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VOLCANIC – SEDIMENTARY METAL DEPOSITION IN PALEOMARGIN ENVIRONMENT: A " PROTORE " OCCURRENCE IN CENTRAL SARDINIA (ITALY)

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Abstract

Several metallogenic periods took place at different moments of the geological evolution of Sardinia, but at places they interacted: the close correlation between the metal parageneses in the Ordovician – Silurian sequences, outcropping in the central part of the island, and the veins and masses associated with the Hercynian magmatism is depicted. The volcanic-sedimentary mixed-sulphide lenses contained in Silurian occurrences show clear sedimentary structures, and the connection with coeval volcanics seems evident. These mineralizations are thought to be the protores for the subsequent metallogenic cycle related with the Hercynian orogenesis which had a strong effect as a promoter of the remoulding of preexisting mineral concentrations to give new ore- and industrial-minerals deposits. Several geochemical campaigns have covered the entire island, and wide areas of the Paleozoic basement, mostly localised in the internal zones, showed high base- and heavy-metals contents. A new prospecting programme has been started in Central Sardinia; it follows the ore-bearing horizon along the Ordovician-Silurian boundary with the purpose to better understand these primary metal depositions, their relationships with geodynamic structures, and ore mobilisation caused by the Hercynian granites. The geochemical anomalies along this horizon detected in the area of "Castello Medusa" support detailed prospecting works.

Key words: *protore, sulfides, Ordovician-Silurian, Sardinia.*

1. Introduction

The present shape, grade and composition of many Sardinian deposits are the final result of recurrent reworkings of original, not always economically interesting accumulations. Among the metallogenic epochs recognizable in the Paleozoic basement of the Sardinian microplate, one took place in the Upper Ordovician to Lower Devonian and yielded different types of deposits that share a common character: they are all syndepositional and partly volcano-sedimentary, at least as far as their protores are concerned (Pretti et al., 1990). These stratiform deposits are essentially located in the central part of the island, in one of the two main recognizable sedimentary areas, the "*internal trough*" (Fig. 1), where volcanics and tuffites are frequent and a Cu-Zn-Pb stratabound mineralization is well developed as a number of generally small, high-grade, mixed-sulphide lenses contained in Silurian black shales (Carmignani et al., 1994); these bodies show evident sedimentary structures

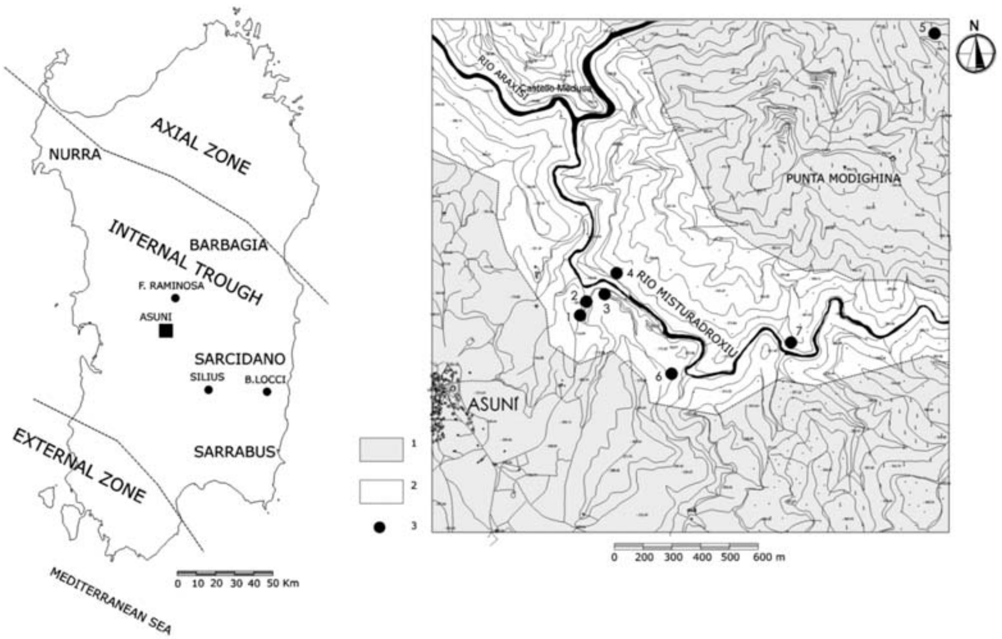

Fig. 1: Left: sketch map of Sardinia showing the three main structural areas; Right: topographic map of the area under study. 1) Silurian-Devonian complex: micaschists, phyllites, arenaceous phyllites; 2) Silurian-Devonian marbles, calcshists; 3) Sampling sites.

(load cast, slumping, diagenetic fracturing, etc). Another type which is characterized by its high Ag grade, at places with recoverable quantities of galena and minor sphalerite, is well known in the Sarrabus district (SE Sardinia), and oolitic iron ore accumulations interbedded with Silurian slates occur in the NW corner of the island (Nurra). The main ore-bearing horizon is made up of lavas and tuffitic rocks probably of Caradocian age. The products of this volcanic cycle, that may represent the cause of the metal supply, are covered almost everywhere by shales, black shales and limestone, of Silurian age. The above subaerial and submarine volcanism started during the Ordovician and exhausted in the Upper Silurian; The ore-bearing horizon seems to represent its upper part, and displays a comparatively modest thickness (50 to 100 m, Garbarino et al., 1980). However important phenomena of ore remobilisation, caused by the Hercynian folding, occurred in this horizon, so that it loosed its spatial continuity and was split and reworked in the nuclei of the folds. Numerous skarn deposits were generated by contact metamorphism of previous protores and/or metasomatic replacement, giving rise to new ore associations and textures (Marcello et al., 1994; Pretti et al., 1990).

A series of geochemical campaigns have covered the entire island, and several base- and heavy-metals showed high contents in numerous, and often wide areas of the Paleozoic basement of Sardinia. Most of these areas are localised in the internal zone.

A five-years prospecting programme was carried out during the eighties in the ambit of CNR-supported "Geodinamica" Project. About 250 samples were collected in the Barbagia region along the above stratigraphic sequences. All the samples have been analised for Pb, Zn, and Cu by AAS and XRF (Tab. 1).

Table 1. M = average content in ppm; S = standard deviation; n = number of samples.

	M	S	n		M	S	n	
Cu	43	41	97	Silurian metasediments (phyllites, black shales, skarn and metalimestones)	30	25	48	Silurian meta-volcanics (metandesites, metarhyolites and their tuffs)
Pb	16	9	97		18	9	48	
Zn	196	246	97		115	28	48	

Table 2. Analytical results of high metal spots from the sampled area, values in ppm.

	PA1A	PA2A	PA3A	PA3B	PA4A	PA4B	PA4C	PA4D	PA4E	PA5	PA6	PA7
Cu	13	8	65	661	16	94	265	329	19	6	15	225
Pb	7	14	6	21	1634	6	8	13	3	3	1612	7
Zn	2	1	21	8	11	40	11	32	24	3	8	7
As	7	23	13	16	6	5	1	1	1	15	5	5
Sb	0.15	2	2	1	1	2	1	1	3	0.4	1	14
Cd	2	0.1	1	1	1	4	1	4	0.1	0.4	1	0
Mo	0.01	0.01	4	3	1	11	10	0.22	0.22	0.01	1	12
Se	0.3	0.3	0.4	1	15	1	1	1	0.02	0.02	13	2
Te	0.009	0.06	0.005	0.03	1	0.2	0.1	0.05	0.005	0.005	1	1.4
Hg	3	2	5	2	4	2	2	2	1	3	4	52
Bi	0.4	0.7	1	1	123	6	2	1	0.3	0.05	122	131
Ni	12	5	95	25	15	94	64	43	19	23	13	5
Co	1	1	22	4	3	14	10	16	6	3	3	157
Ag	0.5	0.8	0.6	6	119	3	3	3	0.2	< 0.005	103	7
Au	0.04	0.01	0.007	0.007	0.011	0.003	0.002	0.003	0.007	< 0.001	0.009	0.053

The aim of this work is to examine some of these areas especially in the pre-Hercynian limestones and shales, in order to detect "spots" having rather high metal content; they could represent a "protore". In the study area of *Castello Medusa* frequent transitions between different lithologies occur: tuffs, tuffites, clastic sediments, black shales, phyllites and limestones are observable; the area also hosts fluorite-galena-bearing veins, which have been exploited in the past. The following step is to recognize disseminated ore minerals and to match the composition of these "protores" with the compositions prevailing in the known ore bodies along the same NW-SE belt. Actually numerous indications of mineralization have been recognized during this field work, which was developed by following the stratigraphic and structural guides.

2. Geological setting

The internal trough, from Sarrabus to Barbagia and Nurra (Fig.1), includes the thickest Palaeozoic sequence of the Sardinia microplate and it is characterized by low grade metamorphism. Lithostratigraphic sequences of the various tectonic units in this zone are composed of a Middle Cambrian-Lower Ordovician pelitic-arenaceous substrate. During the Middle-Upper Ordovician period a subaerial volcanic complex formed and is principally recorded by intermediate-acid metavolcanics with subalkaline affinity. Upper Ordovician deposits are transgressive on the volcanic complex and are represented by terrigenous and, subordinately, carbonate metasediments. Subsequent deposition is recorded by Lower-Middle Silurian pelitic neritic metasediments and by Upper Silurian-Devonian pelagic platform carbonate deposits. The Hercynian deformational history in central Sardinia involved essentially two phases. The first was produced during collision-related shortening, the second deformational event, which appears largely extensional in character, deformed the earlier structures and produced open folds. This orogenic event took place approximately 350 to 290 Ma ago. During the Hercynian cycle tonalities, granodiorites and monzogranites, followed by post-tectonic leucogranites were emplaced, accompanied by porphyrites at the end of the cycle.

3. Sampling and analytical procedures

Data collected during the CNR "Geodinamica" Project have been chosen for a first matching with the results of the present study. Figure 1 shows the sampling pattern and sites along the Rio Misturadroxiu in the Asuni sector where some "stream" samples collected during the above mentioned geochemical campaigns showed high Pb, Zn, Cu, and Au values. Besides base metals, precious elements and PGM have been determined in limestone, marble, and black shale samples by ICP-MS and INAA. These new data are reported in Table 2.

The sampled lithological formations outcropping in the area are mostly composed of Silurian-Devonian shales, black shales, marbles, calcschists, and quartz veins (Fig. 2).

4. Discussion

The most important mineral occurrences are around the paleoreliefs, always at the base of the Silurian limestone or in a synchronous stratigraphic level. Important ore deposits occur around the

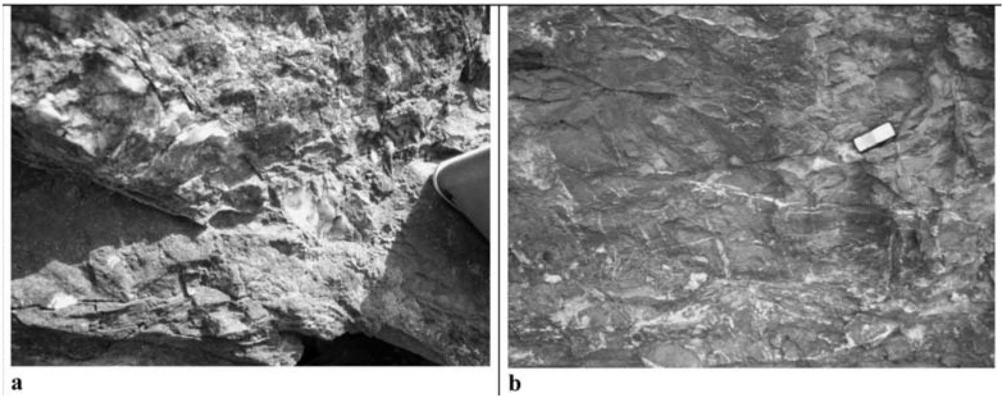

Fig. 2: a) Disseminations of sulfides in silicified limestones, Costa Ualla, Rio Misturatroxiu; b) The "protore" as a tight stockwork of sulfide-bearing quartz veinlets.

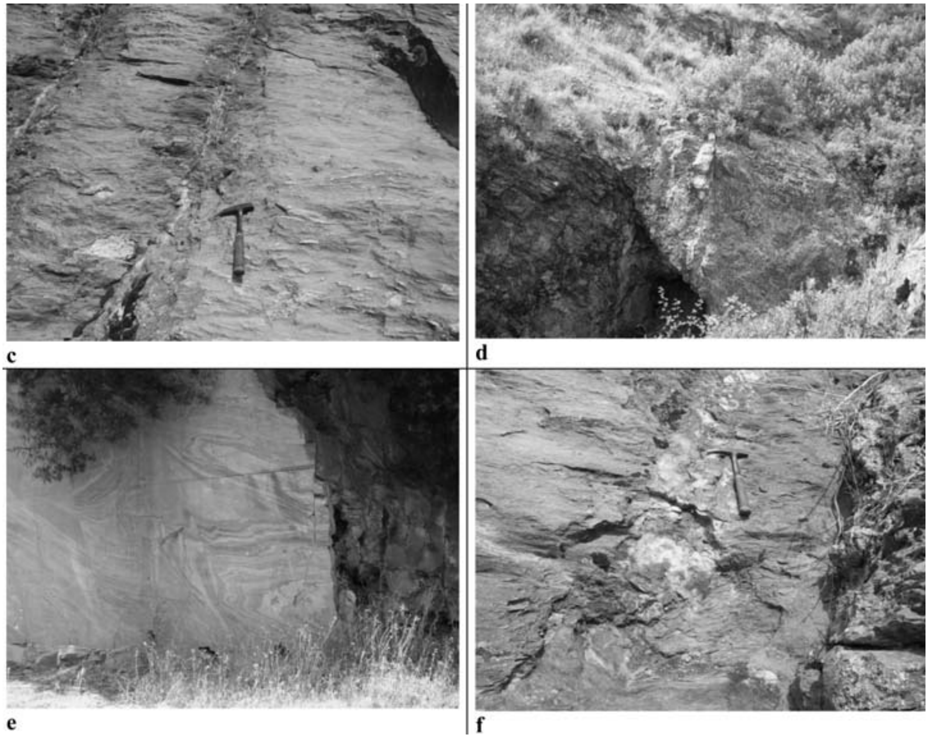

Fig. 2: c) The "protore" as small lenses of squeezed sulfide-bearing quartz. A late mobilization, probably of Hercynian age, formed a sulfide-richer quartz vein; d) Quartz-fluorite-barite-galena vein (an exploration tunnel is visible), as the latest aspect of the ore-level mobilization; e) Asuni marble open pit; f) Oxidized pyrite in quartz vein (in black shales).

thickest volcanic occurrences; they include Fe, Cu, Zn, Ag, and minor amounts of Pb and F. At Funtana Raminosa (chalcopyrite and galena), the ore-bearing horizon reaches its maximum thickness, about 10-15 metres, and the origin of the mineralization has been essentially attributed to concentrations of previous low-grade ores; in fact a fine interpenetration between sulfide and Ca-silicate minerals is present when the ore-content is not very high (Fig. 3).

With increasing ore concentration the structure may become massive and mineralisation assumes the "massive sulfide" structure. In this case the ore bed consists almost exclusively of sulfides; nevertheless a bedding can be frequently recognized in the mineralized layers. Ag was also recovered from the Funtana Raminosa ores. On a microscopic scale the ore occurences of these areas consist of a mixture of sulfides, sulfosalts and oxides; the main ore minerals are sphalerite, galena, pyrite, chalcopyrite, and magnetite; fluorite also occurs.

The ore-bearing horizon overlies the volcanic system and underlies the Silurian–Devonian sequence; it may represent the result of direct deposition and/or replacement phenomena near the sea floor, around the volcanic centres, where sub-marine fumarolic activity was present. However the mineralising processes represent systems in equilibrium with the environmental evolution and they cannot be interpreted as restricted in time and space. The Ordovician-Silurian mixed sulphides have been subjected to the Hercynian orogenesis and have been reworked; the *Filone Argentifero*, and the ore deposit of Baccu Locci in Sarrabus may represent the result of these remobilisation phenomena (Bakos et al., 1988).

Fig. 3: Ore-bearing horizon made up of garnet, epidotes, quartz. The sulfides are finely disseminated in the rock. Crystallization broadly synchronous with the microfolds is visible; S. Gabriele, Funtana Raminosa Mine.

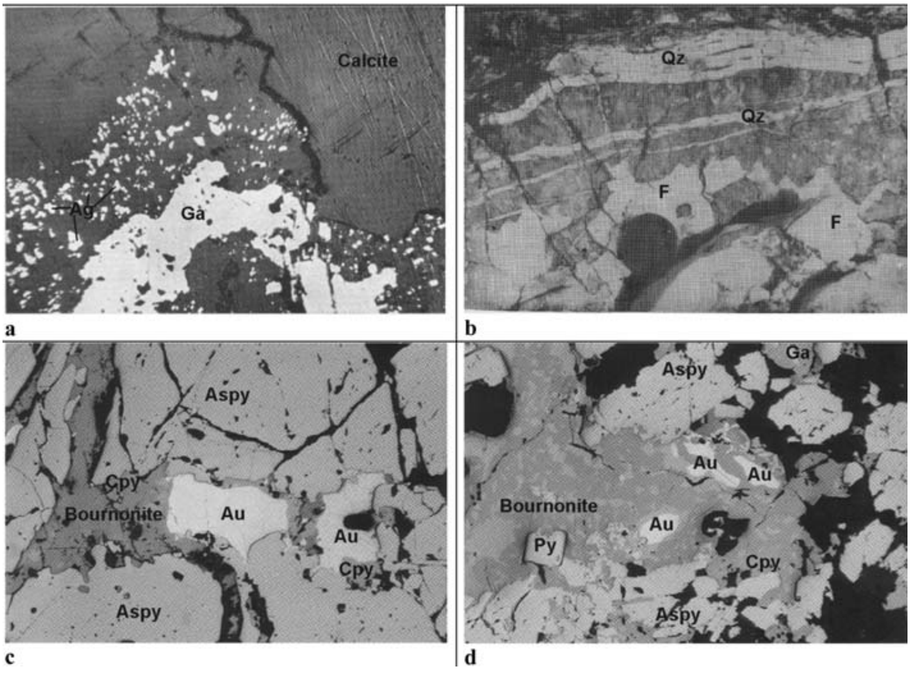

Fig. 4: a) Galena (white) and native silver disseminated in calcite (dark grey), Silver Lode of Tuviois, Sarrabus; b) Fluorite (grey), and quartz, outcrop of Serra S' Angassua, Serra S'Ilixi mine; c) Gold (yellow) accompanying chalcopyrite (brown) and bournonite (grey), galena (medium grey), myrmekitic intergrowth invading fractured arsenopyrite. Reflected light, 660 X (Baccu Locci ore deposit); d) Gold (yellow) in bournonite (grey), galena (medium grey) myrmekitic intergrowth, with chalcopyrite (brown) in fractured arsenopyrite with euhedral pyrite. Black: quartz. Reflected light, 660 X (Baccu Locci ore deposit).

These deposits in fact show a close connection to the Ordovician-Silurian horizon on a regional scale. Fluorine, another element which is likely to have been abundantly supplied by the volcanic activity, often occurs in all the areas from Barbagia to Sarrabus (Fig. 4); the F content in the Or-

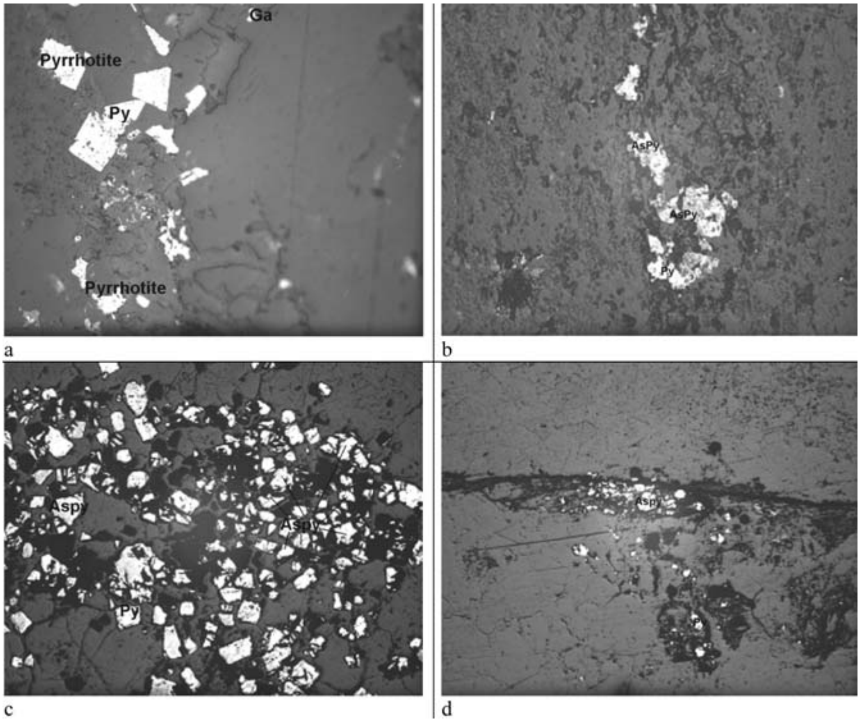

Fig. 5: a) Pyrite, pyrrhotite, and galena in quartz vein in silicified limestone, polished section, 10 X; b) Oxidized arsenopyrite and pyrite in metamorphosed limestone, polished section, 2.5 X; c) Oxidized arsenopyrite disseminated in quartz, polished section, 2.5 X; d) Fine dissemination of pyrite, arsenopyrite in quartz vein, polished section, 2.5 X, Rio Misturadroxiu outcrop.

dovician-Silurian rocks might have been utilized by Hercynian magmatism to give rise to the important veins of Silius (Pani et al., 1988). This mine, a large quartz vein with about 40% CaF_2 and 1.5 % PbS, is still operating and is believed to be one of the most valuable fluorite mines in Europe. The previous geochemical data reported in table 1 suggest the following considerations: lead distributions are very similar between the two groups of formations, but it shows high variability within the same group. Zn shows the highest values and the great differences of distribution between the two group of formations. Cu shows an intermediate behaviour.

However the highest geochemical anomalies are localized in the “skarnoid” horizon, which contains a sort of “spots” having high metal contents. The prevailing metal associations in economic ores, i.e. Fe-Zn-Cu and Pb-Zn, were also found at a geochemical level; when positive anomalies of Pb and/or Pb-Zn are present the Cu contents are rather low; on the contrary positive anomalies of Zn and/or Zn-Cu are always associated with very low Pb contents. The analytical results of the samples from the Asuni sector (Table 2) at least would display a negative correlation between Pb and Cu, in good agreement with the above previous data.

5. Conclusions

The occurrence of high-metal content “spots” detected in the area of Asuni could be interpreted as the result of preconcentration phenomena which began during deposition and diagenesis of Pre–

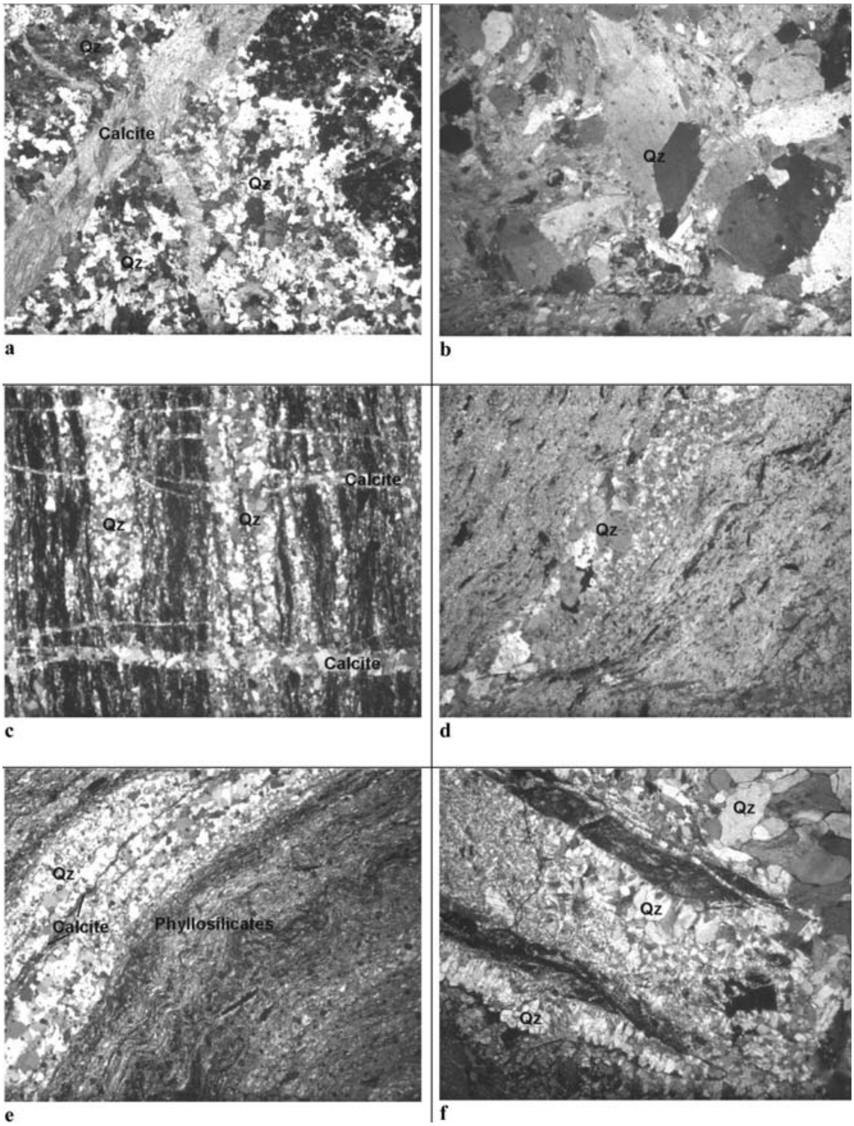

Fig. 6: a) Veinlets of calcite in silicified rock hosting opaque minerals (black), thin section, 2.5 X; b) Quartz veinlet developing idiomorphic crystals in limestone, thin section, 2.5 X; c) Calcite crossing quartz veins and carbonaceous matter, c; d) Quartz and phyllosilicates in limestone; opaque minerals are also visible, thin section, 2.5 X; e) Band of quartz and calcite in phyllosilicate rock that contains the mineralization, thin section, 2.5 X; f) Quartz veinlets, growing in euhedral crystals, alternating with carbonaceous matter bands, thin section, 2.5 X.

Permian, more or less deep sediments, and lasted up to the early Hercynian pulses. These mineralizations (Figs. 5, 6) would represent the Post-Cambrian to Lower Devonian stratabound protore occurrences that mostly formed after a primary volcano-sedimentary metal deposition in a structurally and geodynamically active paleomargin, and then subjected to enrichment phases by several reworking phenomena.

These protores would have been leached, remoulded and remobilised from the older to younger terrains during the Hercynian, by tectonic effects and/or magmatic or post-magmatic fluid circulation phases which contributed greatly to the formation of exploitable ore bodies. However now these deposits in detail exhibit prevalent vein-shaped and other epigenetic features, from pneumatolytic to epithermal, while on a regional scale they show a close connection to the metal-bearing Ordovician-Silurian stratigraphic level.

The "skarnoid" horizon always represents a geochemical anomaly for metals; less mobile elements, such as Pb, Au, Ag, and Bi, were further concentrated by Carboniferous-Permian hydrothermal fluids; on the contrary these fluids dispersed zinc, while barium and fluorine from the Ordovician-Silurian rocks were concentrated as veins of barite and fluorite. Numerous exploration and exploitation works for these industrial minerals are present in the area of Asuni (Bakos et al., 1972). Each mineralising stage seems to be, more or less, connected to the preceding ones. The mineral association of the ores prevailing in Sarcidano and Barbagia, mostly consisting of pyrite-chalcopyrite, sphalerite, and galena, also occur in the area under study even if small variations may occur.

Our recent detailed prospecting in the area of *Castello Medusa* has emphasised the presence of numerous high-metal "spots". These small ore outcrops probably witness the presence of copper-lead-zinc (-silver, -gold) exploitable mineralizations in the areas neighbouring the exhausted mines, and practically in the whole Central Sardinia, where the same stratigraphic and/or geodynamic environment occurs.

6. Acknowledgements

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7. References

Bakos, F., Valera, R., 1972. Il Campo Filoniano di Castel Medusa, (Asuni - Sardegna Centrale) 283-297.

Bakos, F., Carcangiu, G., Fadda, S., Mazzella, A., Valera, R., 1988. The Au-Ag-As-Fe-Cu-Pb-Zn-Sb-W paragenesis of Baccu Locci (SE Sardinia): an example of multistage evolution from a protore of volcano-sedimentary origin. Zuffar' Days – Symposium held in Cagliari, October,10-15, 1988, 9-13.

Carmignani, L., Marcello, A., Musumeci, G., Oggiano, G., Pertusati, P.C., Pretti, S., Salvadori, I., 1994. Paleozoic sequences, extensional tectonics and talc-chlorite deposits of Central Sardinia. Guide-book to the field excursion of the 16th General Meeting of the IMA, 61-72.

Garbarino, C., Grillo, M.S., Marini, C., Mazzella, A., Melis, F., Padalino, G., Tocco, S., Violo, M., Maccioni, L., Fiori, M., 1980. The Paleozoic Metallogenic Epochs of the Sardinian Microplate (Western Mediterranean): An Attempt of Synthesis on Geodynamic Evolution and Mineralizing Processes. *Rend. Soc. It. Min. Petr.*, 39: 193-228.

Marcello, A., Pretti, S., Salvatori, I., 1994. Introduction to the minerogenesis and the economic geology of Sardinia. Guide-book to the field excursion of the 16th General Meeting of the IMA, 37-43.

Pani, E., Valera, R., 1988. Fluorite in the Sardinian metallogenic history. Zuffar' Days – Symposium held in Cagliari, October,10-15, 1988, 71-85.

Pretti, S., Salvatori, I., Uras, I., Valera, R., Zuffardi, P., 1990. The metallogeny of Sardinia. Atti Acc. Lincei, serie IX, 1.