Types of Sulphides in Mantle Xenoliths from the Catalan Volcanic Zone (NE Spain)

/ ERZIKA CRUZ* (1), GUMER GALÁN (1), MERCÈ FERNÁNDEZ-ROIG (1), V. OLIVERAS (1), F.J. MARTÍNEZ (1)

(1) Departament de Geologia, Facultat de Ciències, Universitat Autònoma de Barcelona, Carrer dels Til·lers / Av. de l'Eix Central, 08193 Bellaterra- Barcelona (Spain)

INTRODUCTION

Base metal (Fe, Ni, Cu) sulphides (BMS) appear as accessory microphases in mantle rocks. They capture chalcophile and highly siderophile elements, the Platinum-group elements included, all of them providing crucial insight on mantle processes, such as partial melting, refertilization and metasomatism (Lorand et al., 2013). In addition, BMS are useful to date earlier mantle depletion with the Re-Os geochronometer: this radiogenic system is less susceptible to be perturbed by later metasomatic processes than the conventional geochronometers that rely on lithophile elements hosted by silicates (Harvey et al., 2010).

This abstract includes the first results on BMS in mantle xenoliths enclosed in basaltic rocks from the Neogene-Quaternary Catalan Volcanic Zone (CVZ), in NE Spain (Oliveras and Galán, 2006). Our aim is to establish the amount of BMS in the main types of these xenoliths, the relationships of sulphides with silicates and oxides, the BMS mineral associations, compositions and subsolidus evolution. For such a purpose, the sulphides were observed under transmitted and reflected light microscope, and on backscattered electron images obtained with a scanning electron microscope (a Zeiss EVO-SEM of the Servei de Microscopia, Universitat Autònoma de Barcelona, provided with an energy dispersive spectrometer for semi-quantitative analyses). Also, quantitative major element analyses were performed with a CAMECA SX50 microprobe, in the Serveis Cientificotècnics of the Universitat de Barcelona.

GEOLOGICAL SETTING

The CVZ is part of the Neogene-Quaternary volcanism in the Iberian Peninsula (Ancochea, 2004). The volcanism in this zone is alkaline, within-plate type, and crops out scattered over an area of ca. 700 square kilometers, in the province of Girona. The main volcanic rocks are basanites, leucite basanites and alkali basalts, with subordinate trachytes (Lopez Ruiz and Rodriguez Badiola, 1985), which appear as lava flows, necks, strombolian volcanoes and pyroclasts in three sub-zones: L'Empordà, La Selva and La Garrotxa. These sub-zones are Neogene-Quaternary basins, limited by a NW-SE and NE-SW fracture system, caused by the rift-type extensional tectonic that affected the western Mediterranean since the Miocene (Martí, 2004).

The mantle xenoliths are off-craton type (Galán et al., 2011), mainly composed of anhydrous spinel lherzolites and harzburgites, with rare olivine websterites (Oliveras and Galán, 2006; Bianchini et al., 2007). Amphibole or phlogopite are the only accessory minerals in a few peridotites and pyroxenites (Galán et al., 2011). The lherzolites and harzburgites are interpreted as residues of mantle partial melting (Galán et al., 2008; Galán and Oliveras, 2014), which later were enriched in trace elements by metasomatism. The most widespread metasomatism is of alkaline-carbonatitic type that affected especially the harzburgites. Olivine websterites are interpreted as earlier cumulates from alkaline mafic magmas related to those causing the metasomatism.

PETROGRAPHY OF THE STUDIED XENOLITHS

Fifteen xenoliths were selected, most of them among those previously studied (Galán et al., 2008, 2011). All come from La Banya del Boc and Canet d'Adri volcanoes in La Garrotxa sub-zone. The selected samples are ten lherzolites, three harzburgites and two olivine websterites. Amphibole or phlogopite are accessory minerals in one lherzolite, one harzburgite and in the two websterites. Lherzolites show three main microstructures: protogranular, porphyroclastic and equigranular. Microstructures of harzburgites and websterites are protogranular. All selected harzburgites are trace element enriched by metasomatism, but most of the selected lherzolites are not. Finally, a few lherzolites include pyrometamorphic textures, such as coronae around pyroxenes and interstitial microveins or pockets, composed of either broken xenocrystals or microcrystals in a basaltic matrix or glass.

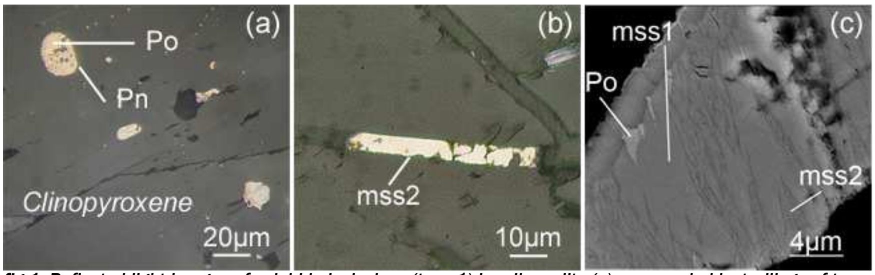

fig 1. Reflected light images of sulphide inclusions (type 1) in a lherzolite (a), surrounded by trailings of type 2 sulphide droplets, and of an intergranular sulphide grain in a harzburgite (b). Backscattered electron image of flame structures between mss1 and mss2 in a type 1 sulphide (c).

TEXTURAL TYPES OF SULPHIDES AND

palabras clave: Sulfuros, Lherzolitas, Harzburgitas, Piroxenitas	key words: Sulphides, Lherzolites, Harzburgites, Pyroxenites

* corresponding author: Erzika.Cruz@uab.cat

MINERAL ASSOCIATIONS

BMS grains are more frequent in lherzolites (15-108 grains) than in harzburgites (21-43) and websterites (11-15). No clear relationships were observed between the different microstructural types of lherzolites and the BMS abundance. Four textural types of sulphide grains are observed: (1) inclusions in silicates and spinel (15-70 µm in size); (2) trails of small droplets (5 µm) following healed microfractures that often radiate from type 1 grains (Fig.1a); (3) interstitial anhedral to euhedral crystals (15-50 µm), often with elongate shape (Fig. 1b); and (4), local anhedral crystals in relation with pyrometamorphic textures (5-30 µm). These textural types are typical of similar mantle xenoliths elsewhere (e.g., Szabó and Bodnar, 1995). Types 1 and 3 grains are equally common in lherzolites, whereas type 3 is the most frequent type in harzburgites. Most sulphide grains are polyphasic. The mineral associations in all types are dominated by two low-temperature monosulphide solid solutions (mss1 and mss2) (Fig. 1c), with pentlandite (Pn) ± pyrrhotite ± Cu-rich sulphides. Alteration to Fe-hydroxide or goethite can affect both types 1 and 3.

SULPHIDE COMPOSITIONS

The mss1 and mss2 are differentiated from Po by showing Ni content> 5 wt%, but mss2 is richer in Ni (25-40 wt%) than mss1 (15-35 wt%). The mss1 would be equivalent to the monoclinic sulphide Fe_7S_8 and the mss2 to the hexagonal sulphide Fe_9S_{10}. The metal/sulphide (M/S) ratio in mss1 is 0.80-0.90, whereas in mss2 is 0.90-1.10. The compositions of mss1 in type 1 and 3 grains are similar, but in type 4 sulphides, related to pyrometamorphic textures, mss1 is Ni-enriched with respect to the former. Pyrrhotite is rare and has M/S between 0.80-0.90. The Ni content in pentlandite is between 32-35 wt% and the M/S ratio is greater than 1.13. The main composition of Cu-rich sulphides is within the intermediate solid solution (iss) range (Fe wt%: 28.7-33.1; Cu wt%: 29.2-33.6%; Ni wt%: <5%), with Cu/Fe ratio close to 1 and M/S ratio between 1.00-1.04.

DISCUSSION AND CONCLUSIONS

The BMS are more abundant in lherzolite than in harzburgite and websterite xenoliths from the CVZ. Four textural types of sulphides are distinguished, all with mineral associations dominated by low temperature monosulphide solid solutions. Late BMS formed by interaction with host basaltic rocks show distinctive Ni-enriched compositions

The mineral associations are characteristic of sulphides quenched at high temperature: they would have been exsolved from high temperature monosulphide solid solution (MSS). Microprobe analyses, obtained with a 50 µm beam diameter, indicate earlier bulk MSS compositions in equilibrium with a Ni-enriched sulphide melt at ca. 1000 °C (Craig and Kullerud, 1969). However, none of the sulphide parageneses register temperatures over 300-200°C (Craig, 1973). Therefore, they would have been reequilibrated at post-eruptive subsolidus conditions, within the host lava.

There are at present two main hypothesis on the origin of BMS in off-craton mantle xenoliths: (i) the MSS would be residual, formed from "blebs" of sulphide melts trapped within restitic minerals, during melt depletion events and (ii), sulphides would be precipitated later from percolating melts, enriched in volatiles and incompatible trace elements, acting as metasomatic agents (Lorand et al., 2013 and references therein). Both generations of BMS could co-exist (Harvey et al., 2010). In the studied case, the fact that BMS are more frequent in lherzolites than in harzburgites, and that lherzolites are less affected by the alkaline-carbonatitic metasomatism than harzburgites, would be in favour of the first hypothesis. However, the distribution of Ni between olivine and MSS does not reflect equilibrium in all lherzolites, which has been used as an argument in favour of a metasomatic origin for the sulphides (Lorand and Grégoire, 2006).

ACKNOWLEDGEMENTS

This study benefited from the MINCINN (MEC) project CGL2011-26700.

REFERENCES

Ancochea, E. (2004): El vulcanismo Neógeno peninsular. In "Geología de España", J.A. Vera ed. Sociedad Geológica de España-Instituto Geológico y Minero de España, Madrid, 671-672.

Bianchini, G., Beccaluva, L., Bonadiman, C., Nowell, G., Pearson, G., Siena, F., Wilson, M. (2007): Evidence of diverse depletion and metasomatic events in lherzolite-harzburgite mantle xenoliths from the Iberian plate (Olot, NE Spain): Implications for lithosphere accretionary processes. Lithos, **94***, 25-45. DOI: 10.1016/j.lithos.2006.06.008.*

Craig, J.R. (1973): Pyrite-Pentlandite assemblages and other low temperature relations in the Fe-Ni-S system. Am. J. Sci., **273***, 496-510.*

—, —. Kullerud, G. (1969): Phase relations in the Cu-Fe-Ni-S system ant their applications to magmatic ore deposits. In "Magmatic Ore Deposits", H. D. B. Wilson ed. Econ. Geol. Monography, 4, 343-358.

Galán, G., Oliveras, V., (2014): Melting and Metasomatism in the lithospheric mantle of NE Spain: Geochemical and Sr-Nd isotopic characteristics. Chem. Geol., **376***, 75-89. DOI:* 10.1016/j.chemgeo.2013.12.011

—, —, —, —, Paterson, B. (2008): Types of metasomatism in mantle xenoliths enclosed in Neogene-quaternary alkaline mafic lavas from Catalonia (NE Spain). In: "Metasomatism in Oceanic and Continental Lithospheric Mantle", M. Coltorti, M. Grégoire eds. Geological Society, London, Special Publication 293:121-153. DOI: 10.1144/SP293.7.

—, —, —, —, —, — , (2011): Thermal and redox state of the subcontinental lithospheric mantle of NE Spain from thermobarometric data on mantle xenoliths. Int. J. Earth Sci., **100***, 81-106. DOI: 10.1007/s00531-009-0503-8.*

Harvey, J., Gannoun, A., Burton, K. W., Schiano, P., Rogers, N.V., Alard, O.. (2010): Unravelling the effects of melt depletion and secondary infiltration on mantle Re-Os isotopes beneath the French Massif Central. Lithos, **74***, 293-320. DOI: 10.1016/j.gca.2009.09.031.*

Martí, J., (2004): La región volcánica de Gerona. In "Geología de España", J.A. Vera ed. Sociedad Geológica de España-Instituto Geológico y Minero de España, Madrid, 672-675.

López Ruiz, J., Rodríguez Badiola, E. (1985): La Región Volcánica Mio-Pleistocena del NE de España. Estud. Geol-Madrid, **41***, 105-126.*

Lorand, J.P., Grégoire, M., (2006): Petrogenesis of base metal sulphide assemblages of some peridotites from the Kaapvaal craton (South Africa). Contrib. Mineral. Petrol., **151***, 521-538. DOI: 10.1007/s00410-006-0074-7.*

—, —, Luguet, A., Alard, O., (2013): Platinum-group element systematics and petrogenetic processing of the continental upper mantle: A review. Lithos, **164-167***, 2-21. DOI: 10.1016/j.lithos.2012.08.017.*

Oliveras, V., Galán, G., (2006): Petrologia y mineralogia de los xenolitos mantélicos del volcán de la Banya del Boc (Girona). Geogaceta, **40***, 107-110.*

Szabó, C.S., Bodnar, R.J., (1995): Chemistry and origin of mantle sulfides in spinel peridotite xenoliths from alkaline basaltic lavas, Nógránd-Gömör Volcanic Field, northern Hungary and southern Slovakia. Geoch. Cosmoch. Acta, **59***, 3917-392.*