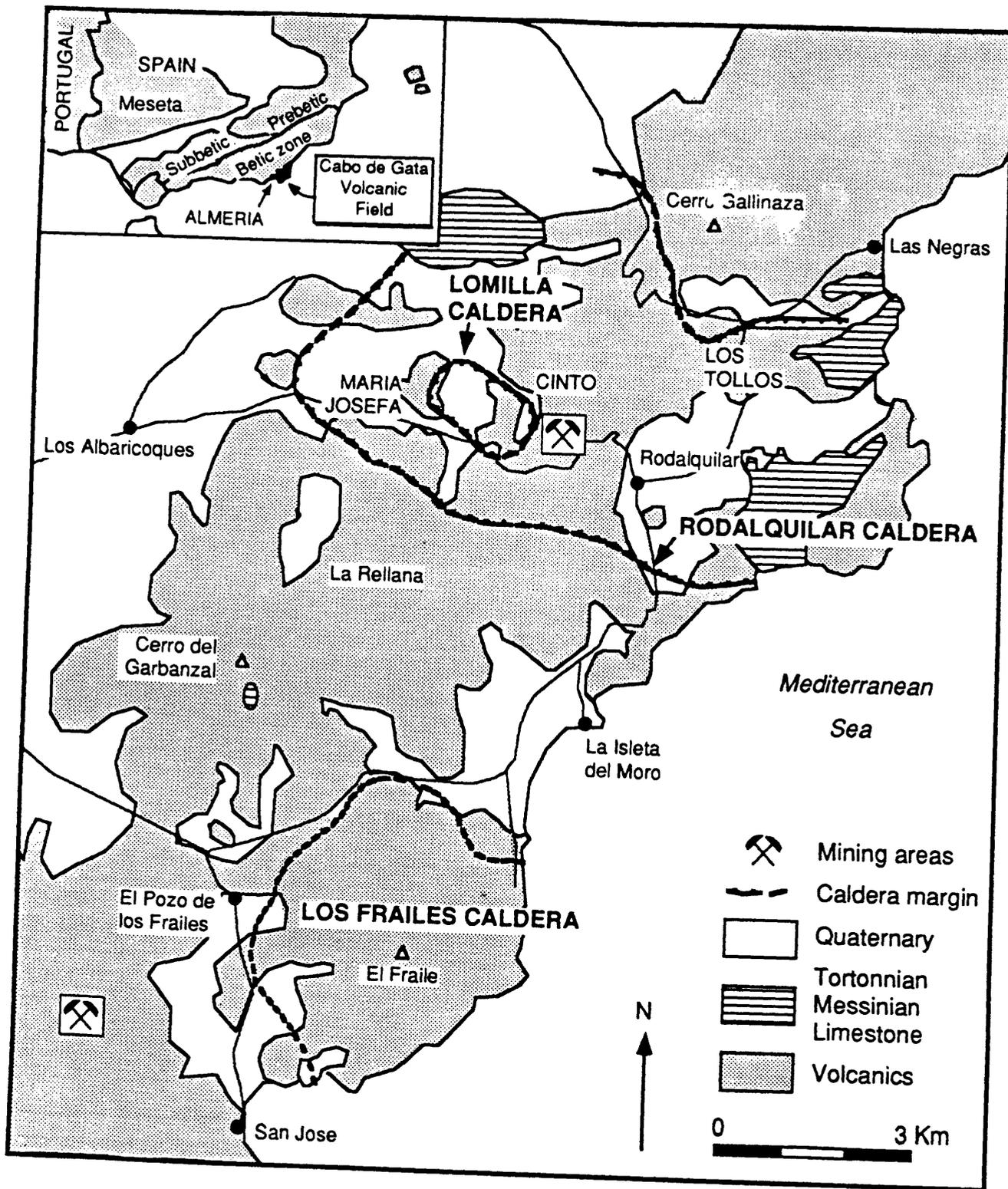


Figure 1. Index map showing location of principal geographic features, margins of calderas and mining districts within the Cabo de Gata volcanic field.

Most of the early studies provide good descriptions of the mineral assemblages and mineralized structures. With respect to the origin of the deposits, De Roever and Lodder (1984) and Lodder (1966) reported that the alteration was limited to an ignimbritic pile and concluded that mineralization and alteration were syngenetic with the ignimbrites in which they occur. They considered most of the mineralized structures as fossil fumaroles and suggested that the zones of greatest concentration of ore veins are localized above the feeders of the ignimbritic materials. León (1967) disagreed with their field observations, arguing that andesitic units below and above the ignimbrites were also affected by the same hydrothermal fluids. Sierra and Leal (1968) and Martín Vivaldi et al., (1971) considered alteration, mineralization and volcanism to be contemporaneous and recognized that the mineralization was "in the subvolcanic zones of volcanic complexes". The present study proposes that alteration and mineralization at Rodalquilar are younger than their host rocks and were produced by rock:water interaction within large hydrothermal systems. These hydrothermal systems were driven by heat released from an andesitic intrusion and localized mainly by faults and fractures developed during collapse and resurgence of calderas. By integrating detailed multidisciplinary geophysical, geochemical and geologic studies, this research provides a three-dimensional picture of the hydrothermal systems that deposited gold at Rodalquilar and establishes the relationship between the evolution of the hydrothermal system and the timing of gold deposition. Therefore, important exploration guides are derived.

## REMOTE SENSING

Landsat-5 and airborne Thematic Mapper (TM) data provided a powerful tool in the initial stages of the study of alteration zones in the Cabo de Gata volcanic field. The usefulness of the data was enhanced by the minimal vegetation cover, the large size of the altered zones, and the acquisition and processing of field and laboratory spectra. As a result, color-ratio-composite images were produced that allowed an excellent discrimination of the altered and mineralized zones.

Fig. 2 is a color-ratio-composite image of the central part of the Cabo de Gata volcanic field in which TM5/TM7, TM5/TM4 and TM3/TM1 band ratio images were projected as red, green, and blue, respectively. In processing data this way, zones of intense argillically and advanced argillically altered rocks are shown as white and yellow. Both white and yellow areas contain hydroxyl- and ferric iron oxides, oxyhydrides, and sulfates; the white areas tend to be brighter in the visible part of the spectrum whereas the yellow areas are darker (Podwysoccki et al., 1985). Two important areas of hydrothermally altered rocks are readily visible. The Rodalquilar area is identified by the yellow and white colors in the center of the image. The yellow zone at the southwestern boundary of the image corresponds to the Cabo de Gata lead-zinc-silver-gold center (Fig. 1). Preliminary investigations of the Cabo de Gata veins suggest that they formed by adularia-sericite type epithermal mineralization. The light blue spots within the Los Frailes caldera and north of the caldera margin correspond to the approximate location of bentonite deposits; the blue color is interpreted as bright in the visible part of the spectrum with weak ferric-iron and hydroxyl absorption. There is a third, less important, altered and mineralized area within the Cabo de Gata volcanic field which lies just to the north of the image surrounding the Palaí Mine, 2 km west of the town of Carboneras (north of the area of Figure 1). Preliminary investigations suggest that this sulfide-gold mineralization formed in a hot-spring environment. The Mina Palaí and Cabo de Gata centers will not be discussed further in this study.

The Rodalquilar district can be divided into two major areas of very intensely altered rocks. In the center of the image, the larger Cinto area (Fig. 1) roughly marks the

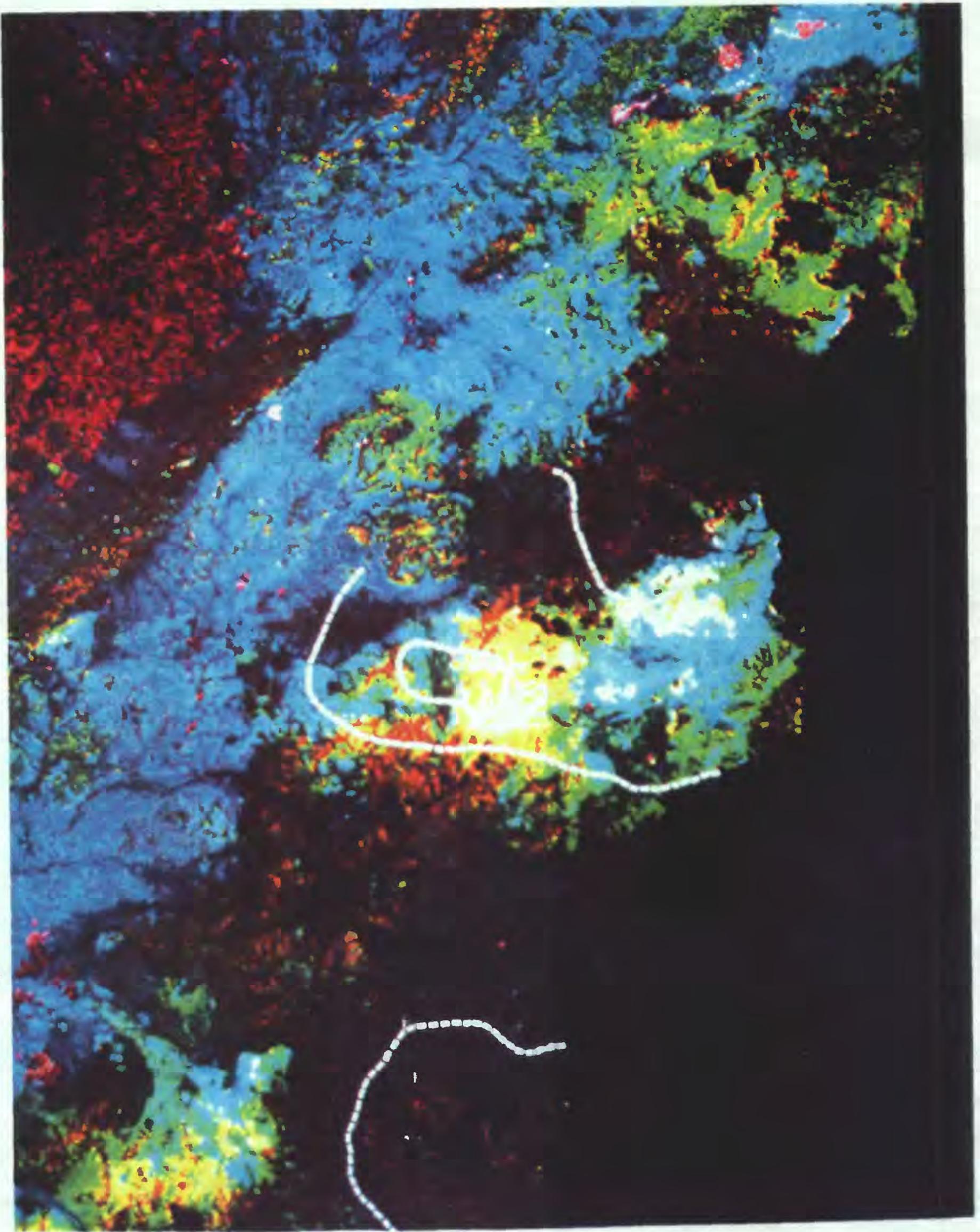


Figure 2. Landsat TM color-ratio-image of the central part of the Cabo de Gata volcanic field. Areas of advanced argillic and argillic alteration appear in white-yellow colors. The large area of alteration is restricted to the Rodalquilar caldera and is most intense around the margin of the nested Lomilla caldera. In contrast, no alteration is present within the older Los Frailes caldera to the south. Photo covers 16 km in east-west direction.

eastern wall of the Lomilla caldera. Most of the gold workings are concentrated in this area. To the northeast, the Los Tollos area shows the effects of advanced argillic alteration with numerous abandoned alunite open pits but gold has not been found there. A third, smaller area, with yellow-orange colors appears about 3 km west of the Cinto area and corresponds to the altered and mineralized area around the (María Josefa mine, Fig. 1). The three areas, María Josefa, Cinto, and Los Tollos, define an east-west trending zone of altered rock centers within the Rodalquilar caldera complex, that coincides with the geophysical anomaly described below.

## INTERPRETATION OF AEROMAGNETIC AND GRAVITY DATA

Aeromagnetic and gravimetric surveys conducted by ADARO in the Rodalquilar caldera show an east-west trending gravity and aeromagnetic anomaly (Figs. 3 and 4). The flight line direction for the aeromagnetic survey was NW-SE with 1 km (and locally 0.5 km) spacing at a constant elevation of 150 m. Tie line direction was NE-SW with a 5 km spacing. An IGRF 1987.28 (1985 model) was subtracted. The gravity data was collected from 287 stations on an irregular grid following available roads; the average distance between stations is 300 m. The source of this geophysical anomaly is considered to be andesitic magma intruded into the base of the volcanic pile late in the evolution of the caldera cycle (Rytuba et al., 1988). This intrusion is regarded as the heat source responsible for hydrothermal circulation. The location of the aeromagnetic anomaly between the two principal areas of altered rocks (Cinto and Los Tollos) suggests that the hydrothermal cells developed concentrically to a central intrusion in a pattern similar to that described by Cunningham et al., (1984) for the replacement alunite deposits in the Marysvale volcanic field, Utah. The aeromagnetic anomaly peak is offset slightly to the north of the gravity anomaly, perhaps reflecting the destruction of magnetic minerals along the southern border of the magnetic high in the area that contains the most intensely altered rock, or near surface emplacement of unaltered andesite dikes. The extrusive equivalents of the dioritic intrusion are hornblende andesites emplaced near the end of volcanic activity in the caldera (Rytuba et al., 1988). This magma is responsible for the last stage of caldera resurgence which was localized in the central part of the Rodalquilar caldera and was important in opening faults and fractures which were subsequently used as fluid pathways by the large hydrothermal systems.

## HYDROTHERMAL ALTERATION

The wall rocks in the Rodalquilar area are so intensely altered that the primary texture of the rock commonly is completely obliterated. Undoubtedly, the possible relation of altered wall rock to ore deposits was obvious to even the first prospectors who witnessed it in numerous metallic deposits in southeastern part of the Iberian Peninsula. Early studies of the Rodalquilar deposits established the genetic link between alteration and mineralization through detailed mineralogical studies (Lodder, 1966; Sierra and Leal, 1968; Martín Vivaldi et al., 1971) but were hampered by the lack of significant drilling data.

### Zonation

The hydrothermal mineral assemblages associated with gold and base-precious metal veins within the Rodalquilar caldera are complex and are typical of acid-sulfate type epithermal deposits. The terminology of the alteration assemblages used in this study follows that of Heald et al., (1987). Figure 5 is a map that shows the distribution of wall rock alteration assemblages in the Rodalquilar caldera complex. Two major areas of intensely altered rock can be distinguished; the central area, Cinto, is better documented at depth because of drilling data, however the surface information suggests that the eastern area, Los Tollos, is similar. Both areas are characterized by centers of silicic alteration

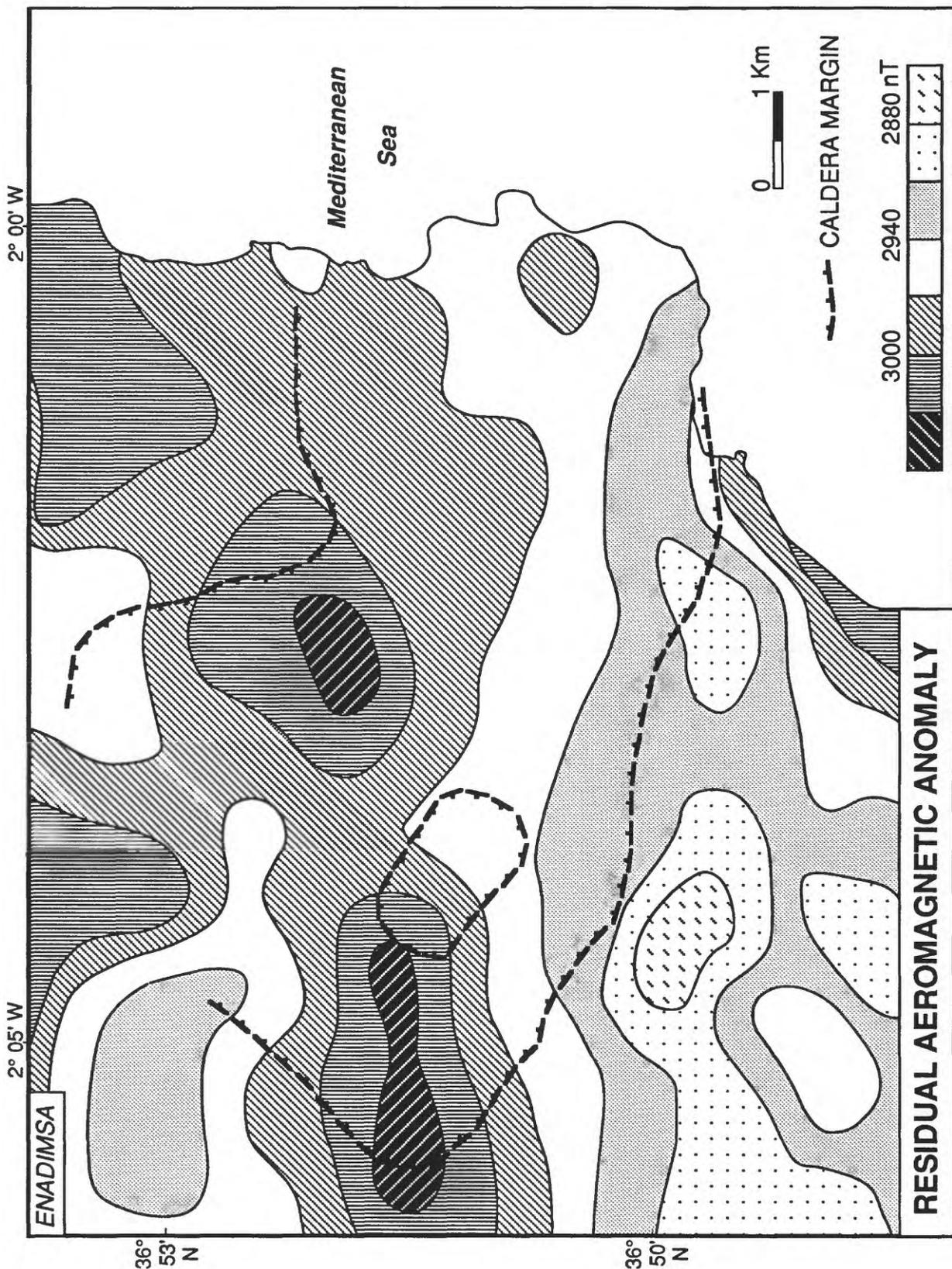


Figure 3. East-west trending aeromagnetic anomaly through the Rodalquilar caldera (simplified from unpublished company maps, by permission from ENADIMSA).

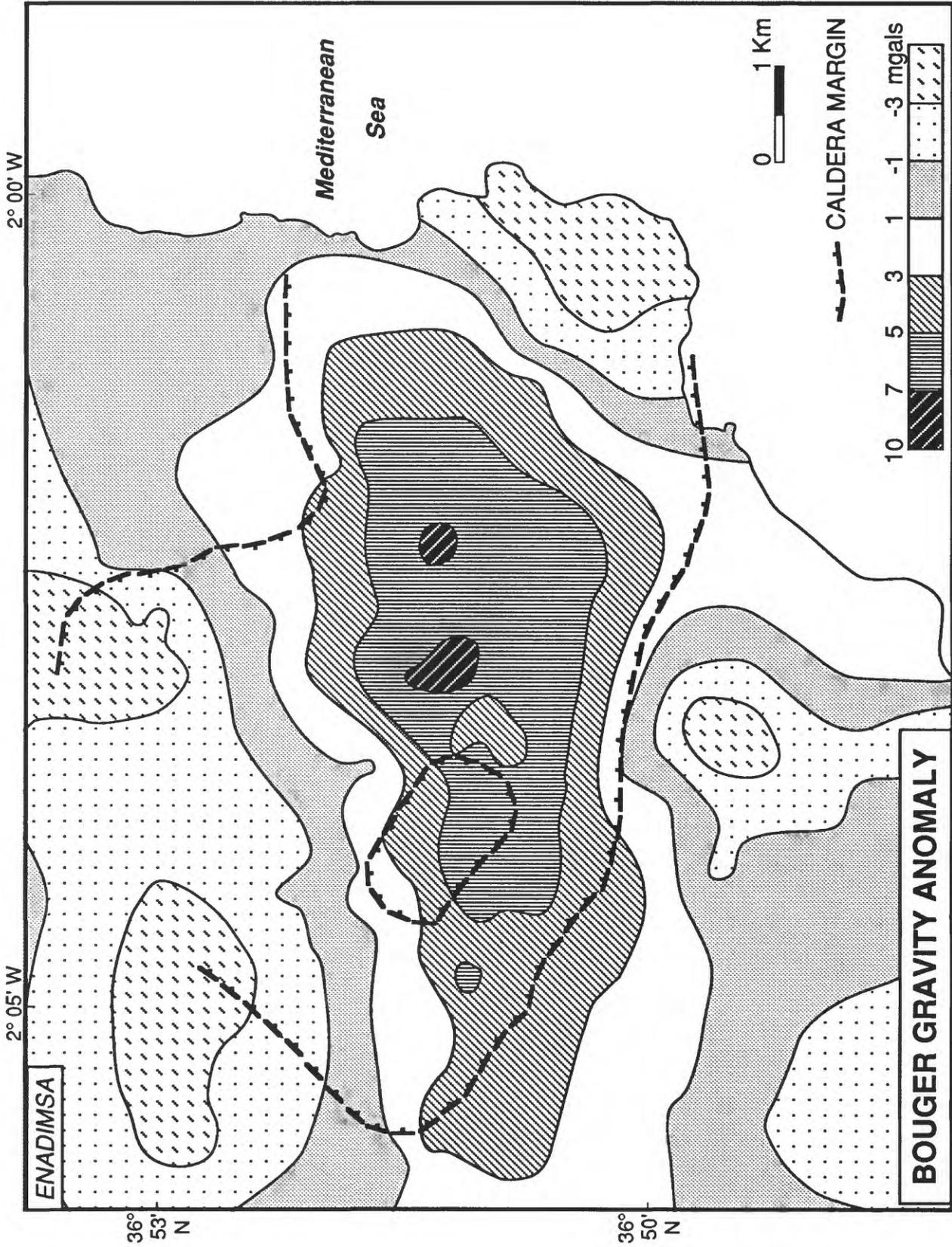


Figure 4. Bouguer gravity map of the Rodalquilar caldera (simplified from unpublished company maps, by permission from ENADIMSA).

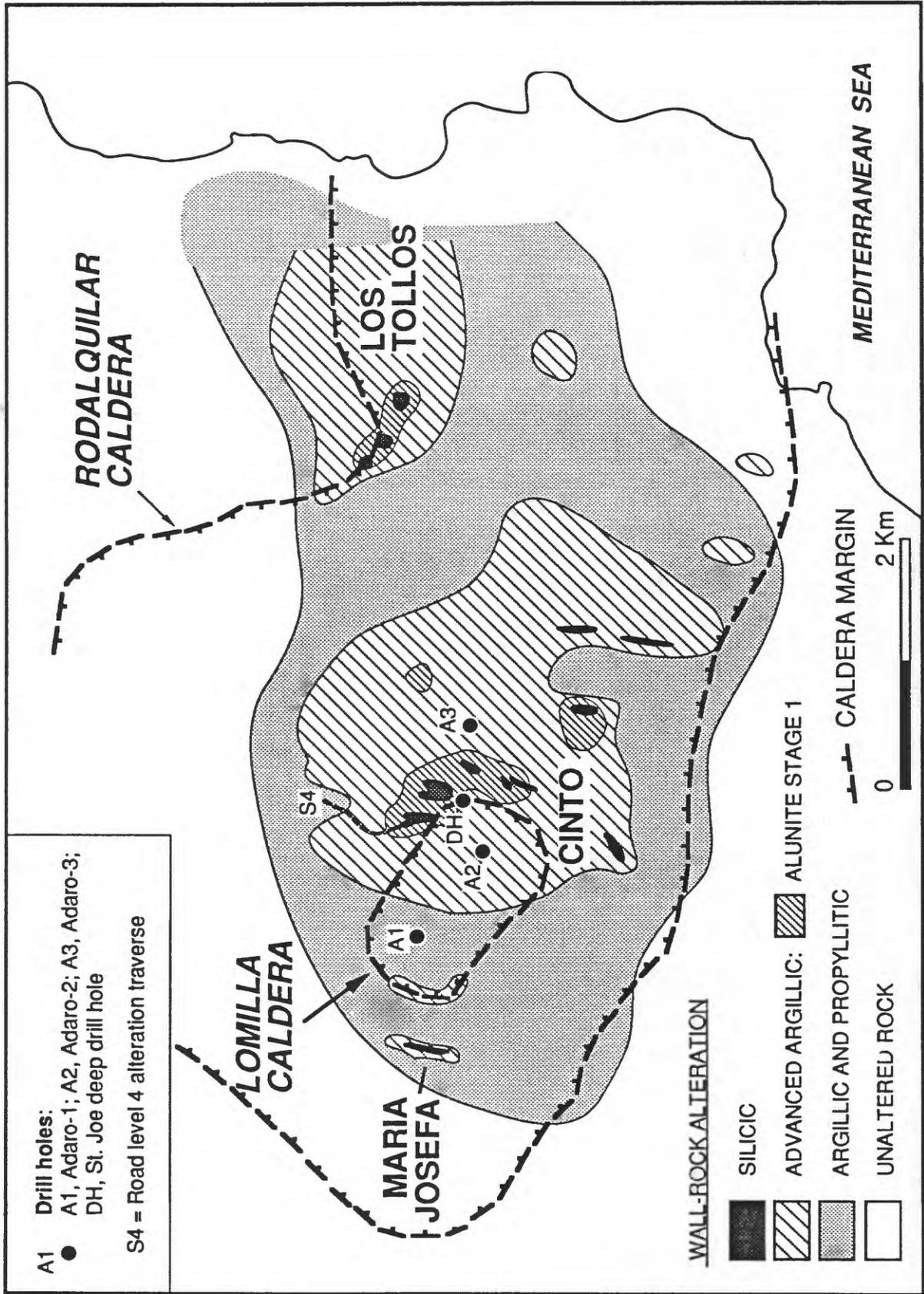


Figure 5. Distribution of major alteration zones and assemblages within the Rodalquilar caldera complex

(vuggy silica as well as introduced silica) and envelopes of advanced argillically altered rocks containing the hypogene assemblage quartz, alunite, kaolinite, pyrite, illite, and minor pyrophyllite as described below. A large area of argillically altered rocks surrounds the centers and has gradational boundaries. This zone contains kaolinite, illite, illite-montmorillonite, quartz, K-feldspar and chlorite and is mineralogically zoned, with kaolinite near the core and chlorite close to the outer boundary. The southern boundary is diffuse because it is difficult to distinguish the subtle alteration related to hydrothermal activity from the deuteritic alteration of the outflow ash-flow tuff. On the north side, unaltered caldera-fill ash-flow tuff and interbedded collapse breccias appear relatively close (~800 m) to the intensely altered core. A particularly good traverse of the zones of altered rocks exists within a lithologically homogeneous rhyolitic dome along the north section of the level 4 road of the Cinto Mine (Fig. 5).

Deep drilling in the core of the Cinto alteration zone shows that hydrothermally altered rocks are present to depths of over 900 m with a gradational change from advanced argillic, to argillic, to sericitic zones (Arribas et al., 1988). Fig. 6 shows alteration mineral assemblages, relative mineral abundances (excluding quartz), and gold contents for the Adaro-1 (A1) drill hole (for location see Fig. 5). This drill hole reached the sericitic zone (Fig. 7) at about 300 m (Fig. 6), and chlorite appears below 430 m (Fig. 6). Gold grades are highest in the top 40-80 m. A similar pattern is defined by other drill holes within the core of altered rocks. In the DH drill hole (Fig. 5), the zone of advanced argillic alteration continued to depths of about 300 m. The depth at which chlorite is present is a good indicator of the outline of the changes of the chemical composition within the hydrothermal system: chlorite is present in the A2 drill hole at a depth of only 20 m, in the A1 drill hole at 430 m, in the DH deep hole at about 500 m, and in the A3 drill hole at 80 m. The pattern defines a classical funnel-shape that flares upwards (Fig. 22).

At the outcrop scale, haloes of altered rock around mineralized structures show a similar zoning pattern. Silica-rich fractures are surrounded by envelopes of vuggy silica which grade into a zone of quartz-alunite and further out into a zone of quartz-kaolinite (Figs. 8 and 9). This distribution reflects the effect of very acidic, sulfate-rich solutions that leached the original rock and were progressively neutralized by reaction with the wall rocks producing the envelope of quartz-alunite and quartz-kaolinite. These zones have very irregular shapes and distribution. The vuggy silica halo is not always present, generally is less than 1 m wide, and locally reaches up to 20 m. The width of the quartz-alunite zone ranges from a few cm to several tens of meters and may overlap other zones if the concentration of fractures is high enough. Mineralization is essentially confined to the silica-rich rocks (chalcedonic vein filling, silicified fracture coatings, and vuggy silica haloes) and to hydrothermal breccias. The distribution of alteration zones described above is typical of acid-sulfate deposits like Summitville, Colorado (Steven and Ratté, 1960; Stoffregen 1987), Chinkuashih, Taiwan (Wang, 1972), Goldfield, Nevada, (Harvey and Vitaliano, 1964; Ashley, 1979), and Nansatsu, Japan (Urashima et al., 1987; Hedenquist et al., 1988).

### **Types of alunite**

Two types of alunite are found in the Rodalquilar district. They contrast strongly in appearance and conditions of origin. Stage 1 alunite is the oldest and occurs in the cores of hypogene alteration (hatched area in Fig. 5), where the concentration of ore veins is greatest (Figs. 10-12). Together with quartz, it is the major component of the quartz-alunite zone where it appears as light pink, fine-grained euhedral crystals embedded in finely-crystalline quartz. It forms pseudomorphs after feldspar and replaces illite. Chemically, Stage 1 alunite is characterized by a high sodium content, up to 35 atomic percent, and is accompanied by kaolinite, pyrite, zunyite, aluminum phosphate-sulfates (svanbergite, woodhouseite, and La-

## RODALQUILAR: ADARO-1 DRILL HOLE

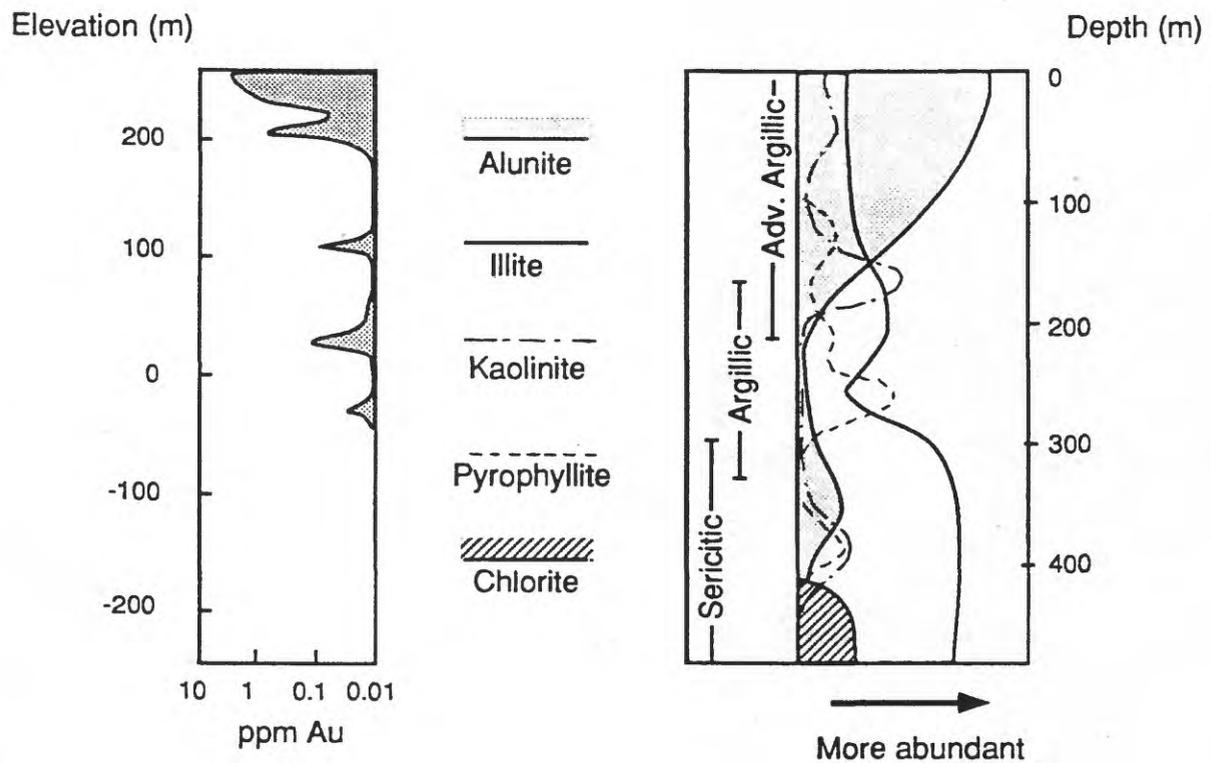


Figure 6. Relative abundances of vertically zoned hydrothermal phases (except silica), range of alteration assemblages and gold concentration profile in the Adaro 1 drill hole (location in Fig. 5) defined by petrography, X-ray diffraction, chemical analysis, and visual estimates. Gold grades from analysis of 2 m intervals.

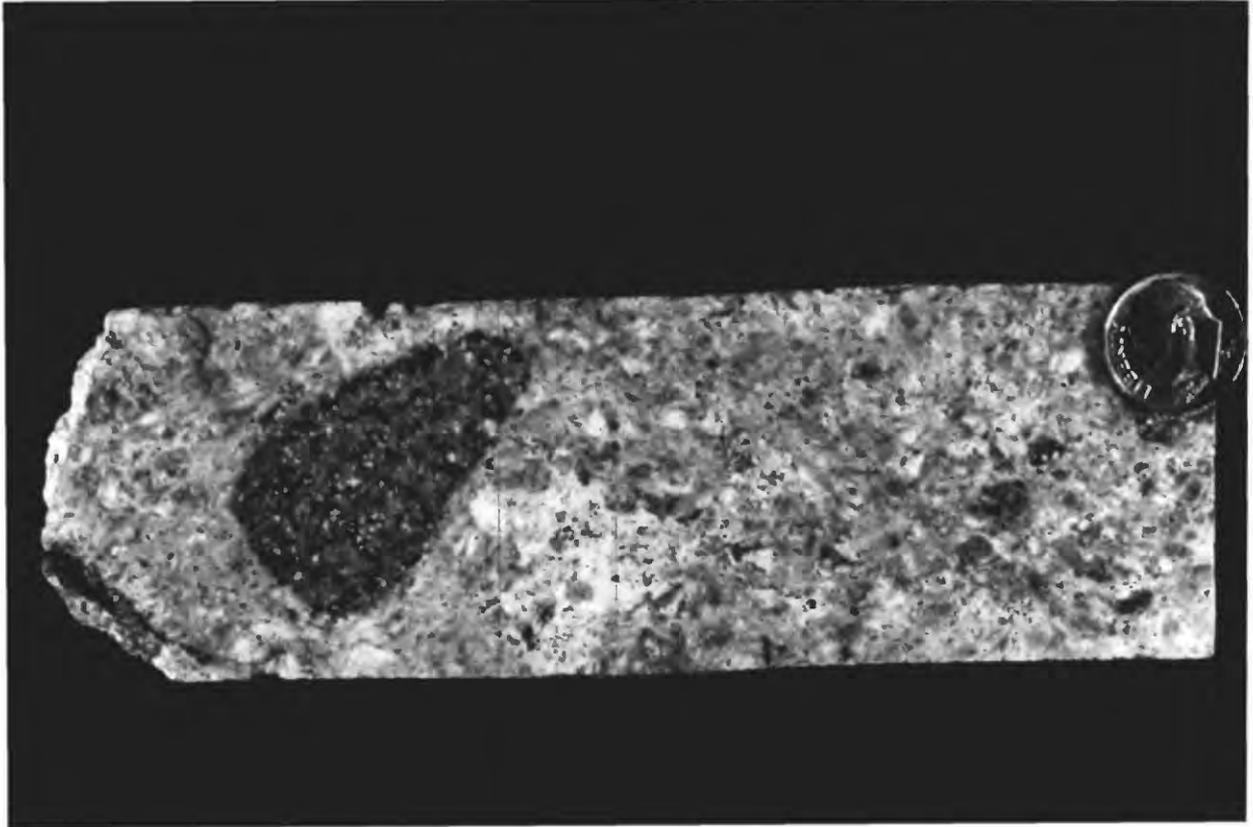


Figure 7. Cinto caldera-fill tuffs altered to quartz, sericite and pyrite, from the sericitic zone at depth (Sample: 87A21, Adaro 1 drill hole, 400 m). This assemblage resulted from the earliest stage of alteration and at higher levels was followed by later oxidation and acidic alteration as the hydrothermal system evolved. A lithic fragment of andesite from the caldera wall contains more pyrite reflecting the greater amount of mafic minerals in the fragment.

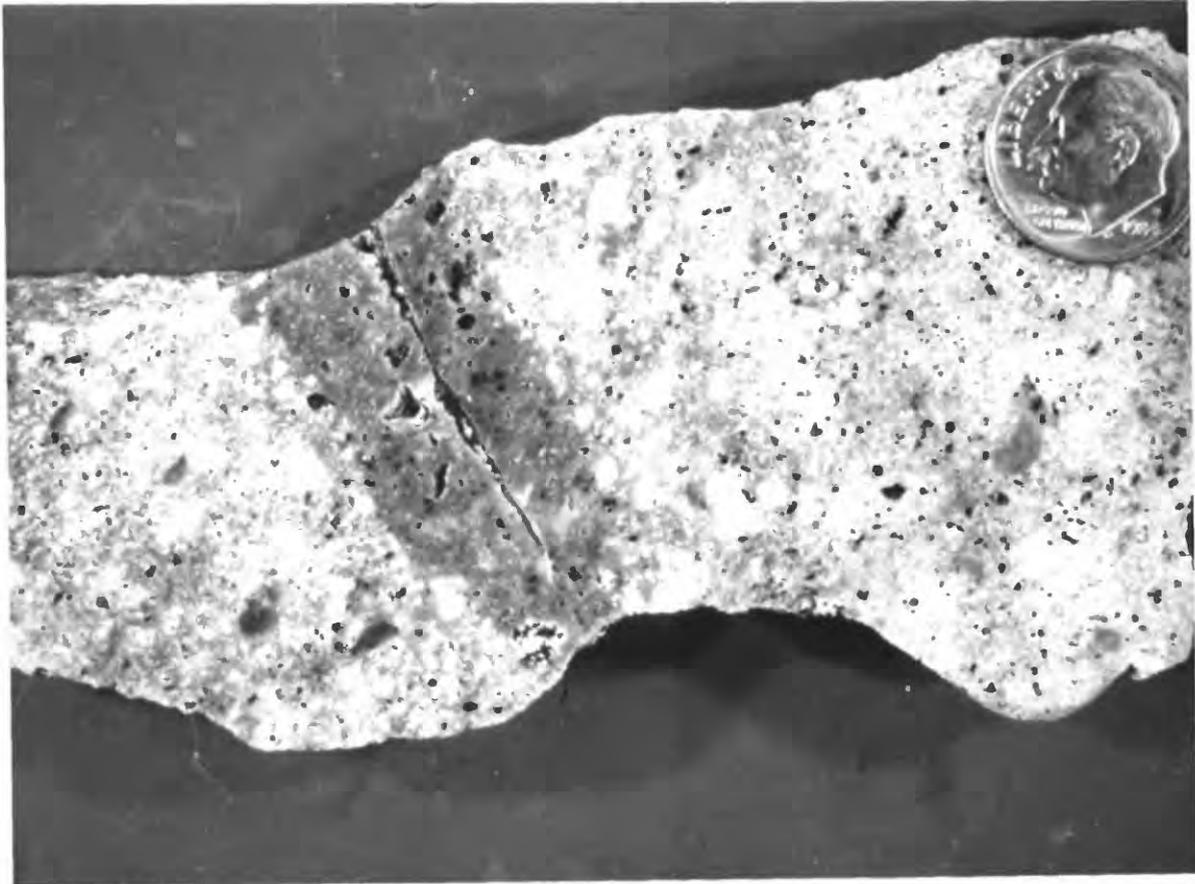


Figure 8. Polished slab of a mineralized fracture (~1 mm wide) showing the envelopes of vuggy silica and of quartz-alunite-kaolinite. Pyrite is present in both zones but is more abundant in the vuggy silica zone. Gold content in a sample of the silicified fracture plus vuggy silica envelope is 20 g/t. Gold content in the quartz-alunite-kaolinite zone is 0.4 g/t (Sample: 87A165, Cinto zone, open pit no.1).

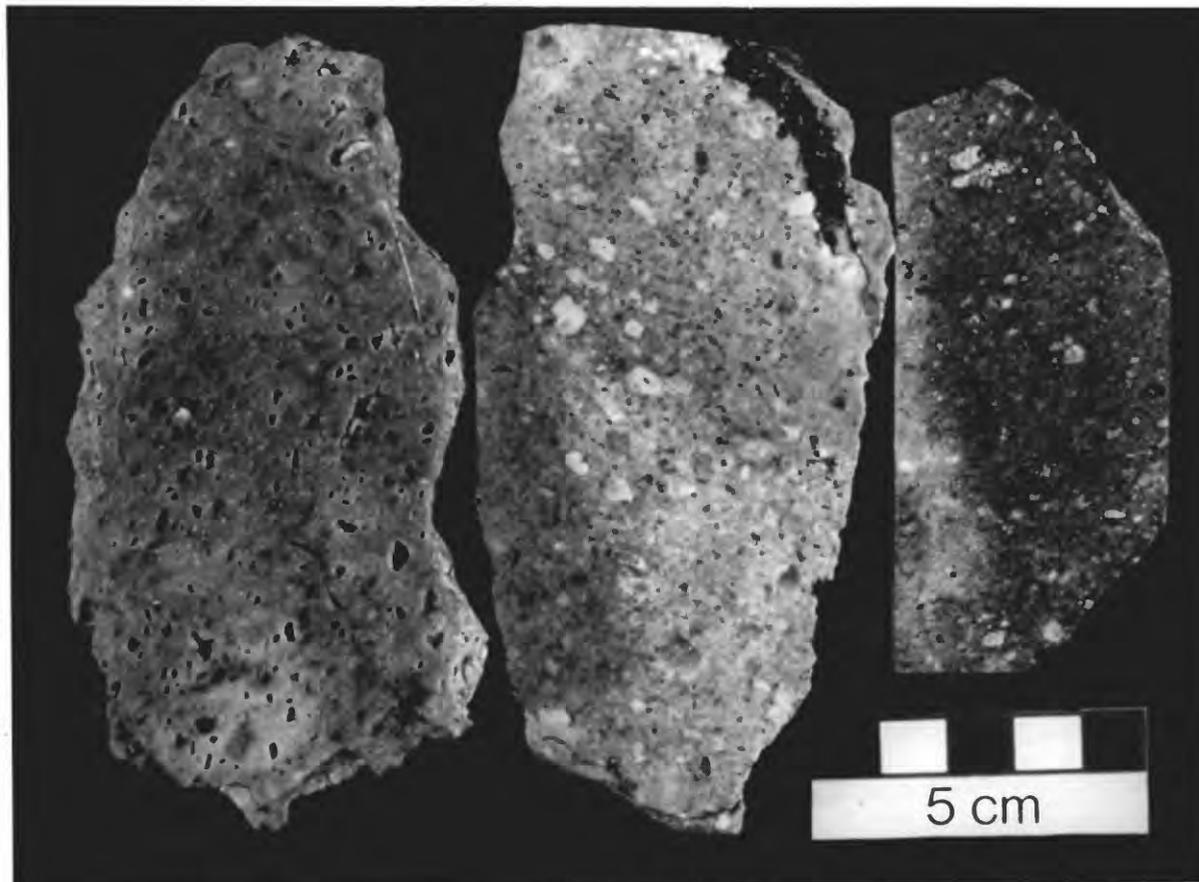


Figure 9. Polished slabs of hydrothermal alteration zones from the core of the Cinto hydrothermal alteration area. Samples were taken at 50 cm intervals from a mineralized vein. A. Porous residual silica -vuggy silica- zone (from the leaching of the original rock by acid fluids). B. Quartz-alunite zone; note the light (pink, in color) alunite crystal aggregates. C. Quartz-kaolinite zone.

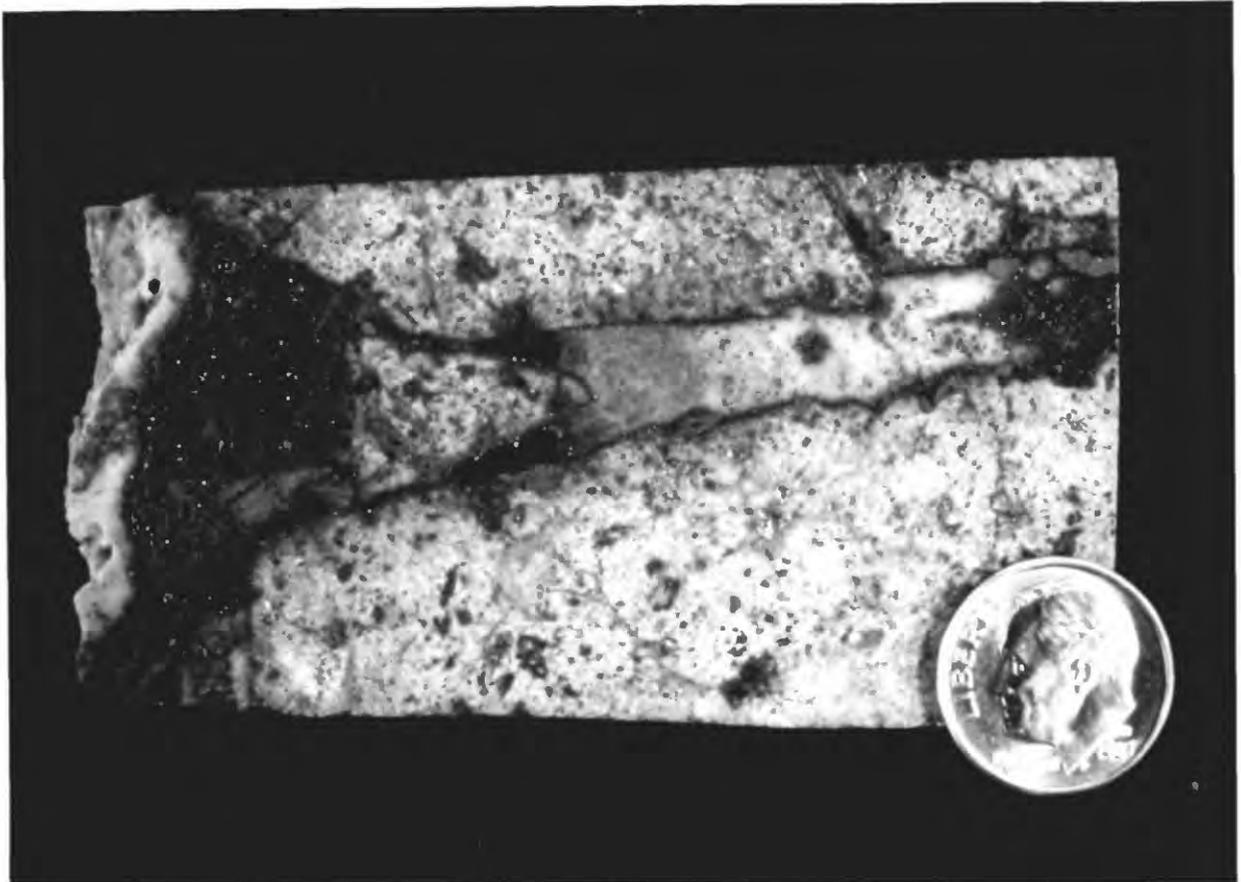


Figure 10. Alunite Stage 1 assemblage. Polished slab of breccia composed of large fragments of altered host rock (f) and matrix of alunite-pyrite-zunyite (m) (87A111, DH deep drill hole m.130).

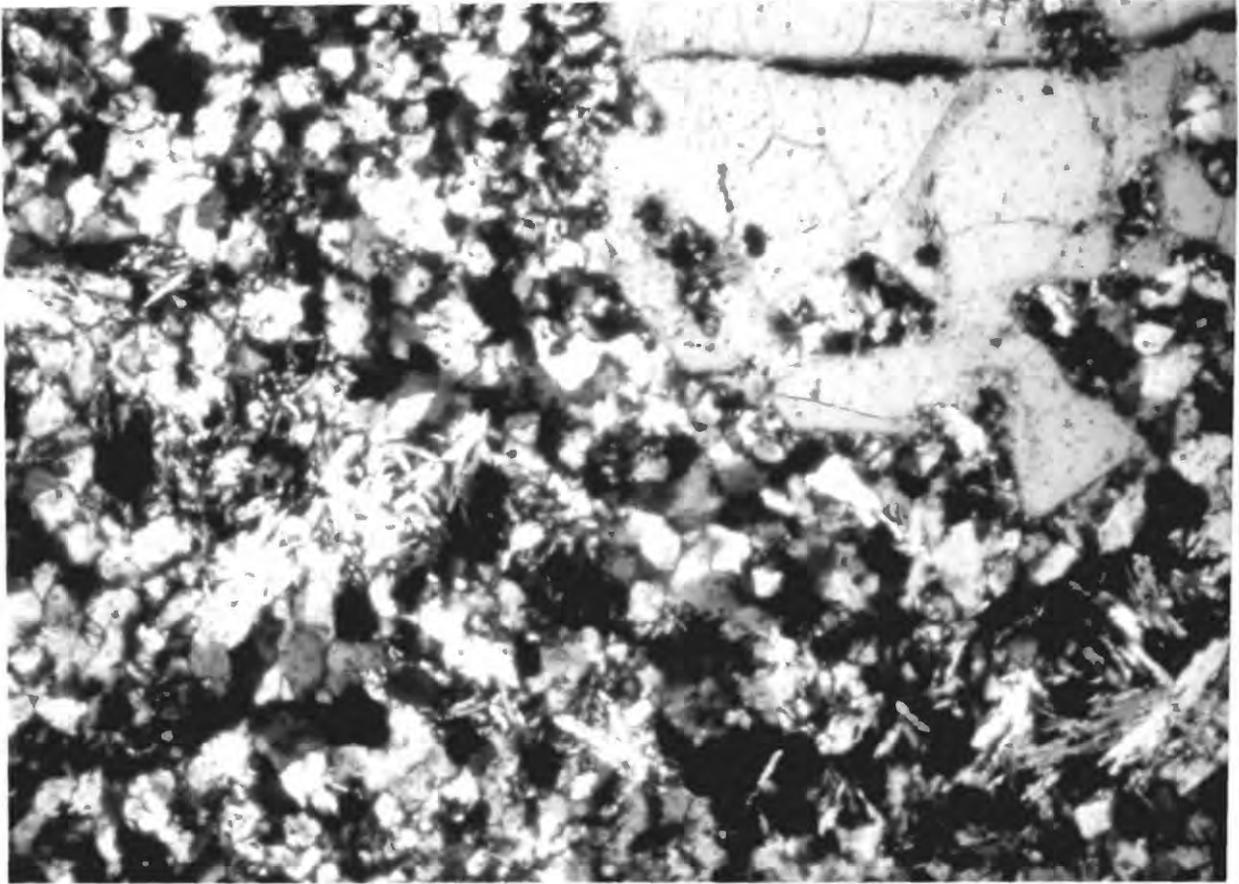


Figure 11. Alunite Stage 1 assemblage. Photomicrograph of typical quartz-alunite alteration. Large, partially reabsorbed, igneous quartz phenocryst enclosed in clear, anhedral, hydrothermal quartz intergrown with bladed alunite and with pyrite. Scale bar is 0.5 mm (Sample: 87A150, eastern wall of the Lomilla caldera).

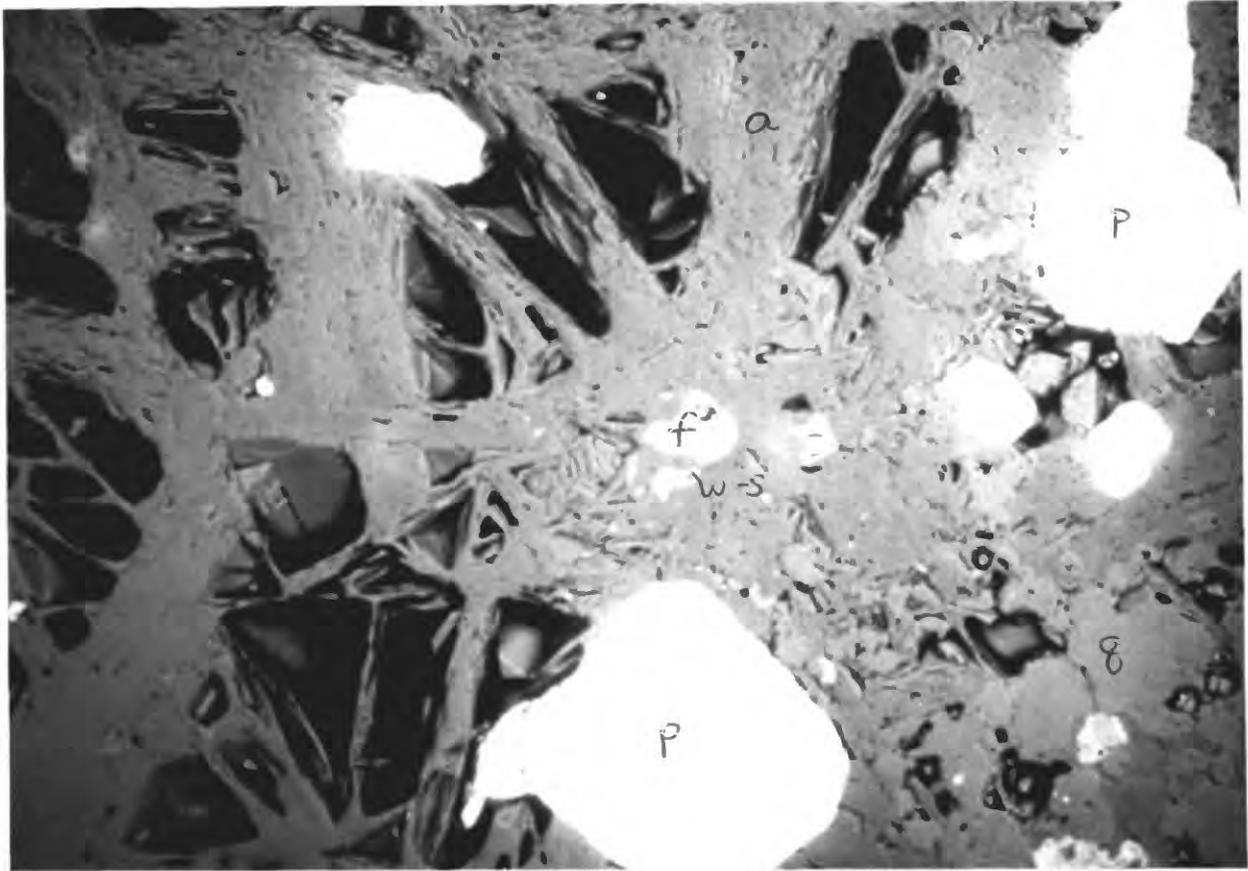


Figure 12. Alunite Stage 1 assemblage. Scanning electron micrograph of alunite Stage 1 assemblage showing bladed alunite (a) with cores of woodhouseite-svanbergite (w-s) and La-florencite (f), pyrite (p), quartz (q) and kaolinite (k). Scale bar is 50 microns. (Sample: 87A120, DH drill hole, m. 191)

florencite), pyrophyllite, hematite, and minor jarosite. The presence of La-florencite within crystals of woodhousite-svanbergite, which in turn occur within alunite crystals, provides evidence of LREE mobilization during hydrothermal activity. In addition, this sequence reflects a geochemical gradient from an early stage of phosphate precipitation (Florencite:  $(La,Ce)Al_3(PO_4)_2(OH)_6$  through an intermediate stage of sulfate-phosphate precipitation (Svanbergite-Woodhousite:  $(Ca,Sr)Al_3(PO_4)(SO_4)(OH)_6$ ) and finally to a stage of sulfate deposition (Alunite:  $(Na,K)Al_3(SO_4)_2(OH)_6$ ) which dominates the paragenesis. The high concentration of strontium in the core of the Cinto area (Crawford, pers. com., 1986) reflects the presence of svanbergite.

The second type of alunite, Stage 2, is very abundant in most of the zone of advanced argillic alteration shown in Figure 5. It is present mainly as shallow, intensely altered, barren areas containing replacement alunite and one to ten cm wide alunite-jarosite veins. These areas generally surround the central cores of Stage 1 alunite but are also superimposed onto them. Figure 13 shows typical Stage 2 alunite alteration replacing an area of previous alteration. The bright (white) host rocks are caldera-fill tuffs replaced by alunite, kaolinite, illite-montmorillonite, jarosite and quartz. The darker colored (yellow) veins are composed of alunite, jarosite and minor quartz and show typical botryoidal texture (Fig 14). Progressive replacement of the wall rock from these veins may produce irregular bodies of pure alunite up to 30 cm wide. Stage 2 alunite contains very little sodium and is not associated with pyrite, zunyite, svanbergite, woodhousite, or florencite. Unlike Stage 1 alunite, Stage 2 alunite is not related to strong silicification of the wall rock. It formed under very oxidizing conditions under which pyrite was not stable. Where the two stages of alunite overlap, Stage 2 alunite is always younger than Stage 1, filling fractures and replacing the previously altered host rock. Stage 2 alunite formed near the paleosurface and, most likely, in the solfataric environment where alunite results from sulfate produced by the oxidation of  $H_2S$ . This interpretation is supported by the stable isotope geochemistry.

## MINERALIZATION

Ore deposits within the Rodalquilar caldera complex consist of alunite, gold-alunite, and lead-zinc-silver-gold veins (Fig. 15). The alunite occurs as vein filling, and massive, replacement alunite hosted within intracaldera Lazaras and Cinto ash-flow tuffs and collapse breccias. The Los Tollos alunite deposits are localized in collapse breccias and intracaldera Cinto ash-flow tuff about 0.5 km from the north-central margin of the Rodalquilar caldera. The deposits were mined by open pit methods and consist primarily of replacement alunite in which the original texture of the collapse breccia and ash-flow tuff is well preserved. Narrow veins of alunite with minor jarosite are locally present but constitute a minor part of the ore body. On the southeast flank of the resurgent dome of the Rodalquilar caldera, an unnamed alunite deposit was developed in intracaldera Cinto ash-flow tuffs and interbedded collapse breccia. The open pit mine is localized along a north-south fracture and consists of several alunite-jarosite veins that individually are up to 30 cm in width. Replacement alunite and small alunite veinlets are widespread throughout the district.

The lead-zinc-silver-gold quartz deposits occur along north-south trending faults and fractures which transect all volcanic units within the Rodalquilar caldera complex except the youngest pyroxene andesite flows (Fig. 15). The Triunfo vein, which cuts the Lazaras tuff in the north-central part of the Rodalquilar caldera, is typical of these. The vein zone is about 2 m wide, includes at least two veins about 30 cm in width, and extends for about 0.5 km a strike of N 5°E. The vein extends northward into the Hortichuela ring dome and alteration extends outward from the vein into the country rock at the contact of the Lazaras tuff and a rhyolite ring dome. The Consulta vein system is similar to the Triunfo

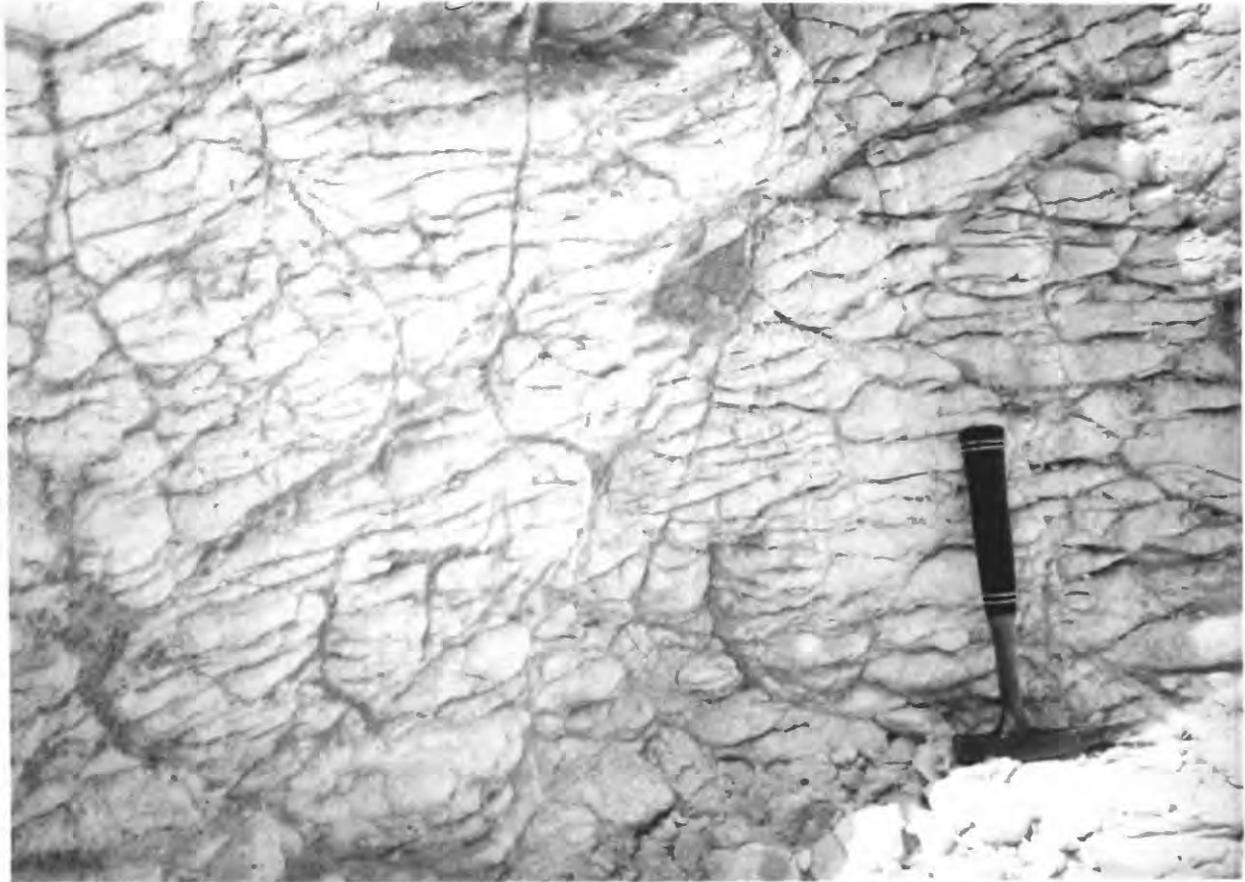


Figure 13. Alunite Stage 2 assemblage. Vein and replacement alunite in Cinto caldera-fill ash flow tuffs. Note the dark (yellow) alunite-jarosite vein stockwork.

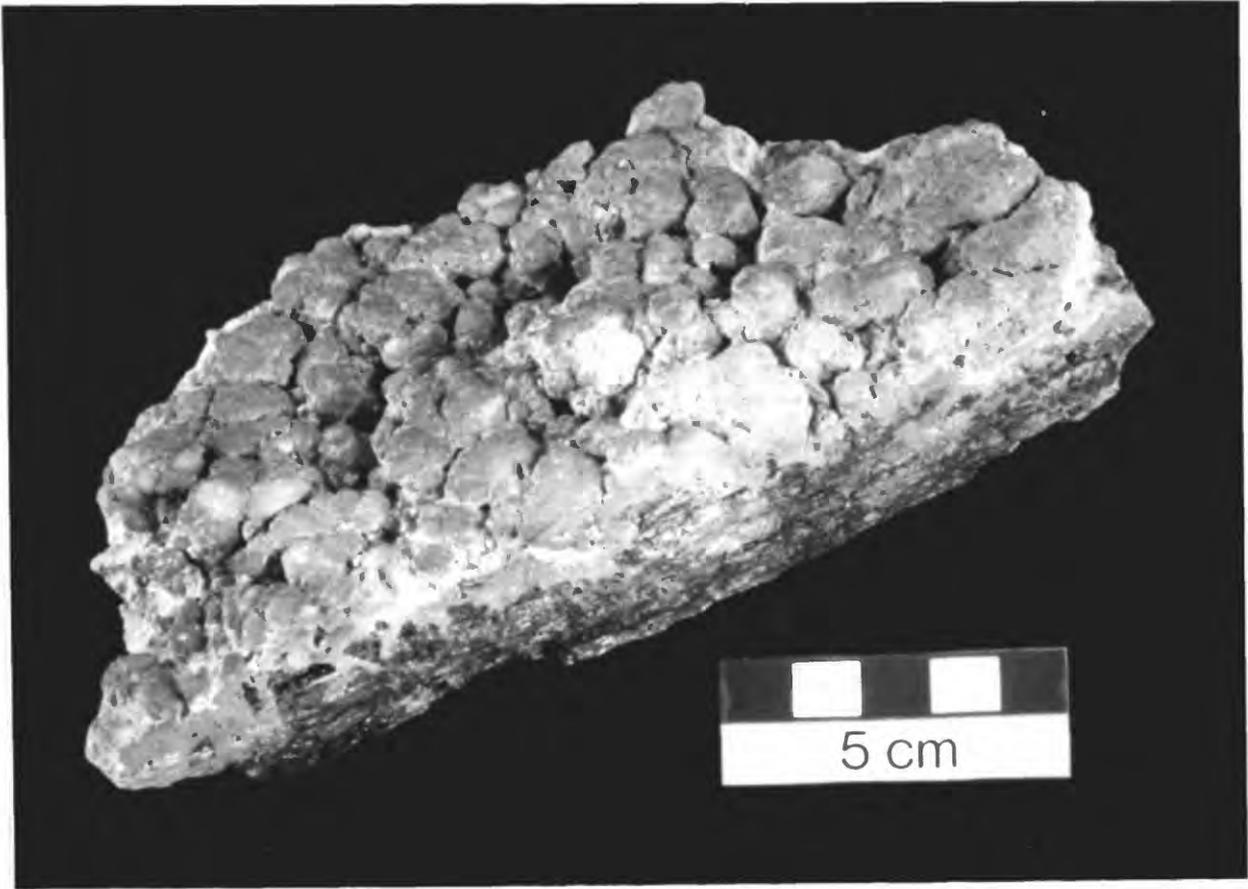


Figure 14. Alunite Stage 2 assemblage. Alunite-jarosite vein.

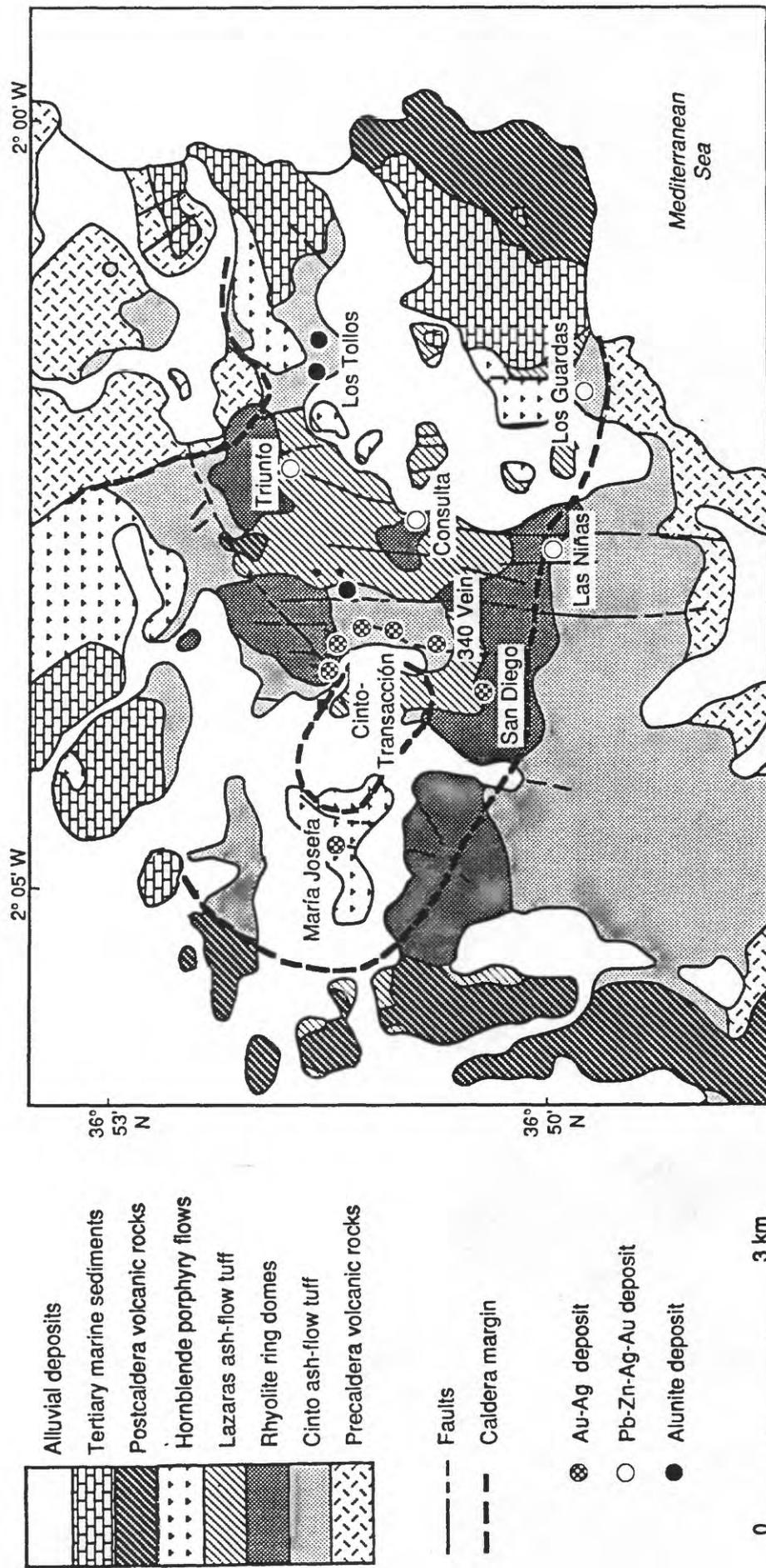


Figure 15. Location of ore deposits within the Rodalquilar caldera complex.

vein and is characterized by bands of massive galena together with minor sphalerite, pyrite, chalcopryrite, covellite and chalcocite in a quartz gangue. The vein system extends for about 1.5 km southward from the central part of the Rodalquilar caldera where it is termed the Las Niñas deposit. It is hosted by rhyolite ring domes and Lazaras ash-flow tuff. Outside the caldera the veins, consisting of unmineralized amethystine quartz, are hosted by the outflow facies of the Cinto ash-flow tuff and by precaldera andesite flows. The Los Guardas vein is hosted by intracaldera Cinto ash-flow tuff just inside the ring fracture of the Rodalquilar caldera.

The gold-alunite deposits are the most economically important deposits in the caldera complex. About 5 metric tons of gold were produced in the period 1943-1966 from these deposits account for over 80% of gold extracted from the Rodalquilar area. These deposits are preferentially localized in ring and radial fractures present in the east wall of the Lomilla caldera. Four main open pits and associated underground workings have been developed in the wall of the Lomilla caldera (Fig. 16). These deposits are hosted by intracaldera ash-flow tuffs, interbedded with collapse breccias, and the northernmost deposits are partly hosted by a rhyolite ring dome which extends into the caldera. The deposits are closely associated with plugs and dikes of hornblende andesite which intrude the intracaldera tuffs and breccias. These intrusives are altered and locally mineralized. Gold mineralization occurs in association with chalcedony veinlets and fracture coatings which cross cut acid-sulfate altered rocks. The gold mineralization extended over a vertical interval of about 100 m from the present surface and changes at depth into a complex sulfide mineralization. Outside the main zone of gold-alunite mineralization, high grade gold veins extend into the ring domes located along the southern margin of the Rodalquilar caldera. The San Diego gold vein is localized in a ring dome emplaced just north of the south-central margin of the Rodalquilar caldera. The vein zone has a maximum width of 8 m and consists of a silicified fracture zone which strikes N 45°E. The 340 gold vein is hosted by collapse breccias and is localized along a northeast trending fracture zone. It consists of a hydrothermal breccia up to 2 m wide in which fragments of vuggy silica rock are enclosed in a chalcedonic matrix. Mining grades in the 340 vein were, at intervals, higher than 500 grams per ton (Sierra and Leal, 1968) and free gold is commonly visible at the boundary of the lithic fragments. Among the ore minerals found in the 340 vein are calaverite, tellurite, native tellurium and the supergene iron chloro-tellurate, Rodalquilarite (Sierra and Leal, 1968; Sierra et al., 1968). The María Josefa vein is localized in hornblende andesite flows and high grade gold is contained in pyritic, chalcedony filling veinlets and open spaces. None of the mine workings at Rodalquilar extended to below 80-100 m. Below that depth, mineralized structures narrowed considerably and gold grades fell sharply.

The analysis of over 120 samples from representative lithologies of the gold-alunite ore (Fig. 17) shows that the highest gold values (0.40 to 380 g/t; median of 8.0 g/t) occur in black, pyritic, banded chalcedony that fills preexisting open spaces and fractures within rock previously altered to vuggy silica (0.13 to 13 g/t; median of 1.2 g/t). This late-stage chalcedony was coeval with, and later followed by, deposition of low-grade white chalcedony (gold values 0.08 to 4.10 g/t; median of 0.4 g/t) which is thought to have been deposited during the waning phase of the hydrothermal system. Black chalcedony is very rare outside the cores of hydrothermally altered rocks and below 80 m from the actual surface. Therefore, the main stage of gold deposition was superimposed on the highest parts of the central zone of quartz-alunite altered rock upwelling fluids following the peak of acidic alteration. Photographs of typical black, pyritic, banded chalcedony are shown in Figures 18 and 19. Banding is enhanced by weathering of pyrite to form jarosite and hematite. Very-fine grained pyrite (<10 micrometers) accounts for 95 percent of the ore minerals and the other five percent includes sphalerite, galena, enargite, covellite, tetrahedrite, Se-metacinnabar, ioderite, collusite, barite, and tellurides. This type of silica-



Figure 16. Overview of the eastern topographic wall of the Lomilla caldera defined by the arcuate scarp in the central part of the photo. Mine workings of the gold-alunite deposits are large open pits in wall of the caldera.

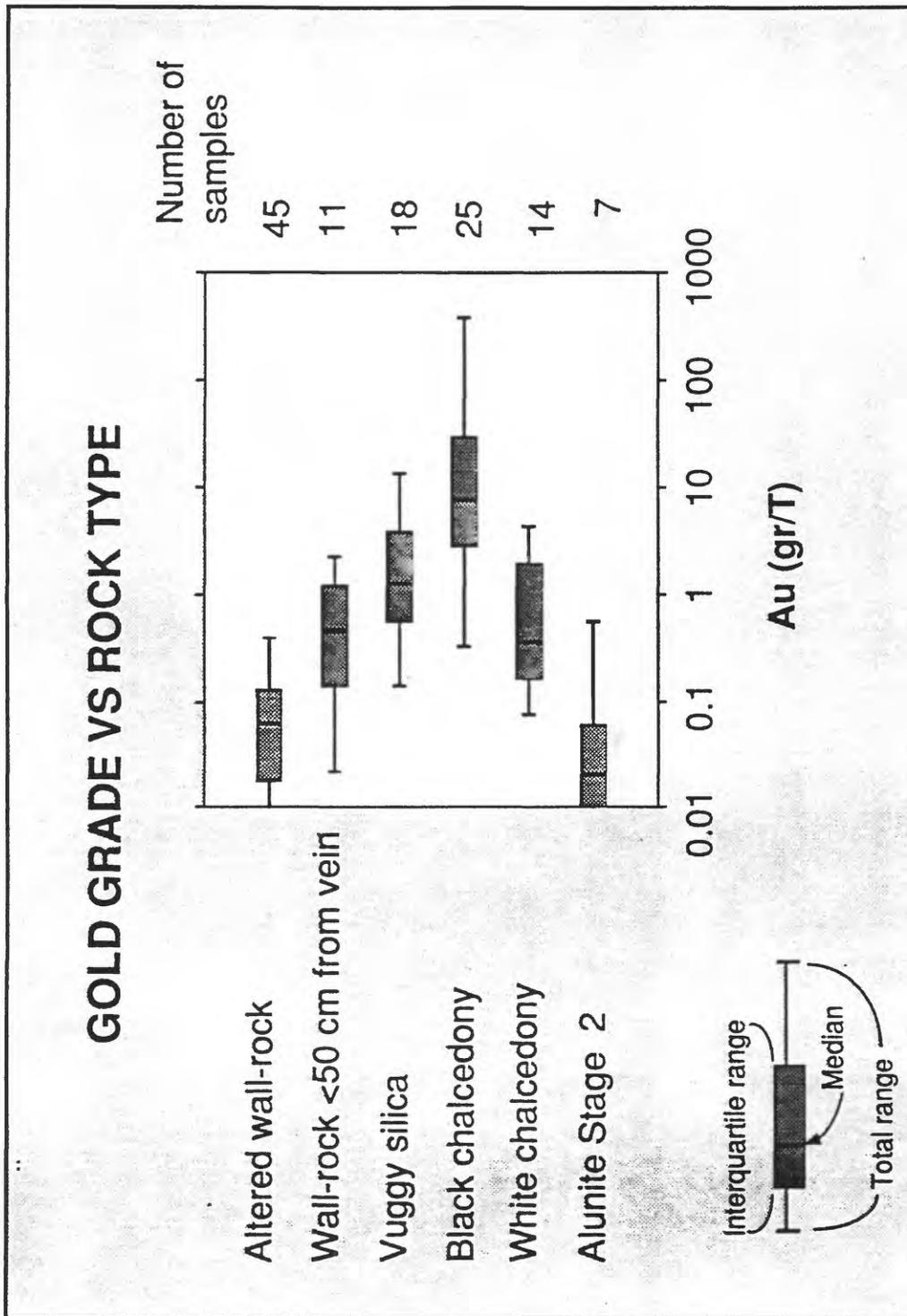


Figure 17. Box plot of 120 gold analyses on the different lithologies that are representative of the gold-alunite deposits within the Rodalquilar caldera. The lithologies are listed in their relative temporal order, younger being at the bottom, except for the altered whole rocks which may include the effects of different episodes of alteration.

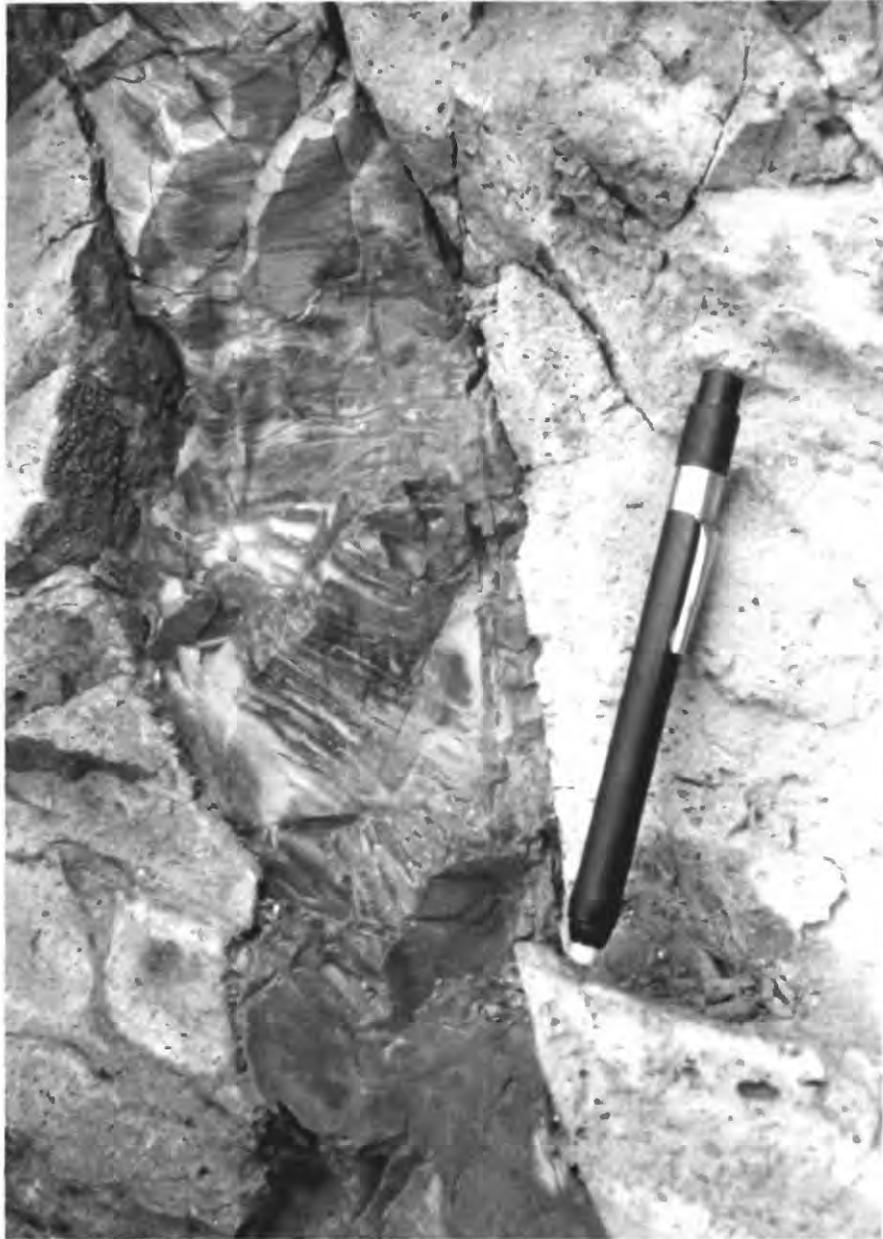


Figure 18. Fracture filled with high grade gold in black, pyritic, banded chalcidony. Some bands apperar light in color, due to weathering of the sulfide. Notice the vuggy silica wall rock. Average gold grade for this vein is 15 g/t.

Figure 19. Typical sample of high grade, pyritic, chalcedony sediment that fills a cavity in intensely altered andesite flows of the Maria Josefa Mine. Gold content, in grams per tonne, is shown for sulfide-rich and sulfide-poor areas.



sulfide precipitate is similar to pool sinter commonly found in the siliceous sinter of hot springs deposits (e.g. McLaughlin, California; Buckskin, Nevada). At the Rotokawa, New Zealand, geothermal system, hydrothermal explosion breccias contain mineralized fragments of pyrite-rich siliceous lake beds that are identical in appearance to the pyritic chalcedony described here (Krupp and Seward, 1987). These observations suggest a very shallow depth of formation for the pyritic, banded chalcedony found at Rodalquilar, within about 200 m of the paleosurface. The preservation of the caldera topographic wall and the zone of solfataric alteration also support this conclusion.

## AGE OF THE MINERALIZATION

Based on stratigraphic constraints, the age of mineralization and hydrothermal alteration within the Rodalquilar caldera complex is younger than the Lomilla caldera and sedimentary and volcanic rocks which fill the moat of the Rodalquilar caldera. The mineralization is closely associated with hornblende andesite intrusions and flows that are among the youngest volcanic rocks within the moat fill sequence of the Rodalquilar caldera. A few of the hornblende andesite flows are altered and mineralized indicating that mineralization occurred during the early phase of andesitic volcanism but ended before the last flows were emplaced at  $9.0 \pm 0.6$  Ma (Rytuba et al., 1989). The youngest volcanic rocks in the Rodalquilar area are unaltered pyroxene andesite flows which occur in the eastern part of the Rodalquilar caldera and have an age of 8.4 to 7.5 Ma (Bellon et al., 1983; Di Battistini, 1987).

Potassium-argon dating of alunite and illite from altered intracaldera tuffs from the eastern wall of the Lomilla caldera range from  $11.3 \pm 0.4$  Ma to  $9.5 \pm 0.5$  Ma and have an average of  $10.8 \pm 0.5$  Ma. These data are presented in Table 1. Illite separates were extracted from drill core samples that intersected the zone of quartz-illite-pyrite alteration located at depth, below the zones of advanced argillic and silicic alteration. Alunite was selected from outcrop samples and from drill core. Stage 1 alunite was sampled from the quartz-alunite zone in the core of advanced argillically altered rocks in the Cinto center and Stage 2 alunite was sampled from an alunite vein in the same area.

Pure illite separates were obtained by selecting the grain size fraction that contained the smallest amounts of any other phases (i.e., chlorite, kaolinite or fine-grained quartz). About 100-200 g of core (depending of the relative proportion of illite) were hand crushed in a mortar, and sieved ( $<1$  mm) to separate large quartz phenocrysts and silicified clots. Fine-grained minerals were disaggregated by shaking in distilled water and the minerals separated by settling in a water column followed by centrifugation. Alunite was separated by microdrilling samples from thick ( $\sim 1$  mm) sections of quartz-alunite rock.

Mineral paragenetic studies indicate that Stage 1 alunite and illite belong to the same hydrothermal event. Illite is abundant at depths of over 300 m, where alunite is a minor phase. Closer to the surface illite is increasingly replaced by alunite, which in places constitutes, with quartz, the major component of the rock. Although it is possible that alunite could be younger than illite, the sequence of alteration minerals seems to reflect a vertical physicochemical gradient, as observed in present geothermal systems. Conventional K-Ar dates obtained for illite are  $11.3 \pm 0.4$ ,  $11.0 \pm 0.3$ ,  $10.8 \pm 0.3$  and  $9.5 \pm 0.5$  Ma, that are for its most part slightly older than measured Stage 1 alunite dates at  $10.6 \pm 0.5$  and  $10.3 \pm 0.40$  Ma. However, they are within the analytical uncertainty of the technique, thus, they are considered essentially contemporaneous. Stage 2 alunite has not been dated, but its age should be the same as Stage 1.

Table 1. Summary of the K-Ar data obtained for the Rodalquilar gold deposit.

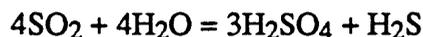
Location and Sample Number	Mineral Dated	Age (Ma)
Lomilla de las Palas (Adaro-1 drill hole, m 480) 87A14	Illite	$11.3 \pm 0.4$
Lomilla de las Palas (Adaro-1 drill hole, m 360) 87A21	Illite	$11.0 \pm 0.3$
Lomilla de las Palas (Adaro-1 drill hole, m 440) 87A10	Illite*	$10.8 \pm 0.3$
Cinto Mine (DH drill hole, m 760) 87A125	Illite*	$9.5 \pm 0.5$
Cinto Mine (open pit 1, surface) 87A150	Alunite (Stage 1)	$10.3 \pm 0.4$
Cinto Mine (DH drill hole, m 130) 87A111	Alunite (Stage 1)	$10.6 \pm 0.5$

\* also contains minor chlorite and quartz

## STABLE ISOTOPE GEOCHEMISTRY

The use of stable isotope data on alunite as a tool to distinguish different environments in fossil epithermal systems has been demonstrated in various studies (Field, 1966; Jensen et al., 1971; Bethke, 1984; Rye et al., 1988). The relation between the stable isotope ratios of alunite and the environment of formation of acid-sulfate alteration was recognized by Bethke et al., (1984) and the genetic process has been documented recently by Rye et al., (1988, 1989) in a comprehensive study of 16 epithermal systems worldwide (including the data presented here on Rodalquilar). In essence, Rye et al., (1989) propose three principal geological environments for the generation of acid-sulfate alteration : 1) oxidation of sulfides in the *supergene* environment, 2) oxidation at the water table, in the *steam heated* environment, of H<sub>2</sub>S released by deeper, boiling fluids, and 3) disproportionation of magmatic SO<sub>2</sub> to H<sub>2</sub>S and H<sub>2</sub>SO<sub>4</sub> at intermediate depths in *magmatic-hydrothermal* systems.

Figures 20 and 21 contain sulfur isotope data from pyrite, and sulfur, oxygen and hydrogen isotope data from alunite, and oxygen isotope data from present-day meteoric waters at Rodalquilar. There is a clear isotopic distinction between Stages 1 and 2 alunites supporting the interpretation of different origins based on field and petrographic observations. The range of values for Stage 1 alunite are:  $\delta^{34}\text{S} = 26 \pm 4\text{‰}$ ,  $\delta^{18}\text{O}_{\text{SO}_4} = 14 \pm 4\text{‰}$ ,  $\delta\text{D} = -25 \pm 5\text{‰}$ , and for Stage 2 alunite are:  $\delta^{34}\text{S} = 7 \pm 1\text{‰}$ ,  $\delta^{18}\text{O}_{\text{SO}_4} = 7 \pm 2\text{‰}$ ,  $\delta\text{D} = -25 \pm 5\text{‰}$ .  $\delta^{34}\text{S}$  from pyrite indicate that the bulk sulfur in the system was  $\sim 7$  per mil. Sulfur isotope data on coexisting pyrite and alunite sampled at the present surface indicate hydrothermal temperatures of 300-250°C. Stage 1 alunite formed in a *magmatic-hydrothermal* environment (Rye et al., 1988) in which requisite amounts of H<sub>2</sub>SO<sub>4</sub> to produce acid-sulfate alteration were generated from the disproportionation of SO<sub>2</sub> derived from a magma, according to the reaction:



The high  $\delta\text{D}$  values probably reflect the proximity of the area to the ocean and possible involvement of sea water in the system. Thermal waters derived from mixtures of meteoric-seawater have been reported in several coastal hydrothermal systems in Japan, Iceland and the Aegean Sea (Arnasson, 1976; Hubberten, 1975; Sakai and Matsubaya, 1974; and Löhnert, 1988)

Stage 2 alunites have values slightly larger than most of the pyrites in the mineralized zone and a large spread of  $\delta^{18}\text{O}_{\text{SO}_4}$  values. Based on the sulfur isotopic ratios and the geologic and paragenetic evidence, these alunites formed by the oxidation of H<sub>2</sub>S in a solfataria or *steam-heated* environment (Rye et al., 1988), in which superficial oxidized waters are heated by steam and other gases, including H<sub>2</sub>S, distilled from deeper boiling fluids. The simple oxidation of hydrogen sulfide, according to the reaction:



is responsible for this spectacular solfataric alteration seen at the surface of many active geothermal systems. This mechanism of alteration was originally proposed over fifty years ago to explain the effects of alteration seen in the Mt. Lassen area (Day and Allen, 1925).



$\delta^{18}\text{O}_{\text{SO}_4} - \delta\text{D}$  OF ALUNITE:  
**RODALQUILAR, ALMERIA, SPAIN**

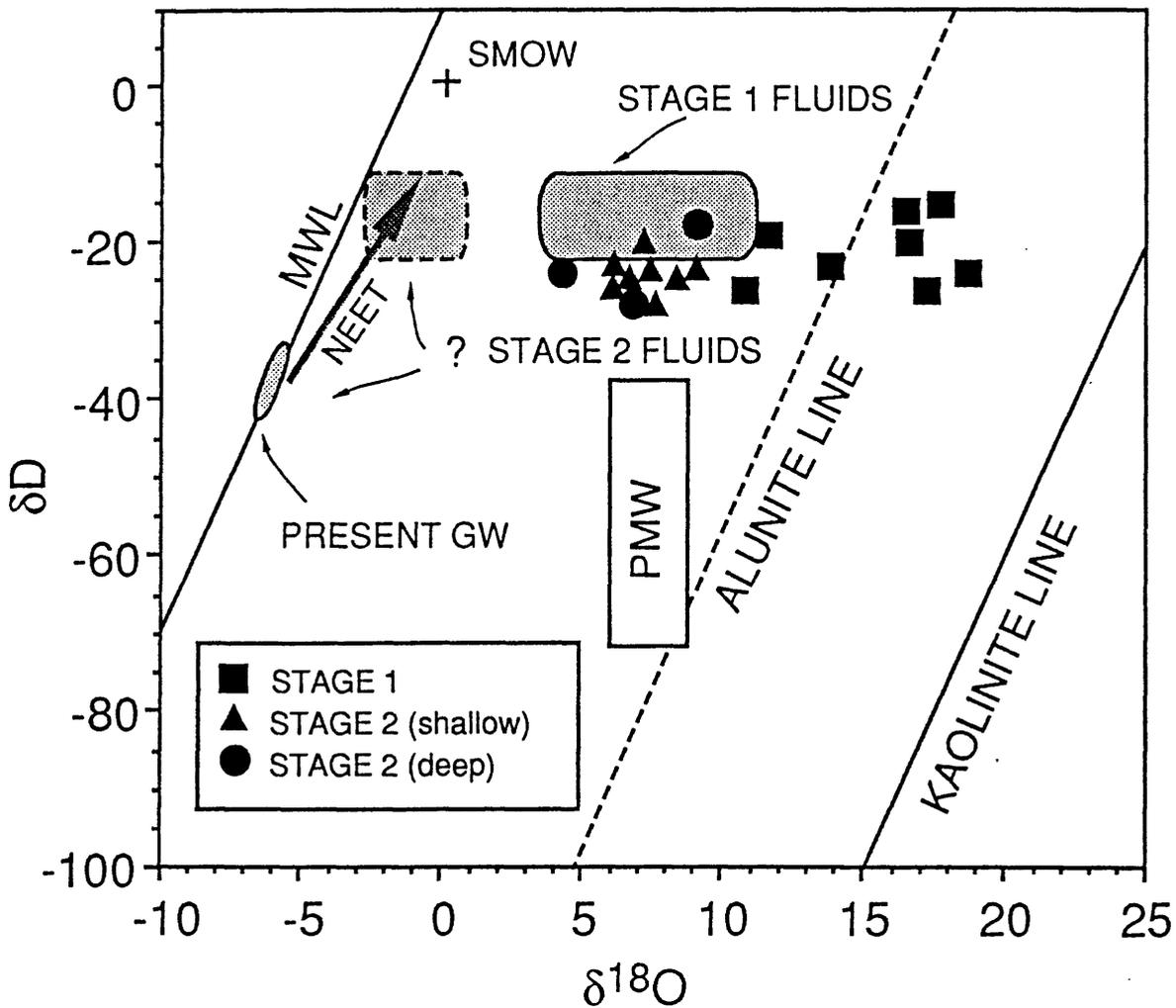


Figure 21. Summary of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data for alunite and calculated fluids. Stage 1 and 2 fluids calculated from experimental oxygen and hydrogen isotope fractionation factors from Stoffregen, Rye, and Wasserman (unpublished data) at 250°C. Such high temperature seems excessive for alunite (Stage 2) formation in the steam-heated environment. Alternatively, if Stage 2 fluids formed in the 100° to 150°C temperature interval believed to be typical of the steam-heated environment, the constraints of the extrapolated experimental  $^{18}\text{O}$  fractionations and geology require that the fluid had  $\delta\text{D}$  similar to present ground water. This in turn would require significant hydrogen isotope fractionations which have not been experimentally verified between alunite and water in the temperature range 100° to 150°C. (MWL = meteoric water line, SMOW = standard mean ocean water, PMW = primary magmatic water, GW = ground water, NEEL = non-equilibrium evaporation trend).

Figure 21 shows two possible compositions for the Stage 2 fluids depending on the temperature of alunite formation and the hydrogen alunite-water fractionations. Most steam-heated alunites probably form between about 100° and 150°C (Rye et al., 1988). Although hydrogen isotope fractionations between alunite and water are small at <50° and >250°C, they could be significant in the above temperature range judging from the shape of the kaolinite-water hydrogen isotope fractionation curve (Liu and Epstein, 1984). The <sup>18</sup>O fractionation curve for alunite-water (Stoffregen, Rye and Wasserman, unpublished) and geologic constraints require that the isotopic composition of the Stage 2 Rodalquilar fluids was close to the present meteoric water if the alunites formed between 100° and 150°C. If the steam-heated alunite formed at high temperatures their fluids must have had hydrogen isotope compositions similar to (or slightly less negative) than those for Stage 1 alunite fluids. Such compositions would suggest that the component of seawater in the steam-heated environment was important. However, waters in acid-hot springs and solfataras (i.e., at Lassen, California and Yellowstone, Wyoming) typically show an enrichment in both deuterium and oxygen relative to the initial meteoric water composition. This enrichment is due to non-equilibrium surface evaporation of steam at temperatures of about 70-100°C and the composition of the waters plot about a line of slope 3 (Craig, 1963; Muffler et al. 1982; Truesdell and Hulston, 1980). A line of this slope originating from the point of present-day ground waters ( $\delta D = -30$  to  $-40\text{‰}$ ) falls on the composition field of fluids responsible for *steam-heated* alteration at Rodalquilar (Fig. 21).

Sulfur isotope ratios of sulfides from Rodalquilar show a narrow range of values of about  $5 \pm 2 \text{‰}$ . This range of values is constant for the different generations of pyrite, disseminated pyrite in the altered wall-rock, pyrite in mineralized chalcedony, and pyrite in base-precious metals veins. Sulfur isotope temperatures on galena-sphalerite pairs from the base-precious metals veins indicate a temperature of ~250°C for the mineralization. Isotopically heavy total sulfur may be explained by an origin from reduced marine sulfate ( $\delta^{34}\text{S} = \sim 20\text{‰}$ ) due to the invasion of the hydrothermal system by seawater. However, the analysis of  $\delta^{34}\text{S}$  on sulfides from the other deposits in the Cabo de Gata volcanic field (Cabo de Gata and Mina Palaí centers) give identical values. Furthermore, north of the Cabo de Gata volcanic field, the important Cartagena base-metals deposit, which is related to the same magmatic province, also has heavy  $\delta^{34}\text{S}$  sulfide values of about 4‰ (Friedrich et al., 1964). From these data, plus trace element, lead, strontium and oxygen isotope considerations (Martín Escorza and López Ruiz, 1988) it is possible to conclude that the sulfur in magmas of the southeastern Spain Miocene volcanic province is heavy and is due to a large crustal component in the genesis of these magmas.

## CONCLUSIONS

Figure 22 shows, in an east-west cross section, the geology and ore deposits of the Rodalquilar caldera complex and integrates the results of the geological, geophysical, and geochemical studies. It is a preliminary model, that will be improved with the addition of further detailed paragenetic and geochemical data. The data presented in the related report by Rytuba et al., (1989) demonstrate that the Rodalquilar caldera and the nested Lomilla caldera resulted from the eruption of the Cinto and Lazaras ash-flow tuffs. The interpretation of the geophysical data is consistent with an intrusion located between the two main hydrothermal plumes at a depth of about two km. This intrusion is interpreted to be the heat source responsible for hydrothermal circulation. Age determinations confirm the close temporal relationship between the caldera cycle and the mineralization at about 11 Ma. An excellent plumbing system was provided by the caldera related fractures and by doming and fracturing caused by the emplacement of the intrusion. Hydrothermal alteration of the

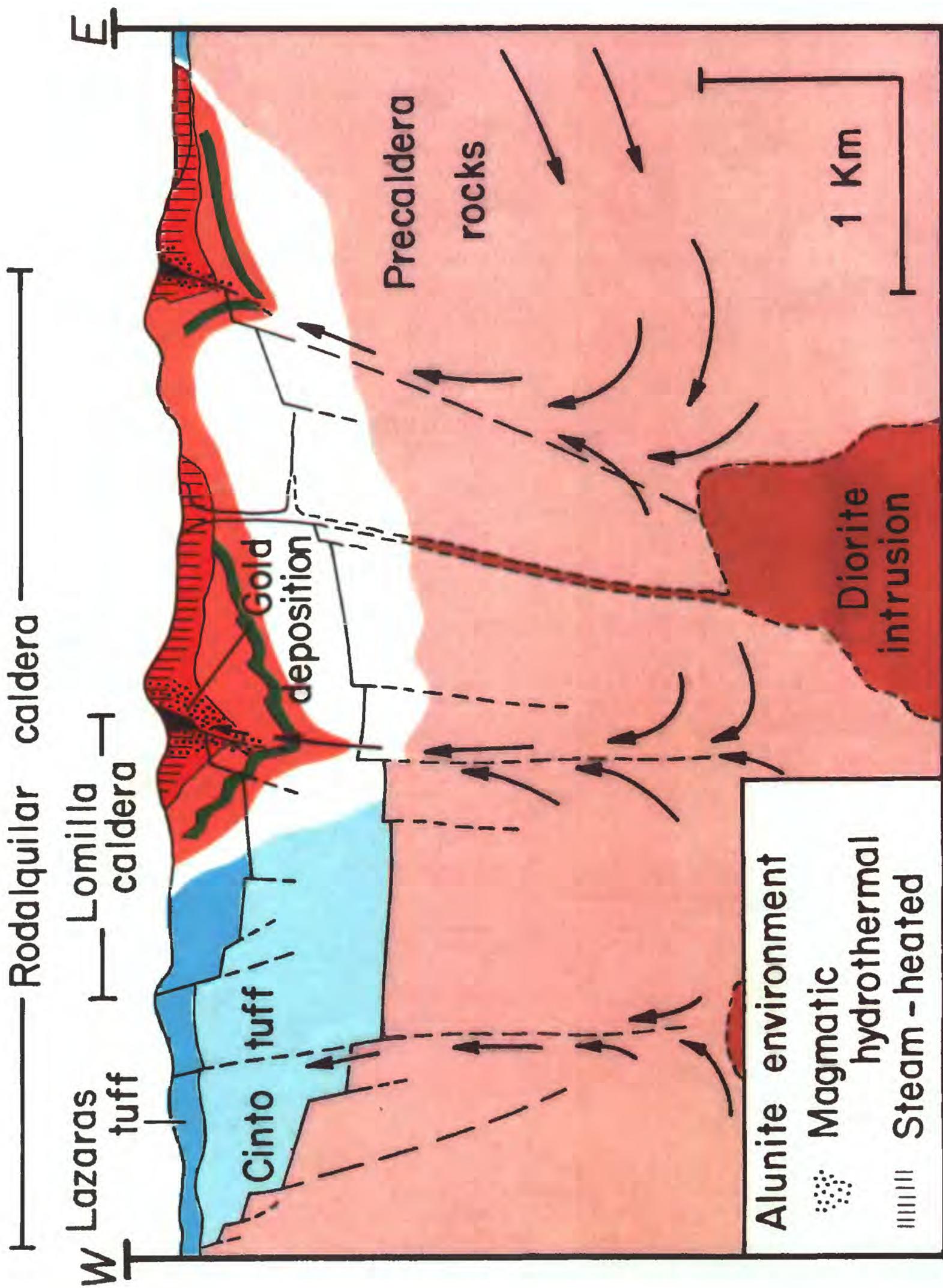


Figure 22. Interpretative east-west cross section through the Rodalquilar caldera complex passing through the Los Tollos, Cinto and María Josefa centers. It shows the size and position of the hypothesized dioritic intrusion at depth. Thickness of the cinto and Lazaras ash-flow tuffs is based on deep drilling data.

tuffs and domes of the caldera complex evolved vertically as well as laterally. An early stage of quartz-sericite-pyrite alteration was followed by acidic solutions responsible for the advanced argillic assemblages. The distribution of chlorite at depth shows the funnel shape of the hydrothermal plumes. The two types of alunite characterized by contrasting isotopic signatures define two types of environment. Stage 1 hypogene alunite, formed in the magmatic hydrothermal environment, is found in the core of the system. Isotopic temperature estimates from alunite-pyrite pairs are about 250 to 300°C. This zone probably coexisted for some time with the surrounding geothermal system in which Stage 2 alunite was formed and was later superimposed on the central hydrothermal system with its collapse. Gold mineralization occurred in the highest parts of the central core along fractures and was associated with silicification and precipitation of sulfides. A large percentage of the gold at Rodalquilar was brought to the surface and deposited as a relatively late feature in the evolution of the hydrothermal system. The introduction of gold postdated the episode of acidic fluids that formed the vuggy silica and hypogene alunite but was prior to the formation of Stage 2 alunite. The collapse of the hydrothermal system resulted in filling of open fractures, fumarolic conduits, and discharge channels, by sediments composed of alteration minerals from the superficial mud pots and hot-springs, lithic fragments of altered wall-rock, and fine-grained pyritic gold precipitates.

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