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Mineral chemistry, fluid inclusion and stable isotope studies of the Suyoc epithermal veins: Insights to Au-Cu mineralization in southern Mankayan Mineral District, Philippines

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Abstract

The Suyoc prospect is an epithermal vein-type mineralization located at the southern part of the Mankayan Mineral District, Northern Luzon, Philippines. The prospect’s epithermal veins are hosted in volcanioclastic rocks and conglomerate, which belong to the Late Oligocene to Early Miocene Balili Formation and the Middle to Late Miocene Suyoc Conglomerate, respectively. These veins are classified into three major types: quartz vein, quartz-sulfide vein, and quartz-carbonate vein. The quartz vein exhibits massive and cockade textures associated with pyrite + chalcopyrite. The quartz-sulfide vein consists of massive and comb quartz associated with pyrite + chalcopyrite + sphalerite. The quartz-carbonate vein has massive quartz associated with
Fluid inclusion measurements in quartz from the three major vein-types revealed 230-250°C formation temperatures and 1.0-3.5 wt.% NaCl equivalent salinity, which are values consistent with epithermal deposits. Quartz textures (e.g., massive, cockade, comb, crustiform) and dominance of liquid-rich fluid inclusions do not suggest that boiling is a primary mechanism of vein deposition. Possible mechanisms are inferred as meteoric water dilution based on homogenization versus salinity trend in quartz vein and presence of rhodochrosite in quartz-carbonate vein, and wall rock interaction based on FeS trend in sphalerite crystals of the quartz-carbonate vein. The presence of pyrite and chalcopyrite in the major vein-types and the FeS mole percent values (0.51 to 8.30) in quartz-carbonate vein indicate an intermediate sulfidation state. The alteration minerals illite chlorite, pyrite and quartz indicate near-neutral pH condition. $\delta^{34}S$ values, which vary from -1.1 to +3.9‰, suggest reduced conditions when compared to the representative bulk $\delta^{34}S$ value for the Mankayan Mineral District. The characteristics and conditions strongly indicate an intermediate sulfidation epithermal (ISE) style of mineralization. Moreover, the $\delta D_{\text{water}}$ (-63 to -66‰) and $\delta^{18}O_{\text{water}}$ (-3.9 to -1.1‰) values from the major vein-types suggest late stage formation in a magmatic-hydrothermal system similar to other ISE deposits in the Northern Luzon Segment (e.g., Victoria, Acupan and Antamok).

Given these, the presence of the Suyoc ISE veins in the underexplored southern part of the Mankayan Mineral District implies potential presence of undiscovered cogenetic porphyry Cu and high sulfidation epithermal mineralization in the area.

1. Introduction
The Mankayan Mineral District in Northern Luzon, Philippines is considered as one of the most well-endowed districts in the Philippines in terms of hydrothermal mineralization. It hosts some of the most well-known and well-studied hydrothermal deposits, such as the Lepanto high sulfidation epithermal Cu-Au deposit (Claveria, 2001; Hedenquist et al., 2017), the Victoria intermediate sulfidation epithermal Au-Ag deposit (Claveria, 2001; Sajona et al., 2002; Chang et al., 2011), and the Far Southeast porphyry Cu-Au deposit (Shinohara and Hedenquist, 1997; Hedenquist et al., 1998; 2017). Other smaller deposits in the district include the Guinaoang porphyry Cu-Au deposit (Sillitoe and Angeles, 1985) and Teresa epithermal Au-Ag vein deposit (Chang et al., 2011). Several studies have been conducted in the district particularly on the Far Southeast, Lepanto and Victoria deposits, which are considered to be genetically linked due to their spatial and temporal relationships (e.g., Arribas et al., 1995; Hedenquist et al., 1998; Chang et al., 2011).

However, there are still other significant mineralization in the district that need to be investigated, as they may provide useful information in identifying other porphyry-epithermal systems similar to the Far Southeast-Lepanto-Victoria. One of these is the Suyoc prospect, which is situated at the less explored southern part of the Mankayan district. The prospect has been mined by artisanal miners for its base metal-rich veins consisting of quartz-carbonate-chalcopyrite (Gonzales, 1967) and is currently managed by Itogon-Suyoc Resources Incorporated (ISRI). In this study, we present the mineralization characteristics of the Suyoc prospect obtained from field investigation, microscopy, fluid inclusion analysis, mineral chemistry analysis, and stable isotope analysis. From these results, its formational conditions are constrained to determine its mineralization style, and ultimately provide insights to the prospective potential of the underexplored southern part of the Mankayan Mineral District.
1.1. Regional Geologic Setting

The Mankayan Mineral District is situated in the Northern Luzon Segment, which forms part of the Taiwan-Luzon Arc that developed from the subduction of the South China Sea Basin (SCSB) along the Manila Trench (e.g., Stephan et al., 1986; Suppe, 1988; Teng, 1990) (Figure 1). The segment experienced major tectonic uplift for the past 4 Ma as a consequence of the subduction of an extinct mid-oceanic ridge manifested as the Scarborough Seamount Chain in the SCSB (Yang et al., 1996). The subduction of this young and buoyant oceanic lithosphere resulted to the initiation of subdued volcanism and emplacement of highly fertile andesite and dacite shallow intrusions, which are considered to be responsible for the Pliocene-Pleistocene hydrothermal mineralization in the Mankayan and Baguio Mineral Districts (e.g., Sajona and Maury, 1998; Cooke et al., 2005; Waters et al., 2011; Deng et al., 2020; Jabagat et al., 2020).

The Luzon island is traversed from north to south by the left-lateral strike-slip Philippine Fault Zone (PFZ). This seismically active fault zone in the Philippine Mobile Belt was formed as a response to the northwestward convergence of the Philippine Sea Plate and southeastward convergence of the Eurasian Plate (Aurelio, 2000; Queaño et al., 2007; Armada et al., 2020). One of the northern splays of the PFZ, which is the Abra River Fault (ARF), cuts the Northern Luzon Segment (Figure 1). The NS- to NNW-trending ARF is a left-lateral fault with thrust component (Mines and Geosciences Bureau (MGB), 2010). Its motion resulted to the formation of NW-trending fault splays, which include the Lepanto fault, host to the Lepanto enargite orebody (Maleterre, 1998). For that reason, the ARF is believed to have controlled the spatial configuration of hydrothermal mineralization in the district (Chang et al., 2011; Manalo et al., 2018).
1.2. Mineralization in Mankayan Mineral District

The Mankayan Mineral District has several hydrothermal deposits and prospects within its ~25 km² area (Chang et al., 2011) (Figure 2a). The general age of this district-wide mineralization is ~1.2 to 3.5 Ma (Arribas et al., 1995). The north-central part hosts a well-defined porphyry-epithermal system composed of the Far Southeast (FSE) porphyry Cu-Au deposit, the Lepanto high sulfidation epithermal (HSE) Cu-Au deposit, and the Victoria intermediate sulfidation epithermal (ISE) Au-Ag deposit. The FSE has a main mineralization stage associated with sericitic alteration that overprints an earlier K-silicate alteration (Hedenquist et al., 1998). Its ore consists of bornite, chalcopyrite and electrum (Concepción and Cinco, 1989), with Bi-Te-bearing tennantite in several areas (Imai, 2000). Located on the shoulder of FSE is the Lepanto HSE deposit. The main Lepanto orebody consists of early enargite-luzonite-pyrite and late gold-telluride associated with tennantite-tetrahedrite. The orebody occurs in vuggy quartz with haloes of alunite, kaolinite and dickite (Hedenquist et al., 1998). On the other hand, the Victoria ISE deposit is situated a few hundred meters southwest of the FSE (Chang et al., 2011). Victoria is characterized by chalcopyrite + sphalerite ± galena ± tennantite ± tetrahedrite sulfide assemblage and gold occurring as native gold and electrum, with associated alteration of dominantly illite-chlorite (Claveria, 2001). A recent study by Manalo et al. (2018) introduced the Northwest quartz-pyrite-gold (QPG) vein mineralization located at the periphery of the main Lepanto orebody. This mineralization occurred after the enargite-luzonite-pyrite stage of Lepanto and is characterized by low-copper, high-gold epithermal veins mainly hosted in the Cretaceous metavolcanic rocks.

Other significant porphyry mineralization in the district include the Guinaoang porphyry Cu-Au deposit and the Buaki and Palidan porphyry prospects. The Guinaoang
deposit is located ~3 km southeast of the FSE and is characterized by Cu-Au mineralization associated with K-silicate alteration overprinted with sericite-clay-chlorite alteration (Sillitoe and Angeles, 1985). Sillitoe and Angeles (1985) reported an advanced argillic cap on top of Guinaoang that has localized enargite mineralization. The Buaki prospect is located ~2 km west of the FSE and is characterized by outcropping porphyry-style stockworks, whereas the Palidan is a porphyry lithocap prospect located ~2 km south of the Victoria deposit (Chang et al., 2011). Vein prospects are also present and are mostly concentrated in the southern portion of the district. These include the Teresa and Nayak prospects characterized by gold-bearing base-metal veins (Chang et al., 2011).

1.3. Local Geology

The lithologies in the Mankayan Mineral District include metamorphic, sedimentary, and volcano-plutonic rocks with ages from Late Cretaceous to Pleistocene (Figure 2b). The basement in the area is the Late Cretaceous to Early Eocene Lepanto Metavolcanics, which consists of indurated andesitic to basaltic lavas with minor turbiditic sequences (Ringenbach et al., 1990). Unconformable over the basement are the Late Eocene to Early Oligocene Apaoan Volcaniclastics and Late Oligocene to Early Miocene Balili Formation. The former is composed of green and red thin-bedded siltstone-sandstone (Garcia, 1991), whereas the latter is characterized by thick sequences of sandstones, volcanic conglomerates, basalt flows, andesitic pyroclastics and breccia (Ringenbach, 1992). The basement and the volcaniclastic rocks are intruded by the Early to Middle Miocene Bagon Intrusive Complex dominantly consisting of tonalite (Sillitoe and Angeles, 1985). This intrusive complex, together with the older formations, is widely exposed at the western portion of the district. The Middle to Late Miocene Suyoc Conglomerate unconformably overlies the older units and is exposed
at the southern area. The conglomerate is polymictic with clasts of well-rounded, pebble- to cobble-sized chert, epidotized volcanic rocks and limestone (Gonzales, 1956). This conglomerate is overlain by the Pliocene to Pleistocene dacitic pyroclastic rocks with associated dacitic dome complexes (Garcia and Bongolan, 1989). These dacitic units are the Pliocene Imbanguila Dacite and the Pleistocene Bato Dacite (MGB, 2010). Both formations are widely exposed at the northeastern and east-central portions of the district. On top of these dacitic units is the Lapangan Tuff, which consists of a thin sequence of ash with an age of 18,820 ± 670 years based on C$^{14}$ dating (Bureau of Energy Development-Japan International Cooperation Agency, 1981).

1.4. The Suyoc prospect

The epithermal veins of the Suyoc prospect is hosted in the volcaniclastic rock and conglomerate (Figure 2b). The volcaniclastic rock forms part of the Late Oligocene to Early Miocene Balili Formation and consists of epiclastic sandstone and conglomerate. The sandstone is a deformed bedded unit consisting of grains of lithic andesite, amphibole, and plagioclase, whereas the matrix- to clast-supported conglomerate is composed of cobble-sized clasts of aphanitic and porphyritic andesite set in a partly silicified matrix (Figure 3a-3b). Overlying the Balili Formation is the Suyoc Conglomerate. It consists of well-rounded, granule- to boulder-sized clasts of andesite, porphyritic andesite, diorite, limestone, mudstone, and sandstone set in dominantly andesitic, silt- to sand-sized matrix (Figure 3c-3d). The Suyoc Conglomerate has a reported age of Middle to Late Miocene based on the dating of foraminifera from a capping limestone (Gonzales, 1956; Maleterre, 1989). Capping the exposures of the Suyoc Conglomerate is the Imbanguila Dacite Pyroclastics which was dated 2.9 ± 0.40 Ma from the K-Ar dating of a biotite in a dacitic lapilli tuff (Sillitoe and Angeles, 1985). The epithermal veins of the Suyoc prospect hosted in the Suyoc
Conglomerate terminate in this pyroclastic unit. Hence, considering such relationship, the veins of the Suyoc prospect can be inferred to be younger than Late Miocene (Suyoc Conglomerate) but older than Middle Pliocene (Imbanguila Dacite Pyroclastics).

A major structure in the area is the north-south trending lineament interpreted herein as a possible southern extension of the Abra River Fault (Figure 2b). This major fault was interpreted by other authors (e.g., Chang et al., 2011; Manalo et al., 2018) to have influenced mineralization in the area. It may have also played a role in the occurrence of structures that host the Suyoc epithermal veins.

2. Methodology

2.1. Sample collection

The field survey was conducted on accessible surface and underground vein exposures in the Suyoc prospect. Underground exposures were observed by accessing the portals of ISRI and small-scale miners (Figure 2a). Surface exposures are intensely weathered that the primary characteristics of the veins were nearly unrecognizable. Hence, megascopic description and identification were only conducted on veins in accessed underground, where exposures are relatively well-preserved. Representative vein samples, together with adjacent altered wall rock samples (within 5-meter peripheral zone), were collected from the Esperanza, Elizabeth and Calixto tunnels at depths of ~80 m, ~130 m and ~100 m from the present surface level, respectively (Figure 2a).

2.2. Petrography

Polished slab-sections with thickness of ~5 mm were produced from the vein-samples for petrographic analysis of opaque minerals (e.g., sulfides, Au). Double-polished thin sections of ~30 μm thickness were also produced for petrographic analysis.
of gangue minerals. The preparation of polished slab and double-polished thin sections was done at the University of the Philippines – National Institute of Geological Sciences (UP-NIGS) using a Pelcon Automatic Thin Section machine and a Topper Diamond Polishing unit. Petrographic analysis was carried out using the Olympus BX53-P polarizing microscope at UP-NIGS.

2.3. Mineral chemistry analysis

Gold-bearing minerals, and sphalerite crystals coexisting with pyrite were subjected to mineral chemistry analysis. The Au-bearing minerals were analyzed for Au and Ag composition, whereas sphalerite crystals were analyzed for Fe, Zn and S. The slab-sections containing the desired minerals were coated with carbon using the 108C Auto Carbon Coater prior to analysis. Mineral chemistry analysis was done using the JEOL JXA-8230 Electron Probe Microanalyzer at the University of the Philippines – National Institute of Geological Sciences. Operating conditions were set to 15kV acceleration voltage with probe current of 10 nA and probe diameter of 3-5 μm. Results obtained were automatically calculated by JEOL software using ZAF correction matrix. The final results are in mass percent values. Detection limits were calculated to range from ~100-200 ppm.

2.4. Fluid inclusion analysis

Double-polished wafer samples of quartz with thickness ranging from 150-200 μm were prepared using similar equipment used for producing thin sections. Microscopic analysis of fluid inclusions was conducted using the Olympus BX53-P polarizing microscope at the University of the Philippines – National Institute of Geological Sciences. Homogenization temperatures and final-ice melting temperatures of the observed primary fluid inclusions were measured using the LINKAM 10002L
heating and cooling stage mounted in a Nikon Eclipse LV100N POL Microscope at the Department of Earth Resources Engineering, Kyushu University, Japan. Salinity values were calculated using the equation of Bodnar (1993) where $\theta$ is the final-ice melting temperature:

$$\text{Salinity (wt. % NaCl equiv.)} = 0.00 + 1.78\theta - 0.0442\theta^2 + 0.000557\theta^3$$

2.5. X-ray diffraction analysis

Representative altered wall rock samples were subjected to X-ray diffraction (XRD) analysis using bulk and oriented methods. For the bulk method, the samples were powdered to $<10$ $\mu$m using an agate mortar and pestle (e.g., Poppe et al., 2001). The powdered samples were analyzed using the Rigaku Ultima IV XRD calibrated with a silica standard at the Department of Earth Resources Engineering, Kyushu University, Japan. For oriented method, samples were sonicated then subjected to centrifugation technique to separate the clay components. Before subjecting these clay components to XRD analysis, three treatments were applied to them: air drying, acid treatment using HCl and glycolation using ethylene glycol.

2.6. Stable isotope analysis

Veins that contain recoverable quartz and pyrite crystals were slightly crushed for oxygen-hydrogen and sulfur isotopic measurement, respectively. Quartz and pyrite grains produced from crushing were separated by picking using stainless tweezers and a binocular microscope. Pure grains of pyrite were recovered, but sulfide impurities were observed in recovered quartz grains. Thus, purification using an aqua regia solution was applied to remove the sulfides (e.g., Tindell et al., 2018). Stable isotope analysis was carried out at the Scottish Universities Environmental Research Centre, University of Glasgow. For oxygen isotope analysis, quartz separates were combusted
with CO₂ laser at temperature >1500°C with ClF₃ as the fluorinating agent (Sharp, 1990). The O₂ gas produced from combustion was reacted to hot graphite to convert O₂ to CO₂ and was subsequently analyzed using VG Optima mass spectrometer. For hydrogen isotope analysis, quartz separates were heated to >700°C in a vacuum to release fluids (Gleeson et al., 2008). Following the method of Donnelly et al. (2001), the fluids were transformed to hydrogen by reaction with hot chromium and were subsequently analyzed using the VG Optima mass spectrometer. Results in oxygen and hydrogen isotope analyses are reported in δ₁⁸O (‰) and δD (‰), respectively, relative to the Standard Mean Ocean Water. For sulfur isotope analysis, liberation of SO₂ gas was done by combusting the pyrite separates at 1075°C using Cu₂O as reagent (Robinson and Kusakabe, 1975). Freed SO₂ gas was analyzed using VG Isotech SIRA II mass spectrometer. Results are reported in δ³⁴S (‰) with respect to the Vienna Cañón Diablo Troilite standard.

3. Results

3.1. Vein-types, mineralogy and textures

The epithermal veins of the Suyoc prospect are classified into three major types: quartz vein, quartz-sulfide vein, and quartz-carbonate vein. The quartz vein is characterized by anastomosing, massive veinlets (Figure 4a), which strike NE-SW and N-S and dips 60-80°SE and 80°W, respectively. The adjacent wall rocks of this vein-type are commonly intensely chloritized. Angular to sub-angular fragments of quartz and intensely silicified wall rock are incorporated within the veins (Figure 5a). These fragments often exhibit cockade texture characterized by bands of massive microcrystalline quartz enclosing the wall rock fragments (Figure 6a). The vein contains low amounts of pyrite and chalcopyrite (<1% vein volume) occurring as
disseminated anhedral crystals (<0.1 mm). This vein-type was observed in the Calixto, Manuit and Antonio tunnels (Figure 2a).

The quartz-sulfide vein has a massive appearance with thickness that reaches up to 0.5 m (Figure 4b). It generally strikes NE-SW and steeply dips to the SE and NW. The vein is characterized by vuggy quartz with massive pyrite and chalcopyrite (Figure 5b). The quartz is micro- to macrocrystalline with massive and comb textures (Figure 6b). Disseminated pyrite and chalcopyrite make up ~10% of the sample. Subhedral pyrite crystals have <1 mm diameter with presence of microfractures. Chalcopyrite has a similar crystal size as pyrite but is mainly anhedral. It occurs as either infill in pyrite microfractures or between pyrite crystals (Figure 6e). Minor sphalerite occurs as intergrowth with chalcopyrite. This vein-type was observed in the Elizabeth and Esperanza tunnels (Figure 2a).

The quartz-carbonate vein exhibits weak crustiform banding of quartz and rhodochrosite. Its thickness rarely exceeds 0.3 m and occurs as continuous veins that sometimes split into two or more branches. It strikes NE-SW and dips 75°NW and 63°NE. Oxidation affected the veins and host rocks that resulted to the formation of malachite, Fe-Mn oxide encrustations and limonite film (Figure 4c). This vein-type is mainly observed at the Elizabeth tunnel and less extensively at the Manuit tunnel. At the Elizabeth tunnel, it crosscuts the quartz-sulfide vein (Figure 4d). The quartz and rhodochrosite layers in this vein type exhibit asymmetric crustiform texture (Figure 5c). The outer or marginal layer is composed of micro- to macrocrystalline quartz crystals of massive texture (Figure 6c). Associated with this layer are intergrowth of pyrite, chalcopyrite, galena, and sphalerite crystals with average diameters of ≤0.5 mm. Sphalerite and galena often display interpenetrating boundaries. Chalcopyrite disease is observed along the rim of sphalerite crystals (Figure 6f). Traces of bournonite
sulfosalts are observed as inclusions in galena (Figure 6g). Au-bearing minerals with diameters of <25 µm commonly occur as inclusions in pyrite (Figure 6h) and occasionally in chalcopyrite and sphalerite. Meanwhile, inner layer of the quartz-carbonate vein is rhodochrosite that occurs as cryptocrystalline and macrocrystalline variety. The cryptocrystalline rhodochrosite is situated in between the quartz layer and the macrocrystalline rhodochrosite (Figure 6d). Very minor sphalerite and galena were observed in the cryptocrystalline layer, whereas sulfides are absent in the macrocrystalline layer.

Gypsum veins were also observed underground particularly in the Manuit tunnel, but of unmapable extent (Figure 4e). They also outcrop on the surface where they are associated with massive pyrite (Figure 4f).

3.2. Elemental compositions

Elemental compositions obtained from the mineral chemistry analysis of Au-bearing minerals and sphalerite in the quartz-carbonate vein are shown in Table 1a and 1b, respectively. Sphalerite crystals that coexist with pyrite as indicated by their interlocking relationship were selected for analysis.

The Au-bearing mineral 1 and 2 have elemental compositions diagnostic of electrum, whereas 3 is of native gold composition (Figure 7). The 3 sphalerite crystals have FeS mole percent values ranging from 0.51 to 8.30 (Figure 8). Sphalerite 1 has 8 analysis points, with the lowest values (< 1 FeS mole percent) recorded near the core (Figure 8a). The subsequent point spikes to a value of 8.30 while the succeeding points dropped to a lower value but still higher than that of the points near the core. Sphalerite 2, which has 5 analysis points, shows a similar trend where FeS mole percent values are <1 near the core but increases up to about fourfold at the rim (Figure 8b). In
sphalerite. However, the core has a relatively high value with 1.02 FeS mole percent while the 2 subsequent points toward the rim have values <1 (Figure 8c). The highest value was recorded at the rim with a value of about twofold of that of the core. In general, an apparent trend characterized by an increase in FeS content from the apparent core to the apparent rim can be observed in the three sphalerite crystals of the quartz-carbonate vein.

3.3. Fluid inclusion petrography and microthermometry

Quartz crystals from the three major vein-types were evaluated for fluid inclusion petrography and microthermometry. For the quartz-carbonate vein, the selected quartz crystals are those associated with Au-bearing minerals. Two groups of liquid-rich inclusions were recognized from petrographic analysis. The first group occurs in clusters, comprising of inclusions with sizes of <5 µm. These inclusions are elongate in shape and have smooth boundaries and are thus interpreted to be of primary type (Figure 9a, b) (Goldstein and Reynolds, 1994). Meanwhile, the second group is composed of irregularly shaped isolated inclusions that had sizes ranging from 5 to 20 µm (Figure 9a, b). This group is interpreted as secondary type (Goldstein and Reynolds, 1994).

Primary fluid inclusions were analyzed in each vein-type. Their homogenization temperature ($T_h$) values and computed salinity from final-ice melting temperature values are listed in Table 2. Modal $T_h$ values in the quartz vein and the quartz-carbonate vein are within a narrow range of 240-250°C while the quartz-sulfide vein has a range of 230-250°C. The modal salinity values have a general range of 1.0-3.5 wt. % NaCl equivalent, with 2.5-3.5 in the quartz vein, 2.0-2.5 in the quartz-sulfide vein and 1.0-1.5 in the quartz-carbonate vein. A positive correlation characterized by a decrease in
temperature with decrease in salinity can be inferred from the values of the quartz vein (Figure 9c). Meanwhile, for the quartz-carbonate and quartz-sulfide veins, values are quite scattered and has very weak correlation (Figure 9d, e).

### 3.4. X-ray diffraction analysis

Narrow alteration zones of around 5 to 10 meters typically surround the epithermal veins of the Suyoc prospect. Results from X-ray diffraction analysis of these alteration zones are shown in Figure 10. Bulk analysis of the altered wall rocks associated with the three major vein-types revealed the presence of pyrite, quartz, calcite, and phyllosilicate minerals such as clay and chlorite/kaolinite. The clay and chlorite/kaolinite peaks detected in bulk analysis were further identified in oriented analysis as illite and chlorite, respectively (Figure 10).

### 3.5. Stable isotope composition

Results of stable isotope analysis are shown in Table 3. The analyzed quartz crystals are of the same variety as those assessed for fluid inclusion studies. $\delta^{18}O$ values obtained are: $+8.7\%o$ and $+7.5\%o$ for the quartz vein, $+5.6\%o$ and $+5.5\%o$ for the quartz-sulfide vein, and $+7.8\%o$ and $+7.7\%o$ for the quartz-carbonate vein. Corresponding $\delta D$ values derived from fluid inclusions are $-65\%o$, $-66\%o$ and $-63\%o$, respectively. Calculated $\delta^{18}O_{water}$ using the equation of Clayton et al. (1972) for 200-500°C quartz-water system resulted in values of -0.7 to -0.2 and -1.9 to -1.4 for quartz vein, -4.4 to -3.4 and -4.4 to -3.4 for quartz-sulfide vein, and -1.6 to -1.2 and -1.7 to -1.2 for quartz-carbonate vein. Sulfur isotope data from pyrite of the quartz-carbonate vein and quartz-sulfide vein revealed values of -1.1, -0.1\%o and 3.8, 3.9\%o, respectively.

### 4. Discussion

#### 4.1. Conditions of formation
The Suyoc epithermal veins are classified into three major types, namely the quartz vein, quartz-sulfide vein, and quartz-carbonate vein. The gypsum vein, with occasional presence of massive pyrite, also forms part of the prospect but is not considered a major vein-type due to its limited extent and minor occurrence. The summary of the characteristics of the three major vein-types that were obtained from the analyses is shown in Table 4.

4.1.1. Mechanism of deposition

Homogenization temperature and salinity values from the three major vein-types have modal range of 230-250°C and 1.0-3.5 wt.% NaCl equivalent, respectively. These values are consistent to what is expected from an epithermal deposit (Bodnar et al., 2014). Vein deposition in epithermal systems can be initiated by processes such as boiling (e.g., Cooke et al, 1996; Moncada et al., 2012; 2017), fluid mixing (e.g., Vikre, 1989; Corbett and Leach, 1998), and wall rock interaction (e.g., Vennemann et al., 1993; Cooke and McPhail, 2001). The major epithermal veins of the Suyoc prospect predominantly display massive quartz texture associated with cockade in quartz vein, comb in quartz-sulfide vein, and crustiform in quartz-carbonate vein. Massive and comb textures can be interpreted as products of slow crystallization (e.g., Dong et al., 1995; Moncada et al., 2012). Meanwhile, crustiform texture and its subtype, cockade texture, may be interpreted as textures associated with fast crystallization (e.g., boiling) when they coexist with rapidly-formed quartz textures like colloform and bladed, among others (Simmons and Browne, 2000). However, the cockade and crustiform textures exhibited by the quartz vein and quartz-sulfide vein, respectively, are associated with massive quartz texture. This suggests that these cockade and crustiform textures are associated with slow crystallization considering the massive texture’s mode of formation (e.g., Dong et al., 1995; Moncada et al., 2012). The dominance of liquid-
rich fluid inclusion hosted in quartz supports this apparently gradual crystallization suggested by the quartz textures. Liquid-rich fluid inclusions are considered to be entrapped during non-boiling condition, in which slow crystallization is typical (e.g., Bodnar et al., 1985; Moncada et al., 2012; 2017).

Evidence supporting the prevalence meteoric water dilution (or fluid mixing) and wall rock interaction for the deposition of the veins in the Suyoc prospect are present. In the quartz vein, apparent decrease in both homogenization temperature and salinity as shown in Figure 9c suggests progressive dilution of hydrothermal fluid by meteoric water (Wilkinson, 2001). In the quartz-carbonate vein, the occurrence of rhodochrosite may also suggest mixing of marginal water (e.g., meteoric) into the system to cause vein deposition (Simmons and Browne, 2000). The FeS content in the sphalerite crystals of the quartz-carbonate vein is generally increasing from core to rim (Figure 8). This progressive increase in FeS content signifies a progressive decrease in sulfidation state, which can be considered to be a result of wall rock interaction (e.g., Barton et al., 1977; Einaudi et al., 2003).

4.1.2. Sulfidation state

In the epithermal veins of the Suyoc prospect, pyrite and chalcopyrite are consistently present. These two sulfides represent the lower and upper stability limit of intermediate sulfidation (IS) state in epithermal conditions, respectively (Einaudi et al., 2003). Hence, the occurrence and coexistence of such sulfides in the epithermal veins of the Suyoc prospect suggest an IS state. This is further supported by the FeS mole percent values in the sphalerite crystals coexisting with pyrite. Obtained values range from 0.51-8.30, which are well within the IS state considering a temperature of 240-250°C from fluid inclusions (Figure 11) (Einaudi et al., 2003).
4.1.3. **pH condition**

The epithermal veins of the Suyoc prospect are associated with wall rock alteration assemblage of illite, chlorite, pyrite, and quartz, with additional calcite observed in the quartz-sulfide and quartz-carbonate veins. These alteration minerals were formed under neutral pH condition in the epithermal environment (Figure 12) (White and Hedenquist, 1995). Pyrite and quartz, although may overlap with acidic condition, still indicate neutral pH condition in this case due to their coexistence with neutral pH minerals (i.e., chlorite, illite, calcite).

4.1.4. **Redox condition**

According to Rye (1993), in a magmatic-hydrothermal system, variations in a sulfide’s $\delta^{34}$S composition relative to the bulk sulfur isotope composition is a function of both reduction-oxidation and temperature. The bulk composition represents the composition of the cogenetic igneous rock or the hydrothermal fluid source (Rye, 1993). Sulfides precipitating from oxidized fluids (H$_2$S$\text{<SO}_2$) are expected to have lower $\delta^{34}$S values relative to the bulk composition, with $\delta^{34}$S values becoming progressively lower as temperature decreases, whereas sulfides precipitating from reduced fluids (H$_2$S$\text{>SO}_2$) only undergo minimal decrease in $\delta^{34}$S values regardless of temperature, resulting to $\delta^{34}$S values not varying much from the bulk composition (Rye, 1993; 2005). Having such concept, it is important to know the bulk sulfur isotope composition representative for the Suyoc prospect in order to interpret its $\delta^{34}$S values then constrain its redox condition.

Imai (2000) and Manalo et al. (2018) have reported a +5‰ bulk sulfur isotope composition for the hydrothermal mineralization in the Mankayan Mineral District (MMD) in which the Suyoc prospect is situated. This value is in agreement with those
in subduction-related volcanic arcs (Sasaki and Ishihara, 1979). Hence, for the
interpretation of the $\delta^{34}$S value of the Suyoc prospect, the +5‰ value suggested by Imai
(2000) and Manalo et al. (2018) is used here. An estimated $\delta^{34}$S compositional
evolution in sulfide through reduced and oxidized cooling pathways in reference to
+5‰ bulk composition is shown in Figure 13. In the figure, it can be observed that the
$\delta^{34}$S values (-1.1 to +3.9‰) of the Suyoc quartz-sulfide and quartz-carbonate veins and
their corresponding temperatures plot within the reduced path suggesting the deposition
of both veins under reduced condition ($H_2S>SO_2$). It is known that mineralizing
hydrothermal fluids, which separate from porphyry intrusions in magmatic arcs such as
in MMD, are originally oxidized ($H_2S>SO_2$) (e.g., Sun et al., 2015; Deng et al., 2017;
Zhang et al., 2017). The reduced condition exhibited by the quartz-sulfide and quartz-
carbonate veins is likely to be caused by the progressive oxygen buffering of fluids by
wall rock during ascent (Einaudi et al., 2003; Sillitoe and Hedenquist, 2003). The
occurrence of gypsum veins in the Suyoc prospect, which accounts for the introduction
of oxidized fluid (Hedenquist et al., 2000), can be hypothesized as a product of later
veining stage when the buffering capacity of the wall rock is already exhausted. This is
similar to other epithermal vein systems in the Northern Luzon Segment showing late
stage deposition of sulfate minerals (e.g., Victoria deposit: Claveria, 2001; Acupan
deposit: Cooke et al., 1996).

4.2. Mineralization style

The conditions of formation of the three major vein-types of the Suyoc prospect
conform to typical intermediate sulfidation epithermal (ISE) style of mineralization.
Sulfide mineralogy from the three major vein-types, as well as FeS content in sphalerite
in the quartz-carbonate vein, indicates that the fluid was at intermediate sulfidation
state. Alteration mineralogy of illite, chlorite, with associated pyrite, quartz, and calcite,
signifies neutral pH fluid condition. Sulfur isotope values recorded in pyrite suggest reduced condition during base and precious metal deposition (i.e., quartz-sulfide vein and quartz-carbonate vein). These constrained fluid conditions are consistent with fluids that form ISE mineralization (Sillitoe and Hedenquist, 2003; Einaudi et al., 2003). In addition, one of the characteristics displayed by the Suyoc prospect that is typical to an ISE endmember is the occurrence of rhodochrosite- and gypsum-bearing veins, which is a characteristic of typical ISE deposit (e.g., Victoria deposit, Philippines: Claveria, 2001; Cayloma deposit, Peru: Echavarria et al., 2006).

Presence of ISE deposits is well-documented in the Northern Luzon Segment. The Victoria ISE deposit (e.g., Claveria, 2001; Chang et al., 2011) north of the Suyoc prospect, and the Acupan ISE vein system in Baguio Mineral District (Cooke et al., 1996), are the best examples. The occurrence of ISE style mineralization in the Northern Luzon Segment can be attributed to its compressive island arc setting (Sillitoe and Hedenquist, 2003; Garwin et al., 2005).

4.3. Timing of formation

As discussed in the previous section, the epithermal veins of the Suyoc prospect belong to the ISE style. ISE mineralization typically occurs in a magmatic-hydrothermal system, in which high sulfidation epithermal (HSE) and porphyry Cu mineralization may co-occur (Sillitoe and Hedenquist, 2003; Einaudi et al., 2003). The theoretical model developed by Shinohara and Hedenquist (1997) about the magma degassing involved during the formation and evolution of the Far Southeast (FSE) porphyry Cu-Au deposit provides a better understanding of the formational timing of specific alteration and mineralization in a magmatic-hydrothermal system. Their model displays the importance of $\delta D$ value as one of the proxies on determining such timings.
According to Shinohara and Hedenquist (1997), two distinct single-phased liquids were involved in the FSE magmatic-hydrothermal system: the early high temperature liquid with $\delta D$ of about -25‰, and the late low temperature liquid with $\delta D$ of about -40‰. More detail about these two liquids is shown in Figure 14a. The early high temperature liquid dissociated to vapor and hypersaline liquid to form advanced argillic and potassic alteration, respectively; whereas the late low temperature liquid formed sericitic alteration that is associated with the main precious- and base-metal mineralization (Shinohara and Hedenquist, 1997; Hedenquist et al., 1998). Hedenquist et al. (1998) provided detailed isotopic composition for the advanced argillic alteration, which represents the vapor, and the sericitic alteration, which represents the mineralized late low temperature liquid. The meteoric water mixing trends of these two fluids, the vapor and the late low temperature liquid, relatively differ, as the former is a product of the earlier, high $\delta D$ value liquid, whereas the latter came from the later, low $\delta D$ value source (Figure 14b).

Looking into the $\delta D$ values of the Suyoc prospect from the quartz of the three major vein-types, the values indicate a source that is low in heavy hydrogen isotope. Such composition can also be observed in other ISE mineralization in the Northern Luzon Segment, which are Acupan and Antamok of the Baguio Mineral District (Sawkins et al., 1979). The low $\delta D$ values of the Suyoc prospect and the Acupan-Antamok show resemblance to that of the late low temperature liquid of the FSE (Figure 14b). This suggests that the formation of these ISE mineralization occurred at the later stage of their respective magmatic-hydrothermal system. Such timing is consistent with the late mineralization stage of the FSE magmatic-hydrothermal system that formed the porphyry Cu, Lepanto HSE (Shinohara and Hedenquist, 1997; Hedenquist et al., 1998), and perhaps the cogenetic Victoria ISE (e.g., Claveria, 2001; Chang et al., 2011).
4.4. Exploration Implications

It is widely accepted that ISE mineralization typically exists with porphyry Cu and HSE mineralization in subduction-related magmatic arcs under near-neutral, mildly extensional, or compressive stress regime (e.g., Hedenquist et al., 1998; Sillitoe and Hedenquist, 2003; Chang et al., 2011; Wang et al., 2019). The MMD in Northern Luzon Segment is no stranger to such kind of mineralization associations considering its tectonic setting (e.g., Sajona and Maury, 1998; Cooke et al., 2005; Waters et al., 2011; Deng et al. 2020; Jabagat et al., 2020). The prime example to it is the Far Southeast-Lepanto-Victoria porphyry-epithermal system, which is just ~3 km north of the Suyoc prospect (Chang et al., 2011).

Considering the prominence of porphyry-epithermal systems in MMD, the existence of the Suyoc ISE veins does imply potential presence of cogenetic porphyry Cu and HSE mineralization in its vicinity (Figure 15). The neighboring Victoria ISE deposit displays a spatial configuration that is at least ~1 km away from its cogenetic Far Southeast porphyry Cu-Au and Lepanto HSE deposits (Chang et al., 2011). Following this configuration, an ~1 km radius of prospective area can be proposed around the Suyoc prospect for potential presence of porphyry Cu and HSE mineralization (Figure 16). Investigation for the presence of lithocap or advanced argillic alteration is highly recommended in this prospective area, as this strongly signifies potential presence of HSE and underlying porphyry (e.g., Sillitoe, 2010, Chang et al., 2011).

5. Conclusions

This study presents the following mineralization characteristics and formational conditions for the epithermal veins of the Suyoc prospect:
1) The veins are mainly hosted in the Middle to Late Miocene Suyoc Conglomerate and Late Oligocene to Early Miocene Balili Formation.

2) The veins are classified into three major types: quartz vein, quartz-sulfide vein, and quartz-carbonate vein. Quartz vein consists of massive and cockade quartz with pyrite + chalcopyrite. Quartz-sulfide vein is characterized by massive and comb quartz with pyrite + chalcopyrite + sphalerite. Quartz-carbonate vein is characterized by massive quartz with rhodochrosite and chalcopyrite + sphalerite + galena + Au/Ag ± bouronite. In addition, there is a minor vein-type of gypsum ± pyrite composition.

3) The general temperature of formation of the veins range from 230-250°C and salinity of 1.0-3.5 wt. % NaCl equivalent. Quartz textures (e.g., massive, cockade, comb, crustiform) and dominance of liquid-rich fluid inclusion suggest the prevalence of non-boiling mechanism of vein deposition. These non-boiling processes are inferred as meteoric water dilution based on homogenization versus salinity trend in quartz vein and presence of rhodochrosite in quartz-carbonate vein, and wall rock interaction based on FeS trend in sphalerite crystals of quartz-carbonate vein.

4) The sulfide assemblage containing pyrite and chalcopyrite and FeS mole percent range of 0.51 to 8.30 indicate intermediate-sulfidation state. Alteration assemblage of illite chlorite, pyrite, quartz with calcite indicates near-neutral pH condition. $\delta^{34}S$ values from -1.1 to +3.9‰ suggest reduced condition when compared to the representative bulk $\delta^{34}S$ value for the Mankayan Mineral District. These characteristics and conditions strongly point to an intermediate sulfidation epithermal style.
δD_{\text{water}} (-63 to -66‰) and δ^{18}\text{O}_{\text{water}} (-3.9 to -1.1‰) values suggest late stage formation in the magmatic-hydrothermal system, consistent with other intermediate sulfidation epithermal mineralization in the Northern Luzon Segment (e.g., Victoria, Acupan and Antamok).

The presence of the Suyoc intermediate sulfidation epithermal veins implies a potential presence of undiscovered cogenetic porphyry Cu and high sulfidation epithermal mineralization in the underexplored southern part of the Mankayan Mineral District.

**Acknowledgements**

We would like to express our gratitude to the Itogon-Suyoc Resources Incorporated (ISRI) for logistical support and access to the Suyoc prospect. Members of the Rushurgent Working Group are also thanked for their fieldwork assistance and their contribution to this study through scientific discussions. The Department of Science and Technology (Philippines) provided the funding support for the Electron Probe Microanalyzer used in this study. This research is partially funded by the University of the Philippines Office of the Vice Chancellor for Research and Development (OVCRD) through the Outright Research Grant to JA Gabo-Ratio. We would also like to thank the comments and inputs of an anonymous reviewer and Dr. Adi Maulana to improve the manuscript.

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**Figure captions**

**Figure 1.** Schematic map showing the features and structures in and surrounding the Northern Luzon Segment, which forms part of the Taiwan-Luzon Arc as defined by Yang et al. (1996). The segment is bounded to the east by the East Luzon Trough, and to the west by the Manila Trench where an extinct mid-oceanic ridge (manifested by the Scarborough Seamount Chain) of the South China Sea Basin is subducting. One of
the major structures traversing the segment is the Abra River Fault, a northern splay of the Philippine Fault Zone (Aurelio, 2000).

**Figure 2.** a) Distribution of the known hydrothermal mineralization in the Mankayan Mineral District (Chang et al., 2011; Manalo et al., 2018) and the surface projection of the epithermal veins and small-scale tunnels of the Suyoc prospect. The location of the Mankayan Mineral District is shown by the red dot on the inset map. b) Geology of the district. Geology of the north and central part was modified from Garcia (1991) and Sillitoe and Angeles (1985), whereas the southern part was derived from the data of Itogon Suyoc Resources Incorporated. Exposures of the Apaoan Volcaniclastcs are located further north, and thus not included in this geologic map. Grey shades are the projections of the location and extent of the mineralized areas in A.

**Figure 3.** Representative photos of the host rocks in Suyoc prospect: a) deformed sequence of epiclastic sandstone of the Balili Formation; b) matrix-supported conglomerate with clasts of aphanitic and porphyritic andesite of the Balili Formation; c) thick beds of conglomerate of the Suyoc Conglomerate; d) silicified, matrix- to clast-supported polymictic conglomerate of the Suyoc Conglomerate.

**Figure 4.** Representative photos of the vein-types and other mineralization features in Suyoc: a) anastomosing quartz vein hosted in chloritized conglomerate inside the Calixto tunnel; b) massive quartz-sulfide vein displaced by a fault (red dashed-line) in argillized volcaniclastic rock at the Esperanza tunnel; c) quartz-carbonate vein exhibiting weak crustiform texture with malachite and Fe-Mn oxide encrustations cutting across a conglomerate with surficial cover of limonite at the Elizabeth tunnel; d) quartz-carbonate vein cutting the quartz vein at the Elizabeth tunnel; e) gypsum veins
hosted in conglomerate inside the Manuit tunnel; and f) an outcrop of massive gypsum
and pyrite in conglomerate. Veins are outlined by white dashed lines.

Figure 5. Hand specimen of the three major vein-types: a) quartz vein consisting of
angular to sub-angular quartz and wall rock fragments exhibiting cockade texture, b)
quartz-sulfide vein characterized by vuggy quartz and pyrite-chalcopyrite exhibiting
massive texture; c) quartz-carbonate vein displaying assymmetrical crustiform texture
characterized by outer quartz and inner colloform to macrocrystalline rhodochrosite (qz
= quartz; rds = rhodochrosite; py = pyrite; ccp = chalcopyrite; cry = cryptocrystalline;
mac = macrocrystalline).

Figure 6. Representative photomicrographs of the different veins: a) silicified wall
rock fragment bounded by microcrystalline quartz; b) prismatic quartz exhibiting comb
texture interlayered with massive microcrystalline quartz; c) micro- to macrocrystalline
quartz displaying massive texture with associated sulfides; d) interlayered massive
quartz and cryptocrystalline to macrocrystalline rhodochrosite; e) fractured euhedral to
subhedral pyrite crystals with chalcopyrite infill intergrown with sphalerite; f)
interlocking pyrite, chalcopyrite, galena, and sphalerite that exhibits chalcopyrite
disease; g) galena with minute inclusions of bournonite; and h) electrum encapsulated
within a euhedral pyrite crystal. (a-d in cross-polarized transmitted light and e-h in
plane-polarized reflected light; qz = quartz; rds = rhodochrosite; SWF = silicified wall
rock fragment; py = pyrite; ccp = chalcopyrite; sp = sphalerite; gn = galena; bno =
bournonite; el = electrum; Au = Au-bearing mineral).

Figure 7. Backscatter electron images of the three analyzed Au-bearing minerals in
pyrite from the quartz-carbonate vein. Red circles are the analysis points. Photos a, b
and c contain the Au-bearing minerals 1, 2 and 3, respectively. (py = pyrite; gn = galena)
**Figure 8.** Backscatter electron images of the three sphalerite crystals in quartz-carbonate vein analyzed for FeS composition and their corresponding FeS mole % diagrams. Photos a, b and c contain sphalerite 1, 2 and 3, respectively. Red circles are the analysis points. (py = pyrite; ccp = chalcopyrite; sp = sphalerite; gn = galena)

**Figure 9.** (a-b) Representative photomicrographs of quartz-hosted fluid-inclusions from the quartz vein (photo a) and the quartz-carbonate vein (photo b). Legend: L: liquid phase, V: vapor phase. (c-e) Scatterplot of homogenization temperature versus salinity from quartz-hosted primary fluid inclusions is shown in diagram c for quartz vein, diagram d for quartz-sulfide vein, and diagram e for quartz-carbonate vein. The x- and y-axis have corresponding histograms to show their modal values. The dashed arrow represents the inferred trend of the values.

**Figure 10.** X-ray diffractograms from bulk and oriented analysis of the altered wall rocks adjacent to the three major vein-types. (chl = chlorite; kln = kaolinite; cly = clay; qz = quartz; cal = calcite; py = pyrite; ill = illite)

**Figure 11.** Sulfur fugacity (log $f_{S_2}$) versus temperature (1000/T) diagram showing the different sulfidation states, with their corresponding sulfide assemblages from Einaudi et al. (2003), and FeS mole percent lines from Barton and Toulmin (1966). The red bar shows the projected sulfidation state of Suyoc prospect’s quartz-carbonate vein plotted using the values of modal homogenization temperature (240-250°C) in quartz (x-axis) and FeS mole percent (0.51-8.30) values from sphalerite crystals coexisting with pyrite (gray dashed lines). (cv = covellite, dg = digenite, py = pyrite, bn = bornite, ccp = chalcopyrite, po = pyrrhotite, asp = arsenopyrite, lo = loellingite)

**Figure 12.** List of the common alteration minerals found in epithermal deposits from the compilation of White and Hedenquist (1995). Highlighted in red are the alteration
minerals present in the altered wall rocks of the three major vein-types of the Suyoc prospect.

**Figure 13.** $\delta^{34}$S versus temperature (°C) diagram showing the sulfide $\delta^{34}$S compositional evolution through oxidized and reduced cooling pathway from a source with ~5‰ bulk sulfur isotope composition ($\delta^{34}$S$_{SS}$). The oxidized and reduced $\delta^{34}$S composition paths were estimated for +5‰ $\delta^{34}$S$_{SS}$ using the $\delta$$_{Sulfate}$–$\delta$$_{Sulfide}$ diagram of Rye (2005). The +5‰ represents the bulk composition for the mineralization in the Mankayan Mineral District based on Imai (2000) and Manalo et al. (2018). Plotted within these oxidized and reduced fields are the sulfide $\delta^{34}$S values and corresponding homogenization temperature of the quartz-sulfide vein and quartz-carbonate vein of the Suyoc prospect.

**Figure 14.** a) $\delta$D composition of the two distinct liquids produced from the causative magma of the Far Southeast porphyry Cu system during its evolution (adapted from Shinohara and Hedenquist, 1997). In the early stage, in which ~30% of the magma is crystallized and magma convection is taking place, single-phase, high temperature liquid with $\delta$D of about -25‰ was discharged from the melt as a result of open system degassing. In the later stage, in which ~50% of the magma is crystallized, with magma convection and degassing being halted, single-phase, low temperature liquid with $\delta$D of about -40‰ is discharged from the melt. b) $\delta$D$_{water}$ vs $\delta^{18}$O water diagram showing the meteoric water mixing trend of advanced argillic alteration and sericitic alteration of the Far Southeast (FSE) porphyry Cu-Au deposit that represent the vapor and late low temperature liquid (LLTL), respectively (Hedenquist et al., 1998). Plotted values and their corresponding references is shown in Table 5. Magmatic water compositions were defined by Taylor (1992). Volcanic waters were derived from Giggenbach (1992).
**Figure 15.** An illustration depicting the potential presence of porphyry Cu and high sulfidation (HS) epithermal mineralization cogenetic with the actual intermediate sulfidation epithermal (ISE) veins of the Suyoc prospect. This interpretation is based on the widely accepted idea about porphyry-epithermal association (Hedenquist et al., 1998; Sillitoe and Hedenquist, 2003; Chang et al., 2011; Wang et al., 2019). This particular illustration is derived from the model of Sillitoe (2010) for a typical porphyry-epithermal system.

**Figure 16.** Map showing a proposed prospective area in the vicinity (~1km radius) of the intermediate sulfidation epithermal (ISE) veins of the Suyoc prospect. This proposed radius follows the spatial configuration of the Victoria ISE deposit with the Far Southeast porphyry Cu-Au deposit and the Lepanto high sulfidation epithermal (HSE) deposit (Chang et al., 2011). Also included are the locations of other known prospects and deposits in the district, as well as the distribution of mapped lithocaps based on Chang et al. (2011).

**Table Captions**

**Table 1a.** Elemental composition of Au-bearing minerals in the quartz-carbonate vein.

**Table 1b.** Elemental composition of sphalerite crystals coexisting with pyrite in the quartz-carbonate vein. The calculated FeS mole % is included.

**Table 2.** Homogenization temperature ($T_h$) and final-ice melting temperature ($T_{fim}$) acquired from microthermometry of primary fluid inclusions from each vein-type. Salinity was calculated from $T_{fim}$ using the formula of Bodnar (1993).

**Table 3.** $\delta D$ from the fluid inclusion in quartz and $\delta^{18}O$ values from the quartz of the three major vein-types. $\delta^{18}O$ values in equilibrium with water ($\delta^{18}O_{water}$) were calculated via the equation provided by Clayton et al. (1972) for 200-500°C quartz-
water system. The temperatures used for the equation were taken from obtained modal homogenization temperature ($T_h$) values.

**Table 4.** Summary of the characteristics of the three major vein-types of the Suyoc prospect. (qz = quartz, rds = rhodochrosite, py = pyrite, ccp = chalcopyrite, sp = sphalerite, gn = galena, Au/Ag = native gold and electrum, bno = bournonite)

**Table 5.** Mean temperature, $\delta D_{\text{water}}$ and $\delta^{18}O_{\text{water}}$ data of the Suyoc prospect, Antamok and Acupan intermediate sulfidation epithermal deposits and the meteoric water in Baguio-Mankayan (~500-1500 masl). Data from the Far Southeast porphyry Cu-Au deposit include compositions of advanced argillic alteration from alunite, and average compositions of potassic alteration from biotite and sericitic alteration from illite. (LLTL = late low temperature liquid). References: 1 = Hedenquist et al. (1998); 2 = Sawkins et al. (1979); 3 = JICA (1984)
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Figure 7.
Figure 8.
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Figure 10.
Figure 11.
Figure 12.
Figure 13.
Figure 14.
Figure 15.
Figure 16.
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Table 3.

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<th>$\delta D_{\text{fluid inclusion}}$ (%)</th>
<th>$\delta^{18}\text{O}_{\text{quartz}}$ (%)</th>
<th>Modal $T_h$ (°C)</th>
<th>$\delta^{18}\text{O}_{\text{water}}$ (%)</th>
<th>$\delta^{34}\text{S}_{\text{pyrite}}$ (%)</th>
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<td>qz+py+ccp+sp</td>
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<td>massive, comb</td>
<td>massive, crustiform</td>
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The Suyoc vein prospect displays typical intermediate sulfidation epithermal signatures. Its δD and δ¹⁸O composition indicates late stage formation in a magmatic-hydrothermal system.

Its existence implies potential presence of undiscovered cogenetic porphyry Cu and high sulfidation epithermal mineralization in the underexplored southern part of the Mankayan Mineral District.

### Table 5.

<table>
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<tr>
<th>Mineral/Alteration</th>
<th>Temp. (°C)</th>
<th>δD&lt;sub&gt;water&lt;/sub&gt; (‰)</th>
<th>δ¹⁸O&lt;sub&gt;water&lt;/sub&gt; (‰)</th>
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Southern Mankayan Mineral District

HYPOTHETICAL

HS epithermal

Porphyry Cu

not to scale

ACTUAL

ISE veins of Suyoc prospect

120.7°E 120.8°E

Prospective area (~1km radius)

Suyoc prospect

Suyoc ISE veins

Lithocap

HSE deposit

ISE deposit

Epithermal prospect

Porphyry Cu deposit

Porphyry Cu prospect