

# Stable Oxygen Isotope Systematics Associated with Epithermal Gold Mineralization, Eastern Cobequid Highlands, Nova Scotia<sup>1</sup>

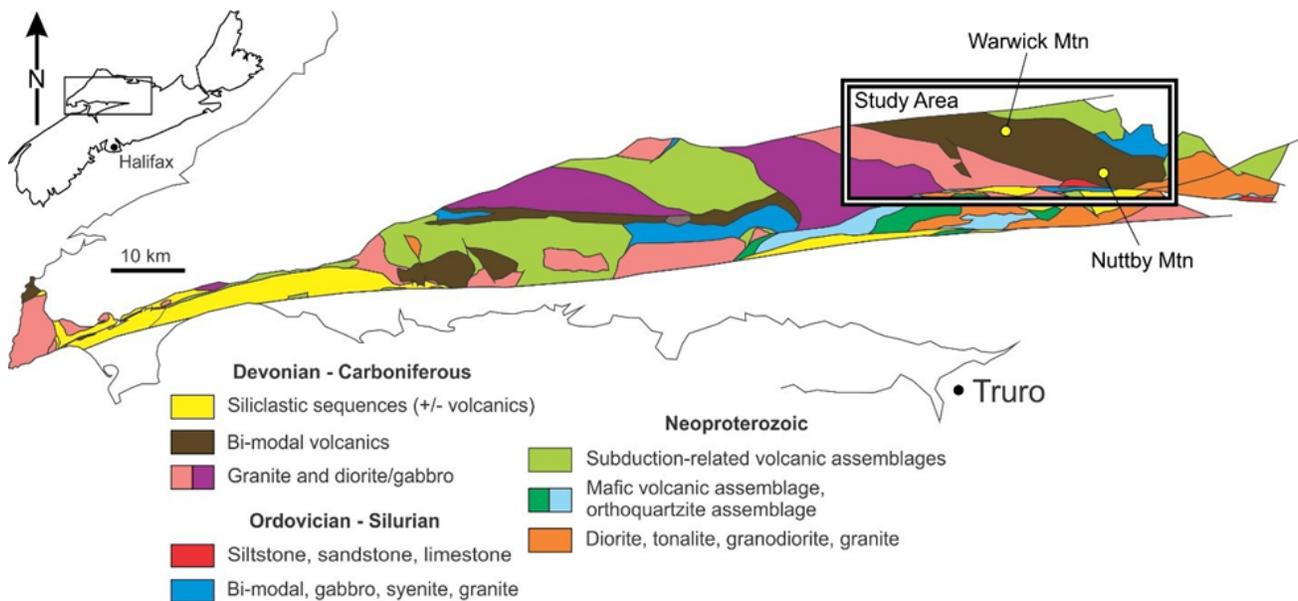
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## Introduction

In the northeastern Cobequid Highlands, Nova Scotia, bedrock mapping and bulk-rock and stream-sediment geochemical surveying by the Nova Scotia Department of Energy and Mines identified a potential epithermal Au system in Late Devonian to Early Carboniferous bimodal volcanic rocks (Fig. 1; MacHattie, 2011, 2013; Baldwin, 2016). The occurrence of low-sulphidation epithermal-style Au mineralization was considered likely in this environment as the geological setting and host rocks show similarities to modern and ancient rift-related, bi-modal volcanic successions hosting such epithermal style mineralization (e.g., the Miocene deposits in the Great Basin, Nevada,

John, 2001). Two Au occurrences (Warwick Mountain and Nuttby Mountain) have been identified and consist of zones of silicified and sulphidized volcanic rocks (rhyolites, basaltic flows, and volcanoclastics) with up to 660 ppb Au reported. Anomalous concentrations of As (up to 4500 ppm), Sb (up to 50 ppm), Se (up to 2.5 ppm), and Hg (up to 600 ppb), which are reported at, or nearby, the locations of elevated Au are consistent with a shallow, low-sulphidation epithermal association (MacHattie, 2011).

The objectives of this research are: (1) to determine if the stable O isotope systematics of quartz and calcite from the hydrothermal mineralizing system vary as a function of position in the epithermal



**Figure 1.** Regional scale map of the Cobequid Highlands. The study area for this project is outlined in the northeast corner of the map. The Warwick and Nuttby Mountain gold occurrences are also labelled. Modified after MacHattie (2018).

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environment (e.g., with depth or proximity to sulphides), relative timing of mineral precipitation, or with variation in mineral textures, and (2) to evaluate whether variability in  $\delta^{18}\text{O}$  within these minerals reflects variability in fluid composition and/or temperature, or some other process known to fractionate or modify stable O isotopes (e.g., boiling, mixing). Ultimately, the goal of the research is to establish criteria that can be used to identify areas where epithermal metal precipitation was likely to have been most efficient, thereby identifying potential drilling targets.

These objectives were met using a subset of samples obtained from two drillholes (SL-11-01 and SL-11-02; Sugarloaf Resources, Whirley Brook area, Colchester County) and surface locations in the Warwick Mountain and Nuttby Mountain areas (Fig. 1). Additional quartz-bearing vein samples from recently discovered epithermal gold mineralization in the Antigonish Highlands (Pictou County; Northern Shield Resources), bearing strong resemblance to the mineralization in the eastern Cobequid Highlands, were also studied for comparison. Following detailed petrography of the textures of hydrothermal quartz and calcite using optical petrography and scanning electron microscopy (SEM), a total of 173 spots within grains of hydrothermal calcite and quartz from 9 sample locations (3 drill core: PR03, PR8B, PR13; 6 surface: 336, 441, 98B, 260B, 4652, 2281) were analyzed for  $\delta^{18}\text{O}_{\text{VSMOW}}$  by secondary ion mass spectrometry (SIMS; University of Manitoba). The analytical instrumentation and procedures utilized for quartz and calcite  $\delta^{18}\text{O}_{\text{VSMOW}}$  determination by SIMS at the University of Manitoba are summarized in Fayek et al. (2002). The  $1\sigma$  error for oxygen isotope analyses is  $\pm 1.2\text{‰}$ .

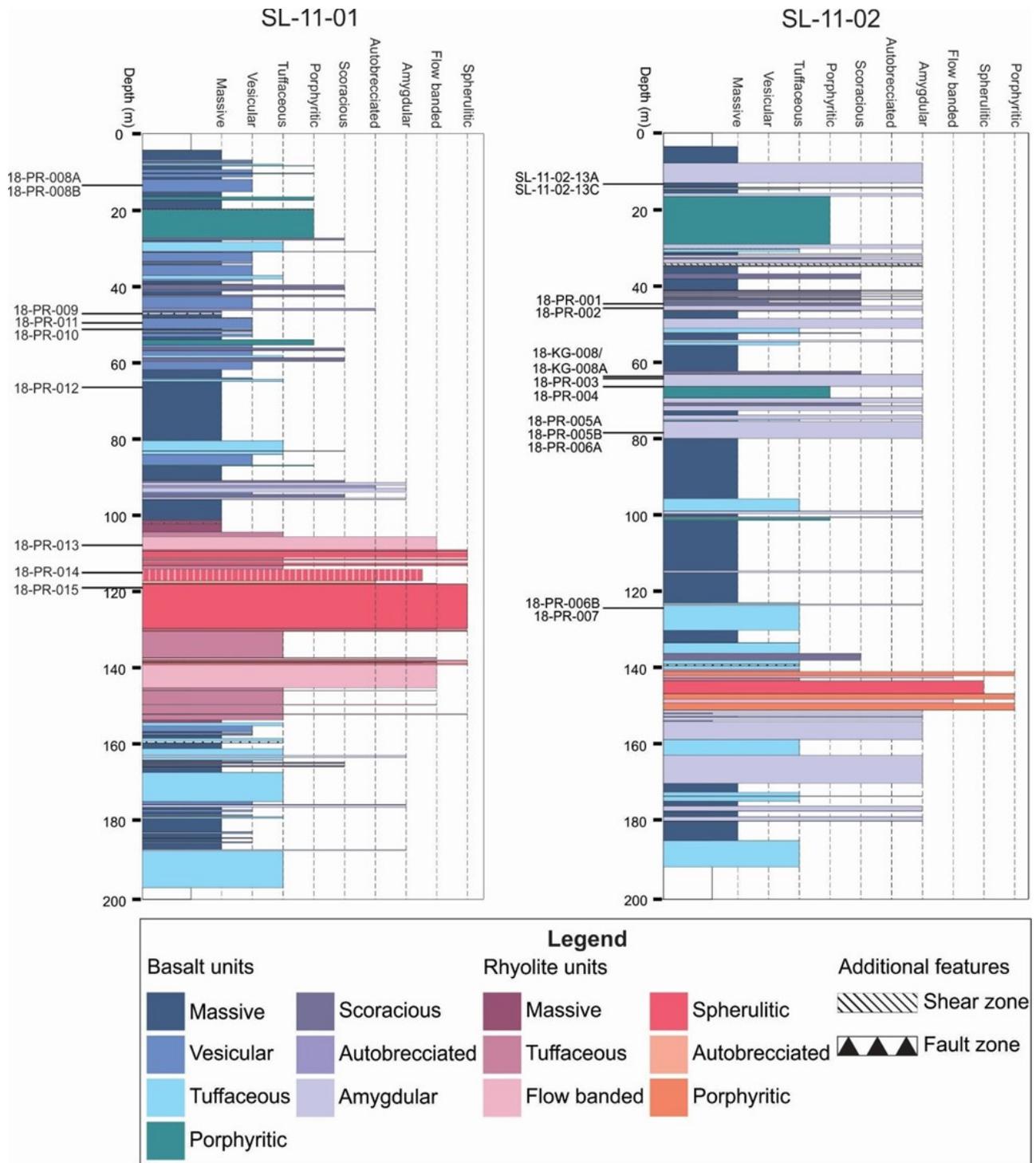
## Results

Petrographic information is summarized in Figures 2 and 3. Graphical vertical logs of the two sampled drillholes (Fig. 2) show basaltic and rhyolitic lithological subunits that are differentiated according to predominant textural features. On these logs the locations of three epithermal quartz-carbonate samples selected for the stable O isotope study are also shown (DDH SL-11-02: PR3 from 56 m below surface DDH SL-11-01: PR8B from 9 m below surface, PR14 from 81 m below surface). Both drillholes are dominated by basaltic rocks,

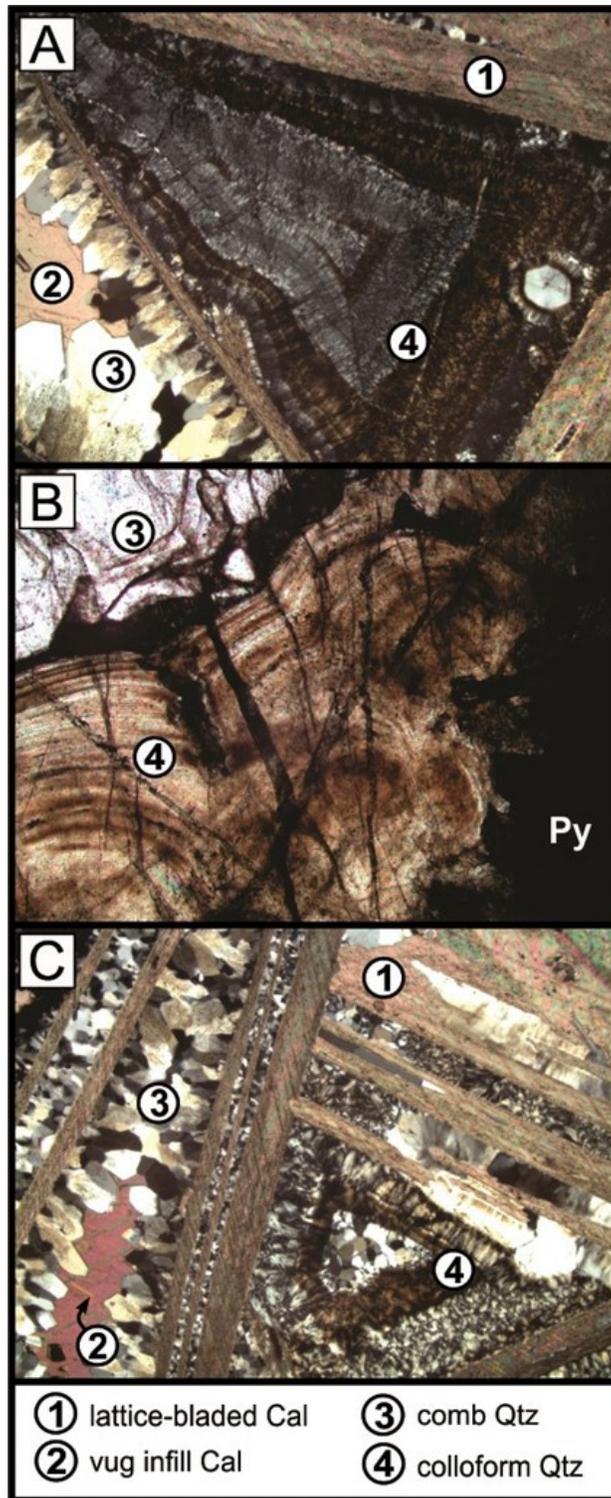
with felsic volcanic rocks intercalated with the basalts near the base of the drillholes. Hydrothermal minerals (quartz, calcite) occur in veins and in the former porosity of the volcanic rocks (e.g., occluding vugs in vesiculated/brecciated basalt and brecciated rhyolite).

Quartz and calcite show textures consistent with a transiently boiling system (c.f. Moncada et al., 2012; Hanley et al., 2019, 2020, and references therein). Stable O isotope data were obtained on three dominant texture variants of quartz and calcite (Fig. 3): (1) colloform-banded quartz (phase “4” in Fig. 3), consisting of concentrically banded, botryoidal accumulations of fine-grained quartz typically precipitated during boiling (Moncada et al., 2012, and references therein); (2) comb-textured quartz (phase “3” in Fig. 3), consisting of variably zoned quartz crystals growing sub-parallel to one another, post-dating and nucleating from colloform-banded quartz surfaces; and (3) vug(gy) infill calcite (phase “2” in Fig. 3) consisting of massive calcite infilling crystal-lined vugs in quartz, post-dating quartz. In some samples, the quartz and calcite were coprecipitated with minor amounts of pyrite (enriched in Au, As, Sb, Hg). A second textural variant of calcite, typically precipitated during boiling (lattice-bladed calcite; phase “1” in Figure 3), pre-dates both generations of quartz and is the paragenetically earliest phase, but was not analyzed by SIMS in this study.

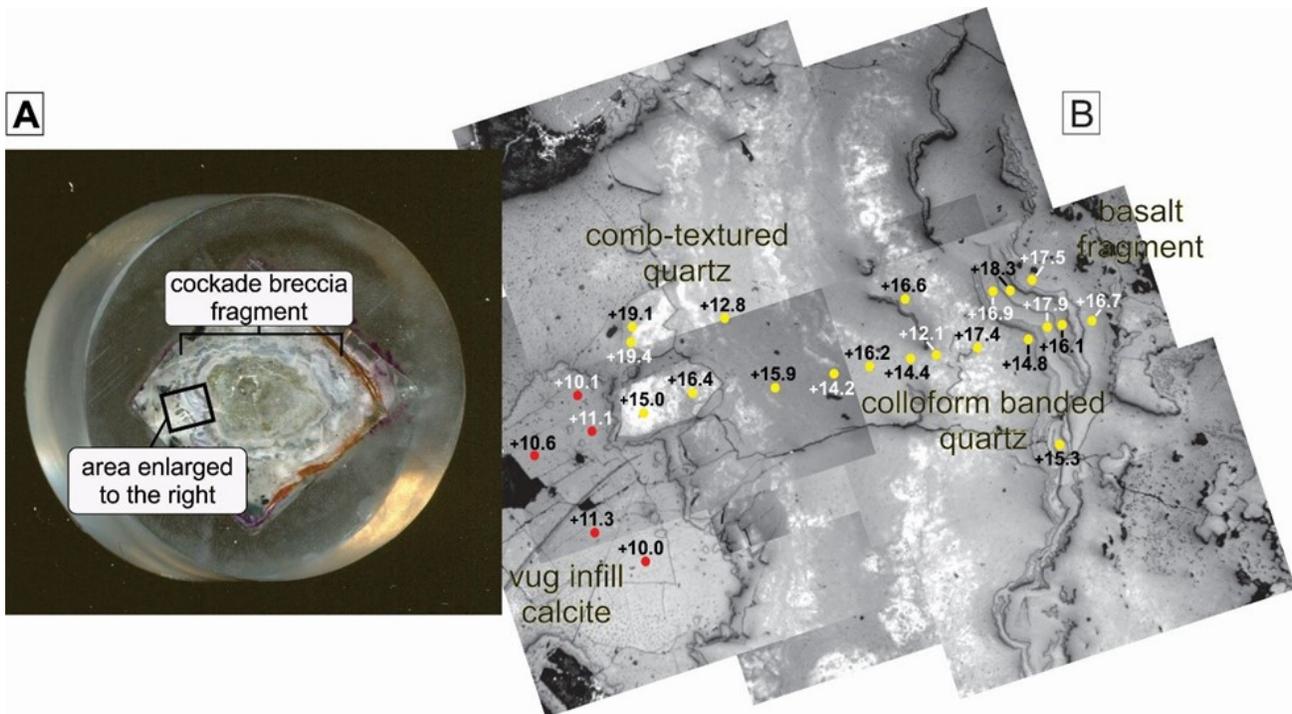
A typical SIMS sample mount and polished sample surface in an area of interest are shown in Figure 4. Figure 4A shows a 1”-diameter Struers polymer mount containing a cut fragment from a polished thin section containing epithermal features of interest in sample PR8B. The sample shows cockade texture, consisting of a fragment of basalt coated in colloform-banded quartz overgrowth, with later comb-textured quartz grown on the outer surface of the colloform quartz accumulation, and a late vuggy calcite infill. Values of  $\delta^{18}\text{O}_{\text{VSMOW}}$  are shown next to the locations of SIMS analysis locations in Figure 4B, a reflected light mosaic showing a  $\sim 2$  mm area of the sample (boxed area in Figure 4A). The *in situ* method allows variations in  $\delta^{18}\text{O}_{\text{VSMOW}}$  to be determined at the microscopic scale within such texturally complex samples. Analyses are obtained from spots  $\sim 20$   $\mu\text{m}$  in diameter (Fig. 4B).



**Figure 2.** Vertical graphic logs through the sampled drillholes (Sugarloaf Resources SL-11-01 and -02) showing basaltic and rhyolitic lithological subunits differentiated according to predominant textural features. Sample locations for this project (stable O isotopes) are shown with the sample markers along the left side of each column.



**Figure 3.** Transmitted, cross-polarized (XPL) and plane-polarized (PPL) images from polished thin sections (30  $\mu\text{m}$  thick) showing representative boiling and non-boiling textures in mineralized volcanic rocks from DDH SL-11-01 and -02. (A) Lattice-bladed calcite ("1"; Cal) with an infilling matrix of colloform-banded ("2") and later comb-textured quartz ("3"; Qtz) followed by end-stage vuggy infill calcite ("4"). XPL image. (B) Early pyrite with thick, colloform-banded quartz overgrowth ("4") and later comb-textured quartz ("3"). PPL image. (C) Similar textured sample as in (A) showing the sequence: early, lattice-bladed quartz  $\rightarrow$  colloform-banded quartz  $\rightarrow$  comb-textured quartz  $\rightarrow$  vuggy calcite infill. XPL. The width of field for all images is 1 mm. Py=pyrite.



**Figure 4.** Images showing petrographic characteristics of epithermal features at different scales that were analyzed by SIMS, and corresponding, spatially resolved O isotope data. (A) Scanned image of a 1"-diameter polymer puck mount containing a cut fragment of a polished thin section at its surface. The thin section fragment contains a cockade breccia fragment with several different textural styles of calcite and quartz. (B) A reflected light photomicrograph mosaic (PPL) showing the area in (A) enlarged, with domains of colloform-banded quartz, comb-textured quartz and vug(gy) infill calcite identified on the surface of the polished sample. Red (calcite) and yellow (quartz) circles show ~20  $\mu\text{m}$  SIMS analytical spots with the corresponding values of  $\delta^{18}\text{O}_{\text{VSMOW}}$  in units of ‰ next to each spot. The width of the mosaic in (B) is equivalent to ~2 mm on the sample surface.

All data are summarized in Figure 5, which shows  $\delta^{18}\text{O}_{\text{VSMOW}}$  data ranges. The most significant findings are described below:

#### *Variation in $\delta^{18}\text{O}_{\text{VSMOW}}$ with mineral species, timing and textural variation*

The range in  $\delta^{18}\text{O}_{\text{VSMOW}}$  values in quartz and calcite are highly variable, with overall values between ~+1 and +24‰ for quartz, and ~+2 and +20‰ for calcite. Ranges in data for individual samples can be as variable (e.g., Fig. 5A, sample 98B-cal), but for most samples there is typically no more than ~5-6‰ difference between the lowest and highest values. The two textural variants of quartz (Fig. 5B, C) show similar values of  $\delta^{18}\text{O}_{\text{VSMOW}}$ . Individual variants of quartz can show significant variation in  $\delta^{18}\text{O}_{\text{VSMOW}}$ . For example, a continuous sequence of colloform-banded quartz in sample PR8B (Fig. 4B) shows a variation of up to ~5‰ between adjacent zones, and in general variations of ~3-5‰ are typical across colloform accumulations. In comb-textured quartz (e.g., Fig.

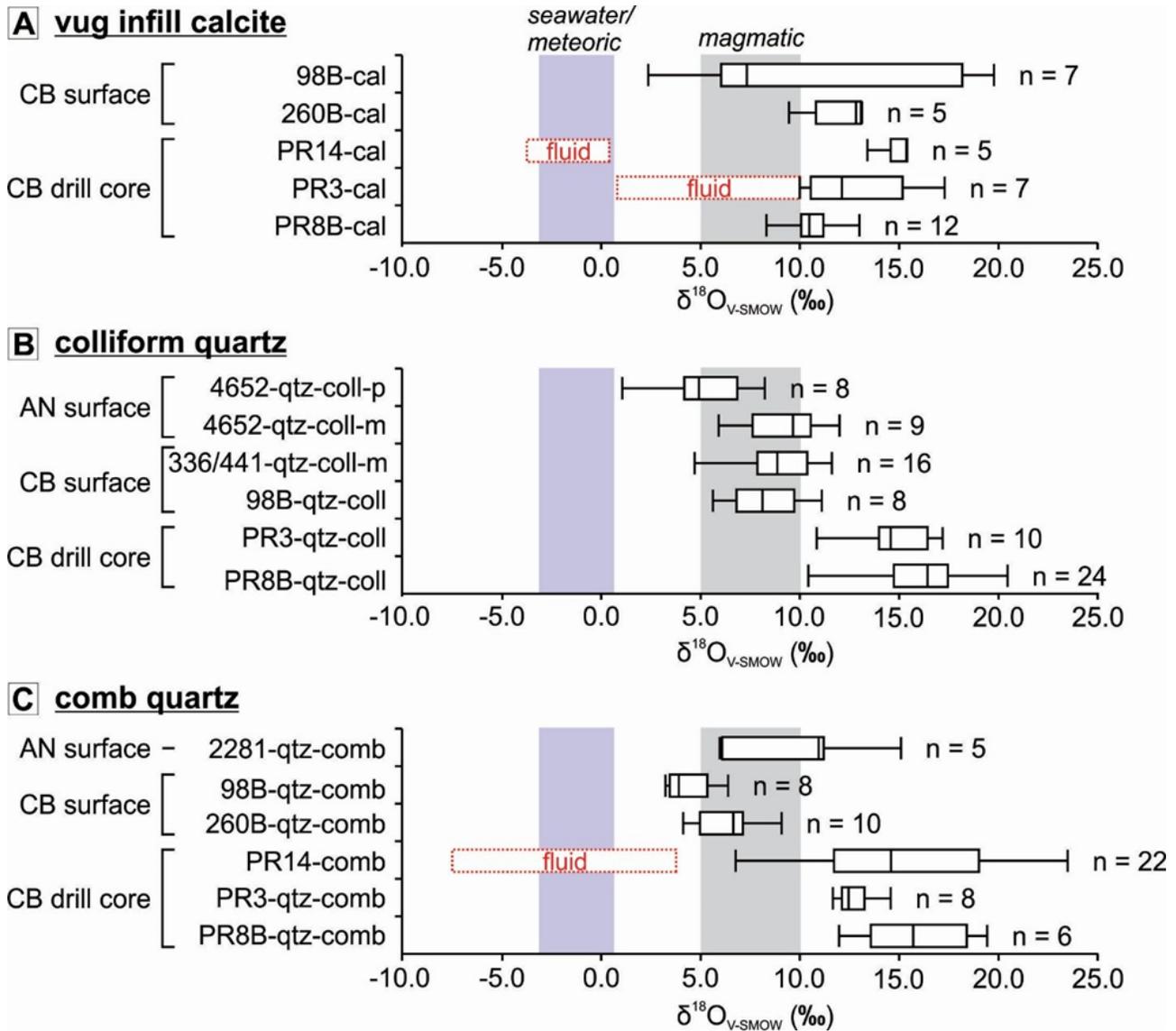
5C) growth zones across single crystals show up to ~7‰ decrease from core to rim, with most crystals showing some decrease, and a minor number of crystals analyzed showing no change from core to rim. Vug(gy) infilling calcite typically shows comparable or lower values of  $\delta^{18}\text{O}_{\text{VSMOW}}$ . For example, calcite in sample PR8B (Fig. 4B) shows values lower than in the adjacent colloform and comb quartz.

#### *Variation in $\delta^{18}\text{O}_{\text{VSMOW}}$ with sample depth*

For quartz, surface samples gave values of  $\delta^{18}\text{O}_{\text{VSMOW}}$  consistently lower than from drill core, shifted by 5-10‰ (Fig. 5B, C), whereas no distinct difference in calcite composition between core and surface samples is evident.

#### *Variation in $\delta^{18}\text{O}_{\text{VSMOW}}$ in pre- vs. syn-mineralization quartz*

Values for syn-mineralization quartz were obtained from three different samples (Fig. 5B, samples 336



**Figure 5.** Box-whisker plot (whiskers=max, min; boxes=median, 1st, 3rd quartile range) of  $\delta^{18}\text{O}_{\text{V-SMOW}}$  in units of ‰ for all quartz and calcite samples analyzed by SIMS. The values of 'n' are the number of SIMS spot analyses per sample. The red 'fluid' ranges are calculated ranges in fluid data for those minerals in specific samples (see text for explanation). The grey field is the range for 'magmatic' waters (Craig, 1963; Taylor, 1968) and the blue range is the range for early Carboniferous meteoric water and seawater (Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003; Bowen et al., 2005; Brand, 2006; van Hinsbergen et al., 2015) in the study area (i.e., at the time of mineralization).

and 441, and sample 4652). These represent quartz that is paragenetically coeval with auriferous pyrite mineralization and yields values between ~5 and 11‰, with the majority of analyses between ~7 and 10‰. For comparison, analyses of pre-mineralization quartz (precipitated before pyrite, as pyrite replaces the quartz) in one of these samples (Fig. 5B, sample 4652) is lower, with values between ~1 and 8‰, and the majority of data between ~4 and 6.5‰.

#### *Comparison of Cobequid Highlands and Antigonish Highlands epithermal Au systems*

Values for colloform-banded and comb-textured quartz from surface samples in the Cobequid Highlands and Antigonish Highlands are comparable (Fig. 5B, C) and values for mineralized colloform quartz from both settings are almost identical (within error).

### *Estimation of fluid source/s*

Two samples from drill core provided the opportunity to constrain the composition of fluids that equilibrated with quartz and calcite. These contained fluid inclusions of primary origin trapped at boiling conditions in quartz and calcite; Hanley et al. (2019, 2020) provide the petrographic rationale for boiling fluid inclusion assemblages in these samples. Therefore, the fluid inclusion data provide absolute temperatures (rather than minimum T) of host mineral growth that, when combined with isotope fractionation calibrations for O between H<sub>2</sub>O and quartz/calcite, can be used to calculate the  $\delta^{18}\text{O}_{\text{VSMOW}}$  of the equilibrating fluid (i.e., the fluid precipitating the mineral). The results of these calculations are shown in Figure 5A and 5C. For a sample of zoned, comb-textured quartz (PR14) the estimated fluid  $\delta^{18}\text{O}_{\text{VSMOW}}$  ranges between -7.5 and +3.5‰ (using the minimum and maximum T data from fluid inclusions, combined with the minimum and maximum  $\delta^{18}\text{O}_{\text{VSMOW}}$  from the growth zones hosting the fluid inclusions). Calcite containing primary inclusions in the same sample yields a narrower range in fluid  $\delta^{18}\text{O}_{\text{VSMOW}}$  that overlaps with the estimated quartz values (Fig. 5A; -4 to 0‰). The calculated fluid isotope composition from this sample lies well outside of the range for “magmatic” fluids (Craig, 1963; Taylor, 1968; Fig. 5) and overlaps with the known range in composition for both seawater and meteoric water in the early Carboniferous (Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003; Bowen et al., 2005; Brand, 2006; van Hinsbergen, 2015). A second sample, PR3, in contrast yields a similarly wide, but much higher fluid  $\delta^{18}\text{O}_{\text{VSMOW}}$  range, from +1 to 10‰, which overlaps with the “magmatic” compositional field.

## Summary

The stable O isotope composition of several texturally distinct stages of hydrothermal quartz and calcite related to epithermal gold mineralization in the eastern Cobequid Highlands of Nova Scotia records large variations in fluid composition that are interpreted to reflect mixing of a fluid of magmatic parentage (estimated fluid  $\delta^{18}\text{O}_{\text{VSMOW}} > \sim 5\%$ ; consistent with fluid inclusion results in the study area; Hanley et al., 2019, 2020) with fluid having an estimated  $\delta^{18}\text{O}_{\text{VSMOW}} < \sim 0\%$ , which when considered with fluid inclusion data (Hanley et al., 2019, 2020) is likely evaporated Carboniferous seawater. Quartz from surface outcrop samples (enriched in Au, in contrast to drill

core samples that are relatively barren) are markedly more depleted in <sup>18</sup>O compared to drill core samples. The reasons for this are not clear, but could be the result of (1) a greater proportion of the low  $\delta^{18}\text{O}_{\text{VSMOW}}$  fluid in the mixture precipitating quartz in shallower parts of former epithermal system; or (2) higher temperatures of quartz precipitation (resulting in less isotope fractionation between fluid and quartz), or both. The results of this study highlight the potential for delineating zones of gold mineralization through stable isotope analysis of mineralization-related gangue minerals. Importantly, recognition of fluid mixing zones through integration of stable O isotope data with fluid inclusion constraints on fluid temperature and salinity may provide a tool for exploration if mixing was a driving mechanism for gold precipitation in the study area.

## Acknowledgments

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