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Geological context and plumbotectonic evolution of the giant Almadén Mercury Deposit

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ABSTRACT

The Almadén mine has been the largest among several mercury deposits that represent the biggest mercury concentration in the world. The deposits form a mining district which is located in a 30 km long and up to 15 km wide WNW–ESE oriented syncline, where a thick Lower Ordovician–Upper Devonian siliciclastic sedimentary sequence outcrops. Most of the deposits are located in the south subvertical syncline flank, which has an opposite vergence to the rest of the region. Of special note is the presence of important NW–SE to WNW–ESE crustal structures that played a major role at several times during the regional geological history and controlled the sedimentary unit distribution, volcanism and deformation. One of these structures seems to have played an important role in the Almadén area, probably having been responsible for the anomalous syncline geometry. This structure acted during the E–W Variscan shortening as a ductile–fragile sinistral shear zone that resulted in a subvertical attitude of the southern Almadén Syncline flank, affecting the sedimentary sequence longitudinally. The Hg deposits in the region correspond to two types, stratabound and stockworks. The former are hosted in well-defined “Criadero Quartzite” orthoquartzite levels of Ordovician–Silurian age. These deposits were folded and sheared during the Variscan deformation. The stockwork deposits filled fractures and veins and partially replaced the volcanic rocks affected by the Variscan shear zones. The replacement process took place at the end of the E–W Variscan shortening

The Almadén deposit belongs to the stratabound type and has three mineralized levels, one located in the lower part and the other two in the upper part of the “Criadero Quartzite”. Of minor relevance, other small stockwork bodies, replacing a volcanic breccia-tuff known as “Frailesca” rock, have also been exploited. This rock formed massive lenticular bodies that have been interpreted as pre-Variscan diatremes. On the basis of field criteria we conclude that the “Frailesca” rock emplacement took place later than cinnabar mineralization. After the “Frailesca” rock was formed, it was cut by sills of quartz-diabase that resulted from a new magmatic event. Both volcanic materials affect the mercury ore, developing small aureoles of contact metamorphism and volatilizing the cinnabar. The deposit shows three sectors, separated by two straight dextral faults, which cut the sinistral WNW–ESE shears bands. The latter affect the mercury ore, mostly in its western area.

Lead isotopes from Almadén cinnabar deposits show a broad range of values, higher than those predicted for the Stacey and Kramers and Cumming and Richards crustal Pb evolution models but largely tallying with the Sardinia evolution line for this sector of the Variscan basement quite well. The data set plotted along the Sardinia curve in several well defined clusters that could be interpreted as a lead extraction by means of large scale convective hydrothermal systems from a lead reservoir located in the upper crust at a time indicated by the Sardinia curve. The estimated ages for this lead model evolution indicate lead extraction as having occurred during the late Silurian–Devonian (420–375 Ma), late Variscan (300 Ma,), Permian–Triassic (290–220 Ma), late Jurassic–Early Cretaceous (200–150 Ma) and Eocene–Oligocene (50–25 Ma), and are coincident with the main extensional tectonic episodes (from late Ordovician to Devonian, Permian to Triassic and Late Jurassic to Early Cretaceous). This shows that cinnabar is likely to have been mostly remobilized–crystallized during the regional extensional tectonic events, capturing lead from the host sedimentary sequence. This lead was mobilized by large scale, long term hydrothermal convective cells at various times, constituting a complex geotectonic history for the ore-forming processes.

1. Introduction

In the Iberian Peninsula two main mercury districts are found, the giant Almadén area (Higueras et al., 2000, 2013; Ortega and

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Hernández Sobrino, 1992; Saupe, 1973, 1990) and the Cantabrian area. Numerous small deposits are found in the latter (Martín-Izard et al., 2009 and references therein). The former mining district has by far the greatest accumulation of mercury in the world. Just 6 mines (Almadén, El Entredicho, Las Cuevas, Vieja Concepción, Nueva Concepción and Guadalperal) accounted for more than 35% of worldwide Hg production. Of these 6 mines, the Almadén Mine was an exceptional deposit and is a clear example of what in metallogeny is known as a Giant Ore Deposit. Moreover, it is no exaggeration to say that Almadén is a unique case with regard to mercury deposits. The exceptional nature of this mining district, particularly the Almadén giant deposit, on a world-wide scale lies in the geological concentration process that has led to the accumulation of this huge amount of mercury, an element with a rather low average content at crustal level (about 67 ppb). Moreover, the Spanish deposits represent a unique geological context and show very different metallogenic characteristics from the rest of the world's mercury deposits, enabling us to speak of the "Almadén type" deposits.

The huge geochemical anomaly represented by the Almadén deposits and the lack of other deposits of such size and equivalent geological features make it difficult to establish a genetic model to explain their formation. In this respect, two hypotheses, both taking into account the important Paleozoic volcanic activity spatially related to the ores in the Almadén area, have been postulated. The first (Saupé, 1973, 1990) assumes a mercury concentration in the host shallow marine sediments that is later remobilized by the volcanic processes and then concentrated in a number of epigenetic structures. The second (Hernández Sobrino et al., 1999; Higueras et al., 2000, 2013; Ortega and Hernández Sobrino, 1992) proposed a deep mantle origin for the mercury, which rises to the surface together with the volcanic rocks, including ultramafic rocks of mantle affinity.

The use of analytical tools to understand the geological processes involved in the genesis of ore deposits gives us information that helps us understand the formation conditions of these mercury mineralizations. Up to the present moment several authors have published S, C and O stable isotope data (Eichmann et al., 1977; Jébrak et al., 2002; Rytuba et al., 1989; Saupé and Arnold, 1992). In all cases the results obtained show a broad range that has made it impossible to confirm either of the two proposed hypotheses.

The use of lead isotopes in cinnabar was not possible until recent times, after some analytical problems had been solved (Chernyshev et al., 2007). Thus, the first lead isotopes from Almadén were obtained using pyrite that appears to be related to mercury mineralization (Jébrak et al., 2002). The first lead isotopes from cinnabar were presented by Higueras et al. (2005), using samples mostly obtained from the El Entredicho mine.

In this paper we present lead isotope results from the Almadén mine using representative samples. Our sampling has taken into account the different main ore-bodies and mineralization types. Some samples from El Entredicho and Las Cuevas mines have also been analyzed to contrast and check previously published data. The results obtained exhibit a wide range of values, making their interpretation difficult. We attempt to explain the results in the geological context and with regard to plumbotectonic evolution of this area of the Variscan massif.

2. Geological setting

The Almadén Mining District is located in central Spain, about 300 km SSW of Madrid and about 260 km to the NE of Seville. In the regional geological context, the Almadén Hg deposits lie in a great syncline near to the southern edge of Central-Iberian Zone (Fig. 1), according to the subdivision of the Variscan Iberian Massif made by Julivert et al. (1972).

The rocks that crop out in the Almadén region are mainly siliciclastic, formed in diverse marine environments. Their original textures have not been altered by metamorphic processes (Saupé et al., 1977). The oldest rocks found in the anticlines include the "Schist-Greywacke Complex" (CEG) that occurs in large areas in the center and the western part of the Iberian Peninsula (Bouyx, 1970; Lotze, 1970). These rocks constitute a monotonous multilayered sequence of shales and greywackes formed in a turbiditic environment. A sequence made up of siltstones, black shales, conglomerates and carbonate lenses unconformably overlies the turbidite sequence in some sectors (Bouyx, 1970; Ortega and González Lodeiro, 1986; Palero, 1993; San José et al., 1990). The age of these rocks is Late Precambrian (Vendian in San José et al., 1990), although some authors indicate that the age could also reach Lower Cambrian (Lorenzo Álvarez and Solé, 1988; Vidal et al., 1994).

A thick Paleozoic sedimentary sequence unconformably overlies the Precambrian rocks and the Almadén Syncline shows one of the most complete Ordovician to Devonian sequences that can be found in the Central-Iberian Zone (Almela et al., 1962; García-Sansegundo et al., 1987a,b; Saupé, 1973). These rocks were formed in a marine shelf basin and the sequence includes abundant volcanic intercalations. The different types of sediment are mainly the results of variations in the sea level in a stable basin, during Ordovician, Silurian and Lower Devonian times, allowing us to define several litho-stratigraphic units based on the predominance of one of the following three lithologies: orthoquartzites, siltstones and black shales. Four orthoquartzite units with good regional continuity outline the general structure on the geological map. These units are, from the bottom to the top (Almela et al., 1962; Pardo and García Alcalde, 1984; Vilas et al., 1999)

"Armonicana Quartzite" of Lower Ordovician (Arenig) age.
"Canteras Quartzite" of Upper Ordovician (Caradocian) age.
"Criadero Quartzite" of Ordovician–Silurian transition (Hirnantian–Llandovery) age.
"Basal Quartzite" of Lower Devonian (Gedinian–Siegenian) age.

The Middle Devonian is not present in the Almadén Syncline (Pardo and García Alcalde, 1984), the basin having been unstable during the Devonian, with strong volcanic activity reflecting extensional conditions. In this respect, it should be pointed out that the magmatic rocks found in the Silurian sequence are mainly dikes, sills and diatremes, while in the Devonian sequence they are mostly volcano-sedimentary.

To the south of Almadén and beyond the syncline, there is a wide and monotonous sequence of black shales, siltstones, greywackes and conglomerates of Lower Carboniferous (Visean) age (Rodríguez Pevida et al., 1990). This sequence is named "Los Pedroches Culm" and was deposited in an unstable marine platform basin (Mira et al., 1987; Pérez Lorente, 1979).

3. The structural context

From a structural point of view, the Almadén area is characterized by a succession of large Variscan folds trending WNW–ESE with subvertical axial planes, slightly verging towards the south (Fig. 1). The general macrostructure of these folds is defined by the "Armonicana Quartzite", which has thickness up to 300 meters and good regional continuity.

The Variscan deformations overprint several pre-Ordovician movements. The general vertical attitude of the turbiditic Precambrian sequence indicates a previous folding. This tectonic event took place before the deposition of the Late Precambrian–Cambrian sequence of siltstones, black-shales, conglomerates and carbonate lenses. This sequence was controlled by important NW–SE crustal faults, which show important vertical block movements prior to sedimentation of Paleozoic rocks. Ortega et al. (1988) proposed a geotectonic model for the southern part of the Central Iberian Zone in pre-Ordovician times in which important tectonic block movements, caused by these NW–SE faults, control the regional distribution of Cambrian and Precambrian rocks.

The Ordovician–Silurian sedimentary sequence apparently took place in a stable marine platform developed on a passive continental

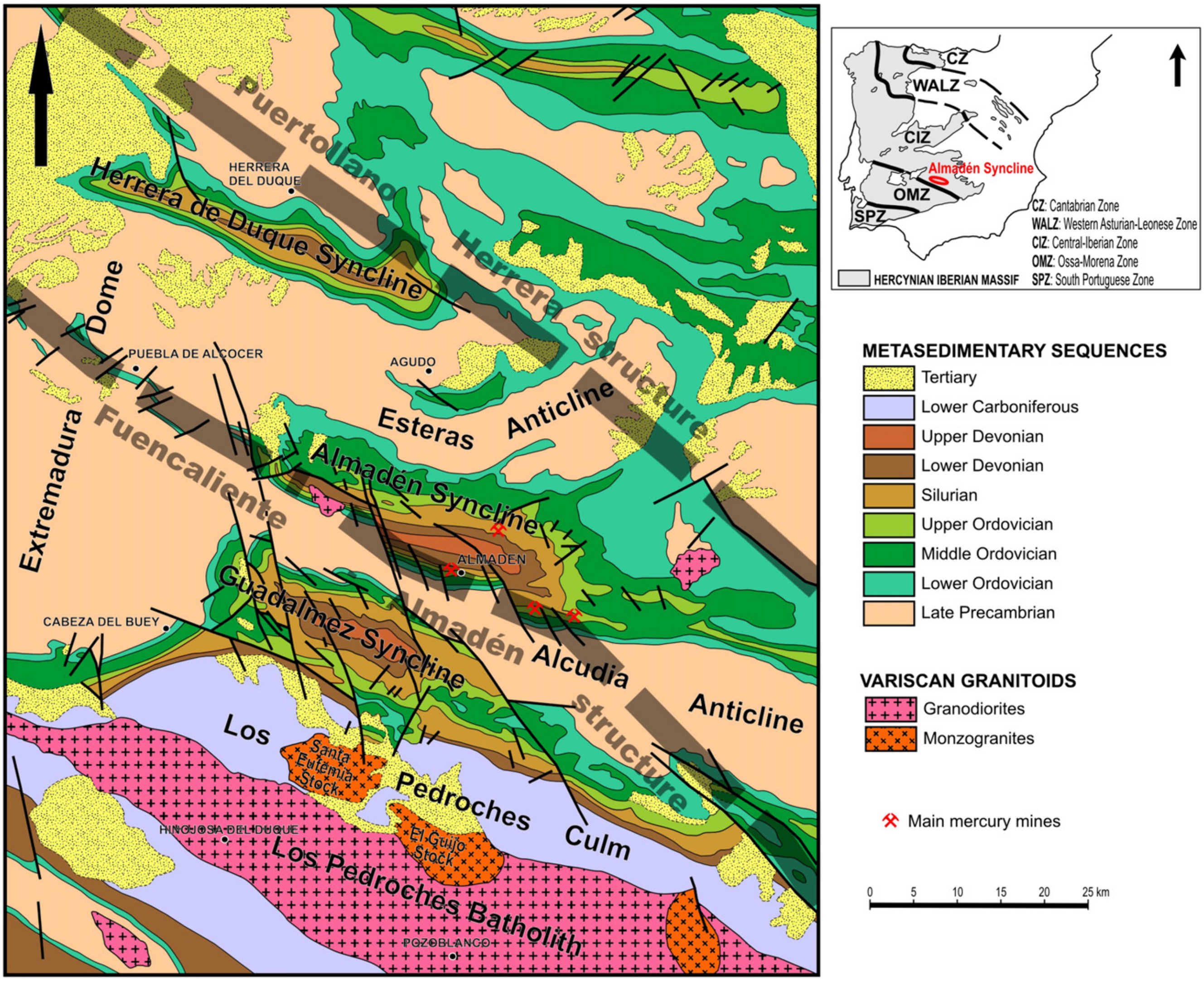

Fig. 1. Geological map of area surrounding Almadén Syncline (modified after Parga et al., 1982: "Mapa Xeolóxico do Macizo Hespérico").

margin where lithostratigraphic units have great lateral continuity. During the Devonian (after the deposition of the "Basal Quartzite"), a basin with strong subsidence was restricted to the Almadén area, where the thicker Devonian sequence of the region is located in this syncline and in the Guadalmez Syncline just to the south. The presence of abundant volcanoclastic material interbedded in the Silurian sequence and, above all, in the Devonian of the Almadén Syncline indicates extensional conditions in this subsiding basin, probably controlled by the NW–SE fractures, one of them present in the southern flank of the Almadén Syncline (Fig. 1). This favored the deposition of the thick sedimentary sequence, which is very rich in volcanic material in a possible pull-apart basin. The NW–SE fractures correspond to the above mentioned important old crustal fracture system that played an important role during Precambrian times and some of which are sealed by the Paleozoic sedimentary sequence (e.g. El Guijo fault located in the Alcudia Anticline, Palero, 1991, 1993).

The Almadén Syncline, which is 30 km long with a maximum width of 15 km, is an asymmetric WNW–ESE trending fold, wider in the east than in the west, since its south-eastern flank is subvertical whereas its north-western flank dips gently (Fig. 2). This is a peculiar feature of the fold, because its north vergence is opposite to that of the regional Variscan structures. This geometry was probably conditioned by the presence of the main NW–SE fracture system affecting the crust, which facilitated the Devonian basin subsidence and in turn facilitated the development of an asymmetric syncline during the Variscan shortening and the subvertical attitude of its south flank that was coincident with the crustal fractures.

At the beginning of the Carboniferous the subsidence moved towards the south, probably due to the elevation and emergence of the basin towards the north during evolution of the Variscan Orogeny, which started at the end of the Devonian in the internal zones. Accordingly, with these field relationships and using Sm-Nd and Rb-Sr isotopes in rocks from the bottom of the sedimentary sequence, Nägler et al. (1992) established an age of 335 ± 15 Ma (Upper Visean), which is interpreted as the age of the first recrystallization due to the Variscan deformation in the region.

The Variscan deformation around Almadén occurred in two stages, the first of which was the main one (Ortega, 1988; Roiz, 1979). In this first widespread stage (F1), due to near N–S shortening, the more important macrostructures and folds were formed on all scales and were generated by buckling. This type of deformation did not result in any important reduction in volume and only incipient development of slaty-cleavage affecting incompetent rocks (black shales) occurred. Metamorphism was practically absent and only certain mafic volcanic rocks gave rise to neo-formed minerals in the zeolite facies (Higueras et al., 1995; Saupe, 1973).

The second tectonic stage (F2) consisted of a heterogeneous deformation produced by E–W shortening. This gave rise to crossed-

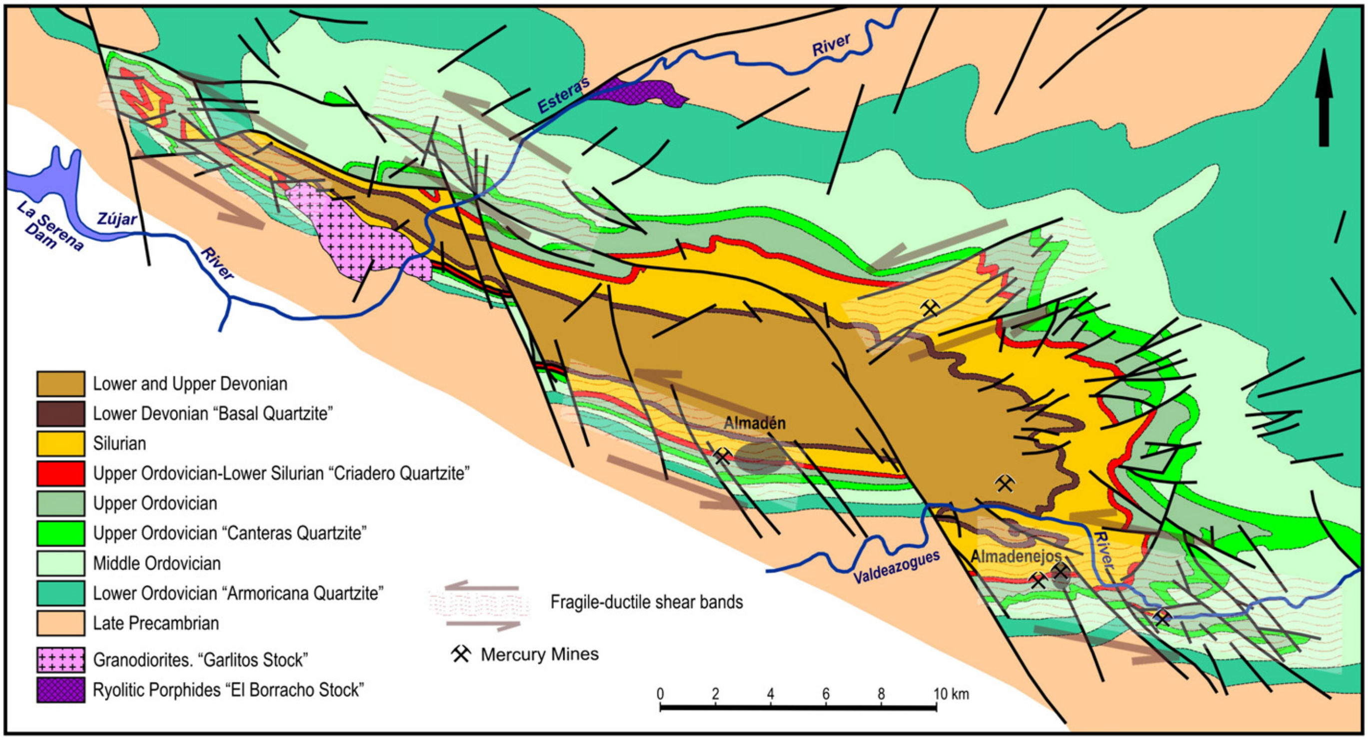

Fig. 2. Geological map of Almadén syncline (modified after García-Sansegundo et al., 1987a, 1987b; Lorenzo Álvarez et al., 2005; Molina Cámara and Fernández Carrasco, 1987).

axes tectonics with F1 folds, which produced interference fold figures such as dome-and-basin interference patterns. However, fragile shear bands were the main structures formed, of which those with NW–SE direction and sinistral displacement predominated over conjugate dextral NE–SW ones. Occasionally, an incipient slaty-cleavage was generated (S2) that transected F1 folds. This tectonic event probably took place during Stephanian times in relation to granite body intrusions. This is also the age of the Puertollano Coal Basin (Wagner, 1983), located about 70 km to the east, which was deposited in a pull-apart structure (Wallis, 1985) formed by a NW–SE shear band with sinistral movement in response to an E–W stress field.

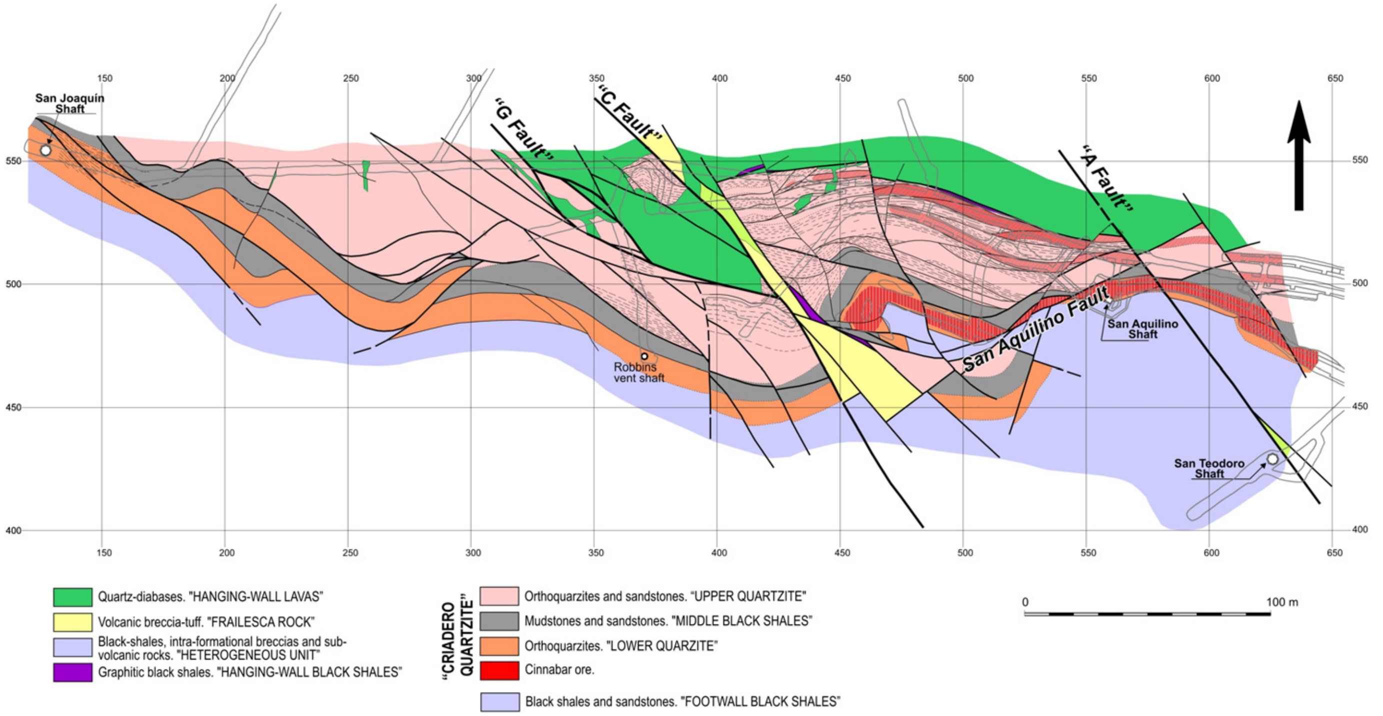

Fig. 3. Geological map of western part of 14th Level, Almadén Mine. The map shows the complex structure produced by the sinistral WNW–ESE shear band, affecting a subvertical multilayer in a similar direction.

The second Variscan stage (F2) affected the Almadén Syncline with variable intensity. It is mainly represented by fragile shear-bands, but conical geometry folds can be found too, resulting in interference between the E–W shortening and F1 folds.

The shear bands can be recognized by strongly dipping faults that are longitudinal with respect to the general structure of the syncline, with a WNW–ESE to NW–SE direction and sinistral displacement. Often these structures are not evident on medium scale mapping, even though more detailed studies show a very complex structure that is produced by shearing in zones with apparently slight deformation (Fig. 3). This fact is especially important when faults interfere with the sub-vertical multilayer sequence in a longitudinal direction. This happens, for example, throughout the southern flank of the syncline, where geological maps do not reflect this very complicated structure (see Fig. 2 and compare with Fig. 3).

After the two main Variscan deformations, some later structures are recognized, mainly new faults and reactivations of pre-existing ones. It is important to point out the existence of faults cross-cutting lithostratigraphic units. These faults make up two conjugate systems, one NW–SE with dextral displacement and the other NE–SW with sinistral movement. They are the result of a new N–S shortening that has been considered to be late-Variscan tectonic movements. Most of these faults are likely to have been inherited, produced during Variscan time deformation and reactivated under later stress fields. This activity must have extended until recent times, as evidenced by the Pliocene–Quaternary basaltic volcanic activity at "Campo de Calatrava" (Gallardo et al., 1998), with outcrops located a few kilometers to the east and northeast of Almadén.

4. Magmatism

Magmatic activity in this part of the Central-Iberian Zone is represented by a Paleozoic mainly syn-sedimentary mafic volcanism and a Variscan felsic magmatism. The former is found distributed in various positions in the Ordovician to Devonian sequence, but it is between the Silurian and Devonian sediments where it is most abundant, particularly in the Almadén Syncline.

The syn-sedimentary igneous rocks are particularly abundant in the sequence above the "Criadero Quartzite", where they appear as sub-intrusive bodies (like dikes and sills), diatremic bodies (mainly explosive breccia-tuffs), or as volcano-sedimentary layers. In general, in the Silurian there is a predominance of sub-intrusive volcanic materials, whereas in the Devonian, the volcano-sedimentary materials are more abundant. At present, the explosive breccia bodies appear limited by faults and tectonized bands, so it is not possible to determine their original relationships with the host rocks. However, it is worth mentioning that the known explosive breccia bodies appear among rocks of ages ranging from Upper Ordovician to Devonian. The breccia-tuffs are very characteristic of the Almadén Syncline and are known as "Frailesca" rock.

The "Frailesca" rock (Fig. 4) is mostly formed by volcanic material, either as fragments or as a matrix, although quartzite and black shale fragments can be found. The volcanic material is mainly basaltic with minor ultramafic rock fragments. The rock displays a distinctive strong carbonatization and sericitization, as seen under an optical microscope in thin sections, where dolomite–ankerite and sericite are the major phases that can be observed. Textural relicts of its original mineralogy are preserved only in some volcanic fragments. The normal appearance of the "Frailesca" rock is a massive breccia-tuff, but sometimes a certain bedding arrangement can be observed, though this does not indicate a true stratification. The interpretation of this peculiar rock has changed since it was first described as a magnesian limestone (Prado, 1846), as a fault rock (Hernández Sampelayo, 1926) or as a volcano-sedimentary material (Almela et al., 1962), and currently, after the studies made at the end of the 20th Century by the Geological Service of the mining company (MAYASA), it is interpreted as diatremic bodies.

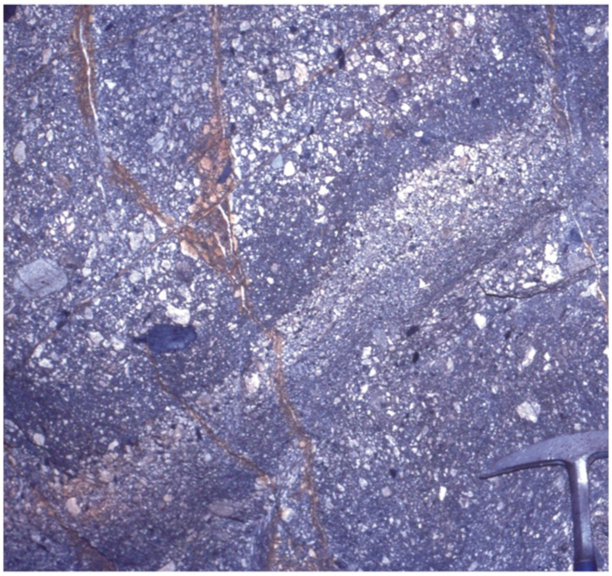

Fig. 4. The "Frailesca" rock on a 5th level tunnel wall, Almadén Mine. The outcropping shows false bedding.

The bedding-like structures that are found in some places within the "Frailesca" body have led to this breccia-tuff being wrongly identified as volcano-sedimentary rock. However, this structural feature is common in diatremes, for example in El Teniente Mine (Chile) or in kimberlite pipes, where Erlich and Dan Hausel (2002) interpreted it as a consequence of volume reduction after the diatreme explosion. Bedding structures in diatremes could also be caused by re-sedimentation in the top of the crater. In this situation it is possible to find volcanic tuff intercalated with fine detrital sediments resulting from the destruction of the crater walls.

Volcanic activity in the Almadén Syncline appears to have taken place in at least 2 events that, as already stated, do not exactly agree with the ideas of Higueras (1994) and Higueras et al. (2000a). The first event would have been an explosive volcanic episode of alkaline basaltic composition that gave rise to the "Frailesca" rock. A network of dikes and sills with ultramafic xenoliths is related to the volcanic breccia-tuffs. Fragments of the same ultramafic material, characterized by the presence of fuchsite, also appear incorporated in the "Frailesca" rock (Morata et al., 2001). The dikes and sills often show peperitic structures, especially when hosted in black shales, evidence that their emplacement took place when the sediments still contained significant amounts of water. The presence of fuchsite is characteristic of the volcanic event related to the "Frailesca" rock, but this mineral is absent in other volcanic rocks that texturally resemble "Frailesca" rock and are in fact, volcano-sedimentary beds, e.g the "ash-tubidites" in the Puebla de Don Rodrigo (Piles Mateo et al., 1989; Pineda et al., 1989) or Solana del Pino (Palero, 1992) Synclines.

The second volcanic event is represented by mafic (tholeiitic) rocks, mainly quartz-diabases, with tholeiitic affinity (Higueras et al., 2000). They mostly appear as large sub-intrusive tabular bodies, paraconcordant with the stratification. They display clear intrusive relationships with the "Frailesca" rock, indicating a later formation than the volcanic breccia-tuffs. These rocks appear with different alteration grades, even in the same body (as in the Almadén Mine or in the Rodoviejo prospect area). In the biggest bodies it is easier to find holocrystalline unaltered rocks made up of hornblende as the main mineral and slightly saussuritized plagioclase. Some shapeless quartz grains appear irregularly distributed, showing corroded rims and strong wavy extinction, in contrast with the rest of the minerals, which are only slightly deformed. This suggests that quartz crystals in these rocks could be xenocrysts.

Higueras et al. (2000a) consider both volcanic series as a single event which evolved more or less continuously from one composition to the other. On the basis of geological field evidence, however, we consider the mafic magmatism a later event from the alkaline. On the 14th level of the Almadén Mine (Fig. 3), the diabases clearly cut the "Frailesca" rock. Also, based on drill core data, the "Frailesca" rock was cut by the diabases. Several porphyritic dikes cut the "Frailesca" body in El Entredicho Mine, producing a very similar appearance to cooling borders in big quartz-diabase dikes and sills. Porphyritic dikes have not been observed to have cut quartz-diabases bodies.

The volcano-sedimentary units, which are mainly hosted in the Devonian units, are difficult to relate to a specific volcanic event. The common heterolithic composition of tuffs and breccias, along with clear evidence of reworked material and strong alteration, makes it difficult establish to which series they belong. Saupé (1990), Higueras et al. (2000) and Higueras et al. (2013) interpret this volcanism as being related to the "Frailesca" rock, assigning to it a mantle origin on the basis of geochemical characteristics. The above mentioned studies did not take into account the temporal relationships between the different volcanic episodes but took all the volcanic material as resulting from a single magmatic activity.

Intermediate volcanic rocks, mainly trachytes, appear sporadically in the core of the Almadén Syncline. These rocks reflect a clear evolution of the volcanism towards a more felsic composition and could either represent a third independent volcanic pulse or an acid evolution of the second event. Higueras et al. (2000a) interpreted these rocks as a differentiated component of the alkaline series, on the basis of geochemical characters. No clear timing criterion has so far been found to confirm either hypothesis.

As the volcanic rocks are intensely altered, they have not been accurately dated, but the work of Hall et al. (1997) using fuchsite from the "Frailesca" rock that produced ages of between 365 and 427 Ma, is noteworthy. However, there is no evidence that the chromium rich mica was formed simultaneously with the volcanic rock; it could be an alteration product.

Field relationships between the "Criadero Quartzite" and the "Frailesca" rock show that the latter cut the former and also include lithified quartzite fragments, perhaps from Criadero beds or other Ordovician quartzites. So it is clear that the "Criadero Quartzite" is older than "Frailesca" diatreme bodies. As the dating is not precise, the field relationships are the only way to understand the relative events involved in the formation of these rocks. Hall et al. (1997) attempted to date the alteration processes of these rocks using samples mainly from Las Cuevas breccia-tuff, which almost certainly belong to a deformed "Frailesca" body. From a structural point of view, the "Las Cuevas" deposit is controlled by Variscan fracturing, and is thus epigenetic (Hall et al., 1997; Hernández et al., 1999). In the Almadén area this deformation took place during Upper Visean to Estefanian (between 330 and 295 Ma). Also, the volcanic rocks underwent several alteration processes, the first one during their own emplacement and the last during the ore formation in Variscan times and later fracture movements. Thus, the illite age (about 360 Ma) obtained by Hall et al. (1997) possibly reflects a mixed composition of all the events to which these volcanic rocks were subjected and is unreliable.

Variscan magmatism is represented by the Fontanosas and Garlitos granite stocks and the large Los Pedroches Batholith. The first two are to the E and the NW of Almadén, respectively, whereas the large batholith occupies a broad band to the south, maintaining its WNW–ESE Variscan orientation (see Fig. 1). At the northern edge of this batholith are two satellite stocks known as Santa Eufemia and El Guijo. These intrusive bodies were emplaced in upper crustal levels and gave rise to a hectometric aureole of thermal metamorphism that overprinted the Variscan folds.

Two main facies of granitic rocks have been identified: granodiorites and monzogranites. The granodiorites are older and their emplacement took place between the two main Variscan deformation stages (Coupez et al., 1988; Escuder and Lorenzo Álvarez, 2002). The monzogranites intruded the granodiorites (Donaire and Pascual, 1992) and constitute the totality of the satellite stocks, and their emplacement was clearly subsequent to the F2 Variscan stage.

Finally, it is worth mentioning that at the NW border of the Almadén Syncline there is a brecciated body in Lower Ordovician units that could be related to a Variscan granodiorite-rhyolite porphyry (Fig. 2).

5. Ore deposits

In the Almadén area only 6 mines have been exploited: Almadén, El Entredicho, Las Cuevas, Nueva Concepción, Vieja Concepción and Guadalperal. In addition there are a dozen small occurrences and registered mines, as well as a new deposit, the so-called Nuevo Entredicho, discovered during the 80s, but which remains unexploited. Altogether these mines and occurrences form a mining district whose geological context is limited to the eastern part of Almadén Syncline (Fig. 5).

The mercury deposits correspond to two different typologies (Hernández Sobrino et al., 1999; Palero and Lorenzo Álvarez, 2008) that can be classified as stratabound deposits (Fig. 6) and stockwork deposits (Fig. 7). The stratabound deposits are larger and are represented by the Almadén, El Entredicho and Vieja Concepción mines. The stockworks are smaller but have higher ore grades, the outstanding examples being the Nueva Concepción and Las Cuevas mines and the unexploited Nuevo Entredicho.

The stratabound deposits are hosted exclusively in the "Criadero Quartzite" unit. The ore appears impregnating the rock and/or as fissure infilling in specific layers in the lower and upper parts of the orthoquartzite unit. The impregnation is the result of cinnabar filling the primary rock porosity, essentially the intergranular spaces or fissure infillings (joints as described by Saupé, 1990). The porosity was sealed prior to cracking, during diagenetic or post-diagenetic compaction processes of the quartzite rock, whereas the joints were clearly infilled post-diagenesis. The paragenesis in these deposits is very simple, with cinnabar (shapeless or micro-crystalline aggregates) as the main mineral, followed by small amounts of pyrite and native mercury. Crystalline quartz, dolomite–ankerite, barite and siderite are present as trace minerals occupying fractures that cut across the mineralized quartzite beds and formed later than the main mineralization.

The stockwork type deposits are mainly hosted in volcanic material, but minor amounts of mineralization can be found in detrital rocks, although in these cases the ores are always related to nearby volcanic rocks. The paragenesis, first established by the Minas de Almadén geological service as epigenetic and related to Variscan deformation, was described by Higueras et al. (1999) and is more complex than in the stratabound type. It is made up of cinnabar and pyrite as major minerals, accompanied by native mercury, pyrophylite, kaolinite, sericite, ankerite and quartz. A later mineralization with barite, siderite, dolomite–ankerite, chalcopyrite, pyrite and recrystallized cinnabar is also present. This later paragenesis is of little volumetric importance. The main mineralization infilled small veins and replaced volcanic rocks, the two processes being intimately related. Clear examples can be observed where the degree of replacement decreases with the distance from the massive cinnabar vein (Fig. 8). In detrital materials, the mineralization only infilled veins. The vein and replacement textures allow us to establish a sequence of crystallization of the main mineralization process. Pyrite was the first mineral to crystallize, followed by pyrophylite and kaolinite, then quartz, and finally cinnabar. The greater abundance of replacement mineralization in the volcanic rocks could be due to the fact that these rocks were easily altered, having previously undergone a strong carbonate alteration, in contrast to the lower susceptibility to alteration of the quarzites.

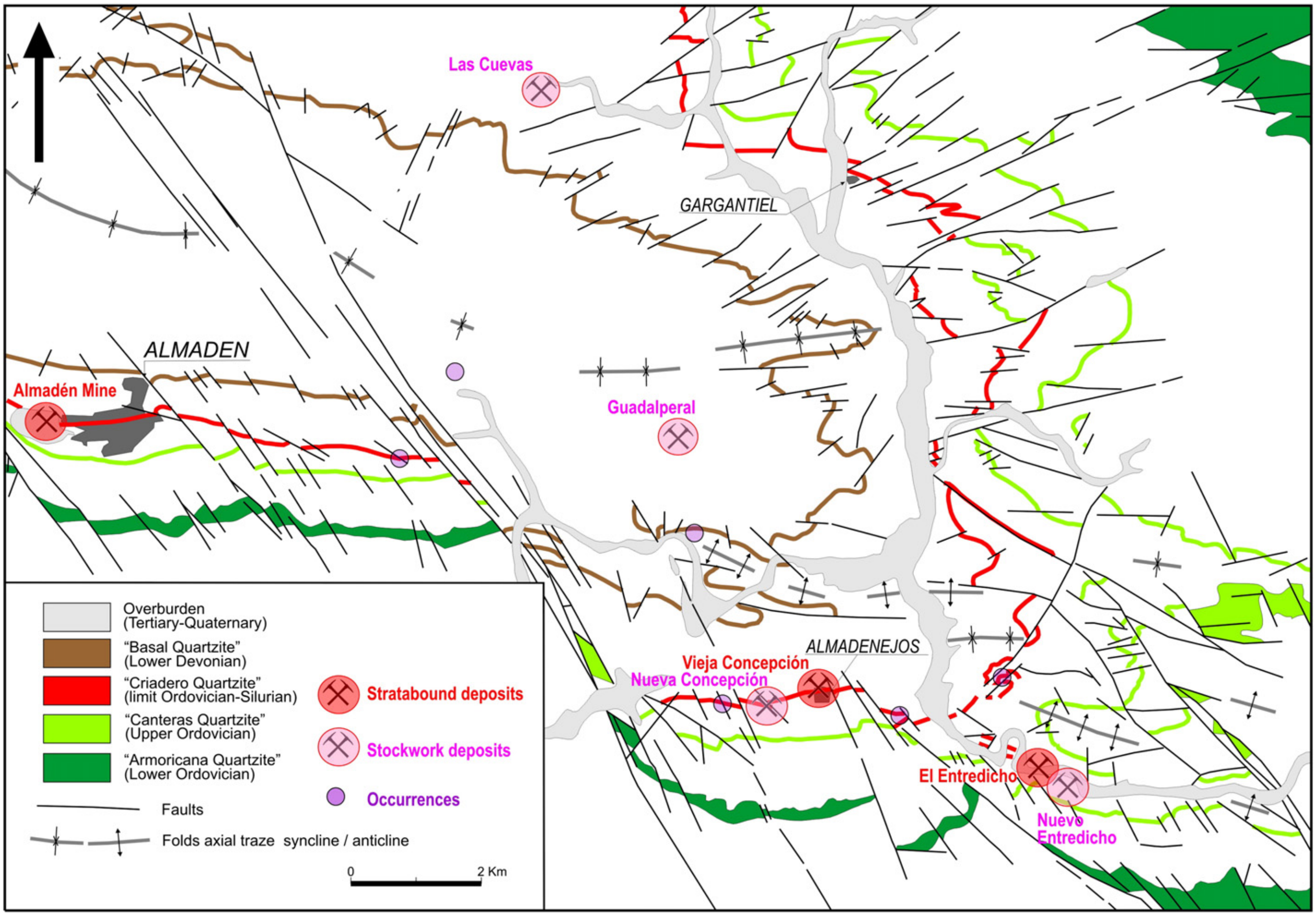

Fig. 5. Geological sketch of eastern part of Almadén Syncline, highlighting traces of orthoquartzite Paleozoic units and marking the main mercury deposits and occurrences.

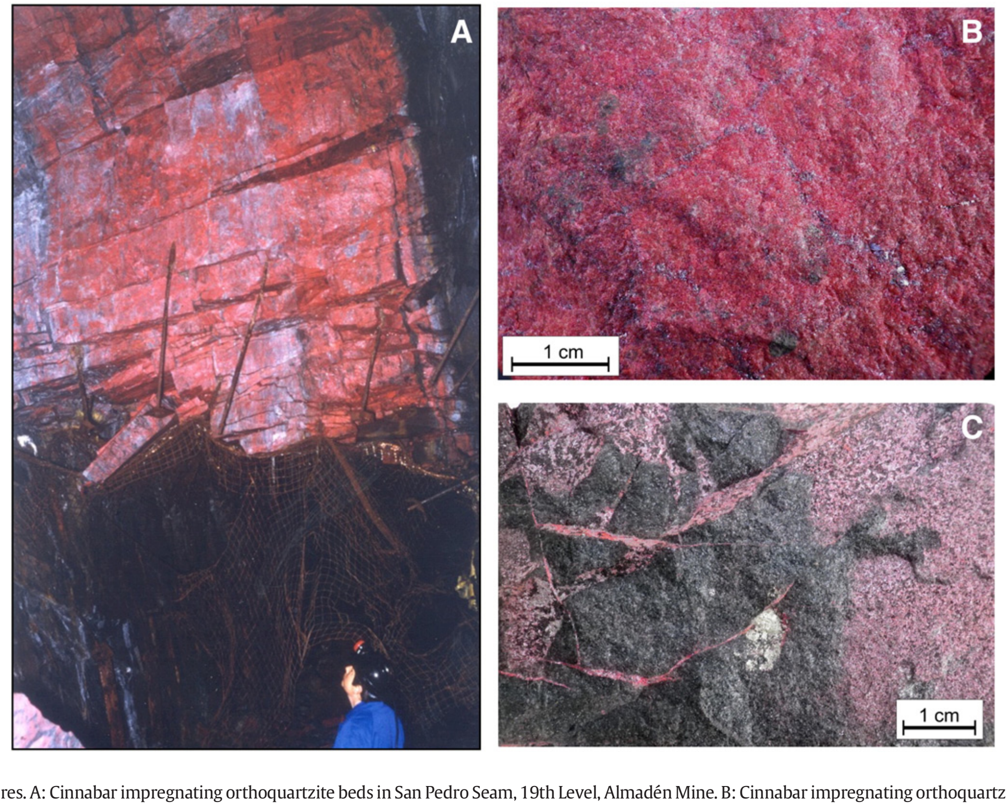

Fig. 6. Stratabound type ores. A: Cinnabar impregnating orthoquartzite beds in San Pedro Seam, 19th Level, Almadén Mine. B: Cinnabar impregnating orthoquartzite of San Francisco Seam, 14th level, Almadén Mine. C: Cinnabar infilling fissures, developing geometrical joints in black orthoquartzites of San Francisco Seam, 21st level, Almadén Mine.

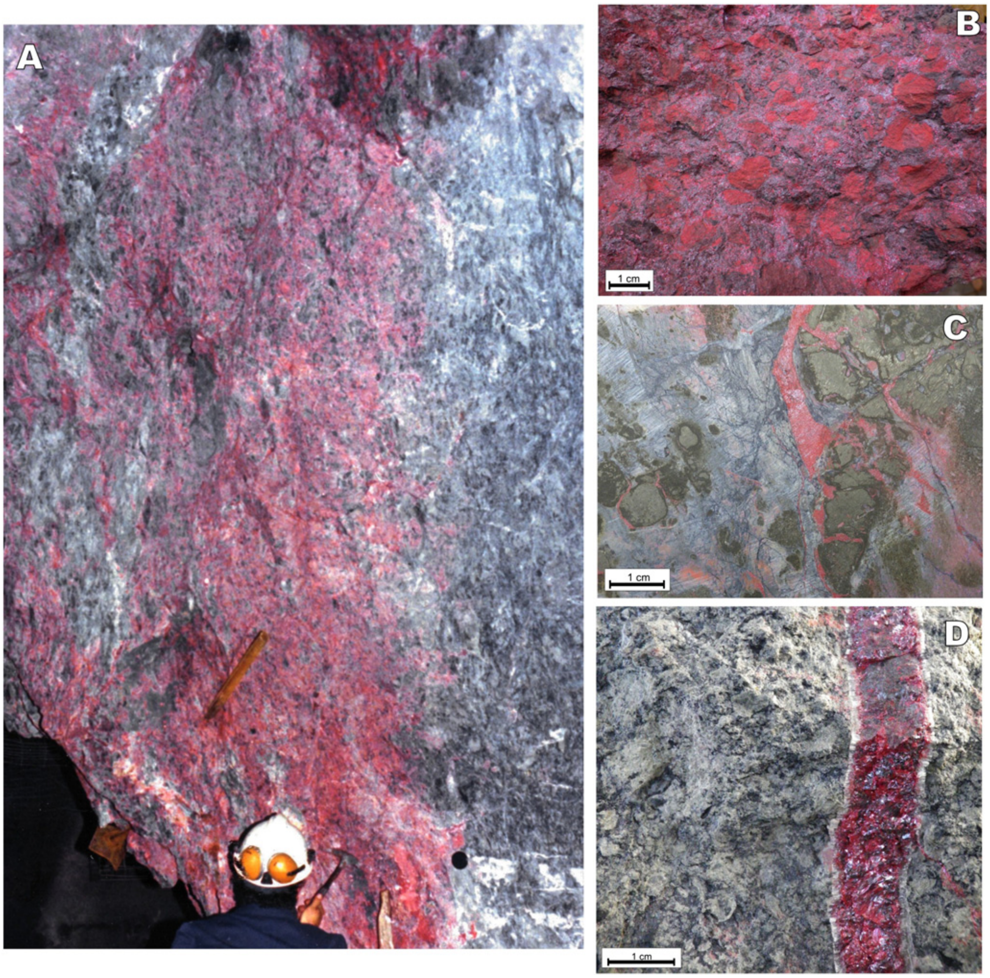

Fig. 7. Stockwork type ores. A: Replacement ore body in volcanic rocks. Western Massif, 175th level, Las Cuevas Mine. B: Massive replacement by cinnabar in breccia tuff rock. The replacement is complete but conserves the original volcanic rock texture. Western Massif, 90th level, Las Cuevas Mine. C: Replacement by pyrite and cinnabar in volcanic rock. Pyritization is previous to "cinnabrization" and Hg ore is formed in places where there are no pyrites. Eastern Massif, 90th level, Las Cuevas Mine. D: Cinnabar vein hosted in breccia tuff. The vein has thin borders formed by pirophyllite and kaolinite. Western Massif, 90th level, Las Cuevas Mine.

The time between the occurrence of the two types of deposit can be established on the basis of the relationships to Variscan deformations. Thus, as the stratabound bodies are controlled by stratigraphic layers, they are clearly affected by the Variscan deformations such as shear zones, and cut by the structures formed during these tectonic events. On the other hand, the cinnabar veins in stockwork mineralization cut the Variscan foliations (slaty and mylonitic). In these vein deposits, ore textures and relationships between the mineralization and the host rocks suggest that the structure was formed in syn-tectonic conditions with respect to the E–W Variscan F2 shortening, just when the deformation changed from ductile to fragile and the rocks became brittle. The progressive deformation resulted in easily recognizable faults, the final stage of which produced minor inverse faults in transpresive zones that cut across the ore bodies.

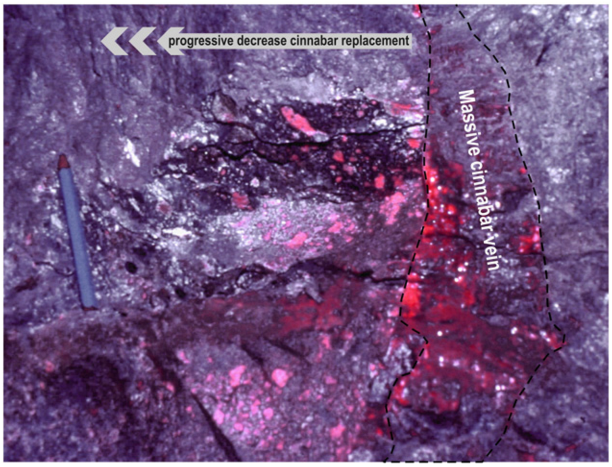

Fig. 8. Progressive replacement by cinnabar in breccia tuff from a massive cinnabar vein. The replacement affects volcanic fragments and is strong near to the vein and decreases with increasing distance from the vein border. Western Massif, 90th level, Las Cuevas Mine.

The spatial coincidence of Hg ores with the "Frailesca" rock has in the past been interpreted as signifying a cause-effect relationship between syn-sedimentary volcanism and mineralization processes (Almela et al., 1962; Hernández Sobrino, 1984; Ortega and Hernández Sobrino, 1992; Saupé, 1973, 1990). This spatial relationship is clear, but it has been verified that some stratabound deposits are previous to the emplacement of the "Frailesca" rock. In the El Entredicho Mine, a sill that includes ultramafic xenoliths related to the "Frailesca" rock may be observed in contact with the mineralized quartzite seam. The sill produced a narrow "thermal metamorphic" border on the mineralized seam through the effect of the heat from the igneous rock. This heating process triggered the removal of cinnabar and also led to recrystallization of the quartzite. This proves that "Frailesca" rock volcanism is younger than the stratabound mineralization, as was previously stated by

Saupé (1990), but they were both probably produced by the same geological process and are not a consequence of one another. The stockwork mineralization post-dated the volcanism, since it is hosted in the volcanic breccia-tuffs and produced alteration that affected the already consolidated and tectonized rocks (Higueras, 1994; Higueras et al., 1999).

The sill with ultramafic fragments do not cut the “Frailesca” rock, but both rocks show similar composition, differing only in textural appearance. In both rocks there are ultramafic fragments (rounded in the sill and angular in the diatreme) and in both rocks, and only in them, is there fuchsite. Field relationships show that the quartz-diabase cuts both rock types, indicating the two magmatic events mentioned above. Also, both magmatic events are later than the stratabound ore, which is affected by them. Generally speaking, kimberlitic diatremes are always rooted in a dike swarm (network) that never cuts the diatremes but frequently reveals pebble-dyke structures and small patches of breccia-tuffs (Dawson, 1971; Kjarsgaard, 2007). This characteristic diatremic disposition can be seen at El Entredicho mine. No dike or sill with ultramafic fragments has ever been found at the Almadén mine, but dikes resembling “Frailesca” rock hosted by the “Footwall Black Shales” (stratigraphic unit below “Criadero Quartzite”), which is also characteristic of diatremes, are visible.

6. Geology of the Almadén Mine

The structure of the huge mercury accumulation in the Almadén area was explained for the first time by Saupé (1973). Knowledge of the deposit geology did not subsequently increase very much until the end of the 20th century, when the Minas de Almadén Geological Survey was working in sectors of complex structure, allowing them to establish a new structural model that clarified the previous models (Palero, 2012; Palero and Lorenzo Álvarez, 2008).

6.1. Ore bodies and host rocks

The ore bodies in the Almadén mine have a stratabound character, with cinnabar located at very specific levels of the “Criadero Quartzite” unit. These ore bodies have been designated “San Pedro–San Diego Seam (SP)”, “San Francisco Seam (SF)” and “San Nicolas Seam (SN)”. The “Criadero Quartzite” in the Almadén mine is in a vertical position and subdivided into 3 intervals. From the lower to the upper parts, these are (Fig. 9):

> “Lower Quartzite”, with 8 to 15 m thick white orthoquartzite beds. This interval includes the San Pedro–San Diego Seam and is 3 to 8 m wide.
>
> “Middle Black Shales”, with 10 to 15 m of carbonaceous rich mudstones with frequent sandy pillow structures. This interval is always barren.
>
> “Upper Quartzites”, composed of 30 to 50 m of multilayered thin grey quartzite and fine micaceous siltstone beds. These beds become increasingly thicker and darker towards the top. “San Francisco” and “San Nicolas” seams are found in this upper part. These seams are from 2.5 to 5 m thick and separated by up to 8 m of fine grained siltstone and carbonaceous mudstone beds. Tectonic wedging is responsible for the variation in thickness, or even absence, of this barren interbedded level.

A black shale unit with marked sedimentary lamination and fine layers of siltstones and mudstones is found underneath the “Criadero Quartzite”. This unit is known as “Footwall Black Shales”. Another black shale unit, the so-called “Hanging Wall Black Shales”, formed by foliated graphitic black shales is found overlying the quartzites. The graphitic shales are partially or totally replaced by intrusive sub-volcanic rock bodies (quartz-diabase) that are known as “Hanging Wall Lavas”. These volcanic rocks show porphyritic texture when the dikes or sills are thin, but show a porphyritic border texture and holocrystalline inner part when they are thick. This can be seen well at the 9th level access ramp, where they produced thermal metamorphic effects in the “Criadero Quartzite”. Also, some propylitic alteration of these rocks gives them a porphyritic texture. In addition to these rocks, within the sedimentary sequence are dikes and sills that cut or are conformable with the bedding. Some are similar in composition to the “Hanging Wall Lavas”, while others have an aphanitic texture that makes it difficult to assign them to either of the volcanic pulses. Spectacular cases of “thermal metamorphism” of these dikes on the mineralized quartzite beds have been observed.

The volcanic “Frailesca” rock forms a massive lenticular body that is in unconformable contact with the rest of the lithological units and is limited by major WNW–ESE and NW–SE faults. The breccia-tuff material is composed of fragments of variable size and composition, including some quartzites and black shales. Heterolithic breccias formed by fragments and blocks of siltstones, orthoquartzites and volcanic rocks showing peperitic structures are found in a spatial relationship with the “Frailesca” rock body, but are limited by faults and thus their relationship with the host rocks is uncertain.

The mineralization of Almadén Mine ore bodies is constituted by cinnabar impregnating and infilling fissures in the orthoquartzite beds. Although in general terms the appearance of the ore is similar in all three seams, there are certain textural differences between San Pedro Seam and the other two seams. Thus, whereas in the San Pedro Seam the impregnating ores prevail, in the San Francisco and San Nicolas seams the infilling joint ores are the more common (Fig. 6).

A small number of stockwork ores are occasionally found hosted in the “Frailesca” rock in specific places. This mineralization has an irregular shape and is bounded by WNW–ESE and NW–SE faults.

The economic mineralization of the Almadén Mine was worked over a maximum length of about 500 m and to a depth of 600 m. It is estimated that production was about 7 million tons with an average grade of 3.5% Hg (approximately 1 flask per metric ton). Grades varied from 1% to 40% Hg above mine cut-off.

6.2. Ore-deposit structure

The Almadén deposit is hosted in the vertical quartzite multilayer of the southern flank of the Almadén syncline, which has an approximately E–W direction and is cut by a diatreme volcanic body of “Fraislesca” rock (Fig. 10A). The quartzite multilayer and the breccia-tuff body were first affected by a fragile-ductile WNW–ESE longitudinal sinistral shear band produced by the E–W F2 Variscan shortening (Fig. 10B) and then by several transverse dextral strike-slip fault systems originated by late-Variscan movements arising from N–S shortening (Fig. 10C). In the multilayer, the shear band produced displacements that follow stratification planes, which form the main anisotropic structure. In the isotropic competent body of “Frailesca” rock the shear band was refracted towards the NW–SE direction and, in consequence, a transpressive zone was created.

The longitudinal shear band structures, which run subparallel to the stratification planes, caused a strong deformation in the deposit, and represent an important network of sub-vertical sinistral strike-slip faults with fragile and fragile–ductile characters (Fig. 10B). They gave rise to significant displacements (up to several hundred meters) and undergo frequent refractions and ramifications in the quartzite multilayer, with different displacement structures that adapted and absorbed the deformation. In the multilayer the shear band produced drag-folds with sub-vertical plunge axes, tectonic wedges, mylonitic bands, etc. Together with the main sinistral WNW–ESE faults, there are two conjugate systems, one dextral NNE–SSW, the other sinistral ENE–WSW.

Transversal strike-slip faults with a NW–SE direction and usually steep dips cut the "Criadero Quartzite" at an obtuse angle. They produced dextral movements and reveal a more fragile character than the

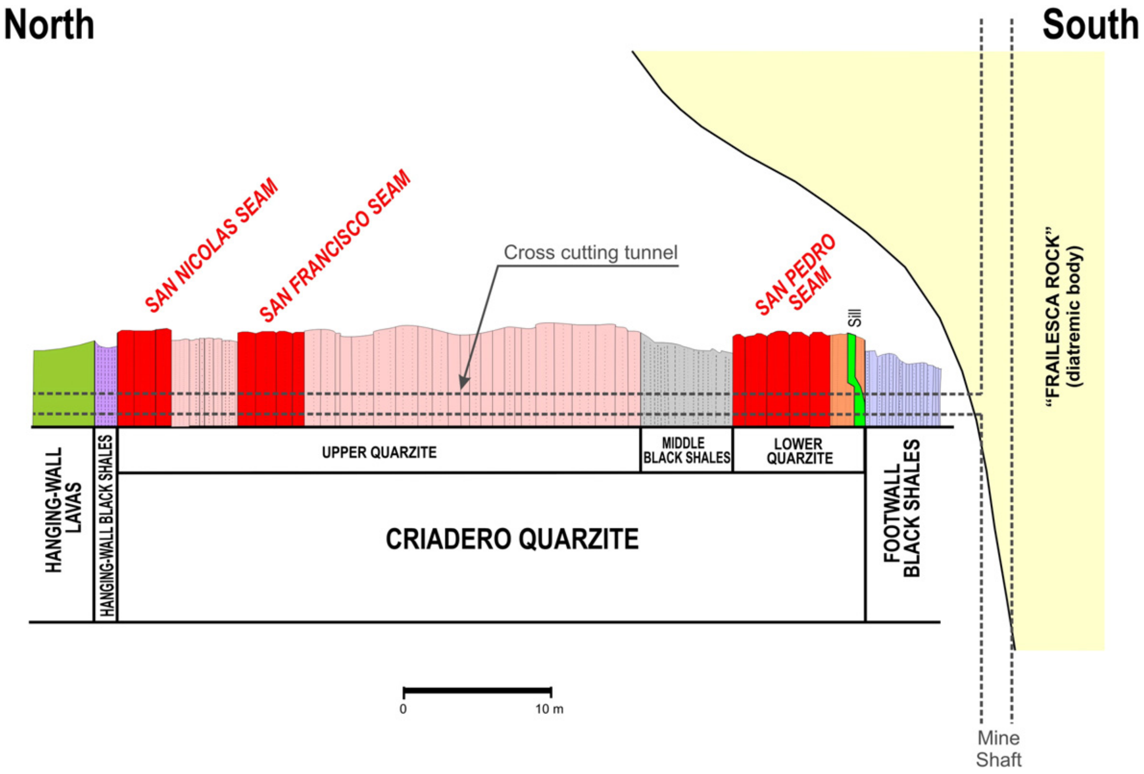

Fig. 9. Typical lithostratigraphic section crossing Almadén Mine, including the three mined ore seams.

longitudinal ones. These faults resulted in displacements of variable magnitude ranging from a few decimeters to several tens of meters.

The intersection of longitudinal and transversal faults with the sub-vertical "Criadero Quartzite" determined the configuration and structure of the deposit (Fig. 10). The general structure can be defined as a large fragmented sub-vertical axis fold of the "Criadero Quartzite", produced by sinistral translation of a wide longitudinal WNW–ESE shear corridor, which cuts across the rigid diatreme body of the "Frailesca" rock. This corridor is crosscut by a dextral transversal NW–SE fracture system that divides the deposit into two parts at the surface, displacing the eastern block southwards in relation to the western block (Fig. 10). These sections basically correspond to the "Rama Mina" in the east and the "Rama Sur" in the west.

Below the 8th level, the transverse NW–SE fracture system is divided into two main faults (A and C) having opposite dips, which then separate the deposit into three mineralized sectors, referred to as "Rama Mina", "Los Masivos" and "Rama Sur" (from east to west).The main distinctive features of these sectors are (Fig. 11):

The "Rama Mina" Sector, with stratabound geometry, is the most characteristic one in the Almadén Mine. The "Criadero Quartzite" is partially fragmented by several transversal NW–SE faults that produced small strike-slip movements. Only one of these faults is worth mentioning, the so-called San Miguel Fault. Mineralization forms the classic three seams mentioned above. The "Frailesca" rock appears to the south of the ore deposit and is separated from the "Criadero Quartzite" by a broad band of "Footwall Black Shales", which becomes wider at depth and towards the east. The contact between the volcanic breccia-tuffs and the black shales is an important fault known as "Southern Fault" ("M Fault" in Figs.), which dips strongly towards the SSW (Fig. 12).

The "Los Masivos" sector is structurally very complex because it is affected by two longitudinal faults that form two sinistral systems, the main one trending WNW–ESE, and the other, the so-called San Aquilino Fault, running ENE–WSW. These faults produced important fragmentations in the "Criadero Quartzite", including duplication of mineralized seams. In addition to the longitudinal deformation, an important network of transversal faults also cut the "Criadero Quartzite". These fault systems are delimited by the two aforementioned "A Fault" to the east and "C Fault" to the west. The "C Fault" is the only one to reach the surface. The classic three seams are mineralized, but the "San Pedro–San Diego Seam" becomes progressively more barren towards the west and at depth. By contrast, the "San Francisco" and "San Nicolas" seams had extraordinarily high grades, hence the name of the sector. Below the 14th level, the grades start to diminish both horizontally and vertically, although San Francisco reaches down to the 21st level. The "Frailesca" rock in this sector is located to the north of the quartzites (Fig. 12), while at lower levels the volcanic breccia-tuffs tend to disappear, being replaced by the quartz-diabases of the "Hanging Wall Lavas" sill. In the southern part, there are small disjointed blocks of the volcanic breccia limited by faults.

The "Rama Sur" sector is located to the west of the "C Fault". It is a structurally complex area affected by longitudinal fault tectonics. A distinctive structural feature is the existence of several sub-vertical axis folds, which absorb much of the translation of the strike-slip faults. The few transverse faults in this area produce minor displacements. Due to strong tectonization, the mineralization is broken into several discontinuous irregular bodies belonging to the San Francisco and San Nicolas seams and finishing above the 14th level (Fig. 12). A great longitudinal fault called the "G Fault" represents the true northern limit between these zones.

The "Frailesca" rock is located to the north of the mineralized quartzite unit and is limited to the East by the "C Fault" and to the south by

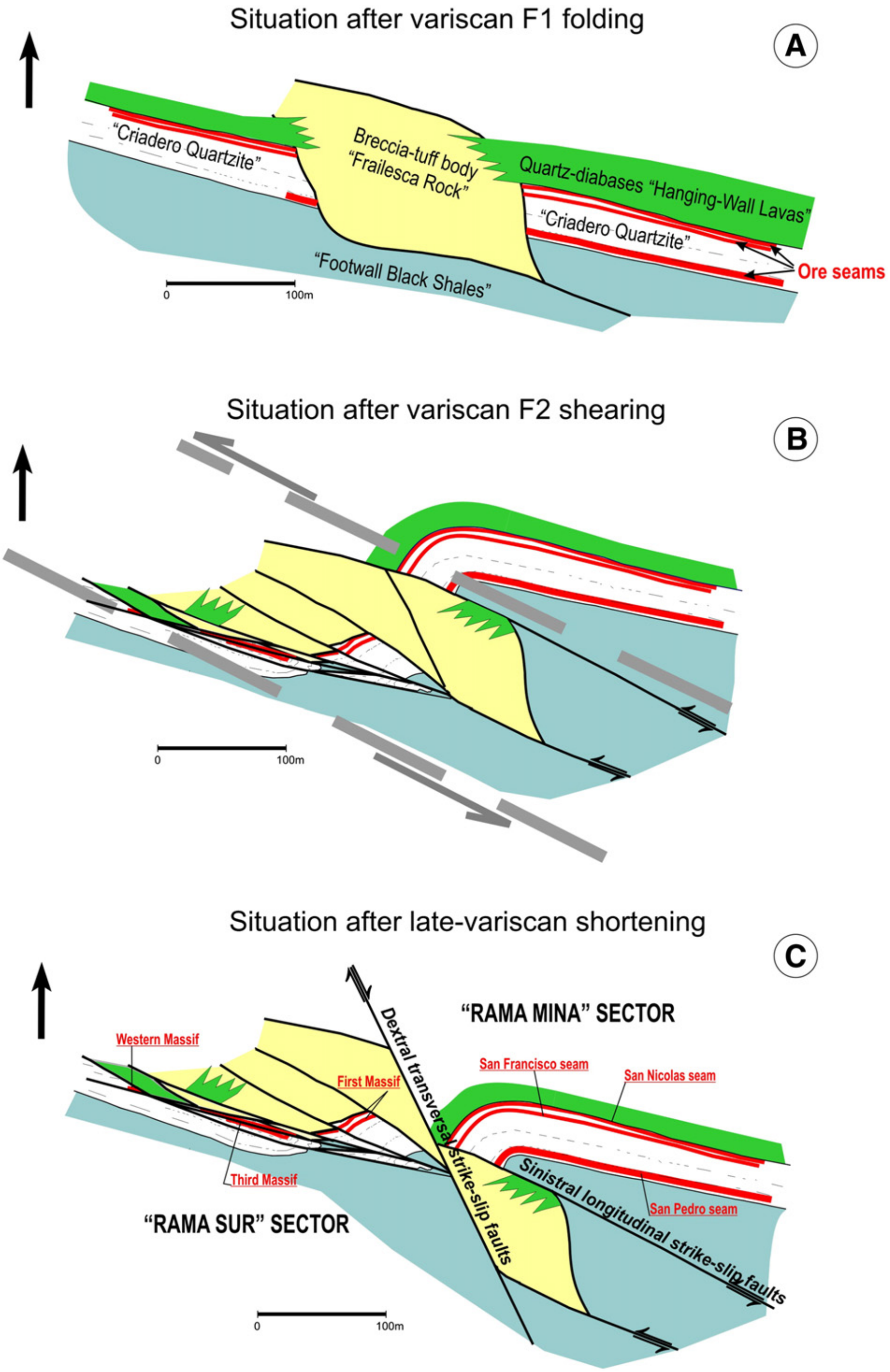

Fig. 10. Structural evolution of Almadén deposit. The sketch refers to mine levels at surface.

the "G Fault" (Fig. 12). From the 7th level downwards, the volcanic breccia-tuffs are intruded and replaced by the diabases of the "Hanging Wall Lavas", with the last bodies of the "Frailesca" rock on the 14th level.

7. Lead isotopes in Hg ores

7.1. Sampling

Samples were selected from the Almadén Mine (10 samples), El Entredicho Mine (2 samples) and Las Cuevas Mine (3 samples) taking into account the different mineralized sectors, the mineralization characteristics and the structural location. We then grouped them into the two metallogenic types: stratabound and stockwork.

The 10 samples from Almadén mine are from:

San Pedro–San Diego seam, 3 samples
San Francisco seam, 2 samples
San Nicolás seam, 1 sample
Rama Sur ore bodies, 3 samples
Stockwork ore in "Frailesca" rock, 1 sample

The Rama Sur samples came from the San Francisco and San Nicolas seams. They are strongly deformed by the longitudinal faults, which occur commonly in these seams.

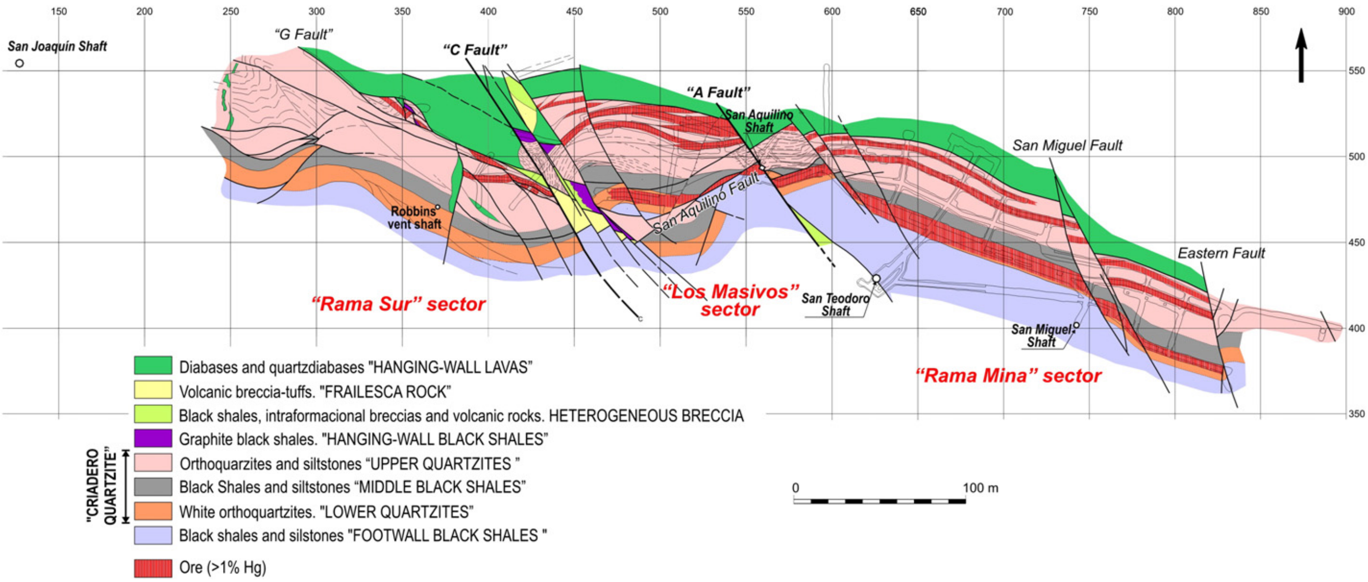

Fig. 11. Geological map of the 13th Level, Almadén Mine. The map shows the three mine sectors with specific structural characters.

The two samples from El Entredicho are stratabound type ore and the three from Las Cuevas are stockwork type ore. Each of these samples represents the different exploited ore bodies in the mining district and their data are comparable with previous data from Higueras et al. (2005) and Jébrak et al. (2002).

All the samples taken are high grade ore. They were crushed by hand using an agate mortar and then sieved. Under a binocular microscope the fractions between 0.25 and 0.125 mm were chosen because cinnabar was liberated, except in one case from Las Cuevas (massive cinnabar in one vein) where we chose the 0.63–0.25 mm fraction. Cinnabar was concentrated by means of elutriation, a very useful method due to the high differences in density between cinnabar and the gangue minerals.

The concentrate was then re-elutriated to separate the cinnabar. The coarse sample from Las Cuevas was purified using heavy liquids because the only contamination was quartz and sheet silicates. Cinnabar concentrates were examined and refined by handpicking under a binocular microscope to obtain more than 250 mg of high purity concentrate.

Table 1 summarizes the samples used, mineral types represented and fractions used. All the deposits are affected by Variscan deformation and structures, making it difficult to recognize the original characteristics (exhalative or replacement or the filling of open spaces) of the deposit. The sampling points in Almadén mine are indicated in Fig. 13.

7.2. Analytical method

Pb isotope analyses were carried out at the University of País Vasco (Spain) by Prof. I. Gil Ibarguchi. 100 mg of cinnabar was dissolved in 7 N HNO_3 for 48 h in closed Savillex recipients heated to 200 °C. After evaporation of the solution at 90 °C, 2 ml of HCl 6 N was added. After 8 h, the solution was re-evaporated. The solid was again diluted in HCl 3.1 N, which was heated for 8 h at 100 °C. Pb was separated using ion exchange resin (Dowex 1-X-8) in a hydrobromic acid medium, following the procedures described by Babinski et al. (1999). After separation, Pb was loaded onto zone-refined rhenium filaments using the silica gel technique and analyzed for isotope ratios in a VG 354 micromass multicollector thermal ionization mass spectrometer. Each measurement represents the average of 105 cycles in Faraday boxes. The mass fraction was internally corrected using the Tl isotope ratio ($^{205}Tl/^{203}Tl$) following the method described by Chernyshev et al. (2007). Precision and reproducibility were confirmed using the NBS981 isotopic lead standard.

The possible interference of ^{204}Hg in the measure of ^{204}Pb is controlled by the presence of ^{202}Hg simultaneously with the other masses ($^{204,\ 206,\ 207,\ 208}$ Pb and $^{203,\ 205}$Tl). The possible presence of ^{204}Hg is calculated taking into account the natural relationship $^{204}Hg/^{202}Hg = 0.230074$, which is subtracted from the total $^{204}Hg + ^{204}Pb$. In the analyzed samples the presence of ^{202}Hg was less than 1%, except for sample MA-02(2) (3%) and for sample MA-03 (4%).

7.3. Pb isotopes results

The lead isotope ratios in the Almadén district are heterogeneous (Table 2), in both our data and those of Higueras et al. (2005). Data from Higueras et al. (2005) largely agree with ours (Fig. 14), their distribution completing and complementing our findings. We also include Pb–Pb data from Almadén mine pyrites obtained by Jébrak et al. (2002) that agree well with cinnabar data for $^{208}Pb/^{204}Pb$ but not for $^{207}Pb/^{204}Pb$, the latter showing a great dispersion. Thus, the data set will be considered together.

The Pb isotope compositions have $^{207}Pb/_{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios higher than those predicted by the Stacey and Kramers (1975) and Cumming and Richards (1975) models for crustal Pb evolution models (Fig. 14). The isotopic data closely fit the two-stage Pb evolution model of Ludwig et al. (1989) for Sardinia, which is a particularly good fit for the $^{208}Pb/^{204}Pb$ ratio but less exact for the $^{207}Pb/_{204}Pb$ ratio. The data plot along the Sardinia curve in several well defined clusters, though in an isolated manner in the case of some samples. Following the ideas of Arribas and Tosdal (1994) and García-Sansegundo et al. (2014), each cluster or sample could be interpreted as lead extraction by means of large scale convective hydrothermal systems from a lead reservoir located in the upper crust at a time indicated by the Sardinia curve. Higueras et al. (2005) previously proposed a similar mechanism of lead extraction by large scale hydrothermal convective cells affecting the Post-Tremadocian sedimentary rocks. The estimated ages for this lead model evolution indicate lead extraction as having occurred during Late Silurian–Devonian (420–375 Ma), Late Variscan (300 Ma, 1 sample), Permian–Triassic (290–220 Ma), Late Jurassic–Early Cretaceous (200–150 Ma) and Eocene–Oligocene (50–25 Ma, 1 sample).

The first age is approximately the same as that of the host rocks. Accordingly, lead in the cinnabar present in the deposit may have been extracted by hydrothermal fluids from the Paleozoic sedimentary rocks during the Upper Silurian–Devonian and deposited in the host Silurian sedimentary sequence. Then, during Variscan times, when mercury

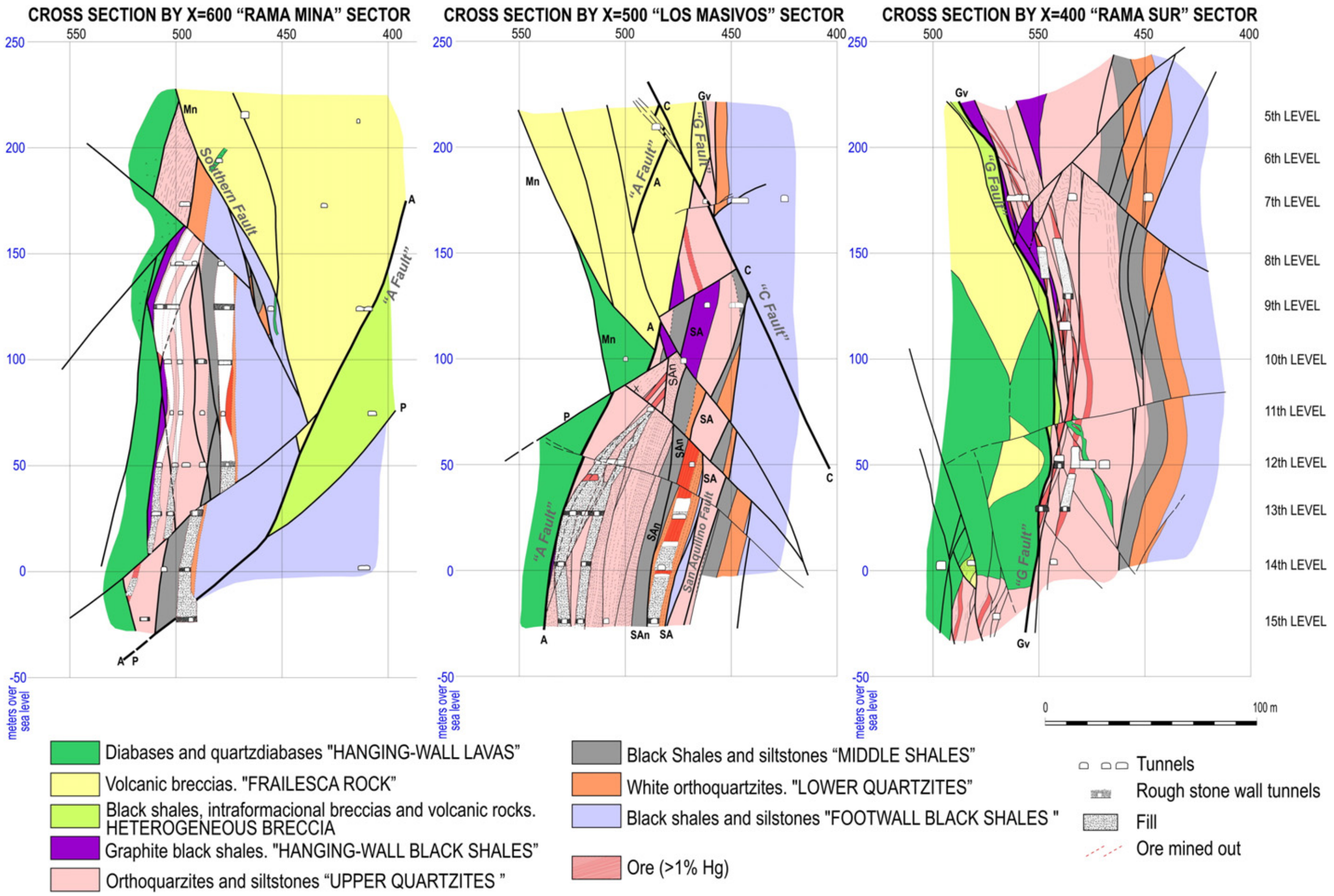

Fig. 12. Representative geological cross sections of the Almadén deposits between 5th and 15th levels (the ore appearing below the 14th level in Fig. 12C belongs to "Los Masivos" sector, the "G fault" representing the true northern limit of "Rama Sur" sector).

minerals were strongly affected by deformation, as previously described, only one sample registered this event. Most of the samples plot after Variscan times, two periods being particularly important, Permian–Triassic and Late Jurassic–Early Cretaceous. Finally, Alpine reactivation of the Variscan basement is registered in one sample.

Remobilizations affected all the Almadén deposits, with all showing variability of lead isotopes. In fact, as far as our samples are concerned, the Silurian ages were obtained from a sample from San Nicolas (Almadén mine) and another from El Entredicho. Also, two Higueras et al. (2005) samples from El Entredicho and Las Cuevas reflect Silurian age, indicating that in all the deposits, both stockwork and stratabound, this first lead extraction is reflected. The rest of the samples from the Almadén, El Entredicho and Las Cuevas mines give ages ranging from Late Variscan to Oligocene.

8. Pb-isotopes related to Southern Europa Variscan deposits

It is noteworthy how well the lead isotopes in cinnabar tally with the Sardinia curve, as happens with lead from galena from other deposits in this Variscan terrain. For such a comparison we have used data from

Table 1
Samples characteristics for lead isotopic analises, mineral types they represent and fractions used.

Sample	Location	Ore Type	Grinding Size (mm)	Concentrate Weight (g)	Comments
MA-01	Almaden Mine. San Pedro Seam, Level 11 Easthern	Dissemination in quartzite beds	0.125–0.08	2.73	
MA-02	Almaden Mine. San Pedro Seam, Level 5 Santa Clara	Dissemination in quartzite beds	0.25–0.125	0.28	Some quartz inclusions
			0.125–0.08	0.61	Some quartz & pyrite inclusions
MA-03	Almaden Mine. San Francisco Seam, Level 14 Westhern	Dissemination in quartzite beds	0.25–0.125	0.4	
MA-04	Almaden Mine. Rama Sur, Level 7 La Patata	Dissemination in quartzite beds	0.125–0.08	0.29	Abundant mixed quartz-cinnabar fragments
MA-05	Almaden Mine. San Nicolas Seam, Level 5 Westhern	Dissemination in quartzite beds	0.125–0.08	0.96	
MA-06	Almaden Mine. San Pedro Seam, Level 19 San Miguel	Dissemination in quartzite beds	0.125–0.08	0.46	
MA-07	Almaden Mine. San Francisco Seam, Level 21 Westhern	Dissemination in quartzite beds	0.25–0.125	1.13	
MA-08	Almaden Mine. Rama Sur, Level 12 Third Massif	Dissemination in quartzite beds	0.25–0.125	5.98	
MA-09	Almaden Mine. Rama Sur, Level 7 Third Massif	Dissemination in quartzite beds	0.25–0.125	1.98	
MA-10	Almaden Mine. Frailesca body, Level 1	Replacement in volcanic rocks	0.25–0.125	1.5	
ME-01	El Entredicho Mine. Lower Seam	Dissemination in quartzite beds	0.25–0.125	4.1	
ME-02	El Entredicho Mine. Upper Seam	Dissemination in quartzite beds	0.25–0.125	0.88	
LC-01	Las Cuevas Mine. Level 1, Westhern Massif	Replacement in volcanic rocks	0.25–0.125	5.25	
LC-02	Las Cuevas Mine. Level 2, Easthern Massif	Infilling joins in quarzites	0.25–0.08	0.89	Abundant pyrite
LC-03	Las Cuevas Mine. Level 1, Westhern Massif	Infilling veins in volcanic rocks	0.63–0.25	3.5	

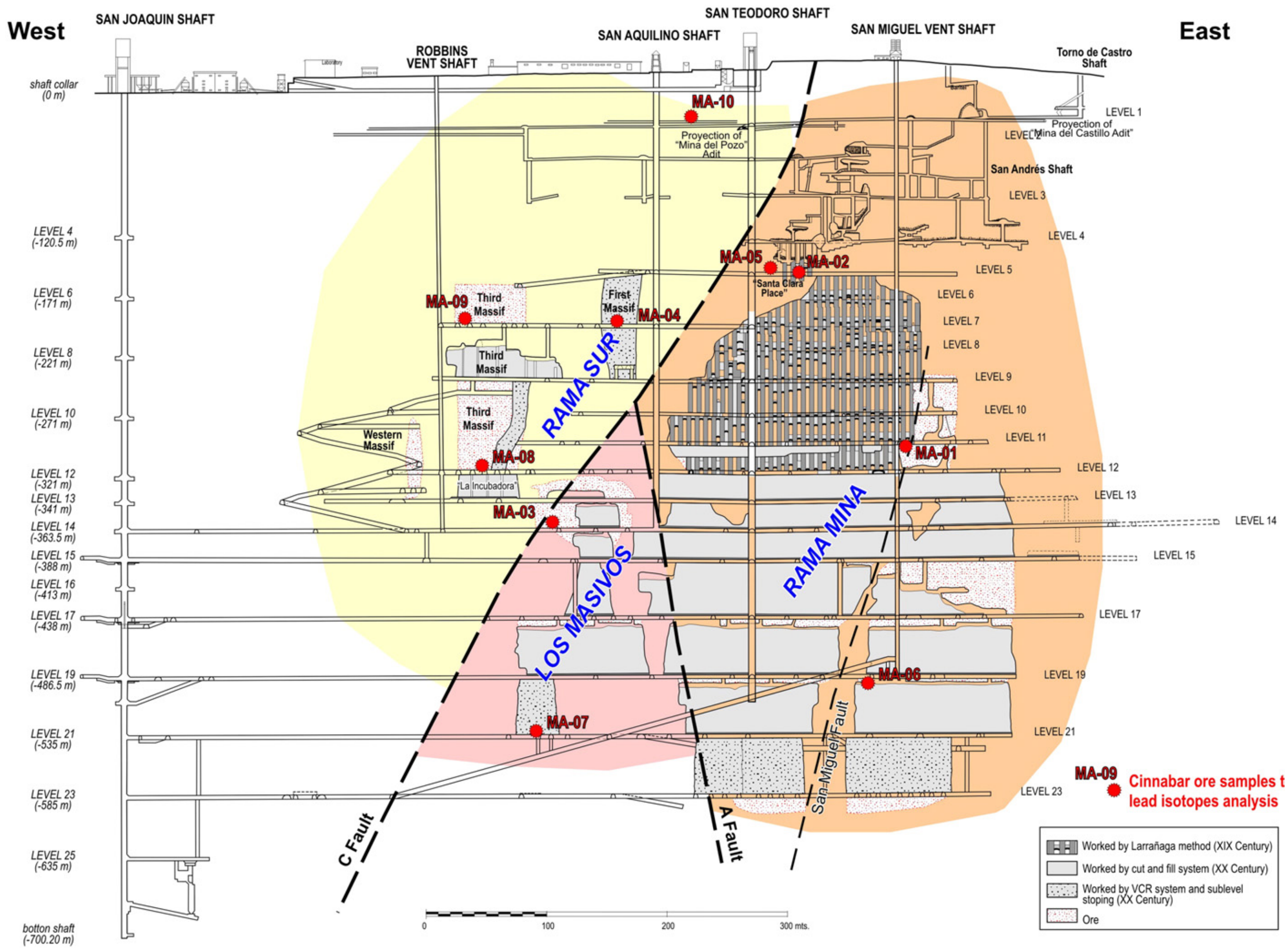

Fig. 13. Schematic longitudinal projection of Almadén Mine. The figure shows the mine sectors and the location of ore samples for lead isotope analysis.

Arribas (1993) and Arribas and Tosdal (1994), García de Madinabeítia (2003) and García-Sansegundo et al. (2014) (Fig. 15).

Most of the pre-Mesozoic basement of the Iberian Peninsula consists of domains of Late Proterozoic to Devonian age, similar to other regions of Western Europe. The Almadén mercury deposit is located in the lead isotope province that includes the Cantabrian, Astur-Occidental-Leonese and Central-Iberian zones, as well as the Central and Eastern Pyrenees. As indicated by Arribas (1993), Arribas and Tosdal (1994), the correlation between the Pb isotope compositions and crustal domains in Western Europe was first illustrated by Vitrac-Michard et al. (1981). Following these authors several others (García-Sansegundo et al., 2014) have provided additional geochemical evidence for the existence of a geological province in south-western Europe characterized by Pb isotope compositions with $^{207}\mathrm{Pb}/_{204}\mathrm{Pb}$ and $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$ ratios that closely fit the two-stage Pb evolution model of Ludwig et al. (1989) for Sardinia.

In order to analyze the relationship of the Pb isotope compositions of cinnabar ores within the Almadén deposits with those of similar southern European lead deposits we compare the results obtained in both. The Pb isotope compositions of our cinnabar ores are plotted in Fig. 15 a and b (modified from Arribas, 1993; Arribas and Tosdal, 1994; García-Sansegundo et al., 2014). This figure also includes data provided by Jébrak et al. (2002) and Higueras et al. (2005) from Almadén and data from García de Madinabeítia (2003), the latter obtained by using galena from the Zn–Pb deposits defined by Palero et al. (2003) and Palero and Martin-Izard (2005) in the Alcudia region (100 km. to the east of Almadén) and hosted in the Ordovician metasedimentary sequence.

We consider the consistent data set shown in Figs. 14 and 15A and B to be a valid working model for the isotopic evolution of Pb in one of the major terrains of the Variscan orogenic belt in Europe. These zones could be included in the domain consisting of Vendée–Cévennes–Drosendorf and Aquitane–Montagne Noire–Moravian geological regions defined by Matte (1991) (Fig. 15C, adapted from García-Sansegundo et al., 2014). As shown in Fig. 15, all the deposits considered occur within the above mentioned domains in the Southern European Gondwana.

With respect to the origin of the ores, it appears that the Pb in the minerals considered here is derived from a pre-Mesozoic basement rock source. The contribution of basement Pb could have occurred as a result of direct leaching or, in the case of pre-Variscan deposits, leaching of first-cycle sediments derived from the basement rocks. As previously indicated by Arribas (1993) and Arribas and Tosdal (1994) and considering the coherence of the Pb isotope trends in all the deposits, the Pb was probably extracted at various times (i.e., Late Silurian–Devonian, Permian–Triasic and Late Jurassic–Early Cretaceous) from a uniform lead reservoir, such as the Late Precambrian through Devonian clastic metasedimentary sequence, which dominates the lead isotope province (Fig. 15 A and B).

Geological factors that contributed to producing consistent ore Pb-isotope compositions with such limited ranges include both homogenization of the original crystalline basement by the erosion and deposition

Table 2
Lead isotopic relationships for cinnabar from Almadén mining district.

Sample	206Pb/204Pb	2σ	207Pb/204Pb	2σ	208Pb/204Pb	2σ
This work cinnabar samples						
MA-01	18.693	0.001	15.687	0.001	38.944	0.003
MA-02 (1)	18.485	0.001	15.694	0.001	38.655	0.003
MA-02 (2)	18.499	0.002	15.690	0.002	38.662	0.005
MA-03	18.519	0.001	15.680	0.001	38.750	0.004
MA-04	18.526	0.001	15.701	0.001	38.737	0.003
MA-05	18.191	0.001	15.708	0.001	38.494	0.003
MA-06	18.484	0.001	15.709	0.001	38.852	0.003
MA-07	18.358	0.001	15.693	0.001	38.632	0.004
MA-08	18.377	0.001	15.683	0.001	38.582	0.004
MA-09	18.523	0.001	15.690	0.001	38.680	0.003
MA-10	18.370	0.002	15.691	0.002	38.553	0.005
ME-01	18.382	0.001	15.698	0.001	38.594	0.003
ME-02	18.148	0.001	15.699	0.001	38.376	0.003
LC-01	18.488	0.001	15.718	0.001	38.748	0.003
LC-02	18.422	0.001	15.696	0.001	38.662	0.002
LC-03	18.312	0.002	15.655	0.002	38.374	0.005
Cinnabar samples from Higueras et al. (2005)						
ETD-1	18.357	0.092	15.663	0.081	38.577	0.083
ETD-2	18.266	0.061	15.641	0.060	38.531	0.062
ETD-2A4	18.132	0.073	15.653	0.057	38.684	0.059
ETD-2A5	18.399	0.006	15.680	0.006	38.667	0.006
ETD-2A6	18.326	0.067	15.654	0.073	38.543	0.069
ETD-2B1	18.429	0.016	15.705	0.017	38.730	0.017
ETD-2B2	18.346	0.040	15.635	0.043	38.555	0.043
ETD-2B3	18.370	0.044	15.686	0.045	38.714	0.046
ETD-2B4	18.409	0.047	15.675	0.041	38.757	0.044
ETD-2B5	18.324	0.018	15.675	0.019	38.654	0.019
ETD-2B6	18.342	0.087	15.662	0.087	38.550	0.088
LC-10	18.112	0.096	15.663	0.086	38.643	0.096
ALMD-3	18.460	0.016	15.681	0.016	38.826	0.017
Pyrite samples from Jébrak et al. (2002)						
14 ME124T	18.350		15.750		38.600	
15 ME124T	18.550		15.760		38.780	
18 ME124R	18.390		15.750		38.590	
22 ME142R	18.380		15.700		38.490	
23 ME142R	18.460		15.730		38.590	

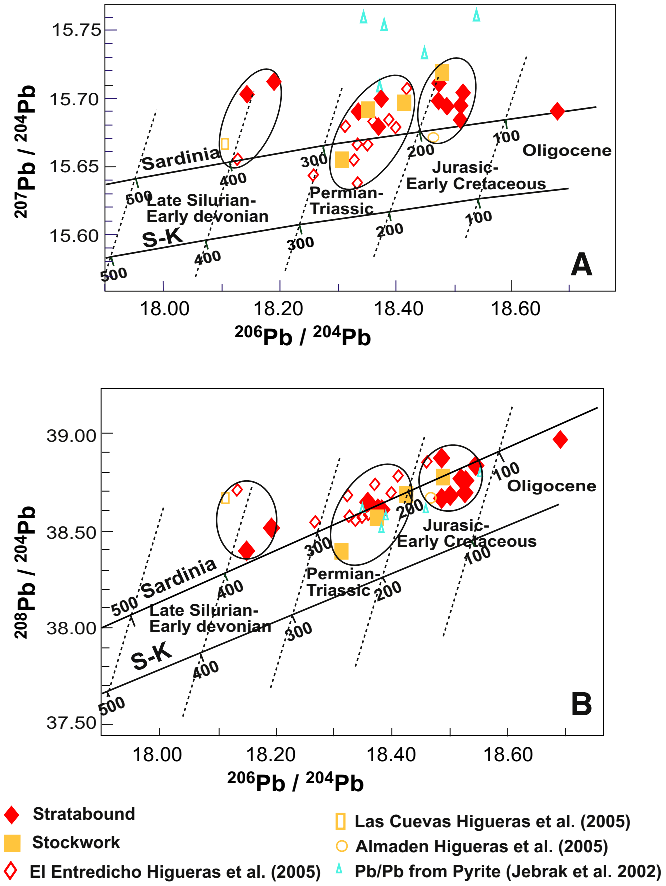

Fig. 14. ^{208}Pb/^{204}Pbvs^{206}Pb/^{204}Pb (A) and ^{207}Pb/^{204}Pbvs^{206}Pb/^{204}Pb (B) diagrams of rocks from the Almadén mines. The isotopic data, listed in Table 2, are taken from referenced publications. **SK** is Stacey and Kramers (1975) growth curve and Sardinia is a two-stage Pb evolution curve proposed by Ludwig et al. (1989).

of thick sedimentary Paleozoic sequences and large scale hydrothermal convection during ore-forming processes that extracted the Pb now found in cinnabar and perhaps other elements also, as indicated by the model ages obtained.

9. Discussion

The Pb isotope data for the ores of south-eastern Europe suggest the Paleozoic sedimentary sequence as having been the main source of Pb during mineralization, an observation that was previously made by Brevart et al. (1982) for the Cambrian deposits of the Montagne Noire region and more recently by Arribas and Tosdal (1994) for the domains dealt with in this study.

Prior to the Variscan Orogeny, during Late Ordovician–Devonian times (García-Sansegundo et al., 2014), these domains suffered extensional tectonics, which in the Almadén area gave way to volcanism, some of it of mantle character (Higueras et al., 2000). The sedimentary sequence was deformed and metamorphosed during the Variscan Orogeny and fractured during Late Variscan times, with orogene collapse and extensional tectonics during Permian–Triassic times. During Jurassic–Early Cretaceous times the opening of the North Atlantic took place and again extensional tectonics developed. During Alpine times a new compressive episode took place.

Unfortunately, the recent seismic profile (Ehsan et al., 2014) across this area does not clearly reflect the structures such as those that could affect the Almadén area. It does, however, detect the presence of an important deep old pre-Variscan NW–SE structure affecting the basement to the south, beyond the Almadén syncline, which could have facilitated the extensional or transtensional tectonics in the region at several stages in its geological history. In the case of the Almadén district, each lead isotope cluster or sample indicates lead extraction from a lead reservoir located in this upper crust at a time indicated by the Sardinia curve. This should be treated with care, however, because if there was recrystallization or remobilization of cinnabar during each episode, lead isotopes could be mixed. Nevertheless, it is surprising how well the lead isotope ratios plot in quite well defined clusters. Taking into account the main episodes in the tectonic evolution of the Iberian Peninsula, the clusters of data are coincident with the main extensional tectonic episodes (from Late Ordovician to Devonian, Permian to Triassic and Late Jurassic to Early Cretaceous). All the deposits studied show first a Late Silurian–Devonian hydrothermal convection that during the first ore-forming stage extracted Pb from the sedimentary Paleozoic sequence. Later, related to three important geological events (late-post Variscan cycle, Middle Jurassic–Lower Cretaceous Atlantic opening and Oligocene Alpine cycle), lead was again removed from the Paleozoic sequence. It appears that during these extensional or transtensional periods large scale, long term hydrothermal convection was established and lead was extracted at various times from a uniform lead reservoir during ore-forming processes.

Thus, we can say that cinnabar is very sensitive to the geotectonic events that affected the Almadén region, having been neoformed and recrystallized during the extensional hydrothermal processes and having captured lead from the metasedimentary host-rock.

During Variscan times the stratabound deposit was intensely deformed, but apparently little or no regional hydrothermal convection was established at that time and little or no new lead was added to the recrystallized - remobilized cinnabar. Only one sample from

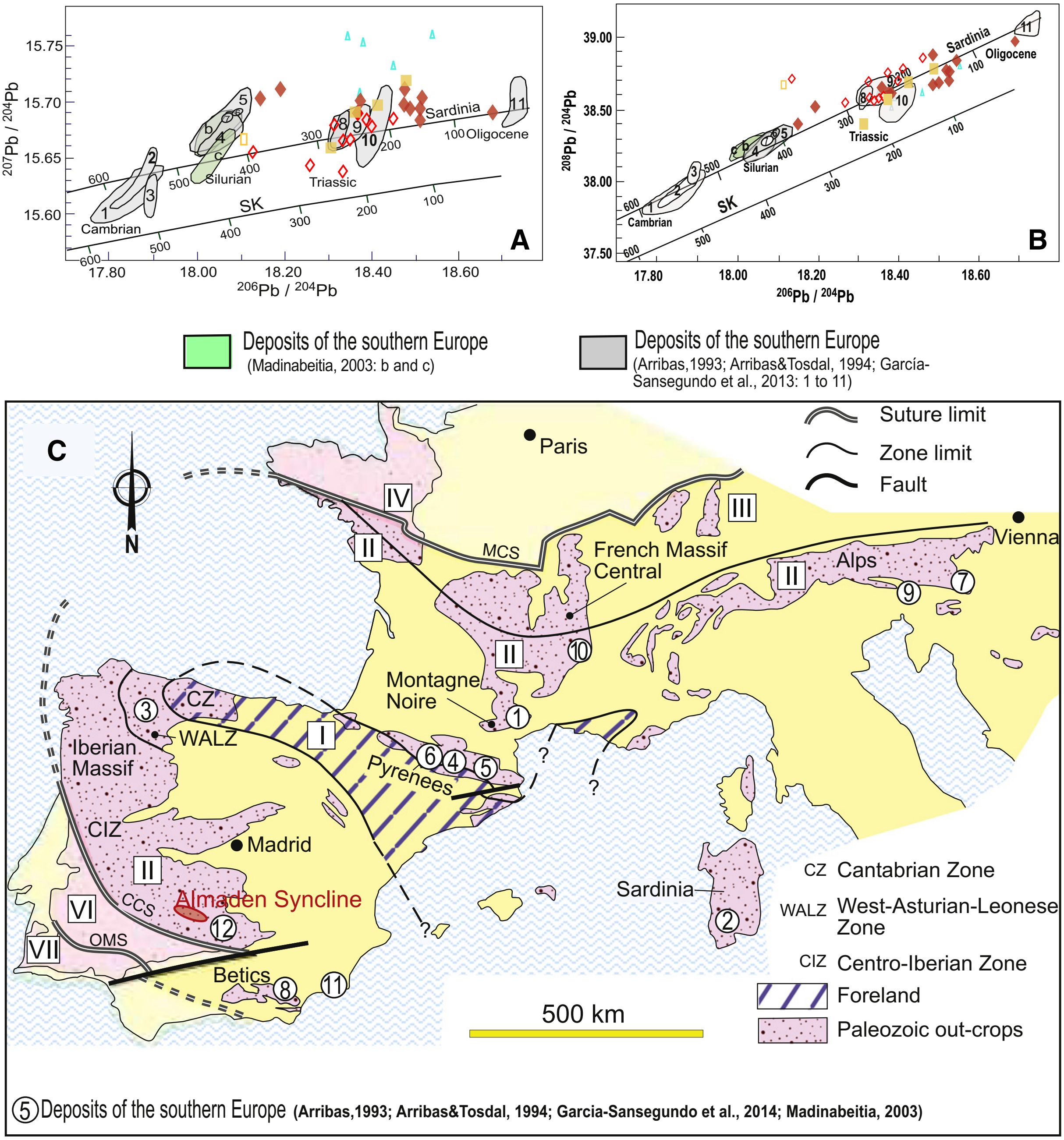

Fig. 15. (A, B) Summary of Pb-isotope variation diagrams of ores from the Iberian Peninsula and selected Pb–Zn deposits of southern Europe (modified from Arribas, 1993; Arribas and Tosdal, 1994). SK is Stacey and Kramers (1975) growth curve and Sardinia is a two-stage Pb evolution curve proposed by Ludwig et al. (1989) for Sardinia. (C) Structural sketch map of the Variscan orogenic belt in Western Europe (simplified from Matte, 1991) showing the outcrop of the Vendée–Cévennes–Drosendorf–Aquitane–Montagne Noire–Moravian terrane and indicating foreland zones and approximate position of mining districts (1 through 10) for which Pb isotope compositions are plotted in b and c. Roman numerals I–VII correspond to the main zones established by Matte (1991). Iberian massif zones of Julivert et al. (1972): CZ = Cantabrian Zone; WALZ = West Asturian-Leonese Zone; CIZ = Central-Iberian Zone. Thick lines represent terrane boundaries: CCS = Coimbra–Cordoba suture, MCS = Massif Central suture, OMS = OssaMorena suture. Stratiform and stratabound deposits in pre-Mesozoic basement: Montagne Noire (1) (Brevart et al., 1982), South-western Sardinia (2) (Boni and Koeppel, 1985; Ludwig et al., 1989); Central (4 and 6) and Eastern (5) Pyrenees (Cardellach et al., 1996; García-Sansegundo et al., 2014; Marcoux et al., 1992), Graz (7) (Köppel and Schroll, 1983). Stratiform and stratabound deposits in Mesozoic rocks: Betic Cordillera (8) (Arribas et al., 1991), southern and Eastern Alps (9) (Köppel and Schroll, 1988). Epigenetic hydrothermal deposits including veins and replacements: Rubiales (3) (Tornos and Arias, 1993), Les Malines (10) (Le Guen et al., 1991), Cartagena, Almagrera, and Mazarrón (11) (Arribas, 1993; Arribas and Tosdal, 1994; Arribas et al., 1991), Alcudia Valley b and c (12) (García de Madinabeítia, 2003).

Higueras et al. (2005) registered the Late Variscan tectonics (around 300 Ma).

In this case, the stockwork deposits appear to be directly derived from the stratabound deposits and were formed by non-convective hydrothermal processes generated by shear bands developed during the E–W Late-Variscan shortening, some samples having maintained the Silurian isotope signature, as in the case of the Las Cuevas sample. This situation could be equivalent to those mentioned by Tornos and Arias (1993) and García-Sansegundo et al. (2014), where Zn deposits located in Variscan structures show Cambrian and Lower Ordovician Pb–Pb model ages, respectively. Also, in the case of the Almadén region, the lead isotope data from García de Madinabeítia (2003) give Ordovician ages and, according to Palero et al. (2003) and Palero and Martin-Izard (2005), the deposits are located in Variscan structures. The same situation may have happened during Alpine times (50-25 Ma).

Comparison of recently published Pb-isotope data from ore deposits of the Iberian Peninsula with data from selected deposits in the Southern European Gondwana indicates the importance of the Variscan sedimentary basement as a source of lead. Furthermore, the lead isotope evolution of the basement rocks provides the geochemical framework for discussion of questions of broad geological interest in the region. In the Almadén district, all the deposits studied show a model age that corresponds to the different extensional periods registered in the Iberian Massif since the Late Ordovician. Identification of the basement lead isotope signature for southern Europe provides a useful constraint in the discussion of regional metallogenic, petrogenetic, and structural questions.

It is worth noting that there is a gap in lead isotope compositions that follows the Sardinia line during the main Variscan times, as if during these times the formation mechanism of Pb–Zn and, in our case, Hg deposits were not related to hydrothermal convective cells. Also, Almadén is the only district that registered lead extraction during the Jurassic–Early Cretaceous.

Taking into account the previous models established for the Almadén district and also the lead isotope distribution of our data and those from Higueras et al. (2005) and Jébrak et al. (2002), the regional convective circulation model is closer to the ideas of Saupé (1990), who proposed a possible explanation for the origin of mercury, but lead remobilization and cinnabar recrystallization took place not only in Silurian–Devonian times but also in two other main periods of extensional tectonics, i.e. Permian–Triassic and Jurassic–Early Cretaceous.

It must be pointed out that lead isotope data better reflect post-Variscan evolution of the deposits and the scarcity of data related to the pre-Variscan and Variscan. This may be due to the sample concentration method that tends to preferentially retain the coarse grained cinnabar which mostly fills fissures and veins or is recrystallized. In all the deposits, this coarse grained cinnabar is scarce and the fine grained, which replaced or impregnated the host rocks, is the more abundant. However, this fine grained cinnabar is lost during the concentration process. At any rate, lead isotopes in cinnabar allow us to reconstruct a large plumbotectonic evolution of this important mine district.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.oregeorev.2014.06.013. These data include Google maps of the most important areas described in this article.

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