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Abstract: Detailed hydrothermal alteration investigations, including petrography, infrared reflectance spectroscopy (IRS) and XRD of the low sulfidation epithermal Co-O mine, located in Eastern Mindanao (Philippines) revealed that both distal and intermediate hydrothermal alteration zones contain dominantly illite and chlorite, whereas the proximal alteration zone comprises mainly illite, chalcopyrite and pyrite. The gold-bearing veins and the proximal hydrothermal alteration zone display a distinct absence of K-rich hydrothermal alteration minerals such as K-feldspar (adularia). Gold mineralization in the Co-O mine is controlled by an extensive quartz-breccia vein system, which is characterized by three distinct stages of vein (incl. breccias) formation. Gold is mainly observed in stages 2 and 3 veins. Stage 1 veins appear as fragments in stage 2 veins and display boiling textures such as quartz pseudomorphs after bladed calcite. These veins further display colloform to crustiform banding and contain pyrite, chalcopyrite and minor gold located in the colloform bands and between banded quartz pseudomorphs. Stage 2 veins comprise mostly banded to massive quartz and contains sulfides parallel to bands or disseminated. These veins are fine-grained with mosaic/jigsaw quartz and contain calcite blebs and/or fragments of stage 1 veins. Gold is in textural equilibrium with chalcopyrite, sphalerite, and locally pyrite. Stage 3 veins consist of quartz and carbonate (locally Mn-rich), and display irregular banded and comb textures. In auriferous veins of this stage gold is in textural equilibrium with chalcopyrite and pyrite (with local abundance of sphalerite). Other sulfide minerals observed with gold in stages 2 and 3 are galena, acanthite and locally jalpaite. The XRD and IRS provide inconsistent results regarding the abundance of K-rich clays (e.g., illite) associated with auriferous veins. Illite, with possibly interlayered swelling clays, such as Al-smectite, was identified in auriferous vein stages 2 and 3 using IRS, but could not be confirmed by XRD. Comparative analysis of the results of these techniques with respect to the ordering of micaceous minerals, suggest less ordered white mica proximal to the veins. Vein textures such as banded quartz, the absence of K-feldspar and the abundance of illite (interlayered Al-smectite) suggest relatively low temperatures of formation of the hydrothermal alteration system and point to a potential boiling horizon located deeper or marginal to the currently exploited levels of the Co-O mine. The absence of K-feldspar may also be related to relatively low temperatures of the hydrothermal fluid, the medium potassium-rich magma series of the host rocks, and/or a relatively low oxidation state of the hydrothermal fluid.
Low potassium hydrothermal alteration in low sulfidation epithermal systems as detected by IRS and XRD: an example from the Co-O Mine, Eastern Mindanao, Philippines

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ABSTRACT

Detailed hydrothermal alteration investigations, including petrography, infrared reflectance spectroscopy (IRS) and XRD of the low sulfidation epithermal Co-O mine, located in Eastern Mindanao (Philippines) revealed that both distal and intermediate hydrothermal alteration zones contain dominantly illite and chlorite, whereas the proximal alteration zone comprises mainly illite, chalcopyrite and pyrite. The gold-bearing veins and the proximal hydrothermal
alteration zone display a distinct absence of K-rich hydrothermal alteration minerals such as K-feldspar (adularia).

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The XRD and IRS provide inconsistent results regarding the abundance of K-rich clays (e.g., illite) associated with auriferous veins. Illite, with possibly interlayered swelling clays, such as Al-smectite, was identified in auriferous vein stages 2 and 3 using IRS, but could not be confirmed by XRD. Comparative analysis of the results of these techniques with respect to the ordering of micaceous minerals, suggest less ordered white mica proximal to the veins.

Vein textures such as banded quartz, the absence of K-feldspar and the abundance of illite (interlayered Al-smectite) suggest relatively low temperatures of formation of the hydrothermal alteration system and point to a potential boiling horizon located deeper or marginal to the currently exploited levels of the Co-O mine. The absence of K-feldspar may
also be related to relatively low temperatures of the hydrothermal fluid, the medium potassium-rich magma series of the host rocks, and/or a relatively low oxidation state of the hydrothermal fluid.

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1. Introduction

The Philippines host one of the largest endowments of gold and copper in the SW Pacific (Garwin et al., 2005), which are amongst others (e.g., porphyry systems) represented in epithermal (low and high sulfidation) deposits. The identification of hydrothermal alteration assemblages and patterns plays a key role in identifying and classifying a mineral deposit. For example, the proximal hydrothermal alteration haloes and/or auriferous veins in low sulfidation epithermal systems are often characterized by quartz, calcite, “sericite”/illite and commonly adularia. Older literature often used the term adularia-sericite or quartz-adularia (e.g., Berger and Henley, 1989; Heald et al., 1987) in regards to the hydrothermal alteration to describe a low sulfidation epithermal system. In contrast, the lack of adularia in some low sulfidation epithermal deposits is rarely discussed or pointed out. Low sulfidation epithermal deposits from the Philippines have been mentioned for their common lack of adularia (Mitchell and Leach, 1991; Sillitoe, 1989). The absence of adularia e.g., in the shallow levels of the Acupan deposit (Philippines) is explained by mixing of magmatic and meteoric/ground waters (Cooke and McPhail, 2001). However, the implications of the lack of adularia the in veins and wallrocks and/or whether there is a relationship between the absence of adularia in
low sulfidation epithermal deposit and the geological setting of the deposits where adularia is reported to be missing from the gold-bearing assemblages, are unclear.

Furthermore, clay minerals associated with hydrothermal alteration haloes are often represented by illite, smectite and inter-layered clays, whereas these minerals cannot be easily separated by conventional XRD analysis. An alternative method to traditional XRD analysis for rapidly identifying clay minerals is infrared reflectance spectroscopy using a portable spectroradiometer. Advantages of this technology over XRD are fast data acquisition, including the detection of clay minerals such as Al-smectite, illite and muscovite, minor sample preparation and its field portability.

Detailed infrared reflectance spectroscopy (IRS) using a Portable Infrared Mineral Analyzer (PIMA) and additional XRD studies were conducted on drill core samples from the low sulfidation epithermal Co-O mine located in Eastern Mindanao in order to define hydrothermal alteration minerals and patterns. Previous studies of this deposit by Kolb and Hagemann (2009) revealed complex hydrothermal alteration mineralogy, but also reported a conspicuous absence of K-feldspar (adularia) in this deposit.

The aims of this study were to: 1) better define and characterize the complex hydrothermal alteration patterns of the Co-O mine by analyzing additional drill core material with IRS and XRD, in order to find distinctive vectors to the high-grade (>1 g/t Au) gold mineralization, 2) investigate the proportion and impact of K-bearing hydrothermal minerals (e.g., K-feldspar and illites) in the low sulfidation epithermal Co-O mine, and 3) evaluate the application of IRS as a modern exploration tool for low sulfidation epithermal systems and compare this method to traditional methods such as XRD.

2. Geological Setting
The tectonic evolution of the Philippines comprises the rotation of parts of the archipelago and the establishment and cessation of several subduction trenches through time (e.g., Hall et al., 1995; Hall, 2002; Pubellier et al., 2003). Mindanao represents the second largest and one of the southernmost islands of the Philippine archipelago and consists of a number of several terranes and blocks (e.g., Pubellier et al., 1991; Rangin, 1991; Sajona et al., 1997). The most important structures in Mindanao are related to the subduction of oceanic crust in two opposite directions and comprise the Negros, Sulu and Cotabato Trenches in the west and the Philippine Trench in the east (Fig. 1b). The Philippine Fault traverses the entire Philippines from the NNW to SSE and separates Eastern Mindanao from Central and Western Mindanao. In the western part of Mindanao the Cotabato Fault represents the boundary between Eurasia (in the east) and the Philippine arc/Philippine Mobile Belt (in the west) (Pubellier et al., 1991; Pubellier et al., 1999; Rangin, 1991) (Fig. 1b).

2.1. The Co-O mine and area

The Co-O area, including the low sulfidation epithermal Co-O mine, is located in Eastern Mindanao in the central western part of the Agusan del Sur region, 170 km north-northwest of Davao City (Fig. 1b). The study area mainly comprises volcanic rocks of Eocene to Oligocene age (basic to intermediate flows and pyroclastic rocks) that are partly overlain by Oligocene to Miocene volcanic and Miocene sedimentary rocks (Fig. 1c). Andesite porphyry plugs of Oligocene age crop out in the central, southern and northern parts of the work area (not indicated on the geological map Fig. 1c as they crop out in only local, smaller locations). Quaternary alluvium deposits conceal the rock formations in the far western Co-O area. Dioritic intrusions of Eocene age are exposed in the western part of the study area. Major faults in the Co-O area trend NE-SW, N-S and locally NW-SE (Fig. 1c). A detailed structural assessment of the Co-O mine and area is presented by Kolb and Hagemann (2009),
who related regional tectonic deformation events, based on structural cross-cutting relationships and vein mineralogy, to specific hydrothermal gold forming stages (Table 1).

Gold mineralization at the Co-O mine is controlled by the following tectonic events and associated major structures and gold mineralization stages (Table 1): 1) \( \text{D}_E \): NE-SW extension, pre-gold stage; 2) \( \text{D}_1 \): NNE-SSW compression, emplacement of stages 1 and 2 auriferous veins; 3) \( \text{D}_2 \): E-W compression, emplacement of stage 3 auriferous veins; and 4) \( \text{D}_3 \): N-S to NW-SE extension, post-gold stage (Kolb and Hagemann, 2009). During the \( \text{D}_1 \) event vein stages 1 and 2 were emplaced in the Co-O mine, which trend parallel to major regional fault trends; these are: 1) NNW-SSE Philippine Fault trend, 2) ENE-WSW Palawan trend, and 3) WNW-ESE Co-O trend (Kolb and Hagemann, 2009). \( \text{D}_2 \) is characterized by the reactivation of these earlier formed faults and is associated with the emplacement of vein stage 3.

3. Mineral Spectroscopy

Infrared reflectance spectroscopy is widely used as a rapid and non-destructive method in mineral exploration to determine major mineral phases related to hydrothermal alteration (Cudahy et al., 2009; Hunt, 1979; Laukamp et al., 2011; Yang et al., 2005). The abundance, composition and crystalline disorder of certain minerals can be inferred from the depth, wavelength position and shape of characteristic absorption features in the shortwave infrared region (SWIR). Absorption features in the SWIR are mainly related to combination and overtones of vibrational processes of molecules and can be used to identify the physicochemistry of the respective minerals. Amongst the SWIR-active minerals are dioctahedral sheet silicates, such as kaolinite, white mica, Al-smectites, trioctahedral sheet silicates (e.g., chlorite), as well as carbonates (e.g., calcite, siderite) and sulfates (e.g., gypsum).
Dioctahedral sheet silicates can be mapped by IRS based on the depth of the absorption feature at around 2200 nm, which can be assigned to the combination of the vibrational stretching and bending of Al$_2$OH in these dioctahedral sheet silicates (Farmer, 1974; Post and Noble, 1993). The composition of the white micas and Al-smectites can be inferred from the position of the 2200 nm feature. In Al-poor white micas (e.g., phengite) this feature is located around 2215 nm, whereas in Al-rich white micas (e.g., muscovite) this feature is located around 2190 nm. As there is a solid solution between these two “end-members” the 2200 nm feature may be located in the range from roughly 2180 to 2220 nm. White micas, such as illite, have an additional major absorption feature at around 2350 nm, which is absent in Al-smectites. Regarding the definition of illite, we follow Srodon and Eberl (1984) who define illite as a clay-size, non-expanding, dioctahedral, aluminous potassium mica-like mineral and can form together with Al-smectites interlayered illite/smectite. Kaolinite was determined with IRS based on the occurrence of its characteristic absorption feature at 2160 nm, which distinguishes it clearly from white mica and Al-smectite. Typical for trioctahedral sheet silicates, chlorites display two characteristic absorption features in the SWIR at around 2250 and 2340 nm, respectively. The wavelength position of the 2250 nm feature, a combination of the vibrational stretching and bending of Al(Fe$^{3+}$,Mg)OH (also commonly known as “FeOH-feature”), can be used to estimate the Mg# of chlorites (McLeod, 1987). Carbonates have an absorption feature with a characteristic short wavelength asymmetry at around 2330 nm, which can be assigned to the 2$^{nd}$ overtone of the asymmetric stretching of CO$_3$ (Gaffey, 1986). The abundance and composition of carbonate is inferred from the depth, asymmetry and position of this feature, which displays a blue-shift in dolomite when compared to calcite. Gypsum has several distinct absorption features related to combinations of OH- or H$_2$O bending, stretching and rotational fundamentals or S-O bending overtones. The most notable
absorption band is located around 1750 nm with a shoulder around 1780 nm and a triplette
feature with absorption minima at 1449, 1488 and 1534 nm (Cloutis et al., 2006).

4. Samples and Analytical Methods

Two sample sets from the low sulfidation epithermal Co-O mine were compiled for this
study. The first sample set comprises 186 PIMA spectra of flat rock surfaces from samples of
nine different drill cores (Fig. 1c). Analyzed areas comprise veins, breccias (mixed vein-
wallrock), intensely altered and weakly altered rocks. For this study we will mainly
distinguish between vein and wallrock and consider the breccias (generally fragments larger
than matrix) as part of the wallrock (e.g. analytical reasons PIMA II acquisition window ~2
cm). However, one sample can comprise all three zones: vein, breccias and altered wallrock.

One entire drill core (#1) was sampled at least every 40 m, related to major changes in the
hydrothermal alteration, to record a complete alteration profile. Eight other drill cores (#2-#9)
were sampled mainly in the “higher grade” (>1 g/t Au) ore zone, to define the proximal
hydrothermal alteration halo (#2-#9), and only locally (#3 and #4) in the lower parts of the
drill core in the low grade (<0.1 g/t Au) ore zone. All drill cores (#1-#9) plunge between 45°
and 71° to the southwest and pierce through at least one of the underground levels of the Co-
O mine.

A second sample set was selected based on the 186 PIMA spectra in order to compare the
IRS results directly with XRD. For this purpose, 36 representative samples (related to
hydrothermal alteration zones) of the complete drill core #1 were carefully selected and
separated using a rock saw into veins, breccia and wallrock. The separated material was
crushed into 1-2 mm chips and milled with a tungsten-carbide mill to a fine rock powder
(particle size 85 % < 20 μm). This second sample set was then analyzed with XRD and
PIMA.
4.1 Infrared reflectance spectroscopy

Infrared reflectance spectroscopy was performed using a Portable Infrared Mineral Analyzer (PIMA II, Integrated Spectronics Pty Ltd) provided by CSIRO Earth Science and Resource Engineering, which records reflectance spectra in the SWIR of the electromagnetic spectrum from 1300 to 2500 nm. The window of acquisition is 2 cm in diameter and the spectral resolution is 7 – 10 nm, re-sampled to 2 – 4 nm. The SWIR data were processed using The Spectral Geologist software (TSG™), where the PIMA measurements are re-sampled to 2 nm resolution. A multiple feature extraction method (MFEM) was applied to extract the mineralogy from the SWIR data (Cudahy et al., 2008; Laukamp et al., 2010). Algorithms used for the identification and characterization of the SWIR active minerals based on the MFEM are listed in Table 2. The depth of a certain absorption feature, which can be used to infer its relative abundance, is abbreviated by the centre of the absorption feature and the letter “D” (e.g., 2200D). Algorithms tracking the wavelength position of a specific absorption feature are annotated with the letter “W” (e.g., 2200W).

4.2 Rietveld XRD

Results from the infrared reflectance spectroscopy were validated with Rietveld XRD on carefully selected 36 representative samples from drill core #1 (listed in Table 3) and three representative samples from high grade sections of drill cores #2 and #4. The X-ray analyses were performed on a Bruker D4 XRD, which uses a Co tube with a Fe filter as X-ray source and a Lynxeye detector. For direct comparisons of the methods, PIMA scans were conducted on powder samples prepared for the XRD. In order to determine Al-smectite and illite or interstratified composites of these two minerals in the XRD-spectra, 26 oriented aggregate mounts were treated with ethylene glycol using a glass rod (applied on all samples where
illite was identified by XRD). Mounts were X-rayed after the liquid was uniformly absorbed. Afterwards these samples were analyzed on a Phillips X’Pert PW3040/00, which uses a Co tube with a Fe filter as X-ray source and a proportional detector filled with Xe gas.

Analysis conducted by IRS and XRD were supported by petrographic studies. For further mineral identification standardless EDS analysis were performed on a Scanning Electron Microscope (SEM) type JEOL 6400 at the Centre for Microscopy, Characterization and Analysis at the University of Western Australia. The same instrument was used for back scatter electron imaging to illustrate the relationship between sulfides and gold mineralization. For sulfide analysis accelerating voltage was set to 20 kV using 3 nA beam and for silicates accelerating voltage was set to 15 kV using 5 nA beam current.

5. Results

5.1 Vein stages and textures, paragenesis, and hydrothermal alteration mineralogy

Vein stages, their type of gangue, textures and paragenesis is summarized in Table 1, which also points out relationships to deformation events described by Kolb and Hagemann (2009). The epithermal Co-O mine displays three gold vein stages. Stage 1 veins display minor gold mineralization (detected by SEM) and occur mainly as fragments incorporated into stage 2 veins (no gold grade applicable). Stages 2 and 3 veins are highly auriferous (5-14 g/t Au). Early carbonate and quartz/chalcedony veins of stage 1 are banded and display locally bladed quartz pseudomorphs after calcite (Fig. 2a), colloform to crustiform bands and/or cockade textures (Fig. 2b). Pyrite and chalcopyrite occur along colloform bands and in-between bladed quartz textures (Fig. 2a and b).
Stage 2 veins display massive grey, white to clear quartz veins, which are 1-3 m wide in underground exposures. The massive stage 2 veins are often banded and display a very fine-grained moss to mosaic/jigsaw quartz matrix with small oat-shaped patches (<1 cm) of calcite (Fig. 2c), locally small bands of calcite (<5 cm) or fragments of stage 1 veins, that give the veins an irregular appearance. Locally saccharoidal (cf. Dong et al., 1995) textures are exhibited by stage 2 veins. Sulfides are mainly located between the quartz mosaics and locally between quartz and calcite grains (Fig. 2c and 3c). Late stage 2 quartz veins frequently host cavities with clear comb quartz, displaying comb and zonal textures, which can be plumose to flamboyant (Fig. 2d).

Stage 3 veins are dominated by quartz and carbonates with most carbonates enriched in Mn and/or Fe (Fig. 3a and b), based on their pinkish and/or greenish color, which was confirmed by SEM studies. The Mn-rich carbonate often display actinomorphic or porous textures (Fig. 3a and b). Sulfides are mainly observed in quartz (Fig. 3d) or at boundaries between quartz and calcite veins/grains. Late stage 3 veins are barren, crosscut all other veins and comprise gypsum and white calcite.

Gold is rarely observed as native gold and occurs mostly as electrum. The electrum in stage 2 veins is mainly in textural equilibrium with sphalerite, acanthite (Ag₂S), chalcopyrite (Fig. 3c and c₁) and locally pyrite and galena. In stage 3 veins gold and electrum are in textural equilibrium with chalcopyrite, pyrite, acanthite and minor sphalerite, galena and jalpaite (Ag₃CuS₂) (Fig. 3d and d₁). Characteristically stage 3 veins contain less sphalerite and more chalcopyrite when compared to stage 2 veins. Vein stage 2 displays a distinct sphalerite-electrum relationship whereby sphalerite-rich and acanthite-poor portions of a vein contain gold with less silver (i.e., gold sensu strictu).
Based on petrographic studies the hydrothermal alteration of the Co-O area is dominated by “sericite” and clay minerals, chlorite, and carbonate. For petrographic studies the hydrothermal alteration halos in and around the Co-O mine were divided into different zones with respect to the gold mineralization observed in veins: a) proximal hydrothermal alteration zone with 10’s m from gold mineralization (> 5 g/t), b) intermediate hydrothermal alteration zone 100’s m but at least more than 50 m away from the gold mineralization, c) distal hydrothermal alteration zone more than 500 m away from the gold mineralization including also rocks around the Co-O mine site (±1-2 km), but no more than 2 km away, and d) last altered hydrothermal alteration zone grading, which is observed about 3-5 km away from the mine site. The dominant (> 7-10 vol. %) proximal hydrothermal alteration minerals are carbonates, “sericite” (and clay minerals), chlorite, pyrite, chalcopyrite, and quartz with minor minerals (< 3 vol. %) such as epidote. With decreasing distance from the gold mineralization (>50 m) the abundance of carbonates, “sericite” and pyrite decreases, chalcopyrite is absent, quartz becomes a more dominant alteration mineral and chlorite with locally epidote is still present in higher amounts (> 10 vol. %). In the distal hydrothermal alteration zone the hydrothermal alteration intensity decreases distinctively with decreasing amounts of hydrothermal alteration minerals such as chlorite (< 7 vol. %), “sericite”, quartz and iron oxides (all < 3 vol. %). The least altered samples are commonly only affected by hydrothermal alteration of minor “sericite” dusting.

Generally, in all hydrothermal alteration zones “sericite”, carbonate and locally, in the more intermediate hydrothermal alteration zones (10-50 m from the ore body), epidote replace feldspars (Fig. 2e and f). Chlorite and locally epidote (in intermediate alteration zones) replace mafic minerals such as hornblendes (Fig. 2g and h). Ilmenite and/or Ulvöspinel are replaced by magnetite, rutile and/or sulfides. Iron oxides are late stage overgrowths and possible related to supergene alteration.
5.2 Hydrothermal alteration minerals identified by IRS and XRD in selected samples from drill core #1

The mineral assemblages interpreted from XRD and IRS analyses for powder and rock surface scans of drill core #1 are listed in Table 3. The formation of veins and hydrothermal alteration halos at the Co-O mine is evidenced in veins, breccias (comprising brecciated veins, wallrock clasts and matrix), and hydrothermal altered wallrock. The extent of the hydrothermal alteration zones is defined by gold values (obtained by fire assays) in the drill cores provided by Medusa Mining Ltd.

The hydrothermal alteration zones form around auriferous stage 2 and 3 veins and can be separated into: 1) proximal zones comprising the alteration halo around the auriferous veins (max. 10 m in width); 2) intermediate zones with a maximum of 50 m distance from gold-bearing veins; and 3) distal zones, which grades into the unaltered wallrocks with more than 50m distance from gold-bearing veins. All hydrothermal alteration zones may include non-mineralized veins, which display also hydrothermal alteration halos. However, the size of the auriferous veins (1-3 m) and their hydrothermal alteration halo is generally of a much larger size than cross-cutting non mineralized veins (1-5 cm).

5.3 Hydrothermal alteration minerals and hydrothermal vein mineralogy identified in powdered rock samples by IRS and XRD in drill core #1

Powdered rock samples analyzed with IRS suggest a dominance of white mica throughout the drill core #1 (Fig. 4a and b, Table 3) and high abundances of chlorite associated with low (<0.5 ppm Au) to barren gold assays. Hydrothermal minerals identified by XRD in powdered
rock samples from drill core #1 are dominated by quartz, calcite, illite, chlorite and locally
higher amounts of anhydrite/gypsum and feldspar/plagioclase (Table 3); pyrite and kaolinite
are detected in generally minor amounts and represent common accessory minerals in the
wallrocks, breccias and veins.

Clay minerals: According to XRD in auriferous veins illite is absent, but is highly abundant
in the proximal and intermediate alteration zone and is observed only in lower amounts in the
distal alteration zone (Table 3). Interstratified clays (illite with possibly interstratified Al-
smectite) were locally present in the proximal and intermediate alteration zones. Al-smectite
(montmorillonite) was only detected in one sample (441_a), together with high amounts (55
wt.%) of kaolinite. Kaolinite is mainly abundant in low amounts (<5 wt.%) throughout drill
core #1 and locally in higher amounts (>10 wt.%) in the proximal to intermediate alteration
zone. Infrared reflectance spectroscopy results of the same powdered samples revealed that
dioctahedral sheet silicates such as white micas (cf. compositional endmembers muscovite,
paragonite, phengite) and Al-smectites (e.g., montmorillonite) trend from Al-poor
composition in the veins to an Al-richer composition in the breccias and wallrock based on
the wavelength position of the AlOH feature (Fig. 4c). The white micas detected in veins plot
closer to the field of kaolinite and/or carbonate when compared with white micas located in
breccias and wallrocks (Fig. 2b). The identification and differentiation of illites and
smectites, based on hyperspectral data, was hindered by overlaps of characteristic absorption
features of the clay minerals with carbonates and chlorite. Therefore, additional sample
preparation and analyses were conducted using XRD, which pointed to the above mentioned
distribution of illites and interstratified clays (see 5.5 Characterization of kaolinite and
hydrothermal clays).

Chlorite: The XRD analyses show that chlorite is absent in auriferous veins, locally abundant
in the proximal but mostly present in the intermediate to distal alteration zone (Table 3). This
is confirmed by the SWIR data, where chlorite is generally not observed in veins and wallrocks displaying higher amounts of gold (Fig. 4d). The location of the FeOH feature at around 2253 nm suggests that chlorites have an intermediate Mg-Fe composition in most of the samples. This was confirmed by EDS analysis and petrography with dominantly light green color of chlorite in normal transmitted light and blue interference colors in transmitted light under crossed nichols (Fig. 2g and h). Chlorites detected by IRS are locally observed in the proximal zones (excluding veins), are most abundant in the intermediate zone, and are also present in the distal zone (Fig. 4d, Table 3).

*Carbonate:* The XRD results indicated that calcite is abundant throughout drill core #1 and commonly present in the auriferous veins as well as in barren veins. Dolomite appears locally in the distal alteration zone, but rarely in the proximal to intermediate alteration zones. The SWIR data clearly show a dominance of calcite (over e.g., dolomite) in the carbonate phases throughout the core. Carbonates are abundant in auriferous veins, but are also present locally in barren veins, and in the wallrock and breccias proximal to the veins (Table 3).

*Sulfates and sulfides:* Gypsum and anhydrite detected by XRD are most abundant in the intermediate to distal alteration zone. Pyrite is abundant in minor amounts (<5 wt.%) throughout all samples, but is generally more abundant in wallrock samples than in veins (Table 3). The IRS measurements of powdered samples detected gypsum only in one breccia and one vein sample (Table 3).

*Quartz and feldspar:* According to XRD quartz is highly abundant mainly in the selected veins, but is present in varying amounts in most samples from drill core #1. With IRS, amorphous quartz was identified in samples that contain almost pure quartz (XRD quartz >90 wt.%). Feldspars are generally not detectable in the SWIR, but plagioclase was locally detected by XRD in the intermediate and distal alteration zone.
5.4 PIMA analysis of rock surfaces from nine drill cores

The 186 results of IRS analysis from samples of nine drill cores from the Co-O mine are considered with respect to observed Au values in drill core samples (gold assays provided by Medusa Mining Ltd.). In this dataset veins are dominated by calcite and poorly ordered illite (and/or interstratified clays) as well as kaolinite (Fig. 5a). High gold values in vein samples are mainly associated with white mica/Al-smectite field and calcite (Fig. 5a). Locally Au-rich veins can also contain kaolinite. Wallrock samples that exhibit high amounts of gold occur mostly in the white mica/Al-smectite or white mica only field (Fig. 5b). Locally, wallrock samples with slightly elevated gold values plot in the field of kaolinite. White micas observed in wallrocks samples show a wide range of white mica disorder when compared to vein samples, which tend to be generally less ordered (Fig. 5c). Most samples that are enriched in gold lack chlorite (Fig. 5d). Only locally samples with low amounts of gold show white mica and chlorite, but most of the samples with this mineral mixture are barren in respect to gold.

5.5 Characterization of kaolinite and hydrothermal clays

Infrared reflectance spectroscopy data were used to map the distribution of clay minerals in the investigated drill cores and were complemented by XRD analyses of selected samples from drill core #1. The powder mounts prepared for XRD were also measured with PIMA.

Kaolinite was identified from the SWIR data on the basis of the characteristic doublet at 2160 and 2200 nm. The absorption feature at 2160 nm is in most samples very shallow compared to the distinct absorption feature at 2200 nm, which suggests a poorly ordered kaolinite. On the other hand, calcite also has a weak 2160 nm absorption feature. However, XRD-results confirm the presence of kaolinite as traces in most of the samples (Table 3). The additional SWIR data acquired from the XRD sample powders lack, in most cases, absorption features characteristic for kaolinite, which suggests that this mineral forms on weathered surfaces of
the exposed drill cores and its abundance in the powder samples, is probably too low to be measured by IRS.

Overlapping absorption features of clay minerals, carbonates and chlorites complicated the mapping of illite and smectite with SWIR data. It was not possible to characterize illite and/or smectite without additional XRD analyses, even though obtained results may provide some clues for the identification of illite and/or smectite in epithermal systems. A number of diffraction patterns showed typical illite patterns, but are characterized by a very wide 001 peak with a peak centre ranging from 10.2 to 10.3 Å and a shallow slope to lower 2θ values, or are even accompanied by a peak at 10.4 Å, which suggest a mixed-layered clay mineral consisting of illite with interlayered smectite. Where white mica and/or Al-smectite were evident from hyperspectral and XRD data (Table 3) diffraction patterns from air-dried and ethylene glycol-solvated mounts were compared to determine shifts of the probable Al-smectite peak positions, which would be the expandable component of an interlayered illite/smectite. No shifts of the peak positions were found, but as pulps of samples 414_a, 438_b, 439a_c and 441_b showed clear expansion when treated with ethylene glycol and no other expandable phase is evident from XRD, a mixed-layered clay, dominated by illite, is proposed for the respective samples (hereafter referred to as illite-IS in the text and in Table 2).

More detailed investigations of the white mica (illite) disorder using SWIR data were based on the ratio of the depth of the Al₂OH feature at 2200 nm (2200D) and the depth of the H₂O feature at 1900 nm (1900D), which provides an estimation of the water abundance in white mica. Figure 4c shows a clear separation of powder samples from drill core #1 in two groups in terms of white mica order. Breccia and wallrock samples show a lower illite order index when compared to most of the vein samples. The decreasing intensity of the water absorption feature shown in Fig. 6 envisages the decreasing water content in illite. Closer observation of
the Al\textsubscript{2}OH features and the overall reflectance though reveals that this estimation is highly
dependent on the reflectance values (Fig. 6). On the other hand, when comparing the
2200D/1900D ratio with the full width half max (FWHM) of the illite 001 peak at 10.1Å
(Kübler index; Kübler, 1964), an apparent correlation between the two parameters is visible
(Fig. 7). The Kübler index is influenced by the mean size of crystal domains, which is
probably strongly affected by the amount of swelling components (e.g., smectite) interlayered
in illite (Guggenheim et al., 2002 and references therein) and therefore provides an estimation
for the disorder of illite (formerly also described in literature as 'illite crystallinity'; e.g.,
Guggenheim et al., 2002).

6. Discussion

6.1 Comparison between IRS and XRD results

Mineral phases inferred from IRS measurements of rock surfaces and powder compounds, as
well as from quantitative XRD analyses are listed in Table 3 for direct comparison. Generally, the results of the quantitative XRD analyses confirm the findings of the IRS
analyses with respect to the SWIR-active phases. However, the identification of mineral
phases using a PIMA is dependent on the number, types, abundances and ratios of mineral
species present in a single sample. Clay minerals are easily detected by IRS, when they are
the dominant SWIR-active minerals (e.g., 435a, 436a), but also when they occur in trace
amounts. Problems regarding the identification of single clay mineral phases in clay mineral
mixtures arise from weathered rock surfaces, such as in sample 422_a, where kaolinite and
illite are evident from XRD, but only kaolinite is apparent from the reflectance spectra. The
lower detection limit of chlorites ranges around 10% (determined with XRD), locally even
lower amounts of chlorite are detectable (e.g., 418_c: 1.3%).
Carbonates can be difficult to detect with IRS, even when a high content is evident from XRD. High kaolinite, white mica and/or chlorite abundance (sample 441_b, 433_b) can obscure carbonate abundance values of up to 20% and more. The asymmetry of the 2340 nm feature can be used in those cases, which remains still problematic, when white mica or chlorites are highly abundant in the same sample (e.g., 438_a). Even very high amounts of calcite can be obscured, when sulfates occur in the same sample (e.g., 432_b, 438_b). Sulfates are very easily detectable with PIMA measurement from rock surfaces, even at very low values (e.g., 433_c).

In contrast to the XRD analyses of the powder mounts, IRS measurements from rock surfaces and powder mounts suggest the abundance of poorly ordered illite in the Au-bearing veins (Fig. 4b, 5a). Variations in the detected minerals are due to different sensitivities of the applied techniques.

6.2 Vein texture and paragenesis

Textures of stages 1 to 3 auriferous veins point towards replacement, recrystallization, and rapid deposition mechanisms of quartz and carbonate. Bladed-lattice, mosaic and saccharoidal textures suggest the replacement of calcite by quartz in veins of stages 1 and 2 (cf. Dong et al., 1995 and references there within). Plumose and flamboyant textures may be associated with recrystallization of chalcedony and/or represent overgrowth textures. Colloform to crustiform quartz textures suggest rapid deposition of stage 1 quartz, where bladed-lattice quartz textures indicate boiling of hydrothermal fluids during vein stage 1 (cf. Dong et al., 1995; Simmons and Browne, 2000). However, the bladed boiling textures are only displayed in stage 1 fragments, which are within stage 2 veins. Therefore a potential boiling zone associated with stage 1 veins cannot be located. The presence of boiling textures in stage 1 veins and the absence of these textures in stage 2 veins may imply higher fluid
emplacement temperatures for stage 1 veins. The high abundances of carbonate in auriferous stage 3 veins, that form actinomorphic textures (Fig. 3a), could be as well related to a boiling environment with rapid precipitation of carbonate due to loss of CO\textsubscript{2} from the fluid during boiling (cf. Dong et al., 1995).

The gold-bearing veins of stages 1 to 3 in the Co-O mine are dominated by chalcopyrite, sphalerite and pyrite, which are all consistent with cooler (<300°C) low-salinity fluid mixtures (cf. Heinrich, 2007). Hedenquist et al. (2000) introduced the term intermediate sulfidation-state deposits (low sulfidation epithermal deposits) in order to distinguish end-member low sulfidation deposits, which are more gold-rich, from low sulfidation epithermal deposits that are more Ag and base metal-rich; potentially related to variations in fluid salinity. End member low sulfidation deposits often display metals such as Au-Ag-As-Sb-Se-Hg-Tl together with various sulfides including cinnabar, marcasite-arsenopyrite, Au-Ag selenides Se sulfates and Fe-rich sphalerite (Hedenquist et al., 2000). In contrast, commonly deeper intermediate sulfidation state low sulfidation deposits display Ag-Au-Pb-Zn, Ba, Mn, Se metals associated with sulfides such as pyrite, sphalerite, galena chalcopyrite and tetraherdite/tennantite, where some intermediate sulfidation-state veins may be adjacent to high sulfidation ore (Hedenquist et al., 2000). The sulfide assemblages at the Co-O mine with sphalerite, pyrite, galena and chalcopyrite are comparable to intermediate sulfidation-state low sulfidation epithermal deposits. The gangue minerals of the Co-O mine may be also more comparable to an intermediate sulfidation-state deposit with quartz-carbonate-rhodonite-sericite-adularia gangue compared to an end-member low sulfidation deposit typically comprising chalcedony-adularia-illite-calcite gangue. However, the ore textures at the Co-O mine with colloform bands, breccias and combs is more comparable to shallow low sulfidation deposits described in Hedenquist et al. (2000). The petrographic study of hydrothermally altered wallrocks indicate chlorite and minor epidote and in the outer
intermediate propylitic alteration zone and a mainly argillic hydrothermal alteration zone proximal to the gold mineralization. A larger vertical extension is expected for intermediate sulfidation-state deposits with possible affiliation to porphyry and/or high sulfidation systems, in contrast to low sulfidation end-member deposits (Hedenquist et al., 2000; Einaudi et al., 2003). In summary, sulfides, host rocks (andesites to dacites), gangue and alteration assemblages suggest that the Co-O deposit had a relative deep formation depth (300-500m; cf. Hedenquist et al., 2000). The Co-O mine is located in an area of epithermal and porphyry style gold mineralization of similar age and a relationship between those may be possible.

6.3 Hydrothermal alteration profile of the Co- O mine and possible fluid source

At the Co-O mine detailed PIMA studies of nine drill cores confirmed by XRD analysis (of mainly one core) revealed a hydrothermal alteration mineralogy that is dominated by white micas (Fig. 8). The proximal to intermediate hydrothermal alteration zones of the deposit are dominated by illite and locally illite-IS (Fig. 8, Table 3). Illite can be associated with low temperatures (200-350°C) and near neutral hydrothermal fluids, whereas illite-IS to Al-smectite point to lower temperatures (160-220°C) and potentially slightly less acidic conditions (e.g., Reyes, 1990; Meunier, 2005; Simmons et al., 2005; Fig. 8).

Higher temperatures may cause a higher degree of crystalline order in clays (from illite-IS to illite), but no specific distribution of ordered/disordered clays in the Co-O mine wallrocks could be identified based on XRD and PIMA (Fig. 4c and 5c). White micas detected by PIMA in vein samples from the Co-O mine are less ordered compared to those detected in the wallrock samples (Fig. 4c and 5c). The occurrence of illite-IS (based on XRD) in the intermediate to proximal alteration zone suggest possible a retrograde conversion of illite to smectite or illitization of smectite (replacement) towards higher temperatures. Based on the
PIMA spectra data of the upper part (0-40m) of the drill core #1 contains higher amounts of illites, which may be partly related to supergene alteration. The distribution of illite in all samples from the different hydrothermal alteration zones in the Co-O mine implies that the hydrothermal alteration of the Co-O mine is related to mixing of descending near neutral ground and meteoric waters with ascending hydrothermal fluids at lower temperatures (cf. e.g., Cooke et al., 1996; Cooke and Simmons, 2000; Hedenquist et al., 2000).

Chlorite is absent in the auriferous veins, is rarely present in the proximal alteration zone and is most abundant in the intermediate and distal alteration zones (Fig. 8). The local abundance of chlorite in the proximal alteration zone could be related to brecciated and overprinted wallrock clasts situated next to veins. The higher abundance of chlorite in the intermediate alteration zone compared to the distal alteration zone is consistent with petrographic studies, which indicate that the distal alteration zone exhibits generally a lower degree of hydrothermal alteration when compared to the intermediate hydrothermal alteration zone. The abundance of chlorite decreases from the intermediate to distal alteration zone, where in thin sections chlorite is generally more abundant than “sericite” in the distal alteration zone.

In both (intermediate and distal) alteration zones original mafic minerals in the wallrock such as hornblende are replaced by chlorite, and feldspars are partly replaced by “sericite”. The decrease in the total amount of hydrothermal alteration minerals from intermediate alteration to distal alteration zone marks the transition into more weakly altered wallrock. Chlorite is consistent with pH neutral and low temperature conditions (cf. Fig. 9), as described for the illites (e.g., Reyes, 1990; Meunier, 2005). The absence of illite in the veins, the high abundance of lower ordered white micas in the proximal to intermediate hydrothermal alteration zone and the rare occurrence of chlorite in the proximal zone represents a distinct vector to gold mineralization in the Co-O deposit.
The presence of poorly ordered kaolinite identified by XRD is likely related to supergene alteration in the upper (40m) of drill core #1 (Fig. 8). The well-ordered kaolinite detected in traces in the vein and in lower amounts in wallrock samples from the deeper parts of the drill core #1 is hypogene. Kaolinite detected by PIMA in rock surface samples and the lack of kaolinite in corresponding XRD samples could be explained due to weathering of the drill core surface. Kaolinite is, therefore, not included in the schematic hydrothermal alteration profile of the wallrocks (Fig. 8). Traces of kaolinite in the auriferous veins are indicated by XRD, which is the most abundant minor accessory mineral together with pyrite.

Carbonates are part of the auriferous veins, the barren veins and the hydrothermal alteration of the wallrock and are present throughout drill core #1 (detected by IRS and XRD). According to petrographic studies carbonates are highly (> 10 vol. %) abundant in the proximal, to a lesser amount (< 5 vol. %) present in the intermediate and absent in the distal hydrothermal alteration zone. However, high kaolinite, white mica and/or chlorite abundance can obscure carbonate abundance in SWIR-spectra with values of up to 20% and more. Therefore, it is difficult to assign carbonate to a specific alteration zone based on IRS and XRD and it was not included in the hydrothermal alteration diagram. Feldspar/plagioclase detected by XRD in the intermediate to distal alteration zone is potentially not a hydrothermal mineral, but is part of the primary rock composition. This is supported by petrographic studies in which the degree of sericitization of plagioclase decreases outwards the deposit. The host rocks are dacitic to andesitic in composition, which is consistent with intermediate to Na-rich plagioclase compositions, confirmed by SEM studies. The occurrence of igneous plagioclase in the intermediate and distal alteration zones indicates a lower degree of hydrothermal alteration in the wallrocks, this is consistent with a decrease of hydrothermal chlorites.
The auriferous veins comprise quartz and often carbonate with traces of clay minerals detected by PIMA. Based on the XRD studies, auriferous veins can contain traces of kaolinite, but lack illite. However, barren quartz veins can contain illite (Table 2). The presence of illite in barren veins may also be explained by a different fluid composition. The lack of K-feldspar and the absence of an alternative K-rich component (e.g., illite) in the auriferous veins suggest an ore fluid that is low in K. The concentration of CO$_2$ together with the fluid salinity, control the fluid pH (Henley, 1985). During boiling CO$_2$ is lost to the vapor and causes the precipitation of calcite, thereby the CO$_2$ loss results in an increase in pH and a potential shift from the illite to the adularia stability field (cf. Hedenquist et al., 2000). However, in this case the adularia stability field was not reached, potentially the hydrothermal fluid was not sufficient enough enriched in K$^+$ or the hydrothermal fluid was not in equilibrium with adularia. The concentration of cations in the ascending hydrothermal fluid is partly influenced by fluid-rock interactions (Giggenbach, 1997), where the degree of fluid-rock interaction is likely rock-dominated in a low sulfidation system (Giggenbach, 1992) and further a magmatic component of up to 14 percent may be linked to the hydrothermal fluid related to andesitic arc-type magmatism (Giggenbach, 1995). The mainly medium-K andesitic to locally low-K dacitic rocks in the Co-O mine (Sonntag et al, submitted) may contain insufficient potassium to support and facilitate the formation of K-feldspar, in contrast to low sulfidation epithermal deposits (comprising adularia) formed during a period of high K magmatism e.g., Acupan, Baguio district (Cooke et al., 1996). On the other hand John (2001) stated that most northern Great Basin (USA) low-sulfidation deposits related to high-K magmatism lack adularia potentially related to lower oxidation states of the hydrothermal fluid. However, the formation of base metal-rich low sulfidation deposits could be explained by low to moderate salinity, metal-rich, oxidized magmatic fluids that react with ground water during late stages magma crystallization (John, 2001).
Salinity of the hydrothermal fluid is supposed to be higher in intermediate sulfidation-state deposits (at higher temperatures) when compared to end-member low sulfidation-state deposits (e.g., Hedenquist et al., 2000; John, 2001).

The total absence of K-feldspar (adularia) in all analyzed (XRD) samples of the Co-O mine, is unusual as K-feldspar is a typical hydrothermal vein and alteration mineral in low sulfidation epithermal systems (e.g., Dong and Morrison, 1995; Cooke and Simmons, 2000; Hedenquist et al., 2000, Simmons et al., 2005). Simmons and Browne (2000) stated that the distribution of K-feldspar and K-mica is especially sensitive to pH-controlled CO₂ gradients around zones of boiling. These authors modeled reaction paths of hydrothermal fluids and showed that the start pH of their model may affect the temperatures at which K-feldspar (and calcite) first reaches their saturation, without affecting the relative position of gold in their modeled depositional sequence. The high abundance of carbonate in stage 3 veins and potentially stage 2 veins, which display carbonate replacement textures, suggest high CO₂ loss presumably related to boiling below K-feldspar saturation.

In the low sulfidation Acupan deposit in the Baguio district (Philippines) Cooke et al. (1996) and Cooke and McPhail (2001) described the presence of adularia in deeper mine levels, whereas the upper mine levels display only hydrothermal "sericite". They explained and modeled their observation by mixing of low temperature ground waters with high-temperature chloride-rich waters in various amounts. This model, in conjunction with the assumption that the formation of K-feldspar is related to the oxidation state of the hydrothermal fluid (cf. John, 2001), suggests that adularia may exist at depth below the present mine levels, (not drilled yet), and that the currently exploited levels at the Co-O mine represents the shallower part of a low sulfidation epithermal system. The intermediate sulfidation-state of the Co-O mine suggests therefore that the vertical extent of the deposit is potentially large (cf. Hedenquist et al., 2000; John, 2001).
Adularia-free and base-metal rich low sulfidation epithermal deposits are described to be typical for the Philippines (Sillitoe, 1989; Mitchell and Leach, 1991), but are also present in other parts of the SW Pacific (e.g., Indonesia) (White et al., 1995) and in America (e.g., Heald et al., 1987; John, 2001).

John (2001) pointed out that the oxidation state and water content of magmas in end-member low sulfidation epithermal systems related to bimodal volcanism in a back-arc settings, vary significantly from low sulfidation systems (often intermediate sulfidation-state) in subduction arc settings. The formation of adularia may not only be a function of fluid mixing and/or temperature, but could also be broadly associated with the oxidation state of the magma related to a specific tectonic setting and how much of these magmatic fluids are related to the hydrothermal fluid forming the ore body.

Taking all identified hydrothermal minerals, their distribution, and the observed paragenesis into account the hydrothermal alteration patterns and mineralogy of the Co-O mine are highly comparable to other low sulfidation (intermediate sulfidation-state) deposits in the SW pacific and worldwide (e.g., Cooke et al., 1996; Cooke and Simmons, 2000; Hedenquist et al., 2000; Simmons et al., 2005). Therefore, the hydrothermal alteration, auriferous veins and their sulfide assemblages at the Co-o mine likely reflect the involvement of neutral hydrothermal fluids with lower temperatures presumably related to the mixing of hotter hydrothermal fluids with cooler ground and meteoric water. This is supported by preliminary fluid inclusion studies at the Co-O mine (unpublished data) analyzing samples from auriferous stages 2 and 3 quartz veins that yielded trapping temperatures between 220 to 270 °C and low (0.7-3.0 wt. % NaCl) salinities for primary fluid inclusion. In addition, the composition of the hydrothermal fluid may be strongly influenced by the composition of the wallrock and the magma source.
7. Conclusions

The study of the hydrothermal alteration assemblages and the auriferous veins paragenesis at the low sulfidation (intermediate sulfidation-state) epithermal Co-O mine in Mindanao, Philippines identified and described low-K hydrothermal alteration zones characterized by the lack of K-feldspar (adularia). In conjunction, the absence of K-feldspar indicate relative low temperatures for the formation of the hydrothermal alteration assemblages (mainly illite and chlorite) and point to a boiling horizon that is located deeper or marginal with respect to the deposit. The deposit formed likely at an intermediate-sulfidation state, which may be typical for low sulfidation deposits related to subduction arc-volcanism, where this deposit has potentially a larger vertical extent and may be related to a porphyry or high sulfidation system. The absence of K-feldspar may also be related to the geochemical composition of the host rocks (e.g., medium to low potassium magma series), high fluid-rock interaction and lower oxidation state of the hydrothermal fluid. There is a distinct possibility that adularia in low sulfidation epithermal systems is not as common as illustrated in the literature. This style of low potassium hydrothermal alteration zonation may prove to be more typical for low sulfidation epithermal deposits with an intermediate sulfidation-state, where its coherence may become more obvious with subsequent studies of epithermal deposits of this type, including the chemical control of host rock composition on the low potassium hydrothermal alteration minerals and zonation.

Vectors to gold mineralization for deposits with low potassium hydrothermal alteration patterns are mainly defined by the presence of white micas and the absence of chlorite proximal to the ore bodies. PIMA can assist greatly in unraveling complex hydrothermal alteration zones due to large datasets that can be generated in a short time period. However,
the interpretation of PIMA spectra needs to be conducted carefully; the separation of clay
minerals e.g., in illite and Al-smectite, may not always be possible, depending on which other
SWIR-active mineral phases are present. Other issues could arise from weathered drill core
surfaces that may exhibit higher amounts of kaolinite, which could obscure the original
hydrothermal alteration mineralogy, especially illite. Therefore, additional XRD analyses are
necessary (in this study), to support PIMA analysis.

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Fig. 1. (a) Map of the Philippines showing Mindanao (in black), with the location of the Co-O mine and study area. (b) Major structures of Mindanao with location of the Co-O area. (c) Geological map of the Co-O area (based on the tectonic map of Pubellier et al., 1993 and the geological map of Sosa 1998), displaying major lithologies, structures, and the drill hole locations of analyzed diamond drill cores.

Fig. 2. Images displaying stages 1 and 2 auriferous quartz veins in transmitted light and hydrothermal alteration of feldspar in the proximal (10s m) and chlorite in the intermediate (50-100 m) alteration zone (abbreviations after Whitney and Evans, 2010): (a) Quartz pseudomorphs of bladed calcite of stage 1 veins (crossed nichols) with chalcopyrite (ccp) between bladed textures. (b) Colloform to cockade banding of quartz and calcite veins of stage 1 with sulfides (pyrite and chalcopyrite) along the bands. (c) Fine-grained mosaic quartz matrix with patches of calcite present in typical stage 2 veins (crossed nichols) with pyrite (py) between quartz and calcite. (d) Fine-grained quartz (left) grading into more coarse grained and finally comb quartz (right) with plumose and flamboyant textures in late stage 2 veins (crossed nichols). (e) Former plagioclase replaced by “sericite” (ser) and carbonate (cb) with outline of feldspar still visible. (f) Same feldspar as (e) with crossed nichols. (g) Former mafic mineral (presumably hornblende) replaced by chlorite (chl) in a (secondary) quartz matrix. (h) Same mineral as in (g) with crossed nichols, where blue interference colors point to intermediate (Fe-Mg) chlorite composition.

Fig. 3. Auriferous quartz veins: (a) Quartz (qz) and actinomorphic Mn-rich carbonate in vein stage 3. (b) Quartz vein (stage 3) with free gold and adjunct porous Mn-rich carbonate, which displays a patchy calcite rim. (c) Stage 2 quartz vein with disseminated sulfides enlarged in (c1) chalcopyrite (ccp) with galena inclusion (gn) and electum (Au) in textural equilibrium.
with sphalerite (sp) and acanthite (Ag$_2$S). (d) Quartz/carbonate stage 3 vein with high abundance of sulfides enlarged in (d$_1$) electrum (Au) in textural equilibirum with chalcopyrite (ccp), pyrite (py), and acanthite (Ag$_2$S).

Fig. 4. Powder samples analysed by IRS. The comparison of the depths (e.g., 2350D) and wavelength position (e.g., 2200W) of selected absorption features identified by IRS allows the identification of major SWIR-active mineral phases: (a) Distribution of selected hydrothermal minerals in all samples with regards to gold assays (in ppm) of drill core #1. (b) Distribution of selected hydrothermal minerals in veins related to gold assays (in ppm). (c) White mica composition (x-axis) of all samples versus the white mica disorder (decreasing with higher values on y-axis), displaying a trend of more Al-poor, less ordered white micas in the veins in comparison to higher ordered and intermediate to Al-rich white mica compositions of breccias and wallrocks. (d) Abundance of chlorite (2250D > 1) and white mica associated with gold, showing that chlorite is nearly absent in the gold (in ppm) enriched parts of the drill core.

Fig. 5. Hydrothermal alteration minerals inferred from diagnostic absorption features in infrared reflectance spectroscopic data obtained from rock surfaces of samples from nine drill cores related to gold assays (in ppm) and analyzed material: (a) Higher amounts of gold in veins are mainly observed in the field of less ordered white mica/Al-smectite and in the carbonate field. Locally, gold-rich veins are displayed in the kaolinite field. (b) Higher gold values in wallrock samples are mostly observed in the field of white mica/Al-smectite. (c) White micas observed in veins (red) are dominated by less ordered white mica when compared to the wallrocks (blue). (d) Most samples enriched in gold plot in the field of white mica, but rarely within the white mica + chlorite field.
Fig. 6. Selected infrared reflectance spectra of powder samples containing illites with/without possibly interlayered smectite with assignments of single features (\(\nu+\delta\): combination of stretching and bending of the respective hydroxyl-groups/water; \(2\nu/2\delta\): first overtone of stretching/bending): sample 417_a containing illite with relatively high water content, sample 411_a containing illite with relatively low water content, and sample 436_c containing low crystalline illite.

Fig. 7. White mica (illite) crystalline disorder in powdered samples measured by XRD and PIMA. X-axis: 2200D/1900D ratio; Y-axis: FWHM of the illite 001 peak at 10.1Å

Fig. 8. Schematic (not to scale) hydrothermal alteration profile of the low sulfidation epithermal Co-O mine displaying the location of alteration zones and their characteristic hydrothermal alteration minerals (excluding plagioclase) based on XRD and IRS results. Intersection of veins was described by Kolb and Hagemann (2009).

Fig. 9. Hydrothermal alteration minerals associated with temperature and activity of alkali to alkaline earth in relationship to the activity of hydrogen (after Utada 1980). Hydrothermal minerals detected by XRD and IRS in the low sulfidation epithermal Co-O mine with grey shaded ellipses representing major hydrothermal minerals in the proximal and intermediate alteration zone, and the hatched ellipses point out dominant hydrothermal alteration minerals in the intermediate and distal alteration zone.
Table 1
Relationship between relative timing of deformation events, paleostress direction, structural elements, vein stages including gangue mineralogy, vein textures and paragenesis.
Deformation events, related structures and auriferous vein stages are after Kolb and Hagemann (2009).

<table>
<thead>
<tr>
<th>Event</th>
<th>Deformation</th>
<th>Structure</th>
<th>Au veins</th>
<th>Gangue Minerals</th>
<th>Vein Textures</th>
<th>Sulfide Paragenesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_E</td>
<td>NE-SW extension</td>
<td>synsedimentary faults, graben</td>
<td>pre-gold mineralization</td>
<td>stage 1 quartz/chalcedony, minor carbonate</td>
<td>collo-, crustiform, bladed calcite</td>
<td>py ± cpy, Au</td>
</tr>
<tr>
<td>D_1</td>
<td>NNE-SSW compression</td>
<td>lateral and frontal ramp, veins in the trends of the Philippine fault (NNW-SSE), the Palawan (ENE-WSW), and the Co-O mine (WNW-ESE)</td>
<td>stage 2 mosaic-jigsaw to brecciated</td>
<td>py - sph - cpy - Au ± py, Ag_S, gal</td>
<td>Ag_S = acanthite, Ag_CuS_2 = jalpaite</td>
<td></td>
</tr>
<tr>
<td>D_2</td>
<td>E-W compression</td>
<td>reactivation of all D_1 structures, N-S trending thrusts, veins in the Riedel geometry</td>
<td>stage 3 quartz and carbonate</td>
<td>banded - comb</td>
<td>cpy - py - Au ± Ag_S, gal, Ag_CuS_2</td>
<td></td>
</tr>
<tr>
<td>D_3</td>
<td>N-S to NW-SE extension</td>
<td>N-S, NE-SW, NNW-SSE trending faults</td>
<td>post-gold mineralization</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 2

Algorithms of multiple feature extraction method (MFEM) used for identification and characterization of SWIR-active minerals based on multiple absorption features in SWIR spectral data (cf. Cudahy et al., 2008; Laukamp et al., 2010). Rx refers to the reflectance at the wavelength x.

<table>
<thead>
<tr>
<th>Product name</th>
<th>Applicable for the listed minerals (examples)</th>
<th>Base algorithm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin abundance index</td>
<td>Kaolin group minerals, namely kaolinite halloysite, dickite and nacrite</td>
<td>2200D (Normalised depth of a fitted 4th order polynomial between 2120 and 2245 nm) Masked with: 2160D ((R2138+R2190)/(R2156+R2179)) &gt; 1.005</td>
</tr>
<tr>
<td>Kaolin composition index</td>
<td>Composition and crystallinity of kaolin group minerals ranging from well-ordered kaolinite to halloysite to dickite (and nacrite)</td>
<td>[(R2138+R2173)/R2156]/ [(R2156+R2190)/R2173] Masked with: 2200D &gt; 0.005</td>
</tr>
<tr>
<td>White mica abundance index</td>
<td>Phengite, paragonite/muscovite, illite/brammalite</td>
<td>2200D Masked with: 2160D &lt; 1.005 and 2350D [R2326+R2376]/(R2343+R2359) &gt; 1.001</td>
</tr>
<tr>
<td>White mica composition index</td>
<td>Phengite, paragonite/muscovite, illite/brammalite</td>
<td>2200W (Wavelength of absorption minimum calculated using the 1st derivative of a fitted 4th order polynomial between 2120 and 2245 nm) Masked with: White mica abundance &gt; 0.005</td>
</tr>
<tr>
<td>Al-smectite abundance index</td>
<td>Montmorillonite, beidellite</td>
<td>2200D Masked with: 2160D &lt; 1.005 and 2350D &lt; 1.035</td>
</tr>
<tr>
<td>Al-smectite composition index</td>
<td>Montmorillonite, beidellite</td>
<td>2200W Masked with: Al-smectite abundance index &gt; 0.005</td>
</tr>
<tr>
<td>Chlorite-epidote abundance index</td>
<td>Chlorite, epidote, (biotite)</td>
<td>2250D (R2227+R2275)/(R2241+R2259) Masked with: MgOH abundance index [(R2270+R2370)/(R2300+R2340)] &gt; 1.06</td>
</tr>
<tr>
<td>Chlorite-epidote composition index</td>
<td>Chlorite, epidote, (biotite)</td>
<td>2250W (Wavelength position of the absorption minimum calculated using a fitted 4th order polynomial between 2240 and 2270 nm with focus between 2245 and 2263 nm) Masked with: Chlorite abundance index &gt; 0.005</td>
</tr>
<tr>
<td>Carbonate abundance index</td>
<td>Carbonates vs. MgOH-bearing silicates, based on left-asymmetry of CO3 feature @ 2340 nm</td>
<td>2340D (Continuum removed depth of a fitted 4th order polynomial between 2320 and 2356 nm) Masked with: MgOH abundance index &gt;1.01 + 2260D (R2240+R2280)/(R2250+R2270) &lt; 1.06 + 2380D (R2360+R2400)/(R2370+R2390) &lt; 1.005 + 2340_left_asym (Asymmetry of the 2340 absorption using a fitted 4th order polynomial between 2326 and 2350 nm focussing between 2336 and 2340 nm) &gt; 0</td>
</tr>
<tr>
<td>Carbonate composition index</td>
<td>separating calcite, dolomite, siderite</td>
<td>2340W (Wavelength of the absorption minimum calculated using a fitted 4th order polynomial between 2290 and 2350 nm) Masked with: Carbonate abundance masks</td>
</tr>
</tbody>
</table>
Table 3
Mineralogical interpretation of infrared reflectance spectroscopy (IRS) and XRD conducted on samples from drill core #1

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Zone</th>
<th>IRS (rock surface)</th>
<th>IRS (powder)</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>410a b</td>
<td>D</td>
<td>wm</td>
<td>wm</td>
<td>ilt, qz, cal, (py, kln)</td>
</tr>
<tr>
<td>411 a</td>
<td>I</td>
<td>wm, chl</td>
<td>wm, (chl?)</td>
<td>ilt, qz, cal, (py, kln)</td>
</tr>
<tr>
<td>414 a</td>
<td>I</td>
<td>wm, chl, Al-sme</td>
<td>wm, chl, Al-sme</td>
<td>qz, ilt-IS, cal, (kln, py)</td>
</tr>
<tr>
<td>416a a</td>
<td>I</td>
<td>wm, chl</td>
<td>wm, chl</td>
<td>ilt, qz, chl, (cal, kln, py)</td>
</tr>
<tr>
<td>417 a</td>
<td>P</td>
<td>wm, chl?</td>
<td>wm, chl?</td>
<td>ilt, qz, cal, (cal, kln, py)</td>
</tr>
<tr>
<td>417 b</td>
<td>P</td>
<td>wm, chl</td>
<td>wm, chl</td>
<td>ilt, qz, cal, (py, kln)</td>
</tr>
<tr>
<td>417 c</td>
<td>P</td>
<td>wm</td>
<td>wm, chl?</td>
<td>ilt, qz, cal, (py, kln)</td>
</tr>
<tr>
<td>418 b</td>
<td>AV</td>
<td>opl</td>
<td>opl</td>
<td>qz, (cal, py)</td>
</tr>
<tr>
<td>418 c</td>
<td>P</td>
<td>wm, chl</td>
<td>wm, (chl?)</td>
<td>qz, ilt, (cal, chl, py, kln)</td>
</tr>
<tr>
<td>422 a</td>
<td>P</td>
<td>kln px</td>
<td>wm, kln px, (chl)</td>
<td>ilt, qz, cal, kln, (py)</td>
</tr>
<tr>
<td>423 a</td>
<td>AV</td>
<td>cal, kln</td>
<td>clay</td>
<td>qz, cal, (kln, py)</td>
</tr>
<tr>
<td>424 a</td>
<td>AV</td>
<td>clay, cal?</td>
<td>clay, cb?</td>
<td>qz, cal, (dol, py, kln)</td>
</tr>
<tr>
<td>425 a</td>
<td>AV</td>
<td>opl, clay</td>
<td>opl</td>
<td>qz, (cal, py)</td>
</tr>
<tr>
<td>426 a</td>
<td>AV</td>
<td>opl, cb?, clay?</td>
<td>opl</td>
<td>qz, (cal, py)</td>
</tr>
<tr>
<td>432 a</td>
<td>I</td>
<td>wm, chl</td>
<td>wm, chl</td>
<td>ilt, qz, chl, fsp, (cal, py, kln, gp)</td>
</tr>
<tr>
<td>432 b</td>
<td>I</td>
<td>gp, cal?</td>
<td>gp</td>
<td>cal, anh, qz, gp, (ilt, chl, py)</td>
</tr>
<tr>
<td>433 a</td>
<td>I-D</td>
<td>kln px</td>
<td>wm, (chl)</td>
<td>ilt, qz, chl, fsp, cal, (kln, py, gp)</td>
</tr>
<tr>
<td>433 b</td>
<td>I-D</td>
<td>wm, chl</td>
<td>wm, (chl?)</td>
<td>ilt, cal, qz, py, (gp, chl)</td>
</tr>
<tr>
<td>433 c</td>
<td>I-D</td>
<td>gp, opl</td>
<td>opl</td>
<td>qz, (cal, ilt, py, gp)</td>
</tr>
<tr>
<td>434 b</td>
<td>D</td>
<td>cal, gp</td>
<td>cal</td>
<td>cal, qz, (gp)</td>
</tr>
<tr>
<td>435 a</td>
<td>D</td>
<td>wm, chl</td>
<td>wm, chl</td>
<td>fsp, qz, chl, ilt, (cal, kln, py, gp)</td>
</tr>
<tr>
<td>436 a</td>
<td>I-D</td>
<td>wm, chl</td>
<td>wm, chl</td>
<td>ilt, qz, chl, (cal, py,)</td>
</tr>
<tr>
<td>436 c</td>
<td>I-D</td>
<td>opl, cal?</td>
<td>opl</td>
<td>qz, (cal, py, kln)</td>
</tr>
<tr>
<td>437 a</td>
<td>I</td>
<td>wm, chl, (cal?)</td>
<td>wm, chl</td>
<td>ilt, qz, chl, (py, cal, kln, gp)</td>
</tr>
<tr>
<td>437 b</td>
<td>I</td>
<td>wm, chl</td>
<td>wm, chl</td>
<td>ilt, qz, chl, (py, cal, kln, gp)</td>
</tr>
<tr>
<td>438 a</td>
<td>P</td>
<td>wm, chl</td>
<td>wm, (chl?)</td>
<td>ilt, qz, chl, (py, gp)</td>
</tr>
<tr>
<td>438 b</td>
<td>P</td>
<td>wm, gp, Al-sme</td>
<td>gp, (wm?), Al-sme</td>
<td>cal, qz, gp, ilt-IS, (py, chl)</td>
</tr>
<tr>
<td>439 a</td>
<td>P</td>
<td>wm, Al-sme</td>
<td>chl?, Al-sme</td>
<td>ilt-IS, qz, (py, cal)</td>
</tr>
<tr>
<td>439 c</td>
<td>AV</td>
<td>cal, clay</td>
<td>cal, clay</td>
<td>cal, qz, (chl, kln)</td>
</tr>
<tr>
<td>441 a</td>
<td>P-I</td>
<td>kln wx</td>
<td>kln wx</td>
<td>kln, qz, cal, (mag, ilt, py, mnt)</td>
</tr>
<tr>
<td>441 b</td>
<td>P-I</td>
<td>wm, kln?</td>
<td>wm, kln?</td>
<td>ilt-IS, qz, cal, kln, (py)</td>
</tr>
<tr>
<td>441 c</td>
<td>P-I</td>
<td>cb</td>
<td>cb</td>
<td>cal, qz, dol, (py)</td>
</tr>
<tr>
<td>442 c</td>
<td>I</td>
<td>kln px</td>
<td>clay</td>
<td>qz, kln, ilt, cal, (chl, mag)</td>
</tr>
<tr>
<td>442 c</td>
<td>I</td>
<td>cal</td>
<td>cal</td>
<td>cal, qz, (py)</td>
</tr>
<tr>
<td>442 c</td>
<td>I</td>
<td>cal, clay</td>
<td>cal, clay, chl</td>
<td>cal, qz, (ilt, chl, kln, py)</td>
</tr>
<tr>
<td>444 a</td>
<td>D</td>
<td>wm, chl</td>
<td>wm, chl</td>
<td>ilt, qz, chl, (kln, mag, py)</td>
</tr>
</tbody>
</table>

Minerals in brackets for infrared reflectance spectroscopy (IRS) are difficult to recognize in the respective dataset. Minor components identified by XRD are in brackets (minerals <5 wt. %). The zone indicates the location of a sample in the hydrothermal system: AV = auriferous vein, P = proximal, I = intermediate, and D = distal zone (to the ore). Abbreviations (after Whitney and Evans, 2010): Al-sme = Al-smectite; anh = anhydrite; cal = calcite; cb = carbonate mineral; chl = chlorite; dol = dolomite; fsp = feldspar; gp = gypsum; ilt = illite; ilt-IS = illite with possibly interstratified Al-smectite; kln wx = well ordered kaoline; kln px = poorly ordered kaoline; mag = magnetite; mnt = montmorillonite; opl = opaline (amorphous) silica; py = pyrite; qz = quartz; wm = white mica.
Co-O mine
normal fault

thrust fault
drill hole

EUR = Eurasia
PMB = Philippine Mobile Belt

PF = Philippine Fault
CF = Cotabato Fault

NT = Negros Trench
PT = Philippine Trench
ST = Sulu Trench
CT = Cotabato Trench

Figure 1
a) Bladed/lattice textures

b) Cockade/colloform textures

c) Calcite "oats"

fine-grained to mosaic quartz

py

d) Plumose/flamboyant textures

fine-grained quartz

e) "ser"

f) Chl

qtz

"ser"

h) Chl

qtz

"ser"

Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
supergene

hypogene

recent surface

kaolin group minerals
+/− illite

auriferous vein

quartz, carbonate

illite, quartz, chlorite
+/− carbonate
+/− ill-IS

illite, quartz, chlorite
+/− plagioclase
+/− carbonate

proximal

intermediate

distal
<table>
<thead>
<tr>
<th>alteration type</th>
<th>mineral zones</th>
<th>cations</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>halloysite, kaolinite, pyrophyllite</td>
<td>$H^+$</td>
</tr>
<tr>
<td>intermediate</td>
<td>smectite, IS mixed layers, illite, K-feldspar</td>
<td>$K$</td>
</tr>
<tr>
<td></td>
<td>smectite, IS and CS mixed layers, chlorite epidote, epidote actinolite</td>
<td>$Ca+Mg$</td>
</tr>
<tr>
<td>alkaline</td>
<td>stilbite, heulandite, laumontite, wairakite</td>
<td>$Ca$</td>
</tr>
<tr>
<td></td>
<td>mordenite-Na, analcite, albite</td>
<td>$Na$</td>
</tr>
</tbody>
</table>

*Figure 9*