Sea-floor massive sulphides
from the Galápagos Rift Zone – mineralogy, geochemistry
and economic importance

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The largest reserves of the Earth's mineral resources are located on the ocean floor. Amongst these, hydrocarbon and metallic resources are of the greatest importance. In 2010, the International Seabed Authority (ISA) adopted rules for documenting new metal resources contained with polymetallic sea-floor massive sulphides (SMS). Russia and China were the first countries to apply to the ISA to acquire the right to commence initial investigation and documentation in the Indian and Atlantic oceans. Apart from copper, cobalt and nickel, modern SMS ores contain inferred significant amounts of gold, silver and PGE. The results described here from Galápagos Rift samples indicate a high concentration of gold (up to 7.24 ppm) and platinum (up to 350 ppb), which are mainly concentrated in low temperature parts of the sulphide mounds. The high content of Au and Pt revealed by this study provides further motivation towards attempting the exploration of marine massive sulphides. This is particularly important in the light of the high prices of metal commodities, and especially the unprecedented price of gold. This paper is the first such detailed scientific account in the Polish scientific literature focusing on the genesis and economic significance of the modern sea-floor sulphides.

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INTRODUCTION

One the 7th of May 2010, the ISA (International Seabed Authority) issued the *Regulations on prospecting and exploration for polymetallic sulphides in the Area* (the Area and its resources are the common heritage of mankind – this term means that the Area is part of the World Ocean under ISA jurisdiction; UNCLOS, 1982). These acts have opened a new chapter in the history of international prospective investigations of oceanic massive sulphides and bring forward the possibility of their extraction. As a consequence of the ISA decisions in 2010, two countries – first China, and later Russia – applied for rights to commence the search for oceanic massive sulphides. China will concentrate its efforts on the Indian Ocean, whereas Russia will focus on the Atlantic Ocean. The scope of the ISA's activity has thus increased considerably. In the near future, ISA should start coordinating the research into gas hydrates, a change which was suggested already at ISA's 2004 anniversary session (Szamałek, 2004*a*, *b*). The expanding activity of China and Russia suggests that the research on mineral metallic resources of the World Ocean has entered a new stage.

Poland is a member state of the Interoceanmetal Joint Organization (IOM) – the registered contractor of International Seabed Authority and is conducting, in the framework of IOM, an extensive program of marine mineral investigation, mainly concentrated on Fe-Mn nodules (Kotli ski, 1999). A general account of marine minerals has been published in Polish in two monographs (Depowski *et al.*, 1998; Mizerski and Szamałek, 2009). However, details concerning the origin and mineralogy of seabed deposits are still needed. Therefore, the sea-floor massive sulphides from the Galápagos Rift were examined.

The reported results are the first SMS examinations presented by Polish mineralogists. The aims of this study were the recognition of the mineralogical composition and geochemistry of sea-floor massive sulphides from the Galápagos Rift Zone. These data, especially the content of noble metals, were used to determine the economic value of the SMS deposit located in the Galápagos Rift Zone.

GEOLOGY OF GALÁPAGOS RIFT AREA

Galápagos Rift Zone is a part of the East Pacific Rise located north of the Galápagos Islands (Figs. 1 and 2). It is a small rift valley 3–4 km wide with walls up to 250 m high. This rift system developed during the Late Oligocene, when the Farallon Plate split into the Cocos and Nazca plates (Silver *et al.*, 1998). Mapping of the magnetic anomalies in the oceanic crust between the Cocos and Nazca plates permits reconstruction of the spreading history that comprises three major tectonic episodes named CNS-01, CNS-2 and CNS-3 (Lonsdale and Klitgord, 1978; Meschede *et al.*, 1998). The oldest (CNS-1) episode, originated *ca.* ~23 to 19.5 Ma, while the next two (CNS-2 and CNS-3) developed in the periods from 19.5 to 14.7 Ma and from 14.7 Ma to the present, respectively (Meschede *et al.*, 1998; Meschede and Barckhausen, 2000).

The sample examined represents sea-floor sulphides created during the youngest (CNS-3) episode.

The spreading at the Galápagos Rift system and its hydrothermal activity is additionally driven by the Galápagos hotspot activity (Ito *et al.*, 1997). This complex interaction of the Galápagos hotspot with the developing mid-ocean ridges is responsible for the high spreading rates, varying from 47 to 63 mm/yr^{-1} (DeMets *et al.*, 1994), which are accompanied by intensive hydrothermal activity along the recent mid-ocean rift. Activity of the Galápagos mantle hotspot caused instability of the upper mantle manifested by upwelling, which resulted in high melt production during their adiabatic melting. As a consequence the less depleted parts of the mantle may supply high amounts of economically important elements, including noble metals, that are partly deposited within the sea-floor sulphides.

GEOLOGY OF MODERN (SMS) AND ANCIENT (VMS) POLYMETALLIC SULPHIDE DEPOSITS

Sea-floor massive sulphides (SMS) can be found on the modern sea-floor in different tectonic settings (Fig. 1). They constitute modern analogies of volcanogenic massive sulphide (VMS) forms that are successfully mined for Cu, Zn, Pb, Au and Ag high-grade ores (Galley *et al.*, 2007). Volcanogenic
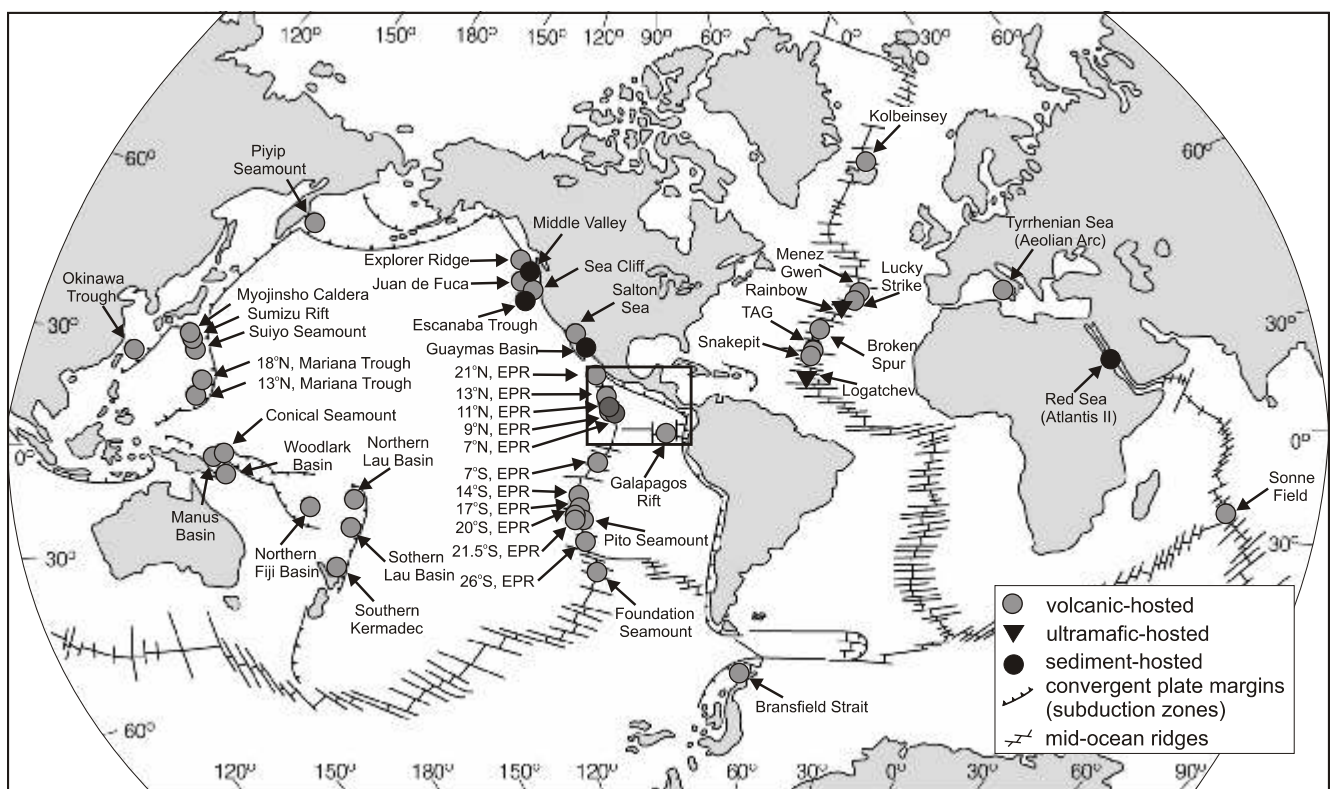

Fig. 1. Location of selected sea-floor massive sulphide (SMS) hydrothermal systems and/or deposits at the modern sea-floor (after Herzig *et al.*, 2002, simplified)

Rectangle marks the study area, for details see Figure 2; EPR – East Pacific Rise, TAG – Trans-Atlantic Geotraverse

massive sulphide (VMS) deposits are sometimes described as volcanic-associated, volcanic-hosted, and volcano-sedimentary-hosted massive sulphide deposits (Galley *et al*., 2007). Because of their polymetallic content, they are characterized also by significant amounts of trace elements such as Au, Ag, Co, Sn, Se, Mn, Cd, In, Bi, Te, Ga, Ge, As and Sb. Therefore they are mostly described as polymetallic massive sulphides (PMS) (Herzig and Hannington, 1995). VMS deposits have distinct stratabound characteristics, and occur as tabular, lensoidal and/or mound-shaped bodies (Fig. 3). They are commonly metamorphosed due to their location in island-arc or orogenic continental crust. These deposits bear high-grade ores, which show different types of massive sulphide textures. The ores have up to 40–50 vol.% of sulphides, while clay minerals, Fe-oxides, Ba-, Ca-sulphates, and different forms of silica are subordinate constituents.

The SMS deposits are the subject of intensive and widespread contemporary studies by many marine institutes and an object of interest of the International Seabed Authority (Herzig *et al*., 2002). Marine polymetallic hydrothermal sulphides were first discovered in 1978 on the East Pacific Rise at 21°N (Francheteau *et al*., 1979). Since the initial discovery, similar deposits have been found in the Galápagos Rift (Malahoff, 1981), the Guaymas Basin (Lonsdale *et al*., 1980), the East Pacific Rise at 13°N (Hekinian *et al*., 1981; Fouquet and Hekinian, 1985), and along the Juan de Fuca Ridge off the coast of Oregon (Normark *et al*., 1982). Additionally SMS have been identified at many locations including the Atlantic and Indian oceans (Scott, 1987). Currently sulphide deposits are known from more than 100 locations (Fig. 1) in the Pacific Ocean, several in the Atlantic Ocean, one in the Mediterranean Sea, one in the Indian Ocean, and in several so called "deeps" of the Red Sea. These deposits are included into separate metalliferous clay groups. At more than 25 locations of SMS "black smokers" were found. Massive sulphides are reported in various tectonic settings on the modern sea-floor, among them mid-ocean ridges, back-arc rifts as well as seamounts. SMS are present along both slow- and fast-spreading ocean ridges. In Pacific fast-spreading (over 12 cm/y) and medium-spreading (6–12 cm/y) zones the massive sulphides form mostly truncated cones up to 5 metres high (sporadically up to 25–35 metres) with base diameters of up to 30 metres. On vol-
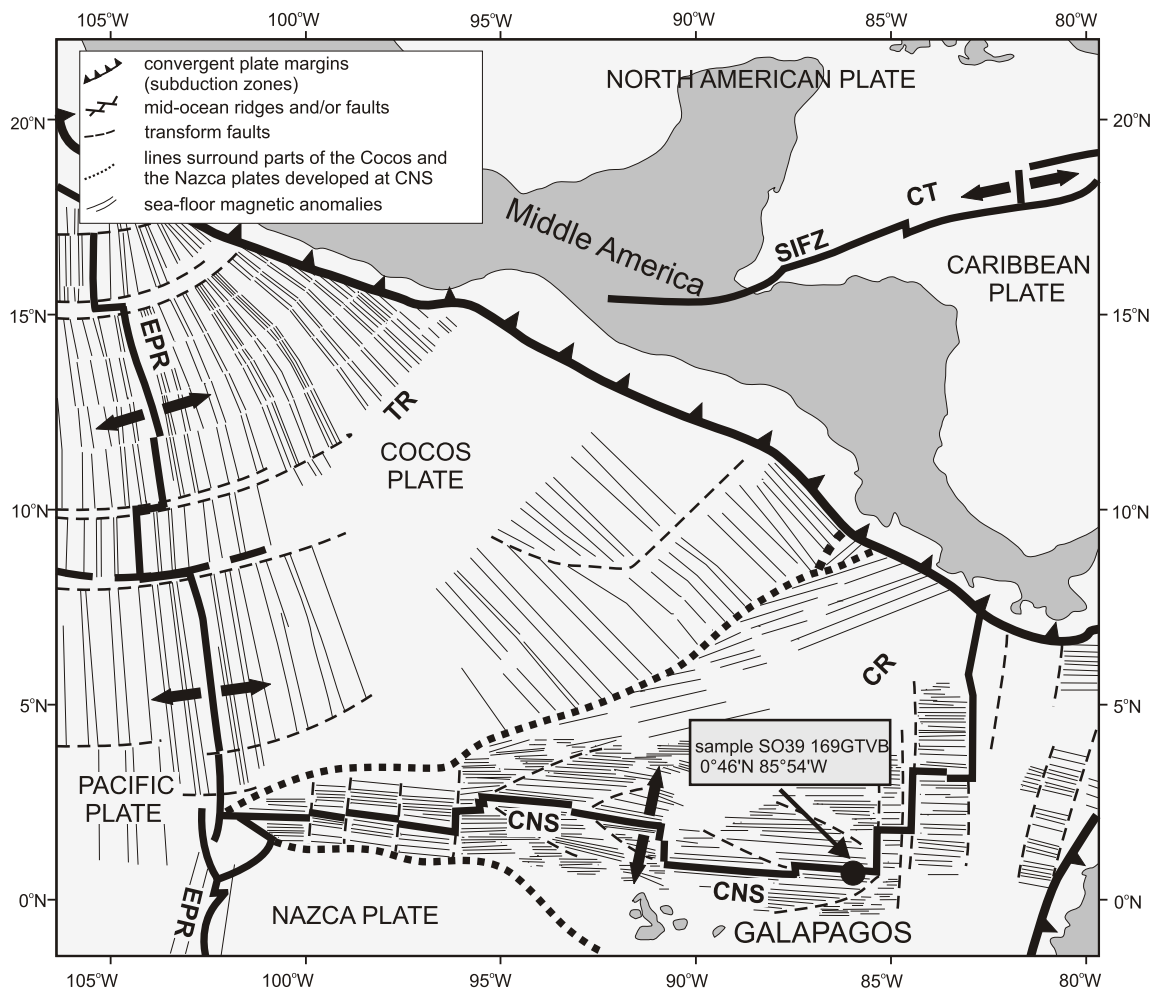

Fig. 2. Tectonic map of the Galápagos Rift Zone (after DeMets *et al*., 2000; DeMets, 2001; Rogers, 2003, modified) showing location of the sample No SO39 169GTVB (0°46'N, 85°54'W)

CNS – Cocos-Nazca Spreading Center, CR – Cocos Ridge, CT – Cayman Trough, EPR – East Pacific Rise, SIFZ – Swan Island Fault Zone, TR – Tehuantepec Ridge
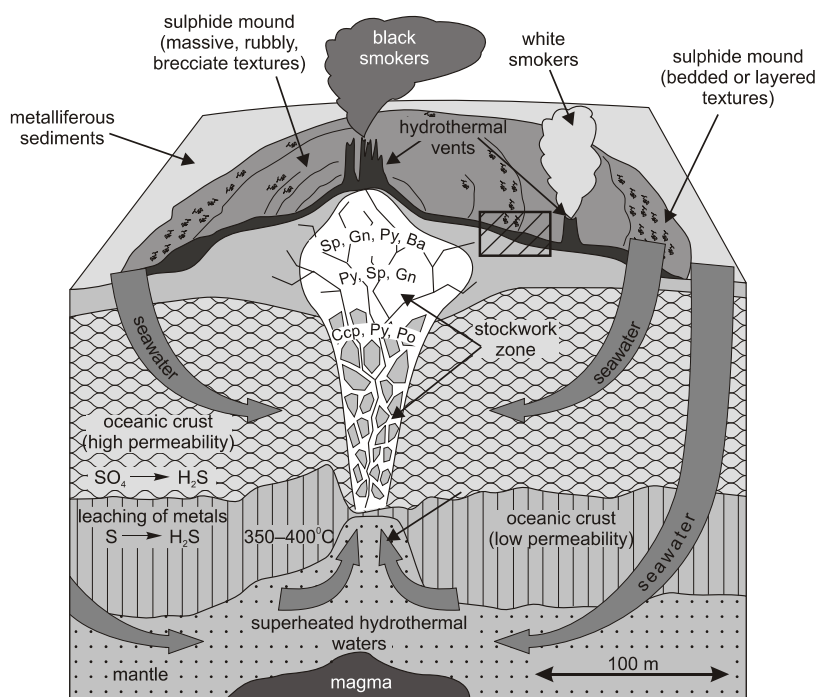
Fig. 3. General model shoving internal structure and genesis of a modern sea-floor massive sulphide (SMS) mound (after Hannington *et al*., 1998, modified)

Rectangle shows presumed place of the sampling area for the SO39 169GTVB sample; Ba – barite, Ccp – chalcopyrite, Gn – galena, Po – pyrrhotite, Py – pyrite, Sp – sphalerite

canic slopes along the spreading axis the sulphide deposits occur in the form of large covers up to $800 \times 500 \times 9$ metres in size (Ajnemer *et al*., 1988).

The origin of SMS is related to percolation of seawater through the upper part of the oceanic crust driven by high heat-flow (Fig. 3). These processes caused intensive hydrothermal alteration of the various basaltic and mantle rocks forming the oceanic crust; they are mainly restricted to transformation of the oceanic crust in the vicinity of mid-ocean ridges and transform faults (Herzig and Hannington, 1995; Fouquet *et al*., 1996). These zones permit easy access for circulating fluids. These processes have a regional character, and the mineralogical changes to the rocks forming upper continental crust were described as ocean floor metamorphism (Coleman, 1977). These metamorphic processes have a typical water-rock character. The intensive water-rock interactions produce large amounts of high-temperature fluids that transport upwards incompatible elements (Rb, U, Th, K, Sr, Ba), chalcophile elements e.g., Mn, Mn, Co, Ni, Zn, Cu, Pb, Ag, Bi, and also noble metals such as Au and

PGE (Pašava, 2004, 2007). The recharged fluid on the sea-floor in the form of the "black smokers" and/or "white smokers" causes spontaneous crystallisation of sulphides which lead to the development of sulphide mounds (Fig. 3). The ratio of the mantle rocks to magmatic basic rocks that occurs in the upper oceanic crust, through which circulation of hydrothermal fluids take place, is probably the main factor that determines the concentration of the noble metals.

SAMPLES AND ANALYTICAL METHODS

The SMS sample examined labelled SO39 169GTVB was collected from the site 0°46'N and 85°54'W during a scientific cruise of the Sonne vessel (Fig. 4). Thanks to the kindness of Prof. P. Herzig it was granted by RWTH Aachen (Rheinisch-Westfaelische Technische Hochschule Aachen) to the Faculty of Geology of Warsaw University for comparative analysis. The macro characteristic of this sample is as follows: 1.55 kg weight, 24 cm length, 8–11 cm width and 5 cm thick (Fig. 4). In order to conduct the examinations, it was cut into two smaller parts (Fig. 5). Six samples from different and macroscopically varied SMS parts were prepared for analysis. Macroscopic analysis of the entire sample revealed small vents up to 12 mm in diameter (Figs. 5 and 6).

The samples were studied using conventional petrographic and geochemical methods at the Faculty of Geology of Warsaw University. Petrographical study, employing mainly reflected light microscopy, was conducted using a *ECLIPSE E600W POL* microscope. EPMA analyses of the
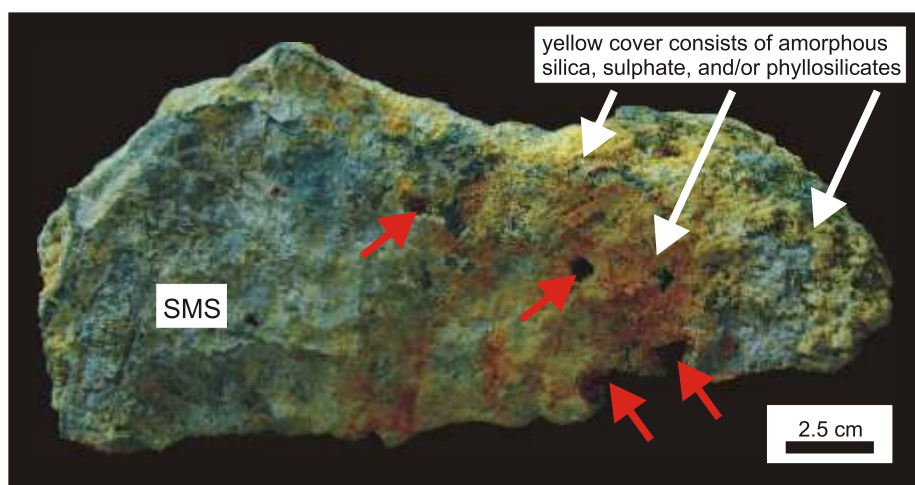

Fig. 4. General view of the SO39 169GTVB sample

Red arrows indicate small unmineralised vents through which hydrothermal water flowed through the massive sulphides, SMS – sea-floor massive sulphides
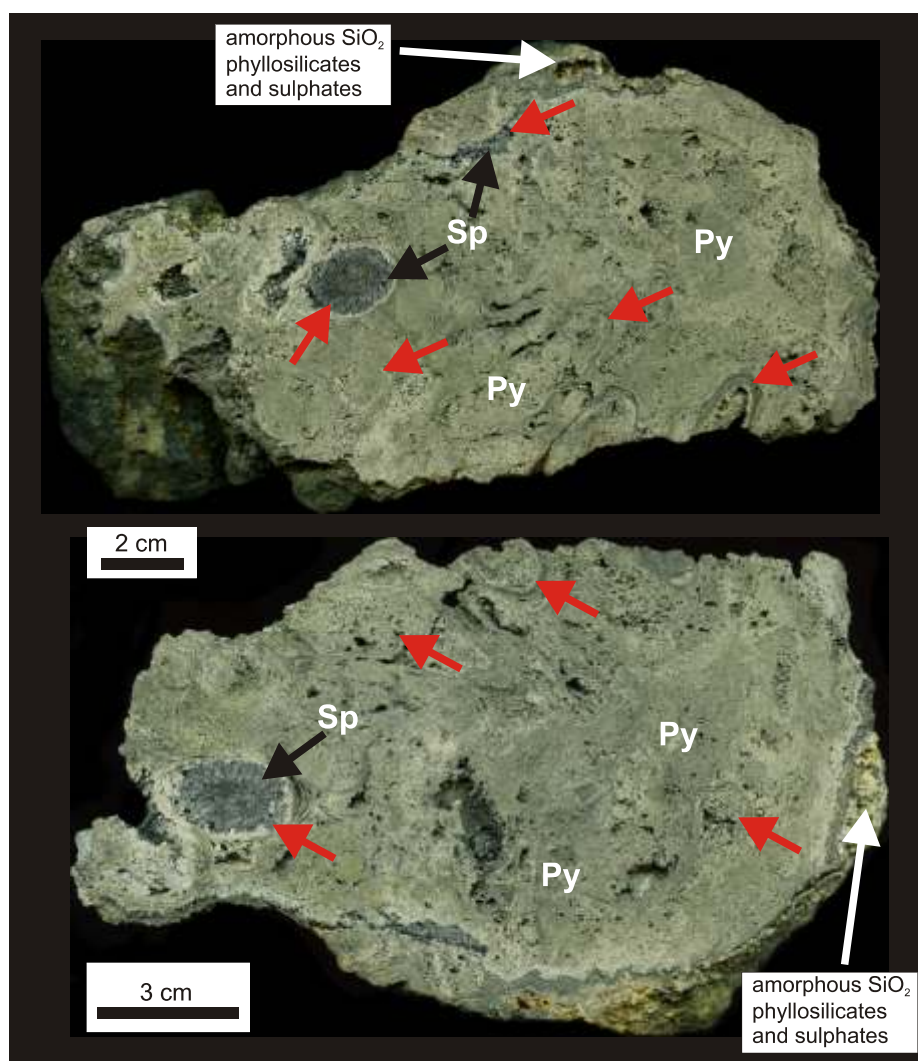
Fig. 5. Texture of the SO39 169GTVB sample

Red arrows mark abandoned old vents completely mineralised by pyrite (Py) and sphalerite (Sp)

massive sulphides were performed using a *CAMECA SX100*. The analyses were done using a focused electron beam, the accelerating voltage and current of the focused beam being 15 keV, and 20 nA, respectively. A 20 s counting time and ZAF correction were applied during analyses. Natural and synthetic standards, supplied by *CAMECA* and SPI (Structure Probe, Inc.), were used as calibrating standards. The BSE and SEM images were recorded using a *JEOL JSM-6380LA* scanning electron microscope.

XRD analyses were performed on a *PHILIPS X'PERT PRO* diffractometer. The samples were manually powdered in an agate mortar, than mounted on a standard metal holder and irradiated with CoKa radiation. Data were collected over the range 2.51 to 75.98° 2Θ, in a step-scan mode employing 0.026 2Θ step-size, and counting time 1 s per step. The acceleration voltage and current intensity were 40 keV and 30 mA, respectively.

The amounts of major and trace elements in the massive sulphide ores were determined by means of the ICP-OES method using an *Optima 5300 DV* spectrometer (Perkin-Elmer). Small chips of the ore, up to 20 g, were taken from different parts of the SO39 169GTVB sample. The preparation procedures, applied before measurement, included powdering of the sample and dissolution in hot hydrochloric acid.

MINERALOGY OF THE POLYMETALLIC SO39 169GTVB SAMPLE: RESULTS OF REFLECTED LIGHT MICROSCOPY, SEM, EPMA AND XRD STUDIES

The samples examined contain mainly pyrite, marcasite, sphalerite, chalcopyrite and galena (Figs. 6–8). Non-sulphide minerals are mainly represented by amorphous silica, phyllosilicates, barite, and subordinate Fe-sulphate and rare native sulfur (Figs. 9 and 10). This mineral association is gener-
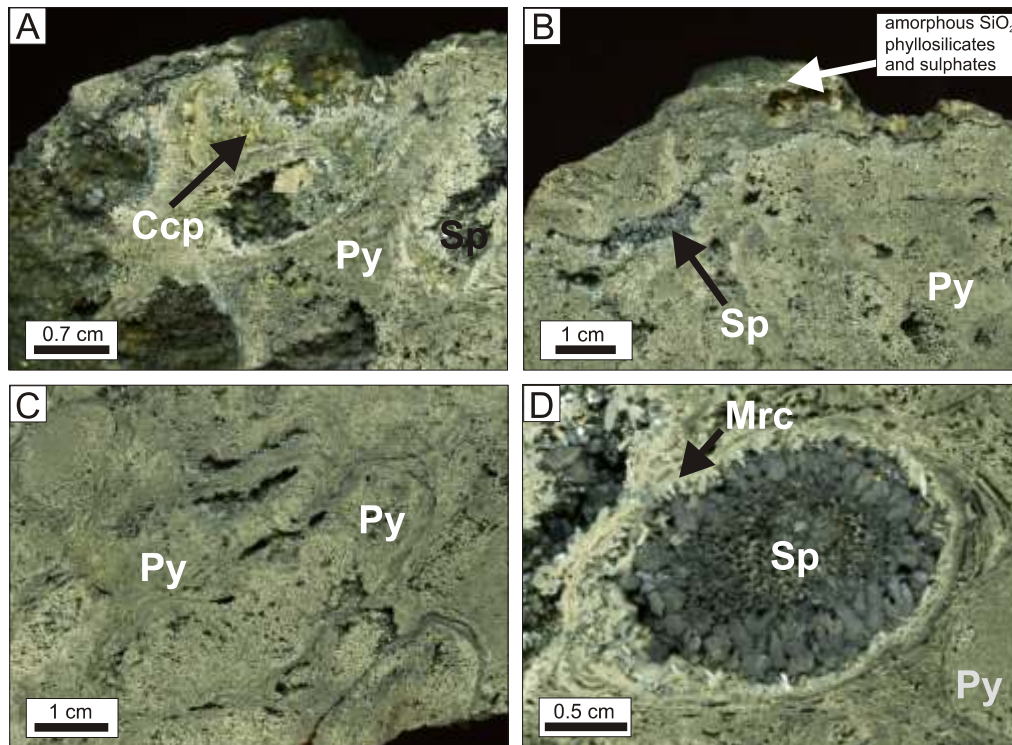
Fig. 6. Photographs showing textural details of the SMS SO39 169GTVB sample

A – association of pyrite and chalcopyrite; B – mineralisation of pyrite and sphalerite coated with amorphous silica, phyllosilicates and sulphates; C – numerous abandoned vents completely filled by pyrite; D – youngest vents concentrically mineralised by sphalerite; Ccp – chalcopyrite, Mrc – marcasite, Py – pyrite, Sp – sphalerite

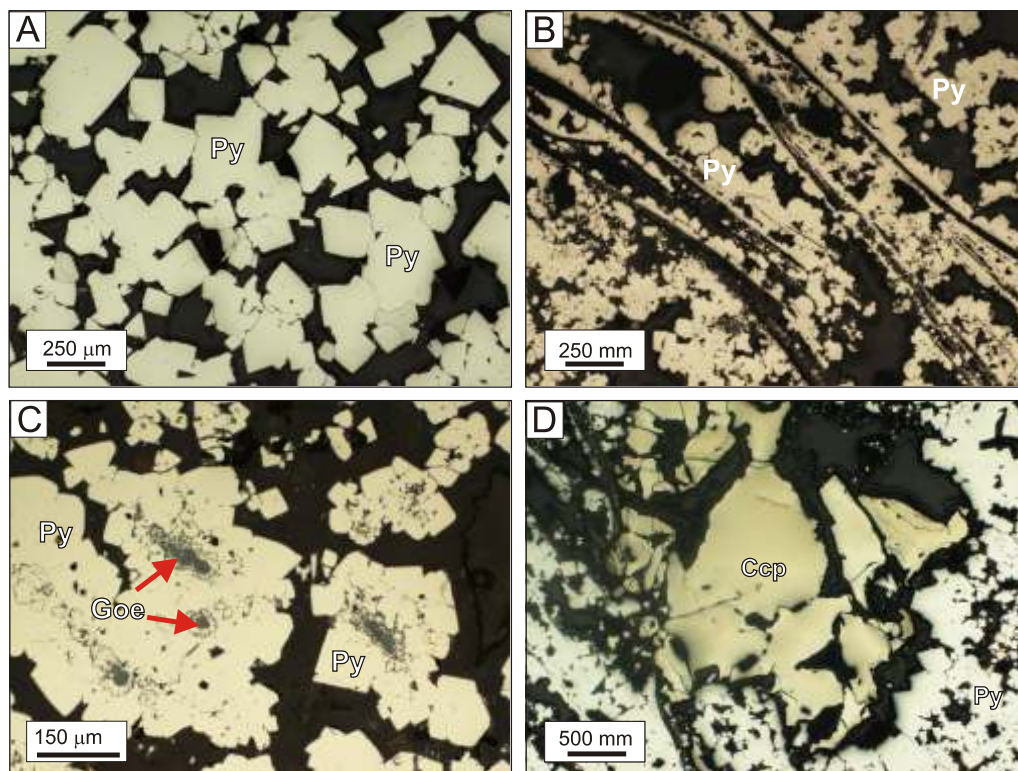**Fig. 7. Textural varieties of pyrite aggregates in the SMS sample studied**

A – euhedral crystals of pyrite (Py) in central parts of mineralised vents; B – crustified texture of pyrite forming sulphide walls of hydrothermal vents; C – aggregates of pyrite around thin channels for hydrothermal waters flowing through sulphide mound; channels are filled by goethite (Goe); D – massive texture of pyrite with chalcopyrite blebs (Ccp)
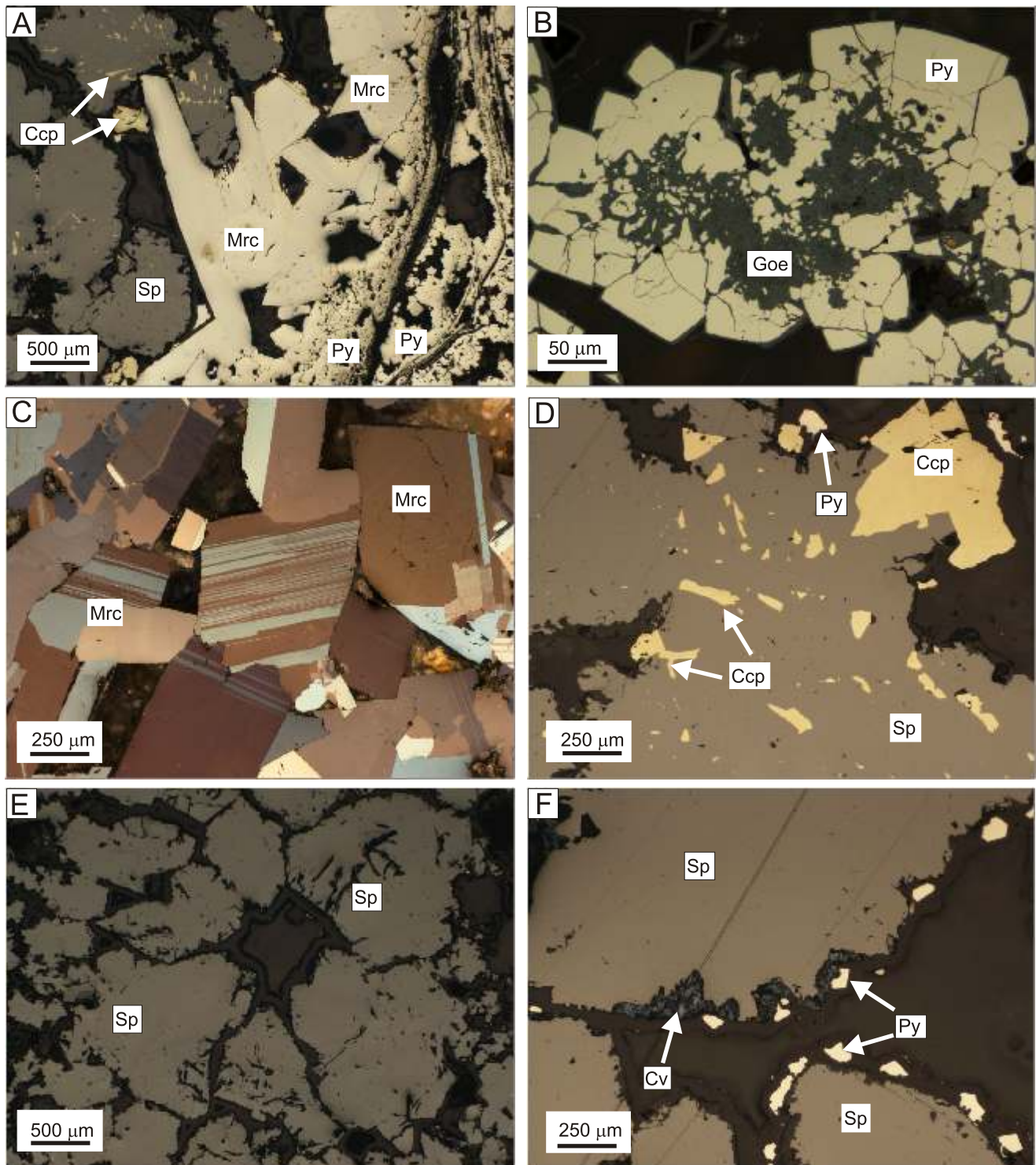
Fig. 8. Ore mineralogy of the SMS sample studied

A – marcasite forming wall of vent filled by later sphalerite with minute inclusions of chalcopyrite; **B** – pyrite and goethite intergrowths; **C** – marcasite crystals with well-developed polysynthetic twinning; crossed nicols; **D** – sphalerite-chalcopyrite composite filling mineralised vent in pyrite ore; **E** – texture of the central part of the sphalerite vent; **F** – sphalerite covered by thin rim of opal intergrown with pyrite and covellite; Cv – covellite, Qtz – opal; for other explanations see Figures 6 and 7; reflected-light microscope, one nicol

ally similar to the results known from other data from sea-floor hydrothermal ore-deposits which consist of massive accumulations of sulphide minerals dominated by pyrite, pyrrhotite, chalcopyrite and sphalerite (Table 1). Pyrite, chalcopyrite together with pyrrhotite, isocubanite and locally bornite are char-

acteristic of high-temperature fluid channels of black smokers and the interiors of sulphide mounds (Fig. 3), while outer parts of sulphide mounds are composed mainly of pyrite, marcasite and/or sphalerite/wurtzite. Anhydrite as a high temperature mineral is later replaced by sulphides, amorphous silica or bar-
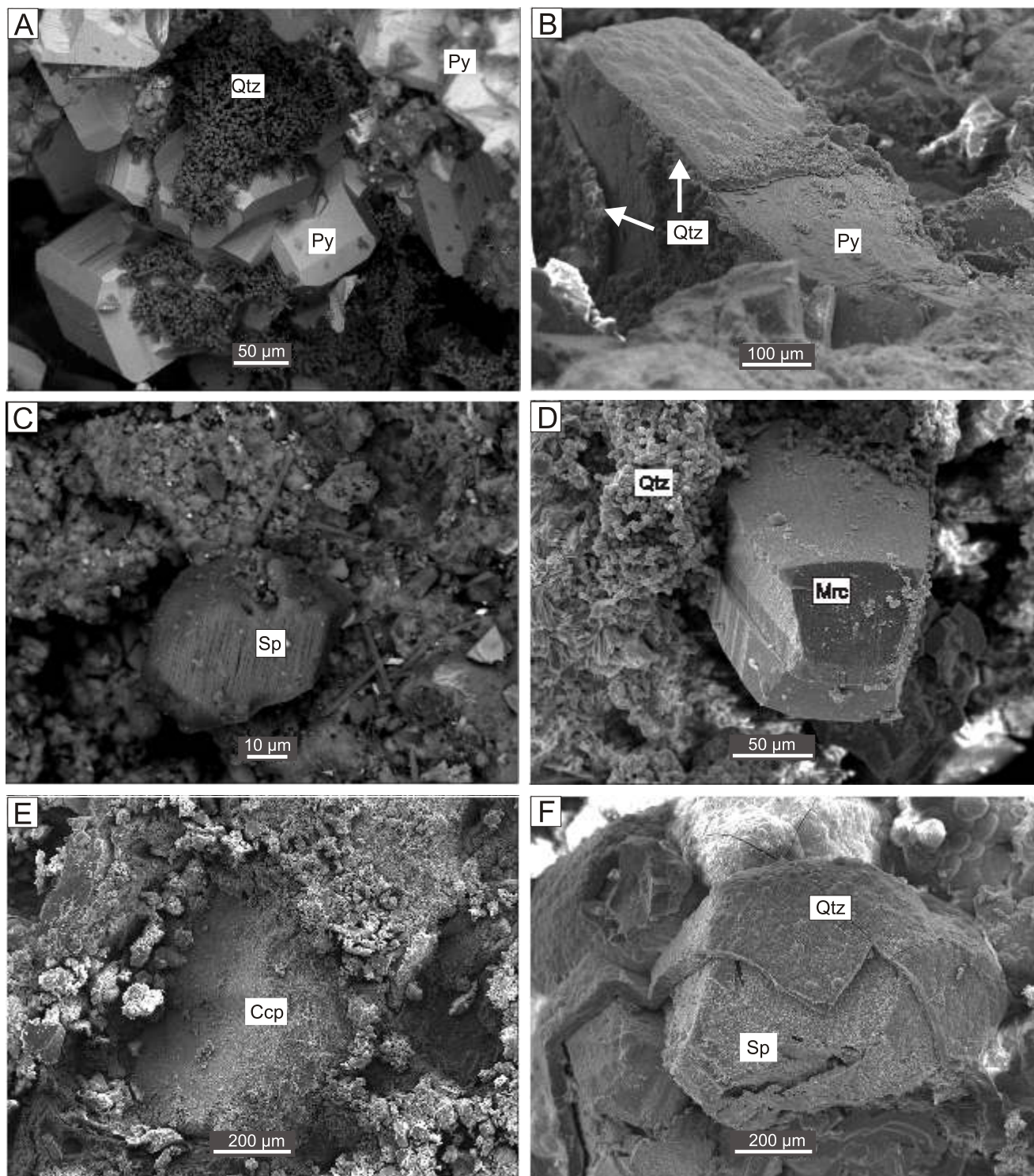
Fig. 9. Morphology of sulphides in the SMS sample studied; electron microscopy images

A – euhedral crystals of pyrite covered by spawn-like opal aggregates; **B** – pyrite and opal intergrowths; **C** – euhedral sphalerite in pyrite ore;
D – marcasite within opal aggregates; **E** – chalcopyrite in pyrite; **F** – euhedral sphalerite covered by opal; for other explanations see Figure 8

ite at lower temperatures (Herzig *et al*., 2002). The characteristic feature of the sample studied is high amounts of amorphous silica occurring together with the sulphides (Figs. 9A–F and 10A). This may correspond to the monomineralic silica chimneys recognized in the Galápagos Rift Zone by Herzig *et al*.

(1988). The mineral composition of the samples under study clearly indicates that their origins are connected with sulphide precipitations at relatively low temperatures.

The paragenetic association of ore minerals in the polymetallic SO39 169GTVB sample is dominated by pyrite
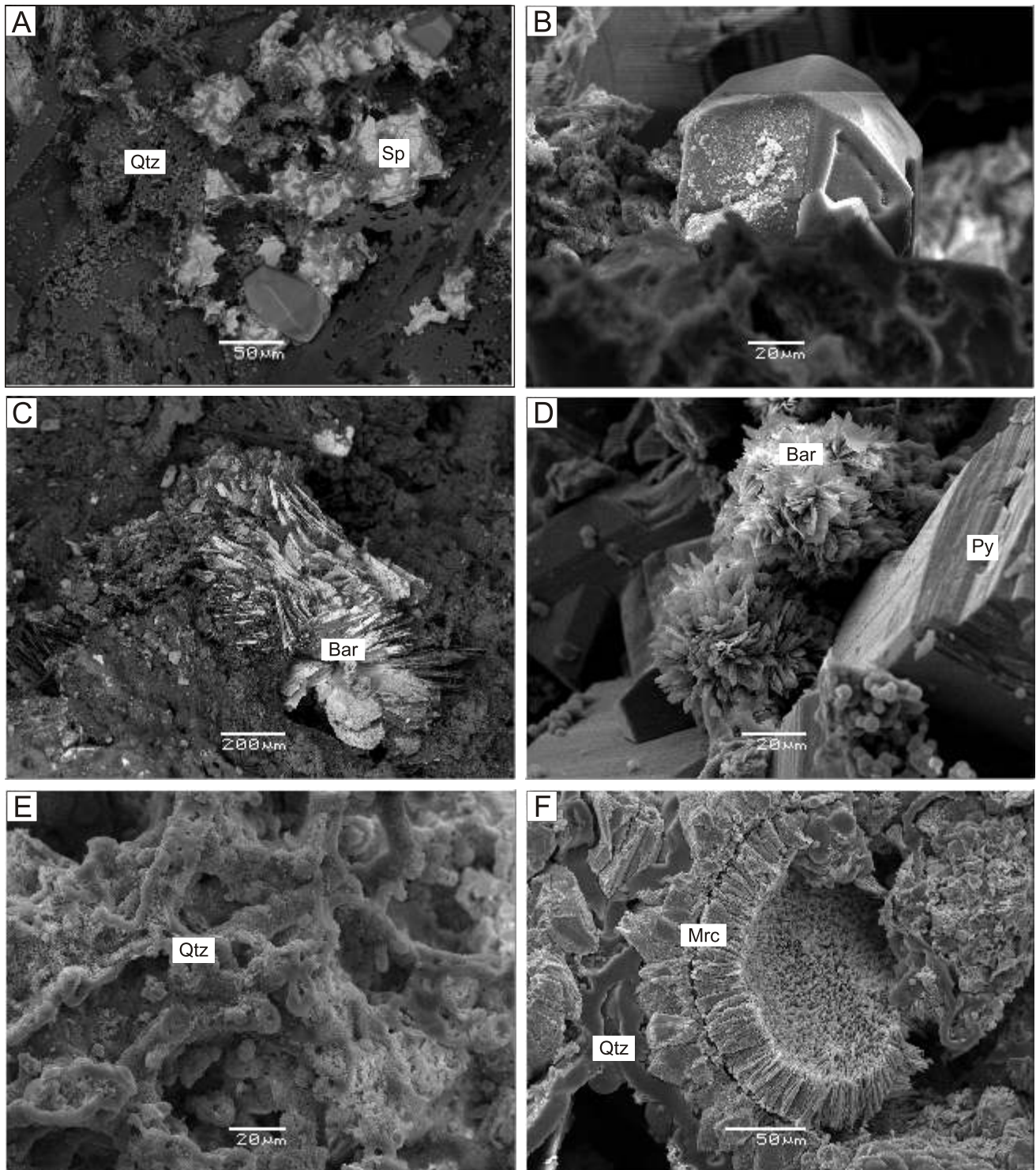
Fig. 10. Morphology of sulphides in the SMS sample studied; electron microscopy images

A – aggregate of sphalerite in the opal groundmass; **B** – euhedral crystal of native sulphur; **C** – aggregate of platy barite (Bar) filling pores within opal; **D** – radial aggregate of barite on the walls of euhedral pyrite crystals; **E** – massive aggregate of opal; **F** – opal coating on the radial aggregates of marcasite; for other explanations see Figure 8

and marcasite (Figs. 7A–D, 8A–C and 11). Trace amounts of chalcopyrite were documented by the XRD method in two samples (VMS-1 and VMS-4; Fig. 11). The marcasite occurs in small amounts, mainly as an incrustation on the walls of late vents cutting the massive polymetallic ore (Figs. 6 and 8A).

The other ore minerals determined include sphalerite (Figs. 6D, 8D–F and 9F), chalcopyrite (Figs. 6A, 7D, 8D and 9E), and covellite (Fig. 8F), which replace minute grains of the chalcopyrite that crystallised on the surface of sphalerite crystals.

Comparison of the mineralogical composition of sea-floor polymetallic sulphide deposits with analysed SMS

Mineral	Back-arc deposits	Mid-ocean ridge deposits	Examined sample SO39 169GTVB
Fe-sulphides	pyrite, marcasite, pyrrhotite	pyrite, marcasite, pyrrhotite	pyrite, marcasite
Zn-sulphides	sphalerite, wurtzite	sphalerite, wurtzite	sphalerite
Cu-sulphides	chalcopyrite, isocubanite	chalcopyrite, isocubanite	chalcopyrite
Silicates	amorphous silica, phyllosilicates	amorphous silica, phyllosilicates	amorphous silica, phyllosilicates
Sulphates	anhydrite, barite	anhydrite, barite	barite
Pb-sulphides	galena, sulphosalts	nd	galena
As-sulphides	orpiment, realgar	nd	nd
Cu-As-Sb-sulphides	tennantite, tetrahedrite	nd	nd
Native metals	native gold	nd	nd

Mineralogical data from back-arc and mid-ocean ridge deposits according to Hertzig *et al.* (2002); nd – minerals that were not recognized in SMS
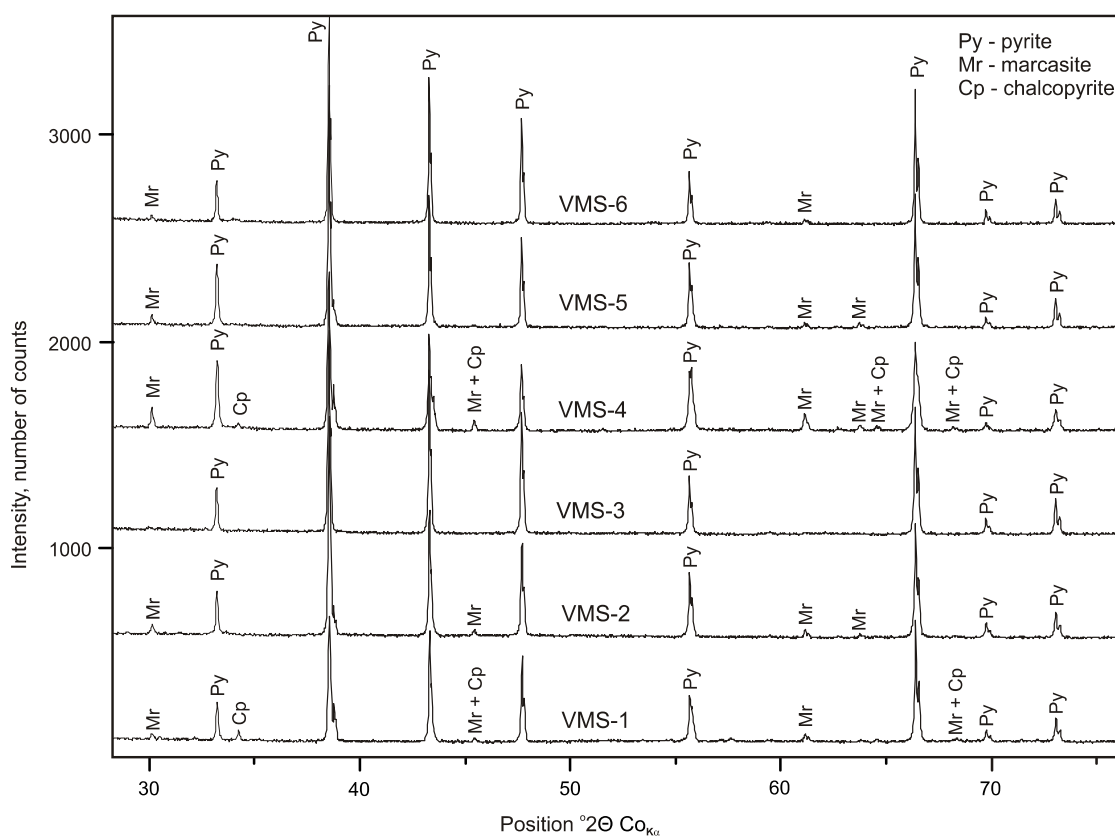

Fig. 11. XRD diffraction patterns of sulphide samples (from VMS-1 to VMS-6) taken from different parts of the SO39 169GTVB sample

The texture of the sulphide ore shows features typical of open space growth. The characteristic feature of the SMS studied are numerous channels, filled mainly by iron sulphides and sphalerite, which generally occur in the youngest channels recognized in the sample (Figs. 6A–D and 8A). The pyrite and marcasite grains usually occur as automorphic grains (Figs. 7A and 8C) and/or their complex aggregates (Fig. 9) that have overgrown thin vent walls (Fig. 7B). The walls of the vents consist of silica minerals and barite. These minerals are common in the spaces between sulphides (Fig. 10).

During scanning electron microscope investigations (SEM), an extensive variety of minerals have been observed (Figs. 9 and 10). This encompasses sulphide minerals, native elements (Fig. 10B) as well as oxidized forms, mostly sulphates (Fig. 10C, D). Pyrite and marcasite that represent primary sulphides occur predominantly in the form of automorphic crystals (Fig. 9A–D). In several cases they are encrusted with amorphic spherical forms of silica, which are often clustered in grape-like aggregates overgrowing sulphide crystals (Figs. 9A–D and 10A). Additionally, pyrite crystals

are covered by Fe-hydroxides and/or sulphates to different extens (Fig. 4). In several cases pyrite has overgrown goethite aggregates (Fig. 8B) which document two contemporaneous processes: crystallisation of sulphides (I) and growth of goethite as a consequence of oxidation of pyrite. Sphalerite (Fig. 9C) is secondary to Fe-sulphides and commonly forms automorphic crystals which are also covered by silica crusts (Fig. 9F). Minor chalcopyrite crystals are also locally over-grown by silica (Fig. 9E). The only native element found is sulphur (Fig. 10B), usually associated with Fe-sulphates. It is plausible that sulphur originated due to oxidation of the primary Fe-sulphides.

Beside sulphides, which constitute the major component of the sample investigated, minerals characteristic of hydrothermal fluid activity were also found. Among these barite in the form of spherical aggregates dominates (Fig. 10C, D). Barite is associated with silica which forms skeletal overgrowths on earlier mineral generations (Fig. 10E). These irregular and porous constructions, spherical in section are characterized by the presence of internal voids which correspond credibly to fluid migration channels. These investigations allowed the tracing of successive stages of mineral crystallisation in the samples examined. This is especially pronounced in the case of marcasite (Fig. 10F). The first stage of its crystallisation is characterized by radial textures, developed during spontaneous nucleation and crystallisation of marcasite from hydrothermal solutions oversaturated with respect to Fe^{2+} and S^{2-}. The second stage is represented by coarse-grained textures, developed during the final stages of crystallisation from undersaturated hydrothermal solutions.

GEOCHEMISTRY OF THE POLYMETALLIC SO39 169GTVB: RESULTS OF ICP-OES STUDY

Chemical analyses of the sample show minor variations in the contents of major elements. The chemistry of this sample is controlled by the dominance of Fe-sulphides (mainly pyrite), in contrast to the average mineralogical compositions of SMS sulphides from different tectonic settings that can be enriched in chalcopyrite, galena and sphalerite, as indicated by average analyses of representative samples (Table 2). The concentration of Fe, Cu, Zn, Pb, and S in the SO39 169GTVB sample ranges from 35.9–39.7 wt.%, 0.1–0.9 wt.%, 0.2–4.8 wt.%, 0.09–0.01 wt.% and 41.6–47.94 wt.%, respectively (Tables 2 and 3). The trace element contents vary widely (see Table 2), therefore correlation between concentrations of trace elements and the mineralogy of the samples studied, determined by means of XRD, was not possible (see Fig. 11 and Table 3). The other economically important metals are represented by Co and Ni that vary from 48.41 to 135.78 ppm and from 4.31 to 8.12 ppm, respectively.

The SMS from the Galápagos Rift Zone revealed high contents of the noble metals including Au, Ag and Pt. The studied SMS is characterized by Au contents that range from 7.24 to 0.3 ppm. The concentration of Ag is highly scattered in the sample studied; in sample VMS-3 up to 24.6 ppm of Ag were determined (Table 3). The samples from VMS-1 to VMS-5 contain extraordinarily high Pt contents which vary from 0.09–0.35 ppm. The Pt concentration in the VMS-6 sample was below the detection limit (<0.01 ppm). Taking into account the amount of Au (in ppm) relative to the sum of Cu, Zn and Pb (in wt.%), the sample examined may be included within the Au-rich VMS deposits (Poulsen and Hannington, 1995).

T a b l e   2

Comparison of the average bulk chemical composition of sea-floor polymetallic sulphide from different tectonic settings (Hertzig et al., 2002) with the sample analysed from the Galápagos Rift system Zone (selected elements)

Element content	Intra oceanic back-arc ridges	Intra continental back-arc ridges	Mid-ocean ridges	VMS-1	VMS-2	VMS-3	VMS-4	VMS-5	VMS-6
[wt.%]									
Pb	0.4	11.8	0.1	0.03	0.05	0.02	0.08	0.02	0.01
Fe	13.0	6.2	26.4	35.9	39.2	39.7	36.7	37.8	37.0
Zn	16.5	20.2	8.5	1.5	0.2	0.2	4.8	4.4	0.2
Cu	4.0	3.3	4.8	0.9	0.1	0.0	0.4	0.2	0.2
Ba	12.6	7.2	1.8	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
[ppm]									
As	845	17500	235	199.36	292.68	197.65	323.66	263.79	168.31
Sb	106	6710	46	53.14	52.78	50.49	56.23	53.75	53.13
Ag	217	2304	113	b.d.l.	b.d.l.	24.60	b.d.l.	b.d.l.	b.d.l.
Au	4.5	3.1	1.2	4.56	7.24	0.3	3.78	5.16	b.d.l.

b.d.l. – concentration below detection limits

T a b l e   3

Chemical composition of examined SMS samples

Element content	Sample					
	VMS-1	VMS-2	VMS-3	VMS-4	VMS-5	VMS-6
[wt.%]						
Fe	35.90	39.16	39.71	36.70	37.85	37.01
S	43.33	46.26	47.94	45.32	45.87	41.60
[ppm]						
Na	174.94	390.98	136.52	599.16	668.62	1078.45
K	60.69	70.15	43.52	114.45	104.01	134.15
Mg	72.14	74.43	66.72	92.95	100.34	140.04
Ca	65.19	50.55	39.82	91.99	74.75	153.60
Sr	0.26	5.80	0.28	2.07	0.85	2.00
Ba	2.78	2.47	3.86	2.47	2.88	3.81
Ti	0.22	0.30	0.00	0.13	0.00	0.86
V	21.72	24.71	24.16	23.14	24.16	24.93
Cr	5.39	7.28	5.90	6.43	5.18	5.35
Mo	0.00	11.74	0.00	62.25	41.70	95.46
Mn	165.02	130.11	105.54	224.43	48.33	29.60
Co	135.28	68.97	92.85	48.41	107.66	135.73
Ni	7.24	7.92	8.12	5.98	4.31	6.77
Pt	0.29	0.30	0.09	0.35	0.35	<0.01
Au	4.56	7.24	0.30	3.78	3.82	0.00
Ag	<0.01	<0.01	24.60	<0.01	<0.01	<0.01
Cu	8915.99	506.88	390.05	4403.72	2246.19	1904.17
Zn	15447.64	2084.081	1734.49	47697.21	44524.47	2502.47
Cd	98.29	10.63	4.29	329.08	173.83	5.46
Al	62.00	24.32	28.67	59.67	75.06	165.60
Si	45.31	50.80	23.12	65.06	70.66	57.53
Pb	296.91	495.94	192.58	783.85	245.56	113.65
P	4847.85	401.27	312.57	2675.55	1550.60	1725.80
As	199.36	292.68	197.65	323.66	263.79	168.31
Sb	53.14	52.78	50.49	56.23	53.75	53.13
Bi	86.32	45.10	41.54	52.48	38.54	46.56

DISCUSSION – GENETIC REMARKS AND THE ECONOMIC IMPORTANCE OF THE SMS FROM THE GALÁPAGOS RIFT ZONE

High contents of some metals in SMS, especially Au, Pt, Ag, Cu, Zn, Pb, makes hydrothermal sulphides a potentially very attractive source for future marine mining. Currently deposits at six locations (Atlantis II Deep, Escanaba Trough, Middle Valley, TAG, seamount at 13°N and southern Explorer Ridge) are within the size range of deposits which could be mined in favorable economic conditions. Among the sea-floor massive sulphide deposits discussed the best potential sites for mining include also those of Galápagos Rift Zone. The most promising ore-bearing zone is located in water depths between 2600 to 2850 m and belongs to the Exclusive Economic Zone (EEZ) of Ecuador (Herzig et al., 2002). It is necessary to emphasize that the ore bodies in this area are sharply distinguished from other rocks and are limited in form and size. The resources of individual SMS deposits often exceed 100 million tons (Herzig et al., 2002). Detailed studies on the northern part

of the Juan de Fuca Ridge has indicated about 8–9 million tons of sulphide ore (Zierenberg et al., 1998) and in the active TAG mound (Atlantic Ocean) there are about 2.7 millions tones of sulphide ore above the sea-floor and about 1.2 million tons of sulphides in the sub-sea-floor stockwork (Hannington et al., 1998). Nautilus Minerals Inc. (Nautilus) company is developing an exploration project called Solwara 1 Seafloor Massive Sulphide Project in the Bismarck Sea, Papua New Guinea (PNG), at a depthwater of 1600 m. This deposit is characterized by a copper grade more than ten times higher than in a typical land-based porphyry copper mine, as well as significant contents of gold (Smith, 2009). The mineralogical, petrographical and geochemical composition of the SMS investigated corresponds with results obtained from earlier studies of the Galápagos Rift.

The high content of the noble metals, including the PGE, influences the economic evaluation of the SMS deposits. These elements are critical to the evaluation of the small volume deposits that dominate among SMS deposits recognized to date. The contents of the selected noble and base metal compared with chemical data from other SMS deposits is shown in Figure 12. Geo-
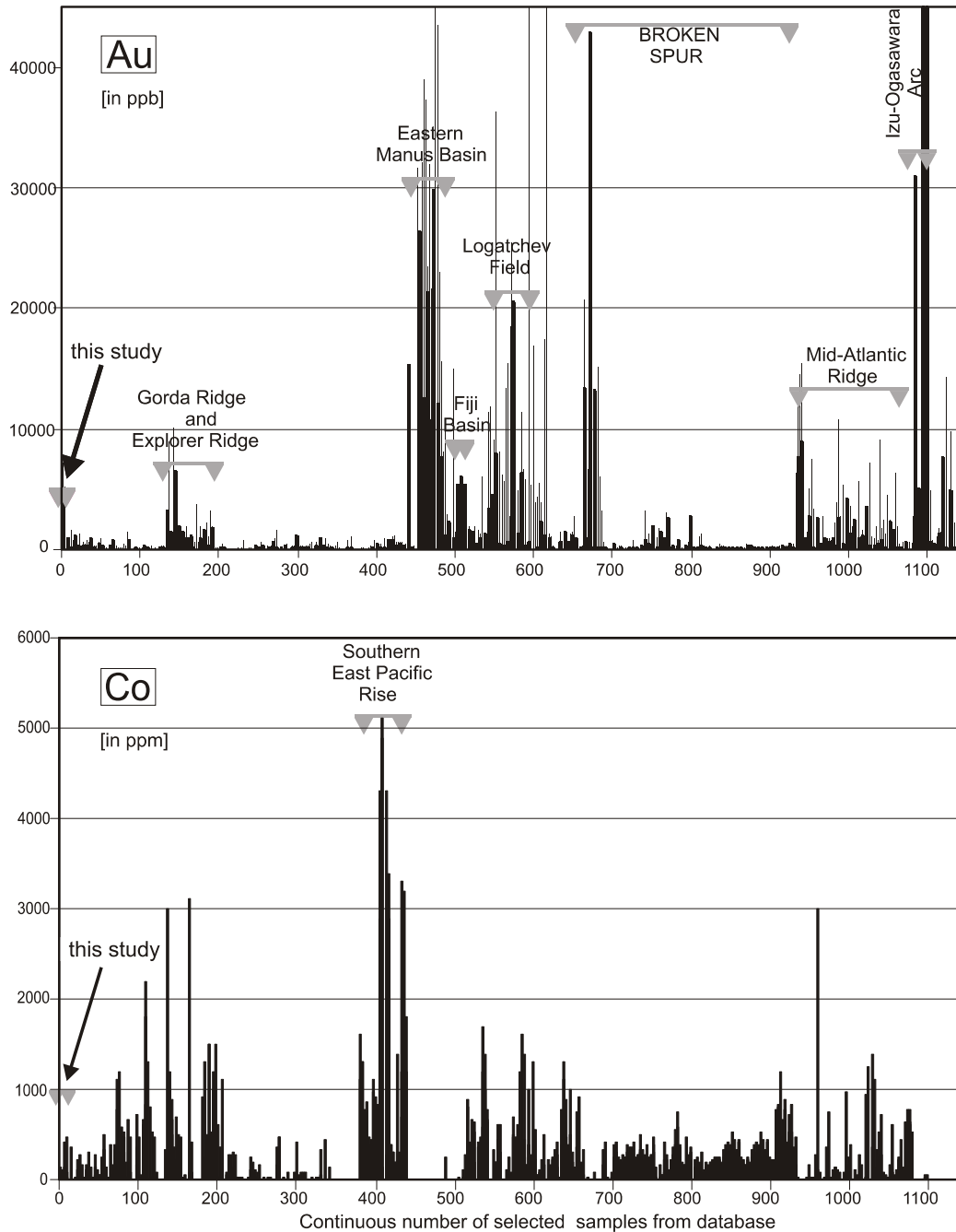
Fig. 12. Comparison of the Au and Co concentrations in the SO39 169GTVB sample examined with concentrations of these metals in known modern sea-floor sulfides

Data for these diagrams were taken from the Central Data Redepository maintained by the International Seabed Authority's (http://www.isa.org.jm/en/home)

chemical data for a comparative study were taken from the databases of the Central Data Redepository maintained by the International Seabed Authority (http://www.isa.org.jm/en/home). The complete dataset hosted at this service comprise 1556 records with chemical analyses of genetically varied PMS types. Samples with determined Au contents were extracted (1138 records). Geochemical data were taken from numerous papers focusing on the geochemistry of PMS from the North and South Pacific, the North Atlantic and Indian Ocean regions (source

http://www.isa.org.jm/en/home, and for detailed localities see Fig. 1). The samples analysed represent different parts of massive sulphides, of active or inactive parts of sulphide mounds and/or chimneys, and each is characterized by a distinct mineral composition.

The concentration of Au, Co and Pt obtained in the sample studied were used to show the potential economic value of the SMS from the Galápagos Rift. The concentration of Au in the polymetallic sulphides from the Galápagos Rift range from

3 to 1550 ppb (http://www.isa.org.jm/en/home). The Au content determined in the SO39 169GTVB sample varies from 0.3 to 7.24 ppm, while the Co content is typical of most recent sea-floor sulphides (Fig. 12). Extremely high Au contents, exceeding 20 ppm, were reported in the SMS's from the Easter Manus Basin, Logatchev Field, Broken Spur and Isu-Ogasawara Arc (Fig. 12). The average gold content determined in the sea-floor sulphides from mid-ocean ridges ranges from 0.2 to 2.6 ppm (Hannington *et al*., 1991; Herzig and Hannington, 1995). The latest investigations of the Ashadze-2 hydrothermal field on the Mid-Atlantic Ridge indicate values up to 8.5 ppm of Au (Cherkashov *et al*., 2008, 2010). The highest Au content, ranging from a few up to 30 ppm, was identified in sea-floor sulphides from back-arc spreading centres, where calc-alkaline volcanics (andesite, dacite and rhyolite) dominate on the sea-floor (Herzig *et al*., 1993; Herzig and Hannington, 1995). High concentrations of Au have also been reported from numerous VMS deposits where concentration of the gold usually ranges from 30 ppm to 0.1 ppm (Vikentyev *et al*., 2004; Galley *et al*., 2007). The Au concentration documented in the SO39 169GTVB sample permits inclusion of the SMS from the Galápagos into the group of sea-floor sulphides which show significant enrichment in Au (Fig. 12). From this point of view SMS from Galápagos may be of interest for future prospecting.

The high Au content may be related to the concentration of the Au in the source rocks, as occurs in a higher Au content in a back-arc setting. The highest contents of gold are reported in low-temperature active hydrothermal moulds, sulphide mounds are dominated by sulphides associated with barite and amorphous silica (Herzig and Hannington, 1995; Hannington *et al*., 1995). In contrast the internal parts of sulphide mounds, dominated by pyrite, isocubanite and chalcopyrite, have significantly lower Au contents, comparable to Au concentration (up to 200 ppb) in hot hydrothermal waters from black smoker chimneys (Hannington *et al*., 1991). The highest Au contents, exceeding 40 ppm (Fig. 12) may document remobilisation (hydrothermal reworking) of gold during intensive venting of the central part of the sulphide mounds by hot hydrothermal waters (for details see Ohmoto and Skinner, 1983; Hannington *et al*., 1995). The other processes responsible for controlling Au concentration are the oxidation state of hot fluids and later oxidation of sea-floor sulphides by oxygen-rich seawater (Herzig and Hannington, 1995). The analysis of different parts of the sulphide sample show considerable variation in gold content (Table 3). These geochemical data together with the texture of the ores (Figs. 4 and 5), where numerous fossil vent channels are well-preserved, strongly support the hydrothermal reworking model of Hannington *et al*. (1995) as an important factor controlling Au content in recent SMS deposits.

Data related to PGE contents in SMS are scarce. From the 1138 analyses collected in the NOAA (National Oceanic and Atmospheric Administration) databases, only 36 samples have been analysed for these elements in amounts exceeding detection limit. The concentration of Ir, Pd and Pt are in the ranges of 3–33, 1–5 and 93–410 ppb, respectively. Generally the concentrations of PGE are rather low, and usually do not exceed a few ppb (Crocket *et al*., 1973; Crocket, 1990; Cave *et*

al., 2003; Pašava *et al*., 2004, 2007). This range of concentrations is also reported from VMS deposits which are ancient analogues of modern SMS deposits (Pan and Xie, 2001; Vikentyev *et al*., 2004). A review of current publications shows that few studies focused on the concentrations of PGE in recent sea-floor sulphides. The most recent reports include Pašava *et al*. (2004, 2007), and references therein, where anomalously high concentrations of PGE were documented. These authors (*op. cit.*) described extremely high Pd and Pt contents in the SMS from the PACMANUS hydrothermal field that reach up to 145 and 356 ppb, respectively. High contents of Pd were also determined in the SMS from the Logatchev hydrothermal field (from 16 to 227 ppb) and varying concentrations of Pd from 1 to 59 ppb in the Turtle Pits (a hydrothermal field on the Mid-Atlantic Ridge). However, individual analyses show extremely high Pd contents of up to 202 ppb (Pašava *et al*., 2007). Extremely high concentrations of Pd, of up to 1000 ppb, were determined in the Zn-rich sea-floor sulphides in the TAG hydrothermal field on the Mid-Atlantic Ridge (Crocket, 1990). Our results show extremely high concentrations of Pt in the sulphides from the Galápagos Rift Zone. The Pt content, varying from 90 to 350 ppb (Table 2), are in the range of the highest concentrations determined in modern sea-floor sulphides.

The SMS examined from the Galápagos Rift Zone shows high noble metal (Au and Pt) enrichment. The concentrations of Au and Pt determined in the SMS examined significantly influenced the economic evaluation of these deposits. A future study of modern sea-floor sulphides elsewhere may show significantly higher noble metal concentrations, comparable to the ranges documented in some VMS deposits where up to 6.04 ppb Pt and up to 0.29 ppb Ir were documented (Pan and Xie, 2001). Our current study shows unequivocally that high concentrations of PGE in SMS may be one of the critical factors which will decide the economic value of recent sea-floor sulphides.

SUMMARY

The SO39 169GTVB sample examined has simple mineralogical compositions which correspond to massive sulphides known from the sea-floor elsewhere. From the mineralogical point of view the sample represents the distal part of a sulphide mound, that crystallised at lower temperatures in comparison to the internal high-temperature part of the sulphide mound. The texture of the ore documents multiple flows of hydrothermal fluids and/or waters, which are responsible for varying concentrations of noble metals determined in different parts of the sample. Despite extensive mineralogical investigations, no noble metal minerals were identified. The lack of correlation between the occurrence of sphalerite and chalcopyrite suggests that pyrite and/or marcasite are major carriers of noble metals. The form of their concentration may be either dispersed in the structure of sulphides or as "invisible" submicroscopic intergrowths inside sulphides and/or in other minerals such as Fe-oxides or Fe-Mn-hydroxides. The high concentrations of Au and Pt, documented in the material examined determine

high economic values of these recent sea-floor sulphides. Our preliminary results from the Galápagos Rift combined with the scarce data related to the concentrations of PGE (see Pašava *et al.*, 2004, 2007) known from the literature and data stored in databases maintained in the NOAA unequivocally display a gap in knowledge as regards PGE concentrations in SMS deposits. High concentrations of PGE in SMS may be one of the critical factors that will determine the economic value of recent sea-floor sulphides.

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