A study of accidental daughter crystals in fluid inclusions in bedded halite from the Permian Opeche Shale and Cedar Hills Sandstone of the midcontinental United States

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A study of accidental daughter crystals in fluid inclusions in bedded halite from the Permian Opeche Shale and Cedar Hills Sandstone of the midcontinental United States

Ryan James Prchlik

Thesis submitted to the
Eberly College of Arts and Sciences
at West Virginia University

In partial fulfillment of the requirements for the degree of

Master of Science
in
Geology

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ABSTRACT

A study of accidental daughter crystals in fluid inclusions in bedded halite from the Permian Opeche Shale and Cedar Hills Sandstone of the midcontinental United States

Ryan James Prchlik

Ancient acid-saline lakes of the midcontinental United States deposited bedded halite during Permian time. These deposits are not typically preserved at the surface, but drill cores of the Opeche Shale of North Dakota and Cedar Hills Sandstone of Kansas contain preserved beds of halite. Halite from these ancient lakes have primary fluid inclusions that contain Permian lake water. Also included are accidental daughter crystals that were trapped inside the fluid inclusions at time of halite precipitation. Both the fluid and daughter crystals inside bedded halite can tell us about the geochemistry of original lake waters of Pangea.

Petrography and laser Raman spectroscopy were used to investigate the fluids and solids in chevron halite crystals. Petrography was used to find and characterize fluid inclusion and daughter crystal targets. Transmitted, polarized, and UV-vis light sources were used at magnifications ranging from 10x to 2000x. Laser Raman spectroscopy was then used to identify chemistry and daughter crystal mineralogy of fluid-phase and accidental daughter crystals. Bisulfate ($\text{HSO}_4^-$) and sulfate ($\text{SO}_4^{2-}$) compounds were detected in fluid-phase; bisulfate that was found in 64% of Opeche Shale fluid inclusions indicate low (<1) pH of lake waters. Anhydrite ($\text{CaSO}_4$), gorgeyite ($\text{K}_2\text{Ca}_5(\text{SO}_4)_4\cdot\text{H}_2\text{O}$), glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$), langbeinite ($\text{K}_2\text{Mg}_2(\text{SO}_4)_3$), celestine ($\text{SrSO}_4$), and magnesite ($\text{MgCO}_3$) were identified. These minerals likely represent crystals that precipitated in the parent lake water and crystals that were transported into the lakes. Bedded halite of the Permian Opeche Shale and Permian Cedar Hills Sandstone likely formed in complex sulfate-rich brines.

This thesis has application to similar ancient acid-saline lake systems on both Earth and Mars. Petrography and laser Raman spectroscopy were both in-situ and non-destructive methods that could be used on valuable Mars samples brought to earth as part of the Mars Sample Return mission. This study shows that petrography and laser Raman spectroscopy can characterize ancient depositional waters through the analyses of fluids and accidental daughter crystals within primary fluid inclusions.
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Introduction

Permo-Triassic bedded evaporites and red-beds have been interpreted across much of Pangea. These bedded evaporites and red-beds are thought to have formed from extensive acid-saline lakes and groundwaters (Benison et al., 1998; Benison and Goldstein, 2002). Three deposits during the formation of Pangea that have been shown to have precipitated from acidic waters are the Permian Nippawalla Group of Kansas, the Opeche Shale of North Dakota, and the Triassic Mercia Mudstone of Northern Ireland (Benison, 1998; Benison and Goldstein, 2002; Eichenlaub, 2016; Andeskie et al., 2018).

A range of methods have been used to characterize the chemistry, sedimentology, and paleoclimate of acid-saline lake systems. Microthermometry has been used to determine the temperature at time of halite precipitation (Benison, 1995; Benison and Goldstein, 1999; Zambito and Benison, 2013). Laser Raman spectroscopy of the fluid-phase of fluid inclusions has identified bisulfate (HSO₄⁻) peaks that characterize the ancient lake waters as having a pH less than 1, and some less than 0 (Benison et al., 1998). Petrography has been done to characterize halite growth and depositional characteristics (Benison and Goldstein, 2000; Benison and Goldstein, 2001; Eichenlaub, 2016; Bernau, 2017). Past studies on these acid-saline lakes have also found and identified the mineralogy of several daughter crystals, but daughter crystals have not been the focus of any of the studies until now (Benison and Goldstein, 2002). This research thesis describes and identifies accidental daughter crystals and their mineralogy from the Permian Opeche Shale and Nippawalla Group (Fig. 1).
Accidental daughter crystals are crystals that were trapped in fluid inclusions as the fluid inclusion sealed. This is in contrast to true daughter crystals that precipitated in fluid inclusions after fluid inclusions were sealed from lake water (Roedder, 1984). True daughter crystals generally form due to large changes in fluid inclusion temperatures between time of entrapment and time they are studied in lab. Petrography of the Permian Nippawalla Group has shown that the bedded halite formed at the Earth’s surface, as evidenced by abundant all-liquid inclusions. In addition, microthermometry of primary fluid inclusions of the Nippawalla Group show temperatures close to the modern day (Benison, 1995; Benison and Goldstein, 1999). The Opeche Shale fluid inclusions contain vapor bubbles, but also appear to be slightly stretched, as they have rounded corners. Petrography reveals chevron and cumulate crystals indicating shallow formation waters, and efflorescent crusts and dissolution pipes indicate desiccation and flooding of the lake systems (Casas and Lowenstein, 1989). So, due to small changes in fluid inclusion temperatures from Permian time to today, daughter crystals in these deposits are all likely accidental daughter crystals.

The Gulf-Romanysyn 2-33-4B core from Billings County, North Dakota and the Amoco Rebecca K. Bounds core from Greeley County, Kansas contain bedded halite with unaltered primary fluid inclusions that contain traces of chemically diverse acid-saline lake waters from Permian time. The Gulf-Romanysyn 2-33-4B core contains bedded halite sequences from the Permian Opeche Shale, whereas the Amoco Rebecca K. Bounds core contains bedded halite from the Permian Nippawalla Group. Halite from subsurface core is the only available source of halite from the Permian Opeche Shale and Permian Nippawalla Group, as halite is not very chemically resistant at the surface.
Petrographic and laser Raman spectroscopic study of fluid inclusions and daughter crystals in halite has application to the study of salts on Mars. Salts have been analyzed on Mars, but their interiors cannot be imaged or analyzed in-situ. Samples brought to Earth as part of the Mars Sample Return mission should be examined using petrography and laser Raman spectroscopy. These techniques are non-destructive and in-situ, and could protect valuable small Mars samples. The techniques could also be used in other ancient acid-saline lake systems.

**Figure 1.** Locations of the Permian Opeche Shale and Permian Nippawalla Group during the formation of Pangea. Bedded halite is alternated by layers of red-beds. Paleogeographic map modified from Ron Blakey of Colorado Plateau Geosystems, Inc. Stratigraphic columns courtesy of Kathleen Benison.
Methods

The primary methods for this thesis included petrography and laser Raman spectroscopy of daughter crystals in fluid inclusions in halite. Petrography served as a means to identify primary fluid inclusions abundant in halite and their accidental daughter crystals. Laser Raman spectroscopy was then used to identify daughter crystal mineralogy, along with the composition of fluids that fill the fluid inclusions.

Drill cores with bedded halite were the main focus, but preliminary investigations were also done on modern halite from Western Australia. Bedded halite samples used came from drill cores of the Opeche Shale and the Cedar Hills Sandstone (Nippawalla Group) of the midcontinental United States from Permian time. Halite of the Opeche Shale is from the Gulf-Romanysyn 2-33-4B core from Billings County, North Dakota. The Nippawalla Group samples are from the Amoco Rebecca K. Bounds core that was drilled in Greeley County, Kansas (Fig. 2).

Sample Preparation

Halite chips were first broken from the drill core with a razor blade, into sizes of about 5 to 10 mm. Once broken off, the pieces were sanded with sandpaper ranging from 200 to 2000 grit in order to create flat chip faces. Once sanded, the halite chips were rubbed against a sheet of glass with a water lubricant to polish the chip faces which improved the clarity of the chip once under the microscope. Chips had thicknesses of approximately 0.5 to 1 mm after being sanded and polished.
Petrography

Petrographic observations were made to identify key depths of each formation that had abundant fluid inclusions containing accidental daughter crystals, and to describe the orientations, sizes, shapes, and phases of primary fluid inclusions. The petrography was completed with an Olympus BX53 microscope with magnification ranging from 40x to 2000x, allowing for the ability to analyze fluid inclusions as small as ~10 microns. Images were taken using SPOT 5 imaging software and an attached digital camera.

Figure 2. Images of bedded halite from the Cedar Hills Sandstone. These two core slices are from the Amoco Rebecca K. Bounds core from Greeley County, Kansas. These upward-oriented images are from the depths of 2350'6" (A) and 2347'6" (B). The dark red colors are an abundance of hematite in the bedded halite.
Plane-transmitted, cross-polarized, and UV-vis light were used during petrography, and each helped to identify key features (Fig. 3). The most used light source was plane-transmitted light, and was used to identify fluid inclusion growth bands and liquid, gas, and solid phases within individual inclusions and other characteristics. UV-vis light was used to test for any fluorescent response emitted by H-C and C-C bonds. These H-C and C-C bonds cause organic features to fluoresce under UV-vis light. Cross-polarized light was effective in finding and characterizing daughter crystals and solid inclusions. The host halite is isotropic, so has no birefringence under polarized light. So, anisotropic minerals were easy to detect with crossed-polars. Most importantly, cross-polarized light was key in making sure that large masses of minerals trapped in solid halite, notably anhydrite, did not lie above or below the fluid inclusions during laser Raman spectroscopy.

Sample chips were chosen from various depths in cores for laser Raman spectroscopy based on petrographic observations and the number and type of fluid inclusions and daughter crystals. Fluid inclusions at least 10 microns in size allowed for successful laser Raman scans. Daughter crystals had to be 3 microns or larger in order to be targeted effectively. Halite chips with large enough inclusions filled with daughter crystals were mapped with a sketch. This study focused on primary fluid inclusions that are representative of parent water from which the halite precipitated. Primary fluid inclusions were determined by identification of growth bands characterized by planes of cubic inclusions. Secondary fluid inclusions were identified by non-cubic inclusions that were along curved planes of inclusions, and that often cut across growth bands and other secondary inclusions. These secondary inclusions formed after halite
precipitation were commonly present, and were noted. However, in this thesis, secondary fluid inclusions are not the focus.

Once key depths and sample chips were identified, the chips were mapped with simple sketches. Sketches detailed the sample chips shape, faces, chevron crystals, cumulate crystals, key fluid inclusions, and the type of daughter crystal inside. The sketches were used to find the fluid inclusions and daughter crystals through the microscope of the laser Raman spectrometer, which has lower magnification and optical clarity than the petrographic microscope.

![Figure 3](image.png)

**Figure 3.** An example of growth bands of primary fluid inclusions shown under transmitted, cross-polarized, and UV-vis light. (A) Transmitted light was the most commonly used light source at the microscope, and was helpful with general halite navigation and documentation of features. (B) Cross-polarized light highlights minerals with birefringence, such as the daughter crystals seen in fluid inclusions in this image. (C) Combined UV-vis and transmitted light highlights many types of organic matter in halite, including fluid inclusions filled with interpreted organic acids seen here.

**Laser Raman Spectroscopy**

Once I had identified key targets with petrography, a laser Raman spectrometer was used to identify daughter crystal mineralogy. The liquid phase of the fluid inclusions were also analyzed. Laser Raman spectroscopy measures the vibrational frequencies of covalent bonds.
Covalent bonds detected appear as peaks in the Raman spectra for each phase analyzed. The Raman shift of a peak corresponds to a specific compound. Halite is ionically bonded, so it gives only a weak background signal in the Raman spectra. Due to the lack of a strong background signal, we are able to use the laser Raman spectrometer on targets inside the halite without any signal from the host halite. For each fluid inclusion analyzed with laser Raman spectroscopy, a measurement was taken for each of the daughter crystals, as well as for the liquid and the surrounding solid halite.

A Renishaw InVia Raman spectrometer was used in this study. The instrument is located in a shared-research facility on the West Virginia University downtown campus in the Chemistry Research Lab building. The spectrometer uses a 532 nm green laser. When focused through a 40x long working distance objective on the attached microscope, the laser beam diameter is ~1 micron. This allows for analyses of phases within fluid inclusions at the micron scale. The microscope attached to the spectrometer has 10x, 20x, 40x, 50x and 100x objectives. Most Raman runs were done with the use of the 40x long working distance objective and a condenser using transmitted light. Each Raman session began with system calibration using a silicon wafer. Calibration consisted of focusing on a silicon wafer with a 50x magnifier, performing a quick calibration, and then running the instrument to ensure it detected a Raman peak for silica at 521 cm\(^{-1}\). The halite chips rested on a glass slide when using the laser Raman spectrometer, but this gave little interference to the Raman spectra. Interference from the halite consisted of a wide hump-like peak around 220 cm\(^{-1}\), near the end of the spectral range. Interference in this range did not present any difficulties in identifying daughter crystals.
The measured wavelength range of Raman spectral detection for each sample was from 200 to 3202 cm\(^{-1}\). Raman spectra were saved as text files and then loaded into CrystalSleuth software. CrystalSleuth is free software developed by the RRUFF database project (Laetsch and Downs, 2006; Lafuente et al., 2006). Spectra were first compared to the RRUFF database of over 4133 spectra samples, and then peaks without a match were searched for in the scientific literature. If features overlapped, such as two daughter crystals, then peaks would be removed so spectra from only one daughter crystal could be compared to the database.

**Results**

Halite chips from three 1 cm sections of bedded halite core were chosen for analysis via laser Raman spectrometer. Two of these three sections came from the Cedar Hills Sandstone from the Nippawalla Group of Kansas at core depths of 2347’6” and 2350’6”. A single section from the Opeche Shale of North Dakota was chosen at a depth of 7411’6”. All three of these sections were chosen due to abundant daughter crystals inside fluid inclusions.

**Petrography of Opeche Shale 7411’6”**

**Primary Fluid Inclusions:** This section of the Opeche Shale had abundant amounts of chevron crystals with primary fluid inclusions. Over 90% of the primary fluid inclusions had a vapor bubble inside, with the air bubble taking up approximately 7% of fluid inclusions volume. Fluid inclusions at this depth varied greatly in size. Most fluid inclusions targeted with laser Raman spectroscopy were between 30 to 40 microns in length. Of the fluid inclusions large enough for laser Raman spectroscopy, approximately 15% had daughter crystals. Daughter crystals that were targeted ranged in size from 3 to 40 microns at their maximum length,
although most fell within ranges of 5 to 10 microns, or 20 to 25 microns. Daughter crystal shape varied from bladed, cubic, needle-like, and spherical crystals (Fig. 4). Thin, needle-like crystals were the most common, but most needle crystals were too thin to accurately target with the laser Raman spectrometer. These needle-like crystals typically had a faint blue birefringence. Cubic and bladed crystals were commonly a neon pink, orange, purple, or blue under polarized light. These cubic and bladed crystals had varying levels of rounded corners. Spherical daughter crystals had a very weak blue birefringence, and were typically subrounded.

![Images of primary fluid inclusions with vapor bubbles and daughter crystals. The most common daughter crystals in the Opeche Shale at 7411’6” were bladed (A), thick needle-like (B), spherical (C), or cubic crystals (C).](image)

**Secondary Fluid Inclusions:** Among the three sections in this study, the Opeche Shale section had the most secondary fluid inclusions. Approximately 10% of fluid inclusions were secondary fluid inclusions. Secondary fluid inclusions were identified by curved planes of fluid inclusions along with the presence of gas bubbles inside, only approximately 5% of secondary fluid inclusions did not have a gas bubble. Gas bubbles in secondary fluid inclusions fluoresced under UV-vis light. No secondary fluid inclusions had any objects that were identified as daughter crystals; they only contained gas bubbles. These secondary fluid inclusions with gas
bubbles most commonly only contained a single gas bubble, but one chip had secondary fluid inclusions with 1 to 7 gas bubbles (Fig. 5).

![Image of fluid inclusions](image)

**Figure 5.** Primary (A, B, and C) and secondary (C and D) fluid inclusions of the Opeche Shale at 7411’6”. The secondary fluid inclusions (C and D) are identified by curved planes of inclusions that cross-cut primary fluid inclusions, and are filled with petroleum.

**Laser Raman Spectroscopy of Opeche Shale 7411’6”**

**Inclusion Liquids:** Raman analysis of liquids was conducted for some inclusions that were studied for daughter crystals. A total of 79 Raman spectra were collected from liquids
within primary fluid inclusions from the Opeche Shale at 7411’6”. In 18% of 79 spectra of inclusion liquids, a sulfate peak at ~983 cm\(^{-1}\) was present (Fig. 15). A bisulfate peak at ~1052 cm\(^{-1}\) was present in a separate 18% of the 79 fluid inclusions. In a separate 46% of the 79 inclusions, sulfate and bisulfate peaks were present together. In 18% of the 79 inclusions, there were neither sulfate or bisulfate peaks in Raman spectra of liquid.

**Daughter Crystal Analyses**

**Anhydrite (CaSO\(_4\))**: A mineral with Raman peaks at ~1018, ~1130, ~1160, ~1112, ~418, ~500, ~628, and ~676 cm\(^{-1}\) was the most common daughter crystal in this section of the Opeche Shale. Anhydrite (CaSO\(_4\)) was matched to these peaks by comparison to several spectra that are part of the RRUFF database. These anhydrite daughter crystals were found 19 times and were typically cubic, bladed, or needle-like crystals. Under cross-polarized light, these anhydrite crystals always had birefringence and were typically a bright shade of blue, purple, or pink.

**Langbeinite (K\(_2\)Mg\(_2\)(SO\(_4\))\(_3\))**: Prominent peaks at ~1001, ~1051, ~457, and ~628 cm\(^{-1}\) were found two times and identified as Langbeinite (K\(_2\)Mg\(_2\)(SO\(_4\))\(_3\)) (Fig. 6). One of these crystals found had a cubic shape, but with the edges rounded a small amount. The other langbeinite found was a subrounded spherical crystal.

**Celestine (SrSO\(_4\))**: An elongated prism with slightly rounded edges had prominent peaks of ~998, ~1092, ~1108, ~1155, ~1188, ~1185, ~451, ~458, ~621, and ~654 cm\(^{-1}\) (Fig. 7). These peaks matched the crystal to the mineral celestine (SrSO\(_4\)).
Glauberite \( \text{Na}_2\text{Ca(SO}_4\text{)}_2 \): A single crystal with peaks at \(~1002, ~1156, ~1140, ~650, \) and \(~619 \text{ cm}^{-1} \) was identified as glauberite \( \text{Na}_2\text{Ca(SO}_4\text{)}_2 \). The crystal was a slightly elongated cube with moderately rounded corners.

![Typical Raman spectra of langbeinite that is found in the Opeche Shale at 7411’6”](image)

**Figure 6. Typical Raman spectra of langbeinite that is found in the Opeche Shale at 7411’6”.** Langbeinite has identifying Raman peaks at \(~1055, ~1001, ~456, ~621, \) and \(~1163 \text{ cm}^{-1} \).

Magnesite \( \text{MgCO}_3 \): Peaks at \(~1095, ~331, ~419, \) and \(~737 \text{ cm}^{-1} \) identified crystals as magnesite \( \text{MgCO}_3 \) (Fig. 8). Four magnesite daughter crystals were found in this section, and were all subrounded spherical crystals with moderate-to-high sphericity.
Figure 7. Raman spectra of the celestine daughter crystal found within an Opeche Shale fluid inclusion at 7411’6”. Identifying spectra are at ~1010, ~991, ~449, ~662, and ~1137 cm$^{-1}$. Also included in the Raman spectra is a bisulfate peak at 1051 cm$^{-1}$.

Figure 8. The Opeche Shale at 7411’6” had some magnesite crystals in fluid inclusions. Prominent peaks that identified magnesite were ~331 and ~1096 cm$^{-1}$. Also included in this Raman spectra is a 1051 cm$^{-1}$ bisulfate peak.
Petrography of Cedar Hills Sandstone 2347’6”

**Primary Fluid Inclusions:** Nearly all inclusions observed at this depth were primary fluid inclusions from chevron crystals. Fluid inclusions in this section rarely had vapor bubbles; whenever vapor bubbles were present, they were small compared to the overall size of the fluid inclusion. Halite from this section had the highest number of daughter crystals per primary fluid inclusion. In several growth bands of this section, nearly all fluid inclusions had daughter crystals. Despite the high number of daughter crystals in this section, many of the fluid inclusions and their daughter crystals were not able to be targeted as they were too small. The primary fluid inclusions that were large enough to be targeted were normally around 30 microns, but ranged in size from 10 to 150 microns. Daughter crystals that were targeted ranged in size from 2 to 30 microns. Most targeted daughter crystals were either bladed, cubic, or rounded spherical crystals. Many of the bladed and cubic crystals were blue to purple to pink under cross-polarized light (Fig. 9). The rounded spherical crystals were often white under cross polars. Many bladed and cubic crystals also had varying degrees of rounded edges.

**Secondary Fluid Inclusions:** This section had the least amount of secondary fluid inclusions, with only approximately 3% secondary fluid inclusions. These secondary fluid inclusions were all-liquid. These inclusions were identified by their orientation along curved planes that cross-cut the primary fluid inclusions.

**Laser Raman Spectroscopy of Cedar Hills Sandstone 2347’6”**

**Inclusion Liquids:** Raman spectra of the primary fluid inclusion liquid from this section included some inclusions with sulfate peaks and then some with neither sulfate nor bisulfate
peaks. Inclusion liquid with sulfate peaks made up 42% of the 70 acquired liquid spectra, whereas fluid with neither sulfate or bisulfate peaks made up the other 58%.

**Daughter Crystal Analyses**

**Anhydrite (CaSO$_4$):** The most common daughter crystal spectra in this section had the most intense peaks centered at 1018 cm$^{-1}$, but additional prominent peaks at ~1130, ~1160, ~1112, ~418, ~500, ~628, and ~676 cm$^{-1}$. These peaks were matched to anhydrite with the formula (CaSO$_4$). Daughter Crystals with these spectra had a varying range of crystal morphology, but were most commonly bladed crystals (Fig. 12). These anhydrite crystals always exhibited birefringence, but varied in color between shades of bright blue, pink, purple, or orange. A total of 22 daughter crystals had spectra that matched strongly with anhydrite.

![Image of anhydrite crystals](image)

**Figure 9.** Transmitted (A) and polarized (B) light images of a section of the Cedar Hills Sandstone at 2347°6” showing plentiful daughter crystals. Included are anhydrite (An), glauberite (Gb), and gorgeyite (Gg).
Glauberite ($\text{Na}_2\text{Ca(}\text{SO}_4\text{)}_2$): Five daughter crystals had matching peaks at ~1002, ~1156, ~1140, ~650, and ~619 cm$^{-1}$ (Fig. 10). This mineral was identified as glauberite ($\text{Na}_2\text{Ca(}\text{SO}_4\text{)}_2$). This mineral normally appeared as a well-rounded crystal, but also appeared as a cubic crystal in one inclusion. These daughter crystals had no observable birefringence.

![Raman spectra of glauberite](image)

**Figure 10.** The Raman spectra of the mineral glauberite has a tall peak at ~1003 cm$^{-1}$, and sets of peaks at ~1139, ~1155, ~651, ~636, ~472, and ~454 cm$^{-1}$.

Gorgeyite ($\text{K}_2\text{Ca}_5(\text{SO}_4)\cdot\text{H}_2\text{O}$): The last type of mineral found in this section of the Cedar Hills Sandstone was gorgeyite. Five daughter crystals had peaks at ~1012, ~473, ~636, ~1145, ~1167, and ~665 cm$^{-1}$, confirming a gorgeyite identification (Fig. 11). These crystals were rounded to subrounded ovals with noticeably rough surfaces. Birefringence of these crystals was always a bright white under cross-polars.
Figure 11. Typical laser Raman spectra of the mineral gorgeyite from the Cedar Hills Sandstone depth of 2347'6". Prominent peaks at ~1012, ~1170, ~1149, ~472, ~432, ~634, and ~665 cm\(^{-1}\) identify it as gorgeyite. There is also a 983 cm\(^{-1}\) peak that is a sulfate peak.

Figure 12. Transmitted light images from the Cedar Hills Sandstone at 2347'6". (A) Overlapping daughter crystals in a primary fluid inclusion, the bladed crystal was identified as anhydrite (An) and the small rounded crystal is magnesite (Mg). (B) Small solid grainy crystals filled this fluid inclusion, laser Raman identified these as anhydrite.
**Magnesite (MgCO₃):** A single daughter crystal with prominent peaks at ~1003, ~1155, ~1139, ~651, ~636, ~472, and ~454 cm⁻¹ was found. This single crystal was magnesite (MgCO₃). This crystal was spherical and rounded with a weak blue glow under cross-polarized light.

**Petrography of Cedar Hills Sandstone 2350’6”**

**Primary Fluid Inclusions:** This depth was characterized as mostly consisting of chevron crystals, which grew directly above a mud-draped layer, seen at the top of Figure 2. Targeted primary fluid inclusions in these chevron crystals ranged in size from 10 to 100 microns, but most were approximately 30 microns (Fig. 13). Daughter crystals were common at this depth, but not as abundant as seen at the 2347’6” depth of this formation. Approximately 5% of fluid inclusions greater than 10 microns had daughter crystals. Targeted daughter crystals also varied from 2 to 60 microns long, but clumped around 3, 12, and 30 microns long. Most daughter crystals were either bladed, spherical, or cubic. Many crystals had perfect edges while others had various degrees of rounding. Nearly all of the targeted daughter crystals were a bright shade of blue, purple, or pink under cross polarized light.

**Secondary Fluid Inclusions:** Similar to the other depth of the Cedar Hills Sandstone, secondary fluid inclusions in this section were all-liquid. Approximately 6% of fluid inclusions were identified as secondary fluid inclusions, by curved planes of fluid inclusions.

**Laser Raman Spectroscopy of Cedar Hills Sandstone 2350’6”**

**Inclusion Liquids:** Laser Raman spectra were collected from 47 fluid inclusions liquids in this section. Raman spectra of the fluid in these fluid inclusions had no sulfate or bisulfate peaks present.
Figure 13. A chevron crystal (A) and two primary fluid inclusions that are part of the chevron crystal (B, C, and D). Images C and D are of the same fluid inclusion, but C is under transmitted light while D is under cross polarized light. All of the daughter crystals were determined to be anhydrite through laser Raman spectroscopy.

Daughter Crystal Analyses

Anhydrite (CaSO₄): Only a single type of daughter crystal was identified in this section. Twenty-three crystals of anhydrite (CaSO₄) were identified by peaks at ~1018, ~1130, ~1160, ~1112, ~418, ~500, ~628, and ~676 cm⁻¹ (Fig. 14). Anhydrite in this section of halite was most commonly blocky, but there were also many crystals that were rounded and spherical. All
anhydrite crystals observed under cross-polarized light were birefringent, and were either a bright shade of blue, pink, purple, or orange.

![Raman spectra from an anhydrite daughter crystal from the Cedar Hills Sandstone at 2350’6”](image)

**Figure 14.** Raman spectra from an anhydrite daughter crystal from the Cedar Hills Sandstone at 2350’6”. Anhydrite is identified by Raman peaks at ~1018, ~1113, ~1130, ~418, ~500, ~610, and ~676 cm\(^{-1}\).  

**Unknown Minerals**

Daughter crystals from each of the three sections in this study were not always able to be identified. These unknown minerals often had sulfate peaks near 1002, 612, and 1131 cm\(^{-1}\), similar to some of the known minerals, but other identifying peaks were not able to be matched through the RRUFF database or in literature. Nine daughter crystals with sulfate peaks were not able to be matched to a known mineral, three of these unknown sulfate minerals also had a water peak near 1650 cm\(^{-1}\), suggesting they may be hydrated sulfate minerals.
Interpretations

Petrography

All fluid inclusions are interpreted to be have been part of bottom growth chevron crystals, identified by their upward-growth orientation. Cumulate crystals were rare in the three sections, and none of the fluid inclusions that were analyzed are interpreted as cumulate crystals. The presence of chevron crystals in the three sections suggests that lake waters were less than ~0.5 meters deep (Shearman, 1970; Artherton, 1973; Lowenstein and Hardie, 1985). We can interpret that the fluid in the inclusions are representative of the depositional lake waters.

There was a diversity of daughter crystal shapes with varying degrees of rounding. Daughter crystals with perfect edges likely precipitated close to the time they were trapped within fluid inclusions. Daughter crystals that had rounded edges, or were completely spherical, indicate they may have been abraded during transportation into the lake via wind blown transportation or flooding. Rounded edges and crystals could have also occurred through partial dissolution of the crystal at times of high precipitation that would have diluted the lake water. It is also possible that some tiny crystals just did not form perfect crystals, and that they are subrounded without any abrasion or dissolution.
**Laser Raman Spectroscopy**

This study characterizes waters as acidic with pHs less than 1, based on criteria developed by Benison et al (1998). Diagnostic criteria for acidity due to sulfuric acid is the presence of bisulfate in fluid inclusions. Bisulfate in laser Raman spectra can be detected by peaks at ~1054, and ~892 cm\(^{-1}\). A 1054 cm\(^{-1}\) peak indicate a pH less than 1, and combined bisulfate peaks of ~1054 and ~892 cm\(^{-1}\) indicates a pH less than 0 (Benison et al., 1998). Sulfate peaks suggest a water with at least ~2000 mg/mL SO\(_4^2-\) (Benison et al., 1997). Sulfate peaks at ~983 cm\(^{-1}\) were noted for each inclusion liquid scanned (Fig. 15). Raman peaks characteristic of neutral to alkaline waters, such as carbonate (CO\(_3^{2-}\)) or bicarbonate (HCO\(_3^-\)) peaks, were not present in any of the fluid inclusions in this study.

The Opeche Shale at 7411’6” had the most variation in combination of bisulfate and sulfate peaks. Bisulfate was detected in 64% of fluid inclusions, indicating 64% of the 79 fluid inclusions tested had pH less than 1. The presence and absence of bisulfate in fluid inclusions may show that water acidity fluctuated over the short time (days) it took for the 1 cm of halite to precipitate from lake waters. This can be seen in modern analogues in Western Australia, where acid-saline lakes fluctuate in acidity as lakes undergo periods of rainfall or drought that affect water levels and acidity. Waters with pH over 1 do not have bisulfate peaks when analyzed by Raman, so these waters may still have been acidic. Inclusion liquids of the Opeche Shale had sulfate peaks in 18% of the 79 inclusions tested, showing high sulfate content.
## Figure 15. Table showing the number of primary fluid inclusion liquids in each section that were analyzed with laser Raman spectroscopy, and whether they contain sulfate (SO$_4^{2-}$) and/or bisulfate (HSO$_4^-$) peaks.

<table>
<thead>
<tr>
<th>Number of Inclusion Liquids Analyzed</th>
<th>SO$_4^{2-}$</th>
<th>HSO$_4^-$</th>
<th>SO$_4^{2-}$ and HSO$_4^-$</th>
<th>no SO$_4^{2-}$ or HSO$_4^-$ peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opeche 7411'6''</td>
<td>79</td>
<td>14</td>
<td>14</td>
<td>37</td>
</tr>
<tr>
<td>Cedar Hills 2347'6''</td>
<td>70</td>
<td>29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cedar Hills 2350'6''</td>
<td>47</td>
<td>0</td>
<td>0</td>
<td>47</td>
</tr>
</tbody>
</table>

Neither of the two sections of halite from the Cedar Hills Sandstone contained bisulfate peaks, indicating a pH of greater than 1 in all of the primary fluid inclusions analyzed. Forty-seven inclusions in halite at the depth of 2350'6'' contained no sulfate peaks, whereas at a depth of 2347'6'', 42% of 70 fluid inclusions had a sulfate peak in the liquid phase. The halite at a depth of 2347'6'' likely precipitated in waters that were more enriched in sulfate.

### Sulfate Minerals

Overall, in this study of the Opeche Shale and Cedar Hills Sandstone, five of the six identified daughter crystal minerals were sulfates. Anhydrite (CaSO$_4$) was the most common of these sulfate minerals (Fig. 16). Of all the daughter crystals in the three sections, anhydrite made up 77% of total daughter crystals. Of the 23 daughter crystals analyzed from the 2350'6'' depth of the Cedar Hills Sandstone, anhydrite was the only daughter crystal identified by laser Raman spectroscopy. Aside from being trapped as daughter crystals, anhydrite was also commonly found trapped as solid inclusions in the halite crystals.
Table of daughter crystals found in each of the three sections:

<table>
<thead>
<tr>
<th>Section</th>
<th>Anhydrite CaSO₄</th>
<th>Glauberite Na₂Ca(SO₄)₂</th>
<th>Gorgeyite K₂Ca(SO₄)·H₂O</th>
<th>Celestine SrSO₄</th>
<th>Langbeinite K₂Mg₂(SO₄)₃</th>
<th>Magnesite MgCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opeche 7411’6”</td>
<td>27</td>
<td>19</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Cedar Hills 2347’6”</td>
<td>33</td>
<td>22</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cedar Hills 2350’6”</td>
<td>23</td>
<td>23</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Figure 16. Count of daughter crystals found in each of the three sections. Anhydrite was the most common type of mineral found across all three of the sections. The table does not include nine daughter crystals that were not able to be identified by laser Raman spectroscopy.*

Glauberite (Na₂Ca(SO₄)₂) was common in the Cedar Hills Sandstone at 2347’6” depth and was rare in the Opeche Shale section. Also common in the Cedar Hills Sandstone at 2347’6” was gorgeyite (K₂Ca(SO₄)·H₂O). This was the only hydrated mineral found within any of the three sections. The Opeche Shale section also had rare occurrences of celestine (SrSO₄) and langbeinite (K₂Mg₂(SO₄)₃). Presence of these minerals suggest brines that had high concentrations of K, Mg, Ca, SO₄²⁻, and Sr. Celestine is not found in evaporites from evaporated seawater, suggesting a groundwater source of the strontium needed for mineral precipitation (Rosenberg, et al., 2018).

**Magnesite**

Magnesite (MgCO₃) is found in the Opeche Shale at 7411’6” and the Cedar Hills Sandstone at 2347’6”. It is the most unusual daughter crystal found in these acid-saline lakes, as it is the only carbonate species found in these sulfate and bisulfate rich waters. In addition, carbonate minerals are noticeably absent from these formations. All magnesite daughter crystals found were sub-rounded to well-rounded, high-sphericity crystals. Several magnesite
daughter crystals in the Opeche Shale at 4711’6” are in fluid inclusions that contain a bisulfate peak at ~1054 cm$^{-1}$, indicating magnesite daughter crystals are in fluid inclusions with acidic water with a pH less than 1. At a pH less than 1, magnesite would be expected to disassociate into solution. Magnesite daughter crystals could have been coated in an iron oxide coating that prevented dissolution, but petrographic observations did not show any signs of this. Magnesite daughter crystals are interpreted to have blown or washed into the lake system based on rounding and lack of magnesite crystal habit. Weathering and erosion of carbonates within the underlying Madison Limestone and Minnelusa Formation could have been the source of this magnesite.

**Unknown Minerals**

Some daughter crystals in fluid inclusions were not able to be matched with a specific mineral. Nine of these unknown daughter crystals are likely a type of sulfate, based on similar peaks seen in known sulfate minerals. There are several possible reasons as to why these daughter crystals could not be identified. These reasons include that the RRUFF database may not have this mineral in their mineral spectra database, that the mineral may have different elements substituted into the minerals crystal structure that would produce a different spectra, or that this is an entirely new and undocumented mineral.
Discussion

Previous Work on Daughter Crystals in Halite from the Opeche Shale and Nippawalla Group

Daughter crystals were previously found in halite from the Opeche Shale and Nippawalla Group, but those previous studies had a more limited focus on daughter crystals. Benison (1997) identified primary fluid inclusions from bedded halite of the Nippawalla Group and Opeche Shale that contained anhydrite, polyhalite, glauberite, and rare magnesite and nahcolite daughter crystals. Smith and Benison (2019) looked at the 2347’10” depth of the Cedar Hills Sandstone, where he identified starkeyite, polyhalite, and gypsum daughter crystals. Despite the different specific minerals found across different depths, similar elemental makeup of daughter crystals suggests similar brine chemistry.

Combined with the results of my study, daughter crystals identified by Smith and Benison (2019) and Smith suggest that anhydrite and glauberite are common across much of the Opeche Shale and Nippawalla Group. Different types of daughter crystals at different depths may suggest unique brines at each depth. This previous work on the Opeche Shale and Nippawalla Group also found common anhydrite included as solid inclusions in halite at different depths. Aside from the halite, anhydrite is shown to be the most common mineral found in all of the acid saline lake halite.

Comparison to the Mercia Mudstone Group and Neoproterozoic Browne Formation

Fluid inclusion studies have been done on other sections of halite interpreted as acid-saline lake deposits. Studies on the Triassic Mercia Mudstone Group of Northern Ireland and
the Neoproterozoic Browne Formation of central Australia analyzed both the fluid, organics, and daughter crystals in fluid inclusions and solid halite.

Eichenlaub (2016) studied unaltered primary fluid inclusions in bedded halite of the Triassic Mercia Mudstone Group from Northern Ireland. Twelve halite beds were analyzed via petrography and laser Raman spectroscopy. In nine of these halite beds, Raman spectra had peaks at ~490 cm\(^{-1}\). These peaks were identified as aluminum sulfate compounds (Frost et al., 2006). In ten of the beds, bisulfate peaks were found at ~1054 and/or ~892 cm\(^{-1}\). If one of these two bisulfate peaks were present then the pH was less than 1, and if both bisulfate peaks were present then the pH was less than 0 (Benison et al., 1998). Some fluid inclusions in bedded halite of the Triassic Mercia Mudstone Group contained daughter crystals. These daughter crystals were bladed and needle-like and most were identified by laser Raman spectroscopy as anhydrite. Use of UV-vis light also identified prokaryotes and possible Dunaliella algae, that fluoresced blue to green (Eichenlaub, 2016).

A study by Bernau (2017) focused on fluid inclusions in bedded halite of the lithologically-equivalent Neoproterozoic Browne Formation of central Australia, and used similar methods to both this thesis and the study by Eichenlaub (2016). Within fluid inclusions from the Browne Formation, Bernau identified multiple types of organics and daughter crystals. Organic material included Dunaliella algae, prokaryotes, and opaque suspect organic-sulfate acids. Two types of daughter crystals were interpreted as accidental daughter crystals. Red angular solids were identified as iron oxides based on color, crystal shape, and Raman spectra. Additional red iron oxides were seen trapped in solid halite. Laser Raman spectra also identified
acicular and tabular solids as anhydrite. Fluid inclusions in the Browne Formation did not produce Raman spectra with sulfate or bisulfate peaks, suggesting that pH was above 1.

These three studies all used petrography and laser Raman spectroscopy to characterize beds of halite from interpreted high salinity lakes. All three studies found plentiful anhydrite as accidental daughter crystals that were typically bladed, acicular, or needle-like. Of these three studies, only sections of halite from the Opeche Shale and Mercia Mudstone Group had bisulfate peaks that confirmed a low pH of less than 1. Halite from the Mercia Mudstone Group had the most confirmed markers for fluid inclusion acidity, including sulfate peaks, aluminum sulfate peaks, and, most importantly, dual bisulfate peaks. The Neoproterozoic Browne Formation fluid inclusions did not have any sulfate or bisulfate peaks, but did have other characteristics of acid saline deposits. These included association with abundant iron oxides, paucity of carbonate minerals, and abundance of sulfate minerals (Benison and Goldstein, 2002). This suggests that Browne Formation parent waters were likely moderately acidic with pHs of 1 to 4 (Bernau, 2017). The halite from the Opeche Shale and Cedar Hills Sandstone that were analyzed in this study had the greatest diversity of daughter crystal minerals, but this may be due to only limited focus on daughter crystals in previous studies.

Comparison to Modern Acid and Neutral Lake Waters

Fluid inclusions in halite from modern acid and neutral saline lakes from Western Australia were analyzed by Jagniecki and Benison (2010). Differences in type of daughter crystals between acid and neutral saline lakes was shown. Neutral saline lakes ranging in pH from 6.8 to 7.3 only had rare daughter crystals, and the daughter crystals that were identified
were rounded grains of quartz that likely had blown into the lakes. Lakes that ranged in pH from 1.7 to 4.2 had more daughter crystals, and these daughter crystals were identified as sulfates. The presence of more types of daughter crystals in more acidic Western Australia lake waters suggests that the absence of non-anhydrite daughter crystals in the Cedar Hills Sandstone at 2350’6” is less acidic when compared to the other two sections in my study where more types of sulfate minerals were found. It’s also possible that the chemistry of the Cedar Hills Sandstone At 2350’6” just had less Sr, K, or Mg to form daughter crystals.

**Anhydrite Morphology**

Anhydrite was the most abundant mineral found in all three of the studied sections, but varied in crystal shape among the three sections of halite (Fig. 17). This range of anhydrite crystal shapes may give clues to crystal history. Despite the wide range in morphology of anhydrite daughter crystals, anhydrite always had birefringence under cross-polarized light. Under cross-polarized light, anhydrite was a range of bright shades of blues, yellows, greens, purples, and pinks, likely due to varying crystal thicknesses that affect birefringence.

Needle-like crystals were abundant in all three sections of this study, but most of these were too small for laser Raman spectroscopy. Only 5 needle-like crystals were confirmed to be anhydrite using laser Raman spectroscopy; most, if not all, unverified needle-like daughter
Figure 17. Transmitted light image of fluid inclusions from the Cedar Hills Sandstone depth of 2347’6” showing the different shapes of anhydrite daughter crystals. Different morphologies included cubic crystals (A), rounded oval crystals (B), and small grain-like solids in clumps (C).

crystals are likely anhydrite. This is based on similarities in crystal shape, texture, and birefringence to confirmed anhydrite daughter crystals. Twenty-one bladed daughter crystals with sharp edges were identified. Fifteen blocky, sharp-edged crystals were found in fluid inclusions. These blocky and bladed crystals likely precipitated in the lake water close to the time of halite precipitation from saline surface waters. The other 24 daughter crystals include 3 bladed crystals with moderately-rounded edges, 16 moderately-to-high sphericity crystals that are moderately rounded, and 5 groups of faded grainy-like crystal clumps. Rounding of these grains may suggest that these anhydrite daughter crystals underwent partial dissolution in the lake water during periods of low lake salinity, or that they were abraded by physical transport.
Are all Daughter Crystals Accidental?

All daughter crystals in primary fluid inclusions were initially considered accidental daughter crystals, to have been trapped in the fluid inclusion before the fluid inclusion seals itself. True daughter crystals are those that precipitate by cooling of inclusion liquid after formation of the fluid inclusion. While most of the daughter crystals in this study are still considered accidental daughter crystals, daughter crystals in fluid inclusions from several growth bands of the Opeche Shale at 7411’6” may be true daughter crystals. One chip of halite from the Opeche Shale at 7411’6” had needle-like daughter crystals that were uniform in shape and size across several growth bands, and were present in all of the fluid inclusions of these growth bands. These uniform needle-like daughter crystals in these few growth bands could be true daughter crystals.

Wang and Lowenstein (2017) used several criteria to establish sylvite daughter crystals as real daughter crystals. The first two criteria are that the daughter crystals occur in all fluid inclusions, and that the fluid inclusions all have a similar daughter crystal-to-fluid ratio. Both of these criteria are met by needle-like anhydrite crystals in several growth bands of the Opeche Shale at 7411’6”. Wang and Lowenstein’s third and fourth criteria use micro-thermometry to see if daughter crystals have similar dissolution and re-nucleation temperatures. Despite the common abundance of these needle-like crystals in fluid inclusions and the similar solid-to-fluid ratios, micro-thermometry would need to be done to see if the third and fourth criteria are met. Further work using micro-thermometry could confirm or deny whether these daughter crystals are true or accidental. Freezing and heating runs in the Jagniecki and Benison (2010) study showed daughter crystals from the Opeche Shale and Nippawalla Group that had no
changes under temperature change. Similar results in these specific growth bands with uniform needle-like crystals would show the needle-like daughter crystals as being accidental daughter crystals.

**Limitations**

Limitations of the research methods in this thesis prevented several original research ideas from being completed. The majority of these were due to limitations of the equipment that prevented easy navigation of halite chips when at the microscope attached to the laser Raman spectrometer. Less than optimal optics of the Raman lab microscope made it so fluid inclusions were often very difficult to find, even with detailed sketches of the halite chips. Focusing of the laser on micron-scale daughter crystals proved difficult. Additionally, many fluid inclusions produced “noisy” spectra that made it difficult to identify any prominent Raman peaks.

Before use of the laser Raman spectrometer, a large collection of halite chips was chosen with the goal of using these chips for laser Raman spectroscopy. These chips were all rich in fluid inclusions that contained daughter crystals, and were chosen based on petrographic observations made when using the Olympus BX53 in the Red Earth Observatory lab. However, when learning to use the laser Raman spectrometer and attached microscope, it was apparent that many of the chosen targets would be difficult to find with the Raman lab microscope.

One initial research idea was to do several detailed maps that showed an entire chevron crystal, and highlighted which type of daughter crystal minerals were in separate growth bands of the chevron crystal. Due to the small size of many of the fluid inclusions in these chevron
crystals, and the poorer optics of the Raman lab microscope, it was too difficult to navigate these chevron crystals.

Initially, laser Raman spectroscopy was to be done on some halite from modern acid-saline lake samples from Western Australia. Preliminary petrography of these modern Western Australia halite samples contained fluid inclusions, but daughter crystals were rare and it became evident that it would not be possible to analyze a meaningful number of daughter crystals. Challenges were due to the difficulties in navigating fluid inclusion crystals with the microscope in the laser Raman spectroscopy lab, and also the small size of many of the fluid inclusions that did have daughter crystals.

Another challenge was the presence of Raman spectra that were too noisy to identify any prominent peaks, due to background noise. Fluid inclusions that had noisy Raman spectra were found in all three of the sections analyzed in this thesis. Fluid inclusions with noisy Raman spectra were randomly assorted, and all components of the fluid inclusions from the liquid to daughter crystals had noisy Raman spectra that made it difficult to match Raman peaks to minerals or other substances. These noisy spectra may have appeared because of a type of solute in the fluids, as these noisy spectra did not appear in the surrounding halite. Approximately 10% of fluid inclusions that were analyzed in this study had Raman spectra that were too noisy to identify any prominent peaks.

**Importance of the Method**

A combination of petrography and laser Raman spectroscopy has applicability to valuable samples to be brought to Earth as part of the Mars Sample Return mission. Acid-saline
lake deposits have been identified on the surface of Mars (Benison and Bowen, 2006; Benison and LaClair, 2003; Benison, 2006). On the Mars 2020 Perseverance Rover, there are two spectrometers, but these are not able to target micron-sized targets in a host rock. Detailed petrography and laser Raman spectroscopy on Earth could be used to characterize ancient lake waters in salt minerals in Mars return samples. Additionally, the non-destructive in-situ nature of the methods will preserve these valuable Mars samples.

**Future Research Ideas**

A future research method that I believe could be helpful to the characterization of ancient lake waters would be the use of laser ablation. Combined use of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) along with cryogenic-scanning electron microscopy-energy dispersive spectroscopy (cryo-SEM-EDS) can give quantitative measurements of major and minor elemental analysis (Welderghebriel et al., 2020). This method of using laser ablation for quantitative elemental analysis could pair well with the more qualitative petrography and laser Raman spectroscopy used in this thesis on daughter crystals. Laser ablation is a destructive method and cannot identify mineralogy, so it could be used after the non-destructive in-situ methods of petrography and laser Raman spectroscopy.

**Conclusions**

Petrography and laser Raman spectroscopy were used to identify and characterize primary fluid inclusions and daughter crystals within those fluid inclusions. These non-destructive in-situ methods were able to identify the mineralogy of micron-sized crystals in halite, along with components of the fluid that reflect original lake water chemistry.
Five different sulfate minerals were identified, along with one carbonate species. In addition to the high Na and Cl concentrations, these minerals may indicate elevated levels of Ca, K, Na, Sr, SO\textsubscript{4}\textsuperscript{2-}, and HSO\textsubscript{4} in the lake water at time of halite precipitation. Laser Raman spectroscopy of primary inclusion liquids in the Opeche Shale at 7411′6″ demonstrated that approximately half had pHs less than 1, and another third of primary fluid inclusions had elevated SO\textsubscript{4}\textsuperscript{2-} content of over 5000 ppm. At the 2347′6″ depth of the Cedar Hills Sandstone, Raman spectroscopy showed high SO\textsubscript{4}\textsuperscript{2-} content in approximately half of primary fluid inclusions.

Depositional waters of the Permian Opeche Shales and Cedar Hills Sandstone were complex acid brines. This thesis shows that combined petrography observations and laser Raman spectroscopic analysis can be successfully used to characterize ancient depositional waters.
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Appendix

**Opeche 7411’6”**

**OP703:** These two fluid inclusions were in large primary growth bands, but were significantly larger than surrounding fluid inclusions. These inclusions had moderately sized vapor bubbles, but most lacked daughter crystals.

**Fluid Inclusion 1:** This inclusion was the smaller of the two, and had two daughter crystals. The first daughter crystal was blocky with 7 µm sides. Raman spectra for the first daughter crystal had significant peaks at 1018, 418, 1130, 676, 629, 1160, 500, 610, and 1051 cm\(^{-1}\). The second daughter crystal was a smaller rounded crystal right next to the first daughter crystal, it had similar peaks as the first daughter crystal, but also had moderately large peaks at 332 and 1095 cm\(^{-1}\).

**Fluid Inclusion 2:** This fluid inclusion did not have any daughter crystals, but was noted for its strong double rimmed wall that appeared fuzzy. Spectra were taken for the liquid of this inclusion and peaks were present at 1052 and 984 cm\(^{-1}\).

**Solid Crystal Inclusion Clump:** This assemblage consists of four well-defined solid crystals trapped in solid halite. Solid A was the largest and was overlapped by the three other solids in certain sections. This solid A had a 40 µm long bladed crystal shape with rounded edges and had peaks at 1018, 629, 1160, 612, 1125, 1113, 677, 418, and 502 cm\(^{-1}\). The other three solids were all blocky with rounded edges, and laid on top of solid A. These three solids all had sides from 5 to 8 µm long. One of these smaller blocky crystals had the same spectra as solid A,
whereas the other two had slightly different Raman spectra with peaks at 1018, 417, 1130, 629, 1151, 1122, 676, 610, and 500 cm\(^{-1}\). Surrounding halite was also scanned with Raman, but there were no significant peaks.

**OP709:** This chip was filled with daughter crystal containing fluid inclusions in clear chevron growth bands, but most were either too small or had extremely noisy spectra.

**Fluid Inclusion 1:** This fluid inclusion had 20 µm sides, with a club-shaped daughter crystal and vapor bubble inside. The club-shaped daughter crystal was 16 µm long and had Raman spectra peaks at 1019, 1052, 1159, 629, and 497 cm\(^{-1}\). The liquid of the inclusion had a single notable spectra peak at 1050 cm\(^{-1}\).

**OP716:** Two fluid inclusions were noted in this chip with plentiful daughter crystals in clear chevron growth rings. These two fluid inclusions were much larger than most others, although many of the smaller fluid inclusions also had daughter crystals.

**Fluid Inclusion 1:** A single daughter crystal was in this 35 µm sided inclusion, along with a vapor bubble. The 20 µm long crystal was blocky with moderately rounded edges. The crystal appears to be rough and chipped in one corner. Under cross-polarized light most of the crystal fades from blue to purple to orange, but the rough chipped corner is a separate blue. Spectra were taken of both parts of this blocky crystal, but each gave peaks of 1018, 610, 1112, 1052, and 502 cm\(^{-1}\). The liquid had a single peak at 1051 cm\(^{-1}\).

**Fluid Inclusion 2:** There were three well-defined crystals in this large 60 µm fluid inclusion, along with a solid inclusion to the side of the inclusion. The first daughter crystal in the inclusion is a 30 µm bladed crystal, the second is a 20 µm rounded oval-like crystal, and the last daughter
crystal in the inclusion is a small 5 \( \mu m \) diameter well-rounded spherical crystal. The bladed crystal had Raman peaks of 1017, 1052, 1160, 1129, 1111, 628, 500, 609, and 417 cm\(^{-1}\). Spectra for the oval-like crystal was very noisy with only a 1050 cm\(^{-1}\) peak. Clear spectra for the spherical crystal gave peaks of 1052, 1098, 331, and 624 cm\(^{-1}\). The solid inclusion outside of the fluid inclusion was another 20 \( \mu m \) long oval-like crystal that had Raman peaks of 1018 and 1129 cm\(^{-1}\). Raman spectra of the liquid portion of the fluid inclusion had two peaks at 1052 and 981 cm\(^{-1}\).

**OP718:** This inclusion had a mix of primary fluid inclusions in chevron growth bands, along with secondary fluid inclusions that are filled with gas bubbles. Most of the primary fluid inclusions were too small to target, although two large fluid inclusions were present that were packed with features including daughter crystals.

**Fluid Inclusion 1:** Many of the features inside this 40 \( \mu m \) fluid inclusion were too small to target, although a 15 \( \mu m \) long bladed crystal was successfully targeted. The bladed crystal had spectral peaks of 1017, 1129, 1160, 628, 1052, 675, and 495 cm\(^{-1}\). The liquid had a wide clear peak from 1049 to 1054 cm\(^{-1}\). Other smaller features inside this fluid inclusion included a large vapor bubble, two needle-like crystals, and what appeared to be several spherical crystals.

**Fluid Inclusion 2:** This 40 \( \mu m \) sided fluid inclusion had a similarly sized vapor bubble, and had several daughter crystals inside that were able to be targeted. The first targeted daughter crystal was bladed and 10 \( \mu m \) long, and had prominent peaks at 1017, 1129, 1160, 1051, 1048, 628, 497, 418, and 677 cm\(^{-1}\). An overlapping cubic crystal with 7 \( \mu m \) sides had Raman peaks of 1017, 1129, 1050 to 1054, 676, 416, 343, 609, and 627 cm\(^{-1}\). There were two spherical...
subrounded crystals on the wall of the fluid inclusion that both had 6 µm diameters and had identical Raman peaks of 1095, 1051, and 331 cm\(^{-1}\). The liquid had a wide 1049 to 1051 cm\(^{-1}\) peak. Several smaller spherical crystals were in this fluid inclusion but were too small to characterize and use Raman on.

**OP713:** There was again a mix of primary and secondary fluid inclusions in this halite chip. Large primary inclusions were plentiful in one arm of a chevron crystal that made up a bulk of the chip. Secondary inclusions in this sample were almost always filled with petroleum bubbles.

**Fluid Inclusion 1:** This was a 20 µm wide fluid inclusion with two daughter crystals and a vapor bubble inside. A larger 10 µm sided cubic crystal had peaks at 1018, 500, 418, 609, 628, 677, 1054, 1130, 1112, 1161, and 1131 cm\(^{-1}\). A small 3 µm diameter spherical crystal was present too, but Raman spectra was too fuzzy to identify peaks. The liquid of the inclusion had a wide sharp peak at 1049 to 1054 cm\(^{-1}\).

**Fluid Inclusion 2:** This was the largest fluid inclusion in the chip and had 60 µm sides, with a vapor bubble and two daughter crystals inside. A small subrounded spherical crystal was too small to target with Raman. However, a 30 µm long bladed crystal with rounded corners was targeted and had peaks at 1018, 1051, 1130, 1161, 1111, 418, 501, 628, 610, and 677 cm\(^{-1}\). Liquid spectra had a peak at 1051 cm\(^{-1}\).

**Fluid Inclusion 3:** Roughly 10 blocky crystals packed this 20 µm sided fluid inclusion, with each of the crystals overlapping several others. Raman scans were done in different parts of this packed fluid inclusion, but they were all too fuzzy to pick out any prominent peaks.
Fluid Inclusion 4: Three daughter crystals and a vapor bubble filled this 20 µm sided fluid inclusion. Spectra from an 8 µm diameter rounded spherical crystal were too fuzzy to identify peaks. A blocky 10 µm long cubic crystal with rounded edges had Raman peaks at 1002, 1043 to 1056, 1138, 1156, 1105, 455, 473, and 617 to 653 cm\(^{-1}\). The last daughter crystal was a 10 µm long rounded oval-like grain that had peaks of 332, 608, 1096, 1148, 1146, and 416 cm\(^{-1}\).

Fluid Inclusion 5: A bladed crystal with slightly rounded corners was inside this 15 µm sided fluid inclusion. The 18 µm long bladed crystal had Raman peaks of 1018, 1051, 1128, 1113, 1161, 610, 628, 677, and 418 cm\(^{-1}\). Liquid spectra had a peak at 1051 cm\(^{-1}\).

OP717: Clusters of fluid inclusions were spread across this chip, most spectra from all parts of these fluid inclusions produced very noisy spectra. Only two fluid Inclusions from this chip had useable Raman spectra.

Fluid Inclusion 1: This inclusion had a 40 µm long needle-like crystal and vapor bubble inside this 40 µm sided inclusion. The crystal had Raman peaks at 1017, 1054, 1130, 628, 498, and 712 cm\(^{-1}\), whereas the liquid had a matching peak at 1054 cm\(^{-1}\).

Fluid Inclusion 2: A vapor bubble and blocky 10 µm long crystal with rounded edges were in this nearby 35 µm sided fluid inclusion. The daughter crystal had Raman peaks 1002, 1051, 460, and 627 cm\(^{-1}\). The liquid had a sharp peak at 1050 cm\(^{-1}\).

OP719: Primary fluid inclusions were again joined by secondary fluid inclusions in this halite sample. The secondary fluid inclusions were all filled with gas bubbles.
Fluid Inclusion 1: Two blocky 25 µm long crystals, a 45 µm long rounded oval-like crystal, and a vapor bubble were inside this 40 µm sided fluid inclusion. The two blocky daughter crystals only produced very noisy spectra. The long oval-like crystal had prominent peaks of 1002, 983, 1050 to 1054, 1168, 1194, 472, 453, and 620 cm⁻¹. The liquid had a matching wide but sharp 1050 to 1054 cm⁻¹ peak.

Fluid Inclusion 2: This 30 µm sided fluid inclusion had four notable features, four daughter crystals and a vapor bubble. The first daughter crystal was a 15 µm long rounded oval-like grain with only fuzzy Raman spectra. The second daughter crystal was a 20 µm long cubic crystal with one side of the crystal being very rounded, notable peaks included 1018, 1053, 1132, 1161, 1113, 500, 418, 610, 629, 677, and 983 cm⁻¹. An additional 20 µm long oval-like crystal had peaks of 1041 to 1043, 1103, 1121, 1217, 432, 630, 667, 502, 535, 220, and 268 cm⁻¹. A final smaller daughter crystal is characterized as being a 5 µm diameter well-rounded spherical crystal with Raman peaks at 1001, 1049 to 1054, 982, 455, 622, and 658 cm⁻¹. Raman spectra of the liquid had peaks at 1048 and 982 cm⁻¹.

722: All fluid inclusions in this chip were primary fluid inclusions, but most were too small to use laser Raman. Of the larger fluid inclusions, only one had features inside.

Fluid Inclusion 1: The only feature in this 15 µm sided fluid inclusion was a daughter crystal that was tabular and 8 µm long. Spectra from this crystal had prominent peaks at 998, 1092, 1108, 1155, 1188, 1185, 451, 458, 621, and 654 cm⁻¹. Liquid spectra did not have any peaks.
**Nippawalla 2347’6”**

**NP804A:** A set of three primary fluid inclusions are present, each approximately 10 µm apart.

**Fluid Inclusion 1:** The first fluid inclusion has 10 µm sides, and has three main features. Crystal A is a 15 µm long subrounded bladed crystal with Raman peaks at 1018, 982, 458, 499, 627, and a broad peak at ~1650 cm\(^{-1}\). Crystal B is a subrounded grain with a ~15 µm diameter, with similar peaks as Crystal A at 1018, 983, 497, 608, 628, 676, and 1161 cm\(^{-1}\). The fluid inclusion also contained a 1 to 2 µm diameter well-rounded sphere that fluoresced under UV-vis light. Raman spectra of the liquid had a broad peak at 1650 and a sharper peak at 983 cm\(^{-1}\).

**Fluid Inclusion 2:** This square fluid inclusion has sides measuring 25 µm and two daughter crystals. The first daughter crystal, crystal A, is a rounded 8 µ diameter sphere with major peaks at 1012, 1146, 1167, 985, 429, 635, and a wide 1650 cm\(^{-1}\) peak. Crystal B is a slightly small well-rounded sphere with a 5 µm diameter, and had identical peaks as crystal A. The liquid alone had peaks of 983 and a wide 1650 cm\(^{-1}\) peak.

**Fluid Inclusion 3:** This is the smallest inclusion with 10 µm sides and is all liquid and has a sharp peak at 983 and a broad 1650 cm\(^{-1}\) peak.

**NP804B:** This area of the chip had one fluid inclusion of interest, surrounding inclusions were much smaller and only contained fluid.

**Fluid Inclusion 1:** Two large daughter crystals are present in this large 40 µm long fluid inclusion. The two large daughter crystals are both rounded oval-like crystals that are 25 and 30 µm long. The larger of these two daughter crystals had noticeable Raman peaks at 1002, 1156, 1140,
1171, 651, 453, 620, and a wide hump at 1650 cm\(^{-1}\). The slighter smaller daughter crystal had peaks at 1018, 1129, 1160, 1112, 417, 500, 609, 628, 676, 982, and a hump at 1650 cm\(^{-1}\). Four smaller masses were also present, three of these looked like small well-rounded spheres with approximate diameters of 3 \(\mu\)m. Spectra from only one of these were gathered with peaks of 1017, 1129, 1161, 1002, 983, 331, 417, 498, 609, 650, and 676 cm\(^{-1}\). The last small mass appeared to be a cluster of much smaller crystals and had peaks of 1017, 983, 1002, 1128, 1155, 331, and 1096 cm\(^{-1}\). A Raman scan of the liquid had a significant peak at 983 cm\(^{-1}\) and a small peak at 455 cm\(^{-1}\).

**NP802:** In this chip large fluid inclusions were scarce, but two present inclusions had notable features. Also, several ‘strings’ of organic material were present that glowed under UV-light a blue to turquoise color.

**Fluid Inclusion 1:** This large 150 \(\mu\)m sided inclusion was composed of a vapor bubble and what appeared to be masses of small crystals clumped together in several different areas of the fluid inclusion. Under cross-polarized light the masses of small daughter crystals were baby blue in color. Raman scans of various crystal masses all produced peaks at 1018, 610, 417, 629, 1111, 1129, 1160, 500, and 629 cm\(^{-1}\). Sections of this large inclusion that were fluid only had no prominent peaks.

**Fluid Inclusion 2:** This notable inclusion was smaller with 30 \(\mu\)m sides, and included three daughter crystals that all overlapped. The first daughter crystal was a 20 \(\mu\)m long bladed crystal that was blue under cross-polarized light and had significant peaks at 1018, 417, 627, 1161 cm\(^{-1}\) and a wide minor hump at 1650 cm\(^{-1}\). A lumpy mass overlaid the end of the first daughter
crystal and had similar peaks as the larger daughter crystal but this may be due to it overlaying the large daughter crystal. A rounded 4 \( \mu \text{m} \) diameter crystal also laid on top of the middle of the larger daughter crystal, under cross-polarized light it had a slight green to blue glow. This rounded crystal also had similar peaks as the larger bladed crystal, which was likely due to it being on top of the larger bladed crystal, but had additional prominent peaks at 1095, 331 and 737 cm\(^{-1}\). Spectra of the liquid had only a wide low peak around 1650 cm\(^{-1}\).

**NP805:** This chip consisted of an arm of a chevron crystal that had plentiful fluid inclusions, with nearly all of the fluid inclusions having one or more daughter crystals. However, most of these fluid inclusions and daughter crystals were too small to perform laser Raman spectroscopy.

**Fluid Inclusion 1:** This 40 \( \mu \text{m} \) fluid inclusion had a single 30 \( \mu \text{m} \) long bladed daughter crystal. Under cross-polarized light the daughter crystal had a similar blue glow, and had peaks at 1018, 418, 500, and 1259 cm\(^{-1}\). The fluid did not have any significant Raman peaks.

**Fluid Inclusion 2:** Two daughter crystals were packed inside this 20 \( \mu \text{m} \) sided fluid inclusion. The first daughter crystal was blocky and about 15 \( \mu \text{m} \) long, and had 1018, 1229, 416, 607, and a wide 1650 cm\(^{-1}\) Raman peak. The second daughter crystal appeared as a twisted oval shape and did not produce any prominent Raman peaks. The fluid inclusion was too packed by the two daughter crystals to get clear Raman spectra of the fluid alone.

**Fluid Inclusion 3:** A 25 \( \mu \text{m} \) long rounded oval was inside this 20 \( \mu \text{m} \) sided fluid inclusion. The crystal produced Raman spectra with peaks at 1017, 610, 501, 419, and 1128 cm\(^{-1}\). The liquid had only a minor 1650 cm\(^{-1}\) peak.
Fluid Inclusion 4: This fluid inclusion had 15 µm sides, and had a single daughter crystal. The daughter crystal was shaped like a short 15 µm long surrounded femur bone. Prominent peaks were at 1001, 1156, 1139, 1108, 650, 635, 473, 455, 618, and 488 cm\(^{-1}\). The liquid again only had a minor 1650 cm\(^{-1}\) hump.

Fluid Inclusion 5: This larger fluid inclusion had sides that were 35 µm long and had three daughter crystals inside. The first daughter crystal was a 20 µm long diamond, or blocky, shape and had prominent peaks at 1017, 1129, 676, 627, 500, 419, and 608 cm\(^{-1}\). The other two crystals were both subrounded 8 µm diameter crystal and had similar peaks at 1001, 1017, 1129, 628, 419, 1161, 677, and a wide 220 cm\(^{-1}\) hump.

NP801: This chip of the Nippawalla formation had the best clarity and number of fluid inclusions along with plentiful daughter crystals. Along with all of the fluid inclusions, there were large amounts of blade crystals encased in solid halite that were found using cross-polarized light.

Fluid Inclusion 1: This fluid inclusion had three similarly sized daughter crystals inside, but all of the spectra being very noisy. One of these daughter crystals was a 10 µm sided cube along the wall of the inclusion, Raman peaks picked out of the noisy spectra were 1002, 1140, 472, and 648 cm\(^{-1}\), a large wide hump was centered around 2050 cm\(^{-1}\). The other two crystals were well-rounded 15 µm diameter crystals stuck together, no peaks were able to be picked out for either of these crystals. The liquid also did not have any noticeable peaks.

Fluid Inclusion 2: Three daughter crystals were inside this 30 µm long inclusion. Like the previous inclusion there was a single blocky inclusion along with two subrounded crystals. The
single blocky crystal was 20 µm long and had significant peaks at 1018, 628, 1159, 1129, and 500 cm$^{-1}$. The two subrounded crystals with 15 µm diameters again had no prominent peaks. The liquid Raman spectra were very noisy and did not have any significant peaks either.

Fluid Inclusion 3: A subrounded crystal along with a bent needle were caught inside this 30 µm wide fluid inclusion. The subrounded crystal had a diameter of 15 µm, whereas the bent needle was 25 µm long and was blue to purple under cross-polarizers. The subrounded crystal had Raman peaks at 1002, 1140, 472, 644, 982, and a wide 1650 cm$^{-1}$ hump. The bent needle had peaks of 1017, 609, 1129, 1111, 676, 500, 983, and another wide hump at 1650 cm$^{-1}$. The liquid of the inclusion had a 983 and a 1650 cm$^{-1}$ wide peak.

Fluid Inclusion 4: This 20 µm long fluid inclusion had three daughter crystals. The first was a narrow 10 µm long needle that was too thin for Raman. The second was a rounded oval-like crystal that was 8 µm long and baby blue under cross-polarized light. This rounded oval-like crystal had Raman peaks at 1017, 1002, 417, 1129, 1160, 628, 610, 676, 651, 500 and a wide 2050 cm$^{-1}$ hump. The last crystal was a subrounded 4 µm long oval-like crystal that was overlapped by the other oval-like crystal. Raman spectra were not able to be collected for the last crystal. Liquid spectra had a 983 cm$^{-1}$ peak and a wide 1650 cm$^{-1}$ peak.

Fluid Inclusion 5: Two daughter crystals were in this 30 µm wide inclusion. The first inclusion was a 10 µm long narrow bladed crystal that was bright white under cross-polarizers, no prominent peaks appeared for this crystal but it may have been too thin to target. The other daughter crystal was a 8 µm long well rounded oval-like crystal that had Raman peaks at 1001,
1140, 1157, 1106, 651, 620, 472, and a wide 2100 cm\(^{-1}\) hump. Raman spectra of the liquid had a wide 2100 cm\(^{-1}\) hump.

**Fluid Inclusion 6:** A single subrounded 15 \(\mu\)m diameter crystal with a rough surface was inside this 30 \(\mu\)m sided inclusion. The subrounded crystal was white under cross-polarized light and had Raman peaks of 1012, 983, 471, 431, 635, 664, 1171, and 1149 cm\(^{-1}\). The liquid had a single Raman peak at 981 cm\(^{-1}\).

**Fluid Inclusion 7:** This 30 \(\mu\)m sided inclusion was very similar to fluid inclusion 6. There was again a 20 \(\mu\)m long subrounded crystal with a rough looking surface and was white under cross-polarized light. Spectra peaks were 1011, 474, 636, 983 and 1141 cm\(^{-1}\). The liquid had a Raman peak at 983 cm\(^{-1}\).

**Fluid Inclusion 8:** There were two daughter crystals in this 20 \(\mu\)m sided inclusion. One was a well-rounded 5 \(\mu\)m long oval-like crystal that was white under cross-polarized light. Spectra for this daughter crystal had peaks at 1017, 609, 500, 675, 1110, 1129, and 1160 cm\(^{-1}\). The other crystal was rounded with a 5 \(\mu\)m diameter with peaks at 1002, 1105, 1140, 619, 645, and a wide low hump at 2400 cm\(^{-1}\). The liquid also had no spectra.

**Fluid Inclusion 9:** This was the last fluid inclusion in this chip, and had dimensions of 20 by 40 \(\mu\)m sides. There were three daughter crystals in this inclusion, with one being blocky and the other two being bladed crystals. The blocky daughter crystal was orange to purple under cross-polarized light and was 18 \(\mu\)m long. Peaks for this blocky crystal were 1017, 1129, 500, 627, 675, and 1160 cm\(^{-1}\). The other two crystals were 15 and 20 \(\mu\)m long bladed crystals that were a
dull purple under cross-polarizers. Spectra for both of these similar looking bladed crystals were 1018, 1129, 417, 675, and 628 cm\(^{-1}\). Liquid spectra were not able to be collected.

**Nippawalla 2350’6”**

**NP812:** This chip is one arm of a large chevron crystal with many fluid inclusions. Most fluid inclusions, however, were too small to target with laser Raman. Most of the daughter crystals in this chip did not have any vapor bubbles.

**Fluid Inclusion 1:** A 15 µm sided inclusion that has three daughter crystals. The largest daughter crystal was a 12 µm sided blocky crystal, another was a rounded 8 µm long oval-like crystal, and the was a rounded 15 µm long more elongated oval-like crystal. All three of these daughter crystals had similar Raman spectra with peaks at 1018, 1129, 1160, 419, 500, 676, 628, and 610 cm\(^{-1}\). The liquid had a wide spectral peak at 1650 cm\(^{-1}\).

**Fluid Inclusion 2:** This fluid inclusion was the largest in this chip with 30 µm sides, and had two similar daughter crystals. Both daughter crystals were subrounded spherical crystals with diameters of 12 and 15 µm. The smaller crystal produced only noisy spectra, but the larger had spectral peaks at 1018, 1128, 1160, 417, 499, 676, 628, and 609 cm\(^{-1}\). The liquid did not have any prominent Raman peaks.

**NP813:** This sample contained both arms of a chevron crystal and had many fluid inclusions, however, many of these inclusions were too small to sample.

**Fluid Inclusion 1:** This large 100 µm sided fluid inclusion had a vapor bubble and three daughter crystals. The largest daughter crystal was blocky with rounded edges and had a length of 60 µm,
Raman peaks were 1017, 1128, 1160, 417, 499, 628, and 675 cm\(^{-1}\). The second crystal was a blocky crystal that was 30 µm long, prominent spectral peaks were 1017, 1130, 1161, 417, 501, 610, 629, 676, and 755 cm\(^{-1}\). The smallest crystal was cubic with slightly rounded edges, but spectra from this sample were too noisy. The liquid spectra was also noisy with no noticeable peaks.

**Fluid Inclusion 2:** A short bladed 10 µm long crystal, along with a vapor bubble, were in this 30 µm long fluid inclusion. The bladed crystal had peaks at 1017, 1128, 1161, 417, 500, 609, and 628 cm\(^{-1}\). Similar to fluid inclusion 1, fluid from this fluid inclusion did not have any peaks either.

**814:** This chip of a chevron crystal was packed with fluid inclusions, many of which had daughter crystals but not vapor bubbles. There were secondary fluid inclusions on one side of this chip.

**Fluid Inclusion 1:** A 20 µm sided inclusion with only a single daughter crystal inside. The crystal is 20 µm long and is bladed. Under cross-polarized light the crystal is blue to purple. Raman spectra peaks were 1018, 1110, 1160, 610, and 499 cm\(^{-1}\). The liquid did not have any peaks.

**Fluid inclusion 2:** Tiny 2 to 3 µm subrounded spherical crystals packed this 30 µm long fluid inclusion. Spectra from various parts of this packed fluid inclusion nearly all gave the same Raman spectra with peaks at 1018, 418, 498, 627, 676, 1160, and 1128 cm\(^{-1}\).

**Fluid Inclusion 3:** This fluid inclusion had 25 µm sides with two overlapping features. A clump of faint ‘squiggles’ lays on top of a 10 µm long bladed crystal. Spectra from the bladed crystal alone and also the ‘squiggles’ on top of the bladed crystal gave matching Raman spectra with
peaks at 1018, 1129, 418, 676, 610, and a wide hump at both 1650 and 1400 cm$^{-1}$. A 1650 cm$^{-1}$ peak was present from a Raman scan of the fluid alone.

Fluid Inclusion 4: A cross-hatched blocky crystal and rounded spherical crystal filled this 30 µm sided inclusion. The blocky crystal with a cross-hatched surface was 10 µm long and had Raman peaks at 1018, 1130, 676, 418, and a wide 1650 cm$^{-1}$ hump. The rounded spherical crystal with an 8 µm diameter had similar peaks at 1018, 1131, 418, 678, 628, and 610 cm$^{-1}$. The liquid lacked any notable Raman peaks.

Fluid Inclusion 5: This fluid inclusion was slightly elongated with 35 and 50 µm sides. Inside was a 12 µm long needle, along with a mass of small bladed crystals each being about 3 µm long. The needle was too thin to be scanned with Raman, but the mass of small bladed crystals had peaks at 1018, 1130, 1161, 410, 500, 610, 628, and 677 cm$^{-1}$. There was a small 1650 cm$^{-1}$ liquid hump.

Fluid Inclusion 6: Two small 20 and 30 µm long subrounded oval-like crystals were inside this 50 µm sided fluid inclusion. The two daughter crystals both had peaks at 1018, 1052, 1113, 1130, 1162, 610, 418, 500, and 488 cm$^{-1}$. The liquid had a peak at 1053 cm$^{-1}$.

Fluid Inclusion 7: A single daughter crystal nearly filled up this entire 10 µm sided fluid inclusion. The 9 µm sided daughter crystal is blocky and has Raman peaks at 1018, 1160, 1130, 418, 628, and 610 cm$^{-1}$. There was not enough open space in the fluid inclusion for a Raman spectra of the fluid to be collected.

Fluid Inclusion 8: Two overlapping daughter crystals were trapped inside this 25 µm sided fluid inclusion. One daughter crystal was a 20 µm long bladed crystal, whereas the other was 15 µm
long and blocky. Both the bladed and blocky crystal had Raman peaks of 1018, 1130, 676, 418, 610, and a wide 1650 cm⁻¹ hump.

815: Three large and notable fluid inclusions were noted in this chip, each having a single daughter crystal. Each of the fluid inclusions are from the same arm of a chevron crystal.

**Fluid Inclusion 1:** A blocky crystal with rough jagged edges was inside this 60 µm sided fluid inclusion. Spectra from this 40 µm long blocky crystal had peaks at 1018, 1130, 1161, 676, 417, 629, 610, 499, 418, and a wide 1650 cm⁻¹ hump. The liquid also had a Raman peak at 1650 cm⁻¹.

**Fluid Inclusion 2:** This 40 µm sided fluid inclusion had a 30 µm long trapezoid shaped crystal, with spectral peaks at 1018, 1129, 418, 610, and a wide 1650 cm⁻¹ hump. Liquid again also had a wide 1650 cm⁻¹ hump.

**Fluid Inclusion 3:** This is another 60 µm sided fluid inclusion, but this one contained a vapor bubble. Also, inside there was a 40 µm long bladed crystal, Raman spectra of this bladed crystal had peaks of 1018, 1130, 1161, 1111, 418, 677, 611, 627, and 500 cm⁻¹. Liquid from this fluid inclusion was missing the 1650 cm⁻¹ wide hump seen in Raman spectra from the other two fluid inclusions in this halite chip.