



INDONESIAN JOURNAL ON GEOSCIENCE

Geological Agency
Ministry of Energy and Mineral Resources

Journal homepage: <http://ijog.bgl.esdm.go.id>
ISSN 2355-9314 (Print), e-ISSN 2355-9306 (Online)



Diagnostic Genesis Features of Au-Ag Selenide-Telluride Mineralization of Western Java Deposits

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Manuscript received: October 9, 2015; revised: March 16, 2016;
approved: March 31, 2016; available online: April 11, 2016

Abstract - The ore mineralogy of the westernmost part of West Java such as Pongkor, Cibaliung, Cikidang, Cikotok, and Cirotan are characterized by the dominance of silver-arsenic-antimony sulfosalt with silver selenides and rarely tellurides over the argentite, whereas the eastern part of West Java including Arinem and Cineam deposits are dominated by silver-gold tellurides. Mineralogy of Se-type deposits at Pongkor, Cikidang, Cibaliung, Cisungsang, and Cirotan and Te-type deposits at Arinem and Cineam shows their different geochemical characteristics. Mineralogical and geochemical differences can be explained by variation of physico-chemical conditions that existed during gold-silver deposition by applying the phase relation among sulfide, telluride, and selenide mineral association in the deposits. The relative values of $f\text{Se}_{2(g)}$, $f\text{Te}_{(g)}$, and $f\text{S}_{2(g)}$ control the actual presence of selenide or telluride minerals within the West Java deposits, which also depend on their concentrations in the hydrothermal fluid. Even though the concentration of selenium in the hydrothermal fluid of Te-type deposits might have been similar or even higher than that in the Se-type, early substitution of selenium in the sulfide minerals prevents its concentration in the hydrothermal fluid to the levels for precipitating selenide minerals. Therefore, early sulfide mineral deposition from reduction fluids will not increase the $f\text{Se}_{2(g)}/f\text{S}_{2(g)}$ ratio to form selenide minerals in Te-type deposits of Arinem and Cineam, other than selenium-bearing sulfide mineral such as Se-bearing galena or Se-bearing pyrrargyrite-proustite.

Keywords: mineralization, fugacity, hydrothermal, selenium, substitution, tellurium

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How to cite this article:

Yuningsih, E.T., Matsueda, H., and ROSANA, M.F., 2016. Diagnostic Genesis Features of Au-Ag Selenide-Telluride Mineralization of Western Java Deposits. *Indonesian Journal on Geoscience*, 3 (1), p.67-76. DOI: [10.17014/ijog.3.1.67-76](https://doi.org/10.17014/ijog.3.1.67-76)

INTRODUCTION

The Miocene-Pliocene mineralization in western Java can be divided into Se- and Te-types with some different characteristic features (Yuningsih *et al.*, 2014). The ore mineralogy of the westernmost part of West Java, *i.e.*, Pongkor, Cibaliung, Cikidang, Cisungsang, and Cirotan is characterized by the dominance of silver-arsenic-antimony sulfosalt with silver selenides and rarely tellurides over the argentite, while to

the eastern part, Arinem and Cineam deposits are dominated by silver-gold tellurides. The Se-type of western Java mineralization mostly lying within and on the flanks of the Bayah Dome is represented by Pongkor, Cikidang, Cisungsang, Cirotan, and Cibaliung, whereas the Te-type is located in the eastern part represented by Arinem and Cineam deposits (Figure 1). Ore petrographic and geochemical studies were undertaken for both Se- and Te-types of these epithermal deposits. Petrographic study was carried out to identify

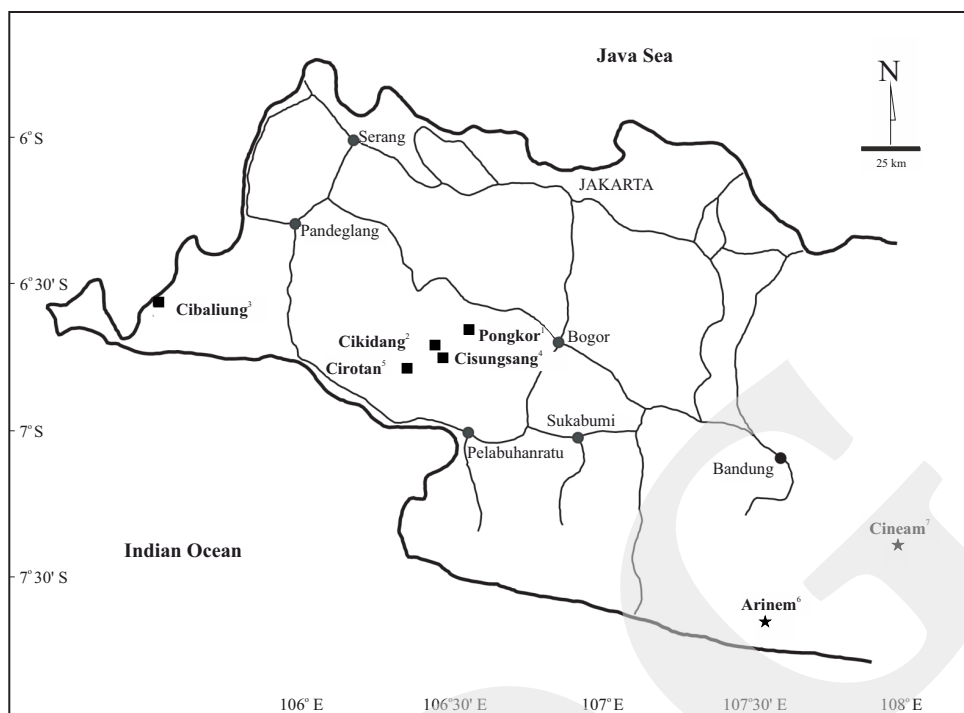


Figure 1. Locality and distribution map of Se (■) and Te (★) type deposits in the western Java, Indonesia (Yuningsih *et al.*, 2014). (1= Pongkor, 2= Cikidang, 3= Cibaliung, 4= Cisungsang, 5= Cirotan, 6= Arinem, 7= Cineam).

the occurrence of selenide minerals in the Se-type deposit with none to rare in the Te-type one. The geochemical analyses of samples from both Se- and Te-types show a similar amount of Se contents. The result indicated that there may be some factors controlling the formation of selenide and telluride minerals in these deposits.

MATERIAL AND METHODS

This study investigates the physico-chemical environment conditions of Se- and Te-types epithermal mineralization in western Java. Ore and alteration minerals assemblage, fluid inclusions, stable and radiogenic isotopes studies were undertaken in certain deposits in western Java in conjunction with literature studies from previous authors. Available thin-, polished-, and doubly polished sections samples were checked under transmitted- and reflected-light microscope. These were combined with fluid inclusion studies, clay mineral identification, and the composition study of ore minerals with microprobe. Minerals for a stable isotope analysis were separated by

hand picking under a binocular microscope and then checked by X-ray diffraction to ensure a purity of >90 %. The sulfide minerals of galena and pyrite were used for $\delta^{34}\text{S}$ analysis. For O and H isotopic analysis, quartz samples were ultrasonically cleaned with dilute HCl to remove calcite and clays, then rinsed with distilled water and dried. The analysis of stable isotopes of sulfur, oxygen, and hydrogen/deuterium was carried out at Activation Laboratories Ltd., Ancaster, Ontario, Canada. The result of this study helps to improve our understanding of the nature and genesis of the Se- and Te-types deposits in western Java. This result was compared to Se- and Te-types epithermal mineralization elsewhere.

RESULTS

Se- and Te-Types Deposit Characteristics in Western Java

Ore mineralogy, ore geochemistry, host rocks, alteration, and temperature formation characteristics of certain Se- and Te-types deposits in western Java, *i.e.*, Pongkor, Cibaliung, Cikidang,

Cisungsang, Cirotan, Arinem, and Cineam are described in detail by Yuningsih *et al.* (2014). The Se-type is characterized by Se- and Se-bearing silver minerals such as aguilarite, naumannite, argentite, polybasite, and pyrargyrite along with various amounts of common sulfide minerals. The Te-type is characterized by the occurrence of hessite, petzite, stutzite, tetradyomite, altaite, and tennantite-tetrahedrite with high amount of sulfide minerals. The iron content in sphalerite of Se-type deposits is in the range of 0.1 to 2.4 mol% FeS, except those of the Cisungsang and Cirotan deposits usually exhibiting a higher Fe content than others. The Fe content in sphalerite of Te-type ranges from 0.5 to around 2.0 mol% FeS. The electrum from both deposits is characterized by various Ag content ranging from 22 to 68 wt%, and 14 to 40 wt% for Se- and Te-types, respectively. Hydrothermal alteration from both types is similar and dominated by clay minerals of chlorite, illite, montmorillonite, kaolinite, mixed layered illite-smectite, and chlorite-smectite. Adularia is identified in Se-type deposits except for Cisungsang. Adularia has not been found in Te-type deposits.

Sulfur Isotope

In general, $\delta^{34}\text{S}$ of Pongkor deposit sulfide is in the range of 0.0 to 3.2‰ and is 0.4 to 2.9‰ for Cirotan deposit. Arinem Te-bearing deposit, represented by Arinem vein, has $\delta^{34}\text{S}$ in the range of -3.6 to (-1.8‰), and $\delta^{34}\text{S}$ of Bantarhuni vein shows the values of -5.5‰, indicating magmatic sources of sulfide sulfur. The slightly lower $\delta^{34}\text{S}$ of Te-type deposit might be the result of phase separation of the ore fluid that possibly took place during the mineralization stage. The high volatility of H_2S relative to oxidized S species, such as SO_2 , may cause an increase in $f\text{O}_2$ in the residual liquid and could produce relatively low sulfur isotope values (Ohmoto and Rye, 1979). This interpretation is supported by the abundance of pyrite and (rare) hematite assemblage occurring in the ore mineralization of Arinem.

Lower $\delta^{34}\text{S}$ values of the Arinem sulfides may also be resulted from the direct addition of magmatic volatiles to the hydrothermal fluid. SO_2 will disproportionate from volcanic gases at

temperatures of below 400°C into reduced and oxidized species and the sulfide will become enriched in ^{32}S relative to H_2SO_4 (Ohmoto and Rye, 1979). Direct addition of magmatic volatiles to the hydrothermal fluids cannot be discarded, because it is still uncertain whether this process can generate $\delta^{34}\text{S}$ values in sulfides as low as -1.8 to -5.5‰ in the Arinem deposit.

Sulfur and Oxygen Fugacities

Sulfur fugacity can be estimated from fluid inclusion homogenization temperatures, FeS content of sphalerite coexisting with pyrite, Ag content of electrum coexisting with argentite (or acanthite), and the assemblages of sulfide minerals. The typical range of log sulfur fugacity of the Se-type is in the range of -18 to -9, and for the Te-type of Arinem deposit is -16.5 to -9 (Figure 2). Diagrams in Figure 2 are constructed mainly based on Heald *et al.* (1987).

Probable ranges of the oxygen fugacity and pH for the Se-type and Te-type are shown in Figure 3. The diagram in Figure 3 is constructed mainly based on Barton *et al.* (1977) and Heald *et al.* (1987) with temperature=200°C and $\Sigma\text{S}=0.005$ molal conditions. The oxygen fugacity of ore fluids responsible for the formation of the Se-type appears to be higher than those of ore fluids responsible for the formation of the Te-type. The log oxygen fugacity of the Se-type of Pongkor, Cikidang, Cibaliung, and Cirotan is in the range of -45.5 to -39 (Rosana, 2004), and the Te-type of Arinem is around -45.5 to -43.

DISCUSSION

The δD and $\delta^{18}\text{O}$ compositions of fluid delivered from analyses of minerals and fluid inclusions of some Se-bearing deposits from Pongkor, Cibaliung, and Cikidang had values in the ranges of -6.2 to 0.3‰ for $\delta^{18}\text{O}$, except for quartz samples from Cibaliung is 4.7 to 9.6‰ (Harijoko *et al.*, 2007) and δD in the ranges of -68 to -44‰ (Syafrizal *et al.*, 2007; Harijoko *et al.*, 2007). These $\delta^{18}\text{O}$ and δD values are near to the meteoric water value, *i.e.* values of Pongkor and Cigomba

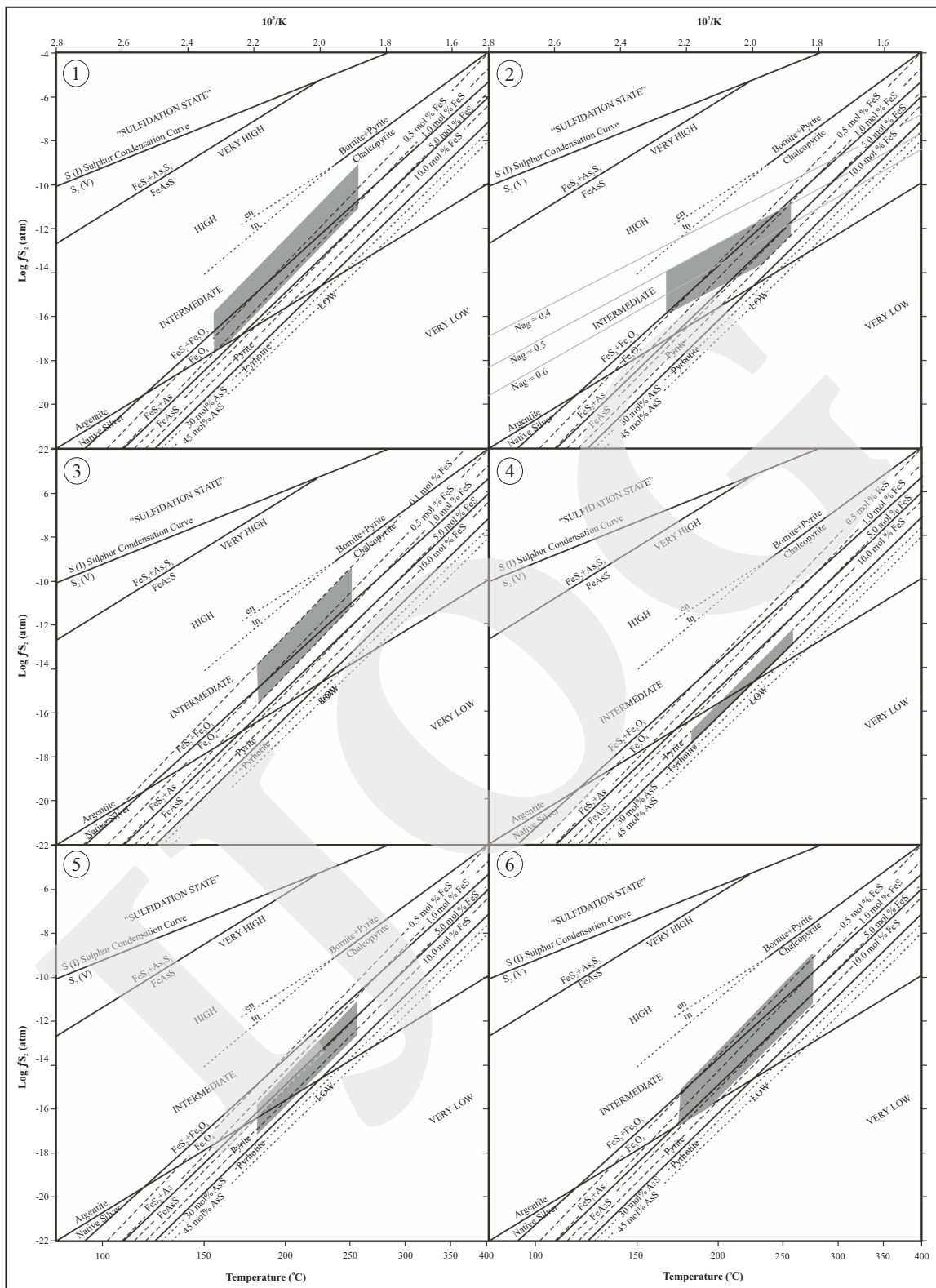


Figure 2. Ranges of sulfur fugacity for Se- and Te-types deposits in western Java (1=Pongkor; 2=Cikidang; 3=Cibaliung; 4=Cisungsang; 5=Cirotan; 6=Arinem).

Rivers which are around -6.1 to -5.8‰ for $\delta^{18}O$ and -36.6 to -35.1‰ for δD .

The oxygen and hydrogen isotope data from the Te-type of Arinem have the value of δD and

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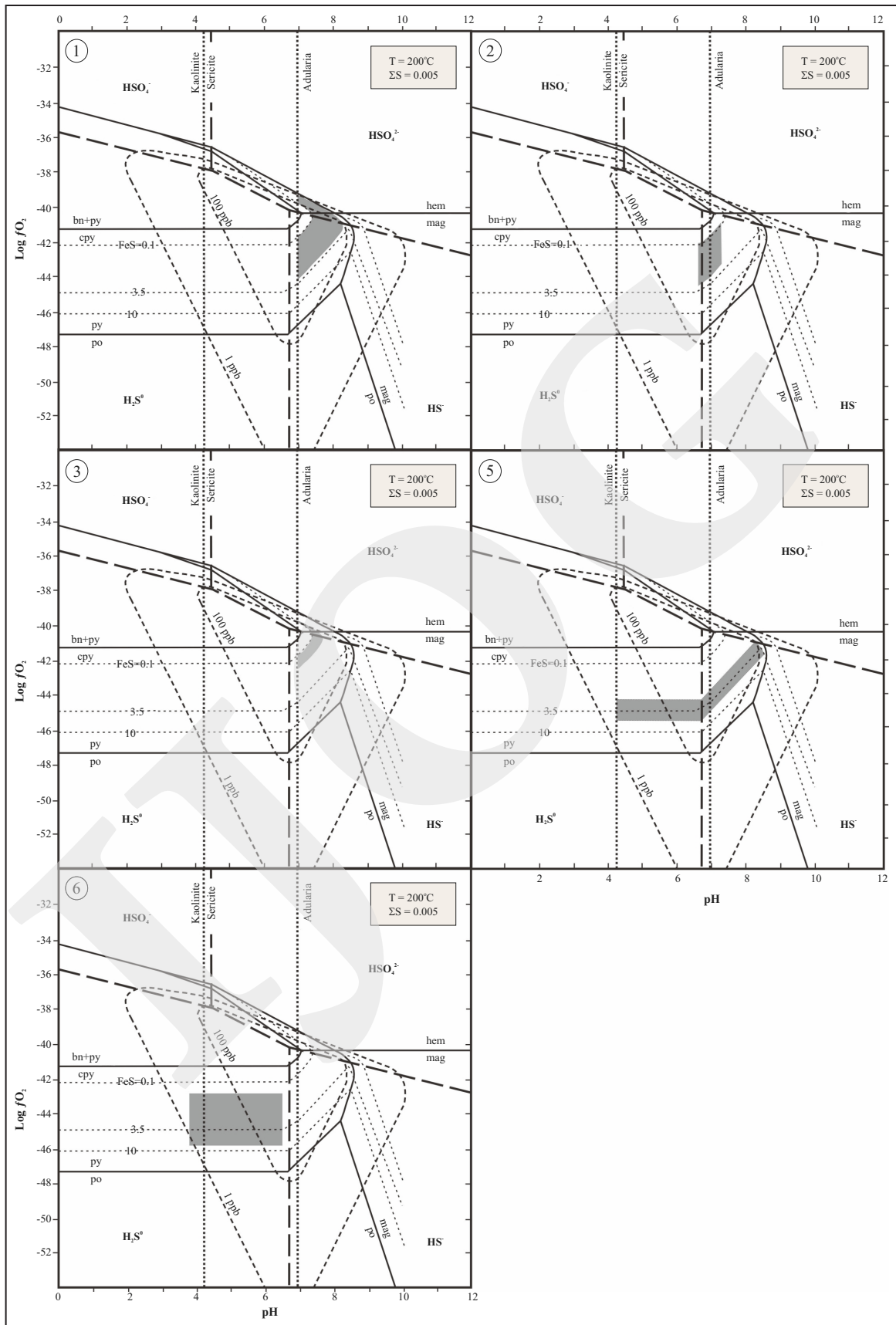


Figure 3. Ranges of oxygen fugacity and pH for the Se- and Te-types deposits (1=Pongkor; 2=Cikidang; 3=Cibaliung; 5=Cirotan; 6=Arinem).

$\delta^{18}\text{O}$ similar to those of Se-type in the range of -6.0 to -0.6‰ of $\delta^{18}\text{O}$, and -66.0 to -34.0‰ of δD . These values indicate that the meteoric water dominates. The depth of the mineralization within the western Java both of Se- and Te-bearing deposits is around 200 to 425 m under the paleo-watertable. The epithermal deposit is dominated by low sulfidation type with some evidence for intermediate to high sulfidation state from several deposit such as Cisungsang and Cirotan (Se-type) and Arinem (Te-type) deposits.

Phase relation among sulfides, tellurides, selenides, and oxides proposed by Afifi *et al.* (1988a, b), Simon and Essene (1996), and Simon *et al.* (1997) were applied to explain the variations of the physico-chemical condition of the Se- and Te-bearing mineral formation for the western Java ore deposits. The fugacity diagrams, as mentioned by those authors, may be used to determine whether the equilibrium was attained or not, and to interpret the probable additional phases which may be present from an incomplete mineral identification.

Those phases can also explain the mineralogy variations within and between ore deposits. The evolution of the mineralizing fluid of western Java deposits was estimated from those fugacity diagrams at a fixed temperature of 200°C since the average of fluid inclusion formation temperature study of Se- and Te-type deposits at western Java is around 170 -220°C and 190 - 270°C (Yuningsih *et al.*, 2014), with an assumption that temperature variations within the deposits were relatively small for those low-temperature epithermal deposits.

Phase relation among sulfide, tellurides, and selenides (Figures 4 and 5) in the Se- and Te-type deposits of the western Java was constructed, except for oxides because of its absence within the Se-type and very rare in Te-type deposits. Those fugacity diagrams show that the value of selenium fugacity is similar in both Se- and Te-type deposits, otherwise the tellurium fugacity is higher than that of the Te-type deposit.

The $f\text{Se}_{2(\text{g})}/f\text{S}_{2(\text{g})}$ diagram in Figure 4 shows that the log values of selenium fugacity is in the

range of -18 to -14 for Se-type, and -18 to -13 for Te-type with log sulfur fugacity between -16 to -10 and -15.5 to -12.5. The value for log tellurium fugacity (Figure 5) in the Se-type represented by Pongkor and Cibaliung, is in the range of -18.5 to -12, and for Te-type of Arinem and Cineam is in the range of -16.5 to -9.5 with log sulfur fugacity of -15.5 to -9.5 and -15 to -11, respectively.

According to Simon and Essene (1996), the selenide minerals were formed from hydrothermal fluids with $f\text{O}_{2(\text{g})}$ below or near the hematite-magnetite buffer and at $f\text{Se}_{2(\text{g})}/f\text{S}_{2(\text{g})}$ ratio lower than unity. The enrichment of selenium in hydrothermal fluid and depositional of selenide minerals were limited by low $f\text{Se}_{2(\text{g})}/f\text{S}_{2(\text{g})}$ ratio and the presence of sulfide assemblages that buffer $f\text{Se}_{2(\text{g})}$ and $f\text{S}_{2(\text{g})}$, except for silver selenides.

The formation of selenide or telluride minerals in ore deposit will depend on the relative values of $f\text{Se}_{2(\text{g})}$, $f\text{Te}_{(\text{g})}$, $f\text{S}_{2(\text{g})}$ and their concentration in the hydrothermal fluid. Thermodynamically, the stability fields of selenide minerals are generally more restricted than those of sulfide minerals, but are larger than those of corresponding telluride minerals for similar condition of $f\text{S}_{2(\text{g})}$, $f\text{Te}_{(\text{g})}$, and $f\text{Se}_{2(\text{g})}$.

Selenium often substitutes sulfur in sulfide minerals due to the similarity in their crystallo-chemical properties. Unlike tellurium, selenium is widely present as an accessory element to replace sulfur in more common sulfide minerals (Table 1). Therefore, tellurium will form individual minerals, whereas selenium more ready to substitute sulfide minerals.

The concentration of sulfide is abundant in the Te-type deposit. The concentration of selenium in the hydrothermal fluid of Te-type might have been similar or even higher than other types of Se-type deposits, but the early substitution of selenium in sulfide minerals prevented its concentration in the hydrothermal fluid to reach the level that is necessary for selenide minerals to precipitate, other than selenium-bearing sulfide minerals. Those are due to the fact that the early deposition of sulfide minerals from reducing ore fluids will not increase the $f\text{Se}_{2(\text{g})}/f\text{S}_{2(\text{g})}$ ratio to the values

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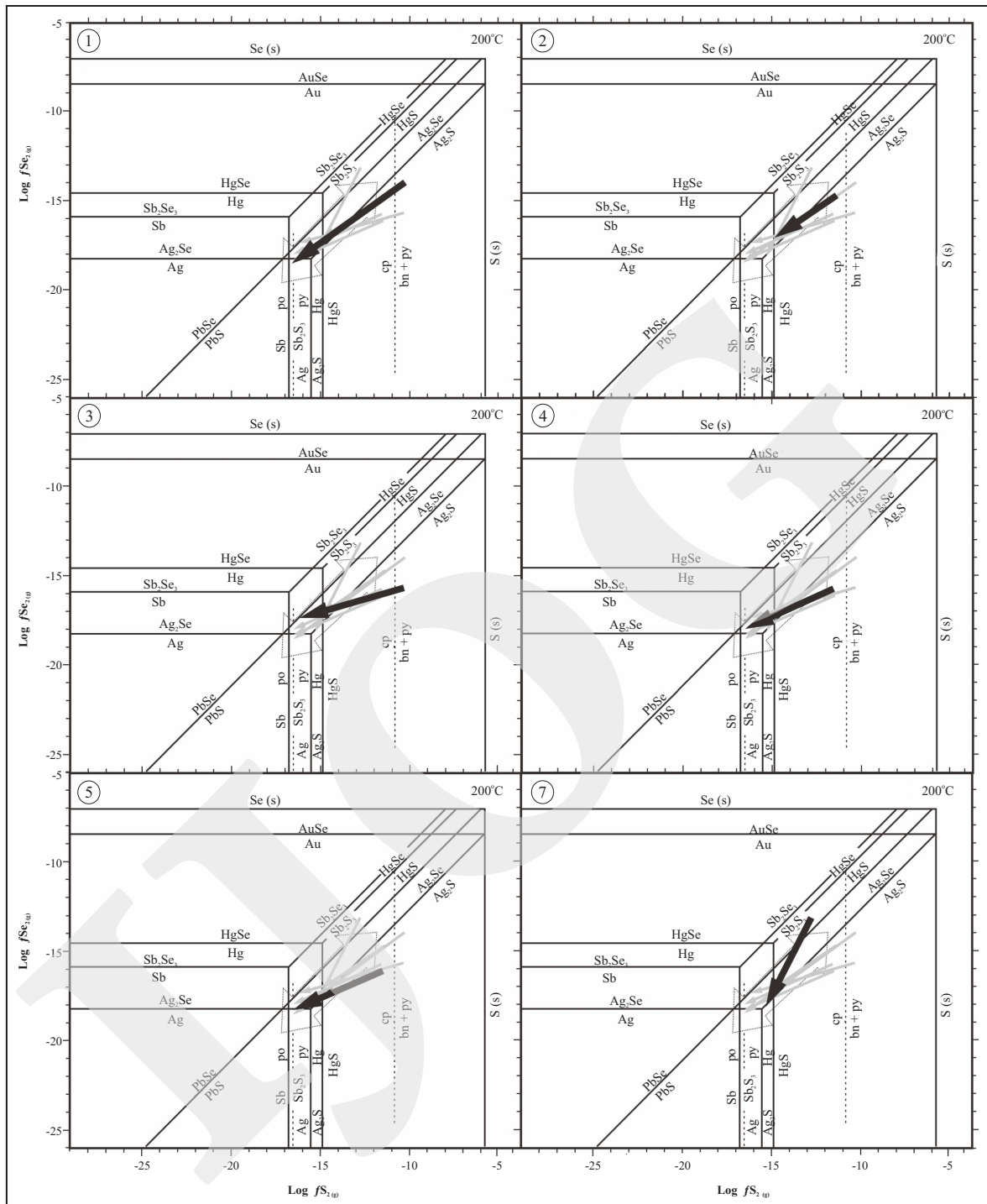


Figure 4. Phase relation between selenides and sulfides of epithermal mineralization within western Java at the temperature 200°C (1=Pongkor; 2=Cikidang; 3=Cibaliung; 4=Cisungsang; 5=Cirotan; 7=Cineam).

that is high enough to form selenide minerals.

Selenide minerals occur favorably in oxidizing environments, not in sulfide-rich deposits. Hydrothermal solutions must also have a high $f_{\text{Se}_{2(g)}}/f_{\text{O}_{2(g)}}$ ratio to prevent the early incorpora-

tion of selenium in sulfides and to form selenides rather than selenium-bearing sulfides. Thus, highly oxidizing conditions are required to form selenide minerals, but these are not common in hydrothermal fluids where the $f_{\text{O}_{2(g)}}$ is usually

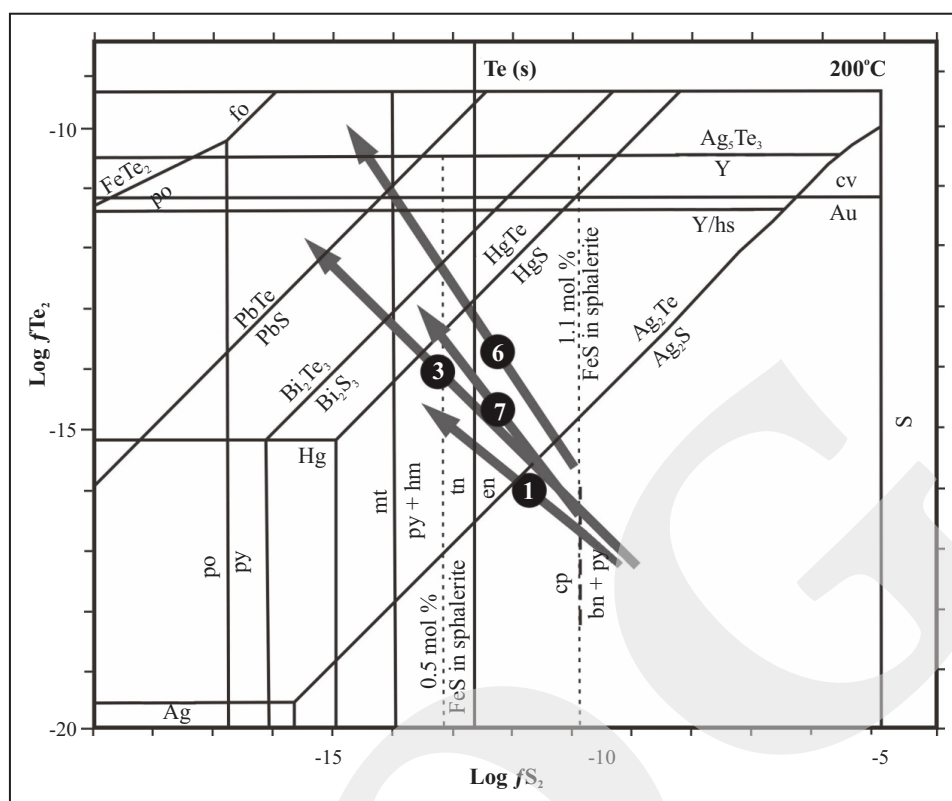


Figure 5. Phase relation between tellurides and sulfides of western Java epithermal mineralization at temperature 200°C (1=Pongkor; 3=Cibaliung; 6=Arinem; 7=Cineam).

Table 1. Electron Microprobe Analyses of Galena and Tetradymite Minerals from Arinem Deposit

Element	Galena ¹					Tetradymite ¹		Tetradymite ²			
	IB	IB	IB	IIB	IIB	IIB	IIB	IIA	IIA	IIA	IIA
Zn	0.04	0.25	0.41	0.00	0.03	0.45	0.20	0.02	0.00	0.00	0.03
Cu	0.71	0.19	0.08	0.39	0.09	0.93	0.27	0.13	0.94	0.32	0.04
Fe	0.09	0.04	0.16	0.24	0.09	0.44	0.09	0.09	0.66	0.31	0.77
Mn	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.03	0.00	0.02	0.00
S	13.45	12.66	12.41	12.13	12.44	3.95	3.51	3.82	4.26	3.76	3.12
Ag	0.00	0.00	0.00	0.51	0.54	0.25	0.36	0.17	0.48	0.21	0.13
Cd	0.15	0.11	0.00	0.06	0.00	0.05	0.13	0.00	0.02	0.00	0.00
As	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Se	0.14	0.56	0.38	1.24	1.07	1.52	1.98	0.74	0.08	0.65	1.31
Sb	0.07	0.06	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	86.13	86.31	87.24	85.81	86.53	0.16	0.83	0.00	0.00	0.00	0.00
Au	0.00	0.22	0.31	0.00	0.00	0.00	0.02	0.00	0.13	0.08	0.39
Te	0.00	0.12	0.20	0.25	0.13	33.83	34.67	34.81	34.81	35.79	35.60
Hg	0.00	0.53	0.20	0.00	0.02	0.00	0.00	0.00	0.00	0.59	0.10
Bi	0.00	0.00	0.00	0.00	0.00	56.54	56.14	58.08	57.76	55.70	57.47
Total (wt %)	100.79	101.04	101.58	100.62	100.94	98.11	98.19	97.88	99.14	97.43	98.95

¹Bantarhuni vein; ²Arinem vein.

controlled by the hematite-magnetite or other less oxidizing buffers. This is probably the main reason why selenide minerals are less common than telluride minerals in the sulfide-rich Te-type deposit in western Java.

CONCLUSION

The $\delta^{34}\text{S}$ of sulfides from the Se-type (-18 to -9) is slightly heavier than that of the Te-type (-16.5 to -9). The present sulfur isotopic study suggests that magmatic volatiles involved in the ore fluids were responsible for the Te and Se mineralization. Hydrogen and oxygen isotopic studies indicate that meteoric water was dominant in the ore fluids for epithermal gold-silver vein deposits of the Se-and Te-types.

Different geochemical behavior of tellurium and selenium elements affects those occurrences in nature. Even thermodynamically selenides may be more widespread than that of tellurides. However, in nature telluride minerals seem to be more common and widespread than selenide minerals. Tellurium tends to form telluride minerals in sulfide ore deposits, because the element is less compatible compare to selenium in the structure of sulfide minerals.

The formation of telluride minerals commonly occur during the late stages of mineralization when $f\text{Te}_{2(\text{g})}/f\text{S}_{2(\text{g})}$ ratios in the ore fluid have been increased by deposition of early sulfide minerals. Thus, the most important requirement to form telluride minerals in ore deposit is simply the source that is rich in tellurium. While for selenide mineral formation, it is only formed in solution with relatively high $f\text{Se}_{2(\text{g})}/f\text{S}_{2(\text{g})}$ ratios, which cannot be achieved in a similar way as that of tellurium.

ACKNOWLEDGEMENTS

The authors would like to thank PT. Antam Tbk., for support on the access to data and samples during field investigation. This work is part of

International Collaboration research funded by the Directorate General for Higher Education (DGHE) of Ministry of Education, Indonesia, and JSPS (Japan Society for the Promotion of Science), Japan.

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