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Mineralogy and formation conditions of Portovelo-Zaruma gold-sulphide vein deposit, Ecuador

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Abstract. The large Portovelo-Zaruma gold field is associated with Early Miocene continental arc magmatism. Quartz-sulphide veins crosscut andesitic lavas and tuffs. Pyrite, chalcopyrite, sphalerite and galena are the dominant ore minerals (5-10 vol.%). Gold occurs in visible and submicroscopic modes, mainly in chalcopyrite (up to 421 g/t, INAA). Petzite, hessite and tetradymite have been identified in druse quartz in assemblages with native gold. There are broad variations in composition of petzite: from Ag_3AuTe_2 to $Ag_3Au(Te_{1.31}S_{0.61})$. Hessite bears 1.56-5.23 wt.% Au, 0.15-0.46 wt.% Fe, 0.0-0.93 wt.% Pb and 0.0-0.48 wt.% Bi. Composition of tetradymite varies from $Bi_{1.9}Te_2S$ to $Bi_2Te_{1.9}(S_{0.6}Se_{0.44})$. Fluid inclusion homogenization temperatures range from 134-331°C. Salinities range from 9.3 to 0.2 wt.% NaCl equiv. (mostly 0.4-2 wt.%). P = 125-50 bar, corresponding to shallow subsurface conditions. Isotope data suggest a magmatic source of sulphur in fluids.

Key words: gold-polymetallic quartz vein, tellurides, epithermal deposit, Portovelo-Zaruma field, Ecuador

Introduction

Zaruma city, founded by Spanish conquerors in 1549, is the oldest mining centre in South America. The Portovelo-Zaruma gold field, southwest Ecuador, is one of the largest vein hydrothermal deposits in the Andean Cordillera. The mine was subsequently deepened to a level 200 m above sea level, 900 m below the uppermost workings.

During the period 1904-1950, 9.1 Mt ore at a cut-off grade of 13.3 g/t Au, 62 g/t Ag, 0.9% Cu and 1% Zn have been mined. Total historic gold production exceeds 4.5 Moz (Spencer et al., 2002; Chiaradia et al., 2004). Recent production is 35,000-50,000 oz Au/year (Spencer et al., 2002) at an average grade of 12 g/t Au, 63 g/t Ag, 1% Cu and 1.7% Zn (Van Thournout et al., 1996). Today, gold production at the deposit is carried out by private companies under the control of the government using shafts, galleries and trenches. The mine delivers more of 60% of the annual Ecuadorian gold production.

Geological setting

In central and southwestern parts of Ecuador, the Eocene to Late Miocene igneous complexes related to epithermal and porphyry-Cu ores originated from mantle-derived calc-alkaline magmas fractionated at shallow levels inside rifted continental crust (Chiaradia et al., 2004).

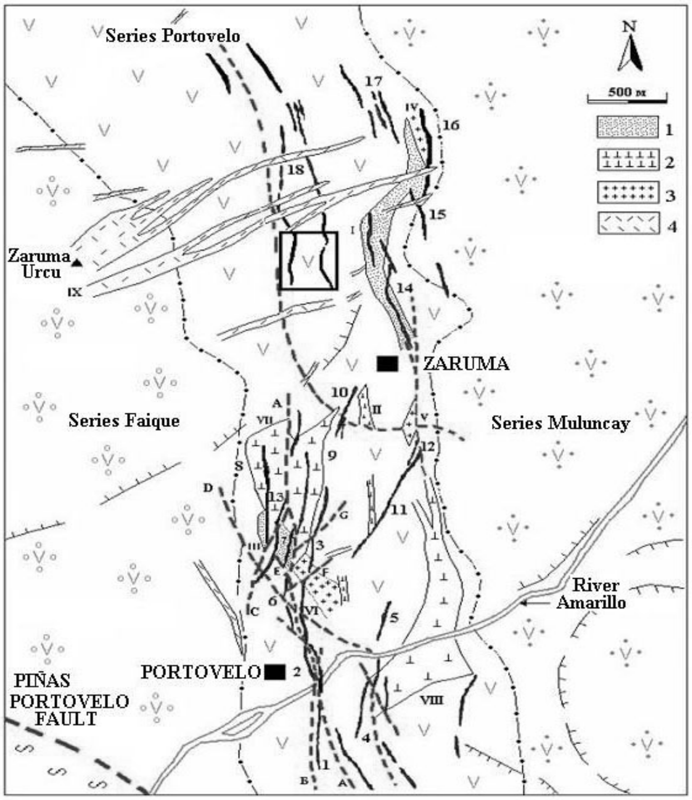

Fig. 1. Map of Portovelo-Zaruma gold field. 1-4 – *intrusives*: 1 - quartz-monzonite, 2 – granodiorite, 3 – diorite, 4 - rhyolite (I- Sesmo, II- Jorupe, III- Soroche, IV- 10 Vetas, V- Tres Reyes, VI- Castillo, VII- Agua dulce, VIII- Curipamba, IX- Zaruma Urcu). *Veins*: 1- Abundancia; 2- Portovelo; 3- Cantabria; 4- Curipamba; 5- Barbazco; 6- 26 y Nudo; 7- Soroche; 8- Tamayo; 9- Agua Dulce; 10- Bomba de Pachapamba; 11- Jorupe; 12- Tres Reyes; 13- Quebrada; 14- Sesmo; 15- Salvador; 16- Veta Ancha; 17- Gobernadora; 18- Vizcaya. *Faults*: A- Abundancia; B- Portovelo; C- Matalanga; D- "25"; E- Cerro Russia; F- "24"; G- Nivel "F"; H- Tres Reyes

Epithermal style gold veins of the Portovelo-Zaruma field (Fig. 1) are associated with Early Miocene continental arc magmatism. The mining district consists of a tectonic block, 7 km in width, with NW-trending fault boundaries. The block is composed of andesites and tuffs of three series (K): Muluncay, Portovelo and Faique. There are numerous sub-volcanic rhyolite dikes and stocks which crosscut the volcanic units.

The Portovelo-Zaruma field comprises a large system of longitudinal gold-polymetallic veins within a surface area of more than 4 x 12 km, aligned along a strike-slip structure. Historical production was focused on the southern part of the system (Portovelo), which is characterized by the highest gold grade.

More than 30 gold-bearing veins are identified. They dip east at angles from 45 to 70°, have lengths of hundreds of m up to 2.5 km, and thickness of 0.8-1.5 m (reaching 3-5 m in some places). The vein system is complicated by the presence of ore shoots with a relatively gentle northern declination. Ore veins are crossed by rhyolite dikes related to the Pisayambo Formation (N_1) that corresponds to the upper limit of gold-sulphide mineralization.

Samples and analytical methods

Our study is based on data resulting from mineralogical mapping of the Vizkaya and Nikol veins at the Zaruma deposit. Mineralogical observations were carried out in polished sections, as well as electron probe microanalyses (EPMA) with Cameca MS-46 and Camebax SX-50 instruments and scanning electron microscopy (JSM-5300 instrument with Link-ISIS EDS detector at IGEM RAS, Moscow. Mineral compositions were determined at 20kV accelerating voltage, 20 nA beam current, 1μm-beam diameter, and 10 s. count times. Standards were pure metals (Cu, Ni, Co, Au, Ag, Bi, Sb, Te, Se, Ge) and compounds (FeS_2, ZnS, HgTe, InAs, PbS, CdS). Contents of Au, Ag, base and rare metals were examined by instrumental neutron activation analysis (INAA) on 20 bulk samples and 69 hand-prepared sulphide concentrates.

Fluid inclusions were optically studied in double polished sections, and then by microthermometry using a THMSG-600 ‘Linkam’ freezing heating stage, calibrated with synthetic fluid inclusions and equipped with an Olympus-80 objective at IGEM RAS. The precision at low temperature (cooling) is about 0.7°C, at high-temperature (heating) of 2°C, respectively). Salinities of aqueous fluids were estimated from final ice melting temperature (T_m) and/or halite dissolution temperature (T_s), according to standard procedures (e.g., Bodnar and Vityk, 1994).

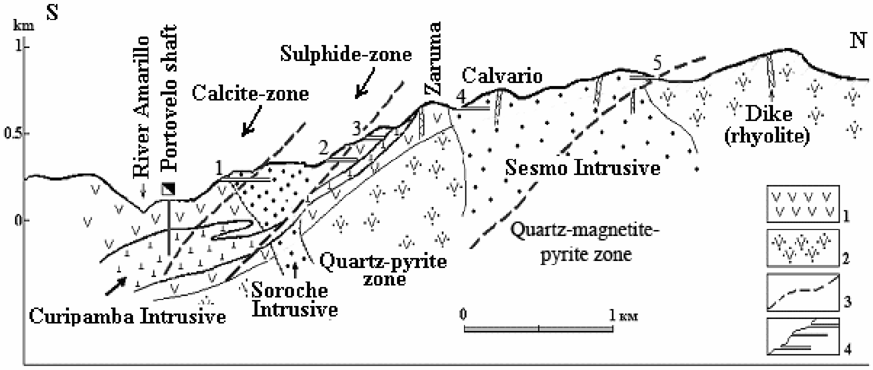

Fig. 2. Simplified longitudinal section of Portovelo-Zaruma field, modified after Billingsley (1926). 1 - Portovelo andesites; 2 - Muluncay andesites; 3 - borders of mineral zones; 4 - galleries to veins: 1) Soroche, 2) Agua Dulce, 3) Bomba de Pachapamba, 4) Sesmo, 5) Ancha

The sulphur isotopic compositions of 15 pyrite, 12 chalcopyrite, 9 sphalerite and 7 galena concentrates were determined using a MI-1311 mass spectrometer at the stable isotope laboratory, IGEM RAS. All samples were checked for impurities with a binocular microscope. The sulphide concentrates were decomposed using CuO at 700-800°C. The evolved SO_2 gas was purified by passing it through a series of cold traps to remove contaminants. All results are reported relative to the Canyon Diablo Troilite (CDT) standard. The reproducibility of the results is generally better than 0.2‰.

Ore mineralogy

Several metals are of major economic importance: Au (5-15 g/t, up to 35 g/t in ore shoots; cut-off grade for current mine production is 6 g/t Au); Ag (up to 220 g/t), Cu (up to 4-5 wt. %), Zn (up to 10 wt. %), Pb (up to 4-5 wt. %). The Ag/Au ratio in ore is typically around 8. According to the INAA data for bulk ore samples, the average gold contents are 20.2 g/t (ranging from 0.08 g/t in quartz-pyrite-chalcopyrite assemblages, up to 175 g/t in polymetallic associations) for the Vizkaya vein and 25.3 g/t (up to 70 g/t) for the Nikol vein.

Pyrite, chalcopyrite, sphalerite and galena are the dominant ore minerals (5-10 vol.%). Bornite, hematite and tennantite-tetrahedrite are common in some parts of Vizkaya and Nikol veins. The tellurides hessite, petzite, and tetradymite, which were previously unknown in the deposit, and native gold, are rare. Magnetite, molybdenite, argentite, freibergite, safflorite, nagyagite, proustite and bournonite are also mentioned for other veins (Van Thournout et al., 1996; Spencer et al., 2002). Quartz is the most abundant gangue mineral; calcite, adularia, epidote, zoisite, actinolite, sericite, chlorite, illite-smectite and barite are common minerals; andradite, tourmaline, apatite, fluorite and gypsum are rare.

Three mineralization stages are distinguished. The *Quartz-pyrite* stage is composed of two parageneses: early quartz-pyrite-chlorite-hematite and late quartz-pyrite-chalcopyrite. Ore formation began with pyritization; veins and veinlets of milk-white quartz were formed later. White and gray quartz fragments are accompanied by chlorite and hematite. Sealing chalcedonic quartz, containing small impregnations of hematite and pyrite, cements the brecciated clasts of previously deposited mineral assemblages. Quartz, pyrite and chalcopyrite of the late paragenesis sometimes carry small inclusions of native gold, several tenths of mm in size.

The *Quartz-polymetallic stage* is an economically important stage. Quartz-galena-sphalerite and late galena-chalcopyrite-fahlore assemblages occur mainly in breccia zones and inside earlier quartz bodies which underwent cataclasis. Gold fills intergranular space between quartz crystals and as cracks in chalcopyrite-I; very rarely gold occurs in galena. Most of the sphalerite, significant parts of quartz, galena and native gold, pyrite-II, chalcopyrite-II, tennantite-tetrahedrite and tellurides crystallized during this stage. Native gold was deposited throughout the stage, but mostly after sphalerite and quartz - together with chalcopyrite-II, tennantite-tetrahedrite and tellurides. The *Quartz-carbonate* stage concludes the mineralizing event. Quartz and calcite are rarely accompanied by pyrite.

In the monomineralic concentrates analyzed by INAA, average Au contents are 16.6 g/t in pyrite (0.45-43.5 g/t), 45.7 g/t in chalcopyrite (0.53-421 g/t), 5.6 g/t in sphalerite and 0.6 g/t in galena for the Vizkaya vein. In the Nikol vein, average Au contents range 28 g/t in pyrite and chalcopyrite and 75.5 g/t in sphalerite; one galena sample gave 140 g/t.

Microprobe analyses of the tellurides, initially associated with native gold in druse quartz (Fig. 3) reveal a number of features (Table 1). We note a broad variation in the sulphur content of petzite: from stoichiometric Ag_3AuTe_2 to $Ag_3Au(Te_{1.31}S_{0.61})$.

Hessite appears to be homogeneous, with little compositional variation within and between grains. We note 0.24-2.02 wt.% S and 1.56-5.23 wt.% Au, 0.15-0.46 wt.% Fe, 0-0.93 wt.% Pb and 0-0.48 wt.% Bi, presumably substituting for Te and Ag, or as admixtures. Compositions indicates minor Ag-Au substitution and a more pronounced tendency for Te-S substitution, resulting in the simplified formula $(Ag,Au)_2(Te,S)$.

Measured tetradymite compositions show the presence of up to 8 at.% sulphur, and a degree of non-stoichiometry, centred around the ideal tetradymite formula, Bi_2Te_2S. Our data are consistent with other studies of natural and synthetic tetradymite, with substantial Se-S substitution (tetradymite-kawazulite solid solution), in this case up to $Bi_2Te_{1.9}(S_{0.6}Se_{0.44})$.

Fluid inclusion and sulphur isotope study

Fluid inclusions in quartz and sphalerite of veins routinely bear two phases. Homogenization temperature (T_h) range from 134-331°C (Table 2). T_h values show a bimodal distribution, with peaks at 260-331 and 134-240°C. Fluid inclusion homogenization in higher temperature zone (331°C) runs to gas phase (vapour). In some samples (V-12, V-23, N-19), there are three-phase fluid inclusions, as well as

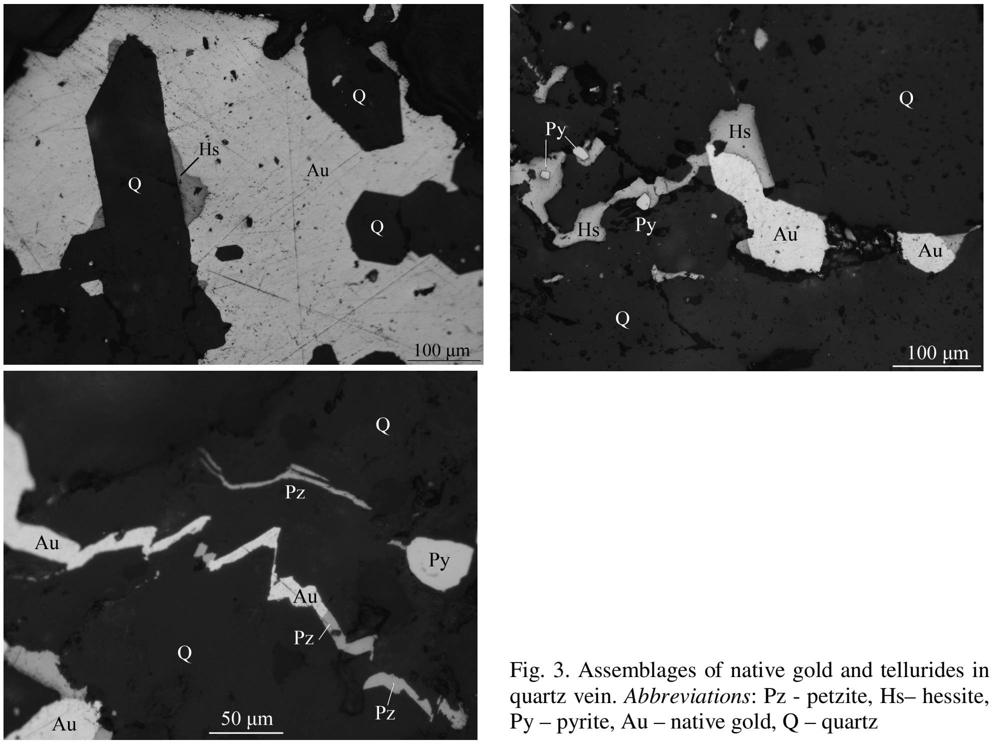

Fig. 3. Assemblages of native gold and tellurides in quartz vein. *Abbreviations*: Pz - petzite, Hs– hessite, Py – pyrite, Au – native gold, Q – quartz

Table 1. Representative electron microprobe analyses (wt.%) of telluride minerals

No	Ag	Au	Fe	Pb	Bi	Sn	Se	S	Te	Sum
					Petzite					
1	41.6	25.13	0.07	0	0	0	0.04	0	33.04	99.88
2	41.52	26.00	0	0.20	0	0.06	0	0.07	32.66	100.51
3	42.51	24.84	0.01	0	0	0	0.04	0.15	32.17	99.72
4	44.25	25.76	0.06	0.14	0	0.04	0	1.68	28.05	99.98
5	44.16	24.78	0.08	0	0.15	0	0.05	1.75	27.74	98.71
6	46.29	23.97	0.07	0.04	0	0	0	2.35	26.43	99.15
					Hessite					
7	60.77	1.56	0.36	0	0	0.09	0	0.24	35.68	98.70
8	61.48	3.16	0.18	0.04	0.40	0.06	0.06	0.80	34.21	100.33
9	60.28	5.01	0.15	0.21	0.48	0	0	1.76	30.9	98.85
10	61.25	5.23	0.46	0.93	0.37	0	0	2.02	29.1	99.36
					Tetradymite					
11	0.22	0.13	0.12	0.15	56.98	0	1.35	4.17	35.68	98.80
12	0.16	0	0.08	0	56.91	0.04	2.99	3.32	36.03	99.53
13	0.10	0	0.12	0.16	57.82	0	3.29	3.38	35.28	100.15
14	0.03	0.08	0.03	0.55	56.21	0	4.76	2.79	34.57	99.02
15	0.31	0	0.06	0.26	57.69	0	4.69	2.64	33.04	98.69

coexisting CO_2+H_2O and gas inclusions, taken as evidence for boiling of the hydrothermal solution. Cryometric study revealed eutectic temperatures (T_e) from -36 to -22°C (-27-28°C in most cases), and ice melting point (T_{ice}) from –6.1 to –0.1°C (typically -1 to -0.1°C).

Table 2. Results of fluid inclusion study

No	Mineral	T_h °C	C, wt % NaCl equiv.	P, bar
V-4	quartz	227-259	0.5-1.4	
V-8	quartz	181-253	2.2-9.3	
V-12	quartz *	265-289	0.9-1.4	50-70
	quartz	238-251	1.4	
V-14	quartz	269-278	0.2-0.5	
	sphalerite	134-275	0.9-2.4	
V-22	quartz	243-262	0.2-0.9	
	sphalerite	162-164	0.4-1.6	
V-23	quartz *	311	1.7	95
V-88	quartz B	265	0.5	
	quartz S	155	0.5	
	quartz M	241-244	0.5	
	quartz E	236-241	0.5	
N-19	quartz *	331 (G)	0.2	125
	quartz *	330	0.4	
	quartz	254	0.7	
	sphalerite	238-245	1.4-3.1	
N-17	quartz	235-258	0.5-0.7	

* - boiling. (G) - homogenization into gas. S - secondary inclusion. Parts of single crystal: B- basement, M– middle part, E– edge zone

Salinity values range from 9.3 to 0.2 wt.% NaCl equiv. (values between 0.4 and 2 wt.% are dominant). Pressure values seem to be ranged between 50-125 bar, corresponding to shallow subsurface conditions of ore genesis.

Na and Mg chlorides predominated in fluids. The following components and metals have been found in fluids of vacuoles (concentrations in g/kg solution): CO_2 (1.05), CH_4 (0.2), Cl(1.0), HCO_3 (3.2), Na (1.5), K (0.32), Ca (0.13), Al (1.08) and metals Fe (0.047), Zn (0.023), Cu (0.013), Sn (0.0007), W (0.0002), Au (0.00002).

$\delta^{34}S$ values in sulphides of ore veins range from –1.7 to +4.1‰ CDT. Such little variations of $\delta^{34}S$ in sulphides can be interpreted as reflecting sulphur input to the hydrothermal fluid from a single homogeneous source – a shallow magmatic chamber, for example.

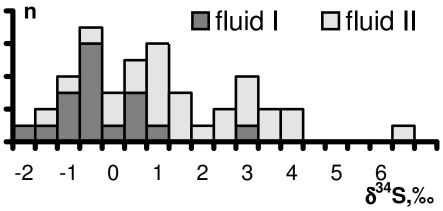

Fig. 4. Calculated sulphur isotope composition for ore-forming hydrothermal fluids of Portovelo-Zaruma field

The S-isotope composition of later generation sulphides is somewhat lighter than those of the early sulphides. Sulphur isotope geothermometry reveals temperature of 133-385°C (including 385-197°C for quartz-polymetallic assemblages).

The S-isotope composition of fluid H_2S ($\delta^{34}S_{fl}$), calculated using T_h and formulae of (Ohmoto and Rye, 1979) ranges from –2.59 to +2.52‰ for quartz-pyrite stage (fluid I, Fig. 4), average ~ –0.5‰. For the economic quartz-polymetallic stage (fluid II), $\delta^{34}S_{fl}$ ranges from –1.95 to +6.24‰ (average ~ +1‰). It can be concluded that juvenile sulphur ($\delta^{34}S$ in the range -3 to +7‰) played a significant role in sulphide formation.

On the other hand, oxygen isotope data for quartz ($\delta^{18}O_{fl}$ ~ –2 to 0‰) reveals the major input of meteoric water. These data are, however, determined from ore vein calcite ($\delta^{18}O_{fl}$~ +3 ‰) and can be explained by mixing of meteoric and magmatic water (Van Thournout et al., 1996).

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