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Alunite veins *versus* supergene kaolinite/halloysite alteration in the Lagoa Salgada, Algares and S. João (Aljustrel) and S. Domingos massive sulphide deposits, Iberian Pyrite Belt, Portugal

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ABSTRACT
Keywords: Alunite veins; supergene kaolinisation; Lagoa Salgada; Aljustrel; S. Domingos; Iberian Pyrite Belt; PIMA SWIR.

The occurrences of alunite veins associated with the Iberian Pyrite Belt (IPB) Lagoa Salgada, Algares, S. João and S. Domingos massive sulphide orebodies is described and correlated with the supergene kaolinite/halloysite alteration observed. The characterization of the hydrothermal and supergene alterations was based on detailed mapping, extensive use of the PIMA short wave infrared spectrometer, petrography, XRD and microprobe. The supergene kaolinisation decreases with depth and forward the massive sulphides (until 90m below the paleo-weathering surface at L. Salgada). The original volcanic textures are usually preserved and the replacement of hydrothermal phyllosilicates by clays is common. At L. Salgada, Western Algares, S. João and S. Domingos up to 5 cm thick alunite veins were identified. Some of these show strong structural control and intense deformation. The vein assemblage includes alunite, natroalunite, minamiite, natrojarosite, jarosite and wavellite. At L. Salgada these veins occur below the paleo-weathering level, in textural equilibrium with unoxidized massive sulphides. The alunite veins occur independently of kaolinisation intensity and are clearly earlier. The presence of Al-bearing sulphates on IPB VMS ores is coherent with very low pH and circulation of oxidising fluids, at low temperature. Current research is aimed at understanding the origin of this alteration: paleo- actual-weathering or a component of high-sulphidation in the hydrothermal system.

Introduction

The strong kaolinisation of volcanic rocks and gossans is well known in the IPB and considered an useful exploration guide for massive sulphides, e.g. Lagoa Salgada, Las Cruces, Lousal and Caveira (Oliveira *et al.* 1998, 2001; Matos *et al.* 2000; Doyle 1996). In the Algares, S. João, S. Domingos, Lousal and Caveira open pits intense kaolinisation can be identified near gossanized massive sulphides by typical whitish-coloured outcrops.

The occurrence of major alunite veining associated with the Lagoa Salgada, Algares, S. João and S. Domingos massive sulphide orebodies was recently identified and compared with the supergene *kln/hal* alteration observed close to gossans in the mentioned orebodies. The first findings, restricted to Lagoa Salgada boreholes (Matos *et al*. 2000), were further completed with geological mapping at outcropping orebodies. The PIMA II portable spectrometer was largely used in this work, as quick and sample-friendly tool for the characterization of sulphates, clays and phyllosilicate assemblages. Current research is aimed at understanding the origin of the alunite veins: weathering (modern or ancient) or, alternatively, a component of high-sulphidation in the hydrothermal system.

Methodology

Hydrothermal and supergene alteration mapping was conducted at the 1/2000 scale at Lagoa Salgada, Algares and S. Domingos. More than 400 rock samples from these VMS deposits, and from the S. João, Lousal and Caveira orebodies were spectrally analysed at CREMINER, with the PIMA II spectrometer. The short wavelength infrared analysis of volcanic lithologies, gossans and pyritic ores, from outcrops and boreholes, was done on fractured and sawed surfaces of dry rocks. The Pima View software (Horsfall 1999) was used to extract parameters such as mineral identification, wavelengths and depths of absorption features, from hull quotient corrected spectra. Selected samples were analysed in detail with the electron microprobe at IGM and by XRD at CREMINER.

Mode of occurrence of alunite veins and supergene kaolinite/halloysite alteration at Lagoa Salgada, Algares, S. João and S. Domingos massive sulphide deposits

- **Lagoa Salgada**

The Lagoa Salgada deposit is a polymetallic massive sulphide body discovered by SFM (IGM) in 1992, on the NW sector of the IPB (Matos *et al*. 2000, Oliveira *et al.* 1998, 2001), under 128 m of sediments of the Sado Tertiary Basin. This sub-vertical deposit is covered by a more than 10 m thick paleo-gossan, which extends downward into a

paleo-supergene enrichment zone and massive sulphides, intersected for more than 60 m. Placed on the overturned limb of an anticline, the orebody is bound underneath by a major fault, locally accompanied by large-scale kaolinisation. Genetically related to the orebody there occurs a large hydrothermal system characterised by *chl+prl*, *chl+ser+carbonates*, *qtz+ser* and *ser* assemblages. The precipitation of pyrophyllite (Relvas *et al.* 1994) and fluid inclusion studies in stockwork chlorite assemblages (Jaques & Noronha 2001) suggest lower pH, at temperatures in excess of 400ºC. Either of these would greatly facilitate higher concentrations of transition metals in the hydrothermal fluid and extreme leaching of the volcanic rocks. The deposit shows a large variation of metal contents, including significant values of Zn, Pb, Sn, Cu, Hg, As, Sb, Au and Ag. Two main volcanic units are recognized (Matos *et al.* 2000): Upper Volcanic Unit (UVU) – intermediate to intermediate-felsic porphyritic volcanics and Lower Volcanic Unit (LVU) - acid porphyritic volcanics with abundant quartz phenocrysts and metric intercalations of volcaniclastic breccias. Recent U-Pb isotope studies (Barrie *et al.* 2002) give identical ages of 356,21±0,73Ma and 356,41±0,8Ma for UVU and LVU volcanic units.

The *kln/hal* supergene alteration is intensely developed near the massive sulphides and proximal stockworks of the UVU (from NW to SE: LS22, LS14, LS11, LS9, LS10, LS4, LS5 and LS6 boreholes) and quartz-sericite metavolcanics with semi-massive sulphides of the LVU (LS 23, LS26 and LS28 boreholes). The intensity of the kaolinisation decreases in depth and extends downward the paleo-oxidation level, until 90-100m below. This ante Palaeogene acid weathering alteration is represented by pervasive matrix alteration of the volcanic rocks. The original volcanic textures are usually preserved and the replacement of hydrothermal phyllosilicates by clays is common. The kaolinisation increases at the main fault zones, probably due to the underground water circulation along these tectonic structures. A similar model is described for the Las Cruces deposit (Doyle 1996). XRD studies detected kaolinite $Al_2Si_2O_5(OH)_4$ and greenalite $Fe_3SiO_5(OH)_4$ in the matrix of volcanic rocks. Halloysite $Al_2Si_2O_5(OH).nH_2O$ was also identified by PIMA.

At Lagoa Salgada centimetric to millimetric alunite veins were identified at the footwall and at the hanging wall of the massive sulphides, respectively at LS4, LS6, LS9, LS10 and LS11, LS14, LS15 boreholes (Matos *et al.* 2000). The spatial distribution of the veins is consistent with a very strong structural control along a NNW-SSE corridor recognized for 400 m, closely associated with the principal thrust faults. The alunite veins depict regularly ptigmatic folds and compression micro fractures, predominant in the earlier veins generations. At the LS14 borehole the veins present a consistent stockwork shape. The veins occur from the paleo-topographic surface to 90m below the paleo-weathering level, in textural equilibrium with unoxidized massive sulphides. XRD study detected alunite $KAl_3(SO_4)_2(OH)_6$, natroalunite $NaAl_3(SO_4)_2(OH)6$, minamiite $(Na, Ca)_{1-x}Al_3(SO_4)_2(OH)_6$. Wavellite $Al_3(PO_4)_2(OH)_3$ $5H_2O$ was identified by PIMA. Veins petrography shows comb structures and late polygonal structures (with *cellular shape)* between fold hinges zones. The nucleus of these polygons and of late globular structures present Na rich sulphates comparing with the veins (K rich sulphates).

- **Algares & S. João (Aljustrel)**

The Algares deposit is one of the two outcropping orebodies of the Aljustrel mining centre. It was intensely mined since Roman times mainly in the supergene enrichment zone. The deposit is located in the SW Aljustrel anticline (Leitão 1997, inc. ref.) and formed by the *Western Algares*, *Central Algares* and *Eastern Algares* massive sulphide horizons with NW-SE direction and 75ºNE inclination (see Fig. 1). The Algares alteration mapping permit a better understanding about the unoutcropping Lagoa Salgada alunites veins and kaolinisation systems. The good exposure of the Algares gossans was essential for the first Al-sulphate veins identification on surface, which occur in both sides of the *Western Algares* horizon. The veins depict regularly ptigmatic folds and compression micro fractures. Along more than 550m of the eastern sector of *Western Algares*, close to the Viana shaft, was recognized a Al-sulphate corridor characterized by a 2m-3m thick layer of multiple generations of centimetric white and locally light pink-brown alunite veins, mainly sub-vertical and sub-concordant with the principal cleavage. Deformed discordant NE-SW veins were also identified, near the compressors house. By XRD was detected natroalunite $NaAl_3(SO_4)_2(OH)6$, alunite $KAl_3(SO_4)_2(OH)_6$, minamiite $(Na, Ca)_{1-x}Al_3(SO_4)_2(OH)_6$. Wavellite $Al_3(PO_4)_2(OH)_3$ $5H_2O$ was also identified by PIMA. At S. João open pit Al- and Fe- sulphate veins were recognised. By XRD was possible the identification of natrojarosite $NaFe_3(SO_4)_2(OH)_6$ and jarosite $KFe_3(SO_4)_2(OH)_6$.

- **S. Domingos**

The S. Domingos abandoned mine is located near the Portuguese-Spanish border, and was intensely exploited between 1857 and 1966 (Carvalho 1971). Kaolinisation is locally observed near the fault zones identified in the northern side of the open pit. At S. Domingos the discordant and planar alunite veins are predominant and associated with NE-SW, E-W and WNW-ESE late faults and fractures (see Fig. 2). The veins occur in a large variety of lithologies: chloritized volcanics, black shales, silicified volcanics, diabases and volcanic breccias. At the SE and deeper sector of the open pit the alunite veins present a stockwork shape, consistently observed in more than 15m. They are hosted in a volcaniclastic polymict breccia, poorly affected by *kln/hal* alteration. The preliminary results, obtained only by PIMA II data, indicate also the presence of barite associated with alunite.

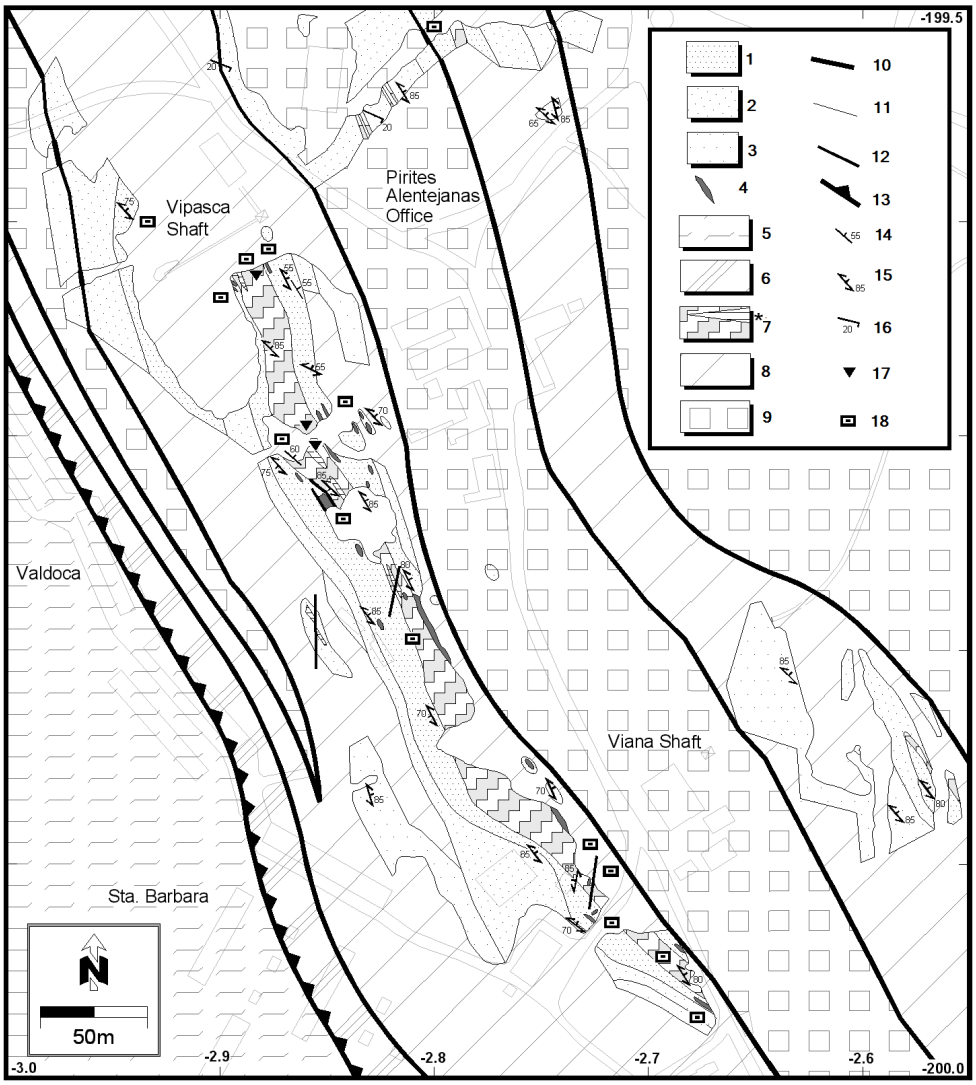

Figure 1 – Geological map of the Algares gossans (Aljustrel), with supergene Kaolinite/halloysite alteration (1 – pervasive; 2 – strong; 3 – weak) and outcropping alunite veins (4). Geology adapted from Leitão 1997: 5 - Flysch Mértola Fm. (Up. Visean); Volcano-Sedimentary Complex (Up. Famenian – Up. Visean): 6 – Paraíso Fm.; 7 – Gossan with cherty horizons (*); 8 – "Mine Tuff" volcanics; 9 – "Megacryst Tuff" volcanics. 10 – Geological limit; 11 – Alteration limit; 12 – Fault; 13 – Thrust fault; 14 – Bedding; 15 – Cleavage; 16 – Diaclase; 17 – Gossan breccias; 18 – PIMA II SWIR measure. Hayford-Gauss coordinates in km.

Discussion and conclusions:

The hydrothermal and weathering alteration mapping done in the four IPB deposits shows a good correlation between alunite veins occurrence and pervasive low pH supergene *kln/hal* alteration (see Table I).

Table I - Occurrence mode of alunite veins and supergene kaolinite/halloysite.

	Lagoa Salgada	**Algares & S. João**	**S. Domingos**
Host rocks	Massive sulphides and proximal stockworks, felsic volcanics	Massive sulphides and felsic volcanics (black shales at S. João)	Proximal stockworks, felsic and basic volcanics, black shales
Supergene kaolinitization	Well-developed, associated with massive and semi-massive sulphides. Decreases in depth. Palaeogenic age.	Well-developed, associated with massive sulphides. Decreases forward the ore horizon. Holocenic age.	Local, associated with proximal stockworks and fault zones. Decreases in depth. Holocenic age.
Alunite veins	Generally with ptigmatic folds, locally with stockwork shape. Observed below hydrostatic level. Independent from *kln* intensity.	Generally deformed (ptigmatic folds and compressive micro-fractures), mainly concordant with cleavage.	Discordant and planar shape are predominant. Millimetric veins are locally folded. Independent from *kln* intensity. Stockwork shape observed.
Tectonic control of *al*	Very strong, NNW-SSE Al-sulphate corridor detected in 400m.	Very strong, NW-SE (Algares) Al-sulphate corridor detected in 550m.	Strong, mainly NE-SW, WNW-ESE and E-W late fractures.

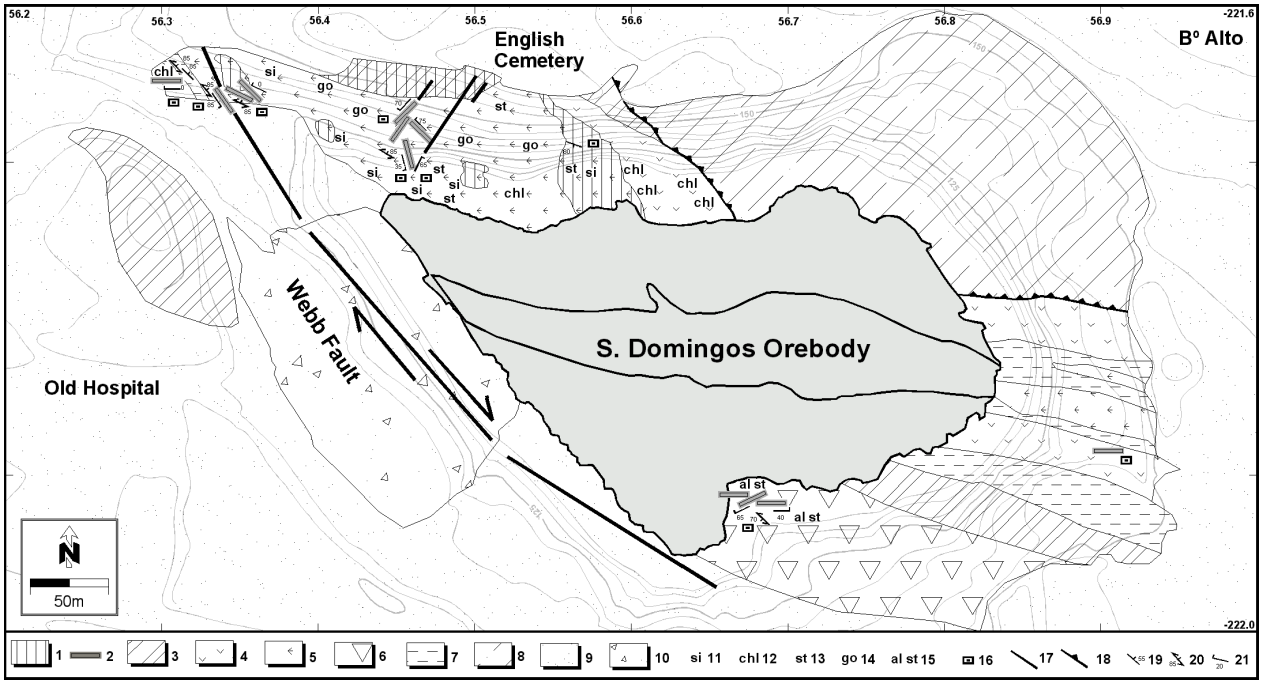

Figure 2 – Geological map of the S. Domingos open pit with supergene Kaolinite/halloysite alteration (1) and outcropping alunite veins (2). Geological limits: personal and unpublished mapping (Mason & Barry 1953, Webb 1958, MEI 1967, Carvalho 1971, Billinton 1984, 1985) - Volcano-Sedimentary Comp. (Up. Famenian – Up. Visean): 3 – Haematitic shales; 4 – Diabases, basic volcanics; 5 – Porphyritic coherent felsic volcanics; 6 – Coarse polymict felsic volcaniclastic breccia; 7 – Black shales; Phyllite-Quartzite Gr. (Up. Devonian) – 8 – Shales and quartzites. 9 – Tailings. 10 – Slag tailings. Hydrothermal alteration: 11 – silica; 12 – chlorite; 13 – pyrite stockwork (± gossanized). 14 – Gossans. 15 – Alunite veins (stockwork type) 16 - PIMA II SWIR measure; 17 - Fault; 18 – Thrust fault; 19 – Bedding; 20 – Cleavage; 21 – Diaclase. S. Domingos orebody projected at 122m mining level. Open pit water level: 107m. Hayford-Gauss coordinates in km.

However, in the deepest and unoxidized sectors of the S. Domingos and L. Salgada deposits, alunite veins are present in a very poorly kaolinitized hosted volcanic rocks. This evidence and the strong deformation and structural control of the alunite veins, observed at L. Salgada and Algares, indicate that alunite veins predates the supergene *kln/hal* alteration and probably has an different origin (hypogenic?). The occurrence of alunite group minerals, which is restricted to veins, is coherent with very low pH and oxidant fluids circulation, at low temperature. Current research is aimed at understanding the origin of this alteration: paleo- actual-weathering or a component of high-sulphidation in the hydrothermal system. Isotope studies will be useful to support these ideas. On the other hand, the occurrence of alunite veins demonstrates a complex geological history after the formation of some of the IPB orebodies. Intense acid fluid circulation correlated with metamorphism, tectonics and acid weathering alteration could be responsible for the ore enrichment observed in several VMS deposits (e.g. Au and Ag high grades at L. Salgada and Algares).

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