Mapping extremely altered pyroclastic rocks at the Casa Biank site, Rodalquilar Volcanic Caldera (Almería - SE Spain)

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To the mappers (an endangered species) and to those who are new to the noble and old art of mapping

On Rodalquilar and Casa Biank: There are four meanings for the term Rodalquilar (*Fig. 1*): the town of Rodalquilar, the volcanic caldera of Rodalquilar, the gold deposits of Rodalquilar (*on the western sector of the caldera: Cinto deposits*), and the Valley of Rodalquilar (*on the eastern sector of the caldera*). There are two cottages on the southern sector of the Rodalquilar Valley, one of them is called Casa Biank and in this work it gives name to an area of intense alteration (*hydrothermal and supergene*) developed in ignimbrites and tuffs of the El Cinto Unit.

The Rodalquilar caldera: The oval shaped, approximately 8 km long, E-W trending Rodalquilar caldera, is part of the calc-alcaline Cabo de Gata Volcanic Zone, where volcanic rocks range in age from about 15 to 7 Ma (*see Oyarzun et al. 2018*). Most of the volcanic rocks at the caldera were emplaced under subaereal conditions, and the volcanic sequence is covered by shallow-marine sedimentary rocks of late Tortonian to Messinian age, the so called Messinian Reef Complex (*MRC*). The best site to observe stratigraphic relationships is on the northern side of the Rodalquilar Valley.

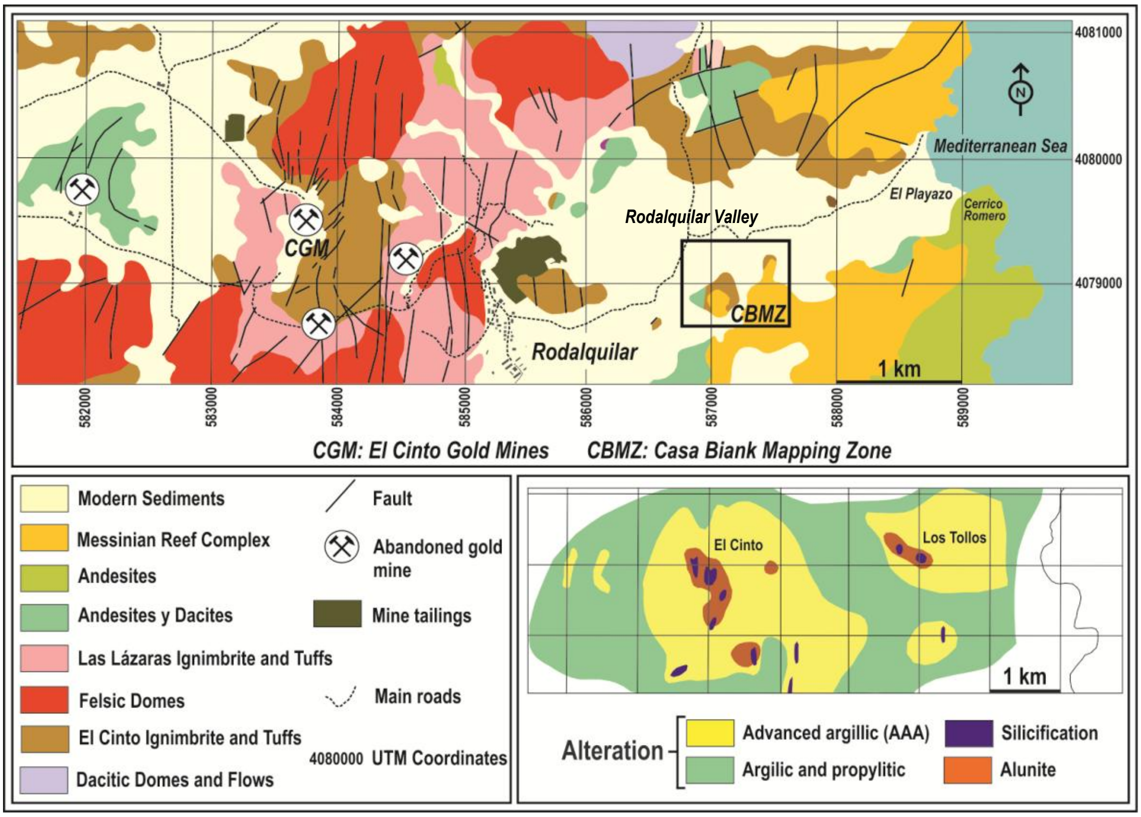


Fig. 1: Geological setting of the Rodalquilar Caldera (volcanic rocks and post caldera marine sediments), mineral deposits, and alteration; adapted from Arribas (1993) and Arribas et al (1995). See location of the Casa Biank mapping zone (CBMZ).

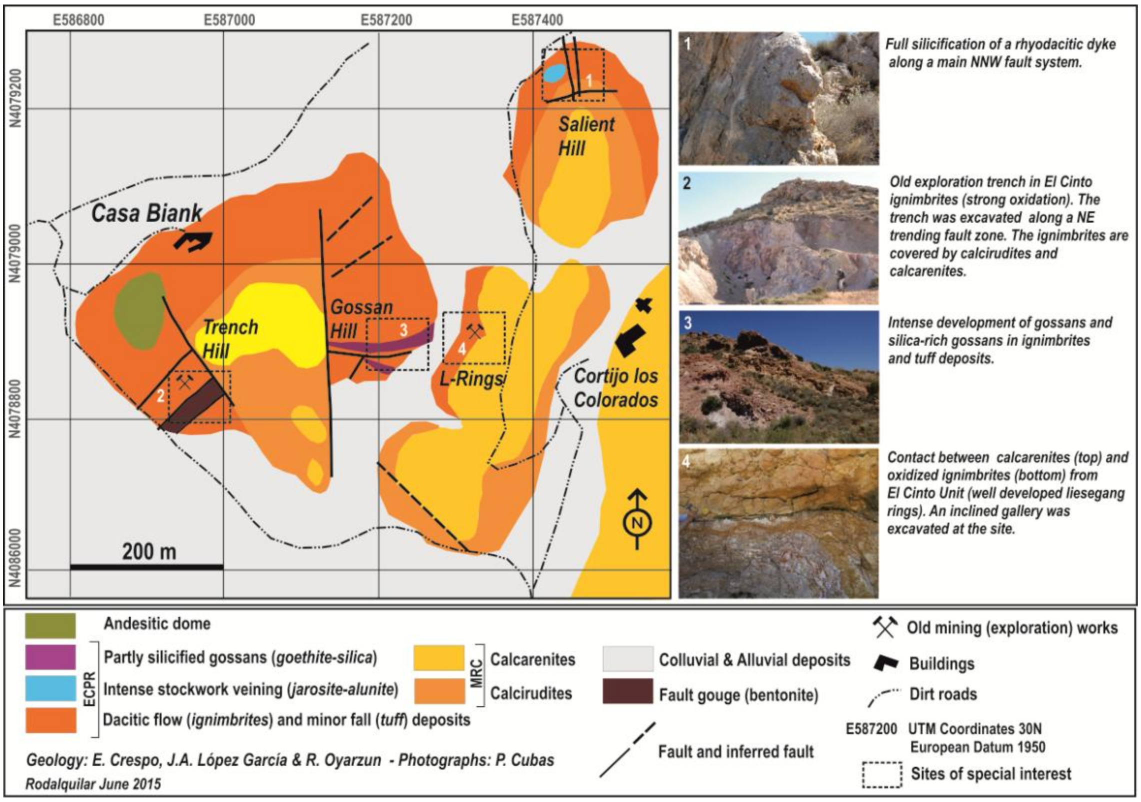
The most relevant volcanic activity at Rodalquilar took place at about 11 Ma (*early Tortonian*) and involved the emission of ignimbrites (*Cinto Ignimbrite*) and formation of the large caldera, closely followed in time by the emplacement of ring felsic domes, the emission of new ignimbrites (*Las Lázaras Ignimbrite*) (*Arribas et al. 1995)* (*Fig. 1*) and the formation of a smaller caldera (*La Lomilla*), where the main Cinto gold epithermal deposits are located. The Cinto Ignimbrite (*Fig. 1*) forms by far the largest unit at Rodalquilar, and a rough conservative estimate (*for an oval shaped area of 8 x 4 km, and a thickness of 200-250 m; Arribas et al. 1995*) may yield a volume ($V = a \times b \times \pi \times h$) of about 20 – 25 km^3 of emitted pyroclastic materials. The alteration model (*Fig.1*) includes cores of silicification surrounded by advanced argillic alteration (*alunite and kaolinite*) (*AAA*) and an external propylitic alteration halo. Massive oxidation of primary sulfides (*mostly pyrite*) and subsequent formation of acid solutions led to mineral overprinting by supergene kaolinite and alunite over the former hydrothermal assemblages. This, together with the widespread presence of limonites (*goethite and jarosite*) gives to the area a characteristic white-reddish color. Gold epithermal mineralization is found on the western sector of the Rodalquilar caldera and consists of two types: 1) epithermal Au-As high sulfidation vein and breccia type (*El Cinto mines*); and 2) low sulfidation (*peripheral*) epithermal Pb-Zn-Cu-(*Au*) veins.

Separating hydrothermal from supergene alteration in the field, not an easy task: Due to the widespread oxidation of sulfides and subsequent leaching-bleaching of the El Cinto ignimbrites, it is somewhat difficult to distinguish in the field whether the minerals typical of advanced argillic alteration (*AAA*) are of hydrothermal or supergene origin. Moreover, given the very shallow depth of the epithermal environment (*oxygen- and water-rich*), both types of processes may overlap in time and space. In this regard, as indicated by Sillitoe (*2015*), hypogene and supergene processes can be transitional in the shallow epithermal environment and, in places, difficult to separate unambiguously. Whatever the case, supergene alteration involving formation of limonite (*goethite and jarosite*) affects most if not all the El Cinto Unit (*see Appendix*). This indicates that pyrite deposition must have been a widespread intense phenomenon throughout the caldera. In this regard, this widespread deposition of pyrite offers some clues to separate hydrothermal and supergene minerals because as noted by Arribas et al. (*1995*), supergene alunite is not associated with pyrite at Rodalquilar. Thus, although at present no pyrite is found on the superficial environment, the presence of either goethite and/or jarosite may serve as an indicator of its previous presence, and as such, associated alunite should be hydrothermal.

Casa Biank: reasons for a mapping exercise: About six years ago two geologists from the Ludwig Maximilian University of Munich, Professor Anke Friederich and Dr Sara Carena (*who also work in Rodalquilar with their students*) called our attention on a peculiar case of tabular-shaped silicified body, cross-cutting the Messinian carbonate rocks. Given that there was not a detailed map of the area we decided to give it a try and on the 06.17.15 we did an express geological survey of the area (*for an equivalent work see also Oyarzun et al. 2021*) which resulted in several interesting findings and a draft map. We mapped geological units, structures, alteration and leached mineralization; the results are shown in Fig. 2. Mapping focused especially on the contact and structural relationships between the volcanics and the overlying sedimentary units (*MRC*) (*calcirudites [that could otherwise be classified as packstones] and calcarenites [finer grained] carbonate rocks*). The volcanics consists of strongly altered dacitic to rhyolitic pyroclastic deposits that comprise both ignimbrite (*dominant*) and tuff facies (*flow and fall pyroclastic deposits*). For the purposes of this map we defined and named four remarkable sites (*Fig. 2*):

- *Salient Hill*, hosting the strongly silicified tabular body: a few decimeters thick felsic dyke.
- *Trench Hill*, an old mining exploration excavation with white to reddish ignimbrites within a wide fault zone; MRC calcirudites and calcarenites cap the El Cinto pyroclastic rocks.

- *Gossan Hill*, hosting a +30 m thick sequence of ignimbrite and tuffs extremely altered (*AAA*) and/or fully transformed into a silicified reddish-brown gossan.
- The *L-Rings* contact, an abandoned inclined old shaft/gallery showing the contact between calcarenites and the Cinto ignimbrite, which displays a beautiful array of liesegang rings.



Full silicification of a rhyodacitic dyke along a main NNW fault system.

Old exploration trench in El Cinto ignimbrites (strong oxidation). The trench was excavated along a NE trending fault zone. The ignimbrites are covered by calcirudites and calcarenites.

Intense development of gossans and silica-rich gossans in ignimbrites and tuff deposits.

Contact between calcarenites (top) and oxidized ignimbrites (bottom) from El Cinto Unit (well developed liesegang rings). An inclined gallery was excavated at the site.

Geology: E. Crespo, J.A. López García & R. Oyarzun - Photographs: P. Cubas
Rodalquilar June 2015

Fig. 2. Geology of the Casa Biank mapping site. ECPR: El Cinto pyroclastic rocks; MRC: Messinian Reef Complex.

Alteration phenomena: Before alteration the silicified tabular body from Salient Hill was a felsic dyke that underwent almost complete silicification to vuggy silica. We recognized the presence of: 1) ghost relic shapes of plagioclase (*and K-*) feldspar phenocrysts, empty and filled with silica; 2) quartz phenocrysts; and 3) exotic limonite (*goethite*) (*Fig. 3*) (*see also Appendix*).

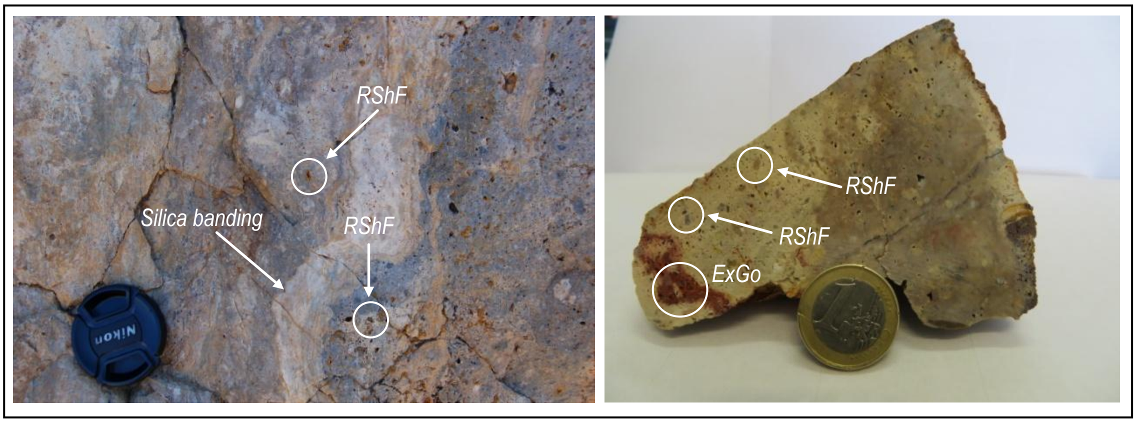


Fig. 3. Field (left) and a hand specimen (right) of vuggy silica silicification at the Salient Hill Dyke. RShF: Relic shapes of feldspars; ExGo: Mostly exotic limonites (goethite) (see Blanchard, 1968 and Appendix).

The ignimbrite and tuffs deposits from Casa Biank (*Fig. 2-4*) display the effects of the large, district-wide hydrothermal event that took place at ~10.4 Ma (*Arribas et al. 1995*) resulting in massive advanced argillic alteration (*AAA*) and sulfide (*now fully oxidized and leached*) veining and dissemination. This event involved the total replacement of feldspars in the rhyodacitic tuffs and ignimbrites by kaolinite together with formation of alunite (*see Appendix*). In addition, there is also a remarkable overprinting of the initial AAA facies by goethite and jarosite (*supergene alteration*), usually in stockwork type structural arrays or in fully developed gossans (*Fig. 4, 5*) thus indicating that hydrothermal sulfide veining must has been ubiquitous. The pyroclastic rocks are strongly bleached and leached, and the best outcrops to observe these phenomena are located in the southern slope of Trench Hill and in Gossan Hill (*Fig. 2, 4*).

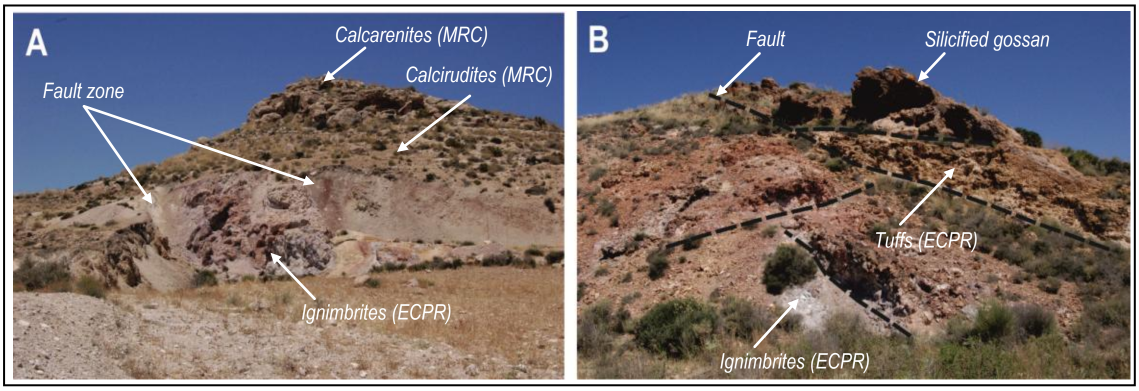


Fig.4. The Trench Hill (A) and Gossan Hill (B) sectors. ECPR: El Cinto Pyroclastic Rocks; MRC: Messinian Reef Complex.

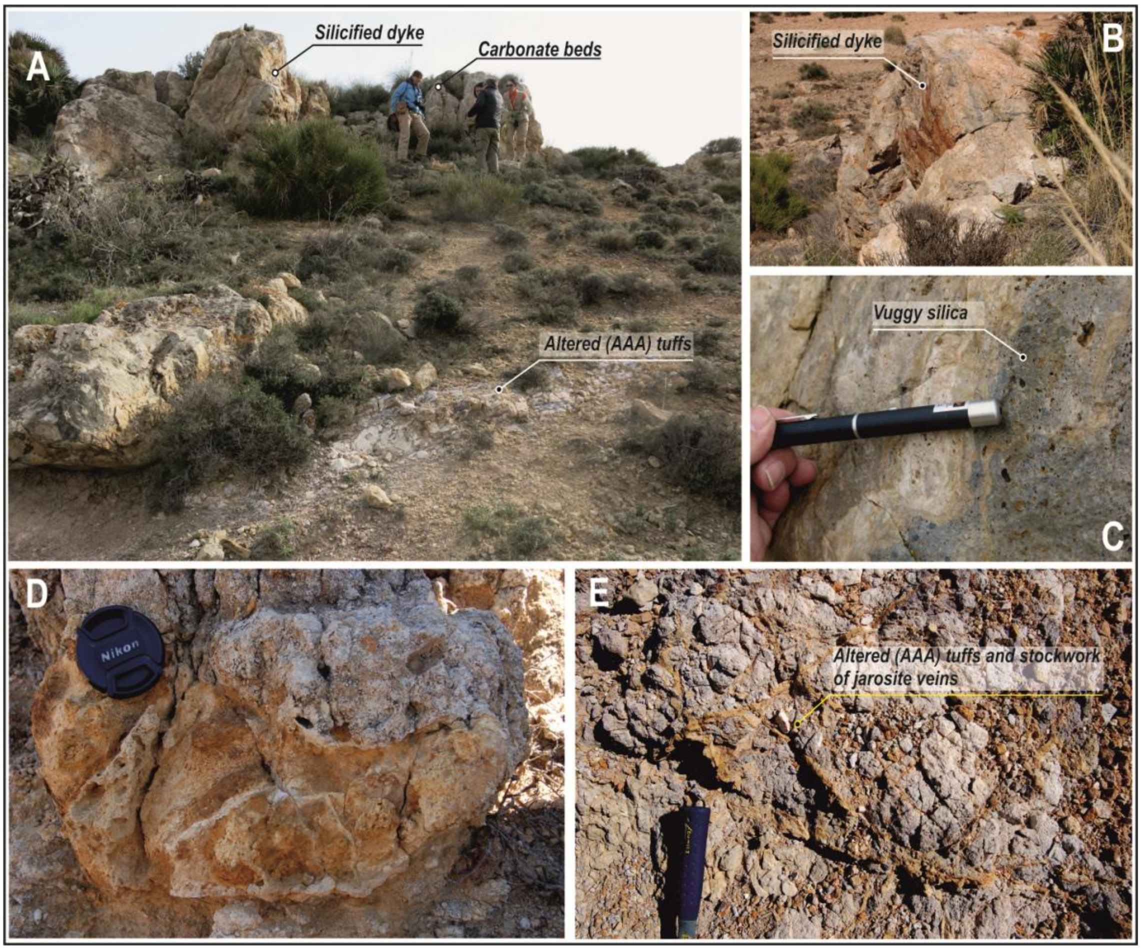


Fig. 5. The silicified dyke on the northern slope of Salient Hill (A and B). C) "Vugs" (cavities) where feldspar phenocrysts were located before complete hydrolysis and leaching. D) Brecciated carbonate rocks near the dyke; E) Tuff with advanced argillic alteration (AAA) cross-cut by a stockwork of jarosite (light brown-yellow veins).

Putting the pieces together in the stratigraphic and chronological puzzle: It is beyond dispute that the most outstanding feature of the Casa Biank geology, and one may say, of the entire eastern sector of the Rodalquilar caldera, is the lonely outcrop of a silicified dyke in Salient Hill; this dyke may hold the key to answer some (*few*) unresolved questions regarding the geology of Rodalquilar. As it has been previously suggested "except for a local occurrence of interbedded carbonate and volcanic strata in the lowest part of the (*carbonate*) section volcanism mostly predated deposition of upper Miocene marine carbonates in the study area" (*Johnson et al. 2005*). These authors further indicate that the basal carbonates (*their DS1A and DS1B sections*) are composed of heterozoan carbonates, which are Tortonian in age (*8.7 - 7.6 Ma; Johnson et al. 2005*). Besides, the aforementioned 'volcanic strata' have an absolute age of 8.5 (*Ma*) (*upper Tortonian*). There are also younger volcanics in the area such as the pyroxene andesites (*Fig.1*) that crop out in the Cerrico Romero hill. These mafic rocks are only 8 Ma old.

In this respect, the comprehensive study of Johnson et al. (*2005*) contains one piece of evidence which is particularly relevant to our work: their DS1A and DS1B basal sequences crop out at Salient Hill and Trench Hill, mostly following the distribution of our calcirudites and calcarenites units (*Fig. 2*) (*see their figure 5*). We know that the dyke (*at least*) cross cuts the calcirudites, therefore this later felsic magmatic episode could be at least as young as 8 Ma (*i.e. something within the age range for DS1A and DS1B*). This age also corresponds to a "mafic" episode of volcanic activity (*the pyroxene andesites*), but given that there are boulders of pyroxene andesite in the base of the calcirudites (*Fig. 6*), the age of the latter must be younger than 8 Ma, and the dyke, even younger than that of the calcirudites.

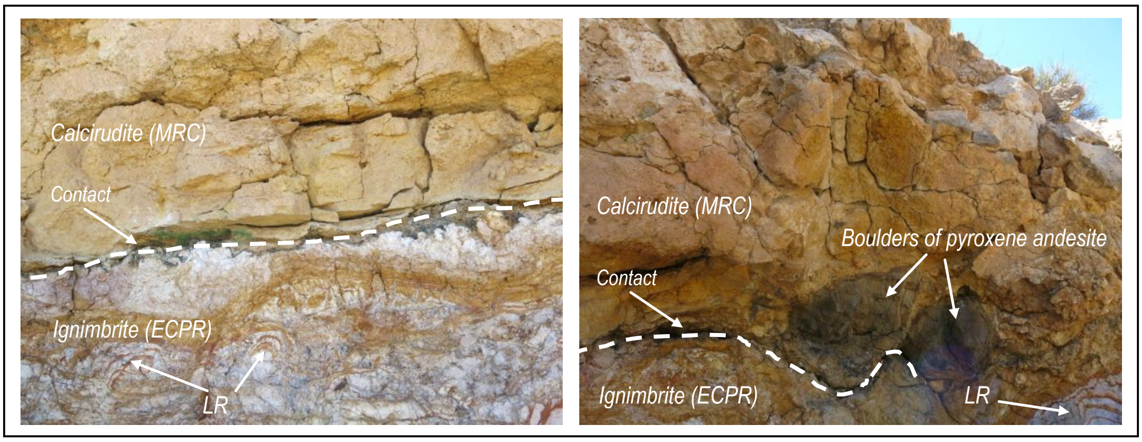


Fig. 6. Contact relationships between the ignimbrites and the calcirudites at L-Rings site (Fig. 2). A) calcirudites resting on top of the El Cinto ignimbrite (with abundant liesegang rings); .B) Boulders of pyroxene andesite at the base of the sedimentary sequence. ECPR: El Cinto Pyroclastic Rocks; MRC: Messinan Reef Complex; LR: Liesegang rings.

However, perhaps this is an oversimplification, because even if the mafic magmatism would have lasted just a mere 10 ky (*10,000 years*), this is more than enough time for these rocks to become deeply eroded. Nature does not need millions of years to remove part of a coastal volcanic sequence; in fact, coastal erosion rates can be as high as 1 my^{-1} (*e.g. Hapke and Plant, 2010*). In this regard, let us put forward just one example: at around 7.7 ky (*lower Holocene*) a barrier shoreline was located approximately 55 km offshore the present Galveston Bay (*Gulf of Mexico*) (*Rodriguez et al. 2004*), which implies a coastal retreat (*and associated erosion*) of 7.3 my^{-1}. Thus, mafic volcanism and coastal erosion at Rodalquilar may have been coexisting phenomena while the sedimentary facies of the MRC were being deposited. If this is correct, then there is no compelling reason to discard the idea of coeval felsic (*Casa Biank dyke*) and mafic (*Cerrico Romero pyroxene andesites*) magmatism (*i.e. bimodal magmatism*). Whatever the case, it is too early to say anything more with the present data. In this respect, finding more outcrops of late felsic volcanics elsewhere in this realm could help a lot to build a more solid model, otherwise we will be stuck with plausible ideas but little more.

To know more about the subject:

A. Arribas (1993) Mapa Geológico del Distrito de Rodalquilar (scale 1: 25,000). Instituto Tecnológico Geominero de España, Madrid

A. Arribas, C.G. Cunningham, J.J. Rytuba, R.O. Rye, W.C. Kelly, M.H. Podwysocki, E.H. McKee & R.M. Tosdal (1995) Geology, geochronology, fluid inclusions, and isotope geochemistry of the Rodalquilar gold alunite deposit, Spain. Economic Geolology 90: 795-822.

R. Blanchard (1968) Interpretation of Leached Outcrops. MacKay School of Mines, University of Nevada, Reno. 196 pp.

J. Daoud & D. Karamanev (2006) Formation of jarosite during Fe^{2+} oxidation by Acidithiobacillus ferrooxidans. Minerals Engineering 19: 960–967.

C. Hapke & N. Plant (2010) Predicting coastal cliff erosion using a bayesian probablilistic model. Marine Geology 278: 140-149.

P. Heald, N.K. Foley & D. Hayba (1987) Comparative anatomy of volcanic-hosted epithermal deposits: acid sulfate and adularia-sericite types. Economic Geology 82, 1−26.

C.L. Johnson, E.K. Franseen & R.H. Goldstein (2005) The effects of sea level and palaeotopography on lithofacies distribution and geometries in heterozoan carbonates, south-eastern Spain. Sedimentology 52: 513-536

J.W. Montoya & J.J. Hemley (1975) Activity relations and stabilities in alkali feldspar and mica alteration reactions. Economic Geology 70, 577−583.

R. Oyarzun, J.A., López García & E. Crespo (2018) The Cabo the Gata Miocene volcanics and the gold mining district of Rodalquilar – SE Spain: a field & teaching guide. Some insights into the geology, ore deposits, mining, and environmental issues. Aula2puntonet – GEMM, https://aulados.net/GEMM/Libros_Manuales/index_libros.html. 80pp.

R. Oyarzun, J. Lillo, J. Oyarzún, H. Maturana, & P. Higueras, P (2007) Mineral deposits and Cu-Zn-As dispersion - contamination in stream sediments from the semiarid Coquimbo Region, Chile. Environmental Geology 53: 283-294.

R. Oyarzun & J.A. López García (2021) 'Express' geological mapping of potential targets during reconnaissance surveys in volcanic terrains: an example from Almería, Spain. Aula2puntonet-GEMM, https://aulados.net/Geologia_yacimientos/Express_Mapping/Express_Mapping.pdf, 3 pp.

A.B. Rodriguez, J.B. Anderson, F.P. Siringan & M. Taviani (2004) Holocene evolution of the east Texas Coast and inner continental shelf: a long-strike variability in coastal retreat rates. Journal of Sedimentary Research 74: 405-421.

R.H. Sillitoe (2015) Epithermal paleosurfaces. Mineralium Deposita 50: 767–793.

Appendix

Chemical processes involved in the generation of advanced argillic alteration and oxidation of pyrite

Enhanced hydrolysis during hydrothermal activity leads to the destruction of feldspars, through subsequent formation of sericite (1), kaolinite (2), and even alunite (3) if H_2SO_4 is present in the system (e.g. Montoya and Hemley, 1975; Oyarzun et al. 2007):

(1) $3KAlSi_3O_8 + 2H^+ \longrightarrow KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2K^+$
(2) $2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \longrightarrow 3Al_2Si_2O_5(OH)_4 + 2K^+$
(3) $KAl_3Si_3O_{10}(OH)_2 + 4H^+ + 2(SO_4)^{2-} \longrightarrow KAl_3(SO_4)_2(OH)_6 + 3SiO_2$

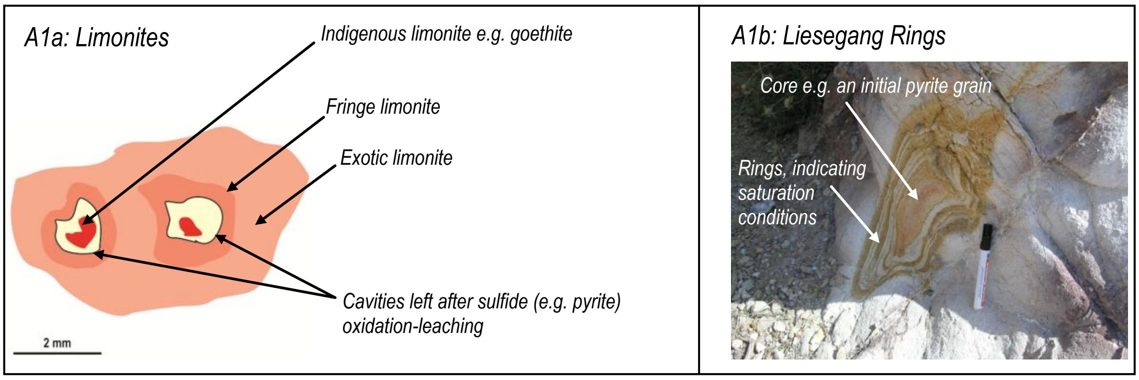
These reactions are common in pyrite-rich high sulfidation (acid sulfate) epithermal systems (Heald et al. 1987), such as those of Rodalquilar). When oxidation of this hydrothermal pyrite begins in the weathering environment, no minerals (such as feldspars) are left (see 1-3) to react with the acid and ferric sulfate generated during oxidation:

(4) $FeS_2 + 3.5O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$
(5) $Fe^{2+} + 0.25O_2 + H^+ \longrightarrow Fe^{3+} + 0.5H_2O$
(6) $4FeS_2 + 10H_2O + 15O_2 \longrightarrow 4FeO(OH) + 16H^+ + 8SO_4^{-2}$

The acid generated by the oxidation of pyrite can also induce formation of kaolinite and alunite (2,3), of supergene origin in this case, and this is the reason why two types of kaolinite and alunite can be found in Rodalquilar. See reaction 6 for the formation of goethite. Jarosite (7) will form only under arid to semiarid conditions (such as the climate of SE Spain) because if the water content increases goethite becomes the only stable limonite phase (Blanchard, 1968). Formation of jarosite can be expressed as (Daoud & Karamanev, 2006):

(7) $3Fe^{3+} + K^+ + 2HSO_4^- + 6H_2O \longrightarrow KFe_3(SO_4)_2(OH)_6 + 8H^+$

Last but not least, oxidation-leaching does not implies that the sulfide grain just vanishes, it leaves traces of its presence in the manner of cavities, that can be (Fig. A1a): i) empty (no sulfide present) but with "indigenous" limonites within the cavity; ii) "fringe" limonites which are near enough to the cavity to relate each other; and finally iii) "exotic" limonites, far enough from the cavity that it is impossible to relate each other (Blanchard, 1968). This is not just a taxonomic classification of limonites because the dominance of one type over the other tells us a lot regarding the chemistry of the system. If indigenous limonites dominate, then the oxidation-leaching and transport was severely restricted. This can occur because the acid reacted with a carbonate rock or a porphyry rich in feldspars. In both cases the acid will be neutralized. If exotic limonites dominate such as at Rodalquilar, then this means that there were no feldspar left after the AAA hydrothermal alteration event took place; therefore, the acid was not neutralized (no hydrolysis took place) and iron could be massively exported to form goethite and jarosite.


A1a: Limonites

A1b: Liesegang Rings

Fig. A1. a) The three types of limonites, in this case, with two isolated small boxworks probably derived from pyrite; the extent of the exotic limonite halo indicates a strong production of acid (and Fe transport) during sulfide oxidation-leaching (based on Blanchard, 1968). b) Liesegang rings in El Cinto ignimbrite (road from Rodalquilar to Los Albaricoques).

Formation of liesegang rings can be regarded as a related phenomenon, in which the rings reflect solution saturation. When part of the iron precipitates saturation conditions disappear, therefore the solution can continue to travel (no rings are formed) until dehydration results in saturation conditions again and iron precipitation, a process which repeats itself several times. The progressive oxidation of iron from Fe^{2+} to Fe^{3+} may also play a role because Fe^{3+} does not migrate in solution, i.e. it goes down as $Fe(OH)_3$, a precursor chemical phase of $FeO(OH)$.