

## Sulfide-, fluorite-, barite-bearing siliceous “crusts” related to unconformity surfaces of different ages in Pyrenees and Alps: a new model in carbonate-hosted deposits?

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### RESUMEN

En numerosos puntos de los Alpes y del Pirineo se han podido reconocer horizontes silicificados, de hasta decenas de metros de espesor, que contienen concentraciones variables de sulfuros y/o barita y/o fluorita. Estas mineralizaciones, que ocupan grandes superficies en las cadenas alpinas mencionadas, tienen un carácter estratoligado y cubren discordantemente a paleosuperficies desarrolladas sobre distintas unidades carbonatadas, de edades comprendidas entre el Paleozoico y el Triásico. En el presente trabajo se plantea, en función de las investigaciones geológicas, mineralógicas y geoquímicas, la posibilidad de que estos yacimientos respondan a un proceso singenético/diagenético característico.

Las mineralizaciones estudiadas separan las unidades carbonatadas de las suprayacentes, de tipo detrítico, por lo que pueden considerarse como unidades litostratigráficas independientes que registran un proceso metalogenético concreto, no sólo en las cadenas alpinas sino a nivel mundial. Desde un punto de vista morfológico, esos yacimientos se caracterizan por presentar diversas estructuras (cuerpos tabulares concordantes con las superficies de erosión, cuerpos columnares discordantes, rellenos de cavidades kársticas, ritmitas y vetas) y por estar sometidos, generalmente, a fenómenos de removilización provocados por procesos diagenéticos o metamórficos. Estos procesos originan el enmascaramiento parcial de los rasgos originales, principalmente la existencia de un conglomerado o brecha en la base del cuerpo mineralizado.

A pesar de las controversias existentes sobre la génesis de algunos de estos depósitos y de que existan algunas diferencias significativas, estas mineralizaciones han sido consideradas como yacimientos de tipo “Mississippi Valley” (MVT). Sin embargo, las características de las mineralizaciones estudiadas (presencia de una inconformidad debajo de la mineralización, existencia de un conglomerado o brecha en la base de la “costra mineralizada”, casi completa silicificación, y abundancia de barita y/o fluorita), difieren claramente de las características

diagnósticas de los yacimientos MVT (presencia de una inconformidad por encima de la mineralización, ausencia de silicificación, y bajos contenidos de barita y/o fluorita), la inclusión de estas costras de cuarzo mineralizadas en el grupo MVT parece incorrecta. Otro hecho que parece confirmar esta opinión es la gran homogeneidad que presentan las principales características de las mineralizaciones estudiadas frente a la variabilidad típica de los yacimientos de tipo MVT.

Teniendo en cuenta los aspectos mencionados, los autores proponen un nuevo modelo metalogenético que denominan “crust-type mineralizations”. La presencia de este tipo de mineralizaciones en otros contextos geotectónicos diferentes al de las cadenas alpinas sugiere la importancia de este modelo a escala mundial.

*Palabras clave:* Mineralizaciones estratoligadas en carbonatos. Discontinuidades. Pirineos. Alpes.

### ABSTRACT

Numerous stratabound sulfide-, barite-, fluorite-bearing siliceous crusts, from dm to some tens of m thick, occur over large areas of the Alpine belt, i.e. the Alps and the Pyrenees. They are linked to unconformity landscapes evolved on various carbonate units of Paleozoic and Triassic sedimentary sequences. Since the study mineralizations constitute the transition between the underlying carbonates and the overlying detrital units, they can be considered as an independent lithostratigraphic units that record a particular metalogenetic process not only in the alpine chains but worldwide. These mineralizations exhibit several morphologies: tabular concordant with the unconformities bodies, columnar bodies, karstic cavity-fillings, laminites and veins. In addition, the study deposits are clearly affected by remobilization process occurred during diagenesis or metamorphism. Such processes are responsible for masking the occurrence of the breccia/conglomerate typically located at the base of the orebodies.

Although the study mineralizations have usually been included in MVT deposit class, contrasting differences between their diagnostic

features and those of MVT mineralizations, suggest that the inclusion of the mineralized crust deposits in the MVT group seem incorrect.

These peculiar ore-bearing quartz-crusts, persistent over large areas and showing an independent and distinct character and constituting an important marker for some sedimentary sequences of different ages in Alpine belts, allow the authors to define a new metallogenic model named as "crust-type" (CT) deposits. Comparable mineralization in other geotectonic environments outside Alpine belts point out to CT deposits being a worldwide significant metallogenic event.

*Keywords:* Carbonate-hosted orebodies. Unconformities. Pyrenees. Alps.

## INTRODUCTION

Numerous carbonate-hosted sulfide-fluorite-barite deposits occur in various geological units and in different stratigraphical positions in the Alpine belt (Eastern and Central Alps, Pyrenees, Fig.1).

A common habit is to class these deposits in the MVT group, notwithstanding the controversial genetic interpretations and the other significant differences.

They may appear to be similar in general characteristics, but a peculiar model could be highlighted owing to

its different and persistent compositional and morphological features. This model concerns pervasively silicified ore-bearing horizons (or "crusts"), up to several meters thick, occurring over large areas in the Alpine belt related to carbonates of different ages. The horizons separate the host-carbonate from overlying, commonly siliclastic formations.

Previous studies dealt with silicified crust-type mineralization related to Devonian and Middle-Upper Triassic carbonates in the Alps (Brigo and di Colbertaldo 1972, Assereto *et al.*, 1976, Assereto *et al.*, 1977, Rodeghiero, 1977, Brigo *et al.*, 1988). In the Central Pyrenees quartz-rich ore deposits related to Devonian carbonates have been studied in France by Pouit (1986, 1993), Pouit *et al.*(1979), Pouit and Bois (1986), and quartz-rich deposits with associated silicification processes, related to Devonian and Carboniferous carbonates in Spain have been described in detail by Martin (1979), and Subias (1993). Recently the authors observed siliceous crust-type mineralization in some deposits of the Argelès-Gazost area in France.

The specific purposes of our correlation researches are (1) to describe the distribution of the silicified crust-type mineralization in the Alps and in the Pyrenees, (2)

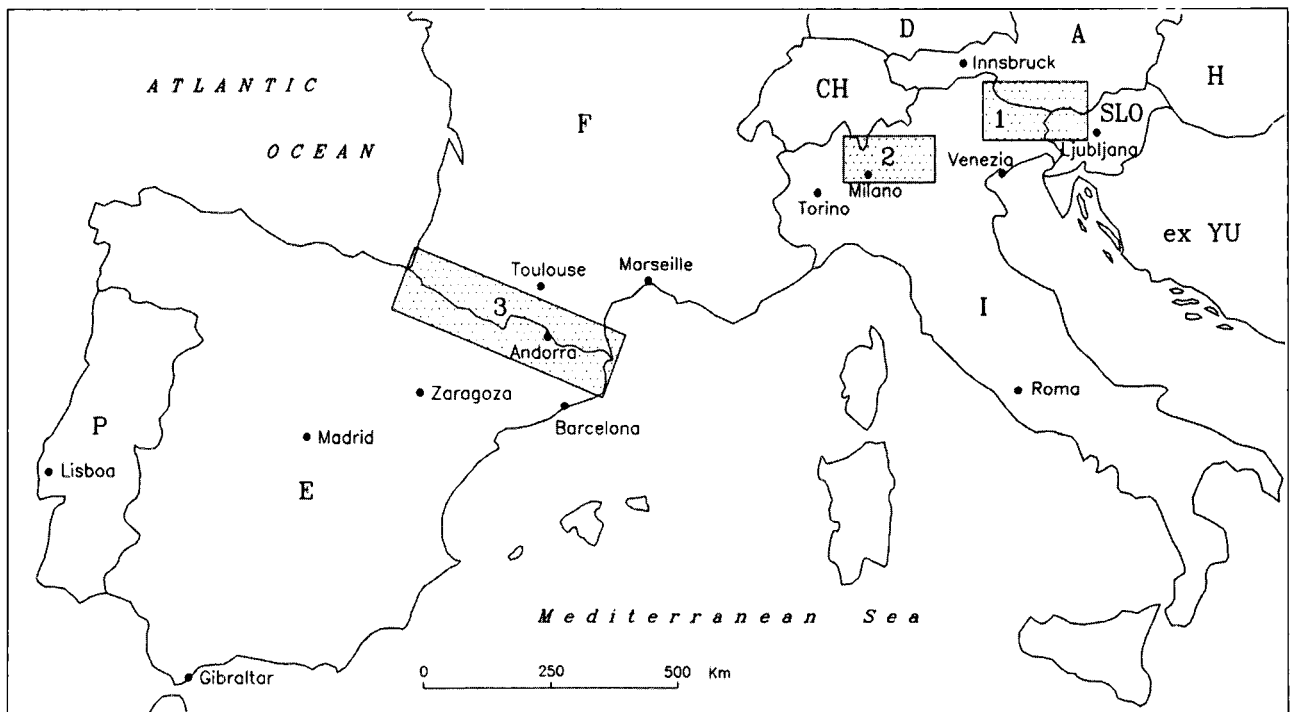


Figure 1.- Geographical location of Paleocarnic chain and Caravanche (1), Orobic Alps (2) and Pyrenees (3).

Figura 1.- Localización geográfica de los Alpes Cárnicos y Caravanche (1), Alpes Oróbcos (2) y Pirineos (3).

to review some selected common features, (3) to define or refine its structural control, suggesting environment and timing of formation, and at last (4) to compare the key characteristics of this quartz-rich mineralization, not unknown in some different geotectonic and lithostratigraphical settings of other localities (e.g., Italy, Spain, USA, China), and of the classical MVT deposits.

However, the authors recognize some major diagnostic features for the studied crust-like mineralization, which cannot be disregarded debating its formation problems: (a) the stable general link to underlying carbonate-unconformity landscapes of different ages, (b) the appearance consistent with an independent and distinctive lithostratigraphical unit, or marker.

#### MINERALIZED SILICEOUS CRUSTS IN THE ALPS

The most significant crust-type mineralization related to the Devonian carbonates of the Paleocarnic chain and of the Caravanche region (Eastern Alps: Italy, Austria and Slovenia) and to the Carnian carbonates of the Orobic Alps (Central Alps: Italy) occurs in the Southalpine domain of the Alps.

#### Eastern Alps: Paleocarnic chain and Caravanche region

##### *Distribution of mineralization*

The ore-bearing Devonian carbonates of the Eastern Alps crop out almost continuously all along the 100 km

of the Paleocarnic chain (Italy and Austria) and continue 50 km to the east in the Caravanche region (Slovenia) (Fig. 2). From west to east some major occurrences were tentatively mined at M.Avanza, Timau, Coccau/Thörl of the Palaeocarnic Chain and at Rus-Stegovinik of the Caravanche region.

##### *Geological setting*

Geological models of Paleozoic sequences of the southern Eastern Alps, with emersion related stratigraphical gaps at the Devonian-Carboniferous boundaries, have been described by Selli (1963), Flügel (1963), Vai (1974). Cantelli *et al.* (1982). Spalletta *et al.* (1982) proposed a new model, recently supported by Venturini (1990), assuming a Hercynian pluriphase tectonic evolution. These authors generalized the validity of their model for the Paleozoic sequences of the Carnic chain as a whole. However, this traditional and well founded sequence of events, as pointed out by Flügel and Schönlaub (1990), contrasts with the large mineralized emersion areas of Devonian carbonates first described by Brigo and di Colbertaldo (1972), and later morphologically defined by paleogeographical, sedimentological and structural studies (Assereto *et al.* 1976, Brigo *et al.* 1988, and unpublished data). Ebner (1991) describes stratigraphical sequences in parts of the Pyrenees and of the eastern Southern Alps, where erosional gaps (subaerial or submarine) are dominating at the Devonian/Carboniferous boundary instead.

The carbonates underwent syndimentary transcurrent horst and graben tectonics producing large and well-limited emersion areas dominated by a major sub-

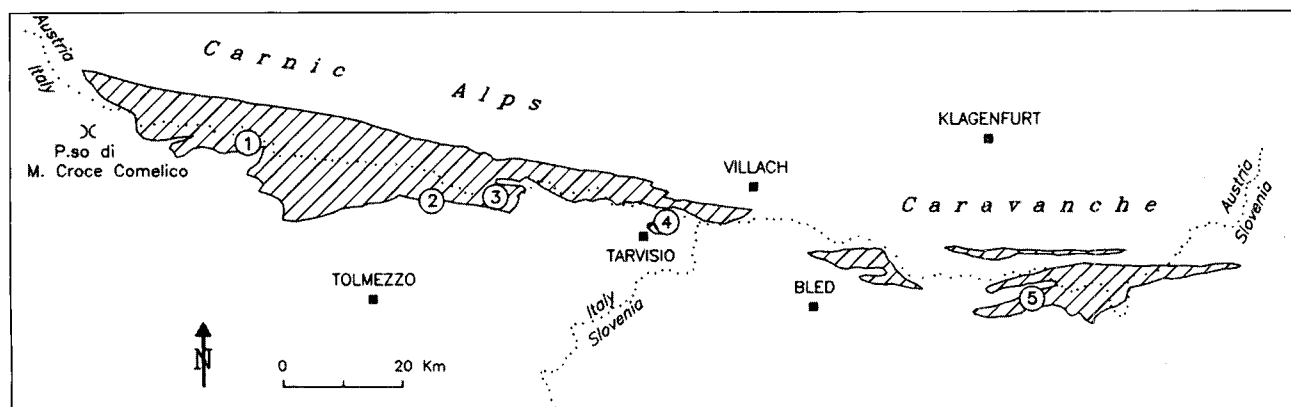


Figure 2.- Paleozoic of Carnic chain and Caravanche (oblique pattern). Deposits: 1 Monte Avanza, 2 Comeglians, 3 Timau, 4 Coccau / Thörl, 5 Rus-Stegovinik.

Figura 2.- Paleozoico de los Alpes Cárnicos y Caravanche (trama oblicua): 1 Monte Avanza, 2 Comeglians, 3 Timau, 4 Coccau/Thörl, 5 Rus-Stegovinik.

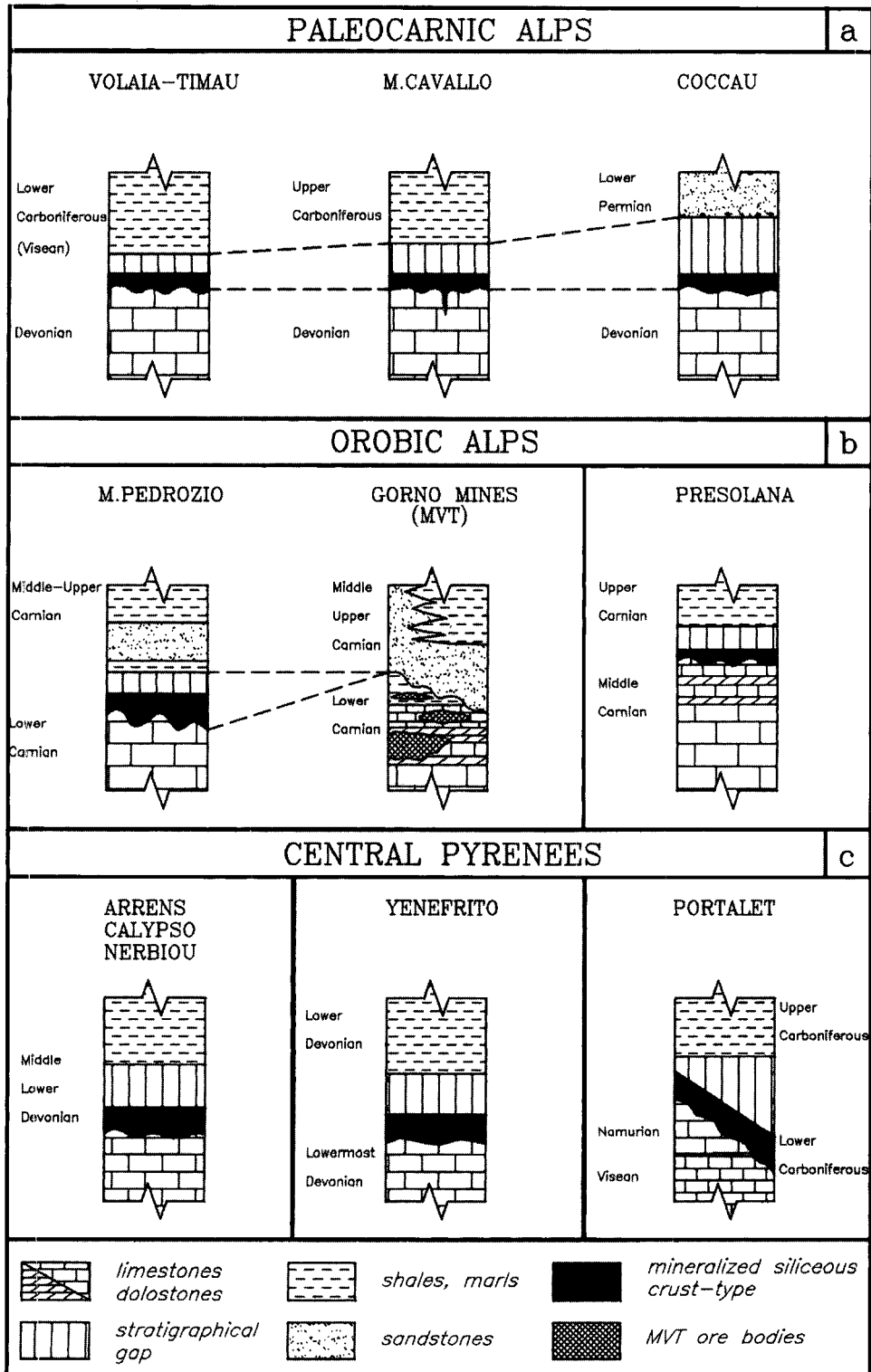


Figure 3.- Schematic stratigraphical profiles. (a) Paleocarnic chain, (b) Orobic Alps, (c) Central Pyrenees: profile in Argelès-Gazost area, France (Arrens mine, and Nerbiou area and Calypso occurrences) and profiles in Valle de Tena, Spain (Yenefrito and Portalet mines).

Figura 3.- Esquemas estratigráficos de (a) Alpes Cárnicos, (b) Alpes Oróibicos, (c) Pirineos centrales: perfiles en el área de Argelès-Gazost, Francia (minas de Arrens, e indicios del área de Nerbiou y Calypso) y en el área del Valle de Tena, España (minas de Yenefrito y del Portalet).

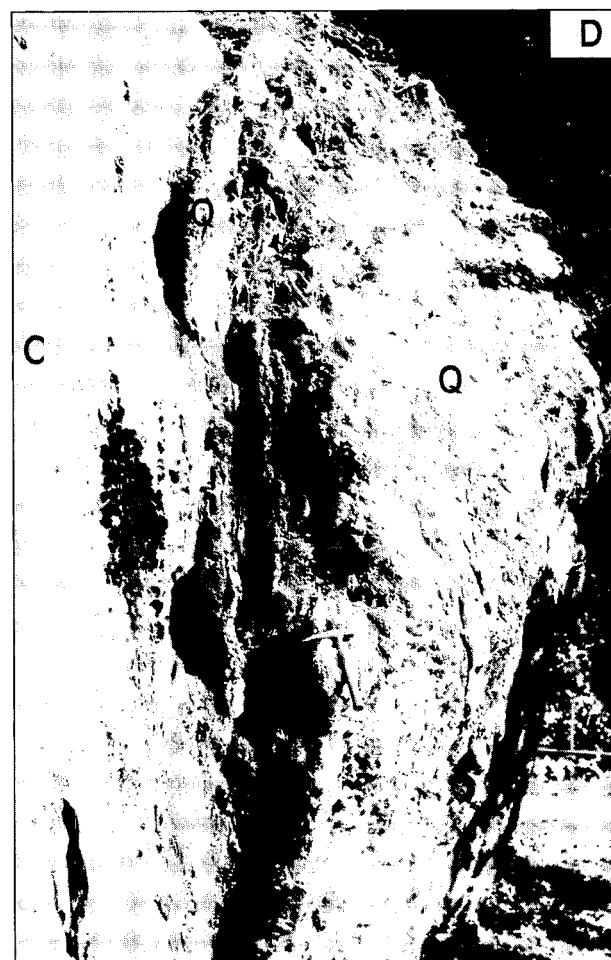
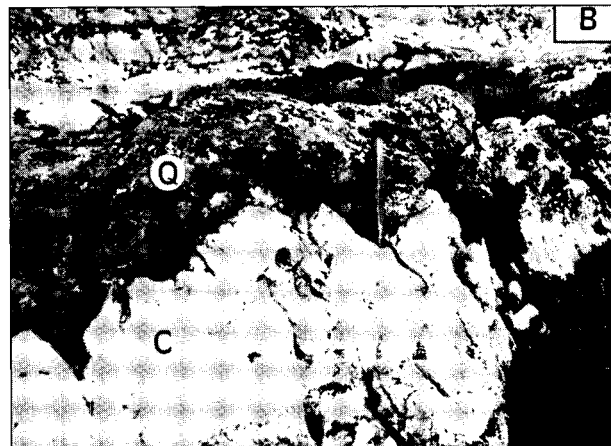


Figure 4.- Siliceous crust-type mineralization which mantles the paleorelief related to carbonates of different ages: (a) Carboniferous in the Valle de Tena area (Portalet mine) of the Central Pyrenees, (b) Triassic in Gorno district (Presolana mine) of the Orobic Alps, (c) Devonian in the Timau-Coglians area of the Carnic Alps, (d) Devonian in the Argelès-Gazost area (Calypso occurrence) of the Central Pyrenees.

Figura 4.- Mineralizaciones de tipo costra silícica cubriendo paleorelieves desarrollados sobre carbonatos de diferentes edades: (a) Carbonífero del Valle de Tena (minas del Portalet) en el Pirineo Central, (b) Triásico en el distrito de Gorno (mina Presolana) en los Alpes Oróbcicos, (c) Devónico en el área de Timau-Coglians en los Alpes Cárnicos, (d) Devónico en el área de Argelès-Gazost (indicio de Calypso) en el Pirineo Central.

Visean unconformity that is marked by karst-solution landscapes. The emersion event was responsible for erosion, reworking, pervasive paleokarst features and mineralization, which affected the uppermost portion of the Devonian-Dinantian limestone platform. The mineralization occur both within the fossiliferous and the low-grade metamorphic Paleozoic sequences.

*Morphology and stratigraphical position.*

In the Paleocarnic chain the mineralization is stratabound to the upper tens of meters of pelagic and shallow water limestones from Middle to Upper Devonian ages (Fig. 3a) and has been referred to by Brigo and di Colbertaldo (1972) as “mineralized quartz crust” (Fig. 4c). It defines an independent stratigraphical unit of the Paleozoic sequence that occurs as, (1) unconformity-concordant flat-lying more or less tabular, (2) discordant, stratabound, columnar bodies, (3) karst-cavity fillings with detrital and chemical deposited minerals, and monomineralic veins. The silicification processes of the mineralized crust did not interested its host-rocks.

The mineralized stratigraphical unit is transgressively overlain by siliciclastic sediments of different ages

(Lower Carboniferous Hochwipfel Formation, Upper Carboniferous Auernig Group, Lower Permian Tarvisio Breccias and Val Gardena Sandstones).

The range of the time gaps between the beginning of the emersion events (Frasnian) and the age of the overlying sedimentary formations varies considerably from 5-10Ma to 70 Ma.

*Composition.*

The mineralized siliceous crusts are dark and spongy in appearance and occur mainly as an almost totally silicified reworked material initially constituted by conglomerates / breccias with clasts of autochthonous Middle to Upper Devonian shallow water and pelagic carbonates and of allochthonous chert, sandstone and siltite of younger (pre-early Visean) stratigraphical units, and of ore-minerals. Fine-grained sandy material appears as open-space filling (matrix) between conglomerate/breccia fragments, frequently with mm cross- or wavy-laminated detrital texture. The major silicification processes consist of an almost complete replacement of this reworked material only above the unconformity by Si-rich, locally Si-F- or Si-Ba-rich solutions.

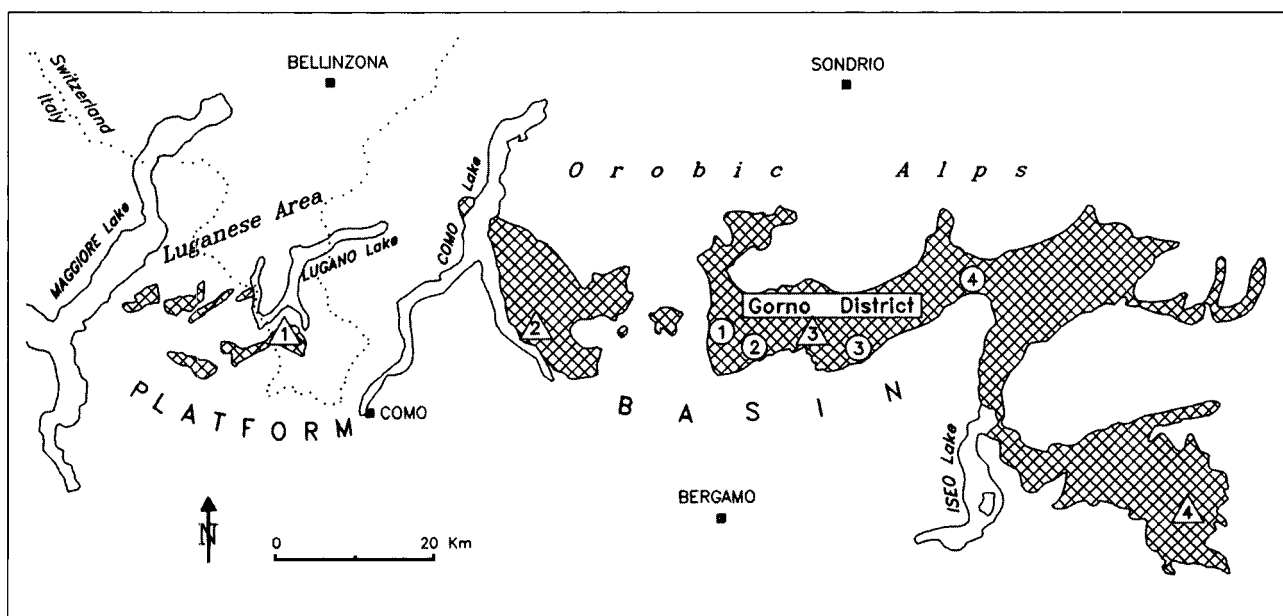


Figure 5.- Middle-Upper Triassic carbonates of the Orobian Alps (crossed pattern). Siliceous crust-type deposits (circle): 1 Cespedosio, 2 Monte Pedrozio, 3 Belloro, 4 Presolana. MVT (Alpine-type) deposits and occurrences (triangle): 1 Besano, 2 Lecco, 3 Gorno mines, 4 Val Sabbia.

Figura 5.- Carbonatos del Triásico medio y superior de los Alpes Oróbianos (trama cuadrada). Con círculos se representan los depósitos de tipo costra silícica: 1 Cespedosio, 2 Monte Pedrozio, 3 Belloro, 4 Presolana y con triángulos los yacimientos MVT (Alpine-type): 1 Besano, 2 Lecco, 3 Gorno mines, 4 Val Sabbia.

The chemical composition of the mineralized silicified crusts shows a silica content varying from ca.50 wt% to 90 wt%, with an average of  $\text{SiO}_2 + \text{Ba} + \text{F} > 70$  wt% (unpublished data).

The polymetallic silicified crust consists of the following mineral assemblage: quartz, fluorite, barite as dominant phases with minor tetrahedrite, chalcopyrite, sphalerite, galena, cinnabar, skutterudite, bournonite, jamesonite, boulangerite, enargite, arsenopyrite (Venerandi Pirri 1977).

## Orobic Alps

### *Distribution of mineralization*

All over the Orobic Triassic carbonates there are both the mineralized quartz crusts above an unconformity surface, and the classical MVT or Alpine type deposits of Gorno district below unconformity surface. The mineralized quartz concentrations were recognized in several localities in the Orobic Alps, both as exploited orebodies and as occurrences. On the map (Fig. 5), the major concentrations are located from west to east, distributed on a distance of about 40 km.

### *Geological setting*

The mineralized quartz concentration areas belong to Upper Triassic carbonates (Esino and Breno Formations) of the Southalpine domain.

The ore-bearing quartz bodies in the Gorno district are mainly concentrated in four distinct areas, or distinct structural belts, from west to east: Cespedosio-Ortighera, Monte Pedrozio, Belloro, Presolana areas.

The host-rocks of the mineralization are represented by limestones and/or dolomites of shallow-water platform of variable thickness and of Carnian age. The carbonate platform facies is characterized by sub-intertidal to supratidal cyclic sedimentation, laterally grading to a basinal facies and upward to a lagoon-facies of restricted circulation and of more siliciclastic supply.

The carbonates underwent synsedimentary horst and graben tectonics producing large and well-limited emersion areas dominated by a pre-Gorno Formation (sub-Middle Carnian) unconformity that is marked by karst-solution landscapes (Assereto *et al.*, 1977 and 1979).

### *Morphology and stratigraphical position.*

The quartz concentrations occurs as: (1) unconformity-concordant flat-lying beds or lenses; (2) discordant and irregular massive bodies, with small and short veins in the footwall limestones, and (3) concordant and discordant karst-cavity fillings. The first two ore-bearing bodies outcrop like crusts, dark and spongy in appearance (Fig. 4b).

The stratigraphical position of the mineralization is strictly linked to the emersion surface developed on carbonate build-up at the Ladinian-Carnian boundary (Fig. 3b), representing the base of mineralization. The minera-

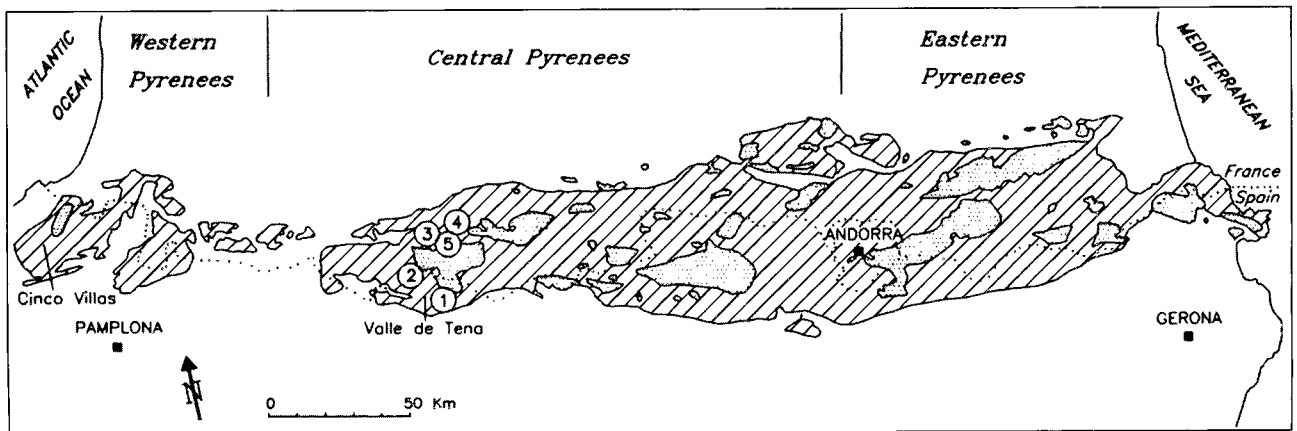


Figure 6.- Paleozoic (oblique pattern) and Hercynian magmatism (dots) in the Pyrenees. Siliceous crust-type deposits: 1 Yenefrito mine, 2 Portalet mines, 3 Arrens mines, 4 Nerbiou occurrences, 5 Calypso occurrence.

Figura 6.- Paleozoico (trama oblicua) y magmatismo hercínico (punteado) en los Pirineos. Con círculos se representan los depósitos de tipo costra silícica: 1 mina de Yenefrito, 2 minas del Portalet, 3 mina de Arrens, 4 indicios de Nerbiou, 5 indicio de Calypso.

lized unit is transgressively overlain by siliciclastic sediments of different age and nature.

#### *Composition*

The mineralized siliceous bodies show mainly breccia-texture, and are initially formed by clasts of carbonate country-rocks, cherts, sandstones, ore-minerals, bitumen. The matrix is composed by sandy and clayey-bituminous material. A typical texture is a mm cross- or wavy- lamination of alternating coarse and fine-grained quartz crystals. An almost total silicification affects the above materials, but it do not interest underlying limestones.

Four main mineralogical associations are observed: quartz-fluorite, quartz-fluorite-Zn-Pb sulfides, quartz-Pb-Zn sulfides (or calamine), quartz-barite (unusual) association.

### MINERALIZED SILICEOUS CRUSTS IN THE PYRENEES

The crust-type mineralization occurs in the Pyrenees mainly in the Central Pyrenees where it is linked to Devonian and Carboniferous unconformities. The major deposits (Fig. 6) are located in the Valle de Tena area, Spain (Yenefrito and Portalet). Recently the authors have observed some comparable deposits in the Argelès-Gazost area, France (Arrens, Nerbiou, Calypso). All these deposits show the same diagnostic features as those described both in the Paleocarnic chain and in the Orobic Alps.

#### **Valle de Tena deposits, Central Pyrenees, Spain**

##### *Devonian carbonates: Yenefrito*

##### *Distribution of deposits*

The ore-bearing siliceous crust-type deposit of Yenefrito occurs in the Bolatica Valley, a lateral branch of Valle de Tena. The mineralization crops out along a striking extension of some kilometers. The Yenefrito deposit was mined for lead and silver until the early seventies.

##### *Geological setting*

The Yenefrito area lies within the Hercynian basement located at the western end of the structural unit re-

ferred to as Gavarnie nappe, an alpine structural unit. This area is marked by a Lower Devonian sequence consisting of thin-bedded limestones overlying by a detrital sequence with intercalated limestones.

##### *Morphology and stratigraphical position*

Essentially, the stratabound ore-bearing quartz crust displays a concordant tabular shape with a thickness of several meters, linked to an unconformity surface developed on the limestones situated at the bottom of the Lower Devonian sequence (Fig. 3c). It appears dark and spongy, producing a strong relief within the outcropping series. It is noteworthy that the silicification process did not interest the host rocks. The deposit is transgressively covered by Lower Devonian detrital sequence. Consequently, the mineralized crust can be considered as an independent lithostratigraphical unit.

##### *Composition*

The lithological composition of the mineralized bodies is represented by a conglomerate/breccia rock affected by an almost complete silicification. Sulfides (sphalerite, galena, pyrite, pyrrhotite, chalcopyrite, calcite, and rare bournonite) are disseminated all over the siliceous crust.

##### *Carboniferous carbonates: Portalet*

##### *Distribution of deposits*

The Portalet deposit is located on both sides of Spanish-French border in the upper Valle de Tena. The stratabound mineralization crops out over an area of about 10 km<sup>2</sup>. The main occurrences were mined only in Spain.

##### *Geological setting*

The Portalet area, included in the Hercynian basement of the Gavarnie nappe, is marked by the outcropping of Lower Carboniferous shallow-marine carbonates. This sequence is divided into two distinctive members, from base to top, (a) the grey unit represented by lidites, intraclastic-bioclastic floodstone, nodular limestone, (b) the black unit, dominantly black limestones with an interbedded intraformational breccia. During the extensional tectonics that predate the Hercynian paroxysm, horst and graben tectonics produced well-limited emersion areas.



### *Morphology and stratigraphical position*

The Portalet mineralized siliceous crusts mantle a paleorelief (Fig. 3c) affecting the described carbonate units. Limestones under the unconformity are not affected by silicification. As the mineralized horizon is transgressively covered by Upper Carboniferous shales and sandstones, ore-bearing siliceous crust can be considered as an independent lithostratigraphic unit whose geometry is determined by the paleotopography of the paleorelief. The mineralized siliceous crusts (Fig. 4a) occur as, (1) paleorelief-concordant tabular or lens-shaped bodies, (2) discordant bodies, i.e. karstified synsedimentary fracture-fillings, (3) karst cavity-fillings and veins resulting from reworked and mobilized original crust material. Fine-grained to coarse-grained laminites are frequently comprised in this crust-framework as open-space filling between conglomerate/breccia clasts. These laminites are constituted by rhythmic repetitions of quartz and fluorite.

### *Composition*

The lithological composition of the quartz crusts appears as an almost totally silicification and/or fluoritization of the original conglomeratic material above the Lower Carboniferous unconformity. The chemical composition shows very high silica content, locally balanced by high F amounts. The mineralogical association consists of quartz, fluorite, calcite, and rare Li-bearing chlorite and pyrite.

### **Argelès-Gazost area deposits, Central Pyrenees, France**

#### *Distribution of deposits*

This area contains several deposit-types: (a) the sedex-type deposits of Pierrefitte and the vein-type deposit of Estaing, they all hosted in the volcano-sedimentary formations of the Upper Ordovician (Bois and Pouit 1976, Pouit 1993), and (b) the Devonian carbonate-hosted stratiform Zn-Pb-(Ba)-(Fe) mineralization (Nerbiou and Arrens mines, among others). The authors opinion is that some of the latter deposits, as Nerbiou Zn-Pb-Fe mine, may be considered as MVT, whereas Arrens Zn-(Pb)-Ba deposit and many other Zn-Pb prospects (i.e., Calypso, Nerbiou area) can be considered as mineralized quartz crusts.

#### *Geological setting* (Fig. 3c).

The study area, lying within the Pierrefitte structural unit, is one of the main districts in the mineralized Pale-

ozoic of the Pyrenean axial zone. The mineralized siliceous crusts and the MVT deposits of the investigated area are associated with the first Devonian massive carbonate formation, Upper Givetian in age. However, whereas MVT mineralizations occur within the above carbonate formation, ore-bearing siliceous crusts occur at the summit of this formation. Erosion and paleokarts features lead us to assume that the mentioned carbonates underwent emersion episodes in the study area.

### *Morphology and stratigraphical position*

The crust-type minealization (Fig. 4d) occurs over the Upper Givetian limestones, as unconformity-concordant lens-shaped bodies of considerable areal extension. The mineralized siliceous bodies show a mainly brecciated texture. An almost total silicification gave rise to the replacement of the original materials above the Devonian unconformity. The ore bodies are covered, in turn, by Upper Devonian black siltstones, occasionally containing some thin lenticular intercalations of ankeritic limestones. Thus, as occur in all the study cases, the mineralized horizon constitutes a stratigraphic unit by itself.

### *Composition*

The polymetallic silicified crust is made of quartz with barite, sphalerite, galena, pyrite, pyrrhothite. Moreover, Pouit and Bois (1986) found in the Arrens mine tetrahedrite, bournonite, Ni-Co sulfoarsenides and sulfoantimonides, rare Ge minerals, celsianite, cymrite, graphite and rutile. It can be locally observed that the base of the ore-bearing horizons are made up of massive barite with minor sulfides and quartz and rare Ba-silicates.

## DISCUSSION

Some selected features, common for the crust-type deposits of the Alpine belt and of other geotectonic environments too, are reviewed in detail, discussed and compared.

### **(a) Regional setting**

The MVT -or Alpine- deposits and the Crust-Type mineralization occur in a well documented rift zone within the Alpine Orogen. On the contrary, the regional setting of the classical MVT deposits is essentially restricted to relatively stable carbonate platforms peripheral to intracratonic (or cratonic) basins. Post-ore deformation

and metamorphism are not unknown in some areas of the Alps and of the Pyrenees, that have undergone structural deformations, although metamorphic grade has remained low (Carnian Alps: M. Avanza, Gamsjoch.).

#### **(b) Morphological characteristics and host-rocks**

The crust-type mineralization of the Alpine belt is stratabound and occurs in large districts closely related to karst-solution unconformity surfaces developing on carbonates of various ages in the same, regionally different (Cambrian, Ordovician, Devonian, Carboniferous, Triassic), chronostratigraphical sequences. Regression leading to karst-solution development in the mineralized carbonates appears related to extensive (transcurrent transtensive) synsedimentary tectonism (horst and graben tectonics) at least. The paleokarst features pervade from the upper few meters to few tens of meters of carbonates and represent the very base of the siliceous crusts. The basic shapes of the orebodies are: (1) unconformity-concordant tabular bodies, (2) stratabound, discordant irregular columnar bodies, and karstified fractures or break trough fillings of various dimensions, (3) karst-cavity fillings with detrital and chemical deposited minerals and monomineralic veins as younger products of reworked or mobilized crust material.

#### **(c) Composition**

The crust-like mineralization occurs in the Alpine belt, and outside too, as a peculiar independent formation of reworked material, dark and spongy in appearance due mainly to an almost total silicification. This formation was initially constituted by conglomerates/breccias with clasts of dominantly autochthonous carbonates and of minor, sometimes sulfide-bearing, allochthonous siliciclastic sediments (protolithes) of younger stratigraphical units. The open-space filling (matrix) among the conglomerate/breccia fragments is represented by fine-grained sandy material (quartz, fluorite, barite, clayey-components), arranged frequently to form coarse- and/or fine-grained laminites. The peculiarity of this independent crust-type formation consists in its almost complete replacement by Si-rich solutions, where high F and Ba contents have played locally an important role. In fact, the zonal decrease of the generally very high SiO<sub>2</sub> content (>70wt%) of all the crusts, is balanced by barite and /or fluorite (unpublished chemical analyses). On the contrary the metallic composition could vary notably, characterizing the crusts with major contents of Cu, of Pb-Zn, of Hg, of Sb. Com-

mon and significant textural patterns of the silicified crusts is the idiomorphic bi-pyramidal and the microcrystalline quartz, recording the diagenetic and the dominant hydrothermal silicification (or replacement) processes.

#### **(d) Some geochemical patterns**

The absence of bedrock alterations proves that the questioned paleoreliefs developed on the carbonates are the very base of the crust-type mineralization. In fact, the carbonate host rock does not exhibit litho-geochemical proximity indicators or any primary geochemical anomalies regarding the base metals. Only minor quantities of trace elements are related to some mineral components (quartz, fluorite, barite, sulfides), remainder element groups are associated with incorporated organic matter, fluid inclusions, detrital grains of protoliths (unpublished chemical and statistical data). REE contents are low in fluorite and calcite and below the detection limits in barite (Brigo *et al.*, 1988; Subias and Fernández-Nieto, 1995). Some fluorite samples show a significant depletion of light REE, indicating severe remobilization. Methodical isotopic analyses of Pb and S are scheduled.

#### **(e) Chronological data**

The timing of formation of the crust-type mineralization, as independent and distinct stratigraphical units, is thought to have ranged from the end of unconformity developments and a closely subsequent relatively narrow time span (including the phreatic and vadose resedimentation of reworked allochthonous and autochthonous sediments and following pervasive silicification and mineralization processes).

#### **(f) Comparable crust-type mineralization in other geotectonic environments**

Other deposits in the Southalpine and Austroalpine units of the Italian Alps could be referred to as crust-type mineralization. Outside the Alpine belt, major comparable deposits are known, in SW Sardinia (Italy), in the Tri-State district of USA, in the central and southern provinces of China.

##### *Italy*

Possible crust-type mineralization occurs in the Alps, (a) in the kinzigitic series (Candoglia marbles) of the

Southalpine Ivrea Verbano Zone (Bigioggero *et al.* 1978-1979) as continue and locally important barite, sulfide and Fe-oxide stratabound mineralization, and (b) in the Austroalpine crystalline basement (Lasa marbles) of Val Venosta/Vinschgau Austroalpine (Venerandi Pirri 1980) as a polymetallic stratabound sulfide mineralization. Outside the Alpine belt the comparable main deposits (dominantly barite) are linked to (c) the Lower-Paleozoic units (Cambrian carbonates) of SW Sardinia (Benz J-P. 1965, Padalino *et al.* 1972, Assereto *et al.* 1976).

## USA

Unlike other Mississippi Valley-type deposits, which occur in Cambrian and Ordovician limestones and dolostones, the Tri-State deposits, one of the greatest lead-zinc districts in the world (100x30 miles extended on the Missouri, Kansas and Oklahoma States), are mainly linked to quartz-rich lithologies which cap unconformably the Mississippian limestones and are overlain by the Pennsylvanian Cherokee shale (Brockie *et al.* 1968). Quartz occurs as chert, jasperoid, quartz druses, and well-formed quartz crystals. Jasperoid, which is closely associated with sulfide minerals, is massive (consists mostly of microcrystalline quartz crystals) but characteristically is very thinly banded and occurs interbedded with chert and fills the spaces between broken chert fragments in the mineralized breccia zones and replaces thin beds and fragments of limestones. The Tri-State district is considered only a major exception among the classical MVT districts because of “..widespread silicification (“jasperoid”) of carbonate..” (Sangster 1988).

## China

Strictly comparable crust-type mineralization, occurring as main Sb deposits (dominantly antimonite) in the Hunan Province, is linked to the widespread Devonian formations (Niansheng and Soufu, 1994; personal observations). Moreover, in the southern provinces of China significant silica-rich formations are described: (a) bedded cherts in Devonian intraplatformal basin of north-west Guangxi Province (Zhou 1990), (b) chert-hosted bedded barite/witherite deposits linked to Lower Cambrian black shale series of Quinling and Jiangnan areas (the deposits are described by Wang and Li (1991) as the richest and most widespread in China, and their abundance suggests some special geological event), (c) bedded cherts (gold source rock of nearby gold fields) of Late Proterozoic (Sinian) series at Gusui, Guandong Province, which are characterized by bedded, laminated, massive and pseudobrecciated structures (Zhou *et al.* 1994).

For all these silica-rich, more or less mineralized formations the source of silica is the debated question.

## (g) Genetic observations

As regards the source of silica (and mineralizing elements), the generation of fluids, and their transport from the source to the depositional site, the present review has revealed some genetic constrains, e.g., the almost total replacement of crust-forming material by silica, the large amount of additional SiO<sub>2</sub> needed to produce the "crusts" and suggested by mass balance estimates, the absence of bedrock alterations, the characteristic lack of igneous rocks associated with crusts, the small time range for mineralized crust formation. Several sources of silica have been suggested by numerous authors, e.g. Hurst and Irwin (1982), Iijima *et al.* (1983), Hesse (1987, 1988, 1989), Thiry and Millot (1987), Houseknecht (1988), Ulmer-Scholle *et al.* (1993), Zhou *et al.* (1994), Lawrence (1994), and some others. These silica sources are: (a) silica originated by hydrothermal systems as emanations in geothermal areas or associated (fossil systems) with volcanism (ophiolite complexes, volcanic arcs, etc.), (b) biogenic silica (microfaunas and diatomaceous sediments), (c) silica originated in pedogenetic environments by weathering (dissolution and leaching) of silica-rich minerals, (d) silica delivered by sources as basinal formations or back-reef units, with pressure solution mechanism (during intermediate diagenesis) of sand or silt grains (quartz and feldspar) and with shale diagenesis mechanism (smectite transformation to illite).

The SiO<sub>2</sub>-rich fluids needed to produce the crust-type mineralization in the Alpine belt, could be generated in siliciclastic basins during burial and compaction with transformation of clay minerals and leaching of metals, and in siliciclastic platform covers during weathering and dissolution of Si-rich minerals, both migrating towards the crust-formation areas.

## CONCLUSIONS

The results of correlation researches carried out in the last years on mineralized siliceous crusts of the Alpine belt are based on circumstantial evidences such as (a) the universal presence of an underlying unconformity in the mineralized areas, (b) the similarities (Fig. 4) of all the studied numerous and large ore-bearing siliceous crusts (geometry of mineralization, fabrics, very high silica average content, absence of bedrock alterations), which

characteristically mantle the carbonate bedrocks “sealing off” the unconformity landscapes, (c) the appearance of silicified crusts consistent with an independent and distinctive lithostratigraphical unit, or marker, (d) the transgressive overlying siliciclastic sediments. This evidence has led to a majority opinion favouring the hypothesis of paleogeographic and metallogenetic evolutions during different geological epochs with ore-forming and silicification processes in nearly identical environments.

The differences between the main diagnostic features of the crust-type mineralization and those of the MVT deposits suggest a different grouping in the framework of the carbonate-hosted deposits. Actually, the most relevant MVT diagnostic features, after Sangster (1988), are: the nearly universal presence of an unconformity above the ore district, the open-space filling of carbonate collapse breccias as the main mineralizing process, the virtual absence of silicification, the usual lack of barite and/or fluorite. By contrast, diagnostic features for crust-type mineralization are: universal presence of an unconformity below the ore-bearing crusts, the extraformational conglomerate/breccia as support of the mineralization, almost total silicification as replacement process, locally dominant barite or fluorite presence.

Consequently, the highlighted differences allow the authors to define the new metallogenetic model: crust-type (CT) deposits. Comparable mineralization in other geotectonic environments outside the Alpine belts point out to CT deposits, being a worldwide significant metallogenetic event.

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#### REFERENCES

- ASSERETO, R., BRIGO, L., BRUSCA, C., OMENETTO, P., ZUFFARDI, P., 1976: Italian ore/mineral deposits related to emersion surfaces: a summary. *Mineral. Deposita*, 11, 170-179.
- ASSERETO, R., JADOUL, F., OMENETTO, P., 1977: Stratigrafia e metallogenese del settore occidentale del distretto a Pb, Zn, fluorite e barite di Gorno (Alpi Bergamasche). *Riv. Ital. Paleont.*, 83, 395-532.
- ASSERETO, R., BRIGO, L., JADOUL, F., OMENETTO, P., PERNA, G., RODEGHIERO, F., VAILATI, G., 1979: Recent studies on Pb-Zn-fluorite and barite deposits in the Mid-and Upper-Triassic series of the Lombardic Prealps (Northern Italy). *Verh. Geol. B.-A.*, 3, 197-204.
- BENZ, J.-P., 1965: Nouvelles observations sur les gisements d'Arenas. In: EDITORES “*Problemi minerari della Sardegna*”, Ass. Min. Sarda, Cagliari-Iglesias, ottobre 1965. Prestampe, 3-7.
- BIGIOGGERO, B., BRIGO, L., FERRARIO, A., GREGNANIN, A., MONTRASIO, A., ZUFFARDI, P., 1978-1979: *Strona Valley (Fe-Ni-Cu) and (Fe-Ba) ore deposits: excursion book*. Mem. Ist. Geol. Miner., Univ. Padova, 33, 33-39.
- BOIS, J.-P. and POUIT, G., 1976: Les minéralisations de Zn (Pb) de l'anticlinorium de Pierrefitte: un exemple de gisements hydrothermaux et sédimentaires associés au volcanisme dans le Paléozoïque des Pyrénées centrales. *Bull. B.R.G.M.*, 2, 543-567.
- BRIGO, L. and COLBERTALDO DI, D., 1972: *Un nuovo orizzonte metallifero nel Paleozoico delle Alpi Orientali*. 2nd Int. Symp. Min. Dep. Alps, 109-124.
- BRIGO, L., DULSKI, P., MÖLLER, P., SCHNEIDER, H.-J., WOLTER, R., 1988: Stratabound mineralizations in the Carnic Alps/Italy. In: J. Boissonnas y P. Omenetto. *Mineral deposits within the European Community*, pp. 485-498, Springer-Verlag, Berlin, Heidelberg.
- BROCKIE, D. C., HARE, E. H., DINGESS, P. R., 1968: The geology and ore deposits of the Tri-State district of Missouri, Kansas, and Oklahoma. In: J. D. Ridges. *Ore deposits of the United States, (1963-1967)*, pp. 400-430, The Mapple Press Company, New York, Pennsylvania.
- CANTELLI, C., SPALLETTA, C., VAI, G. B., VENTURINI, C., 1982: Sommersione delle piattaforme e rifting devono-dinamico e namuriano nella geologia del Passo di M. Croce Carnico. In: A. Castellarin y G. B. Vai. *Guida alla geologia del Sudaipino centro-orientale*. pp. 293-303. Guide geol. reg. S.G.I.
- EBNER, F., 1991: Circummediterranean Carboniferous preflysch sedimentation. *Giornale di Geologia*, 53, 197-208.
- FLÜGEL, H., 1963: Das Paläozoikum in Österreich. *Mitt. Geol. Ges.*, 56, 401-443.
- FLÜGEL, E. y SCHÖNLAUB, H. P., 1990: Exotic limestone clasts in the Carboniferous of the Carnic Alps and Noetsch. In: C. Venturini, K. Krainer. *Field Workshop on Carboniferous to Permian sequence of the Pramollo-Nassfeld Basin (Carnic Alps)*, pp. 15-19.
- HESSE, R., 1987: Selective and reversible carbonate-silica replacements in Lower Cretaceous carbonate-bearing turbidites of the Eastern Alps. *Sedimentology*, 34, 1055-1077.
- HESSE, R., 1988: Origin of chert, I. Diagenesis of biogenic siliceous sediment. *Geosci. Can.*, 15, 171-192.
- HESSE, R., 1989: Silica diagenesis: original of inorganic and replacement cherts. *Earth. Sci. rev.*, 26, 253-284.
- HOUSEKNECHT, D. W., 1988: Intergranular pressure solution in four quartzose sandstones. *J. Sedim. Petrol.*, 58, 228-246.
- HURST, A. Y IRWIN, H., 1982: Geological modelling of clay diagenesis in sandstones. *Clay Miner.*, 17, 5-22.
- IJIMA, A., HEIN, J. R., SIEVER, R., 1983: *Siliceous deposits of the Pacific Region*. Elsevier, New York.
- LAWRENCE, M. J. F., 1994: Conceptual model for early diagenetic chert and dolomite, Amuri Limestone Group, north-eastern South Island, New Zealand. *Sedimentology*, 41, 479-498.
- MARTIN, F., 1979: *Les gisements de fluorine post-hercyniens (karsitiques et filoniens) dans le Paleozoïque de la région du Portalet (Pyrénées atlantiques-province de Huesca)*. Thèse Doct. Univ. Paris VI. 190 p.
- NIANSHENG, J. y SOUFU, J., 1994: *A guide to Xikuangshan Sb deposit and Woxi W-Sb-Au deposit*, Hunan. IX IAGOD Symp., Beijing, 17 p.

- PADALINO, G., PRETTI, S., TAMBURRINI, D., TOCCO, S., URAS, I., VIOLO, M., ZUFFARDI, P., 1972: Carsismi e mineralizzazioni. *Rend. Soc. It. Min. Petrol.*, 28, 215-230.
- POUIT, G., 1986: Les minéralisations Zn-Pb exhalatives sédimentaires de Bentaillou et de l'anticlinorium paléozoïque de Bosost (Pyénées ariégeoises, France). *Chron. rech. min.*, 485, 3-16
- POUIT, G., 1993: Les horizons minéralisés en Zn-Pb (Ba) du Paléozoïque des Pyrénées centrales françaises. *Chron. rech. min.*, 511, 21-31.
- POUIT, G. y BOIS, J.-P., 1986: Arrens Zn (Pb), Ba Devonian deposit, Pyrenees, France: an exhalative-sedimentary-type deposit similar to Meggen. *Mineral. Deposita*, 21, 181-189.
- POUIT, G., BOUQUET, CH., BOIS, J.-P., 1979: Les principaux niveaux minéralisés (Zn, Pb, Cu, Ba) du Paléozoïque des Pyrénées centrales: éléments de synthèse. *Bull. B.R.G.M.*, 1, 23-34.
- RODEGHIERO, F., 1977: Le mineralizzazioni a Pb-Zn, fluorite, barite nel Carnico della zona del Pizzo della Presolana (Prealpi Bergamasche). *Ass. Miner. Subalpina*, 3-4, 453-474.
- SANGSTER, D.F., 1988: Breccia-hosted lead-zinc deposits in carbonate rocks. In: N.P. James, P.Q. Choquette. *Paleokarst*. pp. 102-116. Springer-Verlag, New York, Berlin, Heidelberg.
- SELLI, R., 1963: Schema geologico delle Alpi Carniche e Giulie occidentali. *Giornale di Geologia*, 30, 1-136.
- SPALLETTA, C., VAI, G.B., VENTURINI, C., 1982: Controllo ambientale e stratigrafico delle mineralizzazioni in calcari devonodinantiani delle Alpi Carniche. *Mem. Soc. Geol. It.*, 22, 101-110.
- SUBÍAS, I., 1993: *Yacimientos hidrotermales de Pb-Zn-F del area de Sallent de Gallego-Panticosa, Pirineos occidentales (Huesca)*. Tesis Doctoral. Univ. Zaragoza. Spain. 233p.
- SUBÍAS, I. y FERNÁNDEZ-NIETO, C., 1995: Hydrothermal events in the Valle de Tena (Spanish Western Pyrenees) as evidenced by fluid inclusions and trace-element distribution from fluorite deposits. *Chem. Geol.*, 124, 267-282.
- THIRY, M. Y MILLOT, G., 1987: Mineralogical forms of silica and their sequence of formation in silcretes. *Jour. Sed. Petrology*, 57, 343-352.
- ULMER-SCHOLLE, D.S., SCHOLLE, P.A., BRADY, P.V., 1993: Silicification of evaporites in Permian (Guadalupian) back-reef carbonates of the Delaware Basin, West Texas and New Mexico. *Journal of Sedimentary Petrology*, 63, 5, 955-965.
- VAI, G.B. (1974) Stratigrafia e paleogeografia ercinea delle Alpi. *Mem. Soc. Geol. It.*, 13, 7-37.
- VENERANDI PIRRI, I., 1977: Le paragenesi a Zn, Cu, Pb, Sb, Hg, Ni, As, fluorite, barite nel Devonico della Catena Carnica. *Rend. Soc. It. Mineral. Petrol.*, 33, 821-844.
- VENERANDI PIRRI, I., 1980: La paragenesi a Zn, Pb, Ni, Sb, Cu, Fe, Sn, Co della Val di Lasa. *Rend. Soc. It. Mineral. Petrol.*, 36, 309-322.
- VENTURINI, C., 1990: *Geologia delle Alpi Carniche centro orientali*. Comune di Udine. Ed. del Museo Friulano di Storia Naturale, 36, pp. 220.
- WANG, Z.C. Y LI, G., 1991: Barite and whiterite deposits in Lower Cambrian shales of South China: stratigraphic distribution and geochemical characterization. *Econ. Geol.*, 86, 354-363.
- ZHOU, Y.Z., 1990: Geochemical characteristics of siliceous rocks originated from a fossil hydrothermal system in the upper Devonian strata, Guangxi, southern China. *Acta Sedimentol. Sinica*, 8, 75-83.
- ZHOU, Y., CHOWN, E.H., GUHA, J., LU, H., TU, G., 1994: Hydrothermal origin of Late Proterozoic bedded chert at Gusui, Guangdong, China: petrological and geochemical evidence. *Sedimentology*, 41, 605-619.