The antimony and tungsten deposit of villasalto in south-Eastern Sardinia and its relationship with hercynian tectonics

Autor(en): Carmignani, L. / Cortecci, G. / Dessau, G.

Objekttyp: Article

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen

= Bulletin suisse de minéralogie et pétrographie

Band (Jahr): 58 (1978)

Heft 1-2

PDF erstellt am: **15.05.2024**

Persistenter Link: https://doi.org/10.5169/seals-45197

Nutzungsbedingungen

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern. Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden.

Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

Haftungsausschluss

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

Ein Dienst der *ETH-Bibliothek* ETH Zürich, Rämistrasse 101, 8092 Zürich, Schweiz, www.library.ethz.ch

The Antimony and Tungsten Deposit of Villasalto in South-Eastern Sardinia and its Relationship with Hercynian Tectonics¹)

By L. $Carmignani*)^2$), G. $Cortecci**)^3$), G. $Dessau*)^4$), G. $Duchi*)^5$), G. $Oggiano*)^2$), P. $Pertusati*)^2$) and M. $Saitta***)^6$)

Abstract

The authors have investigated the stibnite and scheelite deposit of Villasalto by field and laboratory techniques (mapping and structural analysis; X-ray fluorescence and mineralogical analyses; isotopes; ore microscopy).

The Ordovician-Devonian series of the Gerrei region in southwestern Sardinia, affected by a Lower Greenschists metamorphism, contains the Graptolitic Black shales of Lower Silurian age. These shales are also locally the main constituent of the tectonic breccia which marks a Hercynian lineament known as the "Villasalto fault", an overthrust of regional importance. The sub-horizontal overthrust surface is conformable with the general schistosity (S₁); this schistosity is associated with isoclinal folds, refolded during the late phases of the Hercynian orogeny.

The local rocks harbour small and undisturbed fissure veins of stibnite. The Black shale *tectonic breccia* contains at Villasalto a more important deposit of stibnite with scheelite. Like all elements of the breccia, the almost pure stibnite is here concentrated in lenses of all sizes (30 m - 10 cm), stretched in E-W direction and flattened within the S_1 .

It is hardly convincing to consider the high-grade almost pure stibnite lenses as due to a diagenetic concentration of the traces of Sb, generally at most a few ppm, of the Black shale formation.

This deposit has been variously interpreted as sedimentary, extrusive-sedimentary or of magmatic-hydrothermal origin, and we incline towards the last alternative. But its tectonic shattering, remolding and transport within the tectonic breccia have obliterated any evidence about its origin.

¹⁾ Research carried out with grants from the Italian Council of Scientific Research, within the framework of the "Progetto finalizzato 'Geodinamica'" (Publication N. 140), and of the "Centro di Studio per la Geologia Strutturale e Dinamica dell'Appennino", Pisa. *) Istituto di Geologia e Paleontologia dell'Università, Via S. Maria 53, I-56100 Pisa, Italia. **) Laboratorio di Geologia Nucleare dell'Università, Via S. Maria 22, I-56100 Pisa, Italia. ***) Istituto di Mineralogia e Petrografia dell'Università, Via S. Maria 53, I-56100 Pisa, Italia. **) Mapping and Tectonics. 3) Isotopes. 4) Coordination, Ore Deposits, Bibliography. 5) Ore Microscopy. 6) X-ray Fluorescence and Mineralogical Analyses.

1. INTRODUCTION

Amongst the mineralizations of the Sarrabus-Gerrei area in south-eastern Sardinia the antimonite-scheelite type of deposit of the Villasalto mine has always been a subject of controversy.

Whereas the veins with galena, sphalerite, barite and fluorite are generally considered to be of hydrothermal origin and related to the Hercynian Sarrabus granites, the stibnite deposit has often been interpreted as being of sedimentary origin, on account of its conformable nature and of its association with black carbonaceous shales of Silurian age.

The present investigation was especially aimed at clarifying the relations between the ores and the complex Hercynian tectonics of the area.

2. THE STRATIGRAPHICAL SEQUENCE

The area of interest (Plate I) is shown near to the eastern margin of Sheet 226 – Mandas (Cavinato and Beneo, 1959, surveyed 1928–1957) of the Geological Map of Italy at the 1:100,000 scale. But on the more modern adjoining sheet 227 – Muravera (Calvino, 1963, surveyed 1956–1959) – the geological column is more detailed.

We can schematically divide the region into a northern and a southern part separated by a regional tectonic lineament, known in the literature as the "Villasalto fault" (Teichmüller, 1931). In the southern part only the "S. Vito sandstones" ("Arenarie di S. Vito" – Or on our geological map) crop out. They are of uncertain age, but on account of their geometrical position are referred to the Ordovician (Calvino, 1972; Cocozza et al., 1974). In the northern portion, the characteristic limestone cliffs of Upper Devonian age (D_c) grade upwards without visible break into Lower Carboniferous limestones; the age of

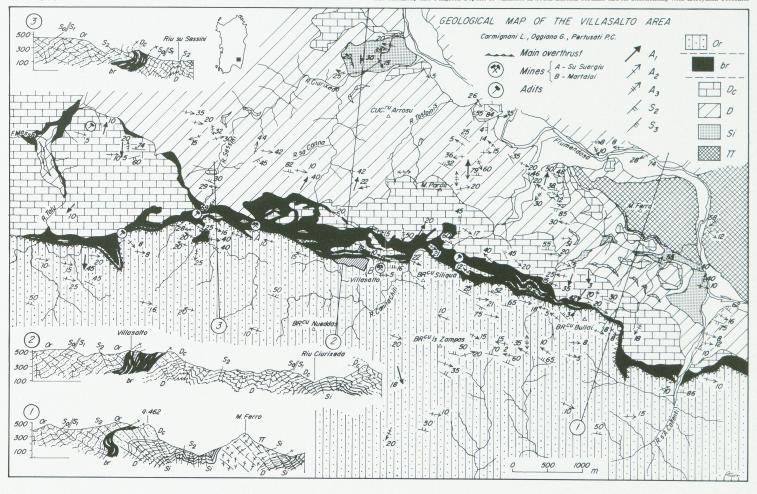
Legend of Plate I

Geological Map of the Villasalto area

Porphyroids and arkoses – Ordovician.
 Si "Black shales", Graptolitic carbonaceous shales, with intercalations of dark limestones, black quartzites (jaspers, "Lydites") and sandstones – Silurian.
 Marly shales, with limestone intercalations – Lower and Middle Devonian.
 Limestones – Upper Devonian-Lower Carboniferous. – This symbol denotes also the biggest limestone lenses included in the Lower and Middle Devonian Marly shales.
 Polygenic tectonic breccias, mainly of Silurian Black shales.
 "S. Vito sandstones" – Ordovician?
 A₁, A₂, A₃ Axes of First, Second, Third phase folds.

The structures shown on the sections are second phase folds, which have refolded the first phase schistosity.

Schistosities of Second, Third phase.



Leere Seite Blank page Page vide

both has been determined through Conodonts (OLIVIERI, 1969; Miss GABRIELLA BAGNOLI, unpublished). Below the limestone cliffs, alternating beds of Devonian shales and limestones (D) crop out; downwards this alternating sequence grades into the Silurian formation of the typical graptolitic Black shales (Si) associated with black quartzites (jaspers, "Lydites") and sometimes with thin layers of limestones.

At various levels in the lower part of this sequence porphyroids and arkoses (π) appear; the first were originally rhyolites, and the second are the product of their reworking.

Between the sandstone area to the south, and the limestone and shale area to the north, a belt of tectonic breccias of varying thickness, running in an E-W direction and generally dipping to the south, marks the Villasalto lineament. This belt contains the only important antimony ore deposit, that of the Su Suergiu-Martalai mine at Villasalto.

3. THE POLYPHASE TECTONICS

Throughout the area one can recognize three phases of folding of different style and orientation, but all belonging to the Hercynian orogenesis. The constant association of the same tectonic phases, as we have verified through the whole of the Gerrei region and along a W-E profile running from S. Basilio in the Campidano-*Graben* to the Tyrrhenian Sea near Muravera and S. Vito, suggests that the tectonic phases are of regional importance.

The first and most important has caused recumbent isoclinal folds, upsetting the original stratigraphic sequence. The Villasalto lineament belongs to this phase. The late phases refold the structures of the first, but with much weaker intensity.

The identification in the Gerrei of polyphase tectonics, like the one since long recognized and described for the Iglesias region, reopens the debate on the interpretation of the tectonic relationship between these two Hercynian domains, up to now considered to be structurally independent.

a) The first phase

The first phase has produced the most intense and penetrative deformations. It is characterized by the presence of a planar anisotropy, which produces in mainly clayey rocks a slaty cleavage parallel to the axial plane of the isoclinal folds.

The transposition of the stratification $(S_0)^7$) along these (S_1) surfaces is often

⁷) Henceforward we shall indicate the bedding surfaces with S_0 and the schistosity surfaces of the three tectonic phases with S_1 , S_2 and S_3 .

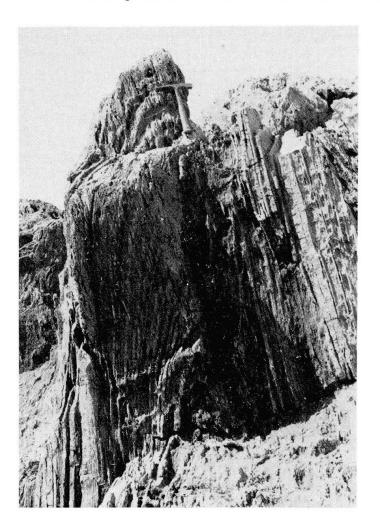


Fig. 1. Silurian shales along the east coast, 1 km S of Capo S. Lorenzo (Muravera). – First phase isoclinal fold, with the hinge torn along a shear surface parallel to the axial planes.

complete. As a consequence, in the outcrop the most evident surface is always the schistosity. Only where hinge areas are exposed, it is possible to distinguish between the two surfaces (Fig. 1).

The S_1 have different appearances depending upon the lithology. In the coarsest arenaceous layers and in the porphyroids the S_1 foliation is poorly developed. The deformation in these rocks often increases through flattening, along the S_1 , of the bigger grains, and their stretching in the direction of tectonic transport, more or less at right angles to the axes of the folds.

In some porphyroid outcrops (for example at Monte Ferro, see our geological map, Plate I) the above-mentioned deformations are clearly visible also at the megascopic scale, whereas in the finer-grained sandstones they appear only under the microscope.

In thin section one notes that the mechanical deformation is often accompanied by an intense recrystallization, above all in the pressure shadows induced by pretectonic rigid bodies, like grains of quartz and pyrite. Where the recrystallization is more advanced, it implies a regional metamorphism of upper greenschists facies.

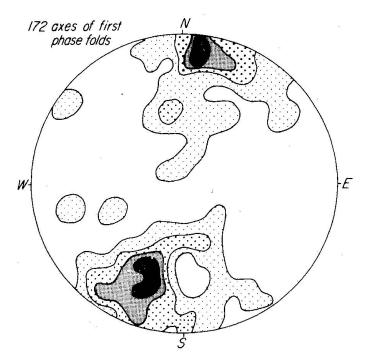


Fig. 2. Statistical diagram of the First phase axes and of the S₀/S₁ intersection lineations. 1%, 3%, 5%, 7% for 1% of the surface. The variability of the strikes between N 10° W and N 50° E is mainly due to the original dispersion of the First phase axes within their own axial planes. The great variability of the dips is due to the Second phase, striking on the average N 120°, which refolds the linear elements of the First phase.

Another characteristic of this first phase is the widespread boudinage of the limbs and the strong thickening of the hinges of the folds.

With the further evolution of the folds, the hinges are torn along shear surfaces parallel to the axial planes (Fig. 1). The tearing is often accompanied by a marked dispersion of the hinge lines within their axial planes. The orientation of the hinge lines is shown on Fig. 2. Shear folds with thickened hinges, synmetamorphic axial plane schistosity, hinge lines dispersed within their axial plane, are all characteristic of tectonics with a dominant tangential component, common to the most important tectonic phases of many Hercynian and Alpine mountain chains. Moreover the association of these structural elements is typical of folds originally having nearly horizontal axial planes (S₁). The present dips of the S₁ are due to subsequent phases.

b) The second phase

The second phase deforms the S_1 and the lineations of the first phase, producing box folds, kink bands, chevron folds, all associated with widespread crenulations (Fig. 3). The folds are often accompanied by conjugate axial plane schistosities, generally of the fracture pattern, but which locally, in the case of favourable lithological types, may evolve into very close schistosity surfaces of strain-slip character.

This phase is evident in the whole belt under consideration, between S. Basilio and the sea. In the area shown on the geological map it exhibits mainly strikes of N 120°, with conjugate axial planes having moderate dips to the NNE and SSW. This structural trend, to which are related the most conspicuous megastructures, has been the only one previously noted in the Gerrei.

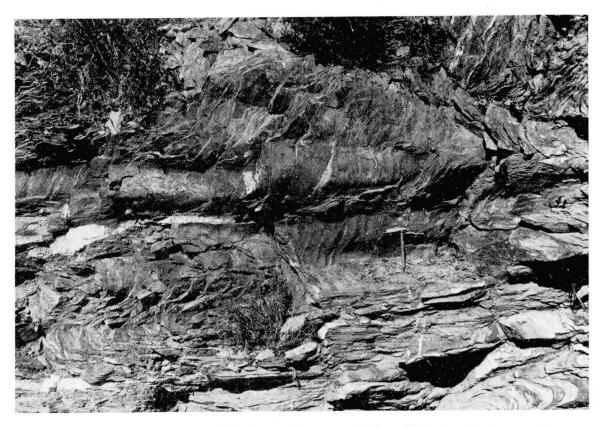


Fig. 3. Devonian limestones near M. Sarbanedda, on road from Villasalto to Arcu sa Panna. – Second phase folds refold a lineation corresponding to the First phase S_0/S_1 intersection.

c) The third phase

The second phase is followed by a deformation event of limited importance, which can be recognized only in some of the outcrops, and the regional distribution of which still awaits definition. This third phase shows crenulations and some open folds with sub-meridian strikes. It is locally accompanied by a fracture cleavage, the surfaces of which are generally rather widely spaced.

On the mesoscopic scale this phase generates fairly open folds and flexures, often associated with shear surfaces. Its structures interfere with those of the second phase, and are nearly orthogonal to them, with deformation of the S_1 into a succession of domes and basins.

Whereas there is no doubt that the first two phases pertain to the Hercynian orogeny, the weak deformations of the third phase may also be attributed to the alpine orogeny, which has affected Sardinia only marginally.

4. THE "VILLASALTO FAULT"

This dislocation was recognized as one of the most important Hercynian lineaments by Teichmüller (1931), who had described it over a long distance

around Villasalto. Later it has been traced from the Campidano-Graben to the Tyrrhenian Sea by Calvino (1959), whose geological map of an adjacent area (Sheet Muravera, 1963) and publications (1959, 1972) have been an useful background for our detail work.

The tectonic significance of this lineament has been interpreted in different ways. In the latest map (in Cocozza et al., 1974) it is shown as a normal fault, with the northern side, consisting of Silurian-Devonian formations, down-thrown with respect to the southern block of Ordovician sandstones. Only Pecorini (1971), on the map of a school atlas by other authors, printed in Cagliari and which hardly is being noticed by the scientific world, calls the "Villasalto fault" "a small overthrust".

This lineament strikes on the average E-W and dips generally to the south; on the whole it is structurally discordant with respect to the underlying Silurian-Devonian series, but on the outcrop scale it is sub-parallel with respect to the S₁ within the series. It is always associated with a thick belt of polygenic tectonic breccias, already described in detail by Calvino (1959).

The breccia contains components of all the rock types from above and below the tectonic contact. These rock fragments, from several metres to a few centimetres in size, and fragments of quartz, are of ellipsoidal shape and flattened within the schistosity surfaces (S₁), and elongated in E-W direction. As we shall see later, in the Villasalto stibnite deposit also the ore bodies are of similar shape and orientation.

In the area shown on our Plate I the matrix is mainly composed of Silurian carbonaceous shales (the "Black shales"), intensely laminated and cut by many shear planes, emphasized by carbonate veins. The ellipsoidal elements often show pressure shadows at both ends, generally containing fibrous quartz and calcite, with their fibres oriented in the direction of maximum elongation. The elements moreover form *boudins*; the *boudinage* lines are at right angles to the longest axes of the ellipsoids, and show the same stretching direction as do the fibrous growths.

We believe that also the large lenticular bodies of sandstones, limestones and porphyroids, wrapped in the breccia, with their sizes ranging from hundreds of metres to kilometres, have the same significance as the smaller elements, and must be interpreted as tectonic slices. Typical examples are the great lenses of sandstone within the tectonic breccia near Monte Atzeri, and of the S. Barbara porphyroid near Villasalto.

Even the shape of the outcrops of the Upper Devonian limestones, with their sudden bottlenecks or complete cut-outs (for example near Su Suergiu), may be interpreted as a gigantic boudinage in N-S direction, having the same kinematic meaning of that observed in the elements of the breccia. This is confirmed by the fact, that in certain cases they also are completely wrapped in the breccia.

We shall now try to fit this regional lineament within the framework of the polyphase deformation.

1. The matrix of the breccia is always crenulated. Its elements are often folded by Second phase fold axes and cut at a large angle by S₂. On the whole, the tectonic contact is bent following the late structural directions (N 120° and sometimes N-S) (Fig. 4 and geological sections on the Plate). Not far to the west of the Villasalto mine, always along the tectonic contact, at Rio Sèssini, an exploratory adit has been driven in a southern direction. It starts in the tectonic breccia and, after crossing several lenses of limestones and sandstones, has advanced for a great length again within the breccia, instead of shortly meeting the sandstones, as had been anticipated on the belief, that the tectonic contact is a simple fault of constant and almost vertical dip.

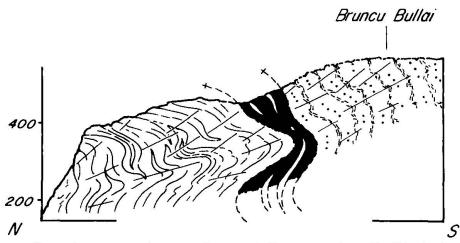


Fig. 4. Natural section near Bruncu Bullai drawn from Su Crispioni.

Instead the tectonic contact is folded by a Second phase fold and the contact changes its orientation from vertical on the surface to sub-horizontal in depth. Therefore the sandstones remain on top of the adit for a long distance (cf. Section 3 on the Plate).

- 2. At the outcrop scale the tectonic contact, the shear surfaces of the tectonic breccia, and the flattening planes of the elements of the breccia, are all subparallel to the S_1 both of the overlying as well as of the underlying rocks.
- 3. In some elements of the breccia we have observed a schistosity which according to its style must be related to S₁ and is unconformable with respect to the shear surfaces of the matrix; therefore this schistosity is older than the formation of the breccia itself. Summing up, the tectonic contact formed certainly prior to the late Hercynian folding phases.

The deformation style of the breccia, characterized by the strong flattening of its elements, and the parallelism between the tectonic contact and the S_1 ,

show that this contact belongs to the First phase. Moreover the presence in the breccia elements of an S₁ older than the brecciation, confirms that the tectonic contact is a late episode of the First phase. Besides, as already stated, one observes also on the macroscopic scale how the folds of the late First phase are torn by the shear surfaces parallel to the axial planes (Fig. 1). Therefore one may suppose that towards the end of the First phase there might have been a transition from a mainly ductile deformation to a more brittle deformation, with development of tectonic slices.

On account of the parallelism of the tectonic contact with S_1 , we believe that also the "Villasalto fault", like the S_1 , should have had initially a sub-horizontal attitude, as is befitting for a structural surface formed in a field of stresses with a strong tangential component, of which the deformations of the First phase are a typical expression.

The orientation of the tectonic contact, which changes from horizontal, for instance at Baccu de Cannas (near S. Vito), to vertical around the Villasalto mine, and is overturned near Bruncu Bullai, is the result of the subsequent folding, which has affected both the S_1 and the tectonic contact together with its breccia.

The structural investigation of the Gerrei has not been limited to the problems connected with the antimony deposits, but has been extended to a far broader area. On the strength of the collected evidence the "Villasalto fault" has to be interpreted as a regional overthrust (CARMIGNANI and PERTUSATI, 1977).

It is more difficult to reach definite conclusions as far as the amount of the translation is concerned. Over a broad area near S. Vito the Ordovician sandstones are clearly overthrust over the Silurian-Devonian series along a subhorizontal contact. In this area the amount of the overthrusting, measured in north-south direction, is of at least 3 km. But the direction of tectonic transport, as inferred from the minor structures, is about east-west, and the vergency of the first phase isoclinal folds (recognized only in the S. Vito sandstones near Muravera, where the polarity of the sediment can be observed) suggests a movement from east to west. With this orientation the amount of the overthrusting of the Ordovician sandstones over the Silurian-Devonian series could be even greater than 35 km – the distance between the Campidano-Graben and the Tyrrhenian sea.

5. RELATIONSHIP BETWEEN HERCYNIAN TECTONICS AND ORE DEPOSITS

The antimony mine known as "Villasalto mine" from the name of the nearest centre, comprises the excavations of Su Suergiu, by far the more important ones and seat of the smelter, and of Martalai.

Both at Su Suergiu and at Martalai lenses of stibnite with scheelite have been mined.

According to published information, mine records, and data supplied by the staff of the mine, as well as to the limited observations still possible underground, all the ore bodies have the shape of lenses of various sizes, flattened more or less parallel to the tectonic contact and elongated in E-W direction. Recrystallized fibrous quartz and calcite appear in the pressure shadows at the ends of the lenses. These, like the matrix and the other clasts, are folded by the late tectonic phases.

The deformations are evident also under the microscope, as beautifully shown on Figs. 5 and 6. The first exhibits stibnite with undulatory extinction, bent in a rather open fold. On the left side of the picture one notices a multiple twin gliding of the ore, parallel to the axial plane of the fold. The composite picture of the second figure shows, in their relationship with the ore ellipsoid from which they have been cut, two polished sections; the one parallel to the elonga-

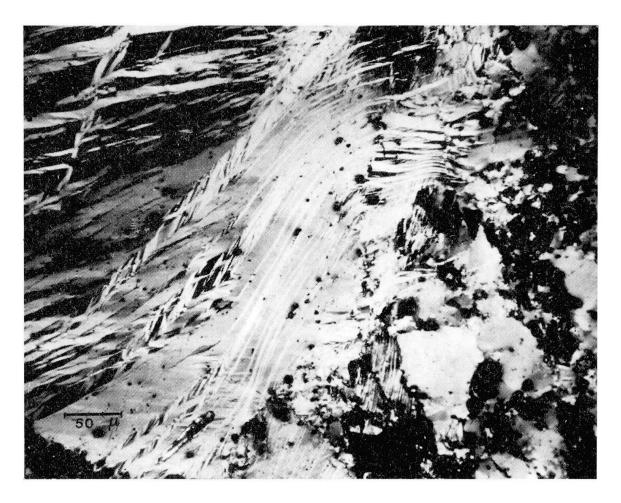


Fig. 5. Stibnite from Su Suergiu mine, deformed according to the open folds of the late tectonic phases. It shows undulatory extinction and twin-gliding parallel to the axial plane of the fold. Polished section, +N.

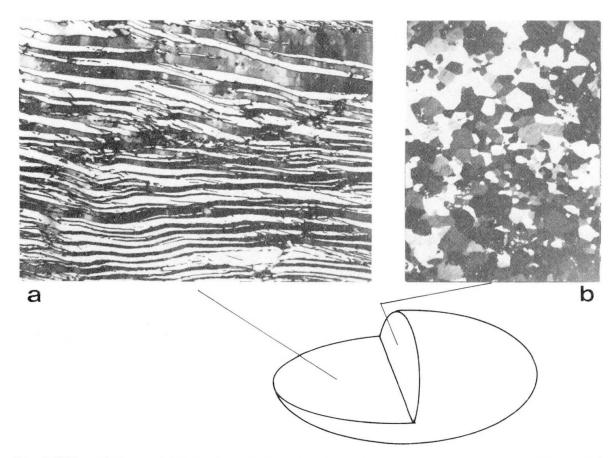


Fig. 6. Ellipsoidal lens of stibnite from Su Suergiu mine. – Photo A: polished section (+N) parallel to the greatest and intermediate axes of the ellipsoid. – Photo B: polished section (+N) parallel to the intermediate and least axes of the ellipsoid. – The stibnite crystals are oriented according to the maximum elongation of the ellipsoid. – Magnification about $100 \times$.

tion of the ore lens exhibits the long stibnite needles oriented according to this elongation; whereas the orthogonal section shows an equigranular texture.

On the strength of field and microscopic evidence alone we can only state that this mineralization, whatever its origin, has undergone a complex tectonic evolution through the greater part of the Hercynian orogeny. It was already in existence before the end of the first tectonic phase, as it has been brecciated at the base of the Villasalto overthrust, and later on repeatedly folded by the late tectonic phases. The ore lenses are flattened according to the lamination surfaces of the breccia, and *not*, as it has often been maintained, conformable with the bedding. Therefore any *direct* evidence of a sedimentary origin of this mineralization is lacking.

6. THE ORE DEPOSITS

The two centres of Sb production in Italy are Tuscany (Dessau, Duchi and Stea, 1972; Dessau, 1974; Dessau, 1976), and the Gerrei area in Sardinia, the latter presently under re-exploration. In this area there were two mining cen-

tres: Su Suergiu and Martalai, near the little town of Villasalto, exploiting the same deposit; and the small mine of Corti Rosas near Ballao, about 8 km north of Villasalto.

The main deposit consists of the tectonic breccia described in the previous pages. It contains lenticular pieces and bodies of stibnite in a matrix of Silurian Black shales, with scattered grains and small layers of pyrite. There are also thin layers and veins of scheelite associated with calcite. No other ore is present. Occasionally big rounded nodules of pyrite are found, with a completely pyritized *Orthoceras*-shell in the centre (Lincio, 1917, 1918; Angermeier, 1964).

The situation in the Corti Rosas mine and in other scattered minor excavations and outcrops, like Brecca-Perda Petunta to the SE of the narrow loop of the Flumendosa river 4 km to the north of S. Vito, and Conca Arroddu near Orroli, is different⁸). Everywhere thin, discontinuous veins of pure stibnite, at times with some tungsten ores, occur in cracks which are younger than the Hercynian compressive tectonics, in the Silurian arkosic sandstones and in the porphyroids below the regularly stratified Black shales. The undeformed stibnite constitutes sometimes stars of radiating flattened crystals, and is accompanied by some quartz. In accordance with Angermeier (1964) and Maucher (1965, 1976) we consider this type of mineralization as "remobilized" through locally derived solutions.

The ore is always associated, directly or indirectly, with Black shales. At Villasalto these are found at two levels: The geometrically lower one occurs in its normal stratigraphic position below the light-coloured calcareous shales with Lower Devonian *Tentaculites* and is devoid of any ore. The ore is instead associated with the Black shales at a geometrically higher level, where they form the matrix and the main component of the tectonic breccia. To the best of our knowledge this is the only Sardinian antimony deposit in such a position. The breccia, which extends over the whole length of the overthrust with variable thickness, at Villasalto reaches an exceptional thickness, well over one hundred metres, and is ore-bearing over a stretch of almost 2 km.

The conditions of the mine, and the scarce interest shown for the scheelite, have almost prevented us from obtaining direct or indirect information about this ore. We know it only from a few abandoned small dumps. It is reported that within the stibnite-bearing breccia it was *not* strictly associated with the sulphide, but rather with thin veins and lenses of white calcite.

a) Evolution of the ideas concerning the origin of the ores

The origin of the ore deposit of Villasalto, known for about one century, has always been controversial. A few quotations from the old literature may be

⁸) A detailed list of outcrops and prospects in the Gerrei area is given by Taricco (1911).

interesting, specially as far as the "sedimentarist", or even extrusive sedimentary views, prevailing during the past century, are concerned.

L. MAZZETTI (1884) and C. DE CASTRO (1890) claimed that the deposit was a true fissure vein along a tectonic lineament. Also G. B. Traverso (1897) was aware of the tectonic lineament, but still considered the ore as sedimentary. A. Ferrari (1897) called it "a contact vein along the unconformable contact ... between Devonian and Silurian", and advised the exploration of the whole length of the latter; according to him there is no relationship between magmatic rocks and the antimony ores. In the ensuing discussion Cattaneo too propounded the sedimentary origin of the deposit. P. Toso (1897) maintained that the contact between the Black shales and the limestones is tectonic, a break or a long fault, and has not been instrumental in the emplacement of the ore; he already inferred, and in a later paper stressed, the syngenetic, extrusive-sedimentary origin of the latter. For U. Cappa (1897, condensed quotation) "waters or vapours, charged with antimony sulphides, entered through fractures the basins in which the shales were deposited". Taricco (1911), while accepting a magmatic origin, posed the question, in consideration of the chaotic nature of the deposit, whether the mineralization be contemporary or later than the dislocation, and opted, although hesitatingly, for the first alternative.

During the 20th century, according to the general trend, magmatic-hydrothermal interpretations prevailed.

A new chapter was opened by the Munich school, with A. MAUCHER and by his pupil H.-O. ANGERMEIER, who had been counsellor to the mine management.

MAUCHER (1965) considers the deposit "extrusive-(exhalative-)sedimentary", syngenetically deposited together with the Black shales, and related to the Silurian volcanism. He mentions the remobilized veins, we have already briefly described. The subject is taken up again, on the same lines, by MAUCHER's paper of 1976.

Both Angermeier (1964), and later Maucher (1976), draw a stratigraphical column of the Villasalto area, showing and describing two regularly interstratified concordant levels of Black shales (or "Graphite schists", as they call them), the lower one at a certain distance above "Lower porphyroids", the upper one just above, or at the same height, as the "Upper porphyroids". The "Upper Graphite schists" are the ore-bearing ones, the "Lower Graphite schists" are barren. Quoting literally, Angermeier states that "contrary to the opinion current in the Gerrei, that the Graphite schists are in every case potentially ore-bearing [for Sb and W], he [Angermeier] has not found in the Lower Graphite schists any indication of a Sb-W mineralization worth mentioning, and in no case for such a primary mineralization." In this we fully agree with him. Angermeier also describes in detail the intense tectonic stresses which have "folded, fractured and sheared" the antimony ore of the "Upper graphite schists", and the undulatory extinction it sometimes exhibits. Still, he states

that most of the ore is present in conformable, sometimes very rich and highgrade lenses, as well as in alternations of thin layers with shales partly with still recognizable sedimentary structures.

Although conceding that he has had more opportunities than ourselves for direct observations, we cannot agree. Both quoted authors have failed to draw the extreme consequences from the tectonized condition, they had well observed, of the ore. The ore lenses belong to a tectonic breccia – their so-called "Upper Graphite schist"-layer – and are conformable with the First phase schistosity.

In their review of the several types of tungsten deposits of Sardinia, Valera and Zuffardi (1970) refer, with some prudence, to connections with magmatic or extrusive-sedimentary events.

Still another chapter in the study of the geology of south-eastern Sardinia started with the investigations by H.-J. Schneider (1972) and of his co-workers (Helmcke, 1973; Helmcke and Koch, 1974; Lehmann, 1975; Biste, 1977).

The paper by Schneider (1972) emphasizes the similarities between the Villasalto ore body and the once so important deposits of the Sarrabus silverbelt to the south; he stresses that they are all within the Black shales, for which he suggests the name of "Monte Narba-formation". By the way, also the 19th century silver miners called the Black shales "the shales of the ore" (S. Traverso, 1890). According to Schneider the stratiform shape of the deposits would be proof of their sedimentary or extrusive-sedimentary origin. We doubt whether he is aware of the actual tectonic emplacement of the Villasalto ore.

Schneider rejects a connection of these deposits with the post-tectonic Hercynian granites. But his sweeping statement that "the greater quantity of metals, fluorite and barite of the Sardinian ore provinces comes from an old paleozoic metallogen, and not from the later Hercynian granites... the Hercynian granite intrusions are sterile", needs qualification. We do not need to quote extensively the enormous deposits of Zn and Pb (and minor ones of other metals) around and in the Arbus granite in southwestern Sardinia. Also in our area there are deposits connected with the Hercynian magmatism, for instance at Perda Majori near Villaputzu, a small pegmatitic-pneumatolitic vein crossing from a granite boss into the surrounding slates, and carrying topaz, wolframite and scheelite, molybdenite, traces of cassiterite and of bismuth, various sulphides and fluorite (Dessau, 1956; cf. also Biste, 1977). Should one even admit (as Jensen and Dessau did, 1966) that the granite magmas might have assimilated preexisting Lower-Paleozoic metallogens, this would not change the actual picture.

An exhalative-sedimentary origin of the Black shale deposits implies con-

⁹⁾ Paper noticed only at the time of proof-reading.

temporary magmatic activity; but the chronological relationships do not provide a definite answer. Helmcke (1973), on the strength of his Graptolite studies, places the Black shale horizons of the Gerrei in the Silurian and Lower Devonian, but mainly in the Upper Silurian.

As far as the magmatism is concerned, it is well known that in the Sardinian Lower Paleozoic, and specially in the Gerrei, there are intercalations of great masses of porphyroids, which are generally believed to be of an Ordovician age. This is also confirmed by Helmcke and Koch (1974) who, after having shown on paleontological evidence that the porphyroids are older than the "Monte Narba-formation", admit the possibility that there might also be younger ones.

Finally Lehmann (1975) reports on a quartz-keratophyric-spilitic volcanism, to which would belong also the "lydites", described as volcanic tuffs. This volcanism would mark the onset of the Hercynian magmatism – a statement which does not seem to agree with the Upper Ordovician age he assigns to it. With the same volcanism he connects the metallogenesis. His few data about the Sb-content of the quoted rocks are of dubious interpretation.

Antonietta Pomesano Cherchi (1960) places all porphyroids in the Silurian, and mentions "typical tuffites intercalated and interpenetrated with the Graphite schists". She considers the antimony deposits related to the Silurian volcanism.

All the quoted research, which is the outcome of necessarily limited efforts of single investigators, is outdated by the team-work of DI SIMPLICIO et al. (1974) on the Paleozoic magmatic and metamorphic rocks mainly of Northern Sardinia. To the times from the Upper Ordovician to the Lower Silurian, and therefore to the end of the Caledonian cycle, belongs the acid magmatism represented by diorites with a consolidation age of 442 ± 30 m. y., and by coeval and more abundant rhyolites and rhyodacites. Their metamorphic equivalents—in keeping with the circumstance that all rocks prior to the late Hercynian were subjected to a regional Hercynian metamorphism—are dioritic orthogneisses and porphyroids, the latter also widespread in our area. Meta-arkoses are the outcome of the sedimentary reworking of the acid extrusives.

A far more limited and distinctly later Silurian magmatism followed, producing basalts with spilitic affinities. It may mark the beginning of the Hercynian cycle.

Successive to the Hercynian metamorphism and post-kinematic is the Sardinian batholite, with monzonites, granodiorites and other related rocks, and characterized by an evolution from a more basic to a more acid composition during a period ranging from 300 to 280 m.y. To it belongs also the quoted Arbus pluton.

Excluding as ore-carriers the acid late tectonic magmatism for chronological reasons, the early Hercynian basalts on account of their limited size and chemical and petrological character, and the late Hercynian plutons again for chro-

nological reasons, the connections between Black shales, "Lydites", ores and magmatism are still in need of clarification.

b) The geochemistry of the Black shales

As already stated, it does not seem to have been fully understood that the Villasalto deposit is localized within the tectonic breccia of an overthrust of regional importance. Thus it is doubtful whether there exists a direct relationship between the shale matrix and the ore.

To obtain more information related to this question we have examined samples of Black shales both from their normal stratigraphical sequence as well as from tectonically disturbed outcrops.

The samples were collected from different localities of southeastern as well as of southwestern Sardinia, on both sides of the Campidano *Graben*. In the normal stratigraphic series, above the main Middle Silurian Black shale horizon, thinner Black shale levels reappear several times. It cannot be totally excluded that some of our samples might come from the higher horizons, although it can be surmised that they belong all to the lowest and thickest one. Their general chemical similarity is confirming evidence.

According to the microscopic examination of a few Black shale samples – partly the same analyzed (see later) and partly from other outcrops – the rock is a fine-grained quartzite with much elemental carbon, and with or without carbonate. S₁ is marked by sericite. But a less cursory study of the thin sections did not yield results of general significance. The rock is by no means homogeneous.

The mineralogical composition was determined approximately by X-ray diffractometry, on the same finely ground, averaged samples submitted to X-ray fluorescence analysis. The results are reported on Table I, which lists the localities where the samples come from. The listing proceeds from samples from tectonic breccias to those in their normal stratigraphic position.

Sample 13 does *not* belong to the Silurian Black shales, but to a more northern Upper Permian anthracite-bearing formation (LAURO, 1970).

Attempts to determine the elemental carbon, not amenable to X-ray analysis, by calorimetry proved unsatisfactory. The same holds for the estimate of C and carbonates from the loss upon ignition of the dried samples, analysis of the CO₂ in the escaping gas, and the dubious assumption that all Ca and Mg (determined by X-ray fluorescence) are present only as carbonates. Therefore we do not quote the results. The widely fluctuating content in elemental carbon may be of the order of 8 percent.

The samples were quantitatively analyzed by X-ray fluorescence, both for major and for trace elements (Tables II and III), and corrections for matrix effects were made according to Franzini, Leoni and Saitta (1975) for major

Table I. List of examined samples, with localities and mineralogical composition (besides carbon)

- 2/Martalai-12 Tectonic breccia rich in Black shales, Villasalto overthrust, very near to Martalai mine, but at a higher level than the excavations. Main components quartz and muscovite about in the same proportion, calcite in somewhat smaller quantity, most probably antigorite, and chlorite as a minor component.
- 1/Cor. Mitz-4 Tectonic breccia rich in Black shales, Villasalto overthrust, near to the Su Suergiu mine, just west of the summit of the Corona Mitziu hill. Main components, in about the same proportion, quartz and muscovite, and some calcite.
- 3/P. Corall-11 Tectonic breccia rich in Black shales, eastern sea coast, sometimes beaten by waves, north of Porto Corallo, near to Nuraghe Su Franzesu. The breccia, between arkoses and Devonian marly shales, probably marks the eastern extension of the Villasalto overthrust, or a subsidiary fault of the same. Mainly muscovite and less quartz; chlorite as minor component.
- 4/SNC. Ball-13 Black shales along a tectonic contact within the Silurian-Devonian sequence, along the road between S. Nicolò Gerrei and Ballao. Main components quartz and muscovite about in the same proportion; chlorite as minor component.
- 9/Flumini-6 Black shales, seemingly not much disturbed, immediately north of the village of Fluminimaggiore. Quartz and muscovite about in the same proportion; chlorite as minor component.
- 5/Armungia-2 Black shales with Graptolites, about 8 km north of Armungia. Main components quartz and less muscovite; chlorite as minor component.
- 6/Goni-7

 Black shales with Graptolites, from the classical locality just above Goni village.

 Main components quartz and muscovite; chlorite as minor component.
- 7/M. Ferro-10 Black shales with "Lydites", clearly at the base of the Devonian sequence (and therefore higher up in the series), from Acqua Caliente in the bed of the Flumendosa river, east of Monte Ferro. Main components quartz and less muscovite; chlorite as minor component.
- 10/Siliqua-3

 Black shales, weathered, from dump next to old shallow water well near Case Sais, south-west of Siliqua. Quartz and muscovite about in the same proportion, chlorite and antigorite as minor components.
- 11/Siliqua-5

 Black shales, other sample from the same dump as previous sample. Quartz and muscovite in the same proportion; chlorite and very probably hypersthene as minor components, the second less than the first.
- 12/Siliqua-1 Dark rock (Black shale?) collected between Case Sais and Case Ferrali southwest of Siliqua. The sample is compact and low in elemental carbon. Mainly quartz, muscovite as minor component, chlorite in traces.
- 8/C. S. Lor-8

 Black shales, from Porto Tramazu on the eastern sea coast, south of Capo S. Lorenzo, 1 m above sea level and beaten by waves. Main component quartz, a limited amount of muscovite and traces of chlorite.
- 13/Ierzu-9 Carbonaceous rock from near Ierzu, belonging to a thin bed inserted between Permian conglomerates and Triassic dolomitic limestones. Small deposits of Permian anthracite have been exploited in the area. Quartz and muscovite about in the same proportion; chlorite as minor component.

N.B. – The listing of the samples proceeds from those surely from tectonic breccias to those definitely in their normal stratigraphic position. Sample 13/Ierzu-9, not of Black shale, belongs to an Upper Permian carbonaceous rock.

Table II. X-ray fluorescence analyses, in percent, of major elements in Black shales

	L.O.I.	Na_2O	MgO	Al_2O_3	SiO_2	$\rm P_2O_{\delta}$	K_2O	CaO	${ m TiO_2}$	M_{n0}	${\rm Fe_2O_3}$	FeO
2/Martalai-12	14.77	0.16	2.67	15.26	40.99	06.0	2.46	14.03	99.0	0.09	8.00	0.00
1/Cor. Mitz-4	21.50	0.09	1.78	14.84	39.02	0.74	2.78	11.29	0.54	80.0	7.31	0.00
3/P. Corall-11	11.43	2.62	2.08	19.73	44.71	0.35	3.86	1.02	0.74	0.00	13.38	0.00
4/SNC. Ball-13	9.95	0.48	1.05	19.83	61.65	0.03	4.96	0.07	0.98	0.00	0.99	0.00
9/Flumini-6	11.40	0.78	3.83	21.91	49.12	0.30	3.88	1.37	0.85	0.04	6.52	0.00
5/Armungia-2	13.70	0.08	0.71	11.25	70.32	0.02	2.33	0.01	0.42	0.01	1.15	0.00
6/Goni.7	10.60	80.0	0.87	10.37	74.87	0.01	2.10	0.04	0.41	0.01	0.64	0.00
7/M. Ferro-10	8.78	0.12	96.0	15.45	66.47	0.43	3.35	0.17	0.48	0.02	3.78	0.00
10/Siliqua-3	13.30	0.53	1.27	20.53	49.59	0.23	3.36	3.86	0.76	90.0	6.49	0.00
11/Siliqua-5	10.80	0.79	1.43	25.08	47.38	0.21	3.94	0.98	1.03	0.04	8.31	0.00
12/Siliqua-1	4.70	0.46	0.41	10.16	79.00	0.09	1.59	0.04	0.39	0.01	3.16	0.00
8/C. S. Lor-8	10.31	1.96	1.49	13.83	69.79	0.61	2.39	4.87	0.59	0.73	5.54	0.00
13/Ierzu-9	20.66	0.16	0.84	12.39	60.40	0.02	2.60	0.35	0.74	0.01	1.84	0.00

Sample 13/Ierzu-9, not of Black shale, belongs to an Upper Permian carbonaceous rock.

Ni \mathbf{Cr} \mathbf{v} Co Pb Ba Ce As836.9 158.9 21.6 274.3 30.3 442.8 2/Martalai-12 160.6 66.7 1/Cor. Mitz-4 131.5 140.6 699.2 19.6 74.0 44.9 608.1 78.6 51.2 3/P. Corall-11 131.5 320.9 11.9 77.7 75.5 3599.5 57.6 4/SNC. Ball-13 638.6 42.3 724.6 102.5 21.4 152.13.6 9.4 9/Flumini-6 141.4 211.2 1509.4 11.2 25.6 27.3 670.5 85.2 5/Armungia-2 15.1 65.1 249.6 3.7 7.0 67.15499.7 90.3 6/Goni-7 27.1 328.2 2.6 37.6 43.4 67.6 3.2 4453.8 7/M. Ferro-10 1388.9 53.8 105.8 153.4 19.1 33.1 5251.0 63.4 10/Siliqua-3 77.8 122.0 367.8 18.7 17.3 26.4 895.2 88.7 11/Siliqua-5 139.2 9.2 1214.0 129.4 44.6 203.9 15.0 4.6 12/Siliqua-1 26.0 54.3 259.4 7.5 36.2 60.4 596.3 46.1 25.260.98/C. S. Lor-8 110.7 74.6 374.4 14.4 53.0 1834.5 13/Ierzu-9 32.1 43.9 79.5 26.2 46.0 302.2 197.8 56.4 RbMo $\mathbf{Z}\mathbf{n}$ Sb Nd \mathbf{Zr} SrCu 105.8 314.7 101.4 30.1 299.7 109.8 1744.5 2/Martalai-12 41.1 1/Cor. Mitz-4 43.0 90.9 192.6115.1 17.6 220.693.4 72.83/P. Corall-11 22.3 91.2 174.8 155.I 10.2 109.8 68.2 17.0 4/SNC. Ball-13 48.2 179.4 229.5 20.9 19.7 4.6 10.3 7.9 27.7 93.5363.0 9/Flumini-6 44.8 138.958.2172.15.436.8 42.6 103.4 13.3 9.8 14.7 7.0 5/Armungia-2 71.4 6/Goni-7 15.5 72.9 16.7 86.8 14.4 8.0 36.7 4.5 7/M. Ferro-10 125.9 54.9 25.0 92.0 38.3 137.0 52.9 15.8 10/Siliqua-3 41.6 118.0 166.3 137.9 8.7 156.9 45.7 1.0 11/Siliqua-5 53.3170.7 187.4 162.0 0.0 113.1 25.3 1.2 12/Siliqua-1 69.0 24.0 49.4 47.3 1.3 21.1 72.1 74.4

Table III. X-ray fluorescence analyses, in ppm, of trace elements in Black shales

elements, and to Franzini, Leoni and Saitta (1972) and Leoni and Saitta (1976) respectively for trace elements. The detection limit should be better than 1–2 ppm. In Table II are shown also the losses upon ignition. All iron was calculated as Fe_2O_3 .

115.4

73.7

331.6

23.6

105.7

1546.6

100.1

5.0

0.3

1.8

5.3

6.7

8/C. S. Lor-8

13/Ierzu-9

31.4

28.0

81.9

341.4

As far as the trace elements are concerned, their fairly uniform distribution is rather striking. There is no correlation between the trace element concentrations and the calcium content of the rocks recognizable, nor differences between the normal Black shales and those from the tectonic breccia. Disregarding the surely contaminated samples from the mine, the average Sb content is 6.1 ppm, or 5.4 when excluding two further samples from tectonic breccias.

Further geochemical data are available through the thousands of samples gathered from sediments of rivers and creeks ("stream samples") for the purpose of geochemical prospecting, with a frequency of about 3 per sq. km, by the "Ente Minerario Sardo", and analyzed in Orléans by the B.R.G.M. for Pb, Zn, Cu, Ag, Sb, Ni, Co, Cr, Mo, Mn and F (Salvadori, 1973; Pretti and Heetveld, 1974; Marcello, Pretti and Salvadori, 1977). A few examples are reproduced on Table IV. The limit of detection for antimony is reported to have been 20 ppm. It appears that Sb anomalies found in the Gerrei belong all to widely scattered places where prospecting or excavation for Sb had been carried out.

Table IV. Specimen of geochemical prospecting by the Ente Minerario Sardo, Cagliari
"Strategical prospecting" "Stream samples" (By permission)

Sample	Pb	$\mathbf{Z}\mathbf{n}$	Cu	$\mathbf{A}\mathbf{g}$	Sb	Ni	\mathbf{Co}	\mathbf{Cr}	Mo	$\mathbf{M}\mathbf{n}$	\mathbf{F}
883	62	411	203	1.25	65	142	35	157	36	2580	1095
6437	26	81.	29	0.25	105	42	24	56	24	1260	555
6464	40	185	88	0.75	350	81	27	125	16	1015	1195
6465	150	548	450	1.75	17,000	181	34	228	38	1020	2350
6472	48	262	124	0.75	5,300	105	28	167	18	1010	1800
6474	108	323	147	0.50	2,750	95	29	144	20	1515	1135
6651	48	102	26	0.75	100	26	16	107	8	920	700
6652	70	168	35	0.25	55	28	18	13	4	910	635
6655	1840	437	71	6.50	260	35	22	88	10	1255	4250
7304	30	182	86	0.25	1600	91	27	146	10	1245	1140
7308	46	153	58	0.25	750	59	24	119	10	1095	825
7309	36	107	28	0.25	85	39	22	98	6	705	770
7318	38	204	89	0.25	1165	82	21	129	14	1015	1260
7319	46	172	67	0.25	250	71	29	121	14	1400	995
7324	42	99	26	0.01	115	34	29	112	4	1080	550

Values in ppm. The following statements about location and geology are roughly approximate. Samples with anomalous Sb values.

Sample 883 - 1:25,000 Map sheet Ballao - Near Ballao village.

Sample 6437 - 1:25,000 Map sheet Ballao - Fosso Massa. Tectonic breccia of overthrust.

Samples 6464 and 6465 - Boundary between Map sheets Villasalto and Ballao. Riu Sèssini near Villasalto, mine smelter slags in the creek.

Sample 6472 - 1:25,000 Map sheet Villasalto. Tectonic breccia of overthrust, near Villasalto

Sample 6474 - 1:25,000 Map sheet Ballao. Accu Foreddas creek, near Margàida, downstream from a prospect of the Villasalto area.

Samples 6651 and 6652 - 1:25,000 Map sheet S. Vito. Riu Piras, to the west of Brecca.

Sample 6655 - 1:25,000 Map sheet S. Vito. Breeca Pb and Sb vein in porphyroids.

Sample 7304 - 1:25,000 Map sheet Ballao. Near to Corti Rosas mine.

Samples 7308 and 7309 - 1:25,000 Map sheet Ballao. Cuile Sermenta, Corti Rosas area.

Sample 7318 - 1:25,000 Map sheet Ballao. Dumps of Corti Rosas mine.

Sample 7319 - 1:25,000 Map sheet Ballao. Near Metzeu prospect.

Sample 7324 - 1:25,000 Map sheet Ballao. Near Metzeu prospect.

c) The microscopic examination of the ores

We have already mentioned the examination of the ores in polished section. Besides stibnite, small grains of pyrite not associated with stibnite and scattered in the Black shale, and scheelite, no other ore minerals were observed.

Figs. 5 and 6 show stibnites with typical deformations and undulatory extinctions due to tectonic stresses.

d) The isotopic analyses

Another approach to the origin of the deposit has been sought through isotopic analyses of the sulphur of the sulphides and of the carbon and the oxygen of the calcium carbonates.

The isotopic compositions (Table V) are given in the δ notation in per mil, i.e. $\delta = [R_{sample}/R_{standard} - 1] \times 10^3$, where R represents the $^{34}S/^{32}S$ or $^{13}C/^{12}C$

+0.94

+1.52

+13.88

+19.36

	Stibnite	Pyrite	Cal	lcite	Devonic limestone
Sample	$\delta^{34}S$	$\delta^{34}S$	$\delta^{13}\mathrm{C}$	$\delta^{18}O$	$\delta^{13}C$ $\delta^{18}O$
1	-0.13				
2	+1.91		-6.54	+13.71	
3	+2.09		-6.79	+16.76	
	+3.43				
4 5 6	-3.62		-5.84	+15.36	
6	-2.22		-5.52	+15.83	
7	+2.16				
8	+1.60				
9	-3.56		-5.76	+15.96	
10	+3.17				
11	+1.14		-7.12	+20.00	
12		+14.48			
13		+19.42	R		6
14	2	+25.55			
15		-1.62			

Table V. Isotopic composition of ore, calcite and limestone samples

Samples 1, 2, 3, 4 Stibnites, partly associated with calcite, Villasalto mine.

Samples 5, 6, 7, 8 Stibnites, partly associated with calcite, from the Bottom level, Villasalto mine; 5, from stibnite lens, with coarse calcite in the pressure shadows; 6, stibnite, probably remobilized, with calcite; 7 and 8, stibnite, fine-grained, from ore lenses.

Sample 9 Stibnite, remobilized, Metzeu, Ballao area.

16

17

Sample 10 Stibnite, remobilized, from veins in sandstone near Black shales, dumps of Ballao mine.

Sample 11 Stibnite with calcite, from fissure veins in Devonian limestone, Malimenta prospect near Armungia.

Sample 12 Pyrite from interbedded Black shale, Villasalto area.

Pyrite from interbedded Black shale, Ballao area. Sample 13

Sample 14 Pyrite from interbedded Black shale, Su Pitzixeddu to the S of Monte Ferro.

Sample 15 Pyrite from lamprophyric dyke, Villasalto area.

Samples 16, 17 Devonian limestone, the first sample enclosed in the tectonic breccia, the second from regular outcrop, Villasalto area.

or ¹⁸O/¹⁶O ratios. The sulphur, carbon and oxygen isotopic compositions are reported relative to the Canyon Diablo troilite, the PDB 1 and the SMOW standards respectively. The accuracy of measurements is about $0.1^{\circ}/_{00}$.

The samples come from mines, prospects and rock outcrops of the Villasalto-Armungia-Ballao area. For further details we refer to Table V. The stibnites 1-5 and 7-8 are from the normal lenticular ore bodies of the Villasalto mine, whereas sample 6 from Villasalto mine, and samples 9-11 from other localities, are probably remobilized stibnite. The δ^{34} S values of all the stibnites, being on the average not far from zero, point towards a magmatic-hydrothermal origin. The sulphur of the pyrites 12-14, all from regularly interbedded Black shales, is clearly organogenic-sedimentary, whereas the sulphur of the pyrite 15, from a lamprophyric dyke, is obviously magmatic.

The δ^{13} C and δ^{18} O values for the two samples, from the breccia and from a

regular outcrop of Devonian limestone, are in keeping with a marine origin. The calcites associated with the stibnite seem to fall, as far as the δ^{13} C are concerned, within the hydrothermal range, but these values could also be due to the mixing of C from the Devonian limestone with the carbonaceous matter of the Black shale.

7. DISCUSSION

After perusing the review paper by Krauskoff (1955) with its very extensive bibliography, we have chosen the Mansfeld Copper shale for a comparison with the Sardinian Black shale, mainly on account of the rich information about the first contained in the paper by Wedepohl (1964) – although the two rocks are not identical. The Mansfeld Copper shale is Upper Permian; it contains Cu, Zn and Pb as major constituents; further data, also about its Polish extension, are found in Vlasov (1968). But neither Wedepohl nor Vlasov supply original information about its Sb and W content. According to Cissarz (1930) it assays between 500 and 100 ppm Sb and between 100 and 10 ppm W, and according to Goedderitz (1951) its maximum content of Sb and W is respectively 500 and 100 ppm.

The Mansfeld Copper shale is bituminous, whereas the Sardinian Black shale is carbonaceous, but it also might have been bituminous prior to the low-grade metamorphism suffered. Both are euxinic sediments, which notoriously scavenge and concentrate from the sea water trace elements, by precipitation through bacteriogenic and putrefactive H₂S and through adsorption on clay minerals. According to the table of Turekian and Wedepohl (1961) the World averages for all shales (without further connotation), and for the majority of trace elements, on the whole are not much below the corresponding figures for the Copper shale and for the Black shale. For Sb the general rather unsatisfactory data of average for shales is only 1.5 ppm (Turekian and Wedepohl, 1961, from Onishi and Sandell, 1955).

In his analysis of the Copper shale sedimentation, Wedepohl (1964) reaches the conclusion that the water must have been enriched with respect to normal sea water at least in the major metals of the Copper shale, Cu, Zn, Pb. But he excludes that this enrichment is due to exhalative action, attributing it instead to fluviatile and marine leaching of the Lower Permian red sandstones "Rotliegendes" (Red beds), which are enriched themselves in metallic ions within the red iron oxyde coating of the sand grains.

Schneider and his school (and we also) have searched for some volcanics which could have supplied the metals to the "extrusive" – or "exhalative-sedimentary" – deposits. As we have seen, however, most even if not all the

magmatic events of Sardinia are either somewhat older (porphyroids) or much younger than the Black shales.

In his two papers MAUCHER (1965, 1976) describes the Villasalto deposit mainly on the basis of Angermeier (1964), who mentions relictic sedimentary structures in the breccia ore, structures we have been unable to trace.

We do not outright reject the extrusive-sedimentary hypothesis, already proposed eighty years ago (Toso, 1897; Cappa, 1897). Equally we share the belief that the undisturbed, usually thin veins of stibnite, sometimes with W minerals, in late joints of porphyroids and arkoses, are due to recirculation of the very small metal content of the regularly interstratified Black shale beds, which are always nearby. We believe, however, that metal-bearing solutions, entering the sea, should spread over distances of at least several kilometres, forming an aureola around the source point, with outwardly decreasing concentration gradients. Up to now, however, nothing of this kind has been reported from Sardinia.

The general metal content of the Sardinian Black shales represents the normal content of an euxinic sediment.

The formation of the unique, high-grade deposit remains difficult to explain. What we see today at Villasalto is the outcome of the Late Hercynian tectonic shattering, transport and remoulding of an extremely concentrated deposit, which even after such a handling has already supplied tenthousands of tons of antimony and some tungsten. Should also this deposit be due to the leaching of the minimal Sb-traces of the Black shales – an impervious sediment, and of limited thickness? How many square kilometres of it need to have been completely leached out?

With an average content of 5 ppm, one cubic km of Black shale could have supplied at most about 12,500 tons of antimony; and for a mean thickness of the shale, assumed to be 25 m, for supplying the 50,000 tons we estimate as the total metal content of the Villasalto-Martalai deposit, at least 160 square km of the shale would have been required.

Or does the original deposit belong to a supposed syntectonic Hercynian metallogenesis, prior or contemporary with the Villasalto overthrust? Such a deposit would be of hydrothermal origin. It had already once been hypothesized (Jensen and Dessau, 1966) that Sardinian granite magmas might have assimilated Cambrian rocks and their ore deposits.

Finally it should be remembered that the isotopic composition of the sulphur of the Villasalto stibnite points to a magmatic origin. Taking everything into account, we rather visualize a primary high-grade epigenetic deposit, prior or contemporary with the overthrust.

In the Sarrabus – the area adjoining to the south the Gerrei – up to the 'nineties thrived a rich mining industry exploiting silver and silver sulphoantimonides within Black shales having a general east-west trend, and squeezed

and tectonized as far as one may guess from the old literature. Similarities with the Villasalto deposit seem obvious, and might have important implications in respect of the silver deposits and of their re-exploration.

Acknowledgements

The access to their records and the generous hospitality of the lessees of the Villasalto mine, the "S.A. Miniere e Fonderie di Antimonio" of the AMMI Group, and the warm, unfailing assistance of the local director Dr. Eng. Giuseppe Mazzari, are gratefully acknowledged. The "Ente Minerario Sardo" has put at our disposal technical documentation on their geochemical prospecting. Dr. Roberto Cioni of the Mineralogical Institute of the University of Pisa has kindly determined the loss on ignition of our samples. Our warmest thanks go to Mr. Roy Kligfield and to Mr. V. Köppel for their patient critical and linguistic revision of the manuscript.

References

- ANGERMEIER, H.-O. (1964): Die Antimonit-Scheelit-Lagerstätten des Gerrei (Südostsardinien, Italien) und ihr geologischer Rahmen. Doktorat-Dissertation, München, 62 p.
- BISTE, M. (1977): Stratabound polymetallic and F-Ba-deposits of the Sarrabus-Gerrei region, SE-Sardinia. V. Report: The hypothermal Cu-As mineralization with occurrence of wolframite-scheelite near Muravera/SE-Sardinia. N. Jb. Miner., Mh., 548-558.
- Calvino, F. (1959): Lineamenti strutturali del Sarrabus-Gerrei. Boll. Serv. Geol. It. 81, 489-556.
- (1963): Carta geologica d'Italia all'1:100000, Foglio 227, Muravera. Roma, Serv. Geol. d'Italia.
- (1972): Note illustrative della Carta geologica d'Italia all'1:100000, Foglio 227, Muravera. Roma, Serv. Geol. d'Italia, 60 pp.
- CAPPA, U. (1897): Relazione della gita geologica fatta alla miniera Su Suergiu nei giorni 11, 12, 13 maggio 1897. Rendic. Ass. Min. Sarda 2 (5), 5-7.
- CARMIGNANI, L. e P. C. PERTUSATI (1977): Analisi strutturale di un segmento della catena ercinica: il Gerrei (Sardegna sud-orientale). Boll. Soc. Geol. It. 96.
- CATTANEO, R. (1897): Rend. Ass. Min. Sarda 2 (4), 10-11.
- CAVINATO, A. e E. BENEO (1959): Carta geologica d'Italia all'1:100000, Foglio 226, Mandas. Roma, Serv. Geol. d'Italia.
- CISSARZ, A. (1930): Die durchschnittliche Zusammensetzung des Mansfelder Kupferschiefers. Metall und Erz 27, 316–319.
- COCOZZA, T., A. JACOBACCI, R. NARDI e I. SALVADORI (1974): Schema stratigrafico-strutturale del Massiccio Sardo-Corso e Minerogenesi della Sardegna. Mem. Soc. Geol. It. 13, 85–186.
- DE CASTRO, C. (1890): Descrizione geologico-mineraria della zona argentifera del Sarrabus (Sardegna). Mem. Descr. Carta Geol. d'Italia 5, Roma, Serv. Geol. d'Italia, 68 pp.
- Dessau, G. (1956): Cenni sul giacimento di tungsteno e molibdeno di Perda Majori (Sardegna). Boll. Soc. Geol. It. 75, 239-254.
- (1974): Die Lagerstätten Toskanas im Lichte der geologischen Entwicklung des Landes. Archiv für Lagerstättenforschung in den Ostalpen, Sonderbd. 2, 51–77, Leoben.
- (1976): Die Antimon- und Quecksilber-Lagerstätten Toskanas und ihre Paragenesen. Freib. Forschungshefte, C 328, Topical Report of IAGOD 7, 47–71, Leipzig.

- Dessau, G., G. Duchi e B. Stea (1972): Geologia e depositi minerari della zona Monti Romani-Monteti (Comuni di Manciano e Capalbio [Grosseto] ed Ischia di Castro [Viterbo]). Mem. Soc. Geol. It. 11, 217-260.
- DI SIMPLICIO, P., G. FERRARA, C. GHEZZO, G. GASPARRI, R. PELLIZZER, C. A. RICCI, F. RITA e G. SABATINI (1974): Il metamorfismo ed il magmatismo paleozoico nella Sardegna. Rend. Soc. It. Mineral. Petrol. 30, 981-1068.
- FERRARI, A. (1897): Sulla regione antimonifera del Gerrei. Rend. Ass. Min. Sarda 2 (3), 3, e (4), 8-11.
- Franzini, M., L. Leoni and M. Saitta (1972): A simple method to evaluate the matrix effects in X-ray fluorescence analysis. X-Ray Spectrometry 1, 151-154.
- (1975): Revisione di una metodologia analitica per fluorescenza-X, basata sulla correzione completa degli effetti di matrice. Rend. Soc. It. Mineral. Petrol. 31, 365–378.
- GOEDDERITZ, A. H. F. (1951): Der Mansfelder Kupferschiefer und die aus ihm gewonnenen Werk- und Rohstoffe. Metallurgie und Giessereitechnik 1, 71–77.
- HEETVELD, H. and S. PRETTI (1975): Geochemical exploration in Sardinia. In: Developments in Geology 1, 119-129. Amsterdam, Elsevier.
- Helmcke, D. (1973): Schichtgebundene NE-Metall- und F-Ba-Lagerstätten im Sarrabus-Gerrei-Gebiet, SE-Sardinien. II. Bericht. N. Jb. Miner., Mh., 529-544.
- HELMCKE, D. und G. KOCH (1974): Schichtgebundene NE-Metall- und F-Ba-Lagerstätten im Sarrabus-Gerrei-Gebiet, SE-Sardinien. III. Bericht. Zs. Deutsch. Geol. Ges. 125, 91–98.
- JENSEN, M. L. and G. DESSAU (1966): Ore deposits of southwestern Sardinia and their sulfur isotopes. Econ. Geol. 61, 917-932.
- Krauskopf, K. B. (1955): Sedimentary deposits of rare metals. Econ. Geol. Fiftieth Anniv. Vol., 411-463.
- LAURO, C. (1965): Il giacimento di antracite di Seui (Barbagia Sardegna). Per. Mineral. 39, Vol. speciale, 209-242.
- LEHMANN, B. (1975): Stratabound polymetallic and F-Ba-deposits of the Sarrabus-Gerrei region, SE-Sardinia. IV. Report. N. Jb. Miner., Mh., 460–470.
- LEONI, L. and M. SAITTA (1976): X-ray fluorescence analysis of 29 trace elements in rock and mineral standards. Rend. Soc. It. Mineral. Petrol. 32, 497-510.
- Lincio, G. (1917): Studi mineralogici e geologici di località sarde. I: Osservazioni petrografiche e genetiche sul giacimento antimonifero di Su Suergiu. Rend. Acc. Lincei, ser. 5, 26, 350.
- (1918): Le gisement de stibine et la pyrite en épigenèse de Nautiloides de Su Suergiu (Villasalto). C. R. Acc. Sc. Paris 166, 737/38.
- Marcello, A., S. Pretti e I. Salvadori (1977): Le prospezioni geominerarie in Sardegna: la prospezione geochimica strategica. Ente Minerario Sardo, Notiziario tecnico-economico, 5 (2-3), 31-59.
- MAUCHER, A. (1965): Die Antimon-Wolfram-Quecksilber-Formation und ihre Beziehungen zu Magmatismus und Geotektonik. Freib. Forschungshefte 186, 173–188.
- (1976): The strata-bound cinnabar-stibnite-scheelite deposits (discussed with examples from the Mediterranean region). In: Wolf, K. H., Editor. Handbook of strata-bound and stratiform ore deposits, 477–503. Amsterdam, Elsevier.
- MAZZETTI, L. (1884): Rivista del Servizio Minerario, Roma.
- OLIVIERI, R. (1969): Conodonti e zonatura del Devonico superiore e riconoscimento del Carbonifero inferiore nei calcari di Corona Mizziu (Gerrei Sardegna). Boll. Soc. Paleont. It. 8, 63–152.
- Onishi, H. and E. B. Sandell (1955): Notes on the geochemistry of antimony. Geochim. Cosmochim. Acta 8, 213–221.

- PECORINI, G. (1971): In: R. PRACCHE e A. TERROSU ASOLE: Atlante della Sardegna. Cagliari, La Zattera.
- Pomesano Cherchi, Antonietta (1962): Ricerche sul vulcanismo Gotlandiano del Gerrei. Ricerca Scientifica, Ser. II, Rendic., Sez. A, 2, 279–283.
- Salvadori, I. (1973): Organizzazione della ricerca mineraria in Sardegna. Boll. Serv. Geol. It. 94, 213-231.
- Schneider, H. H. (1974): Lithostratigraphy of the San-Vito-Formation at San Nicolò Gerrei (SE-Sardinia) and some tectonic considerations on the Villasalto-Fault. Boll. Soc. Geol. It. 93, 927–936.
- Schneider, H.-J. (1972): Schichtgebundene NE-Metall- und F-Ba-Lagerstätten im Sarrabus-Gerrei-Gebiet, SE-Sardinien. I. Bericht. N. Jb. Miner., Mh., 529-541.
- Taricco, M. (1911): Osservazioni geologico-minerarie sui dintorni di Gadoni e sul Gerrei (Prov. di Cagliari). Boll. Soc. Geol. It. 30, 113-150.
- TEICHMÜLLER, R. (1931): Zur Geologie des Tyrrhenisgebietes. Teil 1: Alte und junge Krustenbewegungen im südlichen Sardinien. Abh. Ges. Wiss. Göttingen, math.-phys. Klasse, 3 (3), 1–94.
- Toso, P. (1897): Note sul giacimento di antimonio di Su Suergiu. Rend. Ass. Min. Sarda 2 (4), 11-15.
- Traverso, G. B. (1897): L'antimonio. Alba, Sansoldi, 85 pp.
- Traverso, S. (1890): Note sulla geologia e sui giacimenti argentiferi del Sarrabus (Sardegna). Torino, Casanova, 57 pp.
- Turekian, K. K. and K. H. Wedepohl (1961): Distribution of the elements in some major units of the Earth's crust. Bull. Geol. Soc. Amer. 72, 175-192.
- Valera, R. e P. Zuffardi (1970): La geochimica del Tungsteno nel Paleozoico della Sardegna. Nota I. Rend. Soc. It. Mineral. Petrol. 26, 815–830.
- VLASOV, K. A., Editor (1968): Geochemistry and mineralogy of rare elements and genetic types of their deposits. Vol. III, Genetic types of rare-element deposits. Translated from Russian. Israel program for scientific translations, Jerusalem, 20 and 916 pp.
- Wedepohl, K. H. (1964): Untersuchungen am Kupferschiefer in Nordwestdeutschland: Ein Beitrag zur Deutung der Genese bituminöser Sedimente. Geochim. Cosmochim. Acta 28, 305–364.

Addition in press to the list of references:

Greiling, R. (1977): Die Lagerstättenprovinz Sarrabus-Gerrei (SE-Sardinien/Italien) und ihr geologischer Rahmen. Frankfurt/M., Lang, 145 S.

Manuscript received March 28, 1978.