

SPHALERITES COMPOSITION AND SULPHIDATION STATE OF POLYMETALLIC EPITHERMAL QUARTZ VEINS AT SORIPESA PROSPECT AREA, SUMBAWA ISLAND, INDONESIA

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Abstract

The Soripesa prospect area is located at Maria village, Wawo district, Bima region in the eastern part of Sumbawa Island, Indonesia. This area is related with Cenozoic Calc-alkaline volcanic inner Banda-Sunda Arc. There have five main polymetallic epithermal quartz veins in the Soripesa prospect area, namely, Rini vein, Jambu air vein, Dollah vein, Merpati vein, and Arif vein. The dominant lithology is a lithic-crystal tuff of andesitic and dacitic composition and bedded limestone. Elemental compositions of sphalerites were analysed using Scanning Electron Microscope with energy-dispersive X-ray (SEM-EDX) method to identify their environment of ore deposition. Detected elements in sphalerite are Zn (63.48 wt.%), S (33.3 wt.%), Fe (1.04 wt.%), Ga (0.7 wt.%), Ge (0.54 wt.%), Cd (0.7 wt.%), and Ag (0.2 wt.%). Au content is below detection limit in all sphalerite. Ga/Ge ratios of sphalerites geothermometry indicate that the formation temperatures of sphalerite are between 180°C and 240°C. Based on the Fe mole %, sulfur activity (a_{s_2}) is a little higher and between 10^{-10} – 10^{-11} . Sphalerite are found in pyritic ore fields and low temperature condition. Sulfur activity and formation temperature plots show that ore-forming processes are formed under intermediate sulphidation state of epithermal system.

Keywords: Soripesa prospect area, Tectonic setting, Mineralization, Sulphidation state

Introduction

The Soripesa prospect area is located at Maria village, Wawo district, Bima regency, West Nusa Tenggara Province, Sumbawa Island, Indonesia. The research area is related with the eastern part of Sunda-Banda arc (Neogene). Sunda-Banda arc is the longest in Indonesia, extending from North Sumatra through Java, Bali, Lombok, and Sumbawa, to east Damar (Carlile and Mitchell, 1994). The prospect area is mainly occupied by andesitic and dacitic volcanoclastic rocks and small portion of Tertiary bedded limestones. There have five quartz veins in the Soripesa prospect area including Arif vein, Dollah vein, Jambu Air vein, Merpati vein, and Rini vein, trending nearly north-south. The main ore minerals are chalcopyrite, azurite, malachite, sphalerite and galena forming as polymetallic epithermal quartz veins.

Epithermal Au and Ag deposits of both vein and bulk-tonnage styles may be broadly grouped into high-, intermediate-, and low-sulphidation types based on the sulphidation states of their hypogene sulfide assemblages (Sillitoe and Hedenquist, 2003). In high-sulphidation epithermal deposits, the sulphidation stage ranges from high for copper-rich enargite-bearing assemblages to intermediate for the later gold-rich tennantite-tetrahedrite+pyrite assemblages, with similarities to and overlap with the base metal veins. In intermediate-sulphidation epithermal deposits, the full range of intermediate-sulphidation states is represented by the assemblage pyrite+chalcopyrite+sphalerite+tetrahedrite (Einaudi, et al., 2003). The purpose of this paper is to identify the environment of ore deposition, ore genesis, and ore forming processes of polymetallic epithermal quartz veins at Soripesa prospect area, East Sumbawa, Indonesia.

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Tectonic setting and regional geology

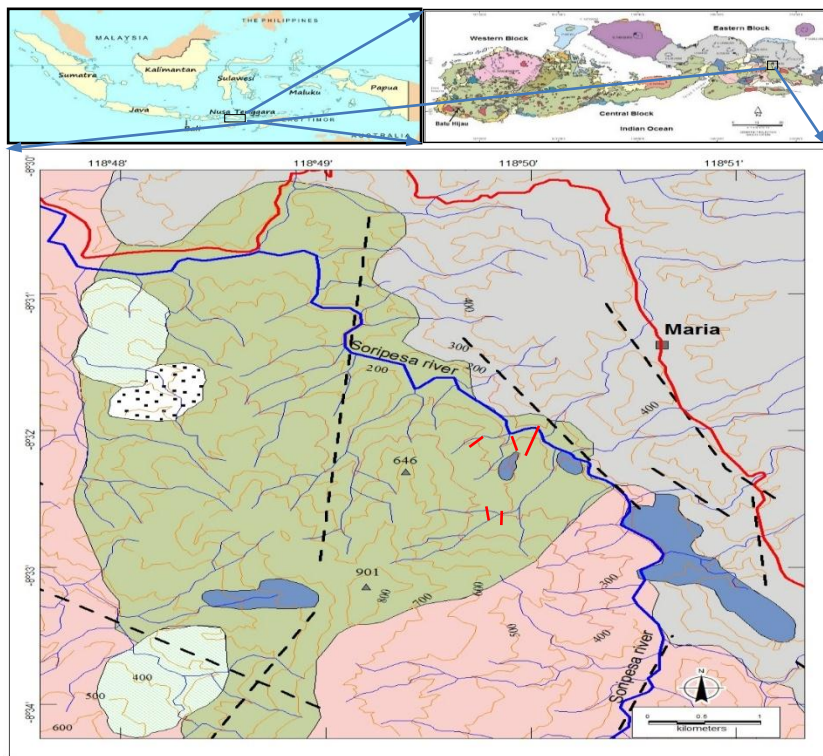
The Sumbawa Island forms as a part of the Cenozoic Calc-alkaline volcanic inner Sunda-Banda arc, which is still active up to present. Sunda-Banda island arc is a volcanic arc formed by the interaction of plate subduction slab in the form of Indo-Australia with Asian plate. The shape of the island arc is now being modified in the east due to collision with the Australian–New Guinea continental margin, including West Flores to East Sumbawa and Alor (Hamilton, 1979).

The East Sumbawa area is largely underlain by andesitic to basaltic lava and breccia of the Lower Miocene, with intercalations of tuff and limestone, and fresh pyroclastic sequences (Noya, et.al., 2009). This sequence is overlain in parts by dacitic tuff and bedded limestone of the Middle Miocene. These units have been intruded by numerous small to medium bodies in the Middle to Upper Miocene including andesite, dacite, diorite, trachyte and syenite (Fig. 1). A signature type of epithermal and porphyry copper mineralization can be recognized in those rock units.

The northern part of Sumbawa Island is dominated by the eruptive products of the active Tambora and Sangeang volcanoes, comprising of lahar, volcanic bomb and lapilli. Sumbawa Island, regionally, is intersected by NW-SE and NE-SW trending structures. However, the formation of quartz veining, alteration and mineralization at Soripesa Prospect are related to the N-S faulting (Noya, et.al., 2009).

Mineralization

The main vein zones which are associated with precious metals (Au-Ag) and base metals (Cu, Pb, Zn) are Rini, Jambu Air, Merpati, Arif, and Dollah epithermal quartz veins (Figure 4). They are nearly vertical ($>70^{\circ}\text{C}$), 1–16 m thick with individual vein to 1000 m length. The vertical outcrop of Rini vein can be observed in the field and it may reach up more than 200 m. The quartz vein and alteration area have a size of $6.7 \times 4.7 \text{ km}^2$ or ± 3150 hectares (Noya, et.al., 2009). Quartz textures of those veins belong to typical characters of low-sulphidation epithermal system and they can help to identify the morphology of veins such as face controlled and parallel-controlled. These parallel-controlled and face-controlled indicate that the epithermal quartz veins in the Soripesa prospect area are formed at the near surface (Khant, et.al., 2012a). Within the veins, multiphases, vuggy, colloform, bedded to massive textures with chalcocopyrite, galena, sphalerite, malachite, azurite, chalcocite, pyrite, and iron oxide minerals are observed. Weak to moderate clay-pyrite alteration intensively developed in the volcanic rocks, especially in the west side of Soripesa. It could be influenced by NW–SE trending structures and andesite to porphyry dacite intrusive rock. The common alteration minerals in this prospect area are quartz, epidote, chlorite, pyrite, illite, and smectite. Minor amount of other alteration minerals are kaolinite, alunite, rutile, and anatase (Khant, et.al., 2012a). Temperature sensitive minerals include Ca-silicates such as epidote and chlorite (stable above $200\text{--}240^{\circ}\text{C}$), near the base of the epithermal environment. At the edges of the quartz veins develop silica clay-chlorite alteration; outward has changed to chlorite-epidote \pm magnetite as the halo alteration.



EXPLANATION

- Lahar and agglomerate rock unit (Quaternary):* Agglomerate to breccias andesitic volcanics
- Volcanic rock unit (Tertiary-Middle Miocene):* Dacitic volcanoclastics, agglomeratic to breccias gradation to fine-grained tuff
- Limestone unit (Tertiary-Miocene):* Fossiliferous and bedded limestone
- Older volcanic rock unit (Tertiary-Early Miocene):* Andesitic volcanoclastics, agglomeratic to breccias gradation to fine-grained tuff
- Argillic alteration (clay-quartz)
- Propylitic alteration (chlorite-epidote)
- Quartz vein with base metals mineralization (azurite, chalcopyrite, malachite, galena, sphalerite, pyrite)
- Spot high
- River and stream
- Motor road
- Contour (m)
- Fault

Figure 1 Geological map of the Soripesa prospect area (modified after [5]).

Material and Methods

Scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX)

For SEM-EDX analyses, 10 sphalerite minerals in polished sections were used to identify mineral chemistry by using a SHIMADZU SS-550 SEM with a Genesis 2000 energy dispersion spectrometer (EDX) at the Center of Advanced Instrumental Analysis, Kyushu University. SEM-EDX analysis has been conducted on some ore samples such as pyrite, galena, sphalerite, azurite, malachite, iron ore minerals, and some unknown ore minerals for elemental identification and compositional information. It can also detect the content of Ag-Au ratio and other important minor elements. Major and minor element compositions of sphalerite ore minerals in this research area can be also compared with other deposits. Based on the elemental compositions, ore minerals can be estimated and identified their ore genesis, and ore forming processes.

Results and Discussions

Minor Elements in Sphalerite

Sphalerite is one of the most useful indicators of the environment of ore deposition because of its refractory nature, wide distribution in natural environments, and wide range of composition resulting from substitution of Zn by Fe (Misra, 1999). Detected minor elements in sphalerite are Fe (1.04 wt.%), Ga (0.7 wt.%), Ge (0.54 wt.%), Cd (0.7 wt.%), and Ag (0.2 wt.%). Au content is below detection limit in all sphalerite. Table (1) shows the elemental composition (wt.%) of sphalerite minerals. Table (2) shows the elemental composition (at.%) of sphalerite minerals

The cadmium content of sphalerite seems to be independent of the conditions of formation; there is no clear indication of systematic differences in sphalerites from low-temperature and high-temperature deposits (Fleischer, 1956). Jonasson and Sangster (1978) investigated the Zn/Cd ratios of sphalerites from some sulphide ores in Canada and concluded that the Cd contents and Zn/Cd ratios in sphalerites vary with the genetic types of deposit (Table 3). The Zn/Cd ratios (average 93.34) in sphalerite from the Soripesa prospect area are close to Zn/Cd ratios (104-214) of sphalerites from hydrothermal deposits (including volcano-hydrothermal deposits) and skarn-hydrothermal deposits. In low iron content of sphalerite, Cd content is towards higher, and higher iron content of sphalerite lesser cadmium amount.

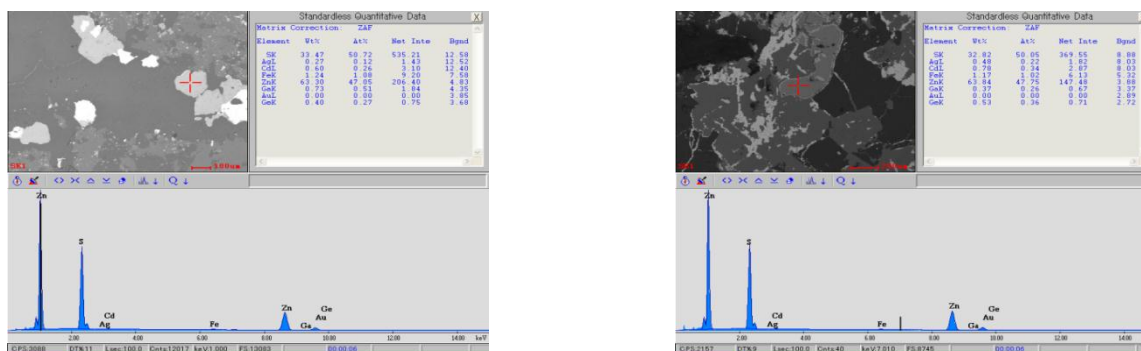


Figure 2 Elemental composition of some sphalerite minerals under SEM-EDX analyses.

Table 1 SEM-EDX analyses of element composition (wt%) of sphalerite minerals.

Element composition (normalized wt%) of Sphalerite minerals										
No.	Samples	Zn	S	Fe	Ga	Ge	Cd	Ag	Au	Zn/Cd
1	Av3-9	62.82	34.14	1.08	0.68	0.29	0.65	0.34	<0.01	96.65
2	Av3-10	63.22	33.81	1.21	0.71	0.54	0.50	<0.01	<0.01	126.44
3	Av3-11	63.30	33.47	1.24	0.73	0.40	0.60	0.27	<0.01	105.50
4	Av3-12	62.29	35.27	0.56	0.65	0.36	0.63	0.25	<0.01	98.87
5	Rvo1-1	64.31	32.62	1.11	0.50	0.48	0.64	0.34	<0.01	100.48
6	Rvo1-2	63.81	33.21	0.93	0.83	0.25	0.71	0.26	<0.01	89.87
7	Rvo1-3	63.38	33.38	0.84	0.59	0.71	0.83	0.27	<0.01	76.36
8	Rvo1-4	64.07	32.00	1.10	0.92	0.65	0.86	0.40	<0.01	74.50
9	Rvo1-5	63.79	32.24	1.17	1.06	0.84	0.77	0.12	<0.01	82.84
10	Mvo4-4	63.84	32.84	1.17	0.37	0.92	0.78	0.48	<0.01	81.85
	Avg	63.48	33.30	1.04	0.70	0.54	0.70	0.27	<0.01	93.34

Table 2 SEM-EDX analyses of element composition (at%) of sphalerite minerals.

Element composition (normalized at%) of Sphalerite minerals									
No.	Samples	Zn	S	Fe	Ga	Ge	Cd	Ag	Au
1	Av3-9	46.48	51.49	0.93	0.47	0.19	0.28	0.15	<0.01
2	Av3-10	46.82	51.05	1.05	0.50	0.36	0.21	<0.01	<0.01
3	Av3-11	47.05	50.72	1.08	0.51	0.27	0.26	0.12	<0.01
4	Av3-12	45.70	52.75	0.48	0.45	0.24	0.27	0.11	<0.01
5	Rvo1-1	48.14	49.78	0.98	0.35	0.32	0.28	0.15	<0.01
6	Rvo1-2	47.56	50.45	0.81	0.58	0.17	0.31	0.12	<0.01
7	Rvo1-3	47.21	50.69	0.73	0.41	0.48	0.36	0.12	<0.01
8	Rvo1-4	48.25	49.13	0.97	0.65	0.44	0.38	0.18	<0.01
9	Rvo1-5	47.90	49.36	1.03	0.75	0.57	0.34	0.06	<0.01
10	Mvo4-4	47.75	50.05	1.02	0.26	0.36	0.34	0.22	<0.01
	Avg	47.29	50.55	0.91	0.49	0.34	0.30	0.12	<0.01

Table 3 Zn/Cd ratios in sphalerites from this research and other deposits.

Type of deposit	Zn %	Cd%	Zn:Cd	Reference
This paper	63.48	0.70	93.34	
Mississippi Valley type	61.10	0.15	398	Jonasson and Sangster (1978)
Alpine type	61.95	0.20	315	Dill (1979)
Volcano-sedimentary Pb-Zn deposit	58.40	0.11	531	Vokes (1976)
Metamorphosed sedimentary Pb-Zn deposit	55.16	0.22	252	Both (1940)

There is general agreement by most workers (Stoiber, 1940 and Fleischer, 1956)) that the gallium content is most likely to be high in sphalerites from low-temperature deposits such as those of Mississippi Valley type and in those from low-temperature quartz veins. In this research, average Ga content (0.7 %) in sphalerites is very high and it means that they may be formed under low temperature condition.

Nearly all of the investigators agree that sphalerite from low-temperature deposits such as those of the Mississippi Valley type tend to be higher in germanium content than those from mesothermal or high-temperature deposits but many exceptions have been noted. In this research, average content of Ge (0.54%) is also very high.

Vaughan and Craig (1997) suggested that a zinc concentrate from a pyritic ore may contain 61-63 wt% Zn, but a concentrate from a pyrite-pyrrhotite ore will often contain only 51-58 wt% zinc and be considerably less valuable. The average content of Zn is 63.48 wt% in sphalerite of this research. It means that sphalerites from this research are related with pyritic ore condition.

Sphalerite Geothermometry

A very interesting recent development is the Ga/Ge geothermometer using sphalerite (Moller, 1985). Ga/Ge can be used to determine temperatures in the source regions of ore solutions and to estimate the degree of mixing of hot parental ore fluids with cool, near surface waters (Evans, 1993). For the study on Ga/Ge geothermometers, we sought geothermometers in the analyzes, obtaining values for Ge and Ga contents in the sphalerites of the study area. 10 samples were simultaneously detected levels for these two elements. The application of these geothermometer results of calculating the logarithm follows:

$$\log [(Ga/Ge) f] \equiv \log [(Ga/Ge) sph] \quad (1)$$

Note that: f - mineraliser fluid; sph - sphalerite.

Determining the values of $\log (Ga/Ge)$ for the analyzes of sphalerite minerals, we obtain the values in the ranges between -0.4 to 1.15. These values are applied to the chart geothermometer Ga/Ge, based on geothermometer of Al/Si, and in this case that of muscovite-chlorite-quartz, given the degree of metamorphism. The chart shows the values of temperatures between 180°C to 240°C. Figure 3 presents the projection of the respective analysis chart that correlates the ratio Ga/Ge with the temperature. This graph is based on geothermometers known systems of Al/Si and published data for reasons of Ga/Ge in many geological systems (Moller, 1985 and 1987).

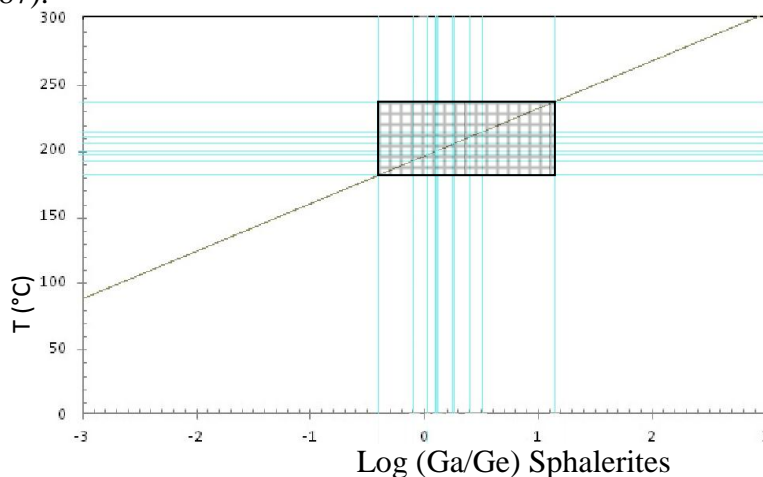


Figure 3 Graph showing the dependence between Ga/Ge ratios in sphalerite and formation temperature. This graph is based on existing Al/Si geothermometers. The musc-chlo-qtz line is the chlorite geothermometer in the Si/Al system (Marquest and Noronha, 2012). Shade area is referred to Ga/Ge ratio (-0.4 to 1.15) and formation temperature (180-240°C).

The results point to low temperatures of formation of the deposit, reaching the values obtained by the method of Ga/Ge between 180°C and 240°C. Marques and Noronha (2012) considers that the presence of Ge is higher in sphalerites that are formed at low temperature. The temperature differences observed between the two geothermometers can be related to the mixing and circulation of fluids late and/or pre-fluid surface Moller, 1985 and 1987). Based on the fluid inclusion data from quartz (host minerals), ranges of homogenization temperature for Merpati Vein is 182°C - 279°C, Rini vein is 185°C -266°C, Dollah vein is 212°C -300°C, Arif vein is 216°C -300°C, and Jambu Air vein is 233°C -297°C (Khant et.al., 2012d).

Sulphur Activity and Sulphidation State

Kullerud (1953) suggested that the FeS content of sphalerite gave a direct measurement of its temperature of deposition. Average Fe content (1.04%) of sphalerite in this research is very low. Mole % FeS in sphalerite is also very low and between 1 – 2%. In Zn-Fe-S of low pressure system, this value (1-2%) falls in pyrite+chalcopyrite field (Fig. 4). Within the pyrite field the decrease in FeS content of sphalerite with increasing sulphur activity (a_{S_2}) is much greater resulting in a close spacing of isopleths near the pyrite-pyrrhotite buffer and in very low FeS contents in sphalerite at high a_{S_2} ($10^{-9} - 10^{-11}$).

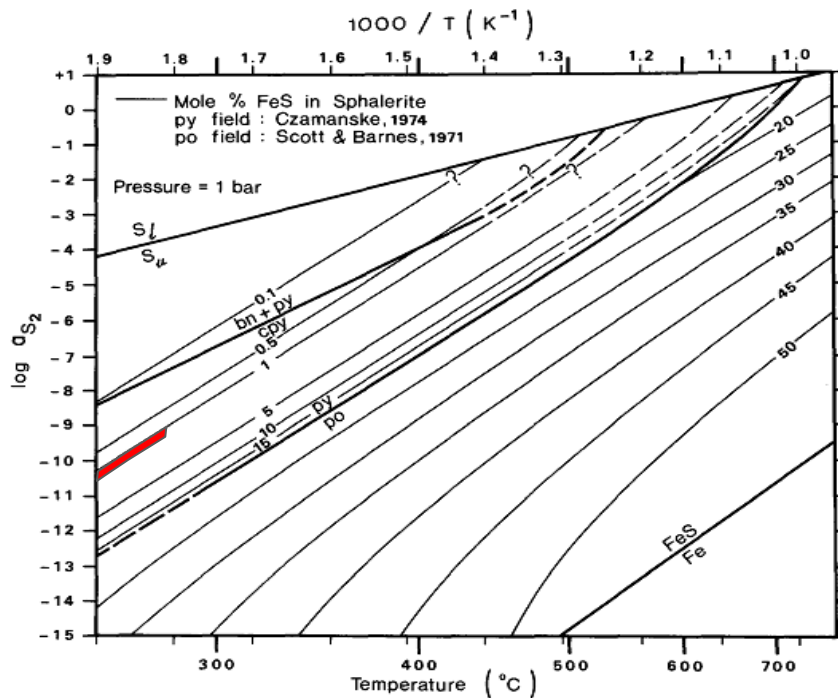


Figure 4 Phase relationships for the Fe-Zn-S system at 1 bar compiled from Barton and Toulmin (1966), Scott and Barnes (1971) and Czamanske (1974) in (Scott, 1983). Red line represents sulfur activity of sphalerite from Soripesa prospect area using Mole % FeS in sphalerite and formation temperature of sphalerite. Abbreviations: bn=bornite; cpy=chalcopyrite po=pyrrhotine; py=pyrite; S_l=liquid sulphur; S_v=sulphur vapour.

In a qualitative sense, it is commonly found that sphalerites formed at high a_{S_2} have a honey yellow to light brown colour with their low FeS contents whereas sphalerites formed at

low a_{S_2} and within the pyrrhotite field are dark brown to black (Scott, 1983). Those factors mean they may be formed in low temperature condition. Based on sulphur activity and temperature, it indicates that plots are fallen in intermediate sulphidation state, pyrite+chalcopyrite field, and magmatic hydrothermal compositional field (Fig. 5). Therefore, epithermal quartz veins at Soripesa prospect area are formed under intermediate-sulphidation state of the fluid condition.

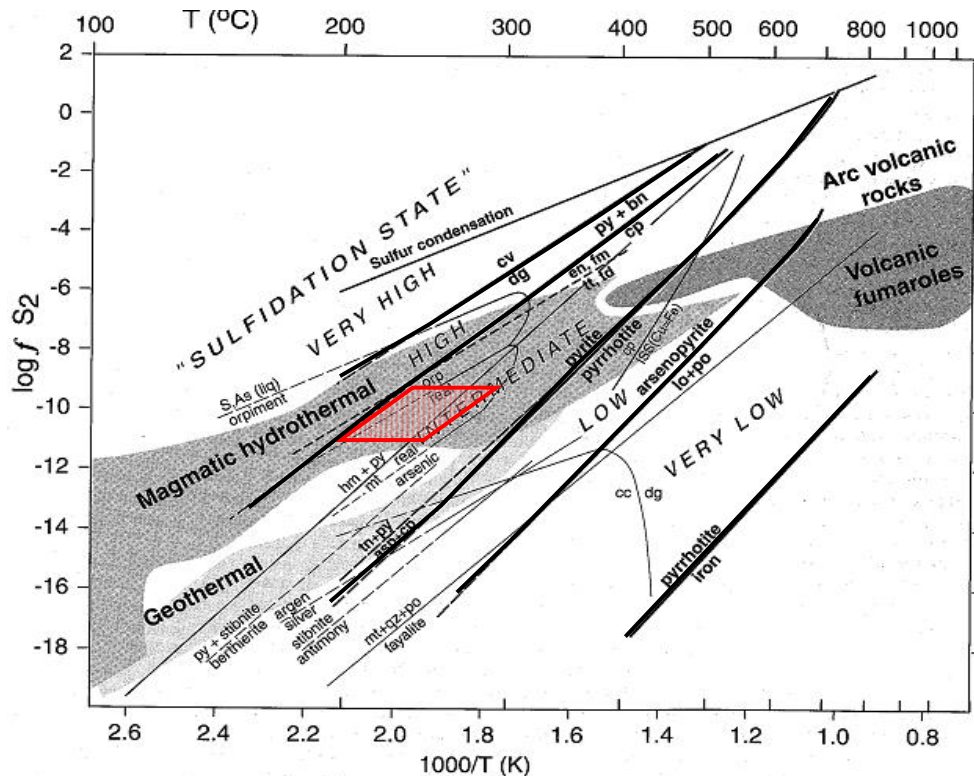


Figure 5 f_{S_2} - T diagram showing the variety of sulfide assemblages in epithermal deposits that reflect sulphidation state from very low through low and intermediate to high and very high. Compositional fields of arc volcanic rocks, high temperature volcanic fumaroles, magmatic-hydrothermal fluids, and geothermal fluids are shown, as discussed by (Einaudi, et.al., 2003 and Sillitoe and Hedenquist, 2003)). Red area is referred to the intermediate sulphidation state of epithermal quartz veins at Soripesa prospect area.

Conclusion

In this research, element composition (average) in sphalerites are Zn (63.48 wt.%), S (33.3 wt.%), Fe (1.04 wt.%), Ga (0.7 wt.%), Ge (0.54 wt.%), Cd (0.7 wt.%), and Ag (0.27 wt.%). Au content is below detection limit in all sphalerite. The Zn/Cd ratios (average 93.34) of sphalerite from this research area are close to Zn/Cd ratios (104-214) of sphalerites from hydrothermal deposits (including volcano-hydrothermal deposits. Average content Ga (0.7%) in sphalerites is very high and it means that they may be formed under low temperature condition. The average content of Zn is 63.48 wt.% in sphalerite of this research. It means that sphalerites from this research are related with pyritic ore condition.

Determining the values of $\log (Ga/Ge)$ for the analyzes of sphalerite minerals are in the ranges between -0.4 to 1.15. The results point to low temperatures of formation of the deposit and estimated formation temperature are between 180°C and 240°C. Mole % FeS in sphalerite is

also very low and between 1% to 2%. In Zn-Fe-S of low pressure system, this value (1-2%) falls in pyrite+chalcopyrite field. Within the pyrite field the decrease in FeS content of sphalerite with increasing sulphur activity (a_{S_2}) is much greater resulting in a close spacing of isopleths near the pyrite-pyrrhotite. FeS contents and formation temperature shows a little high sulphur activity (a_{S_2}) ($10^{-9} - 10^{-11}$). Data from Sulphur activity and formation temperature indicates that ore forming condition is assumed under intermediate sulphidation state, pyrite+chalcopyrite field, and magmatic hydrothermal compositional field.

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