A Comparative Study of Silicified Rock Reservoir in Shunnan 4 well of Tarim Basin with Hydrothermal Chert Reservoir of Parkland Gas Field in Western Canada Sedimentary Basin

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By
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SUPERVISORY AND EXAMINING COMMITTEE

Hang Yin, candidate for the degree of Master of Science in Geology, has presented a thesis titled, *A Comparative Study of Silicified Rock Reservoir in Shunnan 4 Well of Tarim Basin with Hydrothermal Chert Reservoir of Parkland Gas Field in Western Canada Sedimentary Basin*, in an oral examination held on December 22, 2017. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

The silicified limestone reservoirs in the Yingshan Formation of Middle Ordovician, discovered from SN4 well in 2013, have made a high yield in Shunnan area which is located in the center of Tarim Basin, northwest China. Comparing to previous work about the silicification, much more detailed petrographic descriptions have been carried out in this study. The most important diagenetic features to the silicification are identified including replacement quartz, quartz cement (characterized by 4 textures: equant quartz, bladed quartz, overgrowth and quartz cement in later fractures) and three types of calcite cement (CC1-CC3). Geochemical analysis including Si-O isotope analysis on quartz and C-O isotope analysis on calcite cement are processed, together with fluid inclusion studies on both quartz and calcite cement.

Back to the discovery of this unique type of reservoir worldwide, the only comparable one is the hydrothermal chert reservoir interbedded among dolomite and dolomitic mudstone in the Wabamun Group of Upper Devonian, discovered in 1956 in Parkland, NW Western Canada sedimentary basin (WCSB). Due to limited reference in this chert reservoir, detailed work including core and thin section observations have been processed for further understanding. Two types of replacement dolomite and two types of dolomite cement occurring in Parkland comprise fine crystalline dolomite (RD1), medium-coarse crystalline dolomite (RD2), medium-coarse crystalline dolomite cement (CD1) and saddle dolomite cement (CD2), respectively. The chert mainly replaced the original host rock or filled in the fractures/dissolution vugs after the saddle dolomite cement. A third type of silica identified in this study is the euhedral quartz cement. Core-
based geochemical exploration has been put forward including C-O and Sr-O isotope analysis (mainly on RD1, RD2, CD1, CD2 and calcite cement). Fluid inclusion analysis on the saddle dolomite and euhedral quartz cement has also been processed.

Based on the geological setting, the Upper Devonian reservoirs in Parkland show many similarities to those of Ordovician in SN4 well, including original limestone framework and the structural controlled fault systems. The differences mainly display as a pervasive dolomitization before chertification in Parkland, while in the silicified intervals of SN4 well, the dolomite mainly represents as the cement along with stylolites. The textures of the silica which contribute to the reservoir quality in both areas are also dramatically different. Chertification in Parkland formed from Tournaisian to late Viséan at a depth around 3200 m, while in SN4 well, the silicification depth was rather deeper reaching 6600 m and estimated began in the Late Devonian.

The silicified reservoirs in both areas have made breakthroughs in the gas production. A better understanding of the nature and the forming mechanism of these silicified carbonate reservoirs is of critical importance to guide further exploration in both of the areas, which could also be applied in other areas with similar background setting.
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CHAPTER 1

INTRODUCTION

1.1 Preface

Shunnan area, located in the Tarim Basin, northwest China, develops multiplayer and multiphase carbonate reservoirs (limestone and dolomite) in Ordovician (Lu et al., 2015). Shunnan 4 well (SN4 well) is an exploratory well drilled by Sinopec targeting at the oil and gas characteristics of the Lower Ordovician, with total depth of 6668.81 m. In 2013, SN4 well was tested with a high yield of commercial gas flow in Yingshan Formation of the Middle Ordovician (Qi, 2014), revealing a rare kind of reservoir – the porous silicified carbonate reservoir.

The forming of this type of reservoir has attracted a lot of attention from both oil industry and academia. Based on current publications worldwide, the only analogous to the porous silicified carbonate reservoir from SN4 well is the replacement chert reservoir developing in the Wabamun Group of Parkland field, which is located in the northwest of Western Canada sedimentary basin (WCSB), discovered in 1956 with initial gas production tested at 19MMcf/day from the first drilling well 6-29-81-15W (Packard et al., 2001).

Such rare silicified carbonate reservoirs in these two areas were interpreted as hydrothermal origin (Lu et al., 2015; Packard et al., 2001). The main objective of this study is to compare the characteristics of these two silicified reservoirs both in SN4 well and Parkland field, in order to have a better understanding about the nature of these silicified carbonate reservoirs.
1.2 Previous Work and Problems

Considerable research has been done since the silicified reservoir was discovered from SN4 well. Yun and Cao (2014) interpreted that meteoric water lead to multiple erosions during the Ordovician, creating the condition for karstic reservoirs. Han et al. (2014), on the other hand, suggested that the erosion and related meteoric water had little influence on the silicification. They identified several epithermal mineral associations in Shunnan area, including column quartz, iceland spar and anhydrite in the dissolution vugs and fractures. The homogenization temperatures of fluid inclusions in the quartz were much higher than the geotemperature, reflecting that the silicified reservoir was formed through hydrothermal processes. Chen et al. (2015) suggested that the Middle-Lower Ordovician wackstone/grainstone were deposited in an open carbonate platform but the reservoirs did not form until the late diagenetic stage when the siliceous fluids migrated along the fractures due to multiple episodes of volcanism.

The research on Parkland reservoirs was conducted by Packard et al. (2001, 2004). Three possible models were proposed for the silicification in Devonian carbonate the Parkland area (Packard et al., 2001; 2004): mixed marine-meteoric waters, redox diagenetic fronts and hydrothermal-volcanogenic origin. Among the three models, based on the chert microfabric and oxygen isotope signature, the preferred interpretation of silicification was hydrothermal origin.

Even though lots of work has been done for the silicified reservoir in SN4 well including basic petrography, carbon and oxygen isotope analysis, and fluid inclusion analysis, detailed petrography and the corresponding geochemical analyses of quartz were lack in previous publications as geochemical analyses of quartz were based on the
bulk samples, which did not allow differentiation of geochemical signatures from different types of quartz. Therefore, previous interpretations on the nature of silicification and possible different episodes of silicification were compromised, while for parkland, detailed petrography and geochemical analysis about the dolomite was insufficient at all. In order to address the problems outlined above, detailed petrography and the corresponding geochemical analyses were carried out in this study.

1.3 Research Objective and Contents

The main objective of this study is to compare the nature of silicification in Shunnan and Parkland area in terms of petrography, spatial distribution, geochemical attributes, and the processes involved in order to achieve a better understanding about the forming mechanisms of the silicified reservoirs and the principle factors in controlling their development and scale.

The detailed objectives of this research are listed as follows:

(1) To exam and describe the petrography of silicification and associated diagenetic features in SN 4 well in the Tarim Basin and Parkland field in the WCSB.

(2) To compare the nature and quality of silicified limestone from SN4 well with the chert reservoir in Parkland including porosity, permeability and other characteristics.

(3) To identify the mineral association between these two silicified reservoirs through the studies of lithology, mineralogy and geochemistry.

(4) To interpret the forming mechanism of the silicified reservoir of these two areas for further understanding and future exploration.
CHAPTER 2

METHODOLOGY

2.1 Core Examination

Core examination in Shunnan area mainly focused on the cores of SN4 well (Fig 2.1) around 4 m (Table 2.1). The cores were provided by the Northwest Branch of SINOPEC and the examination work was finished in the core storage of Urumchi, Xinjiang Province of China. Core study in Parkland field included cores from 6 wells (Fig. 2.2) approximately 310 m (Table 2.1). The cores were transported to and examined in the Subsurface Laboratory, Saskatchewan Ministry of Economy in Regina, Saskatchewan.

The core description included the depth, color, lithology, porosity, fractures and other diagenetic features. After detailed core examination, a total of 100 samples from two study areas were collected for microscope petrography and geochemical analyses.

2.2 Petrography Study

A total of 110 standard thin-sections (22 for Shunnan and 88 for Parkland) and 20 fluid inclusion thin-sections (8 for Shunnan and 12 for Parkland) from selected samples were prepared by Calgary Rock and Materials Services Inc.. The standard thin sections were made 30 microns thick with blue epoxy. The fluid inclusion thin sections were made 100 microns thick with normal clear epoxy. The thin section petrography study was carried out at the Geology Laboratory, University of Regina, mainly focusing on the lithology, porosity and diagenesis as described in Chapter 4.
Figure 2.1 Core samples of 3rd and 4th core intervals from SN4 well.
Figure 2.2 Well locations of the Parkland area. Six wells where cores were examined are labeled: 10-26 well, 6-29 well, 10-28 well, 6-22 well, 10-11 well and 11-1 well.
Table 2.1 A list of wells, showing the core depth examined from two study areas

<table>
<thead>
<tr>
<th>Study Area</th>
<th>Well Name</th>
<th>Depth Range of Core Interval (m)</th>
<th>Formation/Group</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunnan</td>
<td>SN4</td>
<td>6668.81--6673.52</td>
<td>Yingshan</td>
<td>Ordovician</td>
</tr>
<tr>
<td>Parkland</td>
<td>6-29</td>
<td>3325.80--3477.00</td>
<td>Wabamun</td>
<td>Devonian</td>
</tr>
<tr>
<td></td>
<td>6-22</td>
<td>3328.00--3333.00</td>
<td>Wabamun</td>
<td>Devonian</td>
</tr>
<tr>
<td></td>
<td>10-11</td>
<td>3257.00--3275.00</td>
<td>Wabamun</td>
<td>Devonian</td>
</tr>
<tr>
<td></td>
<td>10-26</td>
<td>3439.20--3504.70</td>
<td>Wabamun</td>
<td>Devonian</td>
</tr>
<tr>
<td></td>
<td>11-01</td>
<td>3318.00--3320.00</td>
<td>Wabamun</td>
<td>Devonian</td>
</tr>
<tr>
<td></td>
<td>10-28</td>
<td>3244.70--3485.00</td>
<td>Wabamun</td>
<td>Devonian</td>
</tr>
</tbody>
</table>
2.3 Cathodoluminescence Microscopy

Selected samples of Parkland were examined for cathodoluminescence (CL) to identify the luminescence features among different kinds dolomite. The thin sections were chosen based on the classification of dolomite both in the matrix and cement. Selected thin sections were put in a vacuum-sealed chamber, exposing to electron radiation at 10-15 kV. The luminescence features of the dolomite were taken by the Nikon Optishot-pol petrographic microscope attached to the chamber.

2.4 Si and O Isotope Analysis

The high resolution isotopic analyses using the secondary ion mass spectrometry (SIMS) with ion microprobe would permit us to obtain Si and O isotopic data with sampling spots of around 10 μm from a single quartz crystal. In this project, a total of 75 Si-isotope and 75 O-isotope analyses were performed on different types of quartz, using SIMS ion-microprobe at the Canadian Centre for Isotopic Microanalysis at the University of Alberta. Thin sections with 100 μm thick were selected from those of SN4 well. Areas with large grains including different types of quartz both in the matrix and cement were marked in the thin sections.

The detailed information about sample preparation, analytical procedures, and accuracy were provided by Dr. Richard Stern, who was in charge of our analysis. “Eight regions of interest (RIOs) were extracted and cast in epoxy along with quartz in a single 25 mm diameter mount (Fig. 2.3) and then lightly polished using diamond grits. The mount was cleaned with deionized H₂O and coated with 7 nm of high-purity Au prior to scanning electron microscopy (SEM). SEM characterization with secondary electrons (SE) and backscattered electrons (BS) was carried out utilizing beam (20 keV, 3-5 nA)
with a Zeiss EVO MA15 microscope. Silicon isotopes ($^{30}\text{Si}/^{28}\text{Si}$) and oxygen isotopes ($^{18}\text{O}$ and $^{16}\text{O}$) in quartz were analyzed following the SEM using a Cameca IMS 1280 multicollector ion microprobe. A $^{133}\text{Cs}^+$ primary beam was operated (20 keV, 2.0 nA) to make measuring spots (20 µm across and 2 µm deep), which were made in pairs, one for silicon isotope and the other for oxygen. Repeated analyses were made using instrumental mass fractionation (IMF) with one analysis known after every 4 unknowns. A single analysis took 255 s for oxygen isotope and 270 s for silicon isotope. All the data were collected utilizing dual Faraday cups.”

After the data collection, together with the SEM mapping, different types of quartz can be identified and analyzed by using scatter between $^{30}\text{Si}/^{28}\text{Si}$ and $^{18}\text{O}$. The results of the analyses will be shown in Chapter 5.

2.5 C and O Isotope Analysis

C and O isotopes were analyzed for 41 calcite cement samples from Shunnan area. 18 of these analyses were performed at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (CUG); the other 23 were analyzed at the Canadian Centre for Isotopic Microanalysis (CCIM), University of Alberta by SIMS. For Parkland, 43 samples with dolomite replacement and dolomite cement were selected for the analysis by the Saskatchewan Isotope Laboratory, University of Saskatchewan.

18 calcite cement samples of Shunnan area were obtained using MicroDrill (with a Nikon-SMZ1500 microscope and OSADA XL-230 drills) and processed with anhydrous phosphoric in the CUG. A GasBench was used to collect the CO$_2$ automatically when the samples were reacting with anhydrous phosphoric. The values were collected and
analyzed with a MAT253 mass spectrometer using the PDB as a standard for δ^{13}C and SMOW for δ^{18}O (precision: δ^{13}C<0.01‰, δ^{18}O<0.02‰). The other 23 calcite cement samples were analyzed using SIMS at CCIM. The preparations for the samples were described in Section 2.4 (Si and O isotope analyses by SIMS) since the selected calcite and quartz was from the same thin sections. The analyzed spots were also made in pairs, one for δ^{13}C and the other one for δ^{18}O. For the calcite O-isotopes (^{18}O and ^{16}O), secondary ion counted rates for ^{16}O\textsuperscript{-} and ^{18}O\textsuperscript{-}, respectively, and the IMF was monitored by repeated analysis of a dolomite primary reference material (RM). Calcite O-isotope data was normalized to the dolomite RM and corrected for a consistent bias of +5.95‰. The calcite C-isotopes (^{13}C and ^{12}C) were conducted from the identical spot location of the preceding O-isotope analyses using similar primary beam and secondary column parameters. The analyses for oxygen and carbon isotopes were made after every 4 unknowns. All the data was collected and analyzed simultaneously in a Faraday cup and electron multiplier.

For Parkland, the detailed process for the carbon and oxygen isotope analysis was provided by Ms. Sandra Timsic, manager of Saskatchewan Isotope Laboratory. “Samples were powdered to 20-50 micrograms and placed into a vacuum oven roasting at 200℃ for about 1 hour to remove the water and volatile organic contaminants that may confound the stable isotope values of the carbonate. Stable isotope values were obtained using a Finnigan Kiel-IV carbonate preparation device directly coupled to the dual inlet of a Finnigan MAT 253 isotope ration mass spectrometer. After reacting with anhydrous phosphoric, the isotope ratios were corrected for acid fractionation and ^{17}O contribution using the Craig correction and converted to VPDB. Data were directly
calibrated against the international standard NBS-19 with the values: δ^{13}C =1.95‰ VPBD and δ^{18}O = -2.2‰ VPBD.”

2.6 Sr Isotope Analysis

22 samples of Parkland were prepared and analyzed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The details of the processes were provided by the Isotope Lab of IGGCAS: “Approximately 100 mg of carbonate rock materials were weighed (to 0.1 mg precision) and then put into Savillex 7.5 mL Teflon-PFA and dissolved on a hotplate at 80°C using 2.0 mL of 0.2 M HCl for 4 hours. After cooled to room temperature for 1 h, the samples were settled into centrifugation for 8 min at 5000 rpm, and then redissolved with 1.0 mL of 2.5 M HCl. The Sr was separated from the matrix after rinsing four times with 0.5 mL of 2.5 M HCl and evaporated to dryness and ready for TIMS analysis. The measurements were performed on a Triton Plus TIMS and acquired in the static collection mode. The mass fractionation of Sr was corrected using exponential law with {^{88}Sr/^{86}Sr}=8.375209. During the data collection, the measured average value of the NBS987 was {^{87}Sr/^{86}Sr} =0.713236 ± 0.000013.

2.7 Fluid Inclusion Study

Petrography and microthermometry are the main focuses during the fluid inclusion analysis. Samples targeting at calcite and quartz cement of Shunnan area were prepared, as well as the dolomite and quartz samples of Parkland.

For both areas, different types of fluid inclusions were identified based on the features of petrography. The fluid inclusion microthermometry was performed at the Geofluids Lab, University of Regina. Fluid inclusions were analyzed using a Linkam
THMGS600 heating-freezing stage, which was calibrated using synthetic fluid inclusions with known compositions. The heating or cycling intervals were 0.1°C for ice-melting temperatures ($T_{m\text{-}\text{ice}}$) in Shunnan area and 1°C in Parkland. The heating intervals for hydrohalite melting temperatures ($T_{m\text{-HH}}$) were 0.1°C in both of the two areas. The homogenization temperatures ($T_h$) heating and/or cycling intervals were 1°C in SN4 well and 2°C in Parkland, respectively.

The bulk salinities were calculated by $T_{m\text{-ice}}$, using the program by Steele-MacInnis et al. (2011). The salinities of the fluid inclusions were calculated using the H$_2$O-NaCl system when the $T_{m\text{-ice}}$ was larger than -21.2°C. If the $T_{m\text{-ice}}$ was less than -21.2°C, the $T_{m\text{-HH}}$ was assumed to be equal to $T_{m\text{-ice}}$ which was used to calculate the maximum NaCl/(NaCl + CaCl$_2$) mole ratios ($R_{NaCl}$) (Chi and Ni, 2007; Steele-MacInnis et al., 2011).

The concept of the fluid inclusion assemblage (FIA) (Goldstein and Reynolds, 1994) was used to guide the fluid inclusion analyses. Detailed classification of the fluid inclusions and microthermometry analyses will be elaborated in Chapter 5.
Figure 2.3 The SEM image of the mounts used for SIMS analysis, showing eight mounts marked in yellow.
CHAPTER 3

GEOLOGICAL SETTING

3.1 Geological Setting of Shunnan area

3.1.1 Location

The Tarim Basin, which is a large composite and superimposed sedimentary basin surrounded by the Tianshan orogeny, the Kunlun orogeny and the Altyn orogeny (Jia, 1997; 1999), is located in the northwest of China, covering an area of $56 \times 10^4 \text{km}^2$ (Jia, 1997; Jin and Wang, 2004). The tectonic framework of Tarim Basin can be divided into seven structural zones based on an integrated study of seismics, outcrops and well data (Jia et al., 1995), including the Kuqa Depression, the Northern Depression, the Southwest Depression, the Southeastern Depression, the Taibei Uplift, the Central Uplift, and the Southern Uplift, respectively (Jia, 1997). The Tarim Basin is characterized with multiple source rocks and oil-bearing rocks, together with periods of hydrocarbon accumulation, reconstruction and adjustment (Jin and Wang, 2004).

The study area, Shunnan, located in Tazhong (in the middle of the Central Uplift), is next to Katakai Uplift and west of Manjiaer Depression. It covers area along the transition between Shuntuogoule Uplift and Guchengxu Uplift (Liu et al., 2004) (Fig.3.1) with a major basement fault, the Tazhong No.1 fault, running through the study area. The target stratum of Shunnan is the Yingshan Formation of the Middle Ordovician, where the silicified carbonate reservoir was discovered in SN4 well.
Figure 3.1 Location and detailed map of Shunnan area. (A) Location of the Tarim Basin including seven major tectonic zones (Modified from report of SINOPEC, 2013). The red box shows the location of the study area—Shunnan; (B) Detailed map of Shunnan area, showing tectonic unit, major faults, and well locations (Modified from Chen, 2015).
3.1.2 Tectonic Evolution

The tectonic evolution of Tarim basin can be divided into five stages: Tarim tectonic orogeny (Late Proterozoic), Caledonian tectonic orogeny (Cambrian to Late Silurian), Hercynian tectonic orogeny (Devonian to Carboniferous), Indosinian-Yanshan tectonic orogeny (Triassic to Cretaceous) and Himalayan tectonic orogeny (since Paleogene) (Jia et al., 1995).

Tazhong area was in the east of intracratonic depression from Cambrian to Middle Ordovician. The Tazhong uplift was initiated at the end of Middle Ordovician related to the Caledonian orogeny, established in the Hercynian orogeny, and further stabiized in the end of Hercynian orogeny. The influence of later Indusinian-Yanshan orogeny on Tazhong uplift was limited (Jiao and Gao, 2008; Liu et al., 2004; Zhang and Jia, 1997).

The north slope of Tazhong area, an area located in the footwall of Tazhong No.1 fault (Fig. 3.1B), can be divided into Guchengxu uplift and Shuntuoguole low-uplift, from southeast to northwest, respectively (Fig. 3.1B). Shunnan is just between these two uplifts (Fig. 3.1B) (Yun and Cao, 2014). In the Early-Middle Ordovician, the whole north slope of Tazhong area was a uniform carbonate platform. In the end of Early Ordovician, the Tazhong No.1 faults become active, and the Katak area was uplifted (Yun and Cao, 2014). In the Late Ordovician, with large-scale marine transgression, the north slope of Tazhong area went through strong folding, which intensified gradually to the southeast concomitant with rapid subsidence (Yun and Cao, 2014).

From Silurian to the Early-Middle Devonian, the north slope of Tazhong area was expressed as low in northwest and high in southeast due to the Early Hercynian orogeny (Yun and Cao, 2014). As a result, the Upper Ordovician and the Silurian to Middle-
Lower Devonian deposits were subjected to erosion in the Guchengxu uplift. The Devonian sediments were totally missing with the pinch-out line along the Shunnan slope area, where the Ordovician carbonate rocks were not subjected to obvious erosion, they went through large-scale karstification (Yun and Cao, 2014). Meanwhile, a series of strike-slip faults accompanied by northwest oriented en-echelon normal faults were developed in the Shuntuoguole low-uplift and Shunnan slope (Yun and Cao, 2014).

From Carboniferous to Permian (Middle-Late Hercynian), the Shuntuoguole uplift was uplifted in the east, concomitant with reactivity of the early faults and strong magmatic activities (Yun and Cao, 2014). From the Mesozoic to Cenozoic (Indosinian-Himalayan tectonics), the Guchengxu continued uplifting due to the compressional stress of the orogenies from the south. As the Shunnan slope evolved from depression to slope, the north slope of Tazhong area was eventually established in Himalayan orogeny (Jia et al., 1995).

### 3.1.3 Depositional Setting of Ordovician and Stratigraphy

The targeted stratum in Shunnan area is the Ordovician Yingshan Formation. The depositional setting and the stratigraphy framework of the study area are summarized below.

The Ordovician in the Tazhong uplift was deposited in a carbonate platform from platform margin, slope, and shallow shelf to basin (Jia, 2004). The main sedimentary environments in Shunnan area include limited platform, open platform, platform margin, slope and shallow shelf (Yun and Cao, 2014). The Ordovician deposits are divided as Lower Ordovician Penglaiba Formation (O₁p), Middle Ordovician Yingshan Formation (O₁₂y), Middle Ordovician Yijianfang (O₂y), Upper Ordovician Qiaerbake Formation
(O_3qeb) and Queerque Formation (O_{3eqy}) (Jia, 1999). The following is a summary of description of these formations based on previous studies (Jia, 2004) (Fig. 3.2).

1) Penglaiba Formation (O_{1p})

The lithology of Penglaiba Formation is mainly grey-white fine-coarse dolomite, intercalated with sparite packstone. Siliceous clusters or lumps can be seen at the base. Integrated analysis from well-logs, cores, thin-sections and seismic data shows that the study area deposited a restricted platform in this period (Liu et al., 2004).

2) Yingshan Formation (O_{1-2ys})

The Ordovician Yingshan Formation is subdivided as Lower Yingshan Formation (O_{1ys}) and Upper Yingshan Formation (O_{2ys}). The Lower Yingshan Formation consists of grey packstone and interbedded packstone-dolomite. The depositional environment of Lower Yingshan Formation was mainly restricted to semi-restricted platform. While in the northern part of Shunnan area, the depositional environment was relatively open due to wide margins, developing thickening packstone of shoal facies. With the rising sea level in the Upper Yingshan Formation, the environment became open gradually, depositing open platform facies such as packstone (Liu et al., 2004).

3) Yijianfang Formation (O_{2yy})

Yijianfang Formation mainly developed wackstone, grey-black in color, where bioclastics (lamellibranch, gastropods, foraminifer, Ostracodes) and algae (algal lump) were locally seen (Liu et al., 2004). During the period of Yijianfang Formation deposited, the depositional environment was open and the water depth was relatively deep.
Figure 3.2 Stratigraphic chart of SN4 well (modified from Yun and Cao, 2014).
(4) Qiaerbake Formation (O$_{3qeb}$)

Integrated analysis shows that the Qiaerbake Formation in the north slope of Tazhong area develops platform margin and wide slope facies with reddish wackstone (Jia, 2004).

(5) Queerqueke Formation (O$_{3eq}$)

The north slope of Tazhong area has a limited distribution for the Queerqueke Formation. According to electronic characters and seismic facies, mudstone and wackstone are the main lithology of this formation with a shallow shelf depositional environment (Jia, 2004).

3.2 Geological Setting of Parkland field

3.2.1 Location

Parkland field is located in the northeast of British Columbia (northwest of the WCSB), adjacent to the boundary of British Columbia and Alberta, close to the Peace River Arch and the Prophet trough (Fig. 3.3A). The major oil/gas fields in the Parkland area include Tangent, Teepee and Gold Creek (Fig. 3.3B). Two normal faults of the Fort St. John graben were identified in the study area, trapping the Parkland on the upthrown sides in the southwest (Fig. 3.3-B). Major gas field was discovered in 1956 in the rare chert reservoir of the Late Devonian Wabamun Group. Together with the adjacent Doe field, these two areas are the only gas fields that sourced from Devonian in the Peace River Block and also northeastern British Columbia (Packard et al., 2001).
Figure 3.3 Location of Parkland and major fields adjacent to Parkland. (A) Location map of Parkland; (B) Location of four major fields including Parkland, Tangent, Teepee and Gold Creek, together with the Fort St. John graben and the following major faults (From Packard et al., 2001).
3.2.2 Tectonic Setting

The WCSB lies in east of the Rocky Mountain with an area of 1.7 million km$^2$, including two major sedimentary basins: the Alberta Basin (in the northwest) and the Williston Basin (in the southeast). The thickness of WCSB reaches the maximum in the west front of Rocky Mountain (almost 6000 m) and pinches out gradually in the eastern part, pinching out on the Canadian Shield (Price, 1986). Tectonic evolution of the WCSB basin is “a continuum including an early rift to passive margin phase (which includes the Middle-Upper Devonian carbonates) to foreland basin in the Middle Jurassic and again from Late Cretaceous to Paleocene” (Moore, 2001).

Four main orogeneses developed during the evolution of the WCSB including the Antler orogeny (Devonian-Carboniferous), the Sonoma orogeny (Permian), the Columbia orogeny (Jurassic-Cretaceous) and the Laramide orogeny (Middle Cretaceous-Neogene) (Fig. 3.4). In Parkland, the current tectonic features include the Prophet trough, the Peace River Arch and the Peace River embayment.

The Prophet trough, extended from southeastern British Columbia to the Yukon Fold Belt (Richards et al., 1991), is regarded as a foredeep which is developed as a downwarp and downfault of the North American plate during the latest Devonian to Early Carboniferous, persisting into the Late Cretaceous (Smith et al., 1993). The trough was exposed during the Late Devonian to the Early Viséan with both Wabamun and later Mississippian carbonate ramps passing westward (Packard et al., 2001).

The Peace River Arch is the cratonic uplift emerging in the Middle Devonian together with the first episode of regional normal faults, then completely buried by carbonate sediments of the Wabamun Group during the Mississippian (Douglas, 1988).
Figure 3.4 Evolution of the Rocky Mountain Foreland Thrust and Fold Belt (From Price, 1986).
Faults formed in the arch during the early time were considered of significant influence on the chert reservoir of Wabamun Group in Parkland (Packard et al., 2001).

The Peace River embayment was a broad, fault-controlled reentrant into the western platform, opening to the Prophet trough. It was formed during the Antler orogeny due to reactivation of Precambrian basement faults (O’Connel et al., 1994). The principal depositional and structural axis of the embayment was coincided with that of the Peace River Arch with extensive faults development (Barclay et al., 1990).

In the Late Devonian, collapse of arch and the embayment may cause the syndepositional extension and shear deformation in the Early to early Middle Tournaisian in Parkland (Eaton et al., 1999). After the evolutions of these essential structures, the Dawson Creek Graben Complex formed, of which the related extension structures played an important role to the development of Parkland trap (Packard et al., 2001).

3.2.3 Depositional Setting and Stratigraphy

The Devonian strata of the WCSB comprise a wide range of shallow-water carbonate systems ranging from pinnacle reefs to epeiric-scale platforms (Switzer et al., 1994). With the feature of a series of W-NW trend carbonate ramps, the Wabamun Group of the WCSB developed a relative open marine sedimentary environment with spherulite and bioclastic carbonate particles, nodular mudstone, limestone and typical absence of reef framework (Packard et al., 2001). In the east and southeast basin, depression of the platforms developed evaporite (Andrichuk, 1956). Eastward to Saskatchewan mainly accumulates argillocalcareous dolomite, shales, anhydrite and red rock layer (Packard et al., 2001).
In Parkland, the Granite Wash and/or Cambrian to Upper Proterozoic directly overlie the Precambrian crystalline basement. The Late Devonian Wabamun Group is the oldest carbonates depositing above the basement. It developed regional hydrocarbon reservoirs associated with chert, cherty dolostone, cherty limestone, dolostone and limestone (Packard et al., 2001). It was subdivided into four units including the Dixonville, Whitelaw, Normandville and Cardinal Lake members, from the oldest to youngest (Halbertsma and Meijer Drees, 1987) (Fig. 3.5).

The Wabamun Group in the study area has a higher proportion of medial and distal-medial ramp facies of quiet-water (and muddier) aspect and the depositional facies can be described in terms of an idealized cleaning and shallowing-upward cycle (Fig. 3.6). This idealized cycle reflects initial marine flooding followed by the progradation (marine offlap) of progressively shallower and higher-energy facies (Packard et al., 2001).

Overlying the Wabamun Group is the relatively thin Exshaw Formation, comprising fine-grained siliciclastics deposited in euxinic-basin to shallow-neritic environments during the Late Famennian and earliest Toumainsian time (Hays, 1985). The Exshaw basal shale ranges in thickness from 2 to 55 m and is present throughout the study area, acting as both the source rock and top seal.
Figure 3.5 Stratigraphic chart in the immediate Parkland and in west-central Alberta. It comprises Mississippian and older formations (From Packard et al., 2001).
Figure 3.6 Idealized shallowing and cleaning-upward cycle in the Wabamun (Parkland) (From Packard et al., 2001).
CHAPTER 4

PETROGRAPHY AND DIAGENESIS

Diagenesis is defined as a series of processes which can influence sediments after deposition (Tucker and Wright, 1990). In Shunnan area, the most prominent diagenetic features in the Yingshan Formation (Ordovician) of SN4 well are quartz replacement and subsequent cementation including calcite and quartz cement. The core and thin section observations indicated that calcite cement is characterized by 3 textures and quartz is characterized by 5 textures together with other diagenetic features. In Parkland, we focus on the pervasive dolomitization, the chert replacement and subsequent cementation in Wabamun Group (Late Devonian). The dolomite is divided into replacement dolomite (2 types) and cement dolomite (2 types). Descriptions of main diagenetic features of the two study areas are discussed in this Chapter.

4.1 Petrography and Diagenetic Features of SN4 well

The Ordovician hydrocarbon reservoirs are identified in 3 strata in Shunnan area including Yijianfang Formation, Yingshan Formation and Penglaiba Formation (Li et al., 2015; Yun and Cao, 2014). The targeted stratum in this study is the Yingshan Formation in SN4 well.

From the 3rd and 4th core intervals of SN4 well, the silicified part recoverable core is 4.64m long. The lithology of the cores, based on the hand specimen examination, is dominated by dark-light grey packstone/grainstone, characterized by grain supported textures with skeletal/peloidal (Fig. 4.1B), as identified in the slightly silicified intervals. The pore spaces are filled with calcite cement. The peloids are normally elliptical and
Figure 4.1 Lithologic column of the silicified intervals of SN4 well. It shows that each section of the intervals develops different degree of silicification.
less than 500 μm (Fig. 4.2A). Low amplitude stylolites are identified with accumulation of organic matter and bitumen (Fig. 4.2E). Dissolution pores and vugs are locally seen filled with calcite cement. Fractures develop from horizontal to high-angle and most of them are generally semi to totally filling with calcite or quartz cement. The variable degree of silicification ranges from the bottom up of the core barrels, which has been divided into four intervals according to the microscopic characteristics as the following list (Fig. 4.1).

(1) Strongly silicified tight packstone/grainstone

At the bottom of the cores (6672.28-6673.52 m), original textures of the packstone/grainstone have been totally silicified. The quartz replacement can be seen packing tightly and leaving no pores among each other (Fig. 4.1A).

(2) Slightly silicified skeletal/peloid packstone/grainstone

The overlying interval consists of skeletal/peloidal packstone/grainstone with original outlines and textures (6670.69-6672.28 m). Pore space among these peloids is filled with calcite cement. Silicification developed within these peloids representing as euhedral quartz (Fig. 4.1B).

(3) Strongly silicified porous packstone/grainstone

Moving stratigraphically upward (6669.49-6670.69 m), the original peloids are strongly silicified. The most distinguished feature from the first silicified interval is the well-developed pore space in this section (Fig. 4.1C), which is considered as the contributor to the high yield gas production.

(4) Siliceous brecciated wackstone/packstone

Capping the cores is light grey wackstone/packstone with local breccias occurring
Figure 4.2 Replacement quartz including CC1, RQ1 and RQ2. (A) RQ1 within the limestone peloids with straight boundaries; CC1 in the pore space among peloids, SN4 well, 6672 m; (B) RQ1 within the limestone peloids with hexagon cross section, SN4 well, 6672 m; (C) RQ1 cut through the original peloids, SN4 well, 6672 m; (D) RQ1 replaced the original grain textures and the calcite cement among the peloids, SN4 well, 6671.64 m; (E) RQ1 was cut by stylolites, SN4 well, 6671.98 m; (F) RQ2 with bending boundaries in the strongly silicified hostrock, SN4 well, 6673.22 m.
from 6668.81 to 6669.49 m. The host wackstone/packstone had been silicified but to a different degree. Pores are not well developed as the third interval. The quartz is mainly in the pore space among the peloids. The distribution of quartz is different from that in the second interval, where the quartz is normally found within the peloids (Fig. 4.1D).

As mentioned above, the most prominent diagenesis in SN4 well is quartz replacement with subsequent cementation. From core and thin section observation, six distinct diagenetic features are identified and discussed as follows.

4.1.1 Quartz

From the samples of SN4 well, replacement quartz and quartz cement (expressed as 4 textures) are identified, based on the size, shape and distribution of the quartz crystals.

4.1.1.1 Quartz replacement

The replacement quartz (RQ) occurring in different abundance can be further divided into 3 textures due to different intensities of silicification described as following.

(1) Replacement quartz in the partially silicified packstone/grainstone (RQ1)

In the matrix of partially silicified peloidal packstone/grainstone, quartz preferentially occurs inside or among the peloids. Quartz inside the peloids develops euhedral crystals with straight boundaries and slender shapes, ranging from 20 μm to 500 μm in length and 5 μm to 10 μm in width. Some quartz represent as hexagon cross sections with the diameter ranging from 20 μm to 60 μm. Almost 70%—90% peloids can be found with this type of quartz (Fig. 4.2A-B). Except for the quartz inside the peloids, much longer and wider quartz can be found replacing the original grain textures and the calcite cement among the peloids, which range from 100 μm to 1000 μm in length and 10 μm to 50 μm in width with straight edges and euhedral crystal shapes (Fig.
4.2C-D). Some quartz can be seen cut by stylolites reflecting that this kind of quartz predates the stylolites (Fig. 4.2E).

(2) Replacement quartz in the completely silicified packstone/grainstone (RQ2)

The host rock completely silicified develops subhedral to xenomorphic quartz with bending boundaries, ranging from 100 μm to several millimeters in length and 10 μm to 30 μm in width (Fig. 4.2F). In the porous interval, pore space is well developed. Quartz is packed loosely with relative straight edges. In the tight silicified cores, quartz is packed tightly with bending boundaries, leaving no pore space left.

(3) Replacement quartz rims on the margin of the completely silicified packstone/grainstone (RQ3)

Moving from the matrix to fractures (or dissolution caves), it appears an obvious rim (between the yellow line in Fig. 4.3) where the quartz was ranging from 10 μm to 50 μm with subhedral to xenomorphic crystals. Quartz in this rim is much smaller than RQ2 and also packing tightly, which can be easily distinguished under the polarized light (Fig. 4.3).
Figure 4.3 Replacement quartz including RQ3. (A) RQ3 distributed in the fracture, SN4 well, 6673.22 m; (B) RQ3 distributed in the dissolution caves, SN4 well, 6670.48 m.
4.1.1.2 Quartz cement

Fractures and dissolution pores/vugs massively develop with quartz and calcite cement semi-filled or fully filled. Based on the size, shape and distribution of the quartz, quartz cement with 4 textures are identified.

(1) Equant Quartz (QC1)

Equant quartz (QC1) has long aixs to short ratio around 1 and distributed along the boundary of fractures (or dissolution pores/vugs) (Fig. 4.4A). Equant quartz ranges from 50 μm to 500 μm in length and 50 μm to 500 μm in width, with straight edges. The quartz ranges from euhedral to subhedral, revealing hexagon-section with diameter less than 500 μm. Equant quartz commonly has a dark rim and a clear core (Fig. 4.4B). The dark rim is related to the occurrence of abundant fluid inclusions (Fig. 4.4C).

(2) Bladed quartz (QC2)

Toward to the center of fractures and/or dissolution vugs, quartz cement is composed of increasingly larger crystals comparing to QC1, ranging from 500 μm to 1000 μm in length and 100 μm to 500 μm in width, which is named bladed quartz (QC2). Bladed quartz is euhedral to subhedral with relative straight edge and most of them are characterized by several dark belts which are full of fluid inclusions (Fig. 4.5A-B). The bladed quartz has a long axis to short ratio above 2.
Figure 4.4 Quartz cement including QC1. (A) QC1 along the edge of fracture, SN4 well, 4-10/11, 6673.22 m; (B) QC1 with seldom inclusions; (C) QC1 with abundant inclusions.
Figure 4.5 Quartz cement including QC2, QC3 and QC4. (A) Bladed quartz with black rims full of fluid inclusions, SN4 well, 4-7/11, 6371.9 m; (B) Annular belt forming by the fluid inclusions, SN4 well, 4-7/11, 6371.9 m; (C-D) Overgrowth quartz at the end of bladed quartz, SN4 well, 4-10/11, 6673.22 m; (E-F) Secondary quartz belt cutting former matrix and cement, SN4 well, 4-10/11, 6673.22 m.
(3) Overgrowth (QC3)

The quartz precipitated in optical continuity with the framework of QC2 is referred to as overgrowth (QC3). The boundaries between QC2 and the overgrowth are commonly irregular which can be easily identified (Fig. 4.5C-D). The width of the overgrowth can range from 10 μm to 70 μm. Fewer fluid inclusions develop in the overgrowth comparing to QC2 crystals (Fig. 4.5C-D).

(4) Quartz cement in later stage fractures (QC4)

Quartz cement filling in late fractures cutting through the early replacement and QC1 to QC3 is identified as the last phase of quartz cement (QC4) (Fig. 4.5E-F). This type of quartz could not be found during the development of regular crystal framework like QC1 to QC3. Many secondary fluid inclusions are distributed along these fractures.

4.1.2 Calcite cement

Calcite cement is found variably throughout host rock with different degrees of silicification. Based on the cores from SN4 well, 3 types of calcite cement have been identified.

(1) Early calcite cement (CC1)

Early calcite cement (CC1) is mainly developing in the pore space in slightly silicified peloidal packstone/grainstone (Fig. 4.2A). The calcite crystals are anhedral and range from 5 μm to 50 μm. It is the most abundant calcite cement before the hostrock is silicified, which may precipitate from synsedimentary seawater when the peloidal packstone/grainstone began to deposit. Replacement quartz (RQ) is found cutting the calcite among the pore space which indicates that the CC1 predate RQ (Fig. 4.2C).
(2) Coarsely crystalline calcite cement in slightly silicified packstone/grainstone (CC2)

Coarsely crystalline calcite cement (CC2) is mainly developing in the fractures in slightly silicified packstone/grainstone. The crystals range from 30 μm to 1000 μm with subhedral to anhedral shapes. The fractures filled with CC2 can be found cutting replacement quartz (RQ), indicating that CC2 postdates RQ (Fig. 4.6A-B). CC2 is also found filling the pore space among RQ (Fig. 4.6C). In some hand specimens, fractures filled with CC2 are cut by those filled with quartz cement (QC1-QC3), suggesting that CC2 predates quartz cement (Fig. 4.6D).

(3) Late-stage calcite cement in strongly silicified packstone/grainstone (CC3)

Late-stage calcite cement (CC3) has larger crystals which can be up to a few centimeters in size with euhedral to subhedral shapes. They are mainly found filling late fractures in strongly silicified packstone/grainstone. These late fractures are firstly occluded with quartz cement, leaving the residual space for CC3, suggesting that CC3 postdates quartz cement (QC1-QC3) (Fig. 4.6E-F).

4.1.3 Dissolution features

Dissolution vugs/pores are the main dissolution features in SN4 well. The majority of these vugs and pores are commonly developing along fractures or near the intersection of conjugated fissures. Only few occurred as isolated vugs. They range from 1 mm to several centimeters in size and are semi-filled or totally-filled with calcite and quartz. Pore space can be found well developed under microscope which is considered as the contributor to the high gas production of the silicified reservoir (Fig. 4.7).
Figure 4.6 Calcite cement in silicified intervals of SN4 well including CC2-CC3. (A) CC2 in the slightly silicified hostrock, cutting the replacement quartz, under plane polarized light; (B) CC2 in the slightly silicified hostrock, cutting the replacement quartz, under Orthogonal light; (C) CC2 distributed in the pore space among RQ; (D) CC2 cut by the quartz cement in hand specimen; (E-F) CC3 postdates quartz cement in late fractures.
Figure 4.7 Dissolution features in the silicified intervals of SN4 well. (A) Dissolution pores distributed along fractures with no fillings inside (SN4; 6673.2 m); (B) Dissolution pores with high porosity, plane polarized light (SN4; 6669.97 m); (C) Dissolution pores with high porosity, cross polarized light (SN4; 6668.3 m); (D) Dissolution vug filled with calcite (SN4; 6668.3 m); (E) Dissolution vug filled with calcite, plane polarized light (SN4; 6668.3 m).
4.1.4 Stylolites

Stylolites are specific interdigitation features forming as a result of intergranular pressure solution (Nenna and Aydin, 2011). Stylolites mainly develop in the siliceous grainstone with low amplitude and cut the floating quartz, reflecting that there develops a stage of compaction after the early silicification (Fig. 4.2E).

4.1.5 Dolomite cement

Dolomite cement is not common in SN4 well. Only small amount are distributed along stylolites together with organic matter. The dolomite crystals have relative euhedral shape and planar-e texture, ranging from 10 μm to 50 μm in size (Fig. 4.8A). They may deposit from the fluid flowing through the stylolites as cement.

4.1.6 Fractures

Fractures are well developed from the cores of SN4 well ranging from horizontal to high-angle. They intersect with each other, forming ‘V’ shaped dissolution vugs and can be generally divided into 3 generations based on the filling cement: (1) fractures filled with calcite cement (CC2) in the slightly silicified packstone/grainstone (Fig. 4.8C); (2) fractures filled with quartz cement (QC1-QC4) in the strongly silicified packstone/grainstone (Fig. 4.8B); (3) fractures filled with quartz cement and late calcite cement (CC3) in the strongly silicified packstone/grainstone (Fig.4.8 D). Fractures with different cement may relate to different tectonic activities.
Figure 4.8 Dolomite cements and fractures in the silicified intervals of SN4 well. (A) Dolomite distributed along stylolite (SN4; 6671.2 m); (B) Fracture filled with quartz in strongly silicified hostrock (SN4; 6672.98 m); (C) Fracture filled with calcite in slightly silicified hostrock (SN4; 6673.4 m); (D) Fracture filled with quartz and late calcite cement (SN4; 6673.1 m).
4.1.7 Diagenetic Paragenesis

The carbonates from Yingshan Formation of Lower Ordovician in SN4 well went through a complex diagenetic alteration including compaction, fracturing, dissolution, silicification and cementation.

Replacement quartz (RQ) can be found both in the slightly and strongly silicified packstone/grainstone in SN4 well, replacing the original peloids and CC1, suggesting that RQ postdates CC1 (Fig. 4.2C). In some samples, RQ can be seen crosscut by early stylolites, suggesting RQ postdates early stylolites (Fig. 4.2E). Fractures filled with CC2 in slightly silicified packstone/grainstone of SN4 well are crosscut by those filled with quartz cement (QC1-QC4) (Fig. 4.6D), indicates that CC2 postdates RQ and predates quartz cements (QC1-QC4). CC3 fills residual space left by quartz cements (QC1-QC4) in fractures in strongly silicified packstone/grainstone (Fig. 4.6F), suggesting that CC3 postdates quartz cement (QC1-QC4). Based on the illustration mentioned above, the paragenetic sequence including mainly diagenetic features is summarized in Figure 4.9.
Figure 4.9 The diagenetic sequence in the SN4 well. Gradual changing boxes indicate that the relative timing of the diagenetic event is ambiguous.
4.2 Petrography and Diagenetic Features of Parkland field

The Wabamun Group of the Upper Devonian is the target stratum of Parkland field. The lithology is dominated by grey dolomite and dark grey packstone/grainstone. Dissolution pores and vugs can be locally seen filled with calcite cement and saddle dolomite. Fractures are well-developed representing as mesh structure semi-filled to totally-filled with cement such as calcite, saddle dolomite and chert. Based on the core examination of 6 wells, massive of the original limestone of has been dolomitic.

Together with the pervasive replacement chert, the dolomitization and silicification are the most fundamental diagenetic features of the Wabamun Group in Parkland field. Along with the observation of thin sections, descriptions of a series of diagenesis are listed.

4.2.1 Dolomite

Dolomite represents as both replacement in the matrix and cement filling the fractures or dissolution pores. Based on the crystal size, surface shape (planar or nonplanar) (Sibley and Gregg, 1987) and distribution, 3 types of replacement dolomite and 3 categories of cement dolomite have been identified.

4.2.1.1 Replacement dolomite

(1) Fine crystalline dolomite (RD1)

RD1 is mainly distributed in the dark grey non-dolomitic or partially dolomitic mudstone/wackstone. Biologic skeleton and sedimentary structures are well preserved in RD1. The RD1 crystals are ranging from 10 μm-50 μm without undulatory extinction and show subhedral with planar-s textures (Fig. 4.10A-B). The crystals are packing tightly with low porosity. The only intercrystalline space is filled with organic matter.
Figure 4.10 Replacement dolomite in Parkland including RD1 and RD2. (A-B) Very fine to finely crystalline dolomite (RD1); (C-F) Medium to coarse crystalline dolomite (RD2).
(2) Medium to coarse crystalline dolomite (RD2)

In hand specimens, RD2 is grey to light grey in color. The crystals range from 100-1000 μm in size and display anhedral to subhedral with non-planar to planar-s textures. The crystals are packing tightly with low porosity and nearly no dark organic matter exists in the remnant intercrystalline space. Most of the crystals have a cloudy core and relatively clear rim. No undulatory extinction is observed. Under cathodoluminescence (CL) light, the crystals display dull red in the cloudy center and bright red luminescence in the rim (Fig. 4.10C-F). Volumetrically, RD2 dolomites make up about 80-90% of the total dolomite matrix volume.

4.2.1.2 Dolomite cement

Dolomite cement is generally developing in the dissolution pores/vugs or fractures in the study area. Based on the crystal size, shape and distribution, two types of dolomite crystals were identified in dolomite cement: medium to coarse crystalline dolomite and saddle dolomite

(1) Medium to coarse crystalline dolomite cement (CD1)

CD1 is either grey or grey-white in hand specimen. The crystals are ranging from 50 μm to 1mm, distributing in the dissolution pores/vugs (Fig. 4.11A). They are euhedral to subhedral with planar-e(s) textures and they display sweeping extinction within a single crystal under cross-polarized light. They show dull red luminescence under CL (Fig. 4.11B).
Figure 4.11 Dolomite cement in Parkland including CD1 and CD2. (A-B) CD1 in Parkland with dull luminescence under CL; (C) Saddle dolomite with brown color; (D-E) CD2 commonly seen in Parkland with dull red luminescence in the crystal center and light red luminescence in the rim.
(2) Saddle dolomite (CD2)

Saddle dolomite is commonly milky white in hand samples which can be easily distinguished from the matrix replacement dolomite. In some samples, the saddle dolomite is light brown which may relate to certain minerals such as sulphide (Fig. 4.11C). The dolomite crystals of the saddle dolomite cement range from 50 μm to 2 mm in size and the crystal shape changes from slightly curved to scimitar-like terminations. Under cross-polarized light, they exhibit distinctive sweeping extinction. Under CL, saddle dolomite cement displays dull red luminescence in the crystal center while the light red luminescence occurs in the rim (Fig. 4.11D-E). Saddle dolomite occurs as cement in fractures or dissolution pores/vugs in the partially or completely dolomitic mudstone/wackstone.

4.2.2 Silicification

The thickness of the silicification varies in different wells of Parkland (8 m in the 10-28 well, 35 m in the 6-29 well, and 5 m in the 10-11 well), with the porosity up to 30% and the permeability reaching 37mD in maximum (Packard et al., 2001). Two forms of the crystalline silica have been interpreted in previous work including chert nodules (consisting of microquartz and chalcedony) and replacement chert (Packard et al., 2001). Based on the core and thin section observations, a third type of silica has been identified which is the euhedral quartz cement. Descriptions of the 3 types of silica are listed combining the previous work by Packard et al. (2001).

(1) Chert Nodule

In hand specimens, chert nodules are found isolated with irregular shapes (Fig. 4.12A). They represent grey to brown in color with diameter size ranging from 4cm to
Figure 4.12 Silicon composition in Parkland including 3 textures. (A) Chert nodule, 10-26-81-16w6 well, 3272.08 m; (B) Stylolite in RD2, 10-28-81-16w6 well, 3371.5 m; (C) Microquartz replacement, 10-26-81-16w6 well, 3469.88 m; (D) Replacement chert in the dissolution pores, 10-28-81-16w6 well, 3279.0 m; (E) Large euhedral quartz filling dissolution pores, 10-26-81-16w6 well, 3459.24 m; (F) Quartz cement in the dissolution pores, 10-26-81-16w6 well, 3439.75 m.
15cm comprising microquartz and chalcedony (Fig. 4.12B). The chalcedony is
distributed in the cover of organism structure with a certain direction.

(2) Chert

The chert is massively developing in the dolostone of 10-28 well (3262.2 m to
3278.7 m) with dark brown in color, which can be easily distinguished from the grey
dolostone. In thin sections, the replacement chert representing as microcrystal ranging
from 10 μm to 100 μm, postdating the earlier dolomite replacement (Fig. 4.12C). It can
also be found as cement filling the fractures or dissolution pores/vugs, postdating saddle
dolomite (Fig. 4.12D).

(3) Quartz cement

In hand specimens, large and clear quartz crystals are found with hexagonal prisms
structures in 10-26 well and 10-28 well (Fig. 4.12E), filling the fractures and dissolution
vugs. Microscopically, the quartz is up to 1 cm in length and 5 mm width occurring as
euhedral crystals. The quartz cement grows after CD2 and calcite cement, suggesting
that it postdates the CD2 and calcite cement (Fig. 4.12F).

4.2.3 Calcite cement

Two types of coarse calcite cement (CC) including CC1-p and CC2-p are identified
based on their distribution. CC1-p is white in hand specimen and mainly distributed in
the dissolution pores/vugs and fractures in slightly dolomitic mudstone/wackstone (Fig.
4.13A-B). The crystals range from 100 μm to 250 μm with subhedral to anhedral shapes.

CC2-p has the same color as CC1-p, depositing after saddle dolomite and quartz in
the fractures of dolostone, suggesting that CC2-p postdates the saddle dolomite and
quartz cement. The crystals can be up to 1mm with subhedral shapes (Fig. 4.13C-D).
Figure 4.13 Fractures and dissolution features in Parkland. (A) Fracture filled with CC1-p in the mudstone; (B) Dissolution pores filled with CC2-p; (C) Pyrite aggregates in the dolomitic mudstone; (D) Dissolution pores/vugs semi-filled with anhydrite cement; (E) Dissolution vugs semi-filled with saddle dolomite; (F) Horizontal stylolite cuts fracture which is filled with saddle dolomite; (G) Multiple stages of fractures forming netted seams.
4.2.4 Pyrite cement

Pyrite develops as small nodule sporadically in the dolomitic matrix or fractures. The nodules range from 0.5 mm to several centimeters. Pyrite aggregates can also be found in the cores such as well 10-28 (Fig. 4.13C). Pyrite is widely spread and can either deposit in early or late stage.

4.2.5 Anhydrite cement

Anhydrite occurs as cement filling the fractures or dissolution pores associated with saddle dolomite, calcite and pyrite (Fig. 4.13D). It displays translucent greyish to white in color and has a form of cleavage masses. Its appearance may relate to an exposure event since anhydrite is most frequently found in evaporate, or associate to mineral deposited fluid flow.

4.2.6 Dissolution features

In Parkland, the carbonate host rocks were subjected to crucial dissolution (Packard et al., 2001). From the core observation, dissolution features are mainly representing as pores and vugs widespread especially in the dolomite cores of 10-26 well and 10-28 well. The dissolution pores and vugs range from 1 cm to tens of cm in diameter with circle to ellipse shapes, partially or completely filled by saddle dolomite, calcite and microcrystalline chert (Fig. 4.13E). Some pores and vugs are found with a special texture which is the grey medium dolomite fill the bottom while the upper space is occluded by white saddle dolomite. This texture is interpreted as geopetal structure (Fig. 4.12D) (Packard et al., 2001).
4.2.7 Compaction

Stylolites are identified in core samples of the study area. The stylolites show different amplitude ranging from 1 mm to 5 mm and develop organic matter nearby. Most of the stylolites are horizontal and only few have a high angle. Figure 4.13F shows that horizontal stylolites cutting a fracture which is filled with saddle dolomite, suggesting that there develops a late stage of stylolite after fracturing.

4.2.8 Fractures

Intensive tectonic activities in the study areas resulted to multiple fractures and fissures development. From core and thin section observations, there develops at least four generations of fractures.

The first generation is observed as thin and horizontal microfractures without any fillings and distributed randomly in mudstone/wackstone. Some are crosscut by closed low amplitude stylolites which indicate that the first generation fractures predate the early compaction. The second generation of fracturing is filled with white calcite cement and crosscut early stylolites, mainly developing in mudstone/wackstone. The width of the fractures is less than 1 cm. The third generation is much wider than the second one and mainly distributed in dolostone. They are found crosscutting the matrix dolomite and occluded by saddle dolomite and calcite. From the cores of 10-26 well and 10-28 well, the third generation represents as both horizontal and vertical. Within some core intervals, the horizontal fractures interlace the vertical forming netted seams. The last generation filled with microcrystal chert cross-cuts the third generation mostly developing in the silicified segments (Fig. 4.13G).
4.2.9 Diagenetic Paragenesis

The Wabumun Group carbonates of Upper Devonian in Parkland have been subject to a complex diagenetic history. Micrite distributed in the original mudstone and/or wackstone has the similar features as those in SN4 well. However, the occurrence of replacement dolomite interbedded with mudstone/wackstone is unique in Parkland area. The paragenetic sequence is summarized in Fig. 4.14.

Chert nodules and the low amplitude horizontal stylolites distributed in the original mudstone and/or wackstone (Fig. 4.12A) are crosscut by hairline fractures, suggesting that the hairline fractures postdate the early chert nodules and stylolites. RD1 is well developed in the slightly dolomitic mudstone/wackstone, replacing the original hostrock (Fig. 4.10A). In some samples, small dissolution pores are filled with internal clastics and calcite cement (CC1) (Fig. 4.13B), suggesting that CC1 postdates RD1. As the buried depth increasing, RD2 becomes abundant (Fig. 4.11A). Stylolites are found crosscutting the crystals of RD2 (Fig. 4.12B), suggesting that there develops at least one stage of stylolite after RD2 depositing. Fractures filled with CD2 (Fig. 4.13E) are well developed in RD2 indicating that the CD2 postdates RD2. Samples of 10-28 well develop chert replacement in RD2 and chert cement in the dissolution vugs (Fig. 4.12D), suggesting that the chert postdates RD2 and CD2. Euhedral quartz crystals fill in the fractures and dissolution vugs after CD2 (Fig. 4.12E), indicating that the euhedral quartz postdates CD2. CC2 can be found filling the residual space of the fractures after the euhedral quartz (Fig. 4.12F), suggesting that CC2 postdates CC2.
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**Figure 4.14** The diagenetic sequence in Parkland. Gradual changing boxes indicate that the relative timing of the diagenetic event is ambiguous.
CHAPTER 5

ISO TOPE AND FLUID INCLUSION STUDIES

Isotope exchange and fractionation can occur during phase transformation, mineral precipitation and diagenetic reactions (Land et al., 1983), which are generally used to analysis the carbonate rocks and fluids during precipitation. As for the SN4 well, three types of calcite components are sampled and analyzed for carbon and oxygen isotopes. Two major types of quartz including replacement quartz and quartz cement are chosen and analyzed for silicon and oxygen isotopes using SIMS. In Parkland, dolomite including replacement dolomite and dolomite cement is analyzed for C-O and Sr-O isotopes, as well as calcite cement.

Fluid inclusions studies contain petrographic descriptions and microthermometric measurements. Microthermometry studies include homogenization ($T_h$), ice-melting ($T_{m\text{-}ice}$) and hydrohalite melting ($T_{m\text{-}HH}$) measuring. $T_h$ can tell the temperature at which two phases are homogenized into a single phase which would provide a minimum temperature when the fluid was trapped. $T_{m\text{-}ice}$ and $T_{m\text{-}HH}$ can provide the compositions of the fluid inclusions. For both of the two areas, different types of fluid inclusions were identified and microthermometry analyses were performed in this study.

5.1 Geochemical analysis results of SN4 well

5.1.1 Carbon and oxygen isotope results

A total of 32 samples were analyzed for the three types of calcite components. The results are listed in Table 5.1 (from Chen et al., 2015) and Table 5.2. Calcite depositing from Middle Ordovician seawater had the $\delta^{13}C$ values of -1.9 – -0.1 (‰ vPDB) and the
$\delta^{18}$O values of -8 – -5.6 (‰ vPDB), based on the study of calcite and phosphatic shells in Phanerozoic seawater (Veizer et al., 1999) (Fig. 5.1).

- On the basis of statistical calculations in this study, the $\delta^{13}$C values of CC1 samples (n=7) range from -0.02 to 0.48 (‰ vPDB) with an average of 0.23 (‰ vPDB) and the $\delta^{18}$O values spread from -8.31 to -4.60 (‰ vPDB) with an average of -6.53 (‰ vPDB) (Fig. 5.1 and Table 5.1).

- The $\delta^{13}$C values of CC2 (n=19) vary from -4.82 to -1.82 (‰ vPDB) with an average of -3.25 (‰ vPDB). The $\delta^{18}$O values spread from -11.73 to -4.87 (‰ vPDB) with an average of -8.89 (‰ vPDB) (Fig. 5.1, Table 5.1 and Table 5.2).

- CC3 samples (n=6) have the $\delta^{13}$C values ranging from -4.2 to -2.89 (‰ vPDB) with an average of -3.57 (‰ vPDB) and the $\delta^{18}$O values from -12.93 to -11.33 (‰ vPDB) with an average of -12.22 (‰ vPDB).

The $\delta^{13}$C values of all the calcite cement are out of the $\delta^{13}$C range of Middle Ordovician marine calcite. Except for some of CC1 and CC2, all the other calcite cement develops different $\delta^{18}$O values with those depositing from Middle Ordovician seawater (Fig. 5.1).
Figure 5.1 Cross plot of $\delta^{13}$C and $\delta^{18}$O of the calcite cement in SN4 well. Isotope signatures of the Middle Ordovician marine calcite are indicated by square of solid red line (Veizer et al., 1999).
Table 5.1 $\delta^{13}$C and $\delta^{18}$O values of calcite (CC1, CC2) in Shunnan area
(from Chen et al., 2015)

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Table 5.2 $\delta^{13}$C and $\delta^{18}$O values of calcite (CC2 and CC3) in SN4 well

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5.1.2 Si and O isotope results

Based on the quartz classification in Chapter 4, eight ROIs were circled on selected standard thin sections including replacement quartz and quartz cement which were large enough (>50 microns) to be processed. A total of 75 pairs of spots were made (20 µm across and 2 µm deep) and measured (one for silicon isotope and the other for oxygen) (Fig. 5.2) in these ROIs. The data of δ\textsuperscript{30}Si (‰ vNBS28) and δ\textsuperscript{18}O (‰ SMOW) are shown in each of the ROIs corresponding to the spots (Fig.5.3~Fig5.5) and listed in Table 5.3. The cross plot of δ\textsuperscript{30}Si and δ\textsuperscript{18}O is shown in Fig. 5.6.

1) Replacement quartz

- Ten pairs of spots were analyzed for RQ1 (Fig. 5.3-5.5). The δ\textsuperscript{30}Si values of RQ1 (n=10) range from 1.90 to 2.56 (‰ NBS28) with an average of 2.31 (‰ NBS28); δ\textsuperscript{18}O values range from 21.30 to 23.22 (‰ SMOW), average of 22.23 (‰ SMOW) (Fig. 5.6 and Table 5.3).

- RQ2 (Fig. 5.3-5.5) spots (n=21) have the average δ\textsuperscript{30}Si value of 2.28 (‰ NBS28) with a spread from 1.91 to 2.74 (‰ NBS28). The δ\textsuperscript{18}O values vary from 20.51 to 24.44 (‰ SMOW), average of 22.45(‰ SMOW) (Fig. 5.6 and Table 5.3).

- The δ\textsuperscript{30}Si values of RQ3 (n=7) (Fig. 5.3 and Fig. 5.5) range from 1.43 to 2.4 (‰ NBS28) with an average of 2.00 (‰ NBS28); δ\textsuperscript{18}O values range from 21.11 to 24.95 (‰ SMOW), average of 23.41 (‰ SMOW) (Fig. 5.6 and Table 5.3).
Figure 5.2 Images of two ROIs showing how the spots were made in pairs on the quartz for silicon and oxygen isotope analysis.
Figure 5.3 ROIs of two samples show spot location and corresponding values of $\delta^{30}$Si and $\delta^{18}$O in SN4 well. (A) ROI of 6670.39 m consists of RQ, QC1-QC3; (B) ROI of 6669.61 m consists of RQ, QC1-QC3.
**Figure 5.4** ROIS of two samples show spot location and corresponding values of $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ in SN4 well. (A) ROI of SN3-18 consists of RQ1; (B) ROI of SN3-3 consists of RQ2.
Figure 5.5 ROI of sample QHR3B show spot location and corresponding values of $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ in SN4 well, including RQ and QC1-QC4.
Table 5.3 $\delta^{30}$Si and $\delta^{18}$O values of quartz (RQ1-3, QC1-QC4) in Shunnan area

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Table 5.3 $\delta^{30}$Si and $\delta^{18}$O values of quartz (RQ1-3, QC1-QC4) in Shunnan area (Continued)

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<tr>
<th>Qz</th>
<th>Sample spot</th>
<th>$\delta^{30}$Si (%NBS28)</th>
<th>$\delta^{18}$O (%SMOW)</th>
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<td>QHR3B@16</td>
<td>2.34</td>
<td>23.84</td>
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</table>

Figure 5.6 Cross plot of $\delta^{30}$Si and $\delta^{18}$O values of quartz both in the matrix and cement (RQ1-RQ3, QC1- QC4) in SN4 well.
(2) Quartz cement

- Thirty eight spots were analyzed for QC1 – QC4. The $\delta^{30}\text{Si}$ values of QC1 (n=8) (Fig. 5.4A) range from 1.66 to 2.46 (‰ NBS28) with average of 1.98 (‰ NBS28); $\delta^{18}\text{O}$ values vary from 22.59 to 25.43 (‰ SMOW), average of 23.72 (‰ SMOW) (Fig. 5.6 and Table 5.3).
- QC2 spots (n=22) (Fig. 5.3 and Fig. 5.5) have $\delta^{30}\text{Si}$ values range from 1.76 to 2.45 (‰ NBS28) with an average value of 2.08 (‰ NBS28); $\delta^{18}\text{O}$ values from 20.47 to 25.36 (‰ SMOW), average of 23.17 (‰ SMOW) (Fig. 5.6 and Table 5.3).
- The $\delta^{30}\text{Si}$ values (n=4) of QC3 (Fig. 5.3 and Fig. 5.5) vary from 1.84 to 2.48 (‰ NBS28), average of 2.24 (‰ NBS28); $\delta^{18}\text{O}$ values range from 22.00 to 23.51 (‰ SMOW) with an average of 22.84 (‰ SMOW) (Fig. 5.6 and Table 5.3).
- The $\delta^{30}\text{Si}$ values of QC4 (n=4) (Fig. 5.5) range from 1.60 to 2.34 (‰ vNBS28), average of 2.02 (‰ vNBS28); $\delta^{18}\text{O}$ values vary 23.36 to 23.84 (‰ SMOW) (mean of 23.66) (Fig. 5.6 and Table 5.3).

5.1.3 Fluid inclusion results

Petrographic descriptions and microthermometric measurements are mainly completed by our collaborator Mr. Lu and all the results have been published elsewhere (Lu et al., 2017). My work mainly focused on the petrography of the silicified rocks in both of the two areas and selected samples for further geochemical analysis. The details of petrography and microthermometry of fluid inclusions are summarized from (Lu et al., 2017) as follows.
5.1.3.1 Petrography

Fluid inclusions can be explained as primary inclusions and secondary inclusions based on the medium in which they were trapped (Goldstein, 2003). Fluid inclusions along growth zones (Fig. 5.7D) are considered to be the primary inclusions, together with those in clusters in this study. Fluid inclusions occurred in trails which crosscut crystal boundaries (Fig. 5.7A-C) are regarded as secondary trapped. Randomly distributed fluid inclusions in one crystal cannot be judged about the origin (Fig. 5.7F).

In CC2, fluid inclusions mainly comprise liquid-dominated biphase, vapor-dominated biphase, vapor-only inclusions and triphase inclusions (Fig. 5.7A-C). Triphase inclusions are randomly distributed and the other three types are mainly in trails. CC3 mainly develops liquid-dominated, liquid-only and triphase inclusions.

In RQ and QC2, liquid-dominated and triphase inclusions are distributed in clusters (Fig. 5.7A-C). In QC3, fluid inclusions in growth zones and clusters comprise liquid-dominated, vapor-dominated and vapor-only types (Fig. 5.7D-E). QC4 mainly develops liquid-dominated, liquid-only and triphase inclusions present in clusters.

5.1.3.2 Microthermometry

From the samples of SN4 well, 134 randomly distributed fluid inclusions in CC2–3, 274 primary fluid inclusions and 133 secondary fluid inclusions in quartz (RQ and QC1–3) are recognized and analyzed by Lu et al., 2017. The data of the fluid inclusions in CC1–3, including the $T_h$, $T_{m-ice}$ and salinities, are listed in Table 5.4. Those in quartz (RQ, QC1–3) are listed in Appendix.

(1) Fluid inclusions in calcite
Figure 5.7 Photomicrographs show fluid inclusion petrography. (A) Fluid inclusions distributed in long trails which crosscut the quartz crystal boundary; plane polarized light; (B) Fluid inclusions distributed in long trails which crosscut the calcite (CC2) crystal boundary; plane polarized light; (C) Liquid-dominated, vapor dominated and vapor-only fluid inclusions coexisted in long trails in CC2; plane polarized light; (D) Fluid inclusions outlined the growth zone in core of bladed quartz (QC2); plane polarized light; (E) Liquid-dominated, vapor-dominated and vapor-only fluid inclusions coexisted in growth zone in core of bladed quartz (QC2); plane polarized light; (F) Fluid inclusions distributed in random populations in CC2; plane polarized light (From Lu et al., 2017).
The fluid inclusions distributed randomly in CC2 have the T\textsubscript{h} values ranging from 124.0°C to 162.0°C with an average of 147.0°C. The T\textsubscript{m-ice} values range from -26.8°C to -14.6°C (average -20.21°C). Salinities spread from of 17.8-25.2 wt% NaCl+CaCl\textsubscript{2} (Table 5.4). Two FIAs in trails (secondary) in CC3 have T\textsubscript{h} values of 183–186°C and 179.0-185.0°C, and a T\textsubscript{m-ice} value of -1.3°C, with a salinity of 2.1 wt% NaCl (Table 5.4 and Fig. 5.8).

(2) Fluid inclusions in quartz

Fluid inclusions in clusters in RQ have T\textsubscript{h} values of 162.0–186.0°C and 173.0–203.0°C, and T\textsubscript{m-ice} values of -19.5 – -19.2°C and -19.7 – -18.6°C, with salinities of 21.8 – 22.1 and 21.4 – 22.2 wt% NaCl+CaCl\textsubscript{2}, respectively (Appendix and Fig. 5.8). Fluid inclusions in clusters and growth zones in QC1 have average T\textsubscript{h} values of 143.0–159.0°C and average T\textsubscript{m-ice} values of -22.3 – -15.0 °C, with average salinities of 18.5 – 23.7 wt% NaCl+CaCl\textsubscript{2} (Appendix and Fig. 5.8). The average T\textsubscript{h} values of the fluid inclusions in QC2 clusters and growth zones range from 154.0°C to 166.0°C and the average T\textsubscript{m-ice} values range from -16.8°C to -10.7°C, with average salinities of 14.7 – 20.0 wt% NaCl+CaCl\textsubscript{2} (Appendix and Fig. 5.8).

QC3 develops both liquid-only and liquid-dominated fluid inclusions in clusters, with average T\textsubscript{h} values of 125.0–132.0°C and average T\textsubscript{m-ice} values of -32.1 to -25.4°C, The average salinities is about 24.8–26.8 wt% NaCl + CaCl\textsubscript{2} (Appendix and Fig. 5.8). Secondary fluid inclusions distributed in trails in replacement quartz and quartz cement have average T\textsubscript{h} values of 172.0–186.0°C and average T\textsubscript{m-ice} values of -6.5 – -0.9°C, with salinities of 1.4–10.1 wt% NaCl (Appendix and Fig. 5.8).
Table 5.4 Microthermometric data of fluid inclusions in calcite samples (from Lu et al., 2017)

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<th>T_m range (°C)</th>
<th>Salinity range (wt% NaCl)</th>
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<td>23.8 – 24.3</td>
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<td>S4-2</td>
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<td>24.1 – 24.3</td>
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<td>2.1 (average)</td>
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<td>Long trails</td>
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<td>179.0 – 185.0</td>
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Figure 5.8 Cross plot of homogenization temperatures ($T_h$) and ice-melting temperatures ($T_{m_{\text{ice}}}$) of fluid inclusions in calcite cement (CC2–CC3) and quartz (RQ, QC1-QC3) in SN4 well.
5.2 Geochemical analysis results of Parkland

5.2.1 Carbon and oxygen isotope results

The results of carbon and oxygen isotopes of dolomite (both in the replacement and cement) and calcite cement are listed in Table 5.5. Calcite depositing from Upper Devonian seawater has the $\delta^{13}$C values of -0.5 – +2.0 (‰ vPDB) and the $\delta^{18}$O values ranging from -7 to -4 (‰ vPDB) (Fig. 5.9) (Veizer et al., 1999). The carbon isotope fractionation has no obvious difference between dolomite and calcite (Land, 1985). That is dolomite depositing from Upper Devonian seawater share the same $\delta^{13}$C trend as the coeval calcite (Land, 1985). As for the $\delta^{18}$O, dolomite would develop a relative higher $\delta^{18}$O value (generally 2‰) than the coeval calcite. Based on the $\delta^{18}$O values of the calcite precipitating from the Upper Devonian seawater, the coeval dolomite has the $\delta^{18}$O values ranging from -5 to -2 (‰ vPDB) (Land, 1985).

Twenty four samples of RD1 and RD2 and fifteen of CD1 and CD2 were selected and analyzed, together with five samples of calcite cement.

- RD1 have the $\delta^{13}$C values ranging from 0.89 to 1.76 (‰ vPDB) with the average of 1.35 (‰ vPDB); $\delta^{18}$O values from -10.39 to -8.03 (‰ vPDB), average of -8.97 (‰ vPDB) (Figure 5.9 and Table 5.5).
- The $\delta^{13}$C values of RD2 range from 0.25 to 1.19 (‰ vPDB) with average of 0.66 (‰ vPDB); $\delta^{18}$O values vary from -11.46 to -8.92 (‰ vPDB), average of -10.82 (‰ vPDB) (Figure 5.9 and Table 5.5).
- The average $\delta^{13}$C value of CD1 is 1.06 (‰ vPDB) with a spread from 0.77 to 1.23 (‰ vPDB). The $\delta^{18}$O values vary from -10.77 to -10.36 (‰ vPDB), average of -10.63 (‰ vPDB) (Figure 5.9 and Table 5.5).
CD2 has the δ\textsubscript{13}C values from -0.47 to 0.91(‰ vPDB) (mean 0.39 ‰vPDB) and the δ\textsubscript{18}O values from -13.02 to -9.85(‰ vPDB) with an average of -11.58(‰ vPDB) (Figure 5.9 and Table 5.5).

The calcite cement analyzed develops the δ\textsubscript{13}C values range from -0.56 to 0.21 (‰ vPDB) with an average of -0.12 (‰ vPDB); δ\textsubscript{18}O values from -12.39 to -11.53 (‰ vPDB), average of -11.81 (‰ vPDB).

All the replacement dolomite (RD1 and RD2) and dolomite cement (CD1 and CD2) fall within the δ\textsubscript{13}C spread of the Upper Devonian marine dolomite. However, the δ\textsubscript{18}O values of all the dolomite are beyond the δ\textsubscript{18}O range of Upper Devonian marine dolomite (Fig. 5.9). The δ\textsubscript{13}C values of the calcite cement are within the δ\textsubscript{13}C range of Upper Devonian marine calcite. While the δ\textsubscript{18}O values are all out of the δ\textsubscript{18}O range of Upper Devonian marine calcite.
<table>
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<th>Phase</th>
<th>Well</th>
<th>Samples</th>
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<th>$\delta^{18}$O_{VPDB} (%)</th>
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<td>B-10-28-41-1</td>
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</tr>
<tr>
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<td>10-28</td>
<td>B-10-28-41-2</td>
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</tr>
<tr>
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</tr>
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Table 5.5 $\delta^{13}$C and $\delta^{18}$O values of dolomite (RD1-RD2, CD1-CD2) and calcite (CC) in Parkland (Continued)

<table>
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<tr>
<th>Phase</th>
<th>Well</th>
<th>Samples</th>
<th>$\delta^{13}$C$_{\text{VPDB}}$ (%)</th>
<th>$\delta^{18}$O$_{\text{VPDB}}$ (%)</th>
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<td>10-28-8-5</td>
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<tr>
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<tr>
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<td>10-26-2-1-6</td>
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<td>10-26-2-2-3</td>
<td>-0.56</td>
<td>-12.39</td>
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</table>
Figure 5.9 Cross plot of $\delta^{13}$C and $\delta^{18}$O of dolomite (RD1-RD2, CD1-CD2) and calcite (CC) in Parkland. Isotope signatures of Upper Devonian marine calcite are indicated by square of solid red line and the coeval dolomite are showed as the dash red line.
5.2.2 Strontium isotope results

18 samples including dolomite and calcite from Parkland were selected and analyzed for Sr isotope. The data was provided by the IGGCAS and listed in Table 5.6. Calcite deposited from Upper Devonian should have a $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio similar to that of Upper Devonian seawater (Burke et al., 1982), which is ranging from 0.708102 to 0.708601 (Fig. 5.10) (Burke et al. 1982).

- Two RD1 samples were analyzed with the $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios 0.712757 and 0.710225, respectively. The average $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio is 0.711491 (Fig. 5.11 and Table 5.6).
- Eight RD2 samples yield $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios from 0.709732 to 0.713449, with an average of 0.711368 (Fig. 5.11 and Table 5.6).
- The $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios of CD1 (n=2) range from 0.714774 to 0.716452, with an average of 0.715613 (Fig. 5.11 and Table 5.6).
- The CD2 samples (n=4) yield $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios from 0.710604 to 0.716128 (mean 0.712802) (Fig. 5.11 and Table 5.6).
- Two calcite samples have the $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios from 0.722599 to 0.725507, with an average of 0.724053 (Fig. 5.11 and Table 5.6).
Table 5.6 $^{\text{87}}\text{Sr}/^{\text{86}}\text{Sr}$ values of dolomite and calcite in Parkland

<table>
<thead>
<tr>
<th>Phase</th>
<th>Sample</th>
<th>$^{\text{87}}\text{Sr}/^{\text{86}}\text{Sr}$</th>
<th>Errors</th>
</tr>
</thead>
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</tr>
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<td>0.000014</td>
</tr>
<tr>
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</tr>
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<td>0.709732</td>
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<td>6-22-1</td>
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</tr>
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<td>0.000013</td>
</tr>
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<td>0.000013</td>
</tr>
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</tr>
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<td>10-26-2-2</td>
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</tr>
</tbody>
</table>
Figure 5.10 Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios through geological time (From Burk et al., 1982).
Figure 5.11 Histograms of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of dolomite (RD1-RD2, CD1-CD2) and calcite (CC) in Parkland.
5.2.3 Fluid inclusion results

In Parkland, fluid inclusions were studied in saddle dolomite and quartz cement. The measurements are mainly completed by our collaborator Mr. Lu in the Geofluids Lab, University of Regina. The data including Homogenization temperatures ($T_h$) and ice-melting temperatures ($T_{m\text{-}ice}$) are listed in Table 5.7.

5.2.3.1 Petrography

Based on phase assemblages present at room temperature, fluid inclusions in the saddle dolomite mainly include liquid-dominated inclusions, occurring in growth zones, clusters or long trails (Fig. 5.12). Quartz cement contains liquid-dominated, liquid-only, vapor-dominated and vapor-only fluid inclusions, mainly distributed in long trails (Fig. 5.13).

Fluid inclusions occur in growth zones, clusters or long trails. Fluid inclusions in long trails that crosscut crystal boundaries are considered to be of secondary origin. Fluid inclusions distributed along growth zones are considered to be of primary origin (Goldstein and Reynolds, 1994). Fluid inclusions in clusters are also considered to be primary in this study, although the possibility that some of them may be secondary or pseudo secondary cannot be discounted (Chi et al., 2016).
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sample</th>
<th>Occurrence</th>
<th>Origin</th>
<th>Size range (μm)</th>
<th>Number of FI</th>
<th>T_h range (°C)</th>
<th>T_m-ice range (°C)</th>
</tr>
</thead>
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<td></td>
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<td>10</td>
<td>132 – 218</td>
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<td>primary</td>
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<td>9</td>
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<td></td>
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<td>Core-cluster</td>
<td>primary</td>
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<td>9</td>
<td>115 – 135</td>
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<td>10</td>
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<td>6</td>
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<td>7</td>
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<tr>
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<td>11</td>
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<td>Core-cluster</td>
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<td>Rim</td>
<td>primary</td>
<td>2 – 3</td>
<td>3</td>
<td>113 – 123</td>
<td>-</td>
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</table>
Figure 5.12 Fluid inclusions in saddle dolomite in Parkland.
Figure 5.13 Fluid inclusions in quartz cement in Parkland.
5.2.3.2 Microthermometry

A total of 137 fluid inclusions are measured for microthermometry, including 59 in long trails in quartz cement, 10 in long trails in saddle dolomite and 68 primary fluid inclusions in saddle dolomite. T_h and T_m-ice are determined for liquid-dominated fluid inclusions with relatively low vapor percentages.

Fluid inclusions in long trails in quartz cement have T_h values of 132 – 140°C and T_m-ice values of -15 – -13°C, with salinities of 17 – 19 wt % NaCl. Some FIAs have T_h values of 132 – 186°C and T_m-ice values of -14 – -9°C, with salinities of 13 – 18 wt% NaCl (Fig. 5.14 and Table 5.7).

In saddle dolomite, the fluid inclusions in long trails in sample 10-26-7 yield T_h values of 152 – 166 °C and T_m-ice value of -12°C, with salinities of 16 wt % NaCl. The primary fluid inclusions in dolomite in sample 10-26-7 have T_h values of 112 – 195°C and T_m-ice value of -25 – -22°C, with salinities of 24 – 25 wt% NaCl+CaCl₂ (Table 5.7). The primary fluid inclusions in saddle dolomite have T_h values of 94 – 108°C and 113 – 123°C, and T_m-ice value of -23°C, with salinities of 24 wt% NaCl+CaCl₂ (Fig. 5.15 and Table 5.7).
Figure 5.14 Homogenization temperatures ($T_h$) of fluid inclusions in late quartz cement of Parkland.
Figure 5.15 Homogenization temperatures ($T_h$) of fluid inclusions in saddle dolomite of Parkland.
CHAPTER 6

DISCUSSION AND COMPARISON

6.1 Silicification

6.1.1 Silicification in SN4 well

Detailed petrography and corresponding geochemical analyses of quartz (RQ, QC1-QC4) have been carried out in this study. Especially the Si-O isotope analysis using SIMS on single quartz crystal has never been done before in SN4 well. The Si-O isotope result shows that there is no obvious relationship among different types of quartz.

(1) O isotope of replacement quartz (RQ) and quartz cement (QC1-QC4)

O isotope of quartz in the silicified rock would be related to temperature and O isotopes of the fluids from which quartz precipitated (Chen et al., 2010, 2015; Zhang et al., 1989). If the temperature of Middle Ordovician seawater is assumed to be 25°C, the δ^{18}O value of Middle Ordovician seawater are from -6 to -3.6 (‰ SMOW), using the δ^{18}O value of coeval marine calcite from -8 – -5.6 (‰ vPDB) (Veizer et al., 1999) and Equation 6.1 (Friedman and O’neil, 1977). The conversion between SMOW and PDB was based on the work done by Coplen et al. (1983).

\[10^3 \ln \alpha_{\text{calcite-water}} = 2.78 \times 10^6 T^{-2} (K) - 2.89 \] (6.1)

where: \[\ln \alpha_{\text{calcite-water}} = \frac{\delta^{18}O_{\text{calcite}} + 1000}{\delta^{18}O_{\text{fluid}} + 1000}\]

\[\delta^{18}O_{\text{SMOW}} = 1.03086 \delta^{18}O_{\text{PBD}} + 30.86\]
The oxygen isotope of quartz is related to the temperature and oxygen isotope of fluid from which quartz precipitate, as expressed in Equation 6.2 (Zhang et al., 1989) and Figure 6.1.

\[ 10^3 \ln \alpha_{\text{quartz-water}} = 3.306 \times 10^6 T^{-2} \text{ (K)} - 2.71 \] (6.2)

where: \( \ln \alpha_{\text{quartz-water}} = \frac{\delta^{18}O_{\text{quartz}}/\delta^{16}O_{\text{quartz}}}{\delta^{18}O_{\text{water}}/\delta^{16}O_{\text{water}}} \)

Using Equation 6.2 with \( T_h \) of fluid inclusions in different quartz analyzed by Lu (2017), the \( \delta^{18}O \) of quartz (RQ and QC1-QC4) measured from SIMS analyses, \( \delta^{18}O \) values of fluids from which quartz precipitated are estimated in Figure 6.1.

RQ occurs in both slightly and strongly silicified packstone/grainstone in SN4 well. The measured \( \delta^{18}O \) values of RQ range from 20.51 – 24.59 (‰ SMOW) and the \( T_h \) values of the primary fluid inclusions in RQ range from 162°C – 186°C (Lu et al., 2017), the \( \delta^{18}O \) values of fluids from which quartz precipitated are estimated in the range of +6.8 to +11.0 (‰ SMOW) (Fig. 6.1), which is much higher than the \( \delta^{18}O \) values of Middle Ordovician seawater.

Quartz cement (QC1-QC4) is mainly distributed in fractures or dissolution vugs in strongly silicified host rock. All the quartz cement have similar range of \( \delta^{18}O \) values, with QC1 from 22.59 – 25.43(‰SMOW), QC2 from 20.47 – 25.36 (‰SMOW), QC3 from 22.0 – 23.51 (‰SMOW) and QC4 from 23.36 – 23.84 (‰SMOW). Combing the \( \delta^{18}O \) values and corresponding \( T_h \) values of the primary fluid inclusions in QC1-QC4 (Lu et al. 2017), the calculated \( \delta^{18}O \) values of fluids from which quartz cement precipitated are
Figure 6.1 Cross plot of homogenization temperature and \( \delta^{18}O \) values of quartz in SN4 well (based on Equation 6.2).
estimated in the range of +4.00 – +11.00 (‰ SMOW) (Fig. 6.1), which is much higher than the $\delta^{18}O$ range of the expected Middle Ordovician seawater.

The fluid from which replacement quartz precipitated has similar $\delta^{18}O$ range to those for quartz cement, suggesting that these fluids may have similar origin. The $\delta^{18}O$ values of these fluids are much higher than that of the expected Middle Ordovician seawater which could be explained as the following two possibilities:

i. The average $\delta^{18}O$ values of these fluids spread from +5.00 – +10.00 (‰ SMOW) (Fig. 6.1) which falls within the $\delta^{18}O$ range of primary magmatic water (+5.5‰ SMOW – +9.50 ‰ SMOW), indicating that these fluids might be derived from the deep-seated magma (Sheppard et al., 1986). This could be possible because intense volcanic activities occurred in the study area during Early Permain (Yun and Cao, 2014), which could provide silica-rich magmatic waters migrating through early faults, modifying the upper carbonate host rock. It is reasonable that, if these magmatic waters were unaltered during the migration, the quartz (including replacement quartz and quartz cement) precipitating from these waters would have congenetic $\delta^{18}O$ values. However, complex fluids exist in the sedimentary basin, such as burial brines which may mix with the magmatic waters, affecting the $\delta^{18}O$ values of the quartz reflecting as the fluctuation of $\delta^{18}O$ ranges in different quartz. In addition, temperature variation during the quartz precipitation would also contribute to the fluctuation of $\delta^{18}O$ ranges (Zhang et al., 1989).

ii. If the siliceous fluids were Middle Ordovician seawater, the heavier $\delta^{18}O$ ranges recorded in different quartz (-6.0‰ SMOW to -3.6‰ SMOW) could be related to
evaporatic (Middle Ordovician) seawater. This evaporatic seawater will have heavy O isotope and high salinity. The primary fluid inclusions measured in replacement quartz and quartz cement have the salinities ranging from 14.7 to 26.8 (wt% NaCl + CaCl$_2$) (Lu et al., 2017), about 5 to 8 times the salinity of seawater together with the heavier $\delta^{18}O$ values of the quartz, supporting the quartz precipitation from the evaporative seawater which could be from any geologic time.

(1) Si isotopes of replacement quartz and quartz cement

Si isotopes, including $^{28}$Si (92.23‰), $^{29}$Si (4.67‰) and $^{30}$Si (3.10‰), have been studied for many years in rocks and minerals (Poitrasson, 2017). The $^{30}$Si/$^{28}$Si of a sample to the standard (NBS-28) is used to present the results of the Si isotope analysis using the following equation (Poitrasson, 2017):

$$\delta^{30}\text{Si (‰)} = \left( \frac{^{30}\text{Si}^{28}\text{Si}_{\text{Sample}}}{^{30}\text{Si}^{28}\text{Si}_{\text{Standard}}} - 1 \right) \times 1000$$

Based on the discussion of oxygen isotope, the origin of the fluid is likely to be fluid with high temperature which is regarded as hydrothermal fluid (Chen et al., 2015). However, it was uncertain about the nature and/or source of the fluids. In order to understand the origin of the fluid, a total of 75 spots are selected for $\delta^{30}$Si analysis (see Chapter 5). The $\delta^{30}$Si values vary from 1.43–2.56 (‰ NBS28) for RQ, 1.66 – 2.46 (‰ NBS28) for QC1, 1.76 – 2.45 (‰ NBS28) for QC2, 1.84 –2.48 (‰ NBS28) for QC3 and 1.6 – 2.34 (‰ NBS28) for QC4, respectively.
Although values are similar to $\delta^{30}\text{Si}$ values measured from seawater, river and granites (Fig. 6.2 and Fig. 6.3) presented in Poitrasson (2017) and Lal and Somayajulu (1984), the most likely origin for the hydrothermal fluid may be related to granites in the Precambrian basement as discussed below.

- The $\delta^{30}\text{Si}$ values of seawater range from 0.5 to 4.4 ($\text{‰ NBS28}$) which cover all our data range. Seawater in a restricted basin could have higher $\delta^{30}\text{Si}$ values due to biological activity such as diatoms which preferentially incorporate light silicon into skeletal, leaving the heavy silicon in water (Poitrasson, 2017). Therefore, if the hydrothermal fluid comes from heated seawater that was in the restricted setting, it would be rich in $\delta^{30}\text{Si}$.

- The $\delta^{30}\text{Si}$ values of rivers range from -0.70 to 4.66 ($\text{‰ NBS28}$) covering the data from this study. The dissolved silicon represented as orthosilicic acid in the rivers is also influenced by biological activity. Moreover, the weathering condition would affect the silicon concentrations in the river which in turn acting on the hydrothermal fluid (Poitrasson, 2017). However, the river water as the source for the silicification seems unlikely because there were no geological conditions to introduce a large amount of river water in the host rock. In addition, the high $\delta^{18}\text{O}$ of fluid for the fluids precipitated quartz does not support river water for quartz precipitation.

- The granites and feldspars from granites both have a relatively large range of $\delta^{30}\text{Si}$ values (0.0-1.8$\%$ NBS28 for granites; 0.3-3.6$\%$ NBS28 for feldspars from granites), which seems most likely related to the hydrothermal silicification fluid in SN4 area as the Cambrian granites in the basement in SN 4 well is also likely
Figure 6.2 The range of silicon isotope composition of various types of terrestrial samples (From Poitrasson, 2017).
Figure 6.3 $\delta^{30}$Si variations in terrestrial and extraterrestrial surface samples (From Lal and Somayajulu, 1984).
to be the hydrothermal source. Hydrothermal fluid from the Precambrian granites might migrate up along fault and fractures during tectonic activities to the host carbonate rock.

Combing the Si and O isotope results, the fluids from which the quartz precipitated come from the evaporatic seawater is preferred. The high temperature could be interpreted as it was heated up during volcanic activities. However, this is a tentative interpretation. The nature of the hydrothermal source needs further investigation.

6.1.2 Silicification in Parkland

Silicification in Parkland mainly occurs as chert nodule, replacement chert and euhedral quartz cement. Chert nodules with microquartz and chalcedony are interpreted to be related to biogenic silica in shallow burial (Packard et al., 2001).

The \( \delta^{18}O \) value of chert nodules varies from 26 – 27 (‰ SMOW), which is more depleted than replacement microquartz that has \( \delta^{18}O \) values of 21-24 (‰ SMOW) (Packard et al., 2001). It is difficult to determine the absolute temperatures at which replacement chert precipitated, because there were limited analyses about the fluid inclusions in replacement chert. Therefore, it can only be constrained based on the paragenesis sequence. Replacement chert was identified postdating matrix dolomite that developed an average \( T_h \) about 140°C measured by Packard et al. (2001). If the replacement chert formed at 140°C following the matrix dolomite, the fluid from which the chert precipitated should have the \( \delta^{18}O \) around +5 (‰ SMOW) (Fig 6.4). It is much higher than the \( \delta^{18}O \) value of the Upper Devonian seawater.

For euhedral quartz cement, no \( \delta^{18}O \) values were measured. \( T_h \) of fluid inclusions
measured were from 130 to 140°C (some FIAs can reach 132–186°C) (Chapter 5), suggesting high temperature for the quartz precipitation. If the similar δ¹⁸O values of the chert are used, the average δ¹⁸O values of fluids from which quartz cement precipitated would be around +6 to +8 (‰ SMOW) (Fig. 6.4), which are much higher than the estimated δ¹⁸O value of Upper Devonian seawater.

The estimated δ¹⁸O values fall within the δ¹⁸O range of primary magmatic water (+5.5 – +9.5 ‰ SMOW) (Sheppard et al., 1986), suggesting that these fluids might also be derived from deep magmatic waters as predicted in SN4 well. A short period of intense hydrothermal activities occurred in early Tournaissian to late Viséan (Packard et al., 2001) support this possibility. These fluids could be unaltered magmatic waters mixed with other brines during migration to the carbonate host rock. Moreover, if the chert and euhedral quartz precipitated in Early Tournaissian (Packard et al., 2001) at burial depth of 200-500 m, the burial temperature should be 32 – 43°C according to the preserved thickness of related strata and using a geothermal gradient 35 °C/km with assumption of surface temperature of 25°C. The estimated burial temperature is much lower than the measured Tₘ in chert fluid inclusions, supporting that the hydrothermal fluids are more likely to be the origin from which the chert and euhedral quartz precipitated.

The pervasive matrix dolomite in Parkland has been interpreted as hydrothermal origin related the granite basement (Packard et al., 2001), which is also reasonable for interpreting the fluid source of the replacement chert and euhedral quartz cement based on the diagenetic paragenesis. However, there is still a lack of accurate evidences for estimating the origin of these fluids from which the replacement chert and euhedral quartz cement deposit. Further research is needed to solve the current problem.
Figure 6.4 A cross plot of homogenization temperature and $\delta^{18}$O values of quartz in Parkland (based on Equation 6.2).
6.1.3 Silicification comparison

The similarities and differences of the silicification between SN area in the Tarim Basin and Parkland area in WCSB can be identified based on the comparison of the diagenetic features and geochemical signatures.

- The host rocks of two areas are limestones that underwent complex diagenesis during the geological time.
- Both SN4 well and Parkland develop porous reservoirs during the silicification.
- From previous research and the current study, the $\delta^{18}$O ranges of quartz in SN4 well are similar to that of the replacement chert in Parkland (Fig. 6.5). The replacement chert in Parkland was interpreted to be precipitated from hydrothermal fluids, according to the close $\delta^{18}$O range, quartz in SN4 well are also precipitated from fluids with a high temperature as indicated in $T_h$ of inclusions.

With respect to the differences, the diagenetic features are the most obvious one. The significant amount of silicification identified in SN4 well consists of mainly subhedral to euhedral quartz both in the matrix (20-500 μm) and cement (50-500 μm). However, the main occurrence of silicification in Parkland is the replacement chert with microquartz crystals (5-10 μm). The euhedral quartz in Parkland only represents as the late cement in fractures or dissolution vugs. The difference textures between two areas may relate to the environment evolution when the silica deposits.
Figure 6.5 The $\delta^{18}$O of different silica compositions in two study areas (based on Packard et al., 2001).
6.2 Dolomitization

6.2.1 Dolomitization in SN4 well

In the silicified intervals of SN4 well, the dolomite only represents as a small amount (less than 5%) of cement along stylolites in the slightly silicified peloidal packstone/grainstone with euhedral crystal shapes (Fig. 4.8A). The dolomite cement was analyzed for the petrography in this study, geochemical analysis has not been processed which still need further exploration.

6.2.2 Dolomitization in Parkland

Dolomite is pervasively distributed in Wabamun Group of Parkland field, including replacement dolomite (RD1, RD2) and dolomite cement (CD1, CD2). Each type of dolomite has been analyzed for carbon, oxygen and strontium isotopes in order to analyze the environment when the dolomite precipitated (see Chapter Five for the data). The estimated $\delta^{13}$C values of Upper Devonian marine dolomite vary from -0.5 – +2.0 (‰ vPDB) and the $\delta^{18}$O values, from -5.0 – -2.0 (‰ vPDB) (Land, 1985; Veizer et al., 1999).

The $\delta^{13}$C values of dolomite are 0.89 – 1.76 (‰ vPDB) for RD1; 0.25 – 1.19 (‰ vPDB) for RD2; 0.77 – 1.23 (‰ vPDB) for CD1 and -0.47 – 0.91(‰ vPDB) for CD2 (Table 5.5). All the $\delta^{13}$C values of replacement dolomite (RD1 and RD2) and dolomite cement (CD1 and CD2) fall within the $\delta^{13}$C range of Upper Devonian marine dolomite (Fig. 5.9), suggesting the source of carbon for the dolomite may be derived from the Upper Devonian seawater. The values of oxygen isotopes of dolomite are controlled by the temperature and O isotopic composition of fluid from which dolomite precipitated as
expressed in Equation 6.3 (Friedman and O’neil, 1977) and Figure 6.6.

\[ 10^3 \ln \alpha_{\text{dolomite-water}} = 3.2 \times 10^6 T^{-2} \text{ (°K)} - 3.3 \] (6.3)

where: \( \ln \alpha_{\text{dolomite-water}} = \frac{\delta^{18}O_{\text{dolomite}} + 1000}{\delta^{18}O_{\text{fluid}} + 1000} \).

The \( \delta^{18}O \) values range from -10.39 to -8.03 (‰ vPDB) for RD1; from -11.46 to -8.92 (‰ vPDB) for RD2; from -10.77 to -10.36(‰ vPDB) for CD1; and from -13.02 to -9.85(‰ vPDB) for CD2 (Table 5.5), respectively. All these \( \delta^{18}O \) values are lower than the estimated \( \delta^{18}O \) values for the Upper Devonian marine dolomite. According to the \( \delta^{18}O \) values of the Upper Devonian marine calcite (estimated from Veizer et al., 1999), the coeval dolomite should have the \( \delta^{18}O \) values of -5 to -2 (‰ vPDB) (Land, 1985). Based on O isotopes of dolomite and \( T_h \) of the dolomite, the O isotopes of the fluids from which dolomite precipitated were estimated range from +1 to +5 (‰ SMOW) for replacement dolomite and +2 to +6 (‰ SMOW) for dolomite cement using Equation 6.3 (Fig 6.6). The O isotopes of dolomitizing fluids are obviously heavier than the \( \delta^{18}O \) values of the Upper Devonian seawater (-4‰ SMOW to -3‰ SMOW). Two possible explanations for the light \( \delta^{18}O \) values of Parkland dolomite:

i. If the dolomite were formed from the Upper Devonian seawater at the surface conditions at 25°C, the \( \delta^{18}O \) values should be conegenetic with the seawater, or heavier if there developed evaporation during which the dolomite precipitated. It is most accepted that the matrix dolomite in WCSB was formed in evaporated context (Fritz and Jackson, 1972; Rhodes et al., 1984). However, the most
Figure 6.6 A plot showing the range of temperatures calculated from the assumed oxygen isotopic composition of the water and the oxygen isotopic composition of dolomite in Parkland, using the fractionation Equation 6.3.
positive $\delta^{18}$O value of RD1(-8.03‰ vPDB) in this study was more depleted than those of expected Upper Devonian seawater, suggesting that the original $\delta^{18}$O values of the dolomite in Parkland should be reset or diagenetically modified at the higher temperatures during deep burial. This could be possible because intense hydrothermal activities occurred in the Early Tournaisian to Late Viséan (Packard et al., 2001) which may provide hydrothermal fluids migrating through early faults and modifying the carbonate host rock. Burial brines with a high temperature may also act as the diagenetic fluid via faults when tectonic activities occurred which can support the impetus for the brines upward, modifying the upper carbonate.

ii. The light $\delta^{18}$O values of Parkland dolomite could be resulted from dolomitization at high temperatures. If the dolomite precipitated in the Early Tournaisian (Packard et al., 2001) at a burial depth of 200-500 m, the burial temperature should be 32–43°C according to the preserved thickness of related strata and using a geothermal gradient 35 °C/km with assumption of surface temperature of 25°C. However, the fluid inclusions results indicated that neither replacement dolomite (mean $T_h$: 140°C) nor dolomite cement (lowest $T_h$: 100°C) could precipitate at a low estimated burial temperature, supporting that the initial Upper Devonian seawater may not contribute to the depleted $\delta^{18}$O values of these dolomite. Evaporative seawater from other geologic time could be potential origin for the lighter $\delta^{18}$O values which is with high salinity and high temperature as well.

The $^{87}$Sr/$^{86}$Sr ratios are 0.712757 and 0.710225 for two RD1 samples; from
0.709732 to 0.713449 for RD2; from 0.714774 to 0.716452 for CD1; and from 0.710604 to 0.716128 for CD1, respectively (Table 5.6). All the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are higher than those of the Upper Devonian seawater (from 0.7081 to 0.7086) (Burke et al., 1982), suggesting that the fluids from which the dolomite precipitate may not be initial Upper Devonian seawater. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of seawater would be affected when it is mixed with other components such as brines or surrounding rock constituents. There is a trend that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio gradually increases with the $\delta^{18}\text{O}$ value decreasing from RD1 to CD2 (Fig. 6.7), which may due to composition variation of the fluids from which dolomite precipitated.

Even though it is still uncertain about the accurate origin of these fluids, potential origins of the dolomite in Parkland could be interpreted combing the analyses of carbon, oxygen and strontium isotopes. It is reasonable that the dolomite in Parkland precipitated from the Upper Devonian seawater fluids due to consistent $\delta^{13}\text{C}$ range. The more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios comparing to the Upper Devonian seawater would be caused by mixing with other components (e.g., volcanic material or continental clastics) when the dolomite precipitated or, modified by later hydrothermal fluids. During Early Tournaisian to Late Viséan, intensive volcanic activities occurred, which could provide hydrothermal fluids (or burial brines) with a high temperature contributing to the depleted $\delta^{18}\text{O}$ values. In addition, evaporative seawater from later geologic time may also act as the dolomitic fluids due to its high salinity. It could be heated up by the volcanic hydrothermal fluids during migrating to upper formations, modifying the original carbonate rock as well.
Figure 6.7 A cross plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and $\delta^{18}\text{O}$ values for dolomite and calcite samples in Parkland. Isotope signatures of Upper Devonian marine dolomite are indicated with the red dash square (based on Veizer et al., 1999).
6.2.3 Dolomitization comparison

Dolomite in the silicified intervals of SN4 well mainly develops one texture with euhedral crystal shapes (10-50 μm) as cement along stylolites. In Parkland, the dolomite is massively distributed both as replacement (RD1 and RD2) and cement (CD1 and CD2). The different amount and textures of the dolomite in two areas may relate to the fluids with different concentration from which the dolomite precipitated. The forming temperature and host rock framework would also have some major influences.

6.3 Calcite Cementation

6.3.1 Calcite cement in SN4 well

Three types of calcite cement were sampled for carbon and oxygen isotope analysis and the results have been listed in Chapter 5. The values of oxygen isotopes of calcite are controlled by the temperature and O isotopic composition of fluid from which calcite precipitated as expressed in Equation 6.1 and Fig. 6.8. The δ18O value of Middle Ordovician seawater was ranging from -6 to -3.6 (‰ SMOW), based on the calculations using δ18O values of -8.0‰ – -5.6‰ (vPDB) for Middle Ordovician marine calcite (Veizer et al., 1999). The δ13C values for Middle Ordovician marine calcite are from -1.9‰ – -0.1‰ (vPDB) (Veizer et al., 1999).

Early calcite cement (CC1) has the δ13C values of -0.02–0.48 (‰ vPDB) and the δ18O values of -8.31– -4.60 (‰ vPDB). CC2 in the fractures of silicified packstone/grainstone or among the replacement quartz has the δ13C values of -4.82– -1.82 (‰ vPDB) and the δ18O values of -11.73– -4.87 (‰ vPDB). Late-stage calcite cement (CC3), distributed in the residual space left by the quartz cement in the fractures of the strongly silicified packstone/grainstone, develops the δ13C values of -4.2 to -2.89
Figure 6.8 A plot showing the range of temperatures calculated from the assumed oxygen isotopic composition of the water and the oxygen isotopic composition of calcite in SN4 well, using the fractionation Equation 6.1.
(‰ vPDB) and more depleted δ¹⁸O values of -12.93 – -11.33(‰ vPDB).

The δ¹³C values of CC1 are higher than those of Middle Ordovician marine calcite, while CC2 and CC3 have lower δ¹³C values, reflecting that CC1 – CC3 may not precipitated from initial Middle Ordovician seawater. However, all the CC1 and half CC2 samples have δ¹⁸O values similar to those of Middle Ordovician marine calcite, reflecting that the fluids from which CC1 and CC2 precipitated may have a connection to the Middle Ordovician seawater. The δ¹⁸O values of CC3 are much depleted than those of the Middle Ordovician marine calcite, reflecting that CC3 may not precipitate from the Middle Ordovician seawater.

Using the O isotopes of Middle Ordovician seawater and measured O isotopes, the calculated temperature of precipitation should be within 10°C – 65°C for CC2 and 45 – 80°C for CC3 (Fig. 6.8). However, the T_h of the fluid inclusions in CC2 range from 124°C to 162°C; and 183 – 186°C and 179 – 185°C for two FIAs in CC3 (Lu et al., 2017). These T_h values suggest that neither CC2 nor CC3 may precipitate from the Middle Ordovician seawater at the calculated temperatures of 10°C – 65°C for CC2 and 45 – 80°C for CC3 (Fig. 6.8).

Based on O isotopes of calcite and T_h of the calcite fluid inclusions, the fluids from which calcite cement precipitated are estimated to have the δ¹⁸O range of +8 – +16 (‰ SMOW) for CC2 and +9 – +10 (‰ SMOW) for CC3 (Fig. 6.8) which are much heavier than the δ¹⁸O values of the Middle Devonian seawater (-6‰ SMOW to -3.6‰ SMOW). Two possible explanations are discussed as follows:

i. Based on the heavier fluid δ¹⁸O ranges estimated for CC2 – CC3 and diagenetic sequence (CC2 postdating replacement quartz and CC3 postdating quartz
cement), it is reasonable that CC2 and CC3 could precipitate from hydrothermal fluids which may come from magmatic waters due to volcanic activities (with δ^{18}O of +5.5 – +9.5‰ SMOW) (Sheppard et al., 1986) or burial brines at a high temperature.

ii. The fluids from which CC1 and CC2 precipitated may have a connection to the initial Middle Ordovician seawater. It is also possible that fluids experienced isotope exchange with the Middle Ordovician limestone during the water-rock reaction, making the fluids with similar δ^{18}O values to the seawater for CC1 and CC2 to precipitate. The lighter δ^{18}O values (from -11.73 – -7‰ vPDB) of the half CC2 samples may be resulted from later diagenetic alteration by fluids with high temperature. The limited ⁸⁷Sr/⁸⁶Sr ratios of CC2 measured by Chen et al. (2014) could add more evidences for the CC2 fluids estimation which range from 0.70949 to 0.70972, higher than that of the Middle Ordovician seawater (i.e., 0.7078 – 0.7085) (Burke et al., 1982). The ⁸⁷Sr/⁸⁶Sr ratios of fluids would be affected when components such as brines or surrounding rock constituents mixing in which may contribute to the differential ⁸⁷Sr/⁸⁶Sr ratios of the congeneric minerals.

### 6.3.2 Late calcite cement in Parkland

Calcite precipitated from Upper Devonian seawater had the δ^{13}C values of -0.5 – +2.0‰ vPDB and the δ^{18}O values from -7 to -4‰ vPDB (Veizer et al., 1999). The δ^{18}O value of the Upper Devonian seawater was calculated ranging from -4 to -3‰ SMOW) based on Equation 6.1. The values of oxygen isotopes of calcite are controlled by the temperature and O isotopic composition of fluid from which calcite precipitated.
as expressed in Equation 6.1 and Fig. 6.9. Late calcite cement (CC2-p) in Parkland have the $\delta^{13}$C values ranging from -0.56 to 0.21 (‰ vPDB) which are similar to those of Upper Devonian marine calcite. But the $\delta^{18}$O values of CC2-p range from -12.39 to -11.53 (‰ vPDB) which are much lower than those of Upper Devonian marine calcite. If CC2-p was precipitated from the Upper Devonian seawater, the calculated temperature of precipitation would be 60°C to 78°C (Fig. 6.9). However, the primary fluid inclusions analyzed by Packard (2001) showed that the $T_{h}$ of calcite cement had two ranges of 140-160°C and 200-240°C, much higher than 78°C.

CC2-p develops similar $\delta^{18}$O values and $^{87}$Sr/$^{86}$Sr ratios with CD2, indicating that the interpretation about the CD2 also works on the late calcite cement as discussed in section 6.2.1. Based on the diagenetic paragenesis, moreover, CC2-p is last stage of cement postdating euhedral quartz cement, providing more logic evidence that it could be formed from (or modified by) late hydrothermal fluids or burial brines with a high temperature during volcanic activities which is interpreted as the most reasonable fluid origin for euhedral quartz.

**6.3.3 Calcite cementation comparison**

In the silicified intervals of SN4 well, the abundance of calcite cement varies due to the degree of silicification. CC1 massively develops in the slightly silicified intervals. The relative late calcite cement (CC2 and CC3) preferentially occurs in the strongly silicified sections. In some completely silicified samples, no calcite is identified. In Parkland, the most distinguishable calcite cement is the relative late one (CC2-p) in the dolomite or silicified dolomite filling the fractures/dissolution vugs. CC3 in SN4 well and CC2-p in Parkland both represent as the last stage of cement after silicification.
Figure 6.9 A plot showing the range of temperatures calculated from the assumed oxygen isotopic composition of the water and the oxygen isotopic composition of calcite in Parkland, using the fractionation Equation 6.1.
6.4 Comparison of the silicification mechanism

In the period of Late Sinian, Cambrian and early Ordovician, the Tarim Basin was at a structural extension stage, manifested as an abundant occurrence of normal faults within the basin (Wu et al., 2007). During Late Devonian, Shunnan area experienced intense uplift and the NE-trending strike-slip faults were re-activated (Han et al., 2016; Qi, 2016; Li et al., 2017), which may serve as the conduits for the hydrothermal fluids. Surrounding host rock with different permeability was silicified in subsection as shown in SN4 well (Fig. 4.1). Mineral association including column quartz, iceland spar, and anhydrite occur represented as cements fillings in the dissolution pores/vugs and fractures (Han et al., 2014). Early calcite cement (CC1) filling the pore space among limestone particles was partially or completely silicified. Late calcite cement was found depositing after the silicification (Fig. 6.10).

The silicification in Parkland is interpreted forming from Tournaisian to late Viséan based on the dolomite veins depositing in late Viséan and the relationships between chert veins and overlying Exshaw Ash (Packard et al., 2001). After the deposition of mudstone/wackstone, early fractures with hot fluids dolomitized the host rock, leaving early hydrothermal karstification. With an increase in burial, hydrothermal fluids with acid composition silicified the original or dolomitic mudstone/wackstone (Packard et al., 2001). Early dissolution pores/vugs and fractures were filled with calcite, saddle dolomite, anhydrite, pyrite and quartz cement. Calcite cement among the original particles was mainly replaced by dolomitized fluids, while remnant was silicified by later acid hydrothermal fluids. Late fluids went through fractures depositing late coarse crystalline calcite cement (Fig. 6.11).
Figure 6.10 Proposed processes and mechanism of the silicification in SN4 well.
Figure 6.11 Proposed processes and mechanism of the silicification in Parkland.
6.5 Reservoir Comparison

6.5.1 Distribution

The cored silicified reservoirs of Yingshan Formation in Well SN4 are approximately 4 m (6668.81-6673.52 m) which have been divided and described in detail in Chapter 4. The Wabamun Group chert reservoirs in Parkland mainly comprise dolostone and chert. The dolomite reservoirs are regionally developed in nodular skeletal wackstone and peloidal-skeletal packstone/grainstone (Packard et al., 2001), while the chert is mainly found in 3 wells including 6-29 well (35 m), 10-28 well (8 m) and 10-11 well (5 m). The depth of the chert is about 3200 m.

Silicification in both of the study areas is limited and selective. As for SN4 well, the peloidal packstone/grainstone is silicified in different degrees. In Parkland, the chert mainly found in dolomite, indicating that the selective dolomite has a relatively higher permeability than the wackstone/packstone. For the depth, silicification of SN4 well is dramatically deeper than that of Parkland.

6.5.2 Reservoir quality

Dissolution vugs and intercrystalline pores are well developed in both areas. The host limestone in SN4 well develops a porosity ranging from 0.2%-3.8% (mainly 0.5%-1.0%) with an average of 0.9% (Han et al., 2014). The permeability varies from 0.001 mD-18.74 mD (mean 1.094 mD) (Han et al., 2014). The silicified intervals display rather better reservoir quality with the porosity spreading from 17.5%-20.5% and the permeability ranging from 23.81 mD-74.37 mD (Han et al., 2014).

In Parkland, the average porosity in dolomite reservoir rarely exceeds 4.0% and the
maximum horizontal permeabilities are 2 mD (Packard et al., 2001). In chert intervals, the porosity ranges from 25% to 30% in pure cherts with an average of 6% in cherty dolostones. The permeabilities vary from 16 md to 40 md in pure cherts, down to 0.08 mD in cherty dolostones (Packard et al., 2001).

The well-developed porosity and permeability in silicified reservoirs show improvement of the reservoir by silicification. The main reservoir space appears to be controlled by the distribution of fractures which act as the conduits for fluid migration moving upward and play a critical role in enhancing reservoir quality.
Conclusions

(1) The silicification in Yingshan Fomation of Middle Ordovician in SN4 well was identified at the depth about 6670 m, with a total core length approximately 4 m. The chert reservoirs of Wabamun Group of Upper Devonian in Parkland are discovered at the depth around 3200 m from the wells including 10-28 well, 6-29 well and 10-11 well.

(2) Fracturing is the priority to the development of high-quality reservoirs. Wells with silicified core intervals in both of the areas are associated with the fault systems. The NE-NNE-trending strike-slip faults in SN4 well and N-NW trending sheer faults in Parkland are of critical importance for the silicification in the respective areas. They act as the conduits for deep acid hydrothermal fluids moving upward, resulting in dolomitization and silicification of the host rock.

(3) The silicification in both of the two areas varies in different lithology. Peloidal packstones/grainstones are preferentially replaced by acid hydrothermal fluids especially the intervals with high. The dissolution related to the silicification then in turn contributes to the reservoir quality with a higher porosity and permeability.

(4) Replacement quartz and quartz cement are found in SN4 well with different textures. Based on the analyses of Si – O isotope from SIMS, the replacement
quartz and quartz cement are considered to deposit from the same or close episode of hydrothermal fluids.

(5) In Parkland, the dolomitization is more pervasive comparing to the silicification. Dolomite replacement including RD1 and RD2 with different crystal features. The values of $\delta^{13}$C - $\delta^{18}$O and $^{87}$Sr/$^{86}$Sr ratios illustrate that both the replacement dolomite and dolomite cement may be related to hydrothermal fluids which have similar $\delta^{13}$C values and $\delta^{18}$O values as the Upper Devonian seawater, and later modified at high temperatures.

**Recommendations**

The aim of this study was to compare the nature of the silicified carbonate reservoirs in the two targeted areas, in order to find out the source of the silica and the forming mechanism of the silicification. So far, a great deal of work and analyses have been processed. As for SN4 well, the Si isotope analysis with SIMS is the first time to make an accurate to single quartz crystal, which has never been published worldwide. It provides insights on the distinctions among different quartz generations, which can help with the detailed diagenetic paragenesis. In this case, such Si isotope analysis using SIMS can be processed in Parkland for future work, in order to study about the time of chertification. Although this may be a relatively small-scale progress, more notable findings could be explored.
REFERENCES


English abstract).


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## APPENDIX

Microthermometry data of fluid inclusions in quartz samples

<table>
<thead>
<tr>
<th>Qz</th>
<th>Sample</th>
<th>Occurrence</th>
<th>N$^1$</th>
<th>T$_s$ range (°C)</th>
<th>Average T$_s$ (°C)</th>
<th>T$_m$ range (°C)</th>
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