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## Chemical composition of submarine massive sulphides in the Lucky Strike hydrothermal field

### Características geoquímicas dos sulfuretos maciços submarinos do campo hidrotermal do Lucky Strike

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**Sumário:** No segmento Lucky Strike, localizado na Crista Média da região dos Açores, existe um dos maiores campos submarinos hidrotermais activos do nosso planeta. Para além da existência de dezenas de chaminés hidrotermais expelindo fluidos a elevadas temperaturas (~325 °C), uma área significativa com cerca de 1 km<sup>2</sup> é constituída por um substrato rochoso formado por placas hidrotermais e sulfuretos maciços polimetálicos. Durante a campanha oceanográfica TTR-10, oito locais desta área foram amostrados resultando um conjunto de rochas que foram incluídos em três grupos: 1) fragmentos de chaminés hidrotermais, com a estrutura original preservada; 2) fragmentos irregulares de sulfuretos maciços sem estruturação (“sulphide rubble”); 3) Fragmentos de rochas basálticas com variáveis graus de alteração hidrotermal. Neste trabalho apresentam-se as principais características químicas (elementos maiores e traço) e mineralógicas destes três tipos de rochas.

**Palavras-chave:** Crista Média Atlântica, elementos maiores e traço, mineralogia principal, tipos de sulfuretos maciços

**Key words:** Mid-Atlantic Ridge, major and trace elements, main mineralogy, massive sulphide types

#### 1. Main features of Lucky Strike hydrothermal field

The Lucky Strike Hydrothermal Field is located approximately 400 km south of the Azores on the Lucky Strike segment of the Mid-Atlantic Ridge (MAR), which is located between 37°00' and 37°35'N. Active and inactive hydrothermal deposits are distributed over a wide area of about 1 km<sup>2</sup> at shallow depths (1630-1730 m), and about 30 vent sites have been identified. Numerous inward-dipping normal faults cut the area and could serve as outflow conduits for fluids (Ondreas *et al.* 2009). Hydrothermal venting is located on extensive deposits of sulphide rubble and hydrothermally cemented hyaloclastite deposits both east and west of a central lava lake (e.g. Humphris *et al.* 2002; Ondreas *et al.* 2009). Hydrothermal discharge occurs as high temperature black smokers, which can reach temperatures of around 325°C.

The hydrothermal deposits consist of a series of sulphide mounds with numerous inactive chimneys that cover large areas of the summit of the Lucky Strike volcano. These deposits include iron- and copper-rich massive sulphides and a typical hydrothermal slab structure (hydrothermally cemented breccia) which forms flat and layered deposits. The mounds can be up to 20 m in diameter and rise several meters above the surrounding seafloor (Barreyre *et al.* 2012). The

most vigorous high-temperature venting chimneys are dominated by chalcopyrite and anhydrite, with minor iron and zinc sulphide minerals, as well as amorphous silica (e.g. Langmuir *et al.* 1997). The spatial distribution and inferred volume of the sulphide rubble suggest that hydrothermal activity has occurred over a long period of time, and that active tectonism, which has clearly influenced the structural development of the central topographic high as it grew, has resulted in a relatively continuous disaggregation of sulphide structures and mass-wasting of the hydrothermal debris.

#### 2. Chemical and mineralogical data for Lucky Strike hydrothermal materials

During the TTR-10 cruise, thirty-five different areas of the Lucky Strike field were sampled using a tv-grab, but only eight sampling stations provided hydrothermal rocks, which were included in three distinct groups: 1) black smoker chimney fragments, with original shape preserved; 2) sulphide rubble fragments; 3) rocks having variable hydrothermal alteration degree.

The chimneys fragments include two different subtypes: a) Cu-rich chimneys and b) Ba-Zn chimneys. The first subtype has a typical mineralogical zonation with chalcopyrite at the inner and at the bottom of the structures and anhydrite at the outer part. They

are very enriched in Cu (20.1-27.4 wt%) and Fe (36.3-52.7 wt%), which are the two most important metallic major elements in these chimneys. The Zn concentrations are below 0.1%. The rare elements, which are critical for high-tech industry and could be enriched in some submarine massive sulphides, are present in very low concentrations (Table 1). These black smoker chimneys are essentially conduits for the escape of high-temperature end-members hydrothermal fluids. The rock fragments collected have a concentric zonation reflecting the sequence of mineral precipitation – an early assemblage of chalcopyrite, pyrrhotite and/or isocubanite (only trace amounts for these two minerals) and anhydrite at high temperatures, followed by pyrite, marcasite and sphalerite at lower temperatures. The chalcopyrite-lined orifices and the outer anhydrite-rich wall constitute characteristic features that distinguish many black smoker vents from other chimney structures.

The Ba-Zn chimneys are primarily composed of variable amounts of barite, very enriched in sphalerite and small amounts of pyrite, marcasite and chalcopyrite (amorphous silica may occur in variable amounts). This mineralogy is expressed, compositionally, in very high concentrations of Zn (20.0-41.4 wt%) and Ba (11.9-28.0 wt%) but lower Fe (2.1-6.1 Wt%) and Cu concentrations (0.1-4.7 wt%). Silica values range from 3,5 to 11.6 wt% (comparatively, Cu-rich chimneys show SiO<sub>2</sub> < 0.62 wt%). In terms of trace element composition, both types of chimneys are indistinguishable, with a slightly increase in Pb and Sb contents in the Ba-Zn chimney types. These chimneys are considered to expel fluids having lower temperatures than the Cu-rich chimneys. They are quite porous and are contain several channels of different diameters. They have complex shapes that could reflect a change in the growth from multiple vent orifices at the base, to a narrower vent at the top. These structures rarely have a central, dominating fluid conduit, and the diffuse flow of fluid through the chimneys is usually via a porous network of interconnecting channels.

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The massive sulphide rubble forms a group of old chimney fragments (without any preserved structure) and, possibly, derived from deposits exposed and later eroded by tectonic movements, which are very frequent in this type of tectonic environment. The sub-types of sulphide rubble were considered based on the relative amounts of Cu, Zn and Fe (Table 1). The Cu-rich rubble stands out for presenting higher concentrations in some of the elements critical for high-tech industry, including Pb, Mo, Ge, Sb and Tl. The rubble samples are essentially made of pyrite and chalcopyrite, but sphalerite is also present (in the Cu+Zn rich types). Barite occurs frequently as transparent euhedral crystals in vacuoles closely associated with sphalerite and is present in variable amounts, reflecting the great Ba contents variation observed among the three types of rubble. In the third type of hydrothermal rocks considered here, only the slabs were analysed. They are predominantly siliceous (~48 wt%), and having only three other elements with concentrations higher than 1%: Al (~ 4 wt%), Fe (27.2 wt%) and S (20.7 wt%). This type of slab represents the hydrothermal rock with the highest degree of silicification, having pyrite as the main metallic mineral disseminated in the matrix (traces of chalcopyrite were also identified).

Tab. 1. Types and chemical compositions of Lucky Strike submarine massive sulphides and hydrothermal slabs.

	Chymneys		Sulphide Rubble			Slab
	Cu-rich	Zn-rich	Cu rich	Cu+Zn rich	Fe rich	
<b>wt%</b>						
Cu (%)	20.1-27.4	0.1-4.7	0.42-0.97	4.0-9.6	0.01-0.20	0.22
Zn (%)	0.04-0.09	20.0-41.4	0.03-0.67	6.1-6.7	0.03-0.08	0.01
Fe (%)	25.4-36.9	1.5-4.3	26.8-43.1	24.1-28.6	40.1-42.2	19
<b>(ppm)</b>						
Ag	1.5-16.7	0.6-5.4	1.1-8.7	<0.5	<0.5	<0.5
Ba	108-3873	11.9-28.0*	24-18120	172-6980	121-24190	412
Bi	<0.1	<0.1	0.1-1.2	<0.1	<0.1	0.5
Co	68-135	37-55	17-319	127-132	74-86	147
Ga	36-71	15-82	2-88	<1	<1	6
Ge	59-87	33-78	1-87	15-22	1	3
In	10.6-20.4	1.8-20.3	0.2-21.3	<0.1-0.2	<0.1-0.2	0.2
Mo	9-73	35-82	10-65	>100	24-80	14
Ni	<20	<20	<20	<20	<20	30
Pb	36-71	53-206	5-436	390-421	36-45	7
Sb	7-39	54-144	1-37	17-34	0.6-2.3	0.7
Sc	2-3	<1	2-3	<1	<1	10
Tl	<0.05	<0.05	0.1-1.0	0.15-10.6	<0.05-0.2	0.34
V	23-59	7-21	18-48	118-126	<5-27	71
REY(T)	0.1-0.7	3.8-6.1	0.1-35.6	<0.4	<2.3	24.5
* values in wt%						