Ammonium Alteration Associated with Epithermal Silver Mineralization in Mexico

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Introduction

Ammonium-bearing minerals have been commonly found in the alteration halos of epithermal precious metal deposits. Since ammonium produces absorption in shortwave infrared (SWIR), a portable SWIR spectrometer is extensively used in exploration. Although, the quantity of ammonium to produce the absorption in the spectrum is unknown. This study was initiated to quantify the ammonium contents in rocks, identify minerals hosting it, and evaluate its source.

Study Location


Fig 1

The study is in the El Zapote I and II prospects in the Tizapa mining district of Mexico The location is east of the Sierra Madre Occidental, known for its rich epithermal silver deposits.

The Ag mineralization forms quartz veins spatially associated with Tertiary rhyolitic igneous rocks, which overlie a Mesozoic basement of phyllite and limestone. Samples were collected within the rhyolite, as outlined in Fig.1.

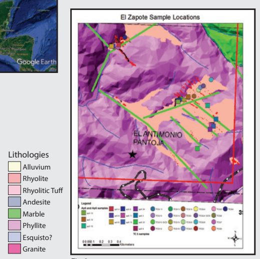


Fig 2

Shortwave Infrared Absorption

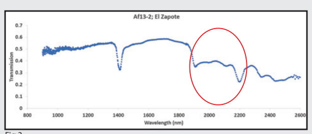


Fig 3

The absorption is characterised by the depressed and undulated zone of the spectrum at 1900 - 2200 nm with minor absorptions around 2000 nm and 2100 nm. This feature is characteristic of the presence of ammonium but does not provide the information related to the ammonium-bearing minerals.

Ammonium is known to replace potassium because of similar ionic radii. Ammonium bearing feldspar and mica are buddingtonite and tobelite, respectively. The samples used in this study show a near-linear correlation of ammonium and K2O contents, demonstrating the substitution of K by ammonium. A positive correlation of N vs K2O, (~0.08 wt% N is ~ 3 wt%K2O) suggests that approximately 9% of potassium is replaced by ammonium.

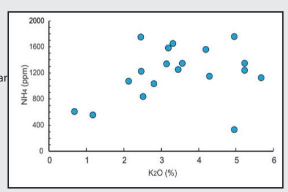


Fig 3

Analytical Methods

Petrographic microscope, scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS) and X-ray diffractometer were used to determine ammonium bearing minerals. SWIR spectra were collected using ArcOptix Rocket FT-NIR spectrometer coupled with Avantes integrating sphere, spectral range of 900-2600 nm and resolution of 8cm-1. Ammonium contents were measured using elemental analyser (EA) and nitrogen isotope compositions were determined with Delta Plus XP gas source mass spectrometer.

Samples

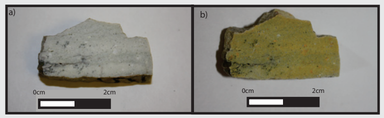


Fig 5: Macro samples of Af13-9 a) before staining; b) after staining

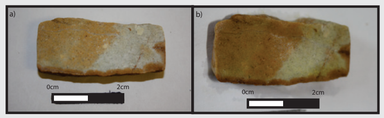


Fig 6: Macro samples of Af13-11 a) before staining; b) after staining

Samples consist of altered rhyolites with phenocrysts of quartz and K-feldspar in the pervasively altered groundmass of fine-grained quartz, illite, muscovite and kaolinite. K-feldspar phenocrysts are commonly replaced by aggregates of illite.

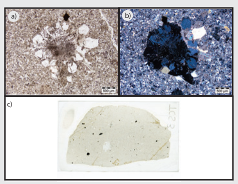


Fig 7: Photomicrographs of Af13-3 a) plain polarized light b) cross polarized light.; c) thin section scan.

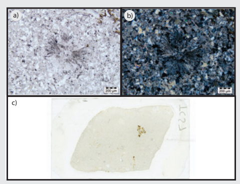


Fig 8: Photomicrographs of Af13-7 a) plain polarized light b) cross polarized light.; c) thin section scan.

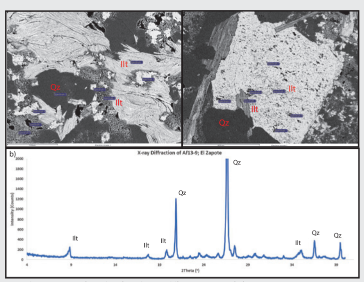


Fig 9: Electron images of samples Af13-9; b) X-ray diffraction pattern of Af13-9

Illite is found in two forms; coarse-grained (1-2 mm) and fine-grained (~200 um) Mg-rich (up to 1.28 wt% MgO) illite as seen in SEM-EDS analysis. High ammonium samples (> 1330 ppm in bulk rock) contain abundant fine-grained illite (~20 wt%), suggesting that ammonium mostly resides in the K site of fine-grained illite.

SWIR Absorption Spectrum

Ammonium content of samples are not correlated with the degrees of SWIR absorption. For example, the sample Af13-8 shows no obvious ammonium absorption feature, yet it contains 1020ppm NH4. The 1900 - 2200 nm zone of the spectrum is only slightly depressed and undulated, characteristic of illite
The sample Af13-5 shows no feature related to ammonium in SWIR absorption spectrum with a significantly lower NH4 content of 330 ppm. The doublet absorptions at 1400 and 2200 nm of the spectrum are characteristic of kaolinite. The presence of kaolinite is confirmed with XRD pattern.

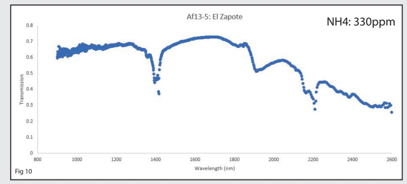
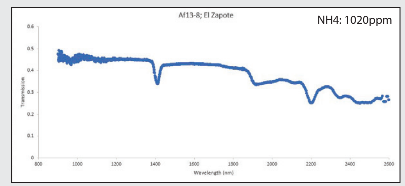


Fig 10



The sample Af13-9 shows a strong absorption due to ammonium in the SWIR spectrum and contains high NH4 content of 1750ppm. In comparison. sample Af13-18c shows a clear ammonium absorption in the 1900nm-2200nm zone of the spectrum yet contains only 540ppm NH4.

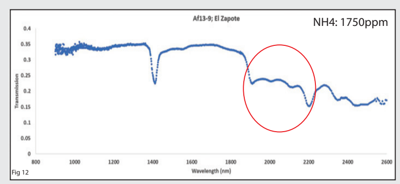


Fig 12

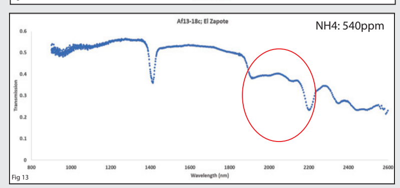


Fig 13

The data indicates the relationship between NH4 content and the SWIR absorption spectra is unclear, potentially controlled by other factors, such as co-existing minerals. The comparison of SWIR absorption features with NH4 content suggest that the SWIR absorption related to ammonium is not reliable for rocks with less than ~500ppmNH4

Source of Ammonium

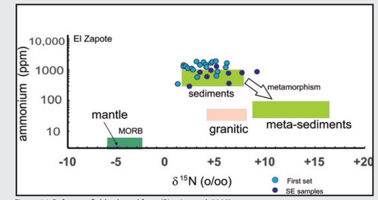


Figure 14: Reference fields plotted from (Pitcaim et al, 2005)

The content of ammonium and its nitrogen isotope compositions suggest that ammonium is likely originated from a sediments (Fig. 9) There are abundant sedimentary rocks in the immediate area, but they are highly metamorphosed. Such rocks would have high 15N. Therefore, we suggest that ammonium sourced from distant sediments.

Conclusions

The major host of ammonium in the Zapote area is illite. Buddingtonite (ammonium feldspar) was not found in the study area.
Samples with high ammonium contents, above 1000ppm, are located near silver deposits, within 200m, with higher concentrations of ammonium in samples closer to veins. SWIR absorption spectra can therefore be used in exploration.

A spectrometer can identify ammonium in rocks containing over 1000ppm NH4, but may not detect ammonium in rocks with < 500ppm NH4.
The δ15N values range from +1.1 to +9.1‰ independent of the ammonium concentrations, suggesting a significant contribution of ammonium from sedimentary rocks to mineralizing fluids.

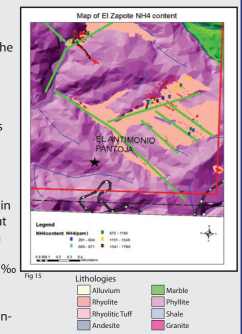


Fig 15

Acknowledgements

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