Fluid Inclusion Study of Calcite and Celestine in DGR-1 and DGR-3 Drill Core Samples from the Bruce Nuclear Site, Southern Ontario

NWMO-TR-2018-13 **August 2018**

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ABSTRACT

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Abstract

As part of on-going research and development activities performed on rock core samples from the Bruce Nuclear Site, which has already been the subject of detailed site investigations, vein-filling calcite in drill core samples from the Devonian Bois Blanc and Silurian Bass Islands Formations have been dated by the U-Pb LA-ICPMS and ID-TIMS methods (Davis, 2016). From five of these dated samples, separate undated pieces were later sent to the University of Bern for fluid inclusion analysis.

The aims of the fluid inclusion study were to (1) place constraints on the temperature of formation of the calcites and (2) estimate the salinity of the parent fluids from which the calcite precipitated. These constraints should aid in enhancing existing understanding about the geological events to which the U-Pb ages apply.

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1. INTRODUCTION

As part of on-going research and development activities performed on rock core samples from the Bruce Nuclear Site, which has already been the subject of detailed site investigations, vein-filling calcite in drill core samples from the Devonian Bois Blanc and Silurian Bass Islands Formations have been dated by the U-Pb LA-ICPMS and ID-TIMS methods (Davis 2016). From five of these dated samples, separate undated pieces were later sent to the University of Bern for fluid inclusion analysis.

The aims of the fluid inclusion study were to (1) place constraints on the temperature of formation of the calcites and (2) estimate the salinity of the parent fluids from which the calcite precipitated. These constraints should aid in enhancing existing understanding about the geological events to which the U-Pb ages apply.

2. SAMPLES AND METHODS

Table 1 shows the samples analysed and the analytical methods employed in this study. Petrographic sections (~100 µm thick) were prepared from all samples. Details of the analytical methods are given in a previous fluid inclusion report (Diamond et al. 2015).

Table 1: Rock Samples and Methods Used to Analyse Fluid Inclusions

Sample	Depth (m)	Formation	Vein minerals	VisTr	UV	µTherm	Raman	Crushing
DGR-1-113.55	113.55	Devonian Bois Blanc	Calcite	X	X	X	X	–
DGR-3-113.26	113.26	Devonian Bois Blanc	Calcite	X	X	X	–	–
DGR-3-133.17	133.17	Devonian Bois Blanc	Calcite	X	X	–	–	–
DGR-3-180.06	180.06	Silurian Bass Islands	Calcite + late celestine	X	X	X	X	X
DGR-3-186.43	186.43	Silurian Bass Islands	Calcite	X	X	–	–	–

VisTr: Transmitted, visible-light microscopy
UV: Reflected, ultraviolet-light microscopy
µTherm: Microthermometry
Raman: Laser Raman microspectroscopy
Crushing: Crushing-stage analyses to detect presence of CO_2 and CH_4

3. RESULTS

Calcite is present in all the samples and, in sample DRG-3-180.06, celestine is observed overgrowing calcite. The results for fluid inclusions in calcite and in celestine are summarized in Figure 1 and are described in order below. Sample photographs and a summary of observations and measurements are given in the Appendix.

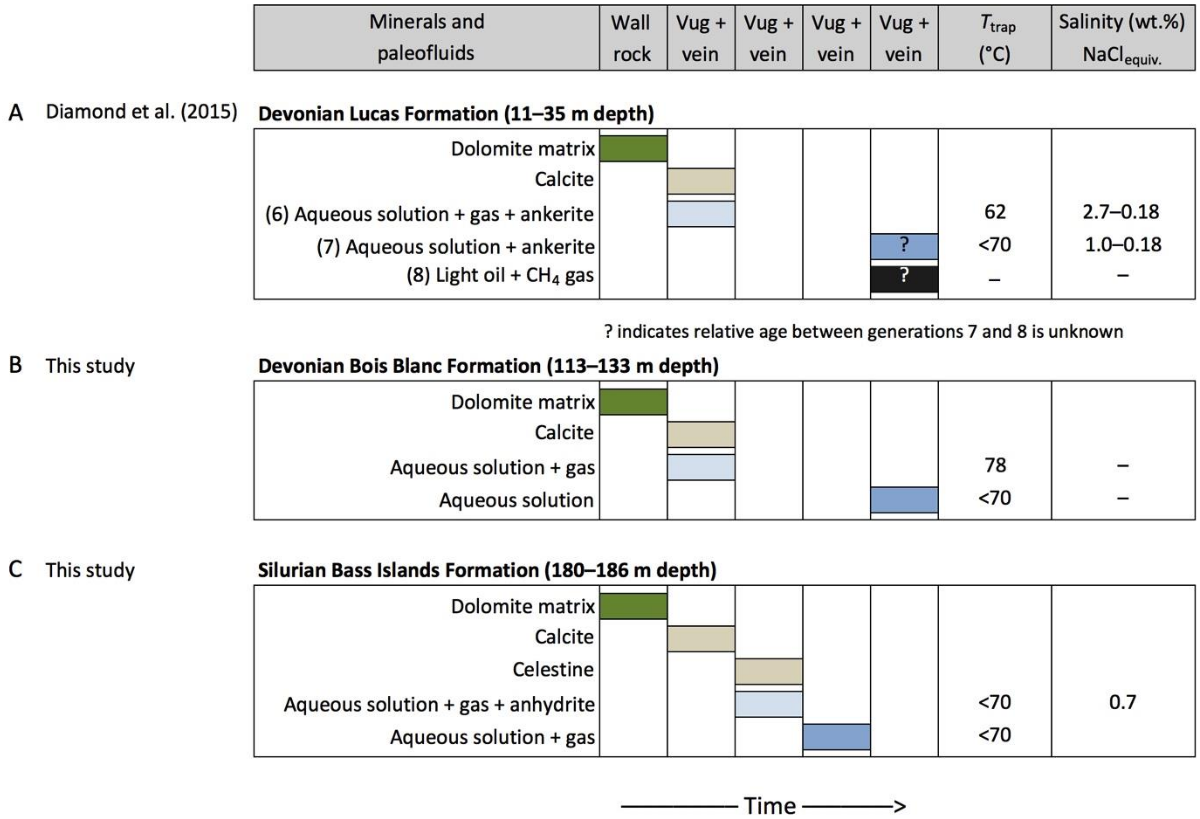

Figure 1: Summary Paragenetic Diagrams of the Petrographic and Microthermometric Results. Time Increases from Left to Right. Primary Fluid Inclusions are Assigned to the Same Time Intervals as the Host Mineral. Secondary Fluid Inclusions are Assigned to Later Events. (A) Results for the Devonian Lucas Formation from Diamond et al. (2015). (B) Results from This Study for the Devonian Bois Blanc Formation. (C) Results from This Study for the Silurian Bass Islands Formation

3.1 Calcite

The vein calcite in all the samples is coarsely crystalline and mostly limpid (e.g., Figs. A2 and A5 in Appendix). Some crystals contain tiny solid inclusions of iron oxide along growth zones (e.g., Fig. 5 in Appendix). Systematic petrographic examination of the samples revealed few fluid inclusions, and all were very small in size. Unfortunately, only sample DGR-3-113.26 contains inclusions large enough to be analysed by microthermometry. None of the inclusions are large enough to yield Raman spectra and none of the inclusions revealed hydrocarbons under UV microscopy.

Sample DGR-3-113.26 (Devonian Bois Blanc Formation) contains liquid+vapour inclusions in 3D clusters within the core of a calcite crystal (Fig. A13). This petrographic texture shows that the inclusions are primary, i.e., they were trapped during calcite growth and hence they represent the parent fluid of the calcite. The liquid:vapour volumetric ratios vary strongly among the inclusions. The textures of the inclusions indicate that this variation is not due to post-entrapment artifacts (so-called "necking down"), therefore the variable liquid:vapour ratios indicate that entrapment was heterogeneous, i.e., from a vein fluid that consisted of an aqueous solution and coexisting bubbles of immiscible gas. No Raman signal could be acquired to identify the gas. The minimum homogenization temperature of the liquid-rich endmember inclusions is 78 °C, which represents the precipitation temperature of the calcite. The inclusions are too small to observe melting phenomena directly, and so their salinity remains unknown.

Calcite in all the samples also contains liquid inclusions arrayed along healed fractures that crosscut the calcite crystal boundaries, i.e. the inclusions are of "secondary" origin and thus they post-date the crystallization of the calcite (e.g., Figs. A3 and A6). The inclusions contain no vapour bubbles (shrinkage bubbles) even though they formed at temperatures high enough for the host fractures to seal by local dissolution-reprecipitation of the calcite walls. Such absence of shrinkage bubbles is very common in fluid inclusions trapped at $T < \sim 70$ °C, and it represents a metastable state due to high surface tension in the liquid phase (see discussion in Diamond et al., 2015, section 3.1.2). Attempts to nucleate bubbles by cooling and heating the inclusions were unsuccessful. Similarly, we were unable to observe any melting phenomena below room temperature and, so, the salinity of the fluid remains unknown.

3.2 Celestine

Sample DGR-3-180.06 (Silurian Bass Islands Formation) contains coarse crystals of celestine (orthorhombic $SrSO_4$) that overgrow (i.e. post-date) vein calcite (Fig. A8). Two generations of fluid inclusions were found. The first contains aqueous liquid and liquid+vapour inclusions that display wide variations in their volume fractions of liquid:vapour (Fig. A10). The 3D distribution of these inclusions within the growth zones of the celestine crystals (Fig. A9) indicates that they are of "primary" origin, i.e. they are of the same age as the celestine and therefore they are trapped samples of the fluid that precipitated the Celestine. A later generation of fracture-hosted secondary inclusions is also present, similarly displaying wide variations in volume fractions of liquid:vapour (Fig. A11).

No gases could be determined by Raman analysis, or by crushing the samples under glycerine, and no hydrocarbons were revealed by UV microscopy. The wide variation in liquid:vapour ratios within coeval inclusions shows that they were trapped heterogeneously, i.e. from a mixture of coexisting gas bubbles and weakly saline water. Since many of the inclusions consist only of metastable liquid at room temperature, it is concluded that all the inclusions were trapped at a temperature below 70 °C.

Microthermometric measurements of the temperature at which ice melts in the primary liquid-rich inclusions (T_m(ice) = –0.4 °C) show that the salinity of the fluid that precipitated celestine was ~0.7 wt.% $NaCl_{equiv}$.

4. CONCLUSIONS

Devonian Bois Blanc Formation:

Vein calcite precipitated in fractures at 78 °C from an aqueous solution that contained bubbles of immiscible gas, presumably a CH_4–CO_2 mixture. The salinity of the solution is unknown. Following growth of calcite the veins were infiltrated by a second aqueous solution that was undersaturated with respect to gas (i.e. without immiscible gas bubbles). The salinity of the solution is unknown. The infiltration occurred at a temperature below ~70 °C.

Silurian Bass Islands Formation:

Vein calcite in this Formation looks very similar to that in the Bois Blanc, but no primary fluid inclusions were found to constrain its formation conditions. Celestine, and tiny amounts of anhydrite, precipitated after calcite from an aqueous solution that contained bubbles of immiscible gas, presumably CH_4 or a CH_4–CO_2 mixture. The salinity of this solution was very weak at 0.7 wt.% $NaCl_{equiv}$. The celestine precipitated at a temperature below 70 °C.

As in the Bois Blanc Formation, a later aqueous solution (undersaturated with respect to gas) infiltrated the veins after the growth of calcite and celestine, also at a temperature below 70 °C.

Comparison with a previous study

Figure 1 allows a comparison of the results of this study with those obtained by Diamond et al. (2015) for the overlying Devonian Lucas Formation. The veins in the three studied Formations appear to have had very similar histories. Celestine precipitated only in the Bass Islands samples, and a late generation of light oil + methane infiltrated only the Lucas Formation. Otherwise, the correlations evident in Fig. 1 suggest that, in all three Formations, vein calcite precipitated from a very low-salinity water (0.2–2.7 wt.% $NaCl_{equiv.}$) that was saturated in gas (presumably a CH_4–CO_2 mixture). Whereas calcite precipitated at 60 °C in the Lucas Formation, it precipitated at 78 °C in the ~100 m deeper Bois Blanc Formation.

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Davis, D.W. 2016. Continued Application of U-Pb Geochronology Methods to the Absolute Age Determination of Secondary Calcite: 2014-2015. Report NWMO-TR-2016-07. Nuclear Waste Management Organization (NWMO). Toronto, Canada. 62 pp.

Diamond, L.W., L. Aschwanden and R. Caldas. 2015. Fluid inclusion study of core and outcrop samples from the Bruce Nuclear Site, Southern Ontario, Canada. Report NWMO-TR-2015-24. Nuclear Waste Management Organisation (NWMO). Toronto, Canada. 138 pp.

APPENDIX A: SAMPLE PHOTOGRAPHS AND PETROGRAPHY

SAMPLE DGR-1-113.55 (Devonian Bois Blanc Formation)

Sample DGR-1-113.55 shows euhedral calcite growing into open space in fractures within a cherty carbonate host rock.

Figure A1: Thick-section of Sample DGR-1-113.55 Showing Calcite Veins Cutting the Cherty Carbonate Host Rock

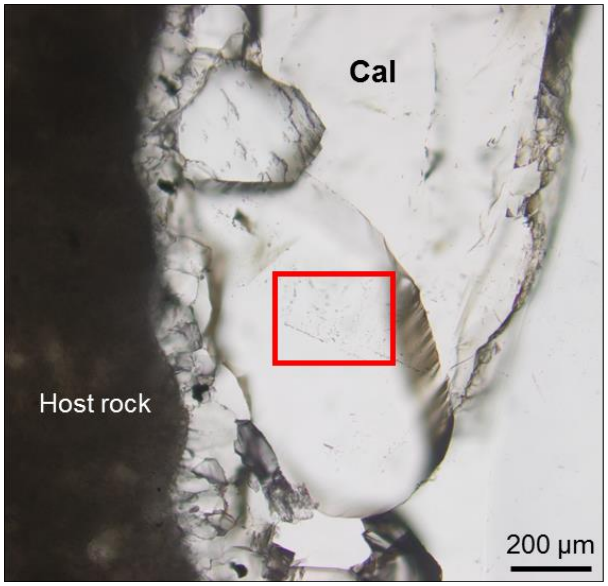

Figure A2: Close-up of Fig. A1. Thick-section Micro-photograph Showing Euhedral Calcite with Healed Fractures Containing Secondary Fluid Inclusions

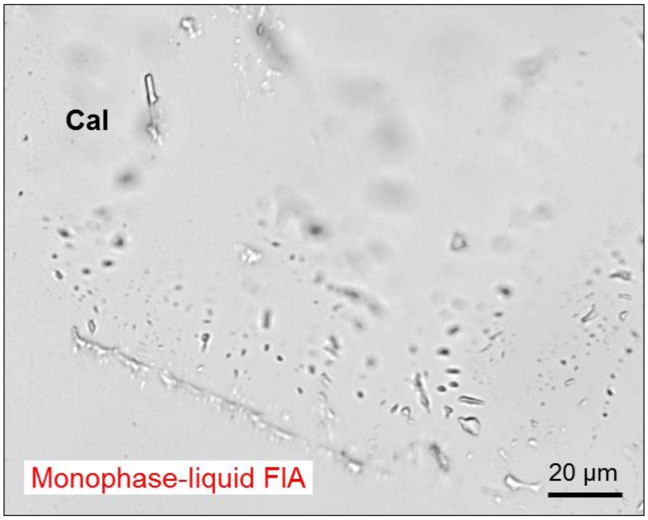

Figure A3: Close-up of Fig. A2. Secondary Fluid Inclusion Assemblage (FIA) Consisting of Homogeneously Trapped Monophase Liquid Inclusions, Demonstrating Trapping Below ~70 °C. No Microthermometric Measurements Could be Conducted on this Sample, Even After Attempting to Nucleate a Vapour Phase Upon Heating and Freezing

SAMPLE DGR-3-186.43 (Silurian Bass Islands Formation)

Sample DGR-3-186.43 showing calcite veins, consisting of euhedral clear crystals, cutting a cherty carbonate host rock.

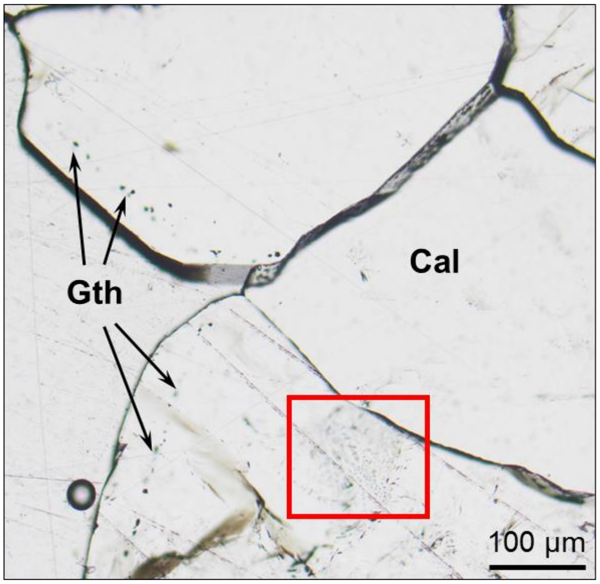

Figure A4: Thick-section of Sample DGR-3-186.46 Showing Calcite Veins Cutting the Cherty Carbonate Host Rock

Figure A5: Close-up of Fig. A4. Thick-section Micro-photograph of Euhedral Calcite with Hematite or Goethite Crystallites Decorating Outer Growth Zones

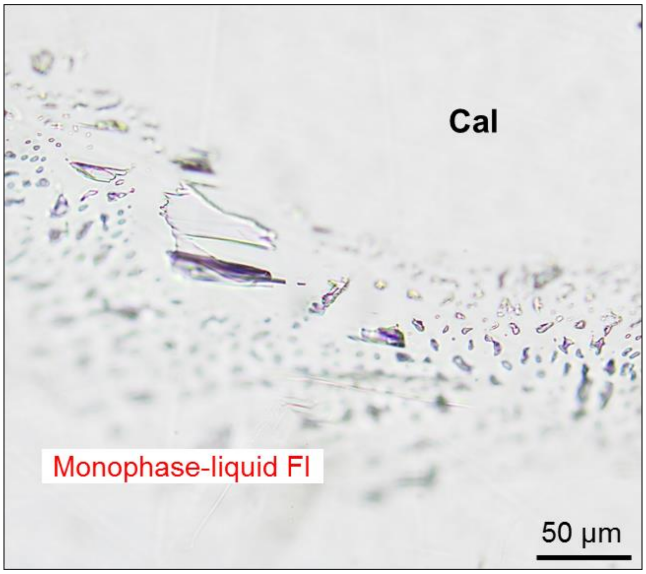

Figure A6: Close-up of Fig. A5. Assemblage of Secondary Fluid Inclusions (FI) Consisting of Homogeneously Trapped Monophase-liquid Inclusions, Demonstrating Trapping Below ~70 °C

SAMPLE DGR-3-180.06 (Devonian Bois Blanc Formation)

Sample DGR-3-180.06 consists of a layered shaly dolostone cut by a vein of euhedral calcite and celestine. Figure A2 shows the temporal relationships between the two minerals, whereby early calcite grows directly from the walls of the vein, overgrown by later celestine.

Figure A7: Thin-section Block of Sample DGR-3-180.06 Showing a Celestine–calcite Vein Cutting the Layered Carbonate Host Rock

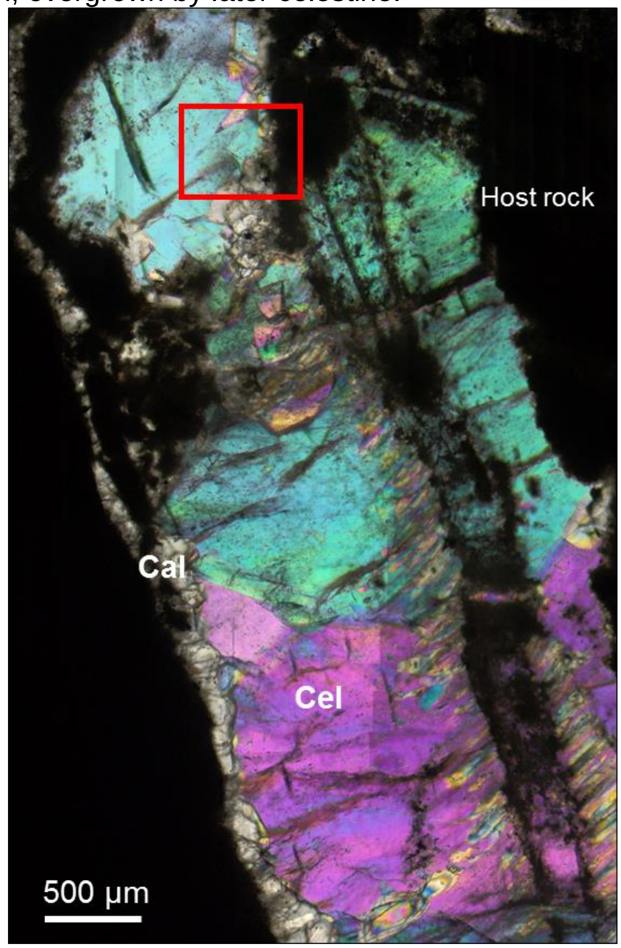

Figure A8: Close-up of Fig. A7. Micrograph of a 100 µm-thick Petrographic Section Under Crossed-polarized Light Showing Early Calcite Along the Edges of the Vein, Overgrown by Later Celestine

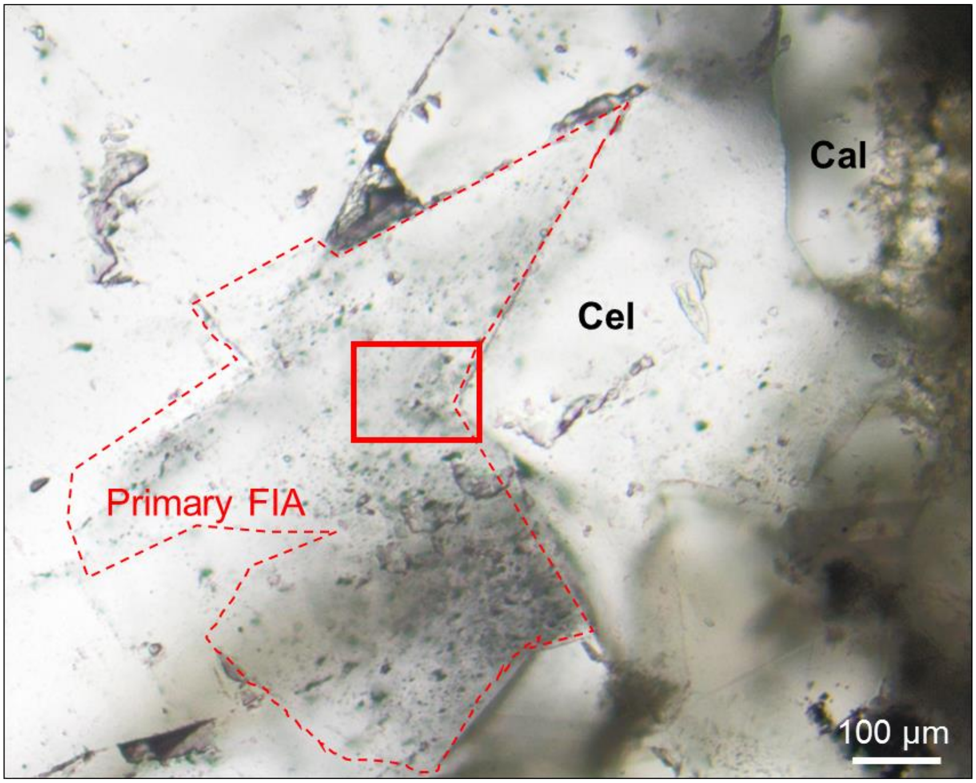

Figure A9: Close-up of Fig. A8. Primary Fluid Inclusion Assemblage (FIA, within red dashed area) in Celestine

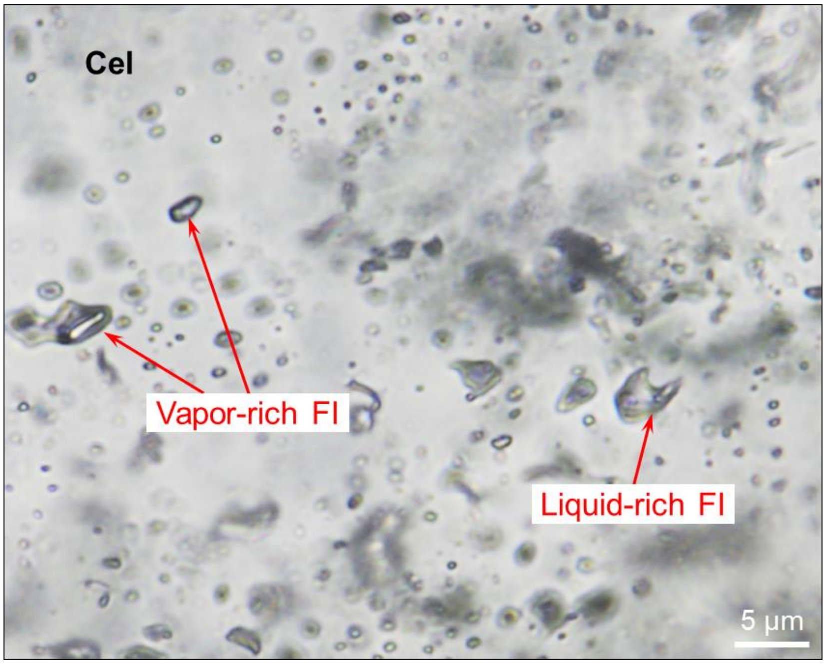

Figure A10: Close-up of Fig. A9. Primary, Heterogeneously-trapped Fluid Inclusion (FI) Assemblage, Consisting of Co-existing Liquid-rich and Vapour-rich Fluid Inclusions in Celestine

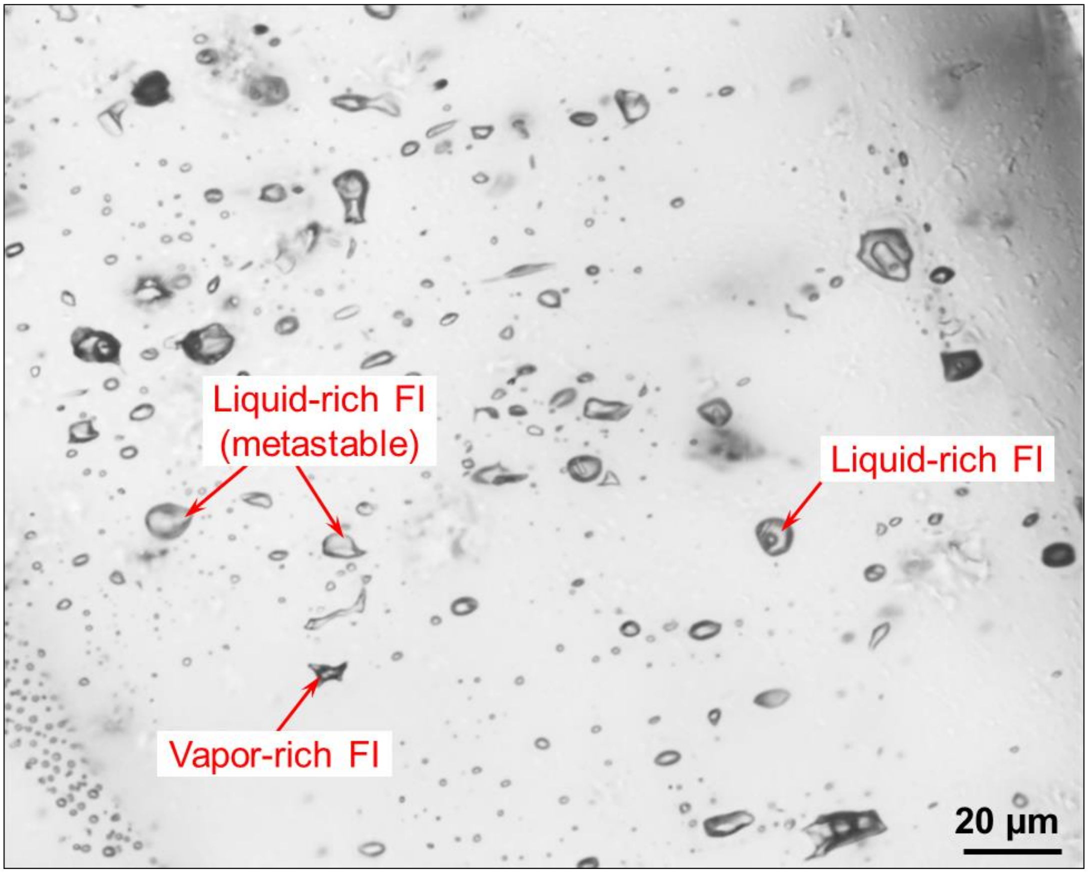

Figure A11: Secondary, Heterogeneously-trapped Fluid Inclusion (FI) Assemblage in Celestine, Consisting of Co-existing Liquid-rich and Vapour-rich Fluid Inclusions. Some of the Liquid-rich Inclusions Contain No Vapour Bubble, Which is a Common Metastable State for Small Fluid Inclusions Trapped at Temperatures Below 70 °C. The Liquid-rich Inclusions Show Ice-melting Temperatures, T_m(Ice), at –0.4 °C, Indicating Entrapment of a Low-salinity Aqueous Solution (0.7 wt.% $NaCl_{equiv.}$).

SAMPLE DGR-3-113.26 (Devonian Bois Blanc Formation)

Sample DGR-3-113.26 shows calcite veins, consisting of euhedral clear crystals, cutting the host rock.

Figure A12: Thick-section of Sample DGR-3-113.26 Showing Calcite Veins with Euhedral Crystals

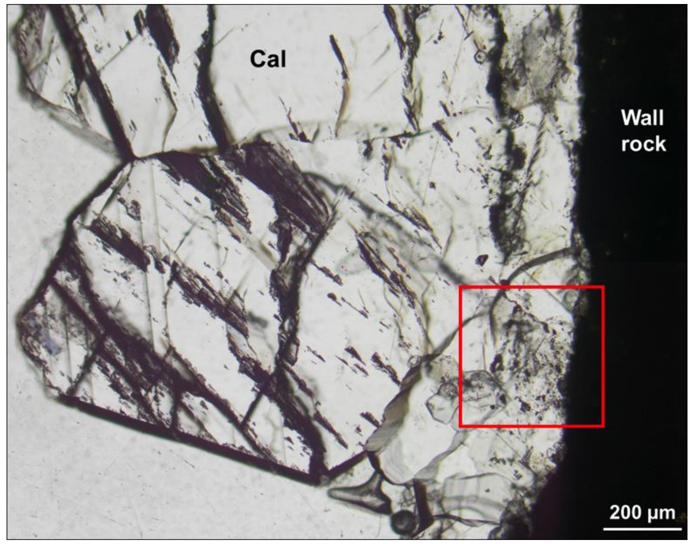

Figure A13: Close-up of Fig. A12. Microphotograph of Euhedral Calcite and the Location of Primary Fluid Inclusions (red box).

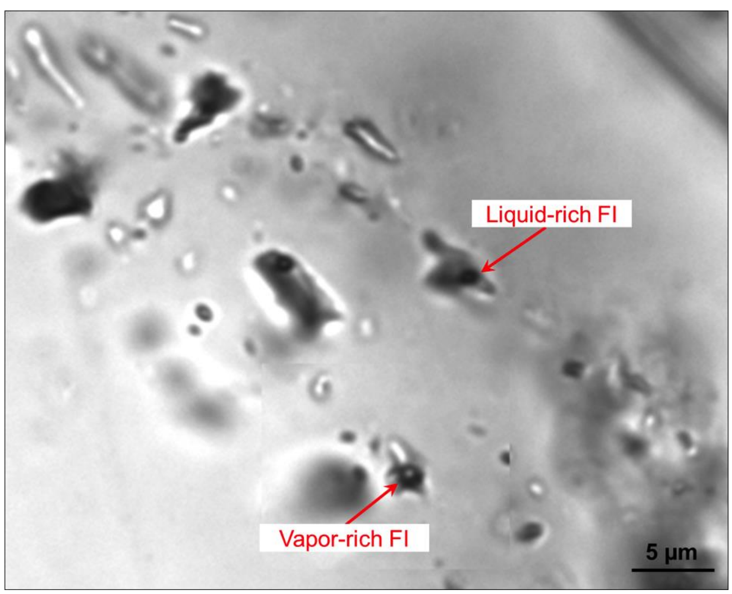

Figure A14: Close-up of Fig. A13. Primary, Heterogeneously-trapped Liquid-rich and Vapour-rich Fluid Inclusions in Calcite. The Liquid-rich Inclusions Homogenize to the Liquid Phase (LV→L) at 78 °C, Which Represents Their Trapping Temperature.