

A THERMOCHRONOLOGICAL HISTORY OF BURIAL AND EXHUMATION AT KEVIN
DOME, NORTHWEST MONTANA INCLUDING THE ORIGIN OF CO₂ IN UPPER DEVONIAN
DUPEROW FORMATION AND THE BAKKEN PETROLEUM SYSTEM AT THE DOME

by

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A dissertation submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Earth Sciences

MONTANA STATE UNIVERSITY
Bozeman, Montana

December 2022

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DEDICATION

I dedicate this dissertation to my best friend, helper, source of strength, and strategist – the Holy Spirit of God.

This milestone in my life is also dedicated to my dear Brother Samuel Olatunji Oluwasesan Otitolaju Okusanya and my Dad, Michael Adeniyi Olukayode Okusanya in eternity. Continue to rest in the bosom of the Lord, until we meet again.

I dedicate all my educational pursuits leading to my doctoral degree to my dear mom, Ruth Bolajoko Okusanya. *“Ninu ikoko dudu ni eko funfun ti jade wa – out of (your) obscurity, a great light has emerged to the world.”* Your immense love, support, prayers, and many sacrifices has fueled my journey across many lands. Thank you for teaching me to endure the process and to shine!

ACKNOWLEDGEMENTS

I would like to thank Dr. Mary S. Hubbard for supporting me throughout the course of my study and my dissertation committee - Dr. Madison L. Myers, Dr. Colin A. Shaw, Dr. David W. Bowen, and Mr. Charles W. Calavan for their insight, patience, and guidance.

I am forever grateful for my wife Dierdre N. Adetoyosi Adeniyi for her constant love and encouragement throughout the process of completing this degree. I am indebted to my mom Mrs Ruth Bolajoko Okusanya, my beautiful sisters and their husbands Ademola and Desola Oloketuyi and Abiodun and Modupe George for supporting me with moral and spiritual support throughout my educational career. Thank you to my niece Temiloluwa, and nephews Boluwatife, Ayomide and Toluwanimi, in Nigeria for bearing with my *absent uncle duties* and for loving me from afar, I hope to make it up to you soon! To my in-laws in the USA, Mr. and Mrs, Donald and Ansala Lee, Xeves and Ashley McCreary, Alissa Lee, and Donald Lee II; I am grateful for your love and support. I would also like to thank every member of Heirs of Love Campus Fellowship at MSU, serving you and doing life with you on campus has been amazing these past years.

I have often said, "*without people, our science is not possible*". Thus, special thanks to all my collaborators on this multi-faceted project, your support and guidance are enormous. Lastly, thank you to the ACS Petroleum Research Fund, Energy Research Institute MSU, AAPG, GSA, Colorado Scientific Society, Rocky Mountain Association of Geologists, National Association of Black Geoscientists, Marathon Oil Company, and the Montana Academy of Sciences for all of your financial support.

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ABSTRACT TO DISSERTATION

Kevin Dome is a geologic structure and historic hydrocarbon producer in northwest Montana. This structure is also a known CO₂ reservoir, yet its development has not been constrained with thermochronological techniques and the origin of the natural ($\sim 283 \times 10^9 \text{ m}^3$) CO₂ of the Upper Devonian Duperow Formation, is not well understood. This work seeks to create a temporal understanding of the burial and exhumation history of Kevin Dome including the hydrocarbon generation and CO₂ emplacement. I constrained the burial and exhumation history at Kevin Dome with low-temperature thermochronology, carbonate clumped isotope thermometry, and thermobarometric proxies. I also tested for microbial, thermogenic, and magmatic CO₂ source(s) as well as CH₄ and N₂ gas sources at the dome with major gas composition, stable and noble gas isotopic geochemistry methods. I found that Kevin Dome rocks were buried to oil and gas generation windows before exhumation during the Late Cretaceous-Paleocene ($\sim 65 - 72 \text{ Ma}$) and the Oligocene-Miocene ($\sim 15 - 26 \text{ Ma}$) at an average rate of $\sim 0.27 \text{ mm/yr}$. My study supports an evolved forebulge-dome origination model for Kevin Dome that is driven by the Late Cretaceous-Paleocene emplacement of the Rocky Mountain overthrust in a Foreland Basin setting in northwestern Montana (and proximal Canada) and an Oligocene-Miocene erosional or epeirogenic event not previously recognized in northwest Montana. I estimated $\sim 4 - 5 \text{ km}$ more overburden erosion than was previously thought in the region and suggest that the Oligocene-Miocene exhumation terminated hydrocarbon generation at Kevin Dome. In terms of CO₂ origin, my data supports a magmatic origin for the Duperow CO₂, with emplacement during the Sweetgrass Hills igneous complex intrusion ($\sim 52 \text{ Ma}$). I also found that the CH₄ and N₂ gases at Kevin Dome were mainly thermogenic in origin. A CO₂ solubility model showed that $\sim 98\%$ of the CO₂ has been dissolved into the groundwater in the Bakken petroleum system's hydrocarbon-bearing reservoirs at Kevin Dome during migration. I present a novel approach of integrating modern t-T sensitive techniques, stratigraphy, thermal maturity data, and isotopic geochemistry to address the structural development of sedimentary basins/domes, hydrocarbon generation, and magmatic CO₂ emplacement and subsequent evolution.

CHAPTER ONE

INTRODUCTION TO DISSERTATION

Premise and Questions Addressed

Kevin Dome is a historic oil and gas producing geologic structure in northwestern Montana (Collier, 1929; Wennekers, 1985). This structure hosts a large known natural CO₂ resource and is a potential site for carbon sequestration in northwestern United States (Spangler, 2011; Bowen et al., 2012; Onishi et al., 2019). The origin of CO₂ trapped in Kevin Dome ($\sim 283 \times 10^9 \text{ m}^3$) has not been studied in detail. Additionally, existing structural evolution models of the dome (e.g., Shepard and Bartow, 1986) are not constrained by modern time-temperature (t-T) sensitive techniques. This dissertation seeks to answer the following four (4) research questions:

1. What are the major exhumation episodes that led to the development of Kevin Dome?
2. How has the burial-and-uplift history controlled the thermal conditions that have led to hydrocarbon generation within the Bakken petroleum system at Kevin Dome?
3. What is the origin and timing of emplacement of the Upper Devonian Duperow Formation CO₂ resource and how has it evolved and migrated through time into the present-day petroleum system?
4. Can we reconcile Kevin Dome's evolution, erosional history, and CO₂ origin with existing structural evolution models for the dome and incorporate it within the framework of existing regional geology?

Objectives and Scope of Dissertation

I integrated various thermochronological, thermobarometric, mineralogic, petrologic, and isotopic geochemistry methods to answer the above questions. The findings of these research efforts were then written into two interdisciplinary journal articles (chapter two and three) for submission to address the research questions highlighted above with relevant techniques.

Chapter Two was co-authored with Colin A. Shaw (Montana State University), Gregory A. Henkes (Stony Brook University), Madison L. Myers (Montana State University), Mary S. Hubbard (Montana State University), David W. Bowen (Montana State University), and Charles W. Calavan (Montana State University) and is in preparation for submission to the *Basin Research* journal. The goal of this prepared article is to address Kevin Dome's structural evolution by examining its burial and exhumation history, and the implications for hydrocarbon generation, including an estimate on the amount of erosion the dome has experienced during its exhumation. I applied: (i) apatite and zircon (U–Th)/He low-temperature thermochronology analyses and HeFTy thermal history modeling on Kevin Dome Archean basement and clastic unit core cutting samples (ii) carbonate clumped isotope thermometry and carbonate petrology (optical microscopy, x-ray diffraction and cathodoluminescence imaging) on Kevin Dome carbonate unit core cutting samples and (iii) igneous petrology (i.e., optical microscopy, bulk rock) major and trace elemental composition, single crystal analysis) and thermobarometry outcrop samples from Gold Butte (Sweetgrass Hills igneous complex). I found two significant exhumation episodes during Late Cretaceous-Paleocene (~65 – 72 Ma) and Oligocene-Miocene (~ 15 – 26 Ma) with an average rate of ~ 0.27 mm/yr at Kevin Dome. I reconciled

Kevin Dome structural development to the evolved forebulge structural evolution model related to (i) the Late Cretaceous-Paleocene deformation associated with evolution of the Rocky Mountain overthrust in northwestern Montana and proximal Canada (Hoffman et al., 1976; Lorenz, 1983; DeCelles and Giles 1996; Sears, 2001; Osborn et al., 2006; Ward, 2007) and (ii) an Oligocene-Miocene erosional or epeirogenic event unrecognized by previous authors in northwest Montana. I also found burial temperature conditions that are consistent with oil and gas generation in the clastic and carbonate units at the dome. This study suggests that the Oligocene-Miocene exhumation event halted hydrocarbon generation at Kevin Dome. I estimated that ~4km – 5km of sediments were eroded from northwest Montana, USA and southern Alberta, Canada regions than earlier accounted for. I present the first data set in the region to constrain the timing of Kevin Dome exhumation and its erosional impact.

Chapter 3 was co-authored with Rebecca L. Tyne (Woods Hole Oceanographic Institution), Peter H. Barry (Woods Hole Oceanographic Institution) Thomas H. Darrah (Ohio State University), Mary S. Hubbard (Montana State University), Madison L. Myers (Montana State University), David W. Bowen (Montana State University), Charles W. Calavan (Montana State University) and Colin A. Shaw (Montana State University) and is in preparation for submission to the *Geochimica et Cosmochimica Acta* journal. The goal of the prepared article is to address the origin, timing of emplacement, and migration history of CO₂ in the Upper Devonian Duperow Formation and its interaction with the Bakken petroleum system at Kevin Dome. The origin of the hydrocarbon and nitrogen gases within the Bakken petroleum system was also addressed. I engaged isotopic geochemistry (i.e., molecular composition, stable isotopes, and noble gases isotopes),

multiple genetic diagram schemes and CO₂ evolution models on (i) the Duperow CO₂-bearing unit; and (ii) Gold Butte (Sweetgrass Hills Igneous complex) igneous fluid inclusions (iii) Kevin Dome and (iv) Ferguson Field (southern Alberta, Canada) hydrocarbon-bearing bulk gas samples. I found that the Upper Devonian Duperow Formation CO₂ and those within the Bakken petroleum system at Kevin Dome to be of magmatic origin. I found that the CH₄ and N₂ gases in the Bakken petroleum system were mainly generated from thermogenic processes during burial with inputs from secondary microbial actions on existing oil during the Early Cretaceous (Dolson et al., 1993; Dyman, 1995; Dembicki, 2017). This study suggests that the magmatic CO₂ was emplaced into Kevin Dome during the proximal Sweetgrass Hills igneous complex intrusion which has been dated at ~52 Ma (Lopez, 1995), and migrated into Kevin Dome. Within Kevin Dome, the CO₂ is trapped within porous and permeable limestones and dolomites of the middle and lower Duperow Formation in a structural trap created by Kevin Dome (Bowen et al., 2009, 2012; Adeniyi and Steuer, 2019). I modeled a major magmatic CO₂ dissolution in the hydrocarbon-bearing reservoirs secondary to groundwater interaction at Kevin Dome (~98%) and at Ferguson Field (~82%). An estimated lesser gas/water ratio at Kevin Dome to Ferguson Field is consistent with more groundwater interaction hence the higher dissolution at Kevin Dome. This study is the first of its kind to characterize CO₂ sources in the northernmost part of the Rocky Mountain region, USA and southern Alberta Basin, Canada.

Lastly, chapter four summarizes the findings of this research, including a section on future research directions that could enhance our research findings.

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CHAPTER TWO

A THERMOCHRONOLOGICAL HISTORY OF BURIAL AND EXHUMATION

FROM KEVIN DOME, NORTHWEST MONTANA

Contribution of Authors and Co-Authors

Manuscript in Chapter 2

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Contributions: Conceptualized the project and analytical approach, completed field work and sample preparations, conducted analyses, performed thermal history and thermobarometry modeling simulations, analyzed the output from the model simulations, interpreted the results and wrote the manuscript.

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Contribution: Supported this research under the U.S. Department of Energy, and the National Energy Technology Laboratory through award number: DE-FC26-05NT42587 to the Energy Research Institute (ERI), Montana State University, helped on the (U – Th)/He analysis, discussed results and edited the manuscript.

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Manuscript Information

Elijah O. Adeniyi, Colin A. Shaw, Gregory A. Henkes, Madison L. Myers, Mary S. Hubbard, David W. Bowen, and Charles W. Calavan.

Status of Manuscript:

- ☒ Prepared for submission to a peer-reviewed journal
- ☐ Officially submitted to a peer-review journal
- ☐ Accepted by a peer-reviewed journal
- ☐ Published in a peer-reviewed journal

Abstract

Thermochronological studies are important for reconstructing the tectonic history, structural evolution, and geologic processes culminating in the development of a basin or dome. Such structures are important in that they commonly have the potential to host a hydrocarbon resource. Kevin Dome is an example of a hydrocarbon bearing structural feature in northwest Montana. Although existing structural evolution models for the development of Kevin Dome have been inferred from stratigraphy and thermal maturity indices, these models are yet to be constrained with time-temperature (t-T) sensitive techniques. In this study, we integrate (U–Th)/He low-temperature thermochronology and thermal modeling of Kevin Dome’s Archean Basement and overlying clastic units with carbonate clumped thermometry of its carbonate units. Thermobarometry analysis of the adjacent Sweetgrass Hills intrusive rocks was also completed to estimate the erosion rates in the region. We find that Kevin Dome rocks reached the oil and gas generation window by burial prior to experiencing two distinct exhumation episodes during the Late Cretaceous-Paleocene (~65 – 72Ma) and Oligocene-Miocene (~ 15 – 26Ma), with exhumation rates that average ~ 0.27 mm/yr. We find that these exhumation episodes are younger than the Early to mid-Cretaceous (ca. 100Ma) onset of exhumation recorded in six basement cored uplifts in southwestern Montana. The Oligocene-Miocene exhumation interpreted at Kevin Dome constrains the timing of regional exhumation that occurred in northern Montana and southern Alberta, Canada. Our study supports the evolved forebulge structural evolution model for Kevin Dome related to (i) the Late Cretaceous-Paleocene emplacement of the Rocky Mountain overthrust in a Foreland Basin setting in northwestern Montana and proximal Canada and (ii) an Oligocene-

Miocene erosional or epeirogenic event not earlier accounted for in the northwest Montana. We estimate that ~4 – 5 km of sediments were eroded from this region, and we suggest that the Oligocene-Miocene exhumation event halted hydrocarbon generation at Kevin Dome. This study presents a novel approach for integrating modern t-T sensitive techniques with conventional stratigraphic and thermal maturity proxies to understand the structural developments of sedimentary basins/domes and how burial-and-uplift controlled thermal conditions influence hydrocarbon generation.

Introduction

Kevin Dome is a geologic structure that initially evolved as part of the Sweetgrass Arch in northwestern Montana (Peterson 1966; Shepard and Bartow, 1986). The dome is an historic oil and gas producing geologic structure which also hosts a large ($\sim 283 \times 10^9$ m³) CO₂ reservoir in the Upper Devonian Duperow Formation and may have significant (~ 1 GT) capacity for carbon sequestration (Collier, 1929; Wennekers, 1985; Bowen et al., 2009; Spangler, 2011; Onishi et al., 2019). Despite the economic importance of Kevin Dome, few studies have been completed focusing on how the dome was formed. The most accepted model involves the formation of an evolved forebulge related to the Late Cretaceous-Paleocene emplacement of the Rocky Mountain Cordillera in the associated foreland basin (Hoffman et al., 1976; Lorenz, 1983; DeCelles and Giles 1996; Sears, 2001; Osborn et al., 2006; Ward, 2007) (see Supplementary information (SI) A). It has been argued that Kevin Dome has experienced repeated episodes of uplift and subsidence during its formation (Shepard and Bartow, 1986; Lochman-Balk and Wilson, 1967; Sandberg, 1965; Sandberg et al., 1988), with deposition punctuated by various erosional and orogenic events (Sloss, 1950; Peterson, 1966, 1981 and 1987) and one of

the net results is an accumulated hydrocarbon resource in the region (Collier, 1929; Nordquist, 1953; Nordquist and Leskela, 1968; Bustin, 1991; Dolson et al., 1993; Jorgensen, 2004; Stein, 2008). These studies, however, were inferred from stratigraphic distribution, erosion/non-deposition evidence and thermal maturity indices and are yet to be constrained with time-temperature (t-T) sensitive techniques such as (U–Th)/He low-temperature thermochronology, carbonate clumped thermometry, and cooling history modeling of the upper crust.

Conventional stratigraphic evidence and thermal maturity indices in rocks may be limited in providing the precise timing, rates, and episodes of exhumation(s) of geologic structures. Thermochronological techniques, however, can be effective in refining the timing of the evolution of sedimentary basins and structural domes because they provide quantitative data on the cooling history of the rocks from which the timing and duration of geologic events can be interpreted (e.g., Peyton and Carrapa, 2013; Flowers et al., 2015; Shenton et al., 2015; Ryb et al., 2021). Low-temperature thermochronology and thermal modeling exhumation studies have facilitated the interpretation of exhumation episodes spanning time frames from Early Cretaceous to Neogene in the Laramide Rocky Mountain foreland basins of New Mexico, Colorado, Wyoming, and southwest Montana (e.g., Peyton et al., 2013; Fan and Carrapa, 2014; Stevens et al., 2016; Rønnevik et al., 2017; Carrapa et al., 2019). Based on Apatite (U – Th)/He (AHe), Apatite Fission Tracking (AFT) and thermal modeling techniques, Peyton et al. (2013) inferred that rapid exhumation began in the Laramide Bighorn Range, WY and Beartooth Range, Montana before ~ 71 Ma and ~ 58 Ma respectively. Additional AFT and thermal modeling work by Stevens et al. (2016) in the Wind River Range, WY established that sedimentary units

were buried deep enough to reach temperatures of approximately 135 – 160 (°C) by the Late Cretaceous-Paleocene prior to uplift and found no evidence for Oligocene exhumation. Using similar methods, Rønnevik et al. (2017) provided no precise timing for the Laramide uplift but indicated that cooling started ~ 65 Ma with Miocene–Pliocene uplift for the Uncompahgre Plateau in western Colorado. From six Laramide ranges (Beartooth, Madison, Gravelly Mountains, Ruby, Tobacco Root Mountains, and Highland Mountains) in southwest Montana, Carrapa et al. (2019) presented strong evidence for Early-to-mid Cretaceous (ca 100Ma), Eocene to early Miocene (ca. 50–20 Ma) and post ca. 25 Ma cooling/exhumation episodes which they associated with Laramide Orogeny, magmatic heating and/or burial and other Basin-and-Range tectonics respectively, using zircon U-Pb geochronology, AFT, zircon (U – Th)/He (ZHe), and AHe proxies. Carrapa et al. (2019) argued that thick-skinned exhumation signifying the onset of the Laramide orogeny (ca 100Ma) recorded in southwest Montana is much older than the Laramide uplift recorded in Wyoming (Fan and Carrapa, 2014; Stevens et al., 2016). Furthermore, carbonate clumped isotope thermometry has been successfully used to investigate thermal history of sedimentary basins in the Rocky Mountains (e.g., Shenton et al., 2015; Lacroix and Niemi, 2019; and Ryb et al., 2021), West Texas, USA (Naylor et al., 2019) and elsewhere (e.g., Xu et al., 2017 and Ingalls, 2019). Naylor et al. (2019) used clumped isotope temperature ($T(\Delta 47)$) measurements to reconstruct burial history curves, past geothermal gradient, identify higher heat flows sources in the Delaware Basin, West Texas USA and also demonstrated the compatibility of $T(\Delta 47)$ with vitrinite reflectance in evaluating the thermal history of basins. Ryb et al. (2021) constrained the peak burial temperature of carbonate strata, (pre-Neogene) total exhumation and amount of sediment eroded from

the Colorado Plateau with $T(\Delta 47)$ measurements. While most of the previous thermochronological studies in the Rocky Mountains are distal to Kevin Dome, the low-temperature work of Carrapa et al. (2019) in southwest Montana and carbonate clumped isotope work in the Colorado Plateau of Ryb et al. (2021) provide some basis for comparison with the new results obtained at Kevin Dome.

The current study aims to reconstruct the cooling history of Kevin Dome to reveal its timing of exhumation(s), thermal history and how thermal conditions drove hydrocarbon generation at the dome. Understanding the cooling history of Kevin Dome's rocks will not only inform the timing of its exhumation but will also allow us to connect its development to local or regional tectonic events. In addition, knowledge gained from reconstructing the timing of Kevin Dome exhumation, and the inferred associated tectonic forces, will allow us to refine existing structural models of the region, and to put forward a new model for Kevin Dome's development. Lastly, determining the thermal history provides needed insight into the maximum temperature that the rocks and fluids have been subjected to and the temperatures which the organic matter trapped in deposited sediments have experienced during maturation and hydrocarbon generation. By integrating (U–Th)/He, carbonate clumped thermometry, and thermobarometric analyses, this study presents a holistic approach and novel opportunity to integrate thermochronological techniques in investigating the various stages of burial, uplift and erosional events associated with Kevin Dome's development and how thermal conditions have driven hydrocarbon generation at the dome.

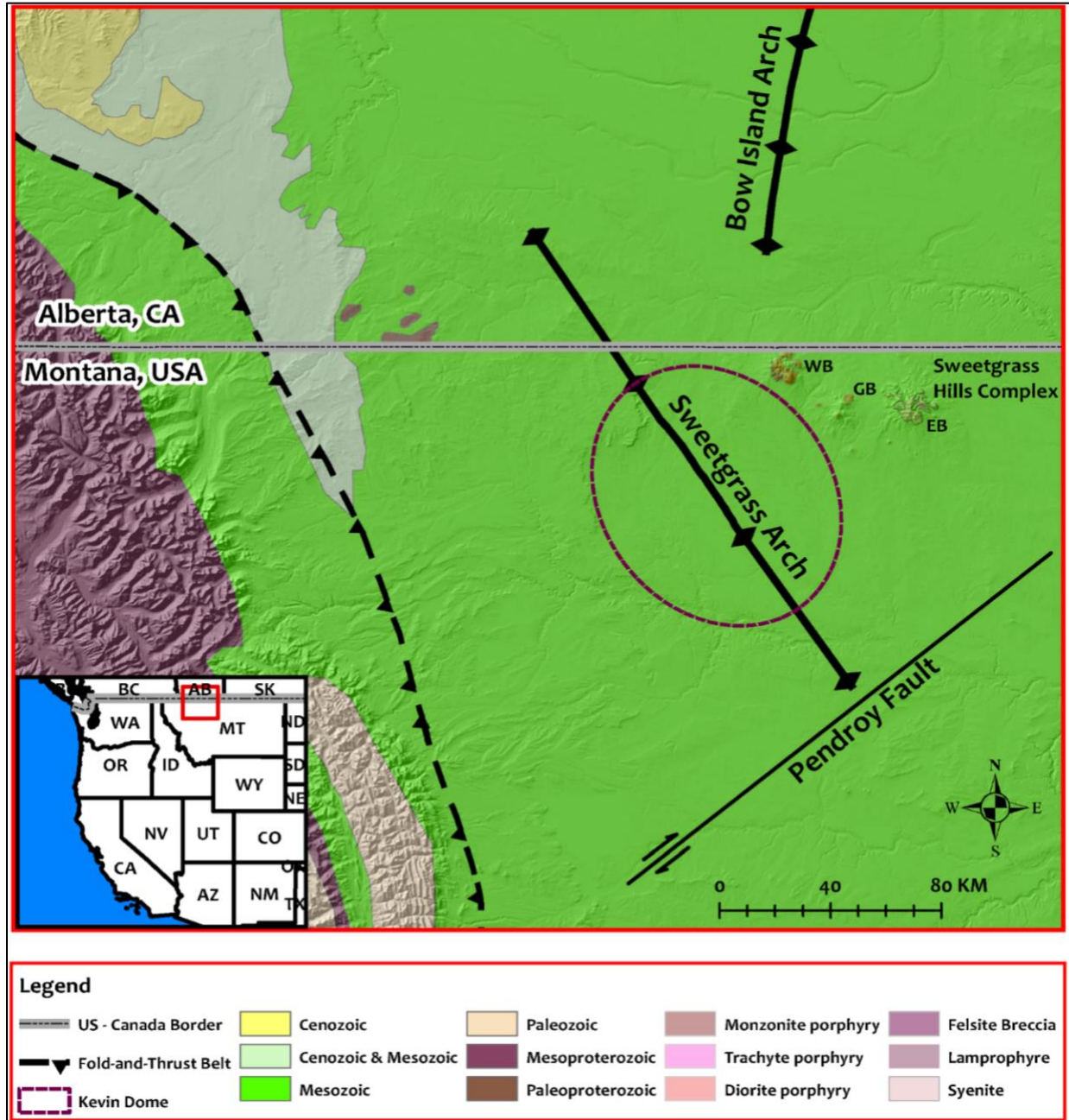


Fig. 1: Regional map of Kevin Dome and various structural elements associated with its development; namely the Sweetgrass Arch, Rocky Mountain Fold and Thrust Belt, the Pendroy Fault, the Sweetgrass Hills igneous complex and the Bow Island Arch, southern Alberta Canada (Shepard and Bartow, 1986; Vuke et al., 2007; Pană et al., 2021). WB – West Butte, GB – Bold Butte, EB – East Butte.

Geologic Setting of Kevin Dome, Northwest Montana

Regional Geology

The Sweetgrass Arch on which Kevin Dome formed is a north to north-northwest plunging anticline that extends for about 266 km from the Little Belt Mountains in central Montana to the north-east trending Bow Island Arch of southern Alberta, Canada (Fig. 1). Proximal to the center of the arch is the northeast-striking, right-lateral Pendroy Fault zone with a ~48 km offset along the hinge of the anticline, thus demarcating the north arch from the south arch. Kevin Dome is a 320 km long, north-plunging structural culmination located on the Sweetgrass Arch in northwest Montana. The dome is bounded to the west by the Rocky Mountain thrust belt and to the east by the Williston Basin (Shepard and Bartow, 1986). Adjacent to and about ~40 km east of Kevin Dome are the Sweetgrass Hills (SGH) igneous complex. The SGH are Eocene (54–49 Ma) igneous intrusions that intruded Phanerozoic siliciclastic and carbonate strata in northern Montana (Rukhlov and Pawlowicz, 2012; Marvin et al., 1980; Lopez, 1995). They are exposed as four main buttes known as the West Butte, Gold Butte, Middle Butte, and East Butte, respectively (Fig. 1).

Tectono-Stratigraphic History

The stratigraphy at Kevin Dome has been greatly controlled by basement faults and offset structures, episodes of uplift and subsidence, and structural instability, with sedimentation punctuated by erosional events (Jorgensen, 2004; Sloss, 1950; Peterson 1966). Fig. 2 shows the Archean Basement and Phanerozoic Sedimentary units at Kevin Dome, including the regional tectonic events, and areas that contain missing time and erosional surfaces associated with its development and strata distribution. Cambrian, Devonian, Mississippian, Jurassic, and Cretaceous aged strata are preserved on Kevin

Dome with a cumulative ~1.7 km thickness (Collier, 1929; Shepard and Bartow, 1986). Michener (1934) estimated that ~1.4 km of sediment has been eroded from the region during uplift. Though present on the western and southern flanks of Kevin Dome, sediment deposited during the Precambrian Belt Basin are missing or interpreted to have been eroded from the dome due to uplift on the Sweetgrass Arch prior to the Mid-Cambrian (Shepard and Bartow, 1986). Similarly, the distribution and thickness of Cambrian, Devonian and Mississippian strata in the region are thought to be controlled by pre-Mid Devonian and pre-Mid Jurassic uplift and erosion. For example, in certain parts of the Kevin Dome, regional pre-Devonian truncation led to the thinning of Cambrian sediment (Lochman-Balk and Wilson, 1967; Peterson, 1966; Shepard and Bartow, 1986). The preserved Cambrian strata on Kevin Dome (limestone and calcareous shales) suggest a moderately stable tectonic setting from Mid to Upper Cambrian periods where the depositional and tectonic conditions consisted of a Foredeep on the west (modern-day Idaho), a broad stable Wyoming Shelf to the southeast and unstable shelf conditions in north-central Montana (Stein, 2008; Shepard and Bartow, 1986; Sloss, 1950). Stable basin conditions favored carbonate deposition during Ordovician and Silurian periods (Blakey and Ranney, 2017). These carbonate strata, however, including lower Devonian rocks, are now absent on the dome due to Mid-Devonian uplift and erosion (Sloss, 1950; Peterson, 1981). As a result, Upper Devonian strata unconformably overlie Cambrian sedimentary units at Kevin Dome. Deposition of Devonian strata occurred during second order sea-level rise resulting in a gently dipping (>10 degrees) shallow marine platform on the western margin of North America that was dominated by carbonate and evaporite

sedimentation (Norwood, 1965; Sandberg, et al., 1988). Upper Devonian units preserved on Kevin Dome include the Souris River, Duperow, Nisku, Potlach, and the Three Forks formations (Sandberg, 1965; McQueen and Sandberg, 1970). The Early Mississippian Bakken Formation is present across Kevin Dome while the Madison Group (Upper Mississippian) unconformably overlies the Bakken Formation. The Madison Group on Kevin Dome includes the Lodgepole, Mission Canyon, and Sun River Formations (Nordquist and Leskela, 1968; Peterson, 1987; Dolson et al., 1993). The Sun River Formation later experienced pre-Jurassic erosion (Nordquist, 1955). The overlying Jurassic and Cretaceous layers are predominantly clastic rocks. Jurassic strata on Kevin Dome include the Sawtooth, Rierdon, Swift and Morrison formations while Cretaceous strata include the Kootenai Formation, the Colorado Group, and the Montana Groups with their respective formations and members.

Methods

Sampling Strategy and Screening

Sampling strategy involved subsurface sampling from the Archean Basement unit and various clastic units for apatite (U–Th)/He (AHe) and zircon (U–Th)/He (ZHe) low-temperature thermochronology while carbonate units were sampled for carbonate clumped isotope thermometry (Fig. 2). We utilized core cuttings from historic wells (n=11) in the Kevin Dome, provided by the Montana Board of Oil and Gas Conservation (MBOGC), and well cores (n=2) provided by the Big Sky Carbon Sequestration Partnership (BSCSP) and the Energy Research Institute (ERI) at Montana State University, USA. Additional igneous rock samples were collected from Gold Butte (SGH) in northwest Montana in the summer of 2020 for thermobarometry analysis (Fig. 2). All

sample preparations were processed at Montana State University prior to being analyzed at chosen lab facilities. To retrieve zircon, apatite, and olivine minerals from the bulk rock samples prior to (U–Th)/He thermochronology and He-Ne-Ar noble gas analyses, mineral separation was completed at GEOSEP Services, Moscow, Idaho (see SI B for details).

(U–Th)/He Analyses

AHe (n=18) and ZHe (n=12) analyses were completed at the University of Colorado Boulder Thermochronology Research and Instrumentation Laboratory (TRaIL). AHe and ZHe measure the concentrations of the daughter product (^4He) and parent nuclide (^{238}U , ^{235}U and ^{232}Th) involved in the radioactive decay process (Peyton and Carrapa, 2013; Reiners et al., 2004a). The ^4He daughter measured during AHe or ZHe is temperature sensitive, and each dating system is defined by a temperature range known as closure temperature (T_c). T_c is a simplified representation of daughter isotope retention over a range of temperatures (Dodson, 1973) in which ^4He is fully retained in the mineral's crystal lattice, and above which ^4He is lost to the external environment (Farley, 2000 and 2002; Peyton and Carrapa, 2013). The T_c range for AHe and ZHe dating systems are $\sim 40 - 75^\circ\text{C}$ and $\sim 170-190^\circ\text{C}$ respectively (Farley, 2000; Flowers et al., 2009; Gautheron, et al., 2009 and 2013; Shuster et al., 2006; Shuster and Farley, 2009; Ault et al., 2019). The operative T_c varies depending on lattice damage and can be estimated using effective uranium (eU).

There are several potential sources of error associated with using core cuttings for (U–Th)/He analyses, including mineral contamination concerns that can occur during drilling and sample mixing due to poor handling. Drilling mud could also contaminate apatite minerals while sample depth recorded for a core cutting may not be its true vertical

depth especially in horizontal drilling (Peyton et al., 2013). To compensate for errors related with depth mixing, the sampling interval was minimized, and sampling was avoided near formation contacts to ensure positioning within the chosen formation (see SI B for details).

Petrographic analysis was conducted on the apatite and zircon grains recovered from mineral separation to select the best candidates for further lab work. The surface area of selected aliquots was measured to determine their volume ratios (useful for the alpha-ejection correction), and photomicrographs were taken. We ensured that samples hosting U-, Th-, and He- bearing impurities (e.g., zircon microlites and inclusions) were avoided, as they pose a challenge to accuracy (Warnock et al., 1997; House et al., 1997). Apatite and zircon grains of similar geometry, morphology and grain size were selected to minimize differences secondary to He diffusivity behavior (Farley, 2000; Beucher et al., 2013; Brown et al., 2013). Successful grain candidates were enclosed in small Niobium tubes then loaded into the ASI Alphachron to degas the grains, and to extract and measure the He content of the emitted gas. These niobium tubes containing the mineral grains were then placed in vials with spiked solutions (i.e., isotopic dilution - in ~50% HNO_3 at ~800°C) to determine the U, Th and Sm isotope compositions using ICP-MS (Evans et al., 2005). The He alpha-ejection correction factor (FT), especially for abraded grains, was factored into the (U-Th)/He apparent date calculation following the methods of Farley et al. (1996).

Carbonate Clumped Isotope Analysis

Carbonate clumped isotope thermometry analyses were performed on Kevin Dome carbonate rock samples (n=17) at the Henkes Stable Isotope Geochemistry Lab, Stony Brook University, NY following analytical procedures described by Passey et al. (2010) and Henkes et al. (2013). Prior to clumped isotope temperature measurements, thin sections were made of each sample (core plugs) to fully characterize and interpret the resultant data within a petrological and mineralogical framework. Carbonate petrology and mineralogy were described using optical microscopy and x-ray diffraction analysis at Montana State University as well as cathodoluminescence microscopy (CL imaging) at Stony Brook University, NY. All descriptions, petrological classification and XRD mineralogical analysis completed on these core plugs can be found in supplementary material: SI C.

Carbonate clumped isotope thermometry is based on the (temperature-controlled) preferential clumping of ^{13}C and ^{18}O into bonds within the carbonate mineral lattice at low and elevated temperatures (Wang et al., 2004; Ghosh et al., 2006; Schauble et al., 2006; Eiler, 2011). The analytical procedure aims to measure the clumped isotope temperature ($T(\Delta 47)$) of the CO_2 gas released from carbonate rocks during acid digestion (Wang et al., 2004). Powdering of the samples is essential for complete acid reaction during carbonate clumped isotope thermometry analysis; thus, the rock matrix and veins/fractures of the samples were hand drilled to make powdered portions of each sample. Measured powdered portions (~ 0.78g) were loaded in silver capsules, arranged sequentially on a sample tray, and positioned to be dropped in a customized acid bath for a carbonate and phosphoric acid reaction ($\rho > 1.9 \text{ g/ml}$) within a vacuum chamber. To

ensure complete reactions and to increase the amount of CO₂ gas released, acid reaction duration and temperature were pre-determined based on the mineralogy of the sample. The gas released from the acid reaction is channeled through different purification lines, traps, and loops to remove unwanted water and gaseous species prior to analysis (e.g., N₂, H₂S, He, and Hydrocarbons). The purification of the gas is based on the freezing point and character of each gaseous species and is set up to isolate pure CO₂ from the gas. Liquid nitrogen and methanol were mixed to create two liquids of different temperatures (-200 and -800 (°C)) and together with pure Nitrogen (-196 (°C)), were placed at different purification line traps and loops until a semi-purified CO₂ was obtained. The semi-purified CO₂ gas was then channeled through a gas chromatography (GC) column (Porapak QTM; 1.2 m Nickel 200 tubing, 1/8" OD, 0.085" ID) in a 20 ml/min Helium carrier gas stream kept at -20 (°C) to remove hydro- and chlorocarbon contaminants. Using mechanical and turbomolecular pumps, the purified CO₂ gas was separated from the Helium carrier gas stream and cryogenically sequestered in a "cold finger" until it expanded in the Thermo Scientific MAT 253 Plus isotope ratio mass spectrometer dual inlet bellows for analysis. The purification line timing and liquid exchange for each stage were controlled by a custom-made software and robot at the Henkes Lab. Each sample was run three times while Oztech reference CO₂ gas (Oztech Trading Company, Stafford, Arizona, USA; $\delta^{13}\text{C} = -3.59\text{‰}$ Pee Dee belemnite [PDB], 24.91‰ standard mean ocean water [SMOW]) was run regularly after seven measurements. Masses of 44–47 signals were used to calculate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope compositions and $\Delta 47$ of the rocks using an O₂ isotope thermometry equation and isotopic classification scheme. More specifically, equation 3 from Bonifacie et al. (2018):

$$\Delta_{47\text{CDES90}} = 0.0422 (\pm 0.0019) * 10^6/T^2 + 0.1262 (\pm 0.0207) (r^2=0.985)$$

was used to compute T (Δ_{47}) while $\delta^{18}\text{O}$ of water in thermodynamic equilibrium with carbonate precipitation were calculated using the T (Δ_{47}) with the Kim and O'Neil (1997) and Horita (2014) equations for calcite and dolomite/anhydrite respectively.

Igneous Mineral Chemistry and Thermobarometry Analysis

Major and trace elemental composition of bulk rocks sampled from multiple outcrops in the Gold Butte (SGH) (n=4) were obtained following Low Dilution Li-tetraborate Fusion x-ray fluorescence techniques for major and trace elements as detailed in Johnson, et al. (1999) at the Hamilton Analytical Lab, NY. Petrographic examination and modal mineral analysis on Gold Butte (SGH) thin sections (n=7) was completed using optical microscopy. The thin sections were described for their mineral phases, textural relationships, and modal composition/abundance. The preliminary petrographic examination was necessary for identifying mineral phases that could provide pressure estimates of formation (i.e., pyroxenes and amphiboles), which were then targeted for chemical analysis. SI D summarizes the Gold Butte (SGH) petrology and petrographic modal analysis from this study. Based on clinopyroxene (Cpx) and amphibole (Amp) mineral abundances, rock samples were selected (n=4 out of 7) from Gold Butte (SGH) for thermobarometry T-P, which can then be used to determine the depth of intrusion.

Cpx and Amp spot analysis mineral chemistry was obtained by using electron probe micro analysis (EPMA) at Oregon State University. For each sample of interest, backscattered electron images (BSE) were obtained. BSE imaging was necessary to better visualize the internal structure of minerals of interest and place spots within the

Rim, Margin (~50 μm from rim) or Core. EPMA analytical conditions were set up following the procedure of Tepley, et al. (2013). A CAMECA SX-100 electron microprobe equipped with five wavelength-dispersive spectrometers (WDS), high-intensity dispersive crystals for high-sensitivity trace element analysis and a CAMECA Peak Site software were used for the EPMA mineral chemistry and BSE imaging data collection. Cpx and Amp mineral chemistry results obtained were validated using stoichiometric principles, with low totals not considered in thermobarometer calculations (e.g., Marroni, et al., 2009; Parry, et al., 1978; Karimpour, et al., 2011; Aulinas, et al., 2011). This work was performed to enhance our understanding of the depth at which these now exposed Eocene SGH intrusions formed, thus providing an independent understanding of the uplift rates in the region.

Results

AHe and ZHe Cooling Dates Distribution and Discrimination

AHe and ZHe cooling dates ($n=30$) were obtained from basement and clastic units at Kevin Dome (Table 1). Using the kernel density functions (Vermeesch, 2012), the density plot of the (U–Th)/He cooling dates for the crystalline basement and clastic units reveal two main clusters at ~ 10 – 48 Ma and ~ 70 – 140 Ma, including three much older dates at ~ 197 Ma, 592 Ma and 637 Ma (Fig. 3). Younger AHe and ZHe cooling dates of crystallization and deposition measured in both basement and clastic units, at Kevin Dome (Table 1) signify that the rocks must have experienced cooling due to exhumation after their crystallization and/or deposition. Our data, however, show wide AHe and ZHe cooling dates disparities from units of the same crystallization/deposition age (Table 1 and Fig. 3). This variety of dates may represent valid, disputable, or uniquely independent dates, depending on the character of the aliquots measured such as its parent isotope

concentration or helium loss by diffusion – a function of radiation damage and effective uranium concentration (eU) as well as its grain size (House, et al., 1997; Kohn, et al., 2008a; Reiners et al., 2008; Meesters and Dunai, 2002a; Hourigan et al., 2005; Reiners and Farley, 2001; Belton et al., 2004; Danisí'k et al., 2008; Gautheron et al., 2013; Orme et al., 2016). Radiation damage, eU, and grain size were thus used to examine the cooling dates obtained, where cooling dates influenced by radiation damage, eU, and/or grain size would show strong correlations in cooling date versus grain size and eU plots (Gautheron et al., 2013; Ault et al., 2013). Kevin Dome AHe and ZHe cooling dates show no correlations with grain size and eU in all the units, so we are not able to clearly discriminate between the cooling dates obtained with eU and grain size (see SI E). The lack of correlation observed is however consistent with areas of multiple episodes of exhumation, protracted cooling, and extended residence in the partial retention zone (PRZ) and partial loss during reheating as well as significant denudation events (Ault et al., 2013; Peyton et al., 2013). Multiple erosional surfaces recorded in Kevin Dome's stratigraphic record (Fig. 2) suggest episodes of exhumation and could be responsible for the dispersed cooling dates and lack of date-eU and date-grain size correlations seen in the data. Helium loss experienced during decay is accounted for mathematically during AHe and ZHe date calculation by a correction factor known as the Alpha-ejection correction (FT). FT is estimated based on an assumption of geometry or size of the grain. Alpha-ejection correction works better for large grains but becomes more uncertain as the grain size decreases or as the mineral density increases which reduces its helium loss e.g., zircons vs apatite (Ketcham, 2011). This relation means that a small zircon grain would have higher FT values compared to an apatite mineral grain of the same size due

to the higher density in zircon. In this study, a baseline of 0.5 was set for the Alpha-ejection correction values (Dr. J.R, Metcalf, personal communications, (2000)). FT values below 0.5 mean that over 50% of the helium produced during decay was ejected out of the mineral crystal lattice and hence unreliable for adequately interpreting the cooling history of the grain. Therefore, AHe (n=6) and ZHe (n=1) cooling dates with FT values below 0.5 were regarded as problematic and disregarded in the thermal history modeling (see Table 1 and Fig. 3).

$\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $T(\Delta 47)$ Trends and Implications

Carbonate clumped isotope thermometry measurements yielded depleted $\delta^{18}\text{O}$ values (-15 to -4 (‰, VPDB)), enriched $\delta^{13}\text{C}$ values (- 1.7 to +4 (‰, VPDB)) and clumped isotope temperatures ($T(\Delta 47)$) that range from 66 to 106 (°C) (Table 2) for Kevin Dome carbonate rocks. Kevin Dome carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures are consistent with marine environments (Jaffrés et al., 2007) and agree with the global increase of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values during the Paleozoic (Veizer et al., 1980; Veizer et al., 1999; Ryb and Eiler, 2018; Lindh, 1983) (see SI F). The $\delta^{18}\text{O}$ formation water composition values ($\delta^{18}\text{O}_{\text{water}}$) are in thermodynamic equilibrium with carbonate precipitation and ranged from - 3.4 to + 4 (‰, VSMOW) and +1 to + 8 (‰, VSMOW) for calcite and dolomite/anhydrite minerals respectively at Kevin Dome. Ideally, near surface $\delta^{18}\text{O}_{\text{water}}$ values of marine settings range between 0 + 2 (‰, VSMOW) and values above +2 (‰, VSMOW) would indicate the presence of an evolved, warmer basinal water as the temperature increases (Taylor, 1974; Zachos, et al., 2001). Except for two outliers, Kevin Dome carbonate rock $\delta^{18}\text{O}_{\text{water}}$ values are greater than +2 (‰, VSMOW) indicating that the carbonate formation waters have been altered through water–rock reactions at warmer temperatures during burial.

Table 1: Kevin Dome AHe and ZHe Results

Well/ Sample		Depth (m)	Aliquot a	Rs (μm) b	⁴ He (nmol/g) c	±2σ	U (ppm) ^c	±2σ	Th (ppm) ^c	±2σ	Sm (ppm) ^c	±2σ	eU ^d	± ^e	Uncorr Date (Ma) ^f	±2σ	F _T comb ^g	Corrected Date (Ma) ^h	±2σ
Well 1	365-13	Three Forks Fm (372 - 359 Ma) ^j																	
		808	a01	30	1.86	0.04	10.83	0.85	69.20	1.98	23.51	1.17	27.1	99.8	12.57	0.50	0.518	24.10	1.81
			a02	18	1.74	0.09	6.24	0.87	11.51	0.61	40.26	5.12	8.9	100	34.64	3.71	0.330	99.62	19.0
			z01	22	0.0	0.1	5.0	0.9	2.5	0.3	0.0	0.0	5.6	0.8	0.7	2.6	0.49	1.3	10.2
			z02	24	246	1.0	534.0	11.1	272.4	1.7	0.0	0.0	598.7	89.8	75.6	1.4	0.53	142.8	5.0
	z03	27	348	1.7	815.2	11.9	295.1	10.7	0.0	0.0	885.3	133	72.5	1.0	0.57	126.7	3.6		
	365-20	Precambrian Unit (3.8 – 2.5 Ga) ^j																	
		1428	a01	32	0.17	0.02	4.73	0.48	2.08	0.19	6.24	0.9	5.2	100	5.97	0.77	0.574	10.34	2.77
			a02	33	5.86	0.03	14.59	0.42	118.38	1.91	35.11	1.15	42.4	100	25.26	0.39	0.542	46.37	1.31
			a03	24	3.50	0.08	47.80	1.58	6.96	0.18	50.36	2.6	49.4	100	13.01	0.50	0.428	30.05	1.74
a04			25	2.56	0.04	22.03	1.25	6.89	0.33	20.73	1.5	23.6	100	19.89	1.05	0.468	42.17	4.14	
Well 2 365-01	Kootenai Fm (120 - 112 Ma) ^j																		
	413	a01	46	3.96	0.03	20.65	0.45	63.78	1.91	18.55	0.4	35.6	100	20.42	0.40	0.736	27.67	1.12	
		a02	31	1.07	0.03	8.63	0.47	51.42	2.34	42.70	0.9	20.7	100	9.34	0.40	0.524	17.64	1.37	
		a03	31	2.16	0.03	20.00	1.18	45.02	1.71	35.50	0.8	30.6	99.9	12.96	0.55	0.438	29.19	1.81	
		a04	29	1.33	0.03	10.48	0.15	49.98	2.29	9.13	0.7	22.2	99.2	10.99	0.36	0.486	22.53	1.34	
		z01	25	427.34	3.88	1050.9	36.6	366.60	5.05	n.m.	n.m	1137.1		69.31	2.25	0.567	121.60	7.84	
		z02	36	383.95	1.94	455.60	8.34	306.55	6.60	n.m.	n.m	527.6		133.42	2.18	0.689	192.67	6.35	
		z03	65	297.72	1.32	525.03	10.8	182.15	2.79	n.m.	n.m	567.8		96.46	1.83	0.824	116.89	4.47	
Well 3	365-10	Bakken Fm (358.9 - 323 Ma) ^j																	
		761	a01	30	12.18	0.09	50.70	2.76	39.95	0.60	31.40	1.8	60.1	99.8	37.30	1.68	0.546	67.88	5.89
			a02	30	12.18	0.09	30.26	1.05	111.28	1.82	47.57	2.7	56.4	100	39.51	0.81	0.524	74.81	2.95
	365-18	Precambrian Unit (3.8 – 2.5 Ga) ^j																	
		1493	a01	28	3.86	0.03	64.16	2.45	26.26	0.96	21.31	0.9	70.3	99.8	10.14	0.35	0.500	20.22	1.11
			a02	33	8.13	0.05	56.94	1.47	21.08	0.30	17.10	0.9	61.9	100	24.26	0.58	0.717	33.78	1.76
			a03	24	5.57	0.06	60.39	1.14	17.53	1.47	17.12	1.31	64.5	100	15.98	0.34	0.535	29.80	1.21
			z01	29	953	3.6	322.0	3.7	523.9	6.0	0.0	0.0	446.4	67.0	385.1	3.6	0.59	637.8	11.9
			z02	29	1156	5.2	477.9	9.9	434.6	4.2	0.0	0.0	581.2	87.2	358.6	6.2	0.59	592.1	20.6
			z03	23	628	2.4	1447.2	37.0	456.6	13.6	n.m	n.m	1556	233.	74.4	1.7	0.52	143.5	6.7
Well 4 365-26	Bow Island Fm (113 - 100.5 Ma) ^j																		
	412	a01	38	5.83	0.04	43.86	1.32	130.20	2.84	52.21	0.8	74.5	100	14.38	0.30	0.625	22.92	0.93	
		a02	33	1.32	0.04	3.52	0.32	57.31	0.77	26.24	1.11	17.0	99.6	14.09	0.51	0.567	24.66	1.84	
		a03	24	19.9	0.14	75.50	0.92	755.57	23.5	44.38	1.14	253.1	100	14.49	0.34	0.413	34.99	1.33	
		z01	29	323.9	3.6	910.58	14.5	571.9	15.6	n.m.	n.m	1046	157	57.2	1.0	0.60	95.2	3.3	
		z03	26	83.4	0.5	229.59	7.9	174.6	1.1	n.m.	n.m	271.2	40.7	56.8	1.6	0.55	102.9	5.7	
		z04	26	69.5	0.6	181.00	10.8	171.1	9.1	n.m.	n.m	221.7	33.3	57.9	2.8	0.56	103.6	10.0	

Notes: a - Sample and mineral being analyzed: a = apatite, z = zircon. b = Rs is the radius of a sphere with an equivalent alpha-ejection correction as the grain, calculated using equation A6 in Cooperdock et al., (2019). c = concentrations of He,

U, Th and Sm computed from their absolute amounts and the estimated dimensional mass reported in Table 1. **d** = eU is effective uranium concentration, calculated as $U + 0.2375 \cdot Th + 0.0012 \cdot Sm$. **e** = uncertainty on eU estimated at 15% of the eU value. **f** = uncorrected date is calculated iteratively using the ^4He production equation defined as equation 1 in Wolf et al. (1998) and assuming secular equilibrium. **g** = combined alpha-ejection correction for the crystal calculated from the isotope specific FT corrections, the proportion of U and Th contributing to ^4He production in Table 1, and assuming homogeneous parent isotope distributions. FT values below 0.5 are written in red (explained in main text). **h** = corrected date is calculated iteratively using the absolute values of He, U, Th and Sm in Table 1, the isotope specific FT corrections in Table 1, and equation 34 in Ketcham et al., (2011) assuming secular equilibrium. **i** = age of deposition/crystallization (see SI H for references). **n.m.** = not measured.

Table 2: Kevin Dome Carbonate Clumped Isotope Thermometry Results

Formation	Well Name	Sample Name	Depth (m)	XRD Dominant Mineral	n	$\delta^{13}C$ ‰, VPDB	±	$\delta^{18}O$ ‰, VPDB	±	$\Delta 47$ ‰	±	$\Delta 47T(^{\circ}C)$ (Bonifacie et al., 2018)	$\delta^{18}O$ ‰, alpha	$\delta^{18}O_{water}$ ‰, VSMOW
Madison	Allen 31-8	21KDo5-2A	467.26	Calcite	3	0.49	0.07	-10.73	0.43	0.42	0.02	104.87	1.015	4.34
		21KDo5-2B		Calcite	3	1.07	0.05	-8.30	0.33	0.48	0.01	70.78	1.020	2.06
		21KDo5-3A	471.22	Calcite	3	0.56	0.15	-15.29	0.47	0.46	0.02	81.56	1.019	-3.42
		21KDo5-3B		Calcite	3	1.42	0.12	-8.81	0.49	0.47	0.01	76.27	1.019	2.37
		21KDo5-3C		Calcite	3	1.70	0.17	-9.50	0.59	0.45	0.02	86.23	1.018	3.11
Potlach	Normont 15-13	21KDo8-5B	772.06	Dolomite	3	-1.64	0.07	-5.61	0.23	0.46	0.01	78.22	1.023	2.48
	Suta 1-34	21KDo6-1B	1016.81	Dolomite	3	-1.76	0.15	-5.64	1.36	0.47	0.01	76.11	1.023	2.13
Nisku	Suta 1-3	21KDo7-2B	1025.04	Dolomite	3	-1.60	0.01	-5.16	0.01	0.47	0.01	76.72	1.023	2.71
Duperow	US 3	21KDo2-1B	956.77	Dolomite	3	4.16	0.25	-7.85	0.53	0.43	0.02	99.08	1.016	6.51
	Inland Empire 1	21KDo1-1B	1038.76	Dolomite	3	1.15	0.13	-7.49	0.44	0.41	0.01	106.27	1.015	7.81
	Danielson 33-17	EADCC2-B	998.46	Anhydrite	3	1.25	0.05	-6.21	0.30	0.45	0.04	84.63	1.022	2.78
		EADCC3-B	1013.46	Dolomite	3	3.80	0.03	-8.93	0.26	0.42	0.01	104.30	1.019	2.52
		EADCC5-B	1044.31	Calcite	3	-0.33	0.07	-8.08	0.45	0.46	0.03	82.51	1.018	4.01
	Wallewein 22-1	EAWCC8-B	1214.02	Dolomite	3	1.38	0.04	-4.84	0.08	0.49	0.01	66.11	1.024	1.40
		EAWCC10-B	1249.07	Dolomite	3	1.69	0.07	-5.60	0.07	0.46	0.01	79.06	1.022	2.60
		EAWCC11-B	1258.00	Dolomite	3	4.11	0.62	-5.92	0.49	0.47	0.01	76.97	1.019	5.39
		EAWCC12-B	1262.63	Dolomite	3	3.72	0.01	-5.33	0.02	0.46	0.00	78.51	1.023	2.80

$\delta^{18}O_{alpha}$ and $\delta^{18}O_{water}$ values were calculated with Kim and O'Neil (1997) and Horita (2014) equations for calcite and dolomite/anhydrite respectively.

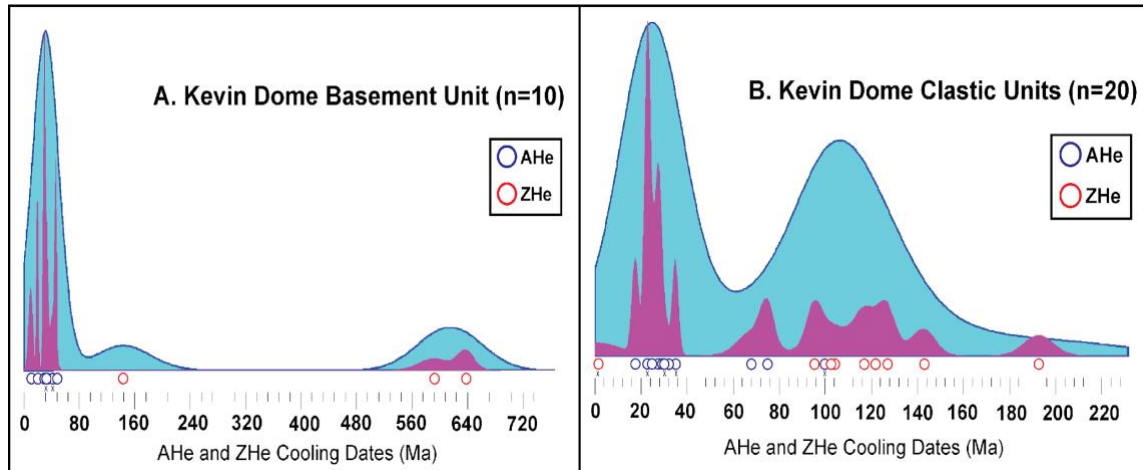


Fig. 3: Kernel density functions of Kevin Dome AHe and ZHe cooling dates probability distribution using Vermeesch (2012) Density Plotter. Cooling dates with FT below 0.5 are marked with X (i.e., problematic).

Kevin Dome carbonate rock $\delta^{18}\text{O}$ values correlate inversely with clumped isotope temperatures ($T(\Delta 47)$) within a -2 to $+6$ ‰ $\delta^{18}\text{O}$ VSMOW equilibrium line range for calcite and dolomite precipitated from water, while its $\delta^{18}\text{O}_{\text{water}}$ correlates positively with $T(\Delta 47)$ within typical crystallization and burial temperature ranges for calcite and dolomite (see SI F). Both clumped isotope $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ trends in this study reveal that burial-controlled temperature increases influenced Kevin Dome carbonate rock $\delta^{18}\text{O}$ values and that their formation water composition was altered by interacting with (more evolved) warmer basinal water as burial temperature increased. The sample with the most depleted $\delta^{18}\text{O}$ value is consistently an outlier in both trends (SI F). This sample may represent carbonates that have been altered either from mixing with (water-buffered) lower $\delta^{18}\text{O}$ fluids or meteoric waters (Machel, 2004; Dale et al., 2014) at some point during the burial or exhumation history of Kevin Dome.

Gold Butte (SGH) Mineral Chemistry, P - T and Depth of Intrusion Estimates

Though now exposed at the surface, the depth at which igneous rocks were emplaced in the subsurface can provide a fixed reference point in time and space. This information can also be used to constrain the average rate of exhumation to the surface through time, provided the age of the igneous rock is known. Results obtained for the major and trace elements composition from Gold Butte (SGH) rocks as well as their Cpx and Amp EPMA mineral chemistry data were used to model emplacement temperature and pressure using the equations of Putirka (2016). By comparing the two independently constrained barometers from Ridolfi et al. (2010)'s Al-in-hbl for Amp and Putirka (2016, Eq 32c) for Cpx we estimated ~1.44 kbar for Gold Butte's (SGH) intrusion pressure. See SI G for the thermobarometry analysis summary and models. Using the thermodynamic formula: $P = h\rho g$, the average depth of intrusion h (km) was estimated as ~ 5.2km, where P is the average pressure in MPa obtained from thermobarometry analysis, ρ is average density of the crust (2800 Kg/m³), and g = acceleration due to gravity (9.8 m/s). The igneous event that emplaced the SGH igneous complex has been radiometrically dated to have occurred at 54-49 Ma (Rukhlov and Pawlowicz, 2012; Marvin et al., 1980), therefore, our modeled ~ 5.2km depth of intrusion suggests that the SGH's rocks have experienced an exhumation rate of about 0.1 mm/yr since the time of intrusion.

Discussion

Kevin Dome Cooling History and Exhumation Episodes

In the following discussions we integrate AHe and ZHe cooling dates, thermal history modeling, carbonate clumped isotope temperatures ($T(\Delta 47)$) of Kevin Dome rocks and depth of intrusion measurements from Gold Butte (SGH) rocks to constrain burial

and exhumation history at Kevin Dome including their influences on hydrocarbon generation. The regional extent of the exhumation and erosional impact is also presented.

Archean Basement and Clastic Units

After eliminating disputable cooling dates, Kevin Dome AHe and ZHe cooling dates (n=23) can be grouped into four main clusters: (a) ~ 10 - 46 Ma and (b) ~ 68 - 75 Ma in Basement and clastic units from AHe; (c) ~ 95 - 144 Ma in Basement and clastic units from ZHe (n=9); (d) ~ 590 - 638 Ma in Basement units only from ZHe. ZHe cooling dates in group (c) whose ages are closer to the depositional ages of host formations (e.g., Kootenai and Bow Island Formations) were interpreted as detrital ages (a situation where detrital zircons have not been buried deep or heated enough since deposition to reset their ages). One of the criteria we used to consider an age to be a valid cooling age was for the sample to have a cooling age significantly lower than the crystallization age for the basement or significantly lower than the depositional age for sedimentary samples. Dates that met this criterion were AHe cooling ages in group (a) and (b) from the Archean Basement, and the Upper Devonian and Early Cretaceous clastic units, and three ZHe cooling dates in group (c) from the Basement and Upper Devonian Three Forks Formation (Table 1). A Neoproterozoic ZHe cooling date from Archean Basement in group (d) was interpreted either as a cooling event represented by the Great Unconformity surface underlying the Flathead Formation ca. 550 – 520 Ma (Chaudhuri and Brookins, 1969) or a response to the unroofing of the Belt Basin (Sloss, 1950; Deiss, 1936; Peale, 1983).

Inverse Thermal History Modeling

Inverse thermal-history models were generated for Kevin Dome with validated AHe and ZHe cooling dates using the HeFTy (version 1.9.3) modeling program (Ketcham,

2017). HeFTy-generated t-T trends reveal the temperature history of rocks through time, including scenarios such as burial/heating and slow or rapid cooling as the rock is exhumed (Stockli et al., 2000; Bernet and Garver, 2005; Zheng et al., 2007; Peyton and Carrapa, 2013; Vermeesch and Tian, 2014; Ketcham, 2017). Invariant cooling dates clustered in a vertical well profile are displayed on the t-T history path as a steep slope indicating a rapid upward change of temperature gradient with depth (Stockli et al., 2000). The onset of this rapid cooling within a well or age-elevation profile indicates the timing of exhumation while the rate of exhumation is calculated from the slope of the rapid cooling trend (Stockli et al., 2000; Peyton and Carrapa, 2013).

HeFTy inputs include the depositional or crystallization age of the unit, (U - Th)/He cooling dates, depositional temperature, present day borehole/well temperature, alpha-ejection correction, mineral concentrations, and thermal maturity indices for the basin/dome to simulate a cooling history path for the sample using Monte Carlo inverse modeling algorithms (Ketcham, 2005 and 2017). Known geologic events and/or exploratory constraints are also added while the software performs an inverse modeling function to choose the best fit t-T paths for the rock after satisfying all the input data (Ketcham, 2005; Vermeesch and Tian, 2014). Because Kevin Dome stratigraphy recorded multiple denudation events represented by erosional surfaces (Fig. 1), our simulations explored thermal histories that allowed for adequate radiation damage to be developed in the grain at the surface before being reburied. To allow long radiation damage accumulation in the mineral grains before reburial, geologic exploration boxes that encourage the model to explore near surface temperatures during thermal history reconstruction were added. The number of paths tried during the simulation were set to

100,000 to effectively reconstruct each sample's thermal history. Through HeFTY we combined the established thermal evolution relationship in samples from the same well (vertical profile), known geological events in the region, thermal gradient assumptions, sediment loading/maximum burial of units, and thermal model viability in order to yield the best-fit t-T path of the input samples. In the software, the Alpha calculation was set to redistribution while the RDAAM calibration of Flowers et al. (2009) and Gautheron et al. (2013) were used for AHe and ZHe data respectively with Ketcham et al. (2011) age alpha and stopping distance calculations. As earlier established, all AHe and ZHe aliquots whose Alpha-ejection correction (FT) values were less than 0.5 were treated as disputable and were not modeled in HeFTy. During the simulations, different modeling scenarios were tested where aliquots from each of the thermochronometers were modeled individually (i.e., a single AHe or ZHe aliquots) or combined (i.e., all AHe, all ZHe or AHe with ZHe aliquots combined). Different geologic constraints were applied to the model until a general trend was observed. SI H summarizes the geologic constraints and justifications of imposed t-T constraints for individual or combined samples from the same well. Fig. 4 shows the representative Phanerozoic thermal history model obtained from HeFTy for Kevin Dome Basement and clastic units.

Integrated AHe and ZHe constrained Phanerozoic thermal history modeling reveals two distinct exhumation episodes at Kevin Dome during the Oligocene-Miocene (~ 15 – 26 Ma), and Late Cretaceous-Paleocene (~ 65 – 72 Ma) in the Archean Basement and clastic units at an average rate of 0.27 mm/yr (Fig. 4). Two wells with Archean Basement, (Upper Devonian to Early Mississippian) Three Forks and Bakken Formations

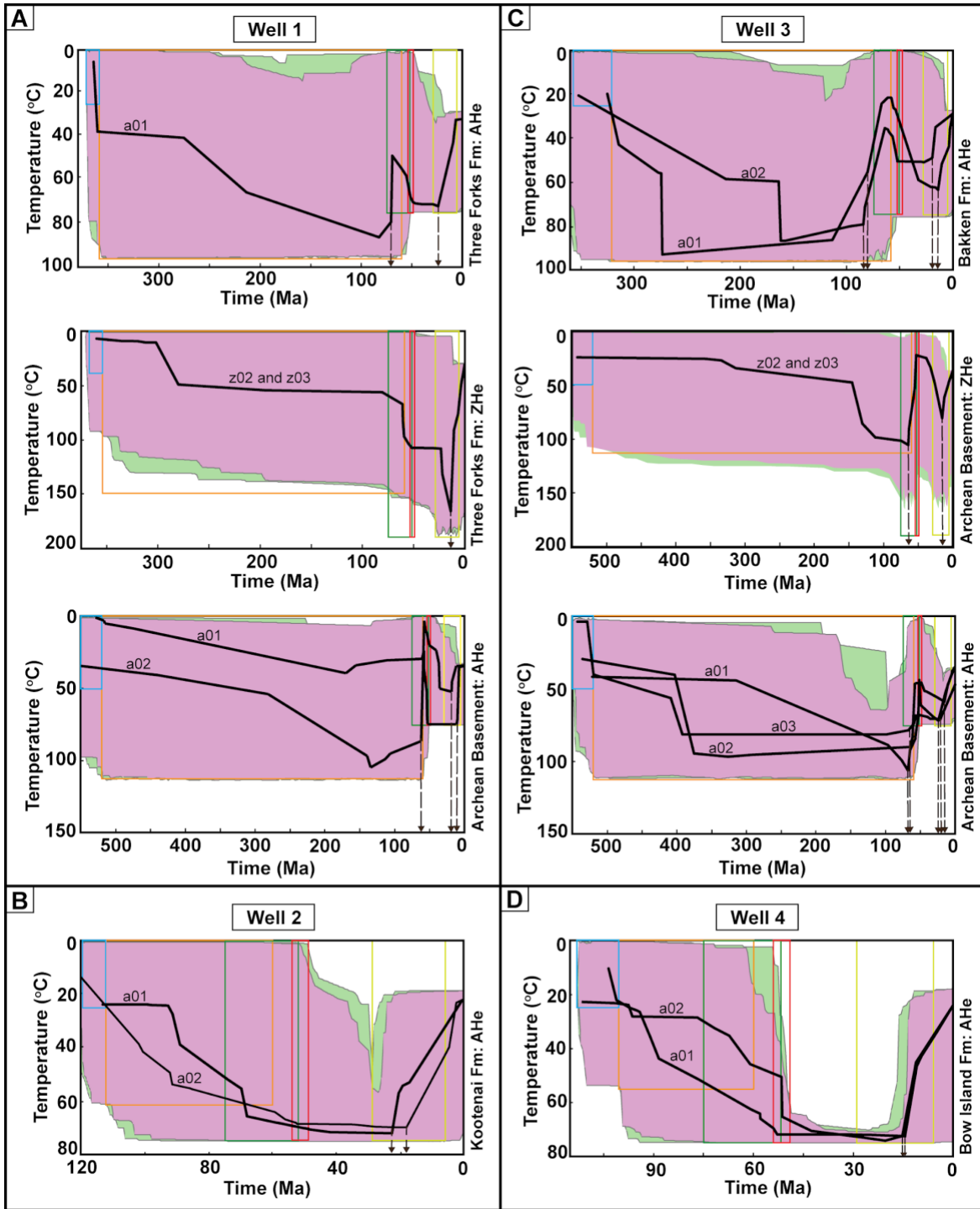


Fig. 4: Representative HeFTy inverse modeling results for Kevin Dome basement and clastic units with sample and analysis labels from four (4) wells. The timing/onset of exhumations in all the models are marked dashed Brown arrows. The rate of exhumation was calculated from the rapid cooling/exhumation t-T paths. Good fits = pink paths; acceptable fits = green paths. Bold black path = "best fit" thermal history. Colored rectangles are the imposed time-temperature constraints based on geologic information summarized in SI H.

samples recorded the two exhumation episodes (Fig. 4 A and C) while (Early to Late Cretaceous) Kootenai and Bow Island Formations recorded only the most recent Oligocene-Miocene exhumation from different wells (Fig. 4 B and D). Oligocene-Miocene and Cretaceous-Paleocene exhumation episodes at Kevin Dome may be related to the evolved forebulge structural evolution model related to (i) the Late Cretaceous-Paleocene emplacement of the Rocky Mountain overthrust induced by the Laramide Orogeny in a Foreland Basin setting in northwestern Montana and proximal Canada (Hoffman et al., 1976; Lorenz, 1983; DeCelles and Giles 1996; Sears, 2001; Osborn et al., 2006; Ward, 2007) and (ii) an Oligocene-Miocene erosional or epeirogenic event not earlier reported in the region. Furthermore, the thermal history generated reveals the maximum burial temperature for the sedimentary units at Kevin Dome. Upper Devonian Three Forks and Early Mississippian Bakken Formations reached $\sim 100 \pm 10$ ($^{\circ}\text{C}$) while Early to Late Cretaceous Kootenai and Bow Island Formations reached $\sim 70 \pm 10$ ($^{\circ}\text{C}$) before exhumation (Fig. 4). The maximum burial temperatures obtained are consistent with oil and gas generation at Kevin Dome. Assuming a thermal gradient of $25^{\circ}\text{C}/\text{km}$ and the upper limit ($\sim 100 \pm 10$ ($^{\circ}\text{C}$)) maximum burial temperature obtained, $\sim 4\text{km}$ of sediments have been eroded from Kevin Dome in connection with the exhumation episodes it has experienced.

Carbonate Units

Integrating the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ trends, computed $\delta^{18}\text{O}$ of formation waters, known isotope signatures in different geologic setting and trends around the globe and the stratigraphic age of carbonate units, we interpret that Kevin Dome carbonates were formed in a marine environment and have interacted with warmer temperatures during burial. This is

consistent with the known burial history of Kevin Dome during the Paleozoic from stratigraphic records (Shepard and Bartow, 1986; Peterson, 1966, 1981 and 1987). Clumped isotope temperatures ($T(\Delta 47)$) of Kevin Dome carbonate units range from 66 to 106 ($^{\circ}\text{C}$) (Table 2 and Fig. 5). Though there are some overlaps, the results reveal that dolomite samples are slightly warmer than calcite containing samples. Since geologic domes are structurally different at the time of basin fill, $T(\Delta 47)$ are ambiguous to interpret because the carbonate horizons are each buried to different stratigraphic depths. Thus, there are two possible interpretations to what the measured $T(\Delta 47)$ of Kevin Dome carbonate units' record. First, Kevin Dome carbonates $T(\Delta 47)$ may represent crystallization temperatures where the carbonates did not experience temperatures warm enough to be partially reordered before exhumation. Second, they could represent solid-state C-O bond reordering temperatures where the strata did experience partial reordering during deep burial prior to exhumation. HeFTy thermal history modeling shows that the Early Mississippian Bakken Formation, and the Upper Devonian Three Forks Formation were exposed to the maximum burial temperature of 100 ± 10 ($^{\circ}\text{C}$) prior to exhumation (Fig. 4 A and C). This estimate implies that the underlying (within 1km depth) Mississippian carbonate units would have experienced a similar 100 ± 10 ($^{\circ}\text{C}$) maximum burial temperature consistent with the maximum (106 $^{\circ}\text{C}$) $T(\Delta 47)$ value obtained. Kevin Dome carbonate $T(\Delta 47)$ trend with depth is also consistent with the minimum and maximum peak-burial temperatures (100 ± 8 ($^{\circ}\text{C}$)) constraints by Ryb et al., (2021) for Mississippian carbonate units (Fig. 5) suggesting a potential regional Palaeozoic carbonate cooling history and exhumation. It is therefore evident that the carbonate units experienced maximum burial temperatures near 100 ± 10 ($^{\circ}\text{C}$) prior to exhumation and

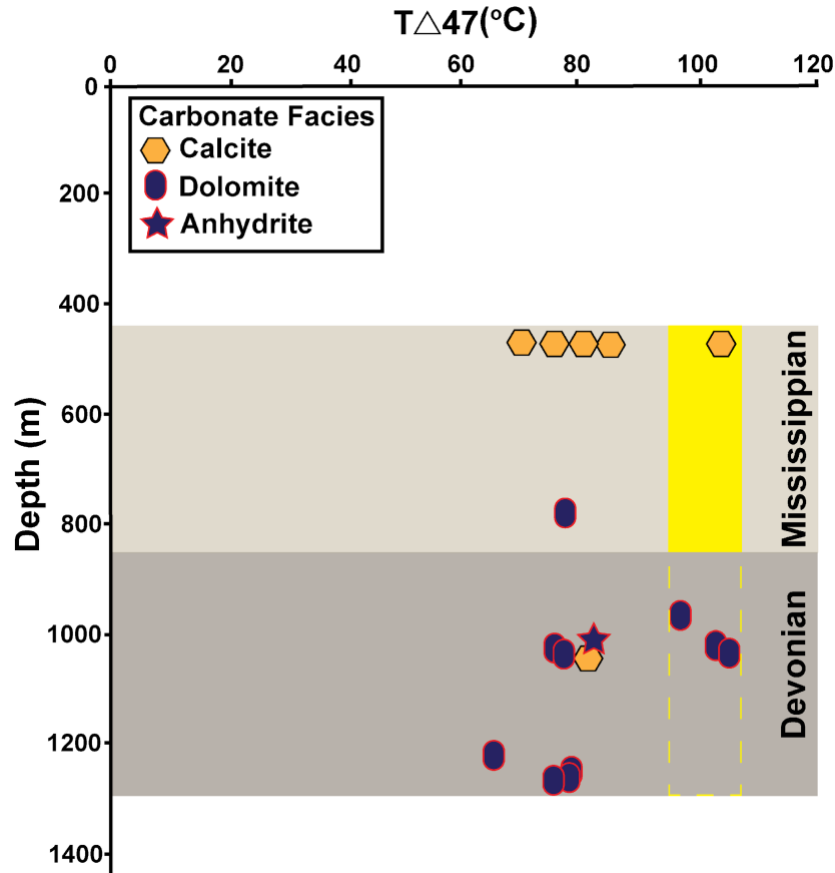


Fig. 5: Kevin Dome carbonate units' sampled depth vs clumped isotope temperatures ($T(\Delta 47)$) showing the 100 ± 8 ($^{\circ}\text{C}$) peak-burial temperature constraint for the Mississippian carbonates (Ryb et al., 2021). The minimum and peak-burial temperature (yellow rectangle) was constrained by integrating AFT and AHe low-temperature thermochronometry peak burial temperature data (Dumitru et al., 1994; Flowers et al., 2008) with carbonate clumped isotope thermometry (Ryb et al., 2021) and is extended here into the Devonian units (dashed yellow rectangle) for experimental purpose only.

by thermal gradient extrapolations have been exhumed by $\sim 4\text{km}$ from their original stratigraphic depth.

Regional extent of exhumation episodes at Kevin Dome

The Late Cretaceous-Paleocene and Oligocene-Miocene exhumation episodes at Kevin Dome interpreted from this study are younger than the Early-mid Cretaceous evidence for the onset of Laramide exhumation (ca. 100 Ma) that is strongly preserved in

six Laramide ranges in southwest Montana (Carrapa et al., 2019). This result suggests that the timing of the onset of the Laramide orogeny (defined as basement involved uplift) is older than the timing of basement involved uplift at Kevin Dome. Our work also suggests that the Laramide event was not recorded at Kevin Dome, or that it may have been overprinted by deformation associated with Late Cretaceous-Paleocene movement within the Rocky Mountain fold-and-thrust belt in northwest Montana and southern Canada (Hoffman et al., 1976; Sears, 2001; Osborn et al., 2006). The most recent Oligocene-Miocene exhumation episode at Kevin Dome is, however, consistent with existing exhumation studies further north of the dome in the adjacent Western Canadian Sedimentary Basin (WCSB). Fraser et al., (2021) reported three young exhumation episodes (i.e., 45–30 Ma, 20–10 Ma, and <10 Ma) from AHe, AFT and thermal history modeling proxies in the Rocky Mountain Trench (RMT) that extends down into northwest Montana (west of the Disturbed Belt) from the Canadian Cordillera. Evidence for a major Neogene exhumation episode from thermal maturity data in the WCSB (Bustin, 1991; Aviles and Cheadle 2015) further supports a regional Oligocene-Miocene exhumation episode in northwestern Montana, USA, and southern regions of the WCSB, Canada.

Several workers have attempted to constrain the thickness of strata that have been eroded from various foredeep sections of the WCSB in Canada (Aviles and Cheadle 2015). Closest to Kevin Dome, Bustin (1991) estimated ~3km of sediment thickness were eroded around Cypress Hill, southern Alberta during the Neogene exhumation based on thermal maturity data. On the other hand, ~1.4km sediment thickness was estimated to have been eroded from Kevin Dome by stratigraphic measurements (Michener, 1934; Collier, 1929; Shepard and Bartow, 1986). Integrated thermochronological techniques on

Kevin Dome rocks coupled with our depth of intrusion estimate for the Gold Butte (SGH) rocks, however, suggest that between ~4 - 5km of strata have been eroded in the region. Our study shows that Kevin Dome's Oligocene-Miocene and subsequent erosional events extended into the southern regions of the WCSB.

Maximum Burial T, Hydrocarbon Generation and Exhumation

Rock cooling history studies are not only important for understanding exhumation episodes but are also applicable for understanding hydrocarbon maturation and generation in sedimentary basins/domes. Conventional investigations of the thermal evolution of sedimentary basins, source rock quality, and petroleum systems modeling rely heavily on organic geochemistry proxies (e.g., Peters, 1986; Peters and Cassa, 1994; Tissot and Welte, 1984; Adeniyi et al., 2018). On the other hand, AHe and ZHe, HeFTy thermal history modeling and carbonate clumped isotope thermometry proxies provide direct and useful information on paleotemperature, burial history and depositional environments. These t-T techniques are also not limited to organic rich rocks unlike organic geochemistry methods such as vitrinite reflectance, RockEval pyrolysis indices,

total organic carbon (TOC) and isotopic composition of organic carbon ($\delta^{13}\text{C}_{\text{org}}$) analyses of organic rich rocks or black shales. Table 3 shows existing thermal maturity data obtained from Upper Devonian and Early Mississippian formations around Kevin Dome, northwest Montana by Dolson et al. (1993) and publicly available data from six (6) wells. The thermal indices of the Upper Devonian and Early Mississippian formations in northwestern Montana reveal that the rocks possess oil-prone Type II and gas prone Type III kerogen and were deposited in a marine or lacustrine environment (SI J).

Fig. 6 shows that the oil generation window is typically within ~60 - 130 (°C)

Table 3: Thermal Maturity Data from six (6) wells in northwest Montana

Well Name	County	Formation	Depth (m)	Tmax (°C)	T.O.C (wt %)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	PI	HI	OI	R _o ** (%)	
15-13	Toole	Lw Exshaw Shale	750.11	436	13.3	4.05	59.40	0.59	0.06	446	4	0.68	
			750.42	439	2.5	1.12	4.86	0.35	0.19	198	14	0.75	
			750.72	434	16.9	6.10	79.70	0.57	0.07	472	3	0.66	
			751.03	435	14.6	5.04	66.00	0.56	0.07	453	4	0.67	
			751.33	435	1.5	0.38	2.29	0.42	0.14	151	27	0.67	
798.27			443	6.1	2.09	15.9	0.27	0.12	263	4	0.82		
800.40			441	7.8	2.53	22.3	0.28	0.1	288	4	0.78		
801.32			442	9.5	3.2	32.6	0.26	0.09	344	3	0.79		
803.45			443	6.5	2.54	20.3	0.31	0.11	313	5	0.82		
804.67			446	2.5	0.94	4.79	0.16	0.16	190	6	0.86		
Quintana Petroleum (1-10 Guith)		Nisku	930.55	429	3.19	1.05	20.77	0.74	0.05	651	23	0.56	
Cardinal State #1 - 5				1186.89	433	11.64	4.52	68.20	0.39	0.06	586	3	0.49
				1187.20	434	10.20	4.05	60.47	0.42	0.06	593	4	
				1187.50	434	15.35	5.06	87.75	0.37	0.05	572	2	0.48
				1187.81	433	12.94	4.80	75.67	0.41	0.06	585	3	
				1188.11	433	8.02	7.27	45.79	0.30	0.14	571	4	
NFX Peacemaker 1-5H	Glacier	“False” Exshaw	1418.84	439	9.3	8.7	25.7	0.9	0.25	274	10	0.74	
		Lw Lodgepole	1435.91	443	3.2	4.6	11.8	0.9	0.28	366	29	0.81	
		Lw Exshaw Shale	1444.75	434	13.6	9.1	58.3	0.6	0.13	428	4	0.65	
Lw Lodgepole		1627.94	429	1.3	0.9	3.5	1.0	0.21	269	79	0.56		
“False” Exshaw		1644.40	438	10.0	2.4	36.3	0.6	0.06	362	6	0.72		
Up Exshaw Shale		1648.66	440	4.8	1.3	18.1	0.7	0.07	374	13	0.76		
Lw Exshaw Shale		1660.55	437	7.6	4.3	22.8	0.5	0.16	299	7	0.71		

Notes: The Total organic carbon content (TOC), Rock-Eval pyrolysis and Vitrinite Reflectance (R_o (%)) data are compiled from Dolson et al. (1993) and publicly available data. Tmax = Temperature index, (°C). T.O.C. = Total organic carbon, wt % S₁ = Free hydrocarbons (mg HC/g of rock). S₂ = Residual hydrocarbon potential (mg HC/g of rock). S₃ = CO₂ produced from kerogen pyrolysis (mg CO₂ / g rock). PI - Production Index = S₁ / (S₁+S₂). HI = Hydrogen index [S₂ x 100 / TOC] (mg HC/g TOC). OI = Oxygen index [S₃ x 100 / TOC] (mg CO₂/ g TOC). ** R_o (%) values are calculated R_o (%) calc. in all the wells except for the Cardinal State #1 – 5 well where R_o (%) values were measured by petrographic methods. R_o (%) calc is estimated from Tmax data using Jarvie et al., (2001)'s equation 5.1 where R_o (%) calc. = 0.018 x (Tmax) – 7.16 (5.1). Lw = Lower, Up = Upper.

temperature range while the gas window overlaps and is typically ~90 - 220 (°C) (Peters, 1986; Tissot and Welte, 1984). This suggest that (Early to Late Cretaceous) Kootenai and Bow Island Formations reached the oil generation window, while (Upper Devonian to Early Mississippian) Three Forks and Bakken Formations reached the gas generation

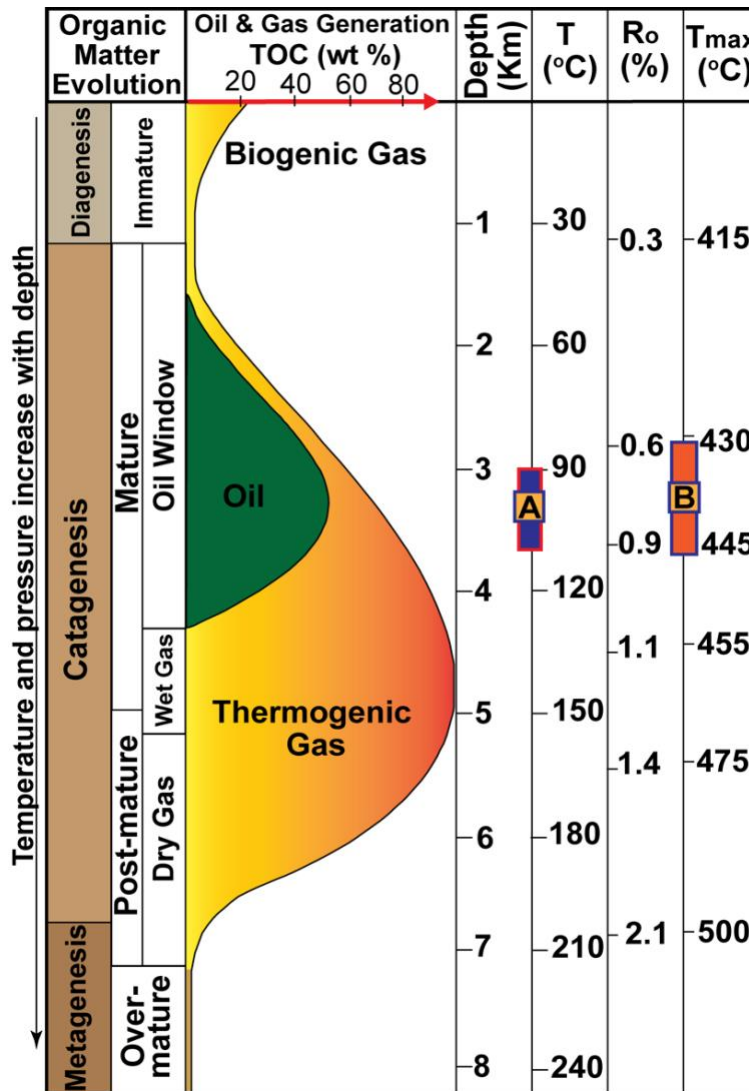


Fig. 6: Integrated thermal maturity indices, thermochronological data and hydrocarbon generation progression with depth at Kevin Dome. We compare two data points - **(A)** and **(B)** from Upper Devonian to Early Mississippian sedimentary units at Kevin Dome, northwest Montana. **(A)** represents the 100 ± 10 (°C) burial temperature and depth of burial prior to exhumation constrained with AHe and ZHe, HeFTy thermal history modelling and carbonate clumped isotope thermometry proxies from Kevin Dome wells (this study) and **(B)** represents existing Vitrinite Reflectance (R_o (%)) and T_{max} values range from studied wells in northwestern Montana. T (°C) represents thermal gradient (30 °C/km). R_o (%) and T_{max} data. (Tissot and Welte, 1984; Peters, 1986; Bjørlykke 1989).

window consistent with the maximum burial temperatures ($\sim 70 \pm 10$ (°C) and $\sim 100 \pm 10$ (°C)) obtained for the units from the thermal history modeling in this study (Fig. 4). The maximum burial temperature and depth constrained in this study using AHe and ZHe,

thermal history modeling and carbonate clumped isotope thermometry proxies in the Upper Devonian and Early Mississippian formations also agrees with the R_o (%) and T_{max} values obtained in previous studies by organic geochemistry methods (Fig. 6). Existing thermal maturity data at Kevin Dome support exhumation episodes obtained in this study. Lower Exshaw Shale thermal indices reveal a thermally matured strata in the oil generation window (Table 3, SI J) at Kevin Dome. The organic rich Nisku Formation ($TOC = 3.19$) from the same area, however, shows lower organic matter thermal maturity (i.e., $T_{max} = 429$ (°C) and production index = 0.05). This data suggests that the Nisku at this location was not buried long enough in the oil generation window prior to being exhumed to the current depth for much of its organic matter to be transformed to hydrocarbon. Deeply buried Nisku rocks, however, generated significant hydrocarbons elsewhere, e.g., in the Williston Basin (Dolson et al., 1993; Dyman, 1995; Dembicki, 2017). Therefore, exhumation episodes could have halted hydrocarbon generation in the Bakken petroleum system at Kevin Dome or aided its expulsion. Our study shows that conventional thermal maturity proxies can be integrated with t-T sensitive proxies. The integrated thermochronological approach in this study provided a novel and complementary approach for understanding thermal conditions of both clastic and carbonate rocks during burial and prior to exhumation including organic matter maturation and hydrocarbon generation at Kevin Dome.

Conclusion

Using a multi-faceted thermochronologic and geothermobarometric approach, this study has constrained the burial and exhumation history at Kevin Dome, northwest Montana and provided an estimate of the amount of erosion in the region. We found:

1. Evidence for Neoproterozoic, Early to Late Cretaceous and Post Eocene cooling events at Kevin Dome, northwest Montana and two distinct Phanerozoic exhumation episodes during the Oligocene-Miocene ($\sim 15 - 26$ Ma), and the Late Cretaceous-Paleocene ($\sim 65 - 72$ Ma) at an average rate of ~ 0.27 mm/yr.
2. Exhumation episodes at Kevin Dome, NW Montana are younger than the Early to mid-Cretaceous evidence for the onset of Laramide exhumation (ca. 100 Ma) strongly recorded in six Laramide ranges in SW Montana (Carrapa et al 2019). Kevin Dome's most recent Oligocene-to-Miocene erosional episode aligns with a similar event in the proximal southern regions of the WCSB (e.g., Bustin, 1991; Aviles and Cheadle 2015; Fraser et al., 2021). Our data set also constrains the timing and the amount of erosion in NW Montana.
3. The timing of exhumation and the thermal history modeled in this study supports the evolved forebulge structural evolution model related to (i) the Late Cretaceous-Paleocene emplacement of the Rocky Mountain overthrust and development of the associated forebulge in the foreland basin in northwestern Montana and southern Canada (Hoffman et al., 1976; Lorenz, 1983; DeCelles and Giles 1996; Sears, 2001; Osborn et al., 2006; Ward, 2007) and (ii) an Oligocene-Miocene erosional or epeirogenic event not previously reported in the region.
4. The thermochronologic approach engaged in this study is consistent with existing thermal maturity data at Kevin Dome, northwest Montana. Both approaches reveal that Kevin Dome rocks reached oil and gas generation windows by burial prior to exhumation to current stratigraphic depths and that the Oligocene-Miocene exhumation event halted hydrocarbon generation at Kevin Dome.

5. Erosional episodes at Kevin Dome and the Sweetgrass Hills igneous complex led to the removal of ~4km – 5km sediment thickness in northwest Montana, USA, and southern regions of the WCSB, Canada. Our estimates exceed the earlier estimated ~1.4km and ~3km of erosion respectively at both regions from stratigraphic and thermal maturity measurements (e.g., Michener, 1934; Collier, 1929; Shepard and Bartow, 1986; Bustin, 1991).

Acknowledgements

This research has been supported in part by funding from the U.S. Department of Energy, and the National Energy Technology Laboratory through award number: DE-FC26-05NT42587 to the Energy Research Institute (ERI) and Big Sky Carbon Sequestration Partnership (BSCSP) at Montana State University and the American Chemical Society Petroleum Research Fund. Thanks to ERI, and the BSCSP for access to the Duperow Formation cores and the Montana Board of Oil and Gas Conservation (MBOGC) for access to historic well core cuttings analyzed in this study. Special thanks to Dr. James R. Metcalf and Dr Rebecca M. Flowers, (TRAIL, CU Boulder, CO), Dr. Gregory Henkes (Henkes Lab, SBU, NY), Dr F., Tepley III (OSU, OR) and Dr K Putrika (CSU Fresno, CA) for analytical assistance and helpful discussions on the results obtained in this study.

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CHAPTER THREE

ORIGIN OF CO₂ IN UPPER DEVONIAN DUPEROW FORMATION AND THE BAKKEN
PETROLEUM SYSTEM AT KEVIN DOME, NORTHWEST MONTANAContribution of Authors and Co-Authors

Manuscript in Chapter 3

Author: E.O. Adeniyi

Conceptualized the project and analytical approach, completed field work and sample collection, conducted analyses, performed CO₂ dissolution modeling, interpreted the results, and wrote the manuscript.

Co-Author: R.L. Tyne

Contribution: Assisted with CO₂ dissolution modeling, discussed the results, and edited the manuscript.

Co-Author: P.H. Barry

Contribution: Contributed to He-Ne-Ar analysis of Olivine minerals, assisted with CO₂ dissolution modeling, discussed the results, and edited the manuscript.

Co-Author: T.H. Darrah

Contribution: Performed noble gas analysis of bulk gas and fluid inclusions, discussed the results, edited the manuscript.

Co-Author: M.S. Hubbard

Contribution: Supported this research through the American Chemical Society Petroleum Research Fund at Montana State University, helped on field work, discussed the results, and edited the manuscript

Co-Author: M.L. Myers

Contribution: Helped on field work, discussed the results, and edited the manuscript

Co-Author: D.W. Bowen

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Manuscript Information

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Status of Manuscript:

- ☒ Prepared for submission to a peer-reviewed journal
- ☐ Officially submitted to a peer-review journal
- ☐ Accepted by a peer-reviewed journal
- ☐ Published in a peer-reviewed journal

Abstract

Carbon capture and storage is a key mitigation strategy in achieving global net zero emissions and therefore it is essential to identify and characterize potential storage repositories. Natural CO₂ accumulations provide an opportunity to understand the subsurface behavior of CO₂. In this study, we investigate the source(s), migration, and storage of CO₂ in the Upper Devonian Duperow Formation at Kevin Dome, northwest Montana, USA. Determining the source of CO₂ at Kevin Dome can help identify secondary migration induced fractionation signals which are crucial for characterization of potential regional carbon sequestration sites. We analyzed fluid inclusions (n=24) from the Duperow Formation for major gas composition, stable and noble gas isotopes and compared them with natural gas samples (n=19) produced from hydrocarbon-bearing reservoirs at Kevin Dome. Using the same methods, additional bulk gas samples from the adjacent Ferguson Field, in southern Alberta, Canada (n=9) and fluid inclusions from the Sweetgrass Hills igneous complex (n=2) were analyzed to understand CO₂ generation and the subsequent processes affecting the CO₂ regionally. We found that CO₂ in the Upper Devonian Duperow Formation is magmatic in origin, likely related to the nearby Sweetgrass Hills igneous complex intrusions (~52 Ma), whereas CH₄ and N₂ gases are generated mainly by thermogenic processes associated with hydrocarbon generation during burial. We also found that since emplacement, the majority of CO₂ in the Bakken petroleum system's hydrocarbon-bearing reservoirs at Kevin Dome (~98%) and the Ferguson Field (~82%) has subsequently been dissolved into the groundwater. We present a simple solubility model and calculate lower gas/water ratios in Kevin Dome versus the Ferguson Field, which are consistent with more groundwater interaction and

more dissolution at Kevin Dome. Understanding the subsurface processes affecting CO₂ is important for future CO₂ storage site selection.

Introduction

The potential of geologic structures to preserve (97-99% pure) CO₂ over geologic time demonstrates the viability of geological carbon sequestration as a key part of the strategy to achieve a net-zero state. Studies suggest that geologic structures such as McElmo Dome, Bravo Dome, Sheep Mountain, Escalante Anticline, and Kevin Dome could provide huge capacity for storing captured anthropogenic CO₂ (Allis et al., 2001; Bowen et al., 2009; Spangler, 2011). Natural CO₂ reservoirs provide an opportunity to study CO₂ origin, characterize CO₂ reservoir rocks and trapping systems, which will help our understanding of the geologic conditions that would favor carbon sequestration.

Kevin Dome is a historic oil and gas producing structure in the northwest United States (Collier, 1929). The dome hosts large volumes of hydrocarbons trapped in Devonian, Mississippian, Jurassic, and Cretaceous reservoirs (Collier, 1929; Nordquist and Leskela, 1968; Wennekers, 1985). Most importantly, Kevin Dome's Upper Devonian Duperow Formation hosts one of the largest known natural accumulations of ~ 96% pure CO₂ in the northwestern United States estimated at ~ 283 x 10⁹ m³ (Bowen et al., 2012; AAL, 2015; Onishi et al., 2019). Additionally, the saline aquifers associated with the Duperow Formation have the potential to sequester large volumes of CO₂ (~1GT) (Bowen et al., 2012). The source, timing of emplacement and subsequent processes affecting the CO₂ in the Upper Devonian Duperow Formation at Kevin Dome, and CO₂ associated with hydrocarbon-bearing reservoirs in the Bakken petroleum system at Kevin Dome and adjacent areas are not well understood.

The CO₂ within the Duperow Formation at Kevin Dome could be microbial, thermogenic, or magmatic in origin. Microbial CO₂ could be generated from the bacterial-oxidation of existing hydrocarbons. Thermogenic CO₂ could be sourced either from the Bakken Shale sequences deeper in the basin west of the dome and in the Disturbed Belt west of the dome (Stein, 2008) or as a byproduct of thermal degassing of Paleozoic carbonate rocks during the felsic igneous intrusions of the Sweetgrass Hills (SGH) igneous complex (~ 40 km northeast) with migration westward along the east flank of the dome into the Duperow (Bowen et al., 2012). Mantle derived CO₂ could also have accumulated in the Duperow during the SGH igneous complex intrusion or from the mantle along basement faults since Kevin Dome sedimentary strata sits directly on Archean basement (Xianbin, et al., 1998; Stevens and Tye, 2004; Zhou et al., 2003).

Previous work on high purity (95–99%) CO₂ gas producing fields (McCallum dome, Sheep Mountain and McElmo dome, in Colorado; Bravo dome, in New Mexico, St Johns dome, in Arizona and New Mexico and Jackson Dome, in Mississippi) showed them to be magmatic in origin (Gilfillan et al., 2008 and 2009; Zhou et al., 2012). However, in lower purity CO₂-rich fields crustal CO₂ appears to be dominant e.g., Mississippian Madison Limestone at the LaBarge Platform (65% CO₂) in Wyoming (Stilwell, 1989; Becker and Lynds, 2012; Merrill et al., 2015) and on the Colorado Plateau (> ~37% CO₂) (Craddock et al., 2017). Crustal CO₂ was identified using associated N₂ + He + Ar in these fields (Craddock et al., 2017).

In this study, we investigate the source(s), migration, and storage of CO₂ in the Upper Devonian Duperow Formation at Kevin Dome. We used CO₂-bearing fluid inclusions from the Duperow CO₂ reservoir as a proxy for the main gas accumulation in

the Kevin Dome. Bulk gas samples from the Kevin Dome and adjacent Ferguson Field were geochemically characterized to understand volatile sources. The Ferguson Field, located in southern Alberta and within the Western Canadian Sedimentary Basin (WCSB) has elevated concentrations (~26%) of CO₂ produced in association with oil from reservoirs within the Early Mississippian Banff Formation and the Middle Bakken Sandstone. The proximity of the Ferguson Field to Kevin Dome and elevated CO₂ concentrations makes its CO₂ gas generation important to this study. Fluid inclusions from the nearby SGH igneous complex were also examined to provide a basis for comparison of fluids from this potential CO₂ source region.

Geologic Setting of Kevin Dome, Northwest Montana

Kevin Dome is a 320 km-long, north-plunging structural culmination on the Sweetgrass Arch in northwest Montana (Fig. 1). The dome is bound to the west by the Cordilleran fold-and-thrust belt and to the east by the Williston Basin (Shepard and Bartow, 1986). Kevin Dome extends over 2590 km², at a surface elevation of 259 m above sea level. Kevin Dome is composed of Cambrian, Devonian, Mississippian, Jurassic, and Cretaceous strata with a cumulative average thickness of 1.7 km (Collier, 1929; Michener 1934; Shepard and Bartow, 1986). More than ~3 km of sedimentary strata is estimated to have been eroded from the Sweetgrass Arch region including Kevin Dome based on apatite and zircon (U–Th)/He and thermobarometry calibrations (Adeniyi et al., 2023). Supplementary information (SI) A shows a regional geologic map of Kevin Dome with various structural elements associated with its development; namely the Sweetgrass Arch, Rocky Mountain Fold and Thrust Belt, the Pendory Fault, the SGH igneous complex and the Bow Island Arch, southern Alberta Canada (Shepard and

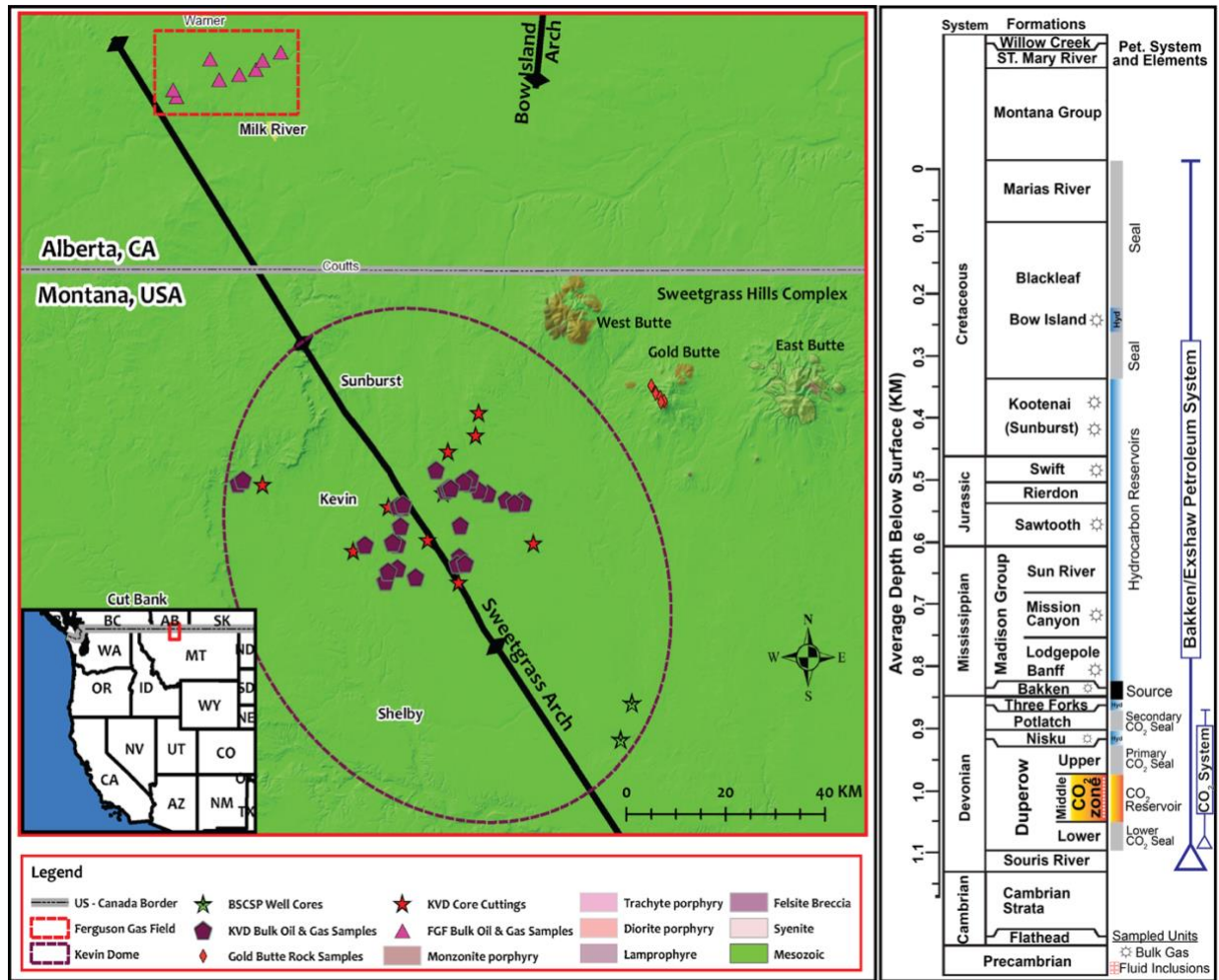


Fig. 1: Sample location at Kevin Dome, northwest Montana and the Ferguson Field, southern Alberta, Canada with a simplified stratigraphic column showing Bakken/Exshaw Petroleum System, the CO₂ System, sampled hydrocarbon-bearing reservoirs and the Duperow CO₂ zones where the fluid inclusions were sampled (Peterson, 1987; Downey, 1986; Bowen et al., 2012).

Bartow, 1986; Pană et al., 2021). The Sweetgrass Arch is a north to north-northwest plunging anticline that extends for about 266 km from the Little Belt Mountains in central Montana to the north-east trending Bow Island Arch of southern Alberta, Canada (Dowling, 1917; Michener 1934; Tovell, 1958; Herbaly, 1974; Shepard and Bartow, 1986; Pană et al., 2021). Proximal to the center of the arch is the northeast-striking, right-lateral Pendroy Fault zone with a ~48 km offset along the hinge of the anticline demarcating the

north arch from the south arch. The Pendroy fault movement is thought to have been associated with the origination of present-day Kevin Dome as a bulge on top of the Sweetgrass Arch crest (Shepard and Bartow, 1986). Kevin Dome has repeatedly experienced episodes of uplift and subsidence, with deposition punctuated by erosional events at different stages during its evolution (Sloss, 1950; Peterson 1966; Lochman-Balk and Wilson, 1967; Nordquist, 1953; Peterson, 1981; Shepard and Bartow, 1986; Jorgensen, 2004). Recent work has shown exhumation at Kevin Dome during the Oligocene-Miocene and is tied to a regional unroofing event across northwestern Montana and the southern part of the WCSB; the timing of which had not previously been documented (Adeniyi et al., 2023). The SGH, ~ 40 km east of Kevin Dome, consists of an igneous complex intruded 54–49 Ma into Phanerozoic siliciclastic and carbonate strata in Northern Montana (Rukhlov and Pawlowicz, 2012; Lopez, 1995; Marvin et al., 1980). These intrusions are exposed as four main buttes: West Butte, Gold Butte, Middle Butte, and East Butte (Fig. 1).

Stratigraphy

The stratigraphy at Kevin Dome is controlled by basement collision, faults, episodes of uplift and subsidence, and sedimentation punctuated by several erosional events (Jorgensen, 2004; Sloss, 1950; Peterson 1966). Wells drilled on Kevin Dome encountered granite in the basement below the dome (Sloss, 1950). Archean basement elsewhere in the Wyoming Craton consists of a complex suite of ortho- and meta gneiss with granitoid intrusive rocks. Proterozoic strata (e.g., Belt Group) are completely absent on Kevin Dome due to erosion from the uplift of the Sweetgrass Arch prior to Mid-Cambrian time (Sloss, 1950). During the Cambrian the limestone and calcareous shales

preserved suggests a moderately stable tectonic setting from Mid to Upper Cambrian periods where the depositional and tectonic conditions consisted of a Foredeep on the west (modern-day Idaho), a broad stable Wyoming Shelf to the southeast and unstable shelf conditions in north central Montana (Stein, 2008; Shepard and Bartow, 1986; Sloss, 1950). In certain parts of the Sweetgrass Arch, regional pre-Devonian truncation led to the thinning of Cambrian sediment, which appears to be strongly localized on Kevin Dome (Lochman-Balk and Wilson, 1967; Peterson, 1966; Shepard and Bartow, 1986). Stable basin conditions favored carbonate deposition during both the Ordovician and Silurian periods (Blakey and Ranney, 2017). These carbonate strata, however, including lower Devonian rocks, are now absent on the dome due to Mid-Devonian uplift and erosion (Sloss, 1950; Peterson, 1981). As a result, Upper Devonian strata unconformably overlie Cambrian sediments at Kevin Dome. Deposition of Devonian strata occurred during second order sea-level rise, over the craton and a gently dipping ($>10^{\circ}$) shallow marine platform on the western margin of North America that was dominated by carbonate and evaporite sedimentation (Norwood, 1965; Sandberg, et al., 1988). Upper Devonian strata preserved on Kevin Dome include the Souris River, Duperow, Nisku, Three Forks, and Potlatch Formations (Sandberg, 1965; McQueen and Sandberg, 1970). The Early Mississippian Bakken Formation is present across the dome. The Madison Group (Upper Mississippian) shares lies unconformably above the underlying Bakken Formation and is unconformably overlain by Jurassic strata (Sloss, 1950; Nordquist, 1955). The Madison Group on Kevin Dome includes the Lodgepole, Mission Canyon, and Sun River Formations (Nordquist and Leskela, 1968; Peterson, 1987; Dolson et al., 1993). The Sun River Formation later experienced pre-Jurassic erosion in parts (Nordquist, 1955). The

overlying Jurassic and Cretaceous layers are predominantly siliciclastic rocks. Jurassic strata on Kevin Dome include the Sawtooth, Rierdon, Swift, and Morrison Formations while Cretaceous strata include the Kootenai Formation, the Colorado Group, and the Montana Group with their respective formations. The Marias River Shale of the Colorado Group is the topmost unit at Kevin Dome (Fig. 1).

Bakken Petroleum System

The Organic-rich Bakken and/or Exshaw Formations are the main regional source rocks in northwestern Montana and southern Alberta, therefore, the petroleum system at Kevin Dome is referred to as either the Bakken Petroleum System, in northwestern Montana, USA, or the Exshaw Petroleum System in southern Alberta, Canada (Schenk et al., 2018). Most of the hydrocarbons trapped in the Bakken Petroleum System are thought to be thermochemically generated and migrated up-dip from the Bakken/Exshaw Shale beneath the Disturbed Belt west of the dome (Dolson et al., 1993). Proximal to the Disturbed Thrust Belt, the Bakken shale source rocks are thermally mature for oil and wet gas generation ($1.5 R_o$ (%)) (Dyman, 1995; Dolson et al., 1993; Dembicki, 2017). Hydrocarbons here are characterized by marine Type II kerogens and about 12 wt.% TOC (Dyman, 1995; Jarvie, 2001; Jarvie et al., 2016). There is also evidence of secondary migration and entrapment within Kevin Dome (Stein, 2008; Shepard and Bartow, 1986), however, not all the reservoirs that are producing elsewhere are present or producing at Kevin Dome. Based on similar depositional environments, Bakken Petroleum System's reservoirs can be broadly grouped into the Devonian-Mississippian carbonates and Jurassic-Lower Cretaceous sandstone units. The Devonian-Mississippian carbonate reservoir units consisting of the (Upper Devonian) Duperow and

Nisku Formations, and the (Mississippian) Madison Group were deposited in evaporite to carbonate cycles and bioclastic carbonate banks that have been highly dolomitized due to near-shore salinity conditions during sedimentation. The Duperow Formation traps a large ($\sim 283 \times 10^9 \text{ m}^3$) natural CO_2 accumulation and downdip associated saline aquifers have the potential to sequester large volumes of CO_2 (Spangler, 2011, Spangler et al., 2020). The Nisku Formation is the oil-bearing reservoir at East Kevin Field while the Madison Group is the major conventional oil reservoir on the dome with production coming from the Lodgepole and Mission Canyon Formations (Romine, 1929; Tonnsen and MGS, 1985; Bowen et al., 2009 and Spangler, 2011). Paleokarst reservoirs are common in the middle and upper part of the Madison Group due to post-Mississippian dissolution (Dyman, 1987; Maughan, 1989). The Jurassic-Lower Cretaceous sandstone reservoirs are a product of local stratigraphic and structural influences. These units, including the Swift, Kootenai (Sunburst and Cutbank members) and Bow Island Formations were deposited from Fluvial, deltaic, and nearshore marine environments and produce oil and/or gas from combination traps on the dome (Hayes, 1984; Dyman, 1995). Dyman (1995) observed that Jurassic and Lower Cretaceous sandstone reservoirs might have been sourced by oil generated within Mississippian source rocks. Seals within the Bakken petroleum system are created mainly by carbonate to evaporite facies changes, shales, and paleosol and karst systems (Dyman, 1995). Evaporite and clastic shales serve as seals in the Devonian-Mississippian strata while only shales seal the Jurassic-Lower Cretaceous reservoirs (Fig. 1). Above the Duperow and Nisku Formations, the Potlach Formation (anhydrite) serves as a tight regional seal while within the Jurassic reservoirs and the Kootenai Formation interbedded shales seal. A detailed facies analysis

and depositional history study of the CO₂ zone within the Duperow Formation at Kevin Dome and the Banff Formation at the Ferguson Field are presented in SI B.

Methods

Bulk oil and gas samples and/or fluid inclusion isotopic geochemistry proxies are useful for unraveling the origin(s) of natural gases (Aulstead et al., 1988; Goldstein, 2001; Zhou et al., 2003; Tseng and Pottorf, 2003; Gilfillan et al., 2008) by allowing for the direct measurements of the isotopic signature of the resource. Fluid inclusions can effectively preserve the history of subsurface fluid movement, migration, and accumulation (e.g., Parnell et al., 2001). In this study, the accumulation of CO₂ at Kevin Dome was estimated using molecular compositional analysis, stable and noble gases isotopic geochemistry analyses of CO₂-bearing fluid inclusions extracted from the Duperow Formation and igneous fluid inclusions extracted from Gold Butte (SGH) rocks. Bulk gas samples were also analyzed from hydrocarbon-bearing formations at Kevin Dome and the Ferguson Field to gain a broader understanding of the origin and processes affecting the CO₂ in the region.

Sampling and Analyses

CO₂-bearing fluid inclusions (n=24) were extracted from the Duperow Formation and produced gases (n=19) were collected at Kevin Dome from the Bow Island, Sunburst, Kootenai, Swift, Bakken, Madison, and Nisku hydrocarbon-bearing reservoirs (Fig. 1). Additional bulk gas samples (n=9) were analyzed from the Banff Formation in the adjacent Ferguson Field, southern Alberta Canada. Finally, igneous fluid inclusions (n=2) from the Gold Butte (SGH) igneous complex, northwest Montana were measured. Well details,

summary of sample preparation and analytical procedures completed on each sample type are summarized in SI C.

Fluid Inclusions

The geochemical composition of fluid inclusions can be used to evaluate the origin and evolution of subsurface fluids in different geologic settings (e.g., Roedder, 1984; Hilton et al., 1993, 2011; Merrill et al., 2015; Barry et al., 2015; Horton et al., 2021). Drilled core plugs were crushed under vacuum to release any trapped volatiles in the fluid inclusions (e.g. Norman and Moore, (1999). The released gas was then purified and measured on a mass Spectrometer. Duperow Formation thin sections were used to locate and describe the types and distribution of its fluid inclusions prior to fluid inclusion isotopic geochemistry analysis (SI C). Olivine is the target mineral of interest in igneous rock studies, as they best preserve the chemistry of the fluids present during intrusion emplacement (e.g., Barry et al., 2015; Horton et al., 2021). He-Ne-Ar data from fluid inclusions in olivines from the Gold Butte (SGH) are summarized in SI C. Duperow and Gold Butte (SGH) fluid inclusion analyses were completed at the WHEEL Noble Gas Lab, Ohio State University, and the Barry Lab, Woods Hole Oceanographic Institution respectively.

Bulk Gas

Bulk gas samples were collected directly from well heads, at Kevin Dome and in the Ferguson Field, in (150 or 300cc) double-ended stainless-steel cylinders following standard ISOTECH Laboratories, Inc., procedures. Major gas abundances were determined by gas chromatography (GC), while the isotopic ratios of the main gases were measured by gas chromatography combustion isotope ratio mass spectrometry

(GC/C/IRMS) techniques respectively at ISOTECH Laboratories, Inc., Champaign IL USA. Noble gas elemental composition and isotopic ratios were analyzed at the WHEEL Noble Gas Lab, Ohio State University following procedures outlined in Darrah et al. (2014 and 2015b).

Results

Measured concentrations and isotope ratios of both the fluid inclusions and bulk gases can be found in SI D table D.1 to D.10.

Duperow CO₂-bearing Fluid Inclusions

Fluid inclusions within the Duperow Formation are located within calcite grain-filled fractures and rock matrix indicating they were formed after crystal growth and thus secondary in nature (SI C). This means they contain information about subsurface fluid processes such as the passage of different fluid pulses or those related to later stages of deposition (Polito et al., 2001; Fairmaid et al., 2011; Kendrick and Burnard, 2012). CO₂ is the most abundant gas in the Duperow fluid inclusions ($85 \pm 10\%$). Other gases were not quantitatively measured in the Duperow fluid inclusions due to analytical limitations, however, noble gas isotopes and their ratios were measured. Measured ³He and ⁴He concentrations were 273 ± 9 pcc/cc and 785 ± 11 µcc/cc respectively. The air normalized ³He/⁴He (R/Ra where Ra is the ratio in air) is $0.26 \pm 4 \times 10^{-3}$. The neon (²⁰Ne) concentration measured was 20 ± 0.3 µcc/cc and the ²⁰Ne/²²Ne and ²¹Ne/²²Ne were within error of air (9.83 ± 0.06 and $0.03 \pm 3 \times 10^{-4}$ respectively). The CO₂/³He was $3.3 \pm 3 \times 10^9$.

Gold Butte (SGH) Igneous Fluid Inclusions

Within the Gold Butte (SGH) olivine mineral fluid inclusion ^3He and ^4He concentrations were $4.8 \times 10^{-8} \pm 3.5 \times 10^{-9} \text{ cm}^3\text{STP/g}$ and $7.7 \times 10^{-7} \pm 9.9 \times 10^{-7} \text{ cm}^3\text{STP/g}$ respectively and the R/Ra was 0.36 ± 0.46 . Measured concentrations of ^{20}Ne were $1.3 \times 10^{-10} \pm 1.3 \times 10^{-10} \text{ cm}^3\text{STP/g}$. Measured $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ were 9.57 ± 0.40 and 0.07 ± 0.04 .

Hydrocarbon-bearing Reservoirs

Kevin Dome hydrocarbon-bearing reservoirs contain higher CH_4 than those observed in the Ferguson Field ($84 \pm 9\%$ vs $47 \pm 7\%$, respectively), while ethane ($3.9 \pm 2.5\%$ vs $7 \pm 1\%$) and propane ($1.7 \pm 1.6\%$ vs $6.3 \pm 1.7\%$) proportions were higher in the Ferguson Field. CO_2 and N_2 proportions are higher in the Ferguson Field compared to Kevin Dome ($26 \pm 10\%$ and $8.7 \pm 2.5\%$ for CO_2 and $1.6 \pm 1\%$ and $4.3 \pm 2\%$ for N_2) except for three outlier samples from the Madison Group and Bakken Formation reservoirs with 10%, 11% and 33% CO_2 at Kevin Dome. No Hydrogen was detected at the Ferguson Field but exists in trace amounts ($0.3 \pm 0.8\%$) at Kevin Dome. Helium ($0.13 \pm 6 \times 10^{-2}\%$) and argon ($0.03 \pm 7 \times 10^{-3}\%$) concentrations were similar in both fields. The $\delta^{13}\text{C}-\text{CH}_4$ at Kevin Dome and in the Ferguson Field were $-54 \pm 3\text{‰}$ vs $-50 \pm 1.4\text{‰}$ respectively and δD was $-259 \pm 15\text{‰}$ vs $288 \pm 14\text{‰}$ respectively. Kevin Dome and Ferguson Field $\delta^{13}\text{C}-\text{CO}_2$ and $\delta^{18}\text{O}-\text{CO}_2$ were $-10 \pm 6\text{‰}$ and $1 \pm 4\text{‰}$ vs $-10 \pm 2\text{‰}$ and $7 \pm 1\text{‰}$ respectively. The $\delta^{15}\text{N}-\text{N}_2$ was $0.2 \pm 1\text{‰}$ vs $-1.0 \pm 0.3\text{‰}$ at Kevin Dome and Ferguson Field, respectively. Measured ^3He and ^4He concentrations within Kevin Dome bulk gas samples were $386 \pm 12 \text{ pcc/cc}$ and $1355 \pm 9 \text{ pcc/cc}$ respectively with an R/Ra of 0.21 ± 0.1 . Kevin Dome ^{20}Ne concentration was $3 \times 10^{-1} \pm 6 \times 10^{-3} \text{ pcc/cc}$, with $^{20}\text{Ne}/^{22}\text{Ne}$ of 9.78 ± 0.05 and $^{21}\text{Ne}/^{22}\text{Ne}$

of $0.03 \pm 2 \times 10^{-4}$. The measured $\text{CO}_2/{}^3\text{He}$ at Kevin Dome was $8.5 \times 10^7 \pm 3 \times 10^6$. Ferguson Field bulk gas samples had 373 ± 12 pcc/cc and 1656 ± 9 $\mu\text{cc/cc}$ of ${}^3\text{He}$ and ${}^4\text{He}$ respectively with an R/Ra of $0.16 \pm 1 \times 10^{-2}$. Measured ${}^{20}\text{Ne}$ concentrations in the Ferguson Field was $3 \times 10^{-1} \pm 2 \times 10^{-1}$ $\mu\text{cc/cc}$, with a ${}^{20}\text{Ne}/{}^{22}\text{Ne}$ of $9.74 \pm 2 \times 10^{-2}$ and ${}^{21}\text{Ne}/{}^{22}\text{Ne}$ of $3 \times 10^{-2} \pm 8 \times 10^{-4}$. The $\text{CO}_2/{}^3\text{He}$ in the Ferguson Field was $5.9 \times 10^8 \pm 4 \times 10^8$.

Discussion

Origin of Gasses

High CO_2 concentrations ($85 \pm 10\%$) measured in Duperow Formation fluid inclusions are consistent with high ($\sim 96\%$) CO_2 concentrations previously measured in the free gas phase (Bowen et al., 2012; AAL, 2015). This suggests that the Duperow serves as the primary CO_2 reservoir at Kevin Dome, northwest Montana, and adjacent regions in Canada (e.g., Lake and Whittaker, 2006; Ryerson, et al., 2013). Elevated CO_2 concentrations within Devonian - Mississippian reservoirs at Kevin Dome and Ferguson Field compared to Jurassic Lower Cretaceous reservoirs at Kevin Dome (Fig. 2) may be the result of stratigraphic proximity to CO_2 source or the primary CO_2 charge into the Duperow. The relationship between the three main gas phases (CH_4 , N_2 and CO_2) at Kevin Dome and the Ferguson Field can yield clues to the gas sources in the area (see SI Fig. E.1). CO_2 is negatively correlated with CH_4 and N_2 in both study areas, while CH_4 and N_2 correlate positively, with the exception of the Lower Jurassic – Cretaceous reservoirs (potentially due to gas mixing from shallower reservoirs). This suggests that CO_2 has a different source to CH_4 and N_2 , which likely have the same.

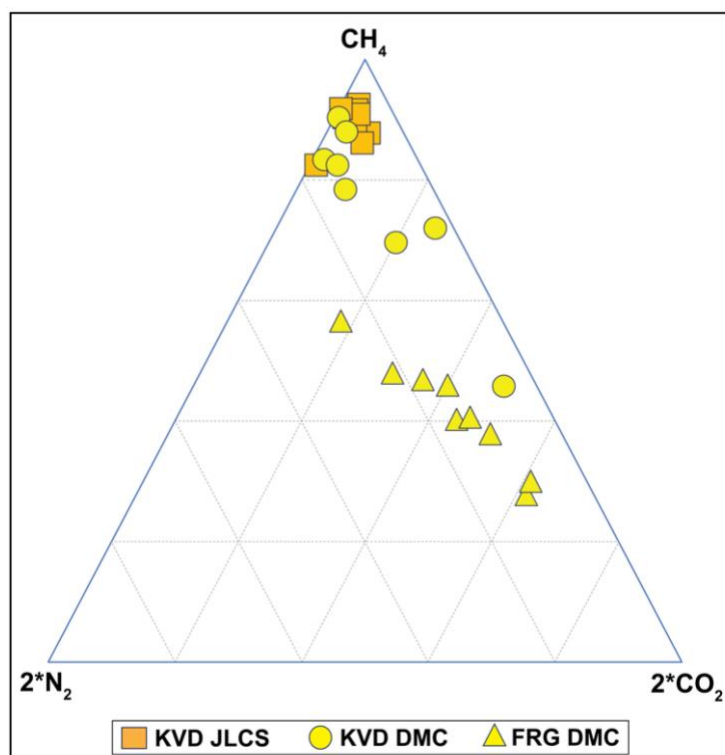


Fig. 2: Kevin Dome, northwest MT USA and Ferguson Field, southern AB Canada bulk gas composition in mole percent (%). CO_2 and N_2 concentrations were multiplied by a factor of 2 to better visualize variations. **KVD** - Kevin Dome; **FRG** - Ferguson Field; **JLCS** - Jurassic-Lower Cretaceous sandstone and **DMC** - Devonian-Mississippian carbonate reservoirs.

Origin of CH_4 and N_2

Stable isotopic signatures of natural gases are indicative of their origin and when combined can help delineate gas origin and subsequent post-genetic alterations (e.g., Bernard et al., 1976, 1977; Whiticar et al., 1986; Whiticar, 1999; Norman and Moore, 1999; Liu et al., 1997 Milkov and Etiope, 2018). The methane at Kevin Dome appears to be oil-associated thermogenic to secondary microbial transition/mix, while in the Ferguson Field methane appears to be early mature thermogenic (Fig. 3a, Whiticar et al., 1986). However, using a Bernard plot, the CH_4 in both study areas plots as early mature thermogenic and oil-associated thermogenic gas (Fig. 3b). The “oil associated

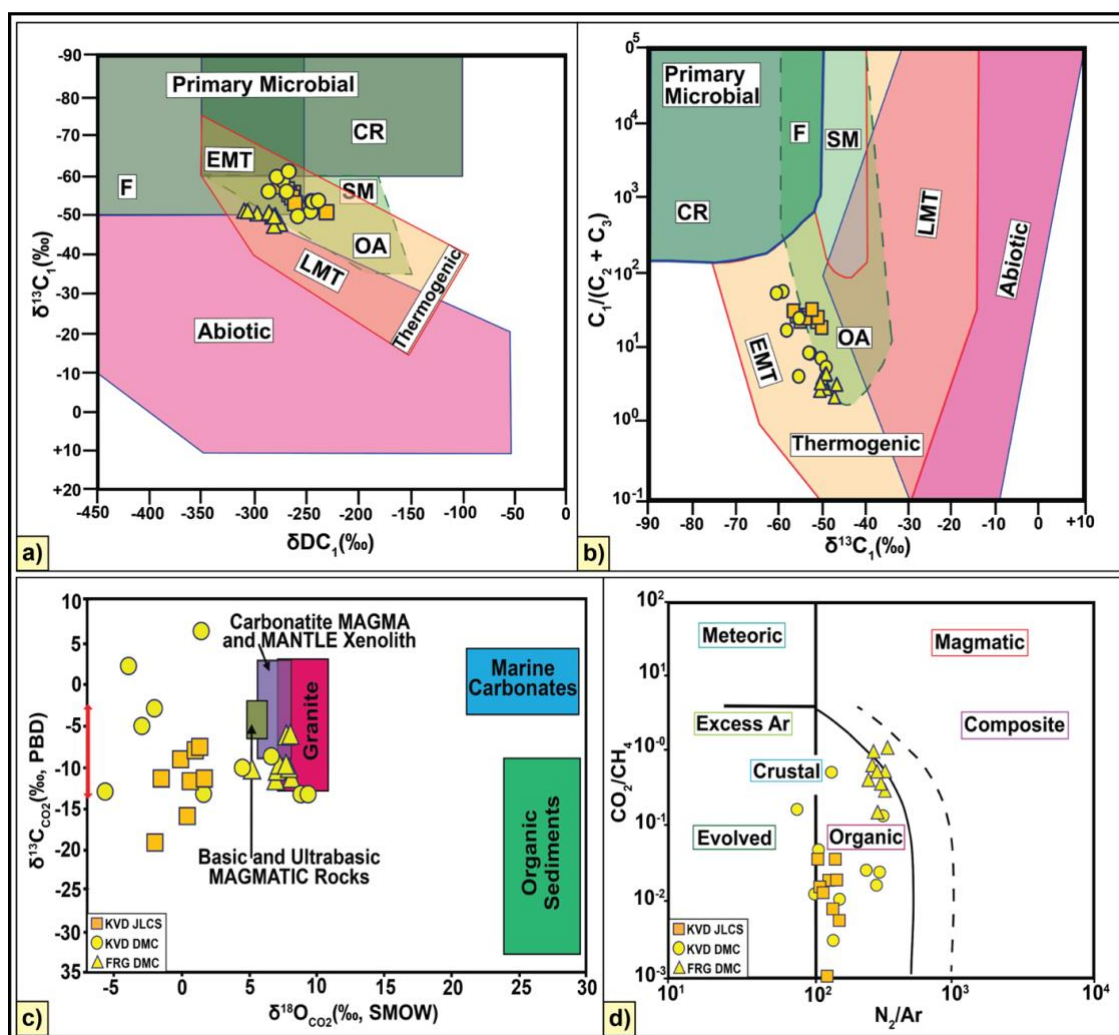


Fig. 3: Kevin Dome, northwest MT USA and Ferguson Field, southern AB Canada major gas origin using stable isotopes signatures: **(a)** Modified Whiticar CH₄ gas genetic classification scheme **(b)** Modified Bernard CH₄ gas genetic classification scheme **(c)** CO₂ origin: $\delta^{13}C$ -CO₂ vs $\delta^{18}O$ -CO₂ classification scheme after Liu et al. (1997). Red arrow highlights where the magmatic and microbial $\delta^{13}C$ -CO₂ value overlaps **(d)** N₂ origin: CO₂/CH₄ versus N₂/Ar ratio and (B) $\delta^{15}N$ of N₂ against N₂ concentration classification schemes after Norman and Moore (1999). KVD - Kevin Dome; FRG - Ferguson Field; JLCS - Jurassic-Lower Cretaceous Sandstone and DMC - Devonian-Mississippian Carbonates reservoirs. CH₄ origin domains: CR – CO₂ reduction; F – methyl-type fermentation; SM – secondary microbial; EMT – early mature thermogenic; OA – oil-associated thermogenic and LMT – late mature thermogenic (Whiticar et al., 1986; Whiticar, 1999; Bernard et al., 1976, 1977; Milkov and Etiope, 2018).

thermogenic” CH₄ at Kevin Dome and Ferguson Field is consistent with oil being present within the reservoirs. The presence of nitrogen in all of the samples suggests an organic

and/or deep crustal (thermogenic) origin (Fig. 3d and SI Fig. E.2). Stable isotopic systematics from both Whiticar and Bernard schemes suggest thermogenic gas sources for CH₄ and N₂ with secondary microbial contributions within the Bakken petroleum system at Kevin Dome and Ferguson Field. Methane could have been sourced from the thermal evolution of organic matter, and/or rocks during burial, with additional input from the biodegradation of generated hydrocarbon, while N₂ could be from the thermogenic evolution of organic matter during petroleum generation or clay minerals in mudrocks within the Bakken petroleum system (Norman and Moore, 1999; Zhu et al., 2000; Faramawy et al., 2016).

Origin of CO₂

Stable isotope-based CO₂ classification schemes of bulk gas samples show an overlap between primary microbial and magmatic sources in both study areas (Fig. 3c, and SI Fig. E.2) especially in the CO₂ rich Devonian-Mississippian reservoirs. On the other hand, noble gas isotopes are useful tracers of CO₂ origin as the mantle has a distinct CO₂/³He range from 1-3 x 10⁹ (Marty and Jambon 1987), whereas crustal CO₂ has a higher CO₂/³He (due to the addition of CO₂ with no associated mantle ³He). CO₂/³He below mantle values is representative of CO₂ loss from the system. Duperow fluid inclusions have CO₂/³He values within the magmatic range, while Kevin Dome and Ferguson Field bulk gas CO₂/³He signatures plot well below the magmatic range (Fig. 4a). This suggests the CO₂ is magmatic in origin and subsequent gas phase loss has occurred. The neon isotope composition in the Duperow fluid inclusions could also exhibit a slight magmatic influence (Fig. 4b), however, we cannot rule out mass dependent fractionation. Gold Butte (SGH) fluid inclusions and the Kevin Dome and Ferguson Field

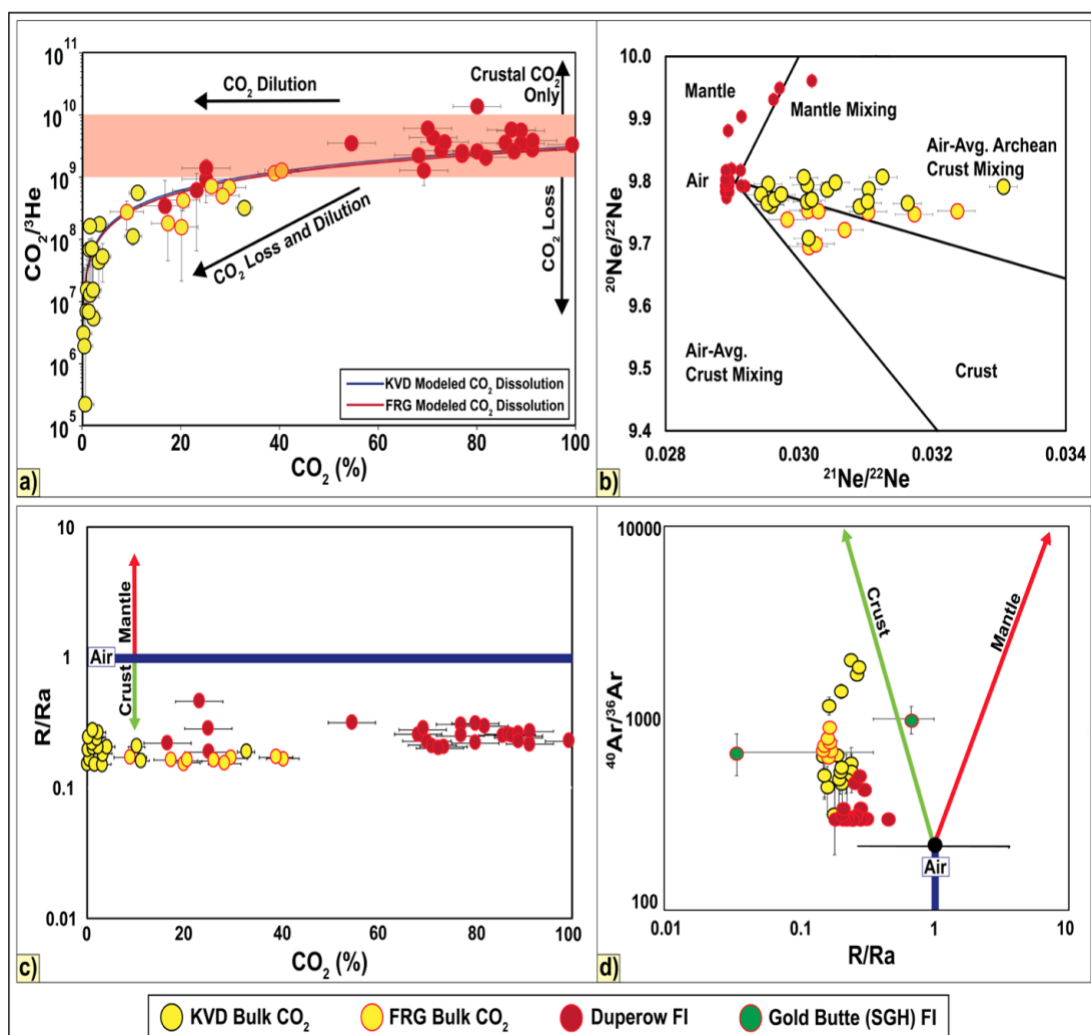


Fig. 4: Kevin Dome, northwest MT USA and Ferguson Field, southern AB Canada bulk gas, Duperow Formation and Gold Butte (SGH) Fluid Inclusions CO_2 origin delineation using (a) $\text{CO}_2/{}^3\text{He}$ vs CO_2 (%) with the magmatic reference range defined by Marty and Jambon (1987), (b) Neon isotopes isotopic ratios (${}^{20}\text{Ne}/{}^{22}\text{Ne}$ vs ${}^{21}\text{Ne}/{}^{22}\text{Ne}$) (c) Helium isotopic ratios (R/R_a) vs CO_2 (%) and (d) Argon isotopic ratios (${}^{40}\text{Ar}/{}^{36}\text{Ar}$) vs CO_2 (%) (Sherwood Lollar et al., 1997 and Ballentine et al., 2001, Ballentine and Burnard, 2002; Prinzhofer, 2013). Solid lines in (a) show the modeled CO_2 dissolution evolution path at Kevin Dome and Ferguson Field respectively (see Supplementary Information Appendix D for CO_2 dissolution model estimation summary). KVD - Kevin Dome; FRG - Ferguson Field; FI - Fluid Inclusions.

bulk gas samples are consistent with air-crust mixing neon isotope signatures (Fig. 4b).

However, helium isotopes in all the hydrocarbon-bearing gas samples and fluid inclusions

are consistent with significant radiogenic production, which has overprinted any magmatic signature present (Fig. 4c-d) (Albarède, 2001; Barry et al., 2015).

Quantifying CO₂ loss from the reservoirs

Dissolution has previously been shown to be a sink for CO₂ in large gas fields around the world (Gilfillan et al., 2008 and 2009; Zhou et al., 2012 and Craddock et al., 2017). The extent of CO₂ dissolution can be estimated using CO₂/³He, whereby a decrease in this ratio in the residual gas phase indicates CO₂ loss due to dissolution. In addition, increases in ⁴He and ²⁰Ne are indicative of gas interacting with groundwater (Gilfillan et al., 2009) and stripping out radiogenic and air-derived species (Fig. 5). An actively flowing aquifer system should have low (i.e., air-like) dissolved CO₂ concentrations and thus could serve as a sink for CO₂ if it came in contact with a CO₂ rich (i.e., magmatic) gas system. If the source of the CO₂ is in fact magmatic, fluid inclusions are predicted to preserve the magmatic CO₂/³He signatures associated with the magmatic CO₂ charge. More importantly, because fluid inclusions are isolated from groundwater influence, they are not affected by secondary processes such as dissolution. Secondary fluid inclusions are found in the Duperow, which represent magmatic CO₂ at the time of emplacement in the dome. Using the Duperow fluid inclusions as the theoretical initial CO₂/³He in Kevin Dome, we modeled dissolution for the Kevin Dome and Ferguson Field bulk CO₂ gas components using CO₂/³He and $\delta^{13}\text{C-CO}_2$ signatures following a simple Rayleigh fractionation model (Gilfillan et al., 2009):

$$\delta^{13}\text{C-CO}_2 = \delta^{13}\text{C-CO}_{2i} + \epsilon_{\text{DIS}} \ln f \quad (\text{Eq. 1})$$

where $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CO}_{2i}$ are the measured and assumed initial $\delta^{13}\text{C-CO}_2$ values of the gas, respectively. f is the fraction of CO₂ remaining in the reservoir. ϵ_{DIS} is the carbon

isotope fractionation for dissolution, which is a function of reservoir temperature, salinity (S), and pH conditions. Table 1 shows the estimated average pH and fraction of CO₂ dissolved within Kevin Dome and Ferguson Field hydrocarbon reservoirs (see SI F for the method summary, parameters and assumptions used). Our model (Fig. 6) predicts that $98 \pm 3\%$ and $82 \pm 13\%$ of CO₂ gas has been dissolved into surrounding fluids with an average pH of 6.12 and 7.25 at Kevin Dome and Ferguson Field hydrocarbon reservoirs, respectively. This is consistent with the shallower (<1km) Kevin Dome gas reservoirs having greater groundwater interaction leading to more CO₂ dissolution, whereas the deeper (>1km) Ferguson Field has interacted with less groundwater flow and thus has less CO₂ dissolution, as is indicated by higher ⁴He and ²⁰Ne (Fig. 5).

Constraining reservoir gas-water ratios

To further quantify the amount of groundwater interaction in both fields we use a zero-order (ZO) total gas-stripping model (Eq. 2) to estimate gas-water (G/W) ratios within the reservoirs (after Barry et al., 2016). The ZO model quantifies the minimum volume of water required to produce the measured concentrations of a noble gas (*i*) and to completely remove it from gas into water phase (Barry et al., 2016). It is expressed as:

$$G/W(ZO) = [C_{i(ASW)}]/Z*[C_{i(meas.)}] \text{ (Eq. 2)}$$

where $[C_{i(ASW)}]$ and $[C_{i(meas.)}]$ are the initial concentrations of noble gas(*i*), in air-saturated water (ASW) and the measured gas phase, respectively. *Z* is the compression factor for converting all parameters measured in STP (273.15 K at 1 bar) to reservoir temperature and pressure (RTP) and is defined as $Z = 273.15 \cdot P/T$ (Barry et al., 2016). Using the measured ²⁰Ne and a ²⁰Ne in ASW of 1.51×10^{-7} cm³STP/g, we estimate a G/W of $0.00024 \pm 1 \times 10^{-4}$ and $0.00033 \pm 1 \times 10^{-4}$ at Kevin Dome and Ferguson Field, respectively

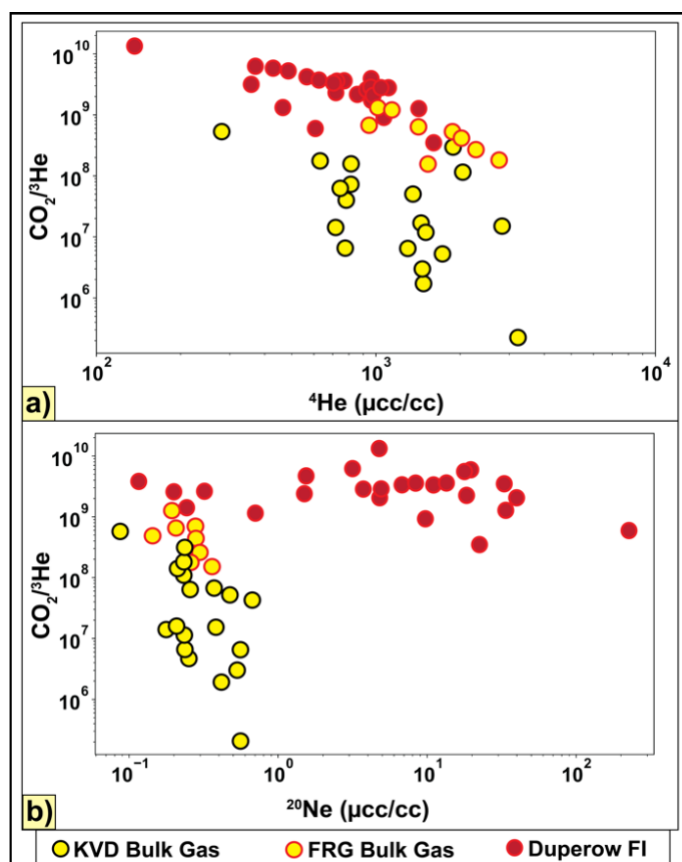


Fig. 5: Kevin Dome, northwest MT USA and Ferguson Field, southern AB Canada bulk gas data with Duperow Formation Fluid Inclusions showing decreasing $\text{CO}_2/{}^3\text{He}$ to increasing radiogenic (a) ${}^4\text{He}$ and (b) ${}^{20}\text{Ne}$ concentrations. Similar trends have been observed in other CO_2 -rich reservoirs across the USA, China, and Europe (Gilfillan et al., 2009). FI – Fluid Inclusions.

Table 1: Average pH and fraction of CO_2 dissolved within Kevin Dome and Ferguson Field hydrocarbon-bearing reservoirs.

RESERVOIRS	BHT (°C)	S (M)	pH	ϵ_{DIS}	$\delta^{13}\text{C} - \text{CO}_2$	$\delta^{13}\text{C} - \text{CO}_{2i}$	CO_2 (%)	Depth (km)	CO_2 Dissolved (%)
Kevin Dome	26	0.17	6.12	2.29	-11.24	0	4.15	0.53	98.04
Ferguson Field	48	1.97	7.25	5.27	-9.55	0	25.55	1.280	82.02

Table 2: Average ${}^{20}\text{Ne}$ G/W ratio within Kevin Dome and Ferguson Field hydrocarbon-bearing reservoirs.

RESERVOIRS	BHT (°C)	P(bar)	Depth (km)	${}^{20}\text{Ne}$	${}^{20}\text{Ne}$ ASW	Z	G/W
Kevin Dome	26	149	0.530	3.5E-07	1.51E-07	1484	0.00024
Ferguson Field	48	347	1.280	2.5E-07	1.51E-07	1976	0.00033

(Table 2). A lower G/W indicates that relatively more groundwater has interacted with the gas in the system and thus there is likely greater groundwater flow (Barry et al., 2016, Tyne et al., 2022). As suggested above, the lower G/W at Kevin Dome is consistent with more dissolution compared to the Ferguson Field (Fig. 7a). In addition, we note a slight trend with depth where the G/W decreases, likely due to groundwater flow being restricted by decreased porosity or different hydrological systems. Again, this is consistent with less groundwater movement and dissolution in Ferguson Field than the shallower Kevin Dome fields (Fig. 7b).

Gas Origin and Kevin Dome's Evolution

In this section we aim to bring together information about gas origins with the geologic setting, stratigraphic framework, and overall evolutionary context at Kevin Dome. Fig. 8 summarizes the orogenic and erosional events that controlled the development and stratigraphy at northwest Montana, USA and southern Alberta, Canada. We also note the hydrocarbon generation events associated with the Bakken/Exshaw petroleum system as well as the CO₂ emplacement events that are presumed to have occurred at Kevin Dome.

CH₄ and N₂ Origin at Kevin Dome

Burial and exhumation history at Kevin Dome and southern Alberta inferred from thermochronological and thermal maturity data show that rocks in this region experienced burial temperatures to the oil and gas generation window (Bustin, 1991; Dolson et al., 1993; Dyman, 1995; Schietinger, 2013; Aviles and Cheadle 2015; Dembicki, 2017; Adeniyi et al., 2023). Oil and gas generation began in the Bakken petroleum system by Early Cretaceous (Fig. 8) but was shut off by an Oligocene-Miocene exhumation associated with a regional unroofing event (Adeniyi et al., 2023). Consistently,

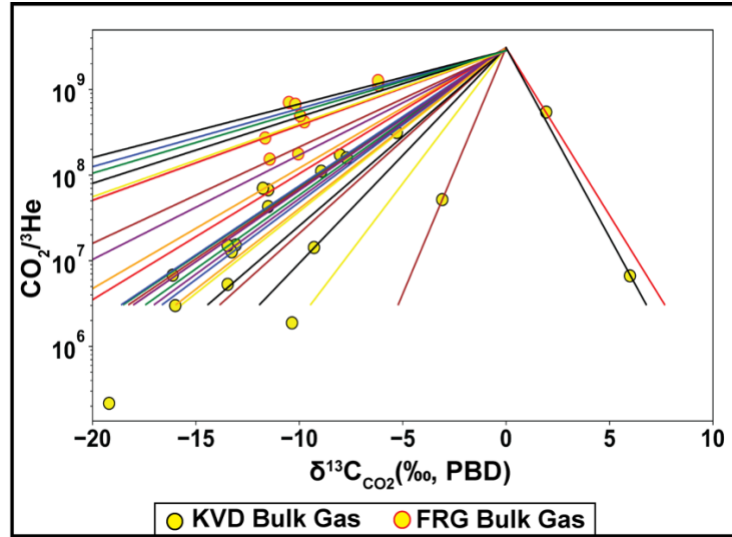


Fig. 6: CO₂ dissolution modeled with changing CO₂/³He and $\delta^{13}\text{C-CO}_2$ with various pH conditions at Kevin Dome, northwest MT USA and Ferguson Field, southern Alberta, Canada. Colored trend lines represent modeled pH conditions for each sample.

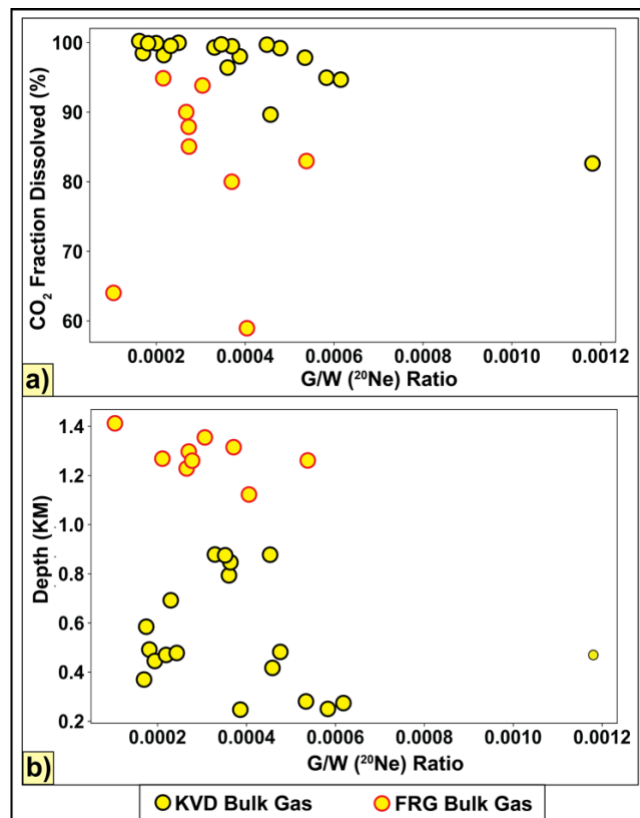


Fig. 7: (a) CO₂ fraction dissolved within Kevin Dome, northwest MT USA and Ferguson Field, southern AB, CA hydrocarbon reservoirs versus ²⁰Ne G/W estimates from our zero-order (ZO) total gas-stripping model and (b) depth versus ²⁰Ne G/W estimates from our zero-order (ZO) total gas-stripping model.

compositional data and stable isotope systematics of Bakken petroleum system gases show that CH₄ and N₂ gasses were generated from the thermal evolution of organic matter, and/or rocks during burial and the biodegradation of the generated hydrocarbon.

CO₂ Origin at Kevin Dome

High purity (95–99%) magmatic CO₂ reservoirs are typically found in close proximity to magmatic centers, igneous intrusions, and/or volcanic regions where basement sutures, shear zones, or faults acted as conduits for CO₂ migration from magmatic intrusions (e.g., Gilfillan et al., 2008 and 2009; Zhou et al., 2012; Karlstrom and Humphreys, 1998; Broadhead, 2005; Craddock et al., 2017). The Duperow gas field is large ($\sim 283 \times 10^9 \text{ m}^3$) and comprised of nearly pure CO₂ ($\sim 96\%$) (Bowen et al., 2012; AAL, 2015), marked by mantle CO₂/³He signatures in secondary fluid inclusions. When considered within the framework of Kevin Dome's geologic context (i.e. proximity to SGH igneous intrusion and basement), these observations suggest a magmatic origin for the CO₂ (Fig. 1 and 8). Due to the lack of evidence of a major basement fault below Kevin Dome from existing seismic data (Bowen et al., 2012), the magmatic CO₂ charge at the dome can be linked to the SGH ($\sim 52 \text{ Ma}$) igneous intrusion (Lopez, 1995). Evidence for elevated CO₂ concentrations in Devonian-Mississippian hydrocarbon reservoirs around Kevin Dome, northwest Montana, and adjacent regions in Canada (Lake and Whittaker, 2006; Ryerson et al., 2013), also suggests that emplaced CO₂ may have migrated into the Bakken petroleum system from the magmatic source. The amount of nearly pure CO₂ preserved in the Duperow suggests that this stratigraphic unit was charged by magmatic CO₂ at $\sim 52 \text{ Ma}$ and was not subsequently modified. The Duperow has two main porosity zones (one located in the Middle Duperow, the other located in the Lower Duperow) and

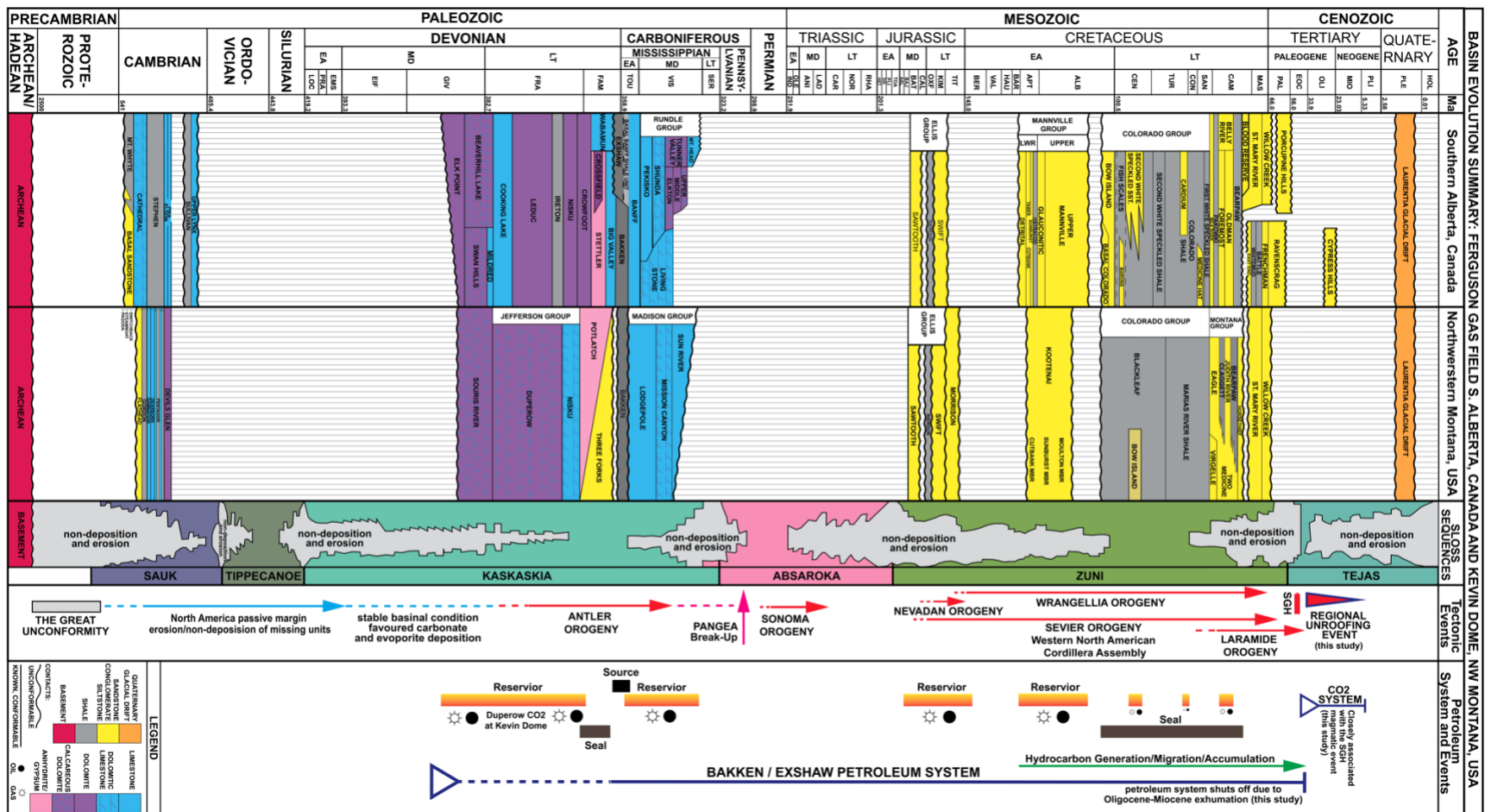


Fig. 8: Basin evolution summary showing tectonic events that controlled stratigraphy, development of the Bakken /Exshaw Petroleum System and the CO₂ system at Kevin Dome, NW Montana, USA and Ferguson Field, S Alberta Canada (Deiss, 1936; Peterson, 1987; Downey, 1986; Dyman, 1995; Smith et al. 1995; Dolson et al., 1993; Vuke et al., 2007; Dembicki, 2017; Core Lab Geo Sci Dept., Canada; Adeniyi et al., 2023).

the stratigraphically higher of these zones is the most porous and serves as the main CO₂ zone. The Upper Duperow has low porosity and permeability and serves as a baffle or seal. The lower Duperow porosity zone also contains significant CO₂ volumes, sealed by a thick anhydrite that separates the upper porosity zone from the lower porosity zone (Bowen et al., 2009, 2012; Adeniyi and Steuer, 2019). The overlying Potlatch Formation also provided a reliable secondary seal for the Duperow CO₂ trap (Fig. 1 and 8). The emplacement of the CO₂ occurred after the Early Cretaceous hydrocarbon generation and trapping at Kevin Dome.

Conclusion

Using a multi-faceted geochemical approach, we have constrained the genetic origin and timing of CO₂ in the Upper Devonian Duperow Formation, Kevin Dome, and the Bakken petroleum system in northwest Montana, USA and southern Alberta, Canada.

We found:

1. CO₂ is the main gas within the Upper Devonian Duperow Formation at Kevin Dome, whilst CH₄ is the dominant gas within the Bakken petroleum system and is associated with varying (trace to elevated) proportions of N₂ and CO₂.
2. CO₂ within the Duperow Formation at Kevin Dome is magmatic in origin (as indicated by CO₂/³He) and has migrated into other hydrocarbon reservoirs within the Bakken petroleum system.
3. CH₄ and N₂ gases were generated mainly by thermogenic processes with inputs from secondary microbial generation from existing oil. The source of the CO₂ at Kevin Dome is tied to the adjacent Sweetgrass Hills igneous complex intrusion and

to the (~52 Ma). Emplacement occurred after Early Cretaceous hydrocarbon generation at Kevin Dome.

4. Groundwater interaction and subsequent dissolution is consistent with CO₂ migration from a magmatic source into hydrocarbon-bearing reservoirs. Using a simple dissolution model, we estimate a CO₂ dissolution of ~98% and ~82% at Kevin Dome and the Ferguson Field, respectively. We suggest that the different fractions of CO₂ dissolved into groundwater, as indicated by G/W estimates, are controlled by stratigraphic depth and different hydrological systems.
5. Radiogenic-produced helium overprinted the initially magmatic He isotope signatures during primary and secondary migration from source to sink. We estimate 98% crustal and 2% mantle components in Kevin Dome hydrocarbon-bearing reservoirs based on helium isotopes.

Duperow formation fluid inclusions preserved the isotopic composition of the CO₂ charge, irrespective of subsequent geologic processes and events at Kevin Dome. In addition, geochemical signatures measured in the adjacent Ferguson Field, southern Alberta Canada, support (CH₄ and N₂) gas thermogenic generation systematics in the region. Identifying gas migration pathways and direction relative to the source is important for geologic characterization of carbon sequestration sites.

Acknowledgements

This research has been supported in part by funding from the American Chemical Society Petroleum Research Fund, U.S. Department of Energy, and the National Energy Technology Laboratory through award number: DE-FC26-05NT42587 to the Energy Research Institute (ERI) and Big Sky Carbon Sequestration Partnership (BSCSP) at

Montana State University. Special thanks to ERI, and the BSCSP for access to the Duperow CO₂ reservoir core including Jerry Croft and John Fugoe (Croft Petroleum, MT., USA); Charles Jansky and Jacob Alborano (SOMONT OIL. MT., USA); Dr. Ted Doughty (PRISEM Geoscience Consulting, WA., USA); Mark Frankiw, Carrie Kukko and Scott Petkau (International Petroleum Corporation, Canada) who allowed the sampling of natural gas from various privately owned and operated oil/gas fields. Additional thanks to Steve Pelphrey (ISOTECH Lab, IL., USA) for analytical assistance and Dr. Andrew Hunt (USGS, CO., USA) for helpful discussions on the data.

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CHAPTER FOUR

DISSERTATION SUMMARY

Main summaries to research questions

In my dissertation, I researched the structural, thermal, and temporal evolution of Kevin Dome and investigated the origin of the existing CO₂ in the Upper Devonian Duperow Formation, as well as the CH₄ and N₂ gas sources in hydrocarbon-bearing reservoirs at the dome. To effectively answer these research questions, I utilized well cuttings and cores to analyze the subsurface at Kevin Dome. I examined the mineralogy, petrology, and geochemistry of the Archean basement and both clastic and carbonate sedimentary units. I also collected and examined bulk gas samples from Kevin Dome and the proximal Ferguson Field, southern Alberta, and outcrop samples from Gold Butte (Sweetgrass Hills igneous complex - SGH) to provide a regional context to the study. I interpreted and compared the results obtained with relevant studies within the Rocky Mountains of Montana and the proximal Western Canadian Sedimentary Basin (WCSB), Canada.

The major findings to the four main research questions asked in my dissertation are summarized below:

1. What are the major exhumation episodes that led to the development of Kevin Dome? – Using apatite (U - Th)/He, zircon (U - Th)/He and thermal history modeling, I found that Kevin Dome was affected by two separate exhumation episodes, one during the Late Cretaceous-Paleocene (~65–72Ma) and the second during the Oligocene-Miocene (~ 15 – 26Ma), with an average exhumation rate of

~ 0.27 mm/yr. These inferred Kevin Dome exhumation episodes are younger than exhumation induced by the Laramide Orogeny (ca 100Ma) that is recorded in southwest Montana (Carrapa et al., 2019). Our results are, however, consistent with exhumation episodes in proximal southern regions in the WCSB (Bustin, 1991; Aviles and Cheadle 2015; Fraser et al., 2021).

2. How has the burial-and-uplift history controlled the thermal conditions that have led to hydrocarbon generation within the Bakken petroleum system at Kevin Dome? I found that the rocks that make up Kevin Dome were buried to the oil and gas generation windows ($\sim 100 \pm 10$ °C) prior to their exhumation to current depths. Integrated results suggest that the Oligocene-Miocene exhumation event halted hydrocarbon generation within Kevin Dome. The ($\sim 100 \pm 10$ °C) maximum burial temperature obtained from the t-T proxies engaged in this study is consistent with existing thermal maturity data for Kevin Dome, inferred by vitrinite reflectance and RockEval pyrolysis indices (Dolson et al., 1993). Though conventional thermal maturity indicators in petroleum studies rely solely on organic-rich rocks, this study demonstrates that thermochronological techniques applied directly to clastic and carbonate sedimentary rocks (e.g., sandstone and limestone) are effective in unraveling the thermal and hydrocarbon generation history of a region, especially where organic-rich rock samples are not available.
3. What is the origin and timing of emplacement of the Upper Devonian Duperow Formation CO₂ resource and how has it evolved and migrated through time into the present-day petroleum system? This study suggests that the CO₂ emplaced into the Duperow Formation, Kevin Dome, which has migrated to other

hydrocarbon-bearing reservoirs in the region, is magmatic in origin and likely related to the adjacent SGH intrusion event (ca 52 Ma). Duperow CO₂ volume ($\sim 283 \times 10^9 \text{m}^3$), bulk gas ($\sim 96\%$ CO₂; Bowen et al., 2012; AAL, 2015), fluid inclusions ($85 \pm 10\%$ CO₂) and mantle CO₂/³He signatures, strongly support a magmatic origin. On the other hand, $\sim 98\%$ and $\sim 82\%$ of the CO₂ in the hydrocarbon-bearing reservoirs at Kevin Dome, Montana and the Ferguson Field, southern Alberta respectively, have been dissolved into the groundwater during migration from the source to sink.

4. Can we reconcile Kevin Dome's evolution, erosional history, and CO₂ origin with existing structural evolution models for the dome and incorporate it within the framework of existing regional geology? Based on the timing of exhumation obtained in this study, Kevin Dome was formed as an evolved forebulge related to the Late Cretaceous-Paleocene emplacement of the Rocky Mountain overthrust in the linked foreland basin in northwest Montana and proximal Canada (Hoffman et al., 1976; Lorenz, 1983; DeCelles and Giles 1996; Sears, 2001; Osborn et al., 2006; Ward, 2007). From our modeling we also interpret and provide the timing for an Oligocene-to-Miocene erosional or epeirogenic event not previously recognized in northwest Montana. These erosional events removed $\sim 4 - 5 \text{km}$ of overburden from northwest Montana, USA, and southern regions of the WCSB, Canada. This erosional thickness is significantly greater than earlier reported estimates of $\sim 1.4 \text{km}$ and $\sim 3 \text{km}$ respectively from stratigraphic and thermal maturity measurements (e.g., Michener, 1934; Collier, 1929; Shepard and Bartow, 1986; Bustin, 1991).

Future Work

Access to additional subsurface fluids and rock samples from Kevin Dome and surrounding regions would lead to more robust constraints to feed into a thermochronological model. Further isotopic geochemistry analysis would also help to further support the findings of this research. Seismic imaging of the substructure of Kevin Dome and the surrounding region could also help identify minor or major faults in the study area that could have served as migration conduits for CO₂ emplacement from magmatic sources.

Apart from isotopic geochemistry on additional samples, another technique that could increase our understanding of the origin of CO₂ in the Duperow Formation, is a technique known as the Advanced Geochemistry Technology (AGT). AGT is a novel method for analyzing diamondoids found in crude oil or gas condensates as proxies for delineating the origin of oil and gas. This technique has been applied to help correlate multiple source rocks, reconstruct migration history, oil cracking, extracting the extent of closed/open connection within petroleum systems, and for determining the age of source-reservoir rock petroleum systems (Landa, and Machacek, 1933; Petrov et al., 1973; Dahl et al., 1999; Nekhaev and Maksimov, 2019 and Atwah et al., 2021). I have collected bulk oil samples from Kevin Dome and the Ferguson Gas Field for AGT analyses. The oil samples collected are being analyzed at the Biomarker Technologies, Inc. CA at the time of writing of this dissertation. I will be performing quantitative diamondoids analysis (QDA), which will provide thermal maturity and hydrocarbon source correlations information, as well as quantitative extended diamondoid analysis (QEDA), which will provide additional hydrocarbon source, migration history and petroleum system

delineation information. The results obtained from these analyses will be included in future publications and will expand our current understanding on the origin of CO₂ and other natural gas resources within Bakken petroleum systems in northwest Montana.

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APPENDICES

APPENDIX A

SUPPLEMENTARY INFORMATION FOR CHAPTER TWO

SI A: A schematic tectonic evolution model for Kevin Dome:

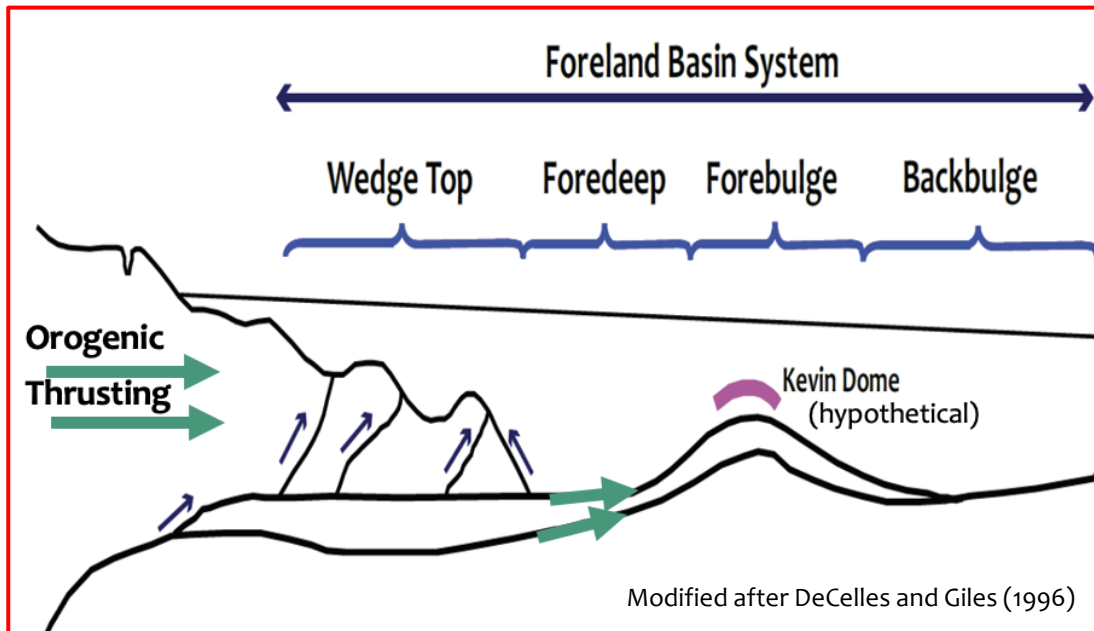


Fig. A1: Evolved forebulge dome-origination model related to Late Cretaceous-Paleocene emplacement of the Rocky Mountain Cordillera in the associated foreland basin (Hoffman et al., 1976; Lorenz, 1983; DeCelles and Giles 1996; Sears, 2001; Osborn et al., 2006; Ward, 2007). The would-be position of Kevin Dome in the context of the sketched model is not to scale.

SI B: Kevin Dome (U-Th)/He Samples

B.1 Well details

Kevin Dome Wells	From (ft)	To (ft)	Interval (ft)	Formation	Lithology	Samples
Well 1 API # 25-101-06724-00-00 Field: Kevin-Sunburst 35N-1W Wh_Sec 17 Coordinates: 48.79633, -111.76803 Well No: 1 Lease: Inland Empire Year Drilled: 1949	1490?	1505	1490 - 1500	Sunburst	Sst	1
	1505?	1510		Morrison		
	1510	1575		Swift		
	1575?	1650		Reirdon		
	1650	1685	1655 - 1685	Sawtooth	Sst	1
	1685	2030		Mission Canyon		
	2030	2455		Lodgepole		
	2455?	2845		Paine		
	2845	3020?		Devonian - DA1		
	3020?	3375		Devonian - DA2		
	3375	4035		DB		
	4035	4855		Barker		
	4855	4890	4855 - 4890	Flathead	Sst	1
Well 2 API # 25-101-24192-00-00 Field: Wildcat 33N-1W Wh_Sec 4 Coordinates: 48.64992, -111.74871 Lease: Plain Kevin Well No: 04-04-33N-01W Year Drilled: 2011	4890		4895 - 4905	Pre-Cambrian	Granite	1
	1385	2379	2370	Madison Group	Dol/Lm	
	2379	2488	2390	Bakken	Shl	
	2488	2515	2480 - 2510	Three Forks	Sst	
	2515	2658		Potlatch		
	2658	2696		Nisku		
	2696	3344		Duperow		
	3344	3648		Souris River		
	3648	4298	44200	Cambrian		
	4298	4446	4310 - 4410	Flathead	Sst	3
Well 3 API # 25-101-23393-00-00 Field: Wildcat 34N-1E Wh_Sec 21 Coordinates: 48.694113, -111.61291 Lease: Montex Well No: 3-21 Year Drilled: 1990	4446		4460 - 4510	Pre-cambrian	Granite	2
	258	535	250-310	Blackleaf	Shl	
	535	691		1st Bow Island		
	691	812		2nd Bow Island		
	812	1020		3rd Bow Island		
	1020	1037		Dakota		
	1037	1420	1060-1410	Kootenai	Sst	6
	1420	1491		Sunburst		
	1491	1508		Morrison		
	1508	1580	1510-1580	Swift	Sst	2
	1580	1616		Swift Shale		
	1616	1706		Rierdon		
	1706	1741		Sawtooth		
	1741	2462		Madison		
	2462	2716		Lodgepole		
	2716	2766	2750-2770	Banff	Sst	
	2766	2774	2770-2780	Bakken	Shl	
Well 4 API # 25-101-24194-00-00 Field: Wildcat 34N-3W Wh_Sec 24 Coordinates: 48.685113, -111.939697 Lease: Plain Kevin Well No: 14-24-34N-03W Year Drilled: 2011	2774	2843	2780-2790	Three Forks	Sst?	
	2843	2999		Potlatch		
	2999	3056		Nisku		
	3056			Duperow		
	844	1320		Kootenai		
	1320	1346		Sunburst		
	1346	1392		Swift		
	1392	1555		Rierdon		
	1555	1587	1560-1580	Sawtooth	Sst	1
	1587	2614		Madison Group		
	2614	2687	2620-2680	Bakken	Shl	
	2687	2726	2690-2710	Three Forks	Sst?	
	2726	2875		Potlatch		
	2875	2940		Nisku		
	2940	3631		Duperow		
Well 5 API # 25-101-23269-00-00 Field: Kevin-Sunburst 35N-4W Wh_Sec 27 Coordinates: 48.759106, -112.10348 Lease: Dickens et al Well No: 1 Year Drilled: 1988	3631	3903		Souris River		
	3903	4613		Cambrian		
	4613	4848	4630-4640	Flathead	Sst	1
	4848		4848-4910	Pre-cambrian	Granite	2
	80	680	420-480		Sst	2
	680	877	750-870	Blackleaf	Shl	
	877	944		Base Fish Scales		
	944	1402	1290	Bow Island	Sst/Shl	
	1402	1433		Dakota		
	1433	1850	1800-1850	Kootenai	Sst	2
	1850	1892	1860-1890	Sunburst	Sst	1
Well 6 API # 25-101-23269-00-00 Field: Kevin-Sunburst 35N-4W Wh_Sec 27 Coordinates: 48.759106, -112.10348 Lease: Dickens et al Well No: 1 Year Drilled: 1988	1892	1954	1900-1910	Swift Sandstone	Sst	1
	1954	1980	1960	Swift Shale	Shl	
	1980	2075	1990-2050	Rierdon	Shl	
	2075	2112	2080	Sawtooth	Sst	1
	2112			Madison		
Key: Sst = Sandstone, Shl = Shale, Dol = Dolomite, Lm = Limestone					Total	28

B.2 Zircon and Apatite Mineral Separation

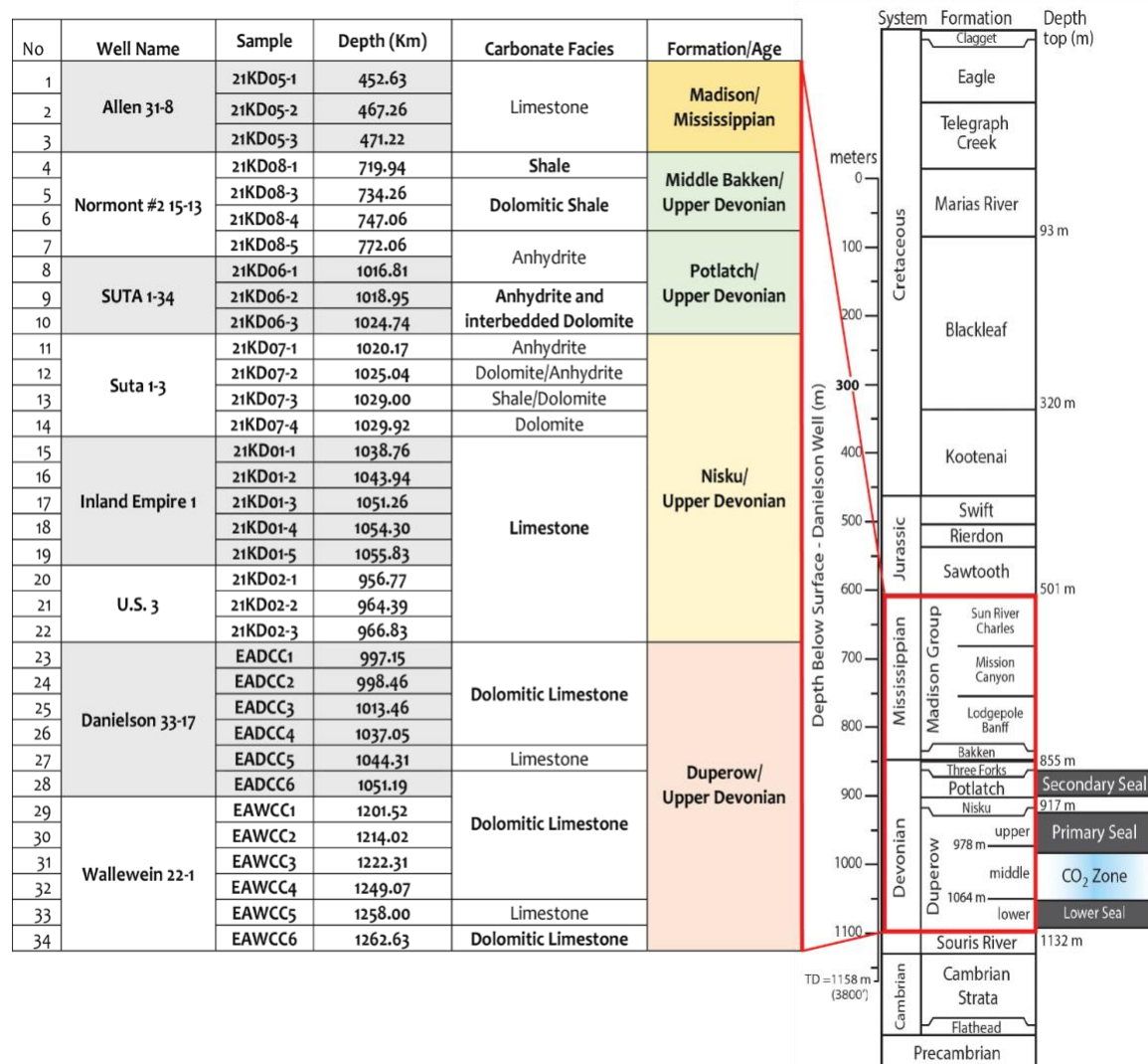
Zircon and apatite minerals from the bulk rock samples were separated by crushing and sieving, followed by magnetic and density separation, at GEOSEPS Services, Moscow, Idaho. Due to the potential to destroy mineral grains during heavy milling, jaw crushers have been noted as an ill-suited method for apatite mineral separation. Therefore, The core cuttings were crushed with a puck mill, secondary to small sample size and unconsolidated grain status at the time of preparation. All the samples yielded a small number of zircon and apatite grains, but enough for the purpose of this project. Table B.2 summarizes the number of zircon and apatite mineral grains recovered from the mineral separation work for each sample.

Table B.2: Kevin Dome Apatite and Zircon minerals yield

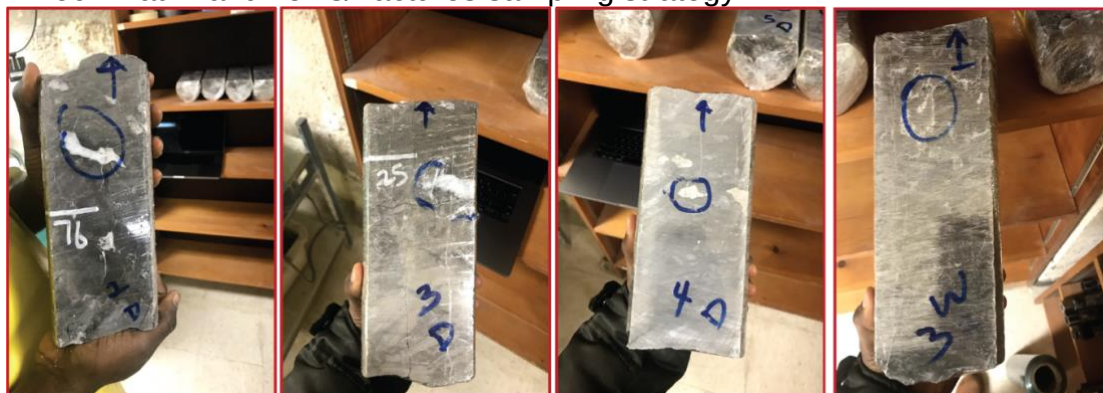
No	Well No	From (m)	To (m)	Interval (m)	Apatite	Zircon	Formations
1	W4	411.48	0.00	0.00	< 10	<100	Bow Island
2	W2	76.20	94.49	18.29	>5	>5	Blackleaf
3	W4	228.60	265.18	36.58	>5	>5	
4	W4	118.87	146.30	27.43	>5	< 10	Colorado
5	W2	393.19	432.82	39.62	10 - 100	10 - 100	Kootenai
6	W2	323.09	374.90	51.82	< 10	>5	
7	W4	548.64	563.88	15.24	<100	10 - 100	Sunburst
8	W4	566.93	576.07	9.14	>5	< 10	
9	W2	460.25	481.58	21.34	>5	< 10	Swift
10	W4	579.12	582.17	3.05	>5	10 - 100	
11	W4	597.41	624.84	27.43	>5	>5	Rierdon
13	W3	475.49	481.58	6.10	>5	< 10	Sawtooth
14	W4	633.98	0.00	0.00	>5	>5	
15	W3	798.58	816.86	18.29	< 10	< 10	Bakken
16	W1	722.38	0.00	0.00	>5	0	
17	W3	819.91	826.01	6.10	>5	0	Three Forks
18	W2	838.20	850.39	12.19	< 10	< 10	
19	W1	755.90	765.05	9.14	< 10	>5	Flathead
20	W1	1313.69	1335.02	21.34	>5	< 10	
21	W4	1472.18	1477.06	4.88	>5	< 10	
22	W1	1338.07	1350.26	12.19	>5	< 10	
24	W3	1411.22	1414.27	3.05	>5	>5	Cambrian
25	W1	13472.16	0.00	0.00	>5	< 10	
26	W3	1477.67	1496.57	18.90	<100	< 10	Precambrian
28	W1	1359.41	1374.65	15.24	< 10	< 10	

SI C: Kevin Dome Carbonate Petrology and XRD Mineralogical Data

C.1A: Carbonate Clumped Isotope Thermometry sampling well details and Kevin Dome stratigraphy highlighting the carbonate units sampled.



C.1B: Rock matrix and veins/fractures sampling strategy:

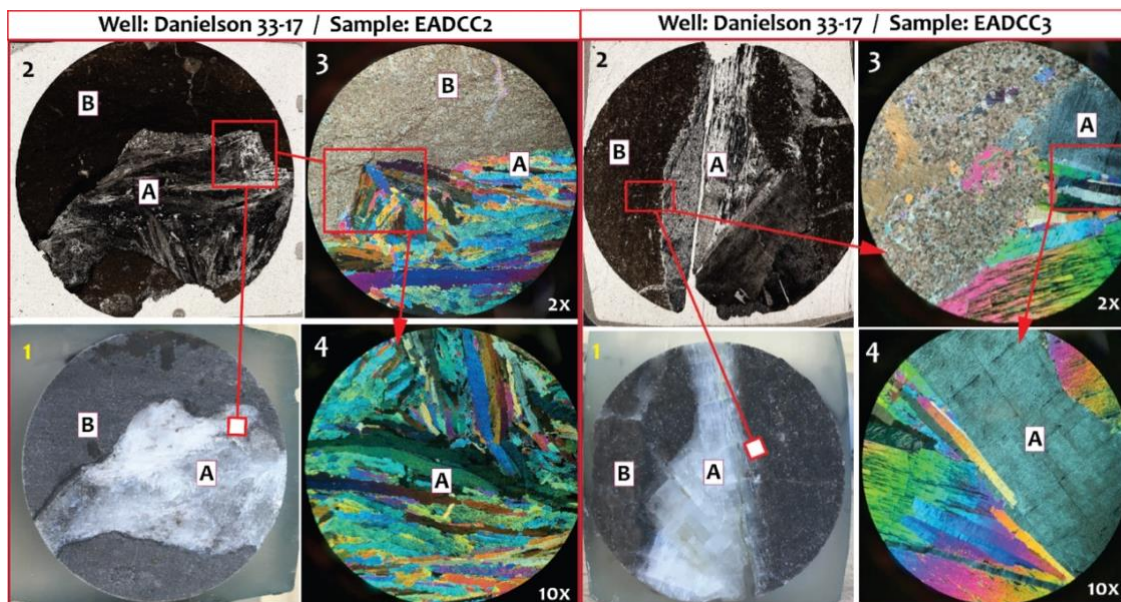


C.2: Carbonate Petrological Classification and XRD Mineralogical Summary

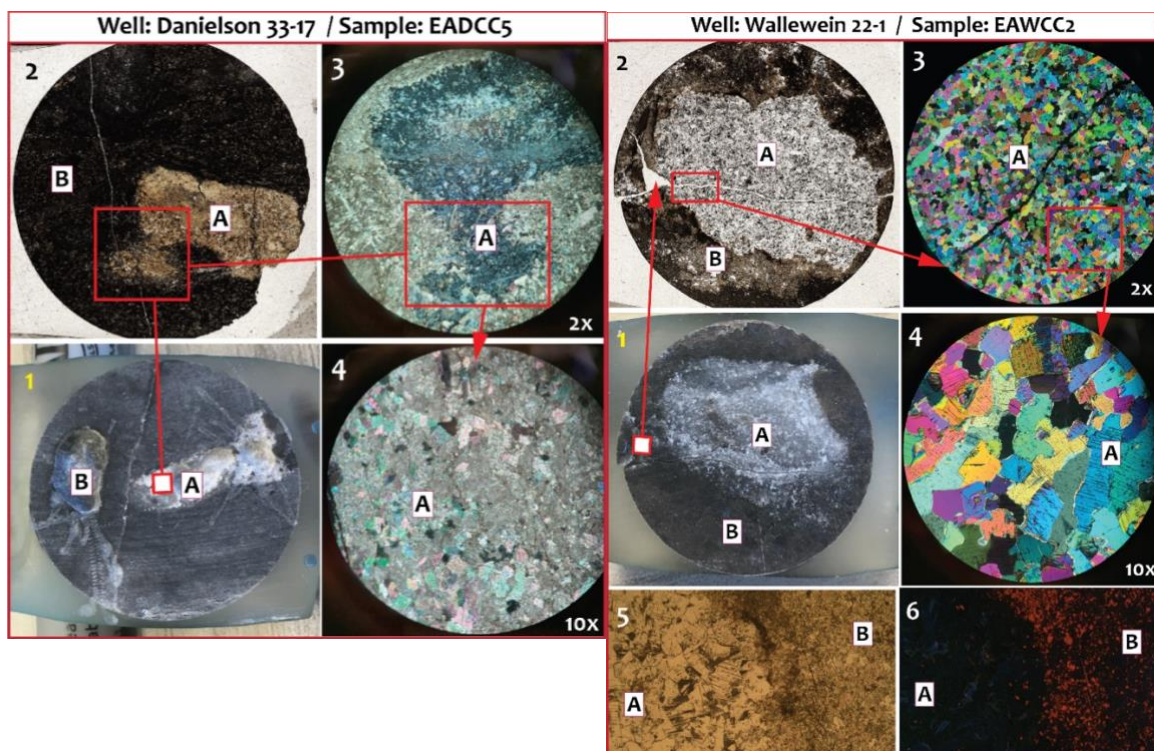
Based on texture and petrological observations, Kevin Dome carbonate veins and fractures are grouped into three petrological classes, namely: Micrite/Dolomicrite (Dm), Microcrystalline (MCr) and Fibrous/Blocky (Cv). The Micrite/Dolomicrite class are nodular in texture and are interpreted to represent the burial history thermal signature of the carbonate strata. Microcrystalline veins/fractures show partial replacement texture representing early-stage alteration while the fibrous/Blocky textures represent secondary or second-stage thermal signatures.

Formation	Kevin Dome Well Names	Sample Names	Rock Facies	Petrological Classifications	XRD Mineralogy
Madison	Allen 31-8	21KD05-2A	LMST	Dm	Calcite (50.7%); Magnesium Calcite (49.3%)
		21KD05-2B	LMST		Magnesium Calcite (100%)
		21KD05-3A	LMST	Dm	Calcite (100%)
		21KD05-3B	LMST		Magnesium Calcite (92.8%); Dolomite (7.2%)
		21KD05-3C	LMST		Quartz (56.5%); Magnesium Calcite (35.8%); Calcite (7.7%)
Potlach	Suta 1-34	21KD06-1B	ANHY		Dolomite (78.3%); Anhydrite (21.7%)
	Normont 15-13	21KD06-5B	ANHY		Dolomite (57.4%); Quartz (31%); Anhydrite (11.6%)
Nisku	Suta 1-3	21KD07-2B	DOL LMST/ANHY		Dolomite (53.1%); Anhydrite (46.9%)
Duperow	US 3	21KD02-1B	LMST		Dolomite (76.5%), Magnesium Calcite (23.5%)
	Inland Empire 1	21KD01-1B	LMST		Dolomite (52.3%) Calcite (47.7%)
	Danielson 33-17	EADCC2-A	ANHY	Cv	Anhydrite (100%)
		EADCC2-B	DOL LMST		Dolomite (61.6%); Minrecordite (24.1%); Anhydrite (14.3%)
		EADCC3-A	ANHY	Cv	Anhydrite (99.4%); Gypsum (0.6%)
		EADCC3-B	DOL LMST		Dolomite (76.4%); Gypsum (14.2%); Calcite (6.8%); Anhydrite (2.6%)
		EADCC5-A	LMST	Dm	Calcite (100%)
	Wallewein 22-1	EADCC5-B	LMST		Calcite (88.5%); Dolomite (11.5%)
		EAWCC2-A	ANHY	MCr	Anhydrite (100%)
		EAWCC2-B	DOL LMST		Dolomite (82.8%); Anhydrite (17.2%)
		EAWCC5-A	ANHY	Cv	Anhydrite (95.6%); Dolomite (4.4%)
		EAWCC5-B	DOL LMST		Dolomite (82.5%); Anhydrite (17.5%)
		EAWCC6-A	ANHY	MCr	Anhydrite (100%)
		EAWCC5-B	LMST		Dolomite (96.3%); Anhydrite (3.7%)
		EAWCC6-A	ANHY	Cv	Anhydrite (100%)
		EAWCC6-B	DOL LMST		Dolomite (85.0%); Minrecordite (15.0%)
Samples A = Vein/Fracture; B = Main Rock/Matrix					
Carbonate Vein/Fracture Petrological Classifications: (1) Dm (Micrite) - Nodular texture representing burial history thermal signature. (2) MCr (Microcrystalline) - (Partial) replacement texture representing early stage alteration. (3) Cv (Fibrous/Blocky) - Fibrous/Blocky texture representing secondary or second stage thermal signature. Rock Facies: LMST (Limestone); DOL LMST (Dolomite/Dolomitic Limestone); ANHY (Anhydrite).					

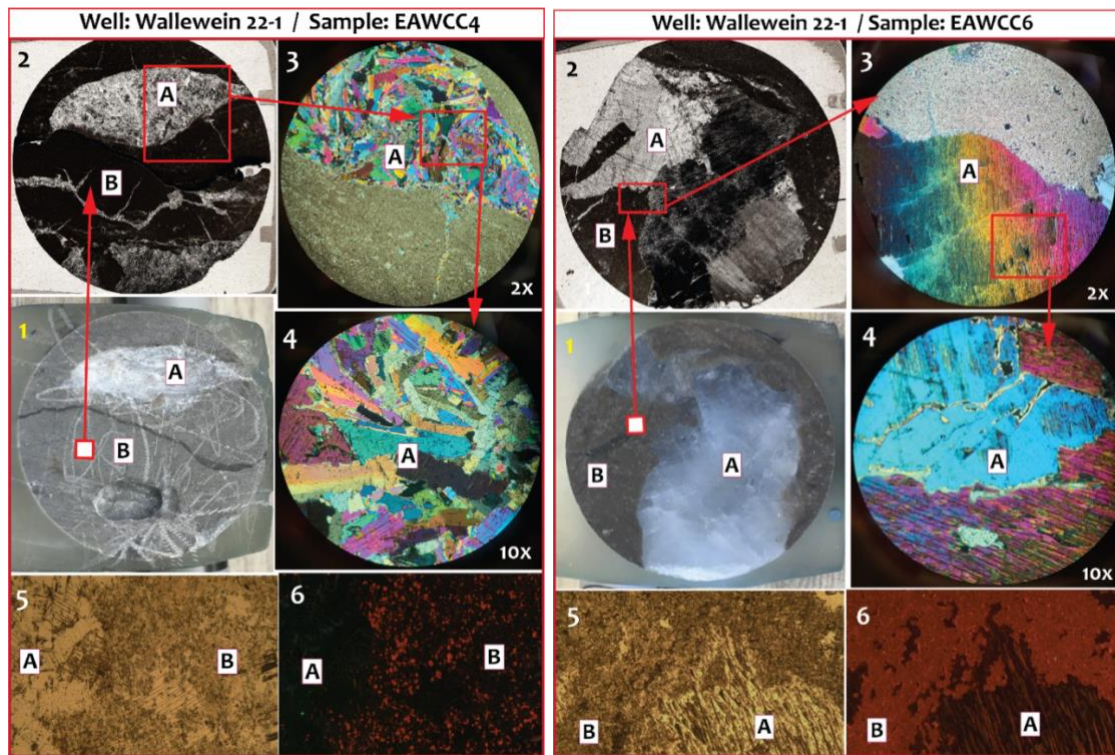
C.3. Representative samples of the carbonate petrology workflow and spot sampling.



Labeling: 1 - Core Plug sample. 2 - Full Thin Section 3 and 4 - XPL Optical Microscopy (at 2x and 10 magnifications respectively). A - Vein/Fracture. B - Main Rock/Matrix.



Labeling: 1 - Core Plug sample. 2 - Full Thin Section 3 and 4 - XPL Optical Microscopy (at 2x and 10 magnifications respectively). 5 and 6 - PPL and CL Images. A - Vein/Fracture. B - Main Rock/Matrix.



Labeling: 1 - Core Plug sample. 2 - Full Thin Section 3 and 4 - XPL Optical Microscopy (at 2x and 10 magnifications respectively). 5 and 6 - PPL and CL Images. A - Vein/Fracture. B - Main Rock/Matrix.

SI D: Gold Butte (SGH) petrology and petrographic Modal analysis summary

Sample - 20GB01	
Modal Abundance (%)	Description
Plagioclase Feldspar (30), Amphibole (25), Quartz (25), Orthopyroxene (5), Clinopyroxene (5), Biotite (5) with Apatite (3) and Zircon (3) as mineral inclusions.	Plagioclase Feldspar and some Quartz make up the groundmass. Larger Plagioclase Feldspar grains exist as euhedral phenocrysts. Quartz, Amphibole grains exist as elongated, euhedral to subhedral grains with some clinopyroxene rimmed within the Amphibole grains. The clinopyroxene exhibits exsolution textures. Microgranular mineral enclaves (MME) of Biotite, Amphibole, Clinopyroxenes and Plagioclase mesh are also present. Apatite and Zircon mineral grains exist as mineral inclusions, especially within the clinopyroxenes.
Sample - 20GB02	
Modal Abundance (%)	Description
Clinopyroxene (25), Quartz (25), Plagioclase Feldspar (15), Calcite (10), Cordierite (10), Amphibole (5), Orthopyroxene (2), Biotite (3), Unidentified (5).	Sanidine groundmass with lots of and plastic deformation (metamorphic) textures. Clinopyroxene grains exist as prismatic with euhedral to subhedral phenocrysts (1-2mm). Microgranular mineral enclaves (MME) of Clinopyroxene, Cordierite and or Quartz, Clinopyroxenes and Plagioclase mesh are also present. It is difficult to identify mineral grains due to either their deformation or grain sizes.
Sample - 20GB03	
Modal Abundance (%)	Description
Plagioclase Feldspar (30), Potassium Feldspar (30), Quartz (20), Amphibole (12), Clinopyroxene (8)	Porphyritic mineral grains texture with Plagioclase Feldspar and (euhedral) Quartz grains as the prominent phenocrysts in medium to fine grained Potassium Feldspar and Plagioclase Feldspar, and quartz groundmass with interstitial texture. Plagioclase Feldspar phenocrysts exist as (5-10mm x 2mm) rectangular euhedral mineral lath showing albite twinning and centrally dissolved mineral zone filled with mineral inclusions (e.g. K-spar and Cpx). Potassium Feldspar are about 0.7 - 2mm grains with Carlsbad twinning. Plagioclase Feldspar, Amphibole and Clinopyroxene exhibit mineral zoning and inclusions of zircons and apatites. Amphibole exists as euhedral to hexagonal mineral grains that are light green and brown in plane polarized light.
Sample - 20GB04	
Modal Abundance (%)	Description
Clinopyroxene (35), Muscovite (20), Biotite (15), Plagioclase Feldspar (12), Potassium feldspar (5), Calcite (5), Amphibole (5), Orthopyroxene (3).	This sample has an overall trachytic-aphanitic texture in Plagioclase Feldspar, Potassium Feldspar and Biotite groundmass. Clinopyroxene and Muscovite exist as elongated grains often forming oriented parallel flows. The Feldspars exist in elongated fine to medium grained trachytic texture while the Biotite exist as singular or microgranular mineral enclaves (MME) i.e. large, anhedral, medium brown Biotite with a mesh of Amphibole, Clinopyroxenes and Muscovite. The predominant clinopyroxene grains exhibited carlsbad twinning and appeared as yellow-green color in plane polarized light while Orthopyroxene showed a display of bright interference colors and euhedral grains throughout the sample. Euhedral calcite grains are also present.
Sample - 20GB05	
Modal Abundance (%)	Description
Plagioclase Feldspar (40), Clinopyroxene (20), Orthopyroxene (15) Biotite (8), Amphibole (8), Biotite (6) Muscovite (2), Olivine (1).	Porphyritic texture predominantly Plagioclase Feldspar and Clinopyroxenes with euhedral and elongated grains of varying sizes. The Muscovite are elongated as in sample 20GB04. Some of the clinopyroxene and anhedral biotite are zoned while most of the pyroxene grains have mineral inclusions. Olivine displays euhedral grains and quartz exhibits undulatory extinction. Microgranular mineral enclaves (MME) of Biotite, Muscovite, Amphibole, Clinopyroxenes mesh are present.
Sample - 20GB06	
Modal Abundance (%)	Description
Plagioclase Feldspar (60), Potassium Feldspar (5), Amphibole (5), Clinopyroxene (5), Orthopyroxene (5), Quartz (5), Biotite (5), Zircons and Apatite Incl (5), Olivine (5).	The sample is made up entirely of Plagioclase Feldspar grains set in interstitial texture with almost equal abundance of Potassium Feldspar, Amphibole, Clinopyroxene, Orthopyroxene, Quartz, Biotite and Olivine mineral grains as phenocrysts and with little to no groundmass. There are numerous mineral intergrowths (e.g. Olivine intergrowths with other mineral grains). Potassium feldspar displays plastic deformation and clinopyroxene exhibits euhedral to rounded grains. Zircons and Apatite exist as mineral inclusions in larger grains and within intergranular groundmass spaces. Olivine crystals are surrounded by a hypocrystalline groundmass. The sample exhibits some fibrous texture that could possibly be a sign of metamorphism.
Sample - 20GB07	
Modal Abundance (%)	Description
Plagioclase Feldspar (40), Amphibole (20), Biotite (15), Clinopyroxene (10), Quartz (5), Cordierite (5), Calcite (5).	Plagioclase Feldspar exists as euhedral and elongated phenocrysts, Amphibole grains exist as euhedral, rounded and elongated grains, Quartz and/or Cordierite as subhedral to rounded grains. Plagioclase Feldspar is the main groundmass with a mix of Amphibole, and Biotite. Many of the Clinopyroxene grains are embedded in some of the Amphibole grains and there is a microgranular mineral enclave (MME) which is made up of a mesh of all the minerals.

SI E: Kevin Dome AHe and ZHe cooling dates trend with Grain size and eU

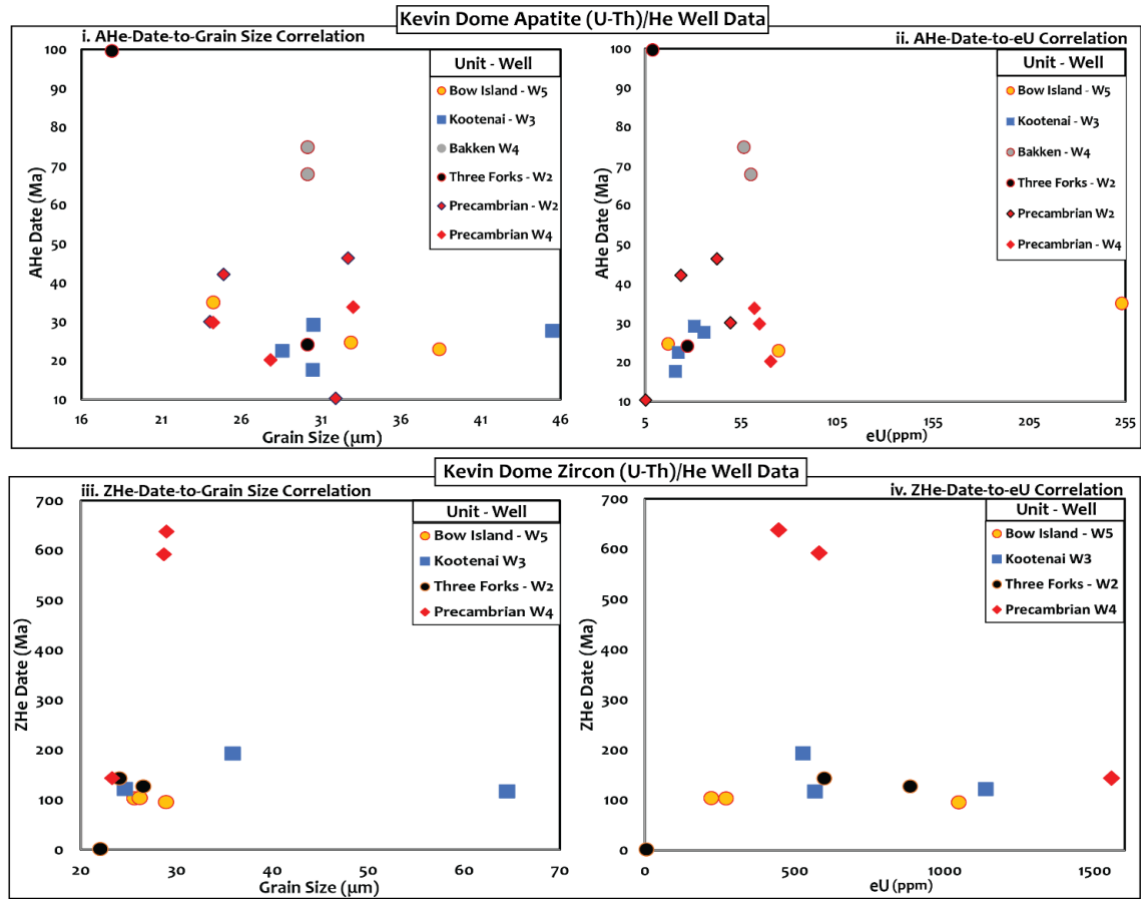


Fig. E: Kevin Dome AHe and ZHe date-to-grain size and date-to--eU correlations.

SI F: $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $T(\Delta 47)$ Trends and implications

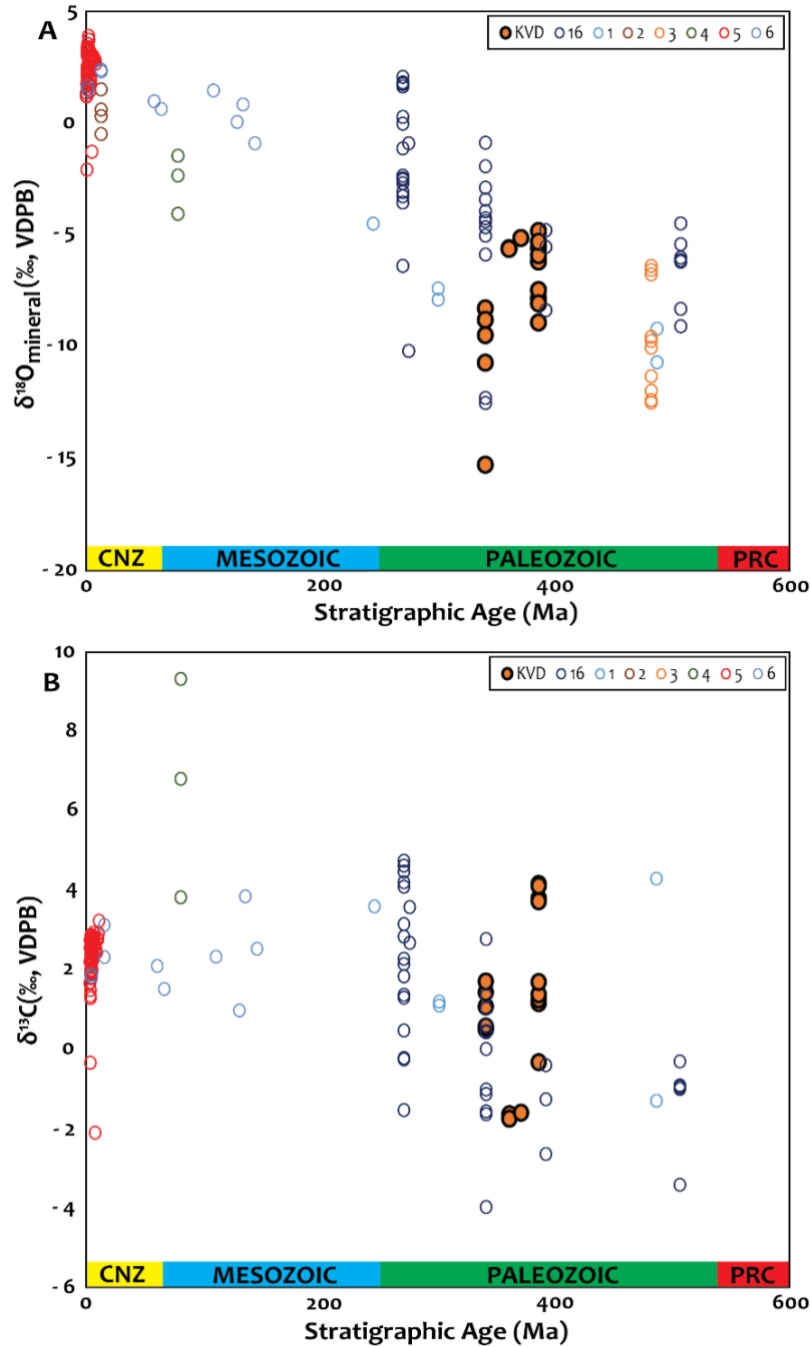


Fig. F.1: (A) $\delta^{18}\text{O}$ (‰, VPDB) and (B) $\delta^{13}\text{C}$ (‰, VPDB) carbonate values vs stratigraphic age (Ma) through the Phanerozoic. Additional data reference coded in figure: KVD – this study; (1) Geske et al. (2015); (2) Loyd et al. (2012); (3) Came et al. (2017); (4) Dale et al. (2014); (5) Murray and Swart (2017); (6) Winkelstern and Lohmann (2016) and (16) Ryb and Eiler (2018). CNZ – Cenozoic, PRC – Precambrian.

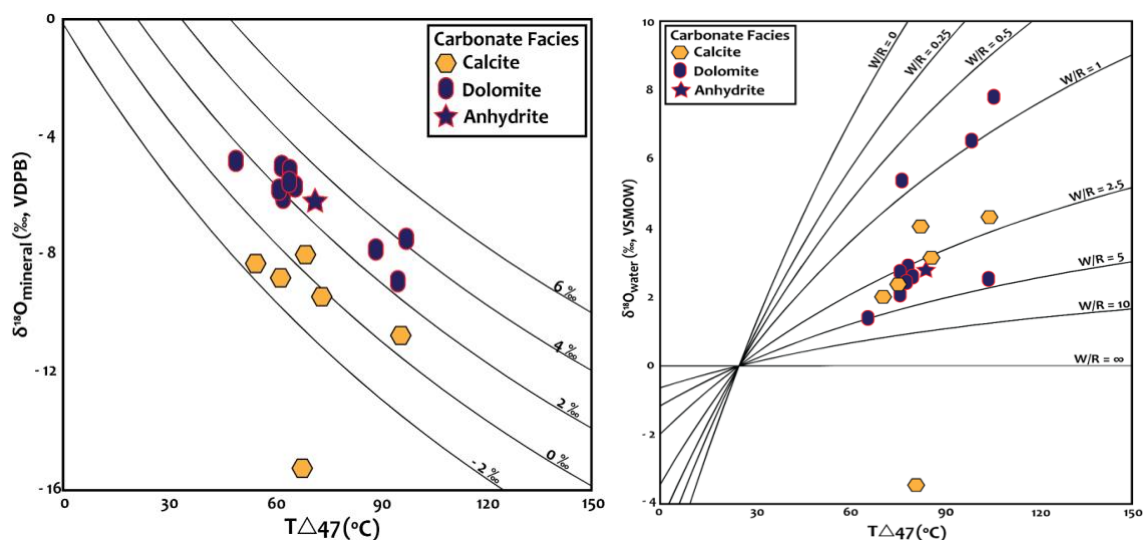


Fig. F.2: (A) $\delta^{18}\text{O}$ (‰, VPDB) of carbonates and (B) calculated $\delta^{18}\text{O}_{\text{water}}$ vs clumped isotope temperatures ($T(\Delta 47)$). $\delta^{18}\text{O}_{\text{water}}$ values were calculated with Kim and O'Neil (1997) and Horita (2014) eqns for calcite and dolomite/anhydrite respectively. $\delta^{18}\text{O}$ of carbonate minerals are at equilibrium with $\delta^{18}\text{O}$ (‰, VSMOW) of -2‰ and $+6\text{‰}$. The water-to-rock ratios (W/R) model for a closed system was estimated with an initial water $\delta^{18}\text{O}_i$ of 0 (‰, VSMOW) known for marine settings, whereas $\delta^{18}\text{O} < 0\text{‰}$ VSMOW were regarded as water-buffered (W/R = ∞) (Taylor, 1974; Sharp, 2007). The initial surface temperature (T_i) where the carbonate rocks were formed were assumed to be 25 (°C) (based on earth's 25 (°C)/Km thermal gradient) which automatically yielded initial rock $\delta^{18}\text{O}_i$ values of 28 and 33 and were used in the W/R model for calcite and dolomite respectively.

SI G – Gold Butte (SGH) Mineral Chemistry Data

Table G.1: XRF Whole-Rock Geochemistry Data

Composition		Samples				RM run as unknown	RM accepted values
		21GB01	21GB03	21GB05	21GB06	AGV-1	AGV-1 GeoREM values*
Major elements (wt % oxides)	SiO ₂	59.72	54.29	59.30	54.88	59.25	59.38
	TiO ₂	0.634	0.406	0.586	0.785	1.060	1.050
	Al ₂ O ₃	16.98	19.46	16.42	17.22	17.11	17.11
	FeO*	5.33	3.15	5.58	6.71	6.07	6.08
	MnO	0.135	0.103	0.119	0.180	0.096	0.097
	MgO	1.68	0.51	2.15	1.84	1.48	1.51
	CaO	3.51	3.76	4.21	6.71	4.95	4.89
	Na ₂ O	4.46	5.56	4.22	4.35	4.26	4.25
	K ₂ O	4.29	5.86	4.83	4.18	2.94	2.94
	P ₂ O ₅	0.291	0.094	0.395	0.359	0.495	0.493
	LOI (%)	1.88	5.33	1.14	1.62	1.50	1.50
	SumMaj + LOI	98.91	98.52	98.95	98.83	99.21	99.29
	sumAll	99.64	99.98	99.68	99.64	99.53	99.63
Volatiles	(wt %)	F >=	0.10	0.25	0.09	0.12	0.04
		Cl >=	0.011	0.006	0.010	0.025	0.013
		SO ₃ >=	0.03	0.16	0.01	0.02	0.01
	(ppm)	Br >=	1	0	1	0	0
		As >=	1	1	0	3	1
Trace elements (ppm)	Ni	27	16	24	15	16	15
	Cr	24	2	24	3	9	9
	V	103	144	103	130	122	119
	Sc	9.6	1.4	12.9	13.2	13.2	12.4
	Cu	25	25	21	16	61	58
	Zn	94	103	65	101	88	87
	Ga	21	29	19	20	21	20
	Ba	3633	6614	3798	3736	1219	1218
	Rb	80	105	96	71	66	68
	Cs	1	20	4	1	1	1
	Sr	1521	2421	1602	1926	667	661
	Y	22	23	20	23	21	20
	Zr	208	305	198	182	226	232
	Hf	3.4	3.0	3.5	2.2	4.9	5.1
	Nb	7.5	61.9	6.3	6.2	14.1	14.5
	Ta	1	1	1	1	1	1
	Mo	3	2	3	3	4	2
	La	48	142	41	52	40	38
	Ce	86	201	70	91	64	69
	Nd	38	66	35	45	31	32
	Sm	7.0	9.4	6.5	8.5	5.9	5.8
	Dy	4.0	3.3	4.0	4.4	4.1	3.6
	Yb	1.9	2.0	1.6	2.4	1.7	1.7
	Th	6	36	9	11	7	6
	U	2	7	3	3	1	2
	Tl	0	1	1	1	0	0
	Pb	32	121	7	35	35	36
	Sn	2	0	1	5	3	5
	Bi	0	0	0	0	0	0
	Sb	3	1	4	2	3	4

Table G.2: EPMA (representative) Cpx Data

Sample	Pt.	Oxides (wt %)												Total
		SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Cr2O3	F	Cl	
20GB03	Core	47.49	0.75	5.13	18.28	0.60	7.37	18.48	1.98	0.03	0.02			100.13
		52.55	0.37	1.90	9.86	0.46	13.92	20.27	0.61	0.02	0.01			99.97
		52.31	0.30	2.28	11.89	0.64	11.64	20.04	1.03	0.01	0.02			100.15
		49.49	0.64	2.92	11.31	0.35	10.84	20.90	1.35	0.03		0.02	0.00	97.85
		50.21	0.47	3.71	14.86	0.68	8.78	19.82	1.97	0.00		-0.02	0.00	100.51
		50.31	0.44	3.63	14.93	0.68	8.87	19.86	1.85	0.01		0.00	0.00	100.57
		49.92	0.27	1.62	9.88	0.40	12.66	20.04	0.83	-0.01	0.00			95.63
		48.43	0.33	2.39	17.05	0.77	7.22	17.91	2.20	-0.02	0.01			96.29
		47.26	0.49	3.95	17.37	0.75	6.68	17.55	2.35	0.02	0.02			96.43
		47.92	0.59	3.71	13.46	0.41	9.56	19.33	1.62	0.00	0.00			96.60
	Margin	50.76	0.48	2.98	19.85	0.76	6.87	17.68	2.44	0.00	0.01			101.82
		50.69	0.59	2.76	17.40	0.39	8.31	18.11	2.32	0.01	0.00			100.59
		50.07	0.29	2.28	19.71	0.73	6.97	17.69	2.25	0.02	0.02			100.01
		48.80	0.57	3.70	17.50	0.59	7.16	18.91	2.49	0.01		-0.04	0.00	99.73
		49.48	0.47	3.10	18.71	0.82	6.29	18.32	2.63	0.00		0.01	0.01	99.82
		50.12	0.45	3.05	17.79	0.72	7.10	18.87	2.32	0.00		-0.01	0.00	100.43
		46.87	0.85	4.39	16.04	0.33	7.88	18.51	2.01	0.02	0.02			96.90
		47.16	0.29	2.23	19.72	0.76	5.54	17.22	2.38	-0.01	0.00			95.31
		45.96	0.48	2.89	20.16	0.69	4.83	16.64	2.69	0.08	0.01			94.43
		49.45	0.41	2.35	12.51	0.39	10.39	19.68	1.45	0.02	0.01			96.65
	Rim	50.65	0.36	2.40	18.93	0.71	7.25	18.00	2.29	0.00	0.02			100.61
		52.11	1.66	3.28	27.79	0.41	0.34	5.20	9.92	0.02	0.01			100.72
		51.42	0.15	0.96	17.05	0.90	8.26	19.00	1.65	0.01	0.01			99.42
		49.71	0.47	3.14	18.11	0.65	6.74	18.58	2.52	0.03		-0.03	0.01	99.96
50.44		0.33	2.27	17.02	0.66	7.61	19.21	2.27	0.04		0.00	0.00	99.86	
49.33		0.39	2.84	17.76	0.63	6.96	18.73	2.42	0.02		0.02	0.00	99.10	
48.43		0.26	1.47	19.84	1.06	5.26	16.96	2.69	0.01	0.01			95.99	
48.58		0.33	2.50	17.25	0.64	7.11	18.13	2.13	0.00	0.01			96.68	
46.73		0.49	3.57	18.16	0.56	5.95	17.06	2.67	0.05	0.02			95.24	
48.18		0.29	2.30	16.63	0.66	7.32	18.07	2.20	0.01	0.01			95.67	
20GB05	Core	53.94	0.20	1.39	5.64	0.16	16.38	22.54	0.45	0.01		0.00	0.00	100.72
		51.22	0.30	1.59	6.51	0.18	15.49	20.97	0.36	0.01	0.02			96.64
		55.00	0.23	1.13	4.50	0.06	18.16	21.34	0.25	0.01	0.03			100.71
		53.97	0.23	1.38	7.10	0.20	16.48	20.37	0.30	0.00	0.08			100.11
		49.93	0.56	3.32	10.54	0.46	12.57	20.73	0.60	-0.01	0.01			98.72
		54.74	0.17	0.76	4.45	0.10	17.96	20.91	0.18	-0.01	0.05			99.31
	Margin	53.64	0.29	1.69	5.59	0.16	16.54	22.34	0.34	0.00		0.02	0.00	100.61
		48.34	0.43	2.75	9.45	0.51	12.53	20.58	0.64	0.01	-0.01			95.24
		51.47	0.42	2.39	10.97	0.25	13.39	20.61	0.43	-0.01	0.01			99.92
		51.87	0.32	2.17	10.40	0.49	13.15	20.84	0.54	0.00	0.00			99.79
		51.29	0.45	3.07	10.68	0.51	12.52	20.59	0.63	0.01	0.01			99.77
		51.29	0.46	2.95	10.34	0.40	12.93	20.84	0.60	0.01	0.02			99.82
	Rim	50.76	0.44	3.14	9.82	0.40	12.82	22.05	0.62	0.01		0.03	0.01	100.09
		49.20	0.38	2.36	9.39	0.49	12.91	20.60	0.64	0.00	0.02			95.97
		51.73	0.41	2.87	9.94	0.38	13.39	20.93	0.53	0.00	0.00			100.17
		52.36	0.29	1.79	9.90	0.54	13.59	20.91	0.48	0.03	0.01			99.90
		50.89	0.46	3.07	10.80	0.46	12.45	20.79	0.67	0.03	0.02			99.64
		52.37	0.35	2.33	10.63	0.48	12.91	20.64	0.62	0.00	0.00			100.34
20GB06	Core	49.22	0.50	2.22	9.65	0.58	13.06	20.37	0.52	0.01	-0.01			96.11
		42.73	2.00	8.98	16.10	0.67	13.41	10.43	2.48	1.48	0.01			98.28
		50.47	0.73	2.68	10.76	0.49	12.37	20.91	0.63	-0.01	0.00			99.05
	Margin	48.97	0.45	1.83	13.92	0.87	10.63	19.74	0.74	0.01	-0.01			97.16
		43.60	1.83	8.88	15.58	0.61	13.66	10.52	2.36	1.58	0.00			98.62
		50.14	0.67	2.55	11.55	0.57	12.10	21.05	0.56	0.00	-0.01			99.19
	Rim	49.55	0.56	1.51	10.55	0.62	12.59	20.31	0.57	0.01	0.00			96.27
		44.24	1.64	8.91	15.93	0.65	13.61	10.37	2.47	1.57	0.02			99.41
		51.52	0.64	2.15	10.17	0.60	13.09	20.66	0.66	0.02	0.00			99.51

Table G.3: EPMA (representative) Amp Data

Sample	Pt.	Oxides (wt %)												Total
		SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Cr2O3	F	Cl	
20GB01	Core	41.08	2.10	12.19	18.35	0.25	10.54	10.29	2.03	1.53	0.08	-	-	98.42
		42.22	1.94	11.76	16.35	0.36	12.14	10.42	2.32	0.96	0.09	-	-	98.55
		42.10	1.79	12.78	16.56	0.28	12.36	10.28	2.55	0.84	0.05	-	-	99.60
		45.85	0.31	11.62	12.09	0.20	15.55	10.42	2.01	0.79	0.27	-	-	99.11
		39.53	2.30	13.87	18.63	0.33	9.41	11.13	2.09	1.65	-	0.04	0.07	99.03
		39.35	2.11	13.72	15.18	0.22	11.93	11.20	2.04	1.51	-	0.13	0.04	97.43
		39.25	2.21	13.24	18.69	0.40	9.62	10.85	2.12	1.80	-	0.13	0.06	98.39
		39.69	2.11	13.21	15.32	0.30	10.99	10.63	2.10	1.58	0.03	-	-	95.97
		38.18	2.38	14.30	16.19	0.26	10.36	10.33	2.01	1.42	0.01	-	-	95.44
	33.86	2.21	13.74	18.70	0.39	7.82	10.28	1.68	2.13	0.01	-	-	90.82	
	Margin	40.08	1.87	13.87	18.75	0.29	10.01	10.34	2.08	1.35	0.06	-	-	98.70
		39.41	2.23	13.70	18.96	0.39	9.82	10.52	1.99	1.79	0.06	-	-	98.87
		38.78	2.46	14.25	21.31	0.37	8.54	10.43	1.98	1.85	0.02	-	-	99.98
		42.23	1.87	12.59	18.92	0.44	10.83	9.85	2.09	1.18	0.02	-	-	100.01
		39.74	2.26	13.88	17.76	0.29	9.69	10.99	2.16	1.56	-	0.12	0.07	98.53
		40.37	2.09	12.84	14.59	0.17	12.25	11.10	2.09	1.58	-	0.13	0.04	97.25
		38.75	2.57	14.00	18.47	0.35	9.21	11.11	2.03	1.76	-	0.13	0.05	98.43
		37.17	2.62	14.40	18.58	0.35	8.52	10.51	1.85	1.81	0.01	-	-	95.82
		39.21	1.78	13.62	15.01	0.27	11.48	10.12	2.20	1.06	0.03	-	-	94.77
	35.97	2.53	13.84	18.06	0.39	8.67	10.27	1.88	1.78	0.01	-	-	93.40	
	38.55	2.01	12.99	19.39	0.31	9.43	10.22	2.15	1.47	0.03	-	-	96.55	
	Rim	39.30	2.31	13.05	21.15	0.56	8.72	10.28	1.92	1.89	0.01	-	-	99.19
		39.90	2.42	13.94	19.02	0.33	10.10	10.53	2.04	1.72	0.01	-	-	100.01
		41.47	1.91	12.52	18.64	0.43	10.92	9.76	2.12	1.19	0.01	-	-	98.96
		38.47	2.51	14.21	19.51	0.32	8.44	11.03	2.06	1.81	-	0.14	0.07	98.57
		39.32	2.01	13.68	17.72	0.25	9.92	10.87	2.19	1.69	-	0.11	0.06	97.80
		39.46	2.44	14.55	19.55	0.37	8.52	11.02	2.10	1.76	-	0.15	0.06	99.98
38.06		2.41	13.01	18.73	0.43	8.76	10.42	1.95	1.87	0.01	-	-	95.63	
38.95		2.17	12.87	15.20	0.24	11.78	10.54	1.97	1.66	0.01	-	-	95.38	
36.48		2.21	13.57	19.96	0.45	7.80	10.31	1.86	1.93	0.00	-	-	94.57	
20GB05	Core	40.03	2.31	13.20	16.94	0.28	10.74	11.12	2.20	1.56	-	0.18	0.08	98.64
		39.76	2.62	12.95	16.67	0.31	10.75	11.12	2.19	1.78	-	0.17	0.09	98.43
		41.23	2.24	12.18	16.10	0.34	11.64	11.25	2.38	1.33	-	0.20	0.07	98.95
		41.14	1.62	11.18	14.15	0.31	12.64	10.13	2.08	1.80	0.02	-	-	95.06
	Margin	39.48	1.88	13.38	16.23	0.29	10.93	10.16	2.01	2.13	-0.01	-	-	96.50
		40.63	2.25	13.13	16.79	0.36	10.83	11.19	2.40	1.53	-	0.14	0.06	99.33
		41.13	2.38	12.86	16.51	0.32	11.13	11.18	2.24	1.75	-	0.16	0.07	99.73
		41.29	2.04	12.56	16.58	0.34	11.50	11.12	2.43	1.34	-	0.21	0.08	99.47
	Rim	37.75	2.05	13.64	21.19	0.42	7.10	9.95	1.92	2.01	0.00	-	-	96.04
		37.40	1.83	13.66	21.64	0.38	7.00	9.91	1.93	2.05	0.02	-	-	95.82
		37.62	1.89	13.80	18.96	0.35	8.37	10.03	1.90	2.22	0.02	-	-	95.17
		39.66	2.32	12.93	17.63	0.40	10.34	11.05	2.08	1.88	-	0.20	0.11	98.59
20GB06	Core	39.80	2.33	12.99	17.43	0.33	10.56	11.18	2.20	1.70	-	0.16	0.09	98.76
		41.37	2.14	13.10	17.07	0.34	11.30	11.23	2.45	1.45	-	0.21	0.09	100.74
		38.86	2.47	12.46	16.90	0.37	10.40	10.45	2.09	1.79	-0.01	-	-	95.79
		38.34	2.45	12.52	16.86	0.41	10.10	10.35	1.95	1.84	0.01	-	-	94.82
	Margin	41.72	1.44	9.10	14.29	0.79	13.35	10.48	2.37	1.47	0.01	-	-	95.01
		42.13	1.39	8.87	14.39	0.70	13.46	10.41	2.40	1.53	-0.01	-	-	95.28
		41.56	1.40	8.93	14.64	0.68	13.43	10.56	2.44	1.52	0.01	-	-	95.18
		43.60	1.88	9.12	14.86	0.69	13.46	10.93	2.56	1.55	-	1.59	0.08	100.30
		37.57	0.92	6.63	10.96	0.44	12.63	18.25	2.25	1.21	-	1.93	0.12	92.92
		42.19	1.43	9.05	14.27	0.64	13.41	10.51	2.40	1.62	0.01	-	-	95.52
		42.58	1.39	9.02	14.48	0.67	13.55	10.40	2.45	1.58	0.00	-	-	96.11
		42.43	1.41	8.96	14.28	0.66	13.52	10.65	2.38	1.57	0.00	-	-	95.86
Rim	43.64	1.77	8.97	14.82	0.63	13.54	11.01	2.60	1.49	-	1.62	0.08	100.16	
	45.20	1.19	8.30	13.02	0.56	15.07	11.23	2.65	1.46	-	1.70	0.12	100.51	
	42.32	1.45	9.21	14.24	0.63	13.60	10.48	2.51	1.61	-0.01	-	-	96.04	
	42.70	1.36	8.85	14.32	0.71	13.81	10.53	2.48	1.57	0.01	-	-	96.33	
43.35	1.18	8.19	12.52	0.61	15.12	10.67	2.49	1.51	0.01	-	-	95.65		
43.50	1.80	8.93	14.56	0.66	13.50	10.97	2.65	1.55	-	1.59	0.09	99.79		
44.99	1.17	8.33	12.90	0.58	15.03	11.18	2.67	1.47	-	1.81	0.13	100.25		

SI H: Geologic constraints and justification for imposed t-T constraints on HeFTy inverse thermal models

H.1A: Basement Unit

Constraints		Time (Ma)	Temp (°C)	Justification
1. Great Unconformity		550 – 520	0 – 50	Missing Precambrian Belt Basin strata at Kevin Dome and the Great Unconformity surface underlying the Flathead Formation require the Basement rocks to have been at the surface ca. 550 - 520 Ma (Sloss, 1950; Chaudhuri and Brookins, 1969; Deiss, 1936; Peale, 1983). Temperatures range of 0 - 50°C caters for near-surface and at least <0.5km of basement cover suggested by Wise (2000).
2. Phanerozoic Burial/Reheating		520 - 60	0 - 113.20	Flathead Fm to the end of Willow Creek FM deposition at Kevin Dome. Maximum burial depth (4.5km) is obtained by adding overlying unit's strata (ending at Willow Creek deposition at 60 Ma) thicknesses to estimate burial temperature with (25°Ckm ⁻¹) thermal gradient. (Vuke et al., 2007; Deiss, 1936; Peale, 1983; Sanberg and Hammond, 1958; Kissling, 1996; Sloss and Laird, 1947; Nordquist, 1953; Perry, 1928; Knechtel, 1959; Collier and Cathcart, 1922; Cobban, 1945; Cobban et al., 1959; Rice, 1976; Oakes, 1966; Peterson, 1966; Stebinger, 1918)
3. Geologic Events			0 – 75 (Ap) 0 – 190 (Zn)	To explore for the contribution of Laramide Orogeny ca. 75 – 52 Ma, the proximal Sweetgrass Hills Complex Pluton emplacement ca. 54 – 49 Ma and the transverse right-lateral Pendroy Fault ca. 29 – 6 Ma (~ 48 km) eastward movement to exhumation (Dickinson et al., 1988; Fuentes et al., 2011; Rukhlov and Pawlowicz, 2012; Shepard and Bartow, 1986). Temperature limits (75 and 190 °C) are set at the closure temperatures for AHe and ZHe systems respectively (Ferley 2000; Reiners et al., 2004).
Laramide Orogeny		75 – 52		
Sweetgrass Hills Complex Pluton Emplacement		54 – 49		
Pendroy Fault Movement		29 – 6		
4. Present/Rock Unit				AHe and ZHe dates obtained from current study. Temperature for each unit is estimated from present depth in the well and (25°Ckm ⁻¹) thermal gradient.
Archean Basement	Well 1	AHe and ZHe	34.18	
	Well 2	Dates	37.18	

H.1B: Clastic Units

Constraints	Time (Ma)	Temp (°C)	Justification
1. Deposition			Stratigraphic age of each FM collated from literature (Vuke et al., 2007; Deiss, 1936; Peale, 1983; Sanberg and Hammond, 1958; Kissling, 1996; Sloss and Laird, 1947; Nordquist, 1953; Perry, 1928; Knechtel, 1959; Collier and Cathcart, 1922; Cobban, 1945; Cobban et al., 1959; Rice, 1976; Oakes, 1966; Peterson, 1966; Stebinger, 1918). Temperatures range of 0 - 25°C caters for uncertainty around sediment accumulation depth, residence time at the surface before burial and encourages the model to explore near-surface temperatures during sediment deposition (Kriš and Ghawi 2008)
Three Forks FM	372.2 – 385.9	0 – 25	
Bakken FM	358.9 – 323.2		
Kootenai FM	120 - 112		
Bow Island FM	113 – 100.5		
2. Phanerozoic Burial/Reheating			End of deposition to end of Willow Creek deposition at Kevin Dome (60 Ma). Burial temperature estimated with cumulative overlying strata's thicknesses and assuming 25°Ckm–1 thermal gradient (Vuke et al., 2007; Deiss, 1936; Peale, 1983; Sanberg and Hammond, 1958; Kissling, 1996; Sloss and Laird, 1947; Nordquist, 1953; Perry, 1928; Knechtel, 1959; Collier and Cathcart, 1922; Cobban, 1945; Cobban et al., 1959; Rice, 1976; Oakes, 1966; Peterson, 1966; Stebinger, 1918)
Three Forks FM	358.9 - 60	0 – 96.10	
Bakken FM	323.2 - 60	0 – 95.30	
Kootenai FM	112 - 60	0 – 61.20	
Bow Island FM	100.5 - 60	0 – 55.08	
3. Geologic Events			To explore for the contribution of Laramide Orogeny ca. 75 – 52 Ma, the proximal Sweetgrass Hills igneous complex emplacement ca. 54 – 49 Ma and the transverse right-lateral Pendroy Fault ca. 29 – 6 Ma (~ 48 km) eastward movement to exhumation (Dickinson et al., 1988; Fuentes et al., 2011; Rukhlov and Pawlowicz, 2012; Shepard and Bartow, 1986). Temperature limits (75 and 190 °C) are set at the closure temperatures for AHe and ZHe systems respectively (Ferley 2000; Reiners et al., 2004).
Laramide Orogeny	75 – 52	0 – 75 (Ap)	
Sweetgrass Hills Complex Pluton Emplacement	54 – 49		
Pendroy Fault Movement	29 – 6	0 – 190 (Zn)	
4. Present/Rock Unit			AHe and ZHe dates obtained from current study. Temperature for each unit is estimated from present depth in the well and (25°Ckm–1) thermal gradient.
Three Forks FM	AHe and ZHe Dates	30.2	
Bakken FM		29.01	
Kootenai FM		20.33	
Bow Island FM		20.28	

SI I: Gold Butte (SGH) Thermobarometry Analysis

Multiple Amp and Cpx geothermobarometer equations developed by several authors (e.g., Nimis and Taylor, 2000; Ridolfi et al., 2010; Ridolfi and Renzulli, 2012; Molina et al., 2015 and Putirka, 2008 and 2016) and incorporated in a Putirka, (2021) calibrated spreadsheet, were engaged to generate and compare the T-P of crystallization and infer emplacement conditions. Amp-mineral chemistry (SI G.3) was discriminated with Putirka (2016) Fe-Mg exchange test of equilibrium (KD) for Amp i.e., removing samples that do not meet eqn. 2: $KD = 0.28 \pm 0.11$ criteria. The mean temperatures calculated for Amp were 888 (°C) and 938 (°C) from Putirka (2016)'s eqn. 5 (pressure independent and with lesser error) and Molina et al., (2015) Amp liquid only equation, respectively. All the Cpx data met the Putirka (2016) Fe-Mg exchange test of equilibrium (KD) eqn ($KD = 0.27 \pm 0.03$). Cpx grains (n=35) yielded mean temperatures of 1099 (°C) from Putirka (2008) eqn 32d and 728 (°C) Nimis and Taylor (2000) eqn which are based on Cpx compositions only (SI G.2). Amp barometers yielded mean pressure values of 0.33 kbar, 2.11 kbar and 1.44 kbar from Putirka (2016) eqn 7b (exhibiting less systematic error at >10 kbar), Ridolfi and Renzulli (2012) liquid only eqn 1c, and Ridolfi et al. (2010)'s Al-in-hbl eqn, respectively after meeting the Putirka (2016) the KD criteria, while the Cpx barometer yields mean pressure of 1.45 kbar from Putirka (2016) eqn 32c (SI G.3). Based on the Gold Butte mineral thermometer data trends (Fig. I) and the strength of the independent thermobarometry eqns used in their estimation, it is plausible to say that the Amp minerals crystallized at about 900 ± 100 (°C) and the Cpx at about 1100 ± 100 (°C). These estimates are consistent with magma emplacement temperature into country rocks from the literature (Annen, 2017). Rusty-colored carbonate veins brecciated and silicified

mudstone, hornfels country rocks and accompanied mineralization along thermal aureoles found in the SGHs gave credence to their thermal impact on the Cretaceous Colorado Group in Northern Montana (Gavin, 1991, Rukhlov and Pawlowicz, 2012). Factors that control the degree of the thermal impact of an intrusion within a country rock are highly dependent on the thickness of the intrusion among other variables (Annen, 2017). Studies have shown that the thermal impact of intruding sills and dikes are localized to about half the width of the intrusion (Galushkin, 1997; Aarnes et al., 2011; Adeniyi et al., 2018). Given the distance of the SGHs intrusion to the Kevin Dome and the lack of thermal aureoles related to contact metamorphism within the Kevin Dome stratigraphy, it is unlikely that the SGH intrusion contributed to Kevin Dome's thermal evolution. On the other hand, Gold Butte's estimated depth of intrusion from geobarometry eqns yielded comparable results to Kevin Dome exhumation and exhumation rates. By comparing the two independently constrained barometers (i.e., Ridolfi et al. (2010)'s Al-in-hbl for Amp and Putirka (2016) eqn 32c for Cpx) Gold Butte intrusion pressure was averaged at 1.44 kbar, implying that the Gold Butte was emplaced at 5.2km depth. This depth suggests that the SGHs rocks have experienced about 0.1 Km/Ma exhumation rates post Eocene contemporaneous with Kevin Dome's exhumation rates.

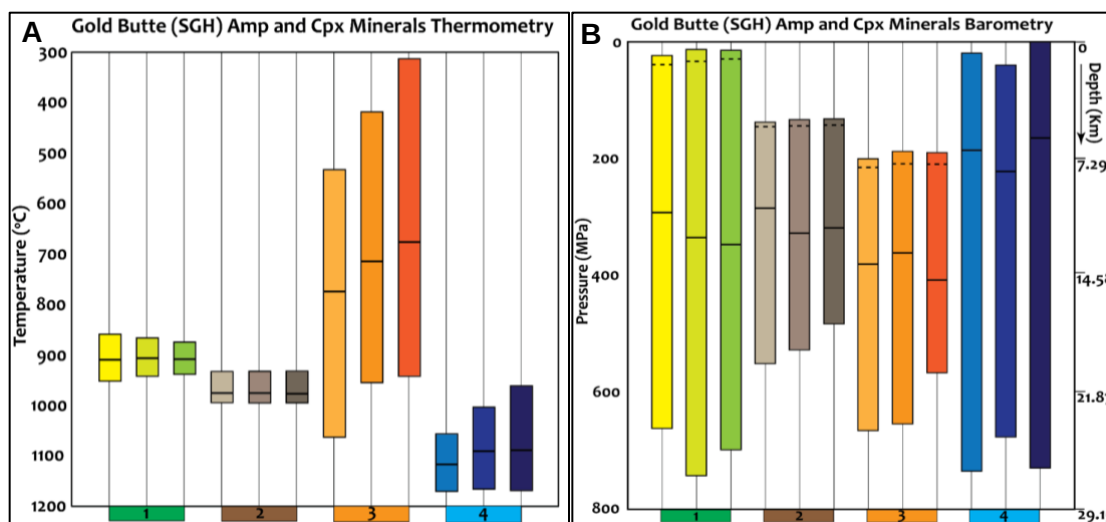


Fig. 1: **(A)** Gold Butte (SGH) Amp and Cpx Minerals Thermometry. The rectangles represent Core-Margin-Rim temperature values for 1: Amp - Putirka (2016)'s eqn 5 (P indep), 2: Amp - Molina et al., (2015) liquid only equation. 3: Cpx - Putirka (2008) equation 32d and 4: Cpx - Nimis and Taylor (2000) equation. Black line represents the GEOMEAN for each data point. **(B)** Gold Butte (SGH) Amp and Cpx Minerals Barometry with Depth of intrusion estimation. The rectangles represent Core-Margin-Rim pressure values for 1: Amp - Putirka (2016) eqn 7b, 2: Amp - Ridolfi and Renzulli (2012) liquid only eqn 1c. 3: Amp - Ridolfi et al. (2010)'s Al-in-hbl equation and 4: Cpx - Putirka (2016) equation 32c. Black line represents the GEOMEAN for each data point while the dotted black lines in samples 1-3 represent the GEOMEAN for values that meet the Putirka (2016) eqn. 2: K_D criteria in the Amp samples.

SI J: Northwest Montana Upper Devonian and Early Mississippian source rocks:
Hydrogen Index vs. Tmax

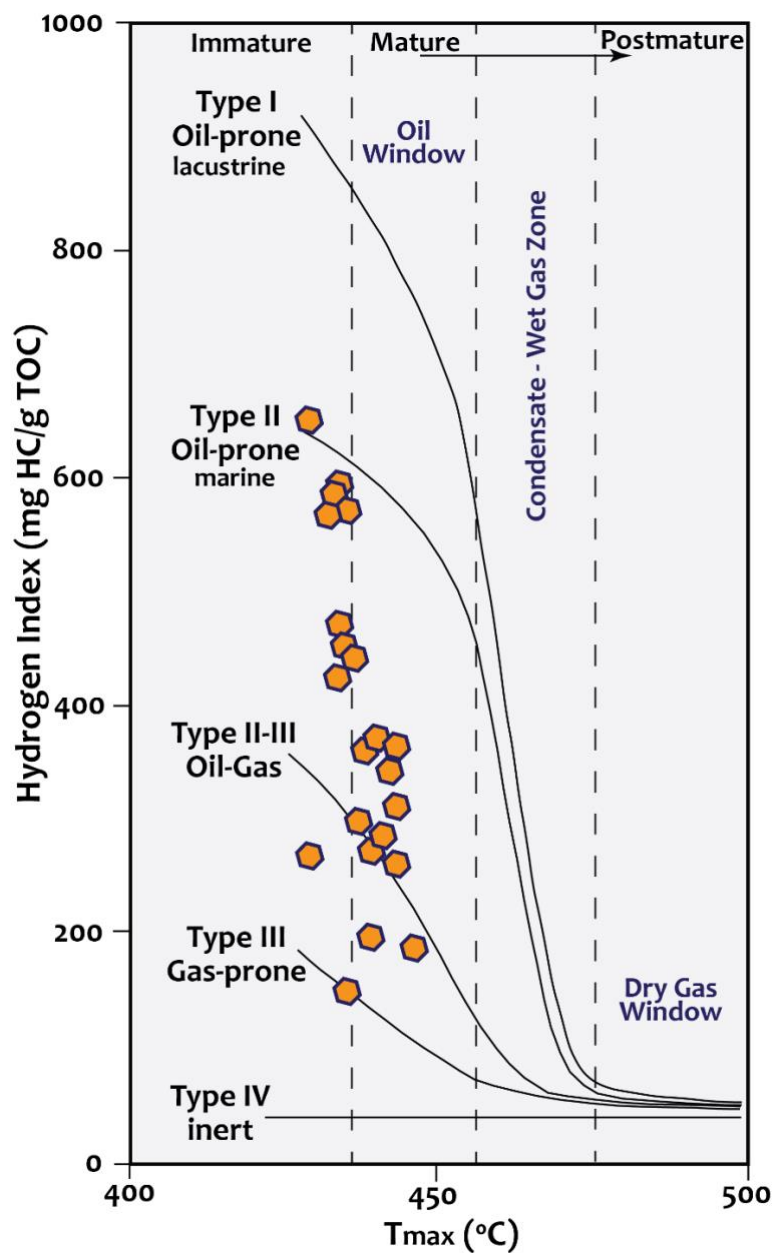


Fig. J: Hydrogen index vs. Tmax indicating northwestern Montana Upper Devonian and Early Mississippian source rocks Kerogen Types and showing that these rocks fall into the Oil-prone and oil-gas prone fields. Hydrogen Index and Tmax data are from Dolson et al. (1993) and publicly available data in six wells (Table 3, chapter 2).

APPENDIX B

SUPPLEMENTARY INFORMATION FOR CHAPTER THREE

SI A: Kevin Dome Regional Geologic Map

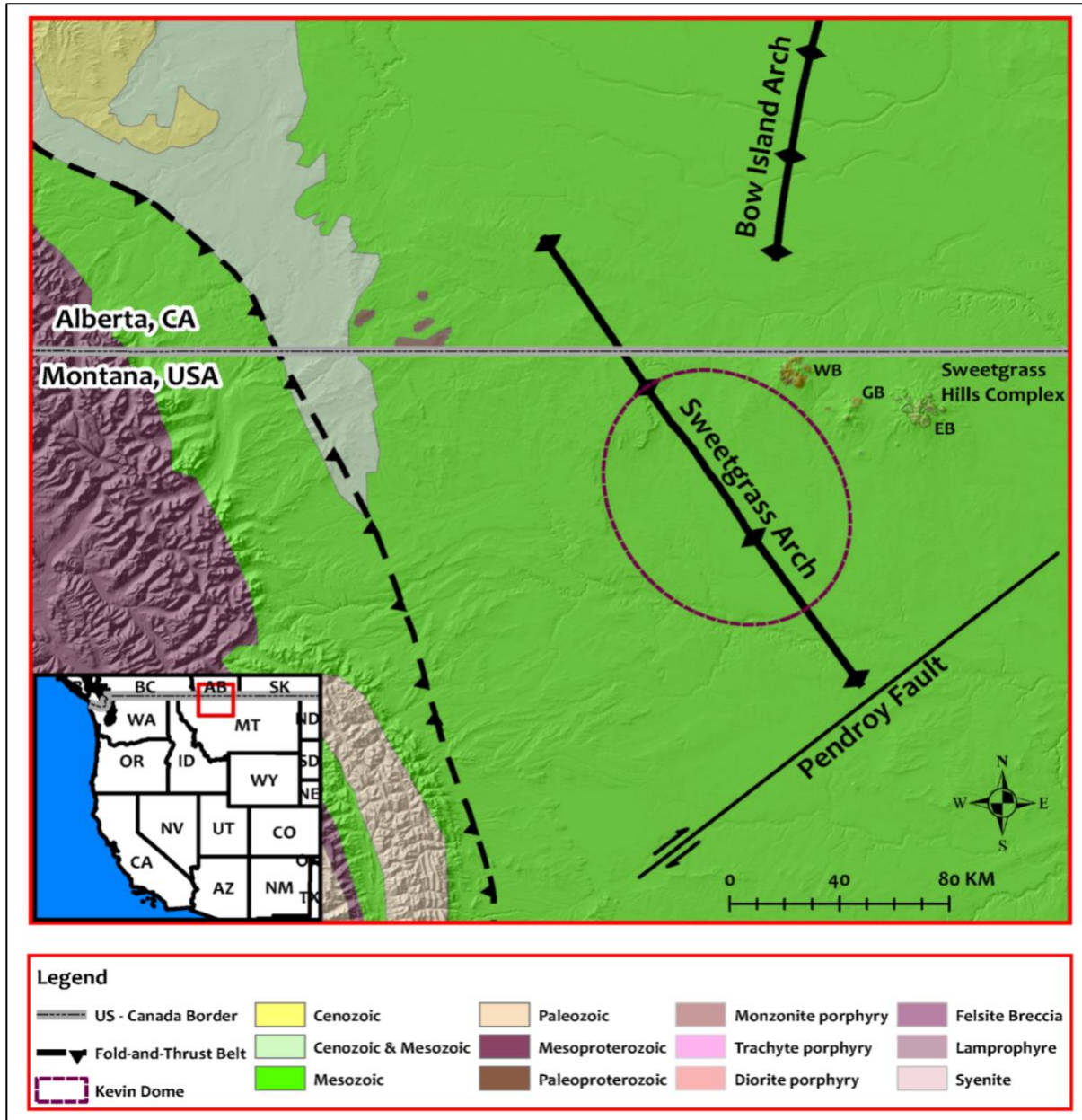


Fig. A1: Regional map of Kevin Dome and various structural elements associated with its development; namely the Sweetgrass Arch, Rocky Mountain Fold and Thrust Belt, the Pendroy Fault, the Sweetgrass Hills igneous complex and the Bow Island Arch, southern Alberta Canada (Shepard and Bartow, 1986; Pană et al., 2021). WB – West Butte, GB – Bold Butte, EB – East Butte.

SI B: Duperow Fm and Banff Fm Depositional History

B.1: Duperow Formation Depositional History

A detailed facies analysis and depositional environment study of the CO₂ sweet spot within Duperow Formation was conducted to adequately understand the facies, facies associations and depositional history of the CO₂ reservoir. Facies analysis was carried out on two well cores provided by the Big Sky Carbon Sequestration Partnership (BSCSP) namely Wallewein 22-1 and Danielson 33-17. The cores were studied by describing their lithology, fossil content, and sedimentary structures. These characteristics were then used to delineate different facies and flooding surfaces, or sequence boundaries interpreted where land-ward and basin-ward shifts in facies were recognized, respectively. Deposition of Devonian strata occurred during second order sea-level rise, over the craton and a gently dipping ($>1^{\circ}$) shallow marine platform on the western margin of North America that was dominated by carbonate and evaporite sedimentation (Norwood, 1965; Sandberg, et al., 1988). Facies analysis and depositional environment studies on the cores show fore-reef, reef, shoal, lagoon, tidal depositional environments. The cores intervals studied represent porous and heavily dolomitized carbonates, and periodic evaporite-rich strata deposited during the Upper Devonian on the Western US Passive Margin (Adeniyi and Steuer, 2019). Furthermore, the Duperow is divided into three porosity zones; upper, middle, and lower (Bowen et al., 2009). The middle Duperow is the most porous and serves as the main CO₂ reservoir zone while the upper and lower Duperow serve as primary and lower seals respectively (Fig. 1, chapter 3). The upper Duperow has tighter carbonate and evaporite-rich beds compared to the lower Duperow zone.

B.2: Banff Formation Depositional History

The Early Mississippian (Tournaisian) Banff Formation of Western Canada Sedimentary Basin (WCSB) is underlain by the Upper Devonian Exshaw Formation in southern Alberta, the Middle Bakken Sandstone member of the Bakken Formation elsewhere and overlain by the basal members of the Early Mississippian Rundle Group; Perisko and Living Stone Formations. The formation can be divided into two units: upper Banff Carbonate unit equivalent to the Madison Group Lodgepole Member and the lower Banff Shale unit equivalent to the upper member black shale unit of the Bakken Formation in Montana and regionally correlative (Smith et al., 1995; Richards et al., 1994; Johnston and Henderson, 2005; Johnston et al., 2010 and Isaacson, 2014). The Banff Formation was deposited in a shallow marine (carbonate-siliciclastic) environment with a distal steep carbonate ramp and a lower slope to starved basin shelf setting within the Prophet Trough and Peace River Embayment on the western North America cratonic platform (Richards et al., 1994). The lower siliciclastic shale unit was deposited during sea level rise in a transgressive system tract separated by a maximum flooding surface and a thin gradational contact to the upper (shallow-marine shelf and slope) carbonate unit (Richards et al., 1994; Smith et al., 1995). The Banff lower shale unit also known as the Banff sand is the primary reservoir and producing oil and gas unit of the Banff Formation at the Ferguson Field. The unit is primarily composed of quartz (hence the name “Banff Sand”), sourced from terrigenous sand and is very high in organic content. The upper fine grained limestone carbonate unit serves as the seal for the Banff sand reservoir unit and both units are part of the Mississippian-Devonian petroleum system within the WCSB. Biostratigraphic evidence from conodont faunas reveal that the deposition and

stratigraphy of Upper Devonian to Lower Mississippian strata at southern Alberta, WCSB were controlled by tectonic elements such as the Sweetgrass Arch or basement faults similar to the depositional events, unconformities, non-deposition and/or erosional hiatuses observed at Kevin Dome and across North America and the globe (Johnston et al., 2010; Jorgensen, 2004; Sloss, 1950; Peterson 1966).

SI C: Sampling and Analyses

Table C.1: Kevin Dome, northwest MT USA, and Ferguson Field, southern AB Canada sampled wells details.

No	Well Name	Reservoirs	Operator	Study Area
1	BARGER 28-34-1	Bow Island, Sunburst	Croft Petroleum	Kevin Dome Montana USA
2	FED 28-34-1			
3	JONES 28-34-1			
4	ROGERS 5-22			
5	GIBLER #1	Sunburst		
6	BAILEY 1	Kootenai	Somont Oil Company, Inc.	
7	WALL 4-34	Bow Island, Dakota, Sunburst, Swift	Croft Petroleum	
8	STATE 2-21			
9	LUNDIN 5-4	Swift		
10	GREEN WELL 14-14	Madison		
11	ARCUS 1981/B 18		Somont Oil Company, Inc.	
12	BARGER 9		Croft Petroleum	
13	FEDERAL 1-6-19			
14	FLYING J #1	Bakken	Somont Oil Company, Inc.	
15	ANDERSON 14-29			
16	J.P. JOHNSON 1D	Nisku	Sands Oil Company	
17	NORWOOD 32-35		D & H Energy, LLC	
18	ZIMMERMAN REALTY 2		Croft Petroleum	
19	LEONARD BASHER 1			
20	D3EXP 1-20 HZ FERG. 1-22-3-16	Banff	International Petroleum Corp. Canada	Ferguson Field, southern Alberta Canada
21	D3EXP 9-27 HZ FERG. 4-30-3-15			
22	D3EXP 14-21 HZ FERG. 15-23-3-16			
23	D3EXP 4-26 HZ FERG. 4-27-3-17			
24	D3EXP 8A-14 HZ FERG. 6-18-3-16			
25	D3EXP 15E-18 HZ 1 FERG. 1-24-3-17			
26	GXO 3B – 8HZ FERG. 5-7-3-17			
27	D3EXP 120-8 HZ 1 FERG. 1-14-3-18			
28	GXO 12C – 8HZ FERG. 15-12-3-18			

C.2: Duperow Formation CO₂ Reservoir Fluid Inclusions

Twenty-Four (24) core samples were selected within the Middle Duperow CO₂ zones from two Kevin Dome wells - Danielson 33-17 and Wallewein 22-1. The well cores were provided by the Big Sky Carbon Sequestration Partnership at Montana State University. Doubly polished thin sections were prepared from these samples for petrographic examination prior to isotopic geochemistry analyses. Optical Microscopy was used to locate, describe the types and distributions of the fluid inclusions found in the Duperow (Fig. C.1. The geologic setting of where the fluid inclusions were found i.e., either in mineral overgrowths, cements, calcite veins, faults, and fractures or within rock matrices was noted as it helps to put the geochemistry interpretations in context (Parnell et al., 2001). Microthermometry PVTX analyses could not be completed to further characterize the fluid inclusions PVT conditions due to the size of the inclusions identified (Jim Reynolds, personal communications, November 29, 2019). Duperow fluid inclusion gas was liberated through stepwise heating using a Teledyne Cetac Diode Laser or double-walled furnace and measured with Thermo Fisher Helix SFT MS at the Water Health Energy and Environment Laboratory (WHEEL) Noble Gas Laboratory, Ohio State University by analytical procedures summarized in Darrah and Poreda, (2012) and Darrah et al. (2015).

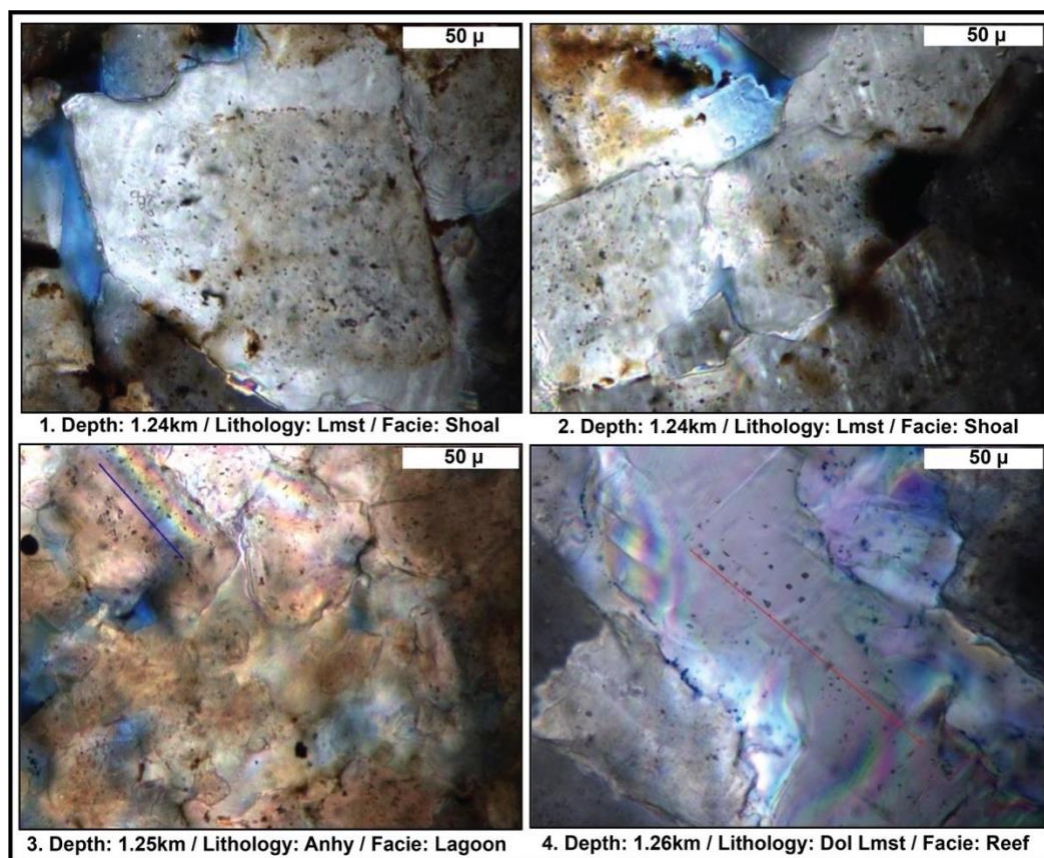


Fig. C.1: Photomicrographs of Wallewein 22-1 core Fluid Inclusions. Secondary fluid inclusions were found within calcite grain-filled fractures and rock matrix of Duperow Formation, Kevin Dome.

C.3: Gold Butte Fluid Inclusions

Seven (7) rock samples were selected for igneous He-Ne-Ar fluid inclusion analyses from the Gold Butte. Gold Butte is one of the SGH igneous complex surface expressions near Kevin Dome (Fig. 1, chapter 3). Mineral separation procedures were completed on the bulk rock samples at GeoSep Services (GSS), Idaho to secure the olivine mineral separates. Table C.4 lists the Gold Butte Olivine mineral yields from each sample. Based on the olivine mineral yield and quality, two samples were selected and analyzed for their trapped-gases He-Ne-Ar analyses. He-Ne-Ar analytical protocols described in Horton et al. (2021) were followed in this study. To remove residual pyrite

[illegible]

C.5: Gas Composition and Stable Isotopes Geochemistry

Isotopic geochemistry analyses were conducted on Kevin Dome and Ferguson Gas Field bulk gas samples to examine their gas composition, concentration, stable elements, noble gas, and their isotopic ratio systematics. Full natural gas composition for major gas abundance (CH_4 , C_2H_6 , C_3H_8 , CO_2 , N_2 , O_2 , He, Ar, and H_2) were analyzed by gas chromatography (GC), while the isotopic ratios of the main gases ($\delta^{13}\text{C}$ and δD of CH_4 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 and $\delta^{15}\text{N}$ of N_2) were measured by gas chromatography combustion isotope ratio mass spectrometry (GC/C/IRMS) techniques respectively at ISOTECH Laboratories, Inc., Champaign IL USA (Darrah et al., 2014; Darrah et al., 2015b; Jackson et al., 2013; Osborn et al., 2011). The GC system - Shimadzu 2010 is custom designed for ISOTECH by Shimadzu and equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors, though only the TCD is used for quantifying fixed gases. This GC system is a helium purged flow system that uses automatic valve switching between different packed columns after each sample gas is released into the loop and adjusted to atmospheric pressure. Lab technicians monitor all the baselines to ensure accuracy of the chromatographs shown and to ensure that all components are detected; they also evacuate the sample loop between each sample load. GC solutions software is used to process the totals could vary between 96% - 104%. ISOTECH uses multiple calibration standards to calibrate their GC system by running a reference sample at every tenth analysis performed. The equipment and supplies required for GC/C/IRMS include 3 SRI 8610C Gas chromatographs, evacuated transfer system, copper oxide combustion furnace, dry ice, isopropyl alcohol, liquid nitrogen, electronic manometer, electronic vacuum gauge, helium, and oxygen and gas-oxygen torch. $\delta^{13}\text{C}$ and δD of

carbon and hydrogen were measured in two stages – (1) separate individual hydrocarbons of interest from the bulk sample, then (2) convert the hydrocarbon to CO₂ and water for mass spectroscopic (MS) analysis. The configuration for separating individual hydrocarbons consists of sample injection syringes, SRI 8610C gas chromatographs, several flow-control valves, and a personal computer. The isolated hydrocarbon is then passed into the combustion-collection unit comprising of quartz combustion tubes filled with cupric oxide (CuO), and vacuum lines. In the combustion-collection unit, the hydrocarbon is converted into CO₂ and water, collected, and sealed off separately in Pyrex tubing for MS analysis. The Pyrex tubing used for the water of combustion contains a weighed quantity of zinc turnings as reagents. $\delta^{13}\text{C}$ and δD of methane, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}_2$ in carbon analyses were performed simultaneously with a Finnigan MAT Delta S Isotope Ratio Mass Spectrometer. This is a dual inlet spectrometric analysis configuration where the spectrometric analysis is completed by comparing the sample to a reference standard. Two internal reference standards are used at ISOTECH. The internal references were calibrated multiple times relative to several standards (graphite, oil, carbonates, waters, etc.) at the International Atomic Energy Agency and the National Institute of Standards and Technology. Both internal references held in aluminum cylinders were mounted permanently on the MS inlet system. A primary reference standard is also introduced via the standard side of the inlet system, and this gas is gradually used for the entire session. The sample (already sealed in the Pyrex tubing) is mounted via an evacuated inlet system and tube-cracker. The sample is released by breaking the Pyrex tubing and allowing the gas to fill a variable volume bellows. The actual analysis is computer initiated and managed by the manufacturer's

software. The software calculates the difference between the sample and an internal reference standard value measured relative to the primary standard:

$$\delta X (\text{sample}) = [(R \text{ sample} - R \text{ standard}) / R \text{ standard}] \times 1000$$

where X is the isotope of interest, $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$, and R stands for the ratio of $\delta^{13}\text{C}/\delta^{12}\text{C}$, or $\delta^{18}\text{O}/\delta^{16}\text{O}$. The δ value is expressed in terms of per mil (‰), or parts per thousand. All gas component carbon isotope values were reported on a scale defined by a two-point calibration of LSVEC and NBS 19. Nitrogen separated by the GC column, is measured when introduced directly into the Mass Spectrometer. $\delta^{15}\text{N}$ in Nitrogen is measured following the same procedure highlighted above but using Finnegan's Isodat software for peak detection and quantification. In all the analyses, the isotopic composition of hydrogen is relative to Vienna Standard Mean Ocean Water (VSMOW), carbon is relative to Vienna Pee Dee Belemnite (VPDB), calculations for BTU and specific gravity are as per ASTM D3588 and all gas component carbon isotope values are reported on a scale defined by a two-point calibration of LSVEC and NBS 19. ISOTECH Lab gas compositions data are normalized to 100% and measured in Mol. % ($\approx$ vol. %).

C.6: Noble Gases Isotopes Geochemistry

Noble gas elemental ([He], [Ne], [Ar], [Kr] and [Xe]) and isotopic ratios ($^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$, $^{21}\text{Ne}/^{22}\text{Ne}$, $^{38}\text{Ar}/^{36}\text{Ar}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $^{20}\text{Ne}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$, $^{132}\text{Xe}/^{84}\text{Kr}$) were analyzed at the WHEEL Noble Gas Lab, Ohio State University. WHEEL Lab also measured the molecular and stable isotopic composition of the gas samples. Darrah and Poreda (2012), Darrah et al. (2013), Hunt et al. (2012), and Poreda and Farley (1992) highlighted the analytical and purification procedures for noble gases elemental composition and isotopic

ratios. The current analyses were completed with Thermo Fisher Helix Split Flight Tube MS with precision and reproducibility error (2σ) of $\pm 1.61\%$. Using analytical procedures summarized by Tedesco et al. (2010) and Harkness et al. (2017), individual noble gases precision values were obtained from Lake Erie, Ohio air, synthetic natural gas standards from Praxair (i.e., referenced/cross-validated laboratory standards of N_2 , CO_2 , O_2 , C_1 - C_5 and Yellowstone MM standard) as ^4He - (0.69%), ^{22}Ne - (1.09%), ^{36}Ar - (0.31%), ^{84}Kr - (1.51%), and ^{132}Xe - (1.72%). Molecular compositional analysis of the major gas abundance was completed by similar analytical procedures already stated above and earlier summarized in Darrah et al. (2013) and Hunt et al. (2012). WHOI and WHEEL Labs measured gas compositions in ccSTP/g and ccSTP/cc respectively.

SI D: Full Analytical Results Data Tables

Table D.1: Duperow Formation Fluid Inclusions CO₂ Gas and Noble Gases Isotopic Composition values*

Sample ID	CO ₂ %	± 1σ	³ He pcc/cc	± 1σ	⁴ He μcc/cc	± 1σ	²⁰ Ne μcc/cc	± 1σ	²¹ Ne μcc/cc	± 1σ	²² Ne μcc/cc	± 1σ	³⁶ Ar μcc/cc	± 1σ	³⁸ Ar μcc/cc	± 1σ	⁴⁰ Ar μcc/cc	± 1σ	⁸⁴ Kr ncc/cc	± 1σ	¹³² Xe ncc/cc	± 1σ
EAD1	80	3.4	59	2.1	138	1.2	4.7	8E-2	1.4E-2	5E-4	0.48	1E-2	22.1	22.1	4.16	0.03	6559	163.1	532.03	22.37	20.6	0.95
EAD2	80	3.9	311	7.7	1024	9.3	1.5	2E-2	4.4E-3	1E-4	0.15	3E-3	7.08	7.1	1.34	0.03	2144	53.5	158.63	5.53	6.5	0.30
EAD3	77	2.9	274	9.5	981	8.7	4.7	7E-2	1.4E-2	5E-4	0.48	1E-2	23.59	23.6	4.55	0.03	7104	164.6	1010.95	43.52	61.8	2.97
EAD4	91	4.8	329	15.2	1091	5.6	3.8	6E-2	1.1E-2	3E-4	0.39	9E-3	10.56	10.6	1.97	0.03	3196	136.4	262.75	7.81	12.0	0.63
EAD5	17	1.0	491	12.1	1610	11.2	22.0	4E-1	6.5E-2	2E-3	2.24	5E-2	110.88	110.9	20.80	0.03	33188	1037	2566.15	80.68	70.0	2.88
EAD6	25	0.9	272	9.6	1052	11.2	9.7	1E-1	2.9E-2	9E-4	0.98	2E-2	38.87	38.9	7.28	0.03	11642	290.6	979.12	39.50	31.0	1.67
EAD7	77	2.9	303	10.5	965	13.4	6.9	1E-1	5.4E-2	2E-3	0.70	2E-2	71.98	55.1	13.46	0.03	21393	869.4	2250.90	69.04	56.7	3.73
EAD8	99	3.3	244	11.1	699	5.6	13.2	2E-1	2.0E-2	6E-4	1.35	3E-2	55.05	79.2	10.22	0.04	16642	623.1	1500.34	51.61	86.7	2.65
EAD9	86	4.5	162	5.9	483	4.3	17.6	2E-1	3.9E-2	1E-3	1.80	4E-2	79.24	82.0	14.76	0.04	23757	686.6	2568.74	80.66	101.9	5.03
EAD10	89	3.3	153	4.3	427	3.5	18.6	3E-1	5.2E-2	2E-3	1.90	3E-2	82.00	37.6	15.29	0.04	24322	630.2	2808.22	109.35	39.0	5.47
EAD11	87	4.6	384	13.5	603	6.2	224.9	3E+0	5.5E-2	2E-3	22.95	5E-1	37.57	1085	7.06	0.03	11212	258.6	1244.16	34.76	1242.4	1.59
EAD12	23	1.1	261	6.7	750	12.5	32.8	5E-1	6.6E-1	2E-2	3.35	8E-2	1084.56	252.5	202.54	0.03	320555	9313	35785.62	1469.6	267.9	75.13
EAW1	89	4.6	342	12.1	983	18.5	18.1	3E-1	9.7E-2	3E-3	1.85	5E-2	252.45	72.0	47.77	0.03	74866	2339	8029.83	258.51	85.9	13.53
EAW2	69	2.7	548	14.3	1418	17.5	33.4	5E-1	9.9E-2	2E-3	3.41	8E-2	74.34	74.3	14.08	0.03	22053	641.2	2382.12	68.23	81.8	3.97
EAW3	82	4.6	399	13.8	967	16.0	39.4	6E-1	1.2E-1	3E-3	4.03	9E-2	152.47	152.5	28.54	0.04	45250	730.3	4763.23	155.11	187.1	10.04
EAW4	77	3.1	306	14.1	722	7.0	0.2	2E-3	5.9E-4	2E-5	0.02	4E-4	0.19	0.2	0.04	0.03	80	4.1	5.12	0.26	0.2	0.01
EAW5	91	4.6	239	8.3	635	55.1	0.1	1E-3	3.5E-4	1E-5	0.01	3E-4	0.10	0.1	0.02	0.03	52	3.2	5.91	0.36	0.2	0.01
EAW6	88	2.3	342	8.3	968	16.1	0.3	4E-3	9.7E-4	3E-5	0.03	7E-4	0.19	0.2	0.04	0.03	86	3.3	6.17	0.25	0.5	0.02
EAW7	25	1.5	182	6.3	463	7.2	0.2	4E-3	7.2E-4	2E-5	0.02	6E-4	0.36	0.4	0.07	0.03	120	5.0	12.63	0.40	1.7	0.10
EAW8	68	2.4	308	7.7	864	8.3	4.8	9E-2	1.4E-2	4E-4	0.49	1E-2	6.90	6.9	1.30	0.03	2101	54.8	132.11	5.24	10.1	0.65
EAW9	71	2.6	166	6.0	566	5.4	1.6	3E-2	4.6E-3	1E-4	0.16	4E-3	1.90	1.9	0.36	0.03	633	19.1	41.24	1.90	3.3	0.14
EAW10	55	3.3	157	6.8	359	4.0	11.2	2E-1	3.3E-2	1E-3	1.15	3E-2	21.77	21.8	4.13	0.03	6445	168.1	674.77	29.62	55.1	2.58
EAW11	74	3.1	203	7.0	709	6.4	8.0	1E-1	2.4E-2	7E-4	0.82	2E-2	15.30	15.3	2.96	0.03	4703	131.9	475.10	19.23	16.7	0.81
EAW12	70	2.6	117	3.2	369	3.4	3.2	5E-2	9.4E-3	3E-4	0.32	8E-3	13.49	13.5	2.53	0.03	4102	119.3	427.99	12.74	26.3	1.23

*Data obtained at WHEEL Noble Gas Lab, Ohio State University.

Table D.2: Duperow Formation Fluid Inclusions Noble Gases Isotope Ratio values*

Sample Name	$\frac{^3\text{He}}{^4\text{He}}$	$\pm 1\sigma$	$\frac{^{20}\text{Ne}}{^{22}\text{Ne}}$	$\pm 1\sigma$	$\frac{^{21}\text{Ne}}{^{22}\text{Ne}}$	$\pm 1\sigma$	$\frac{^{38}\text{Ar}}{^{36}\text{Ar}}$	$\pm 1\sigma$	$\frac{^{40}\text{Ar}}{^{36}\text{Ar}}$	$\pm 1\sigma$	$\frac{^4\text{He}}{^{20}\text{Ne}}$	$\pm 1\sigma$	$\frac{^{20}\text{Ne}}{^{36}\text{Ar}}$	$\pm 1\sigma$	$\frac{^{84}\text{Kr}}{^{36}\text{Ar}}$	$\pm 1\sigma$	$\frac{^{132}\text{Xe}}{^{84}\text{Kr}}$	$\pm 1\sigma$	$\frac{\text{CO}_2}{^3\text{He}}$	$\pm 1\sigma$
EAD1	0.31	4E-3	9.82	7E-2	2.9E-2	3E-4	0.189	9E-4	297	1.1	29	1.2	0.21	7E-3	0.02	1E-3	0.04	2E-3	1.4E+1	7.5E+8
EAD2	0.22	3E-3	9.90	7E-2	2.9E-2	3E-4	0.189	9E-4	303	1.1	683	30.8	0.21	7E-3	0.02	1E-3	0.04	2E-3	2.6E+9	1.4E+8
EAD3	0.20	2E-3	9.81	6E-2	2.9E-2	3E-4	0.193	9E-4	301	1.1	207	9.1	0.20	7E-3	0.04	2E-3	0.06	4E-3	2.7E+9	1.4E+8
EAD4	0.22	2E-3	9.82	7E-2	2.9E-2	3E-4	0.186	9E-4	303	1.1	285	11.2	0.36	1E-3	0.02	1E-3	0.05	3E-3	2.8E+9	1.9E+8
EAD5	0.22	3E-3	9.81	6E-2	2.9E-2	3E-4	0.188	9E-4	299	1.1	73	3.1	0.20	7E-3	0.02	1E-3	0.03	1E-3	3.4E+8	2.3E+7
EAD6	0.19	2E-3	9.88	7E-2	2.9E-2	3E-4	0.187	9E-4	300	1.1	108	4.7	0.25	8E-3	0.03	1E-3	0.03	2E-3	9.2E+8	4.9E+7
EAD7	0.23	2E-3	9.82	6E-2	2.9E-2	3E-4	0.186	9E-4	302	1.1	140	6.2	0.13	4E-3	0.03	1E-3	0.04	2E-3	3.3E+9	1.6E+8
EAD8	0.25	2E-3	9.82	7E-2	2.9E-2	3E-4	0.186	9E-4	300	1.1	53	2.2	0.17	5E-3	0.03	1E-3	0.03	2E-3	3.5E+9	2.4E+8
EAD9	0.24	3E-3	9.78	6E-2	2.9E-2	3E-4	0.187	9E-4	297	1.1	27	1.2	0.21	7E-3	0.03	2E-3	0.04	2E-3	5.5E+9	2.9E+8
EAD10	0.26	3E-3	9.78	6E-2	2.9E-2	3E-4	0.188	9E-4	298	1.1	23	0.9	0.49	1E-3	0.03	1E-3	0.03	2E-3	5.7E+9	3.4E+8
EAD11	0.46	6E-3	9.80	5E-2	2.9E-2	3E-4	0.187	8E-4	296	1.1	3	0.1	0.21	6E-3	0.03	2E-3	0.03	3E-3	6.0E+8	3.6E+7
EAD12	0.25	5E-3	9.79	6E-2	2.9E-2	3E-4	0.189	9E-4	297	1.0	23	1.0	0.13	5E-3	0.03	1E-3	0.03	2E-3	3.4E+9	2.0E+8
EAW1	0.25	3E-3	9.79	5E-2	2.9E-2	4E-4	0.187	9E-4	297	1.1	54	2.3	0.25	9E-3	0.03	1E-3	0.04	2E-3	2.2E+9	1.2E+8
EAW2	0.28	4E-3	9.80	6E-2	2.9E-2	3E-4	0.189	9E-4	297	1.1	42	1.9	0.45	2E-3	0.03	1E-3	0.03	2E-3	1.3E+9	5.9E+7
EAW3	0.30	5E-3	9.77	5E-2	2.9E-2	3E-4	0.187	9E-4	297	1.1	25	1.1	0.26	9E-3	0.03	1E-3	0.04	2E-3	2.1E+9	1.4E+8
EAW4	0.31	5E-3	9.93	6E-2	3.0E-2	3E-4	0.189	9E-4	424	1.6	3629	149.0	1.06	4E-3	0.03	2E-3	0.03	2E-3	2.5E+9	1.5E+08
EAW5	0.27	3E-3	9.96	6E-2	3.0E-2	3E-4	0.189	9E-4	498	1.9	5447	523.5	1.12	4E-3	0.06	4E-3	0.04	3E-3	3.8E+9	2.3E+8
EAW6	0.26	3E-3	9.95	6E-2	3.0E-2	3E-4	0.199	9E-4	461	1.7	2996	121.1	1.72	6E-3	0.03	2E-3	0.08	5E-3	2.6E+9	9.3E+7
EAW7	0.28	4E-3	9.79	6E-2	2.9E-2	3E-4	0.189	9E-4	334	1.3	1914	79.6	0.68	2E-3	0.04	2E-3	0.14	9E-03	1.4E+9	9.5E+7
EAW8	0.26	4E-3	9.79	5E-2	2.9E-2	3E-4	0.189	9E-4	305	1.1	180	7.1	0.70	2E-3	0.02	9E-4	0.08	6E-3	2.2E+9	9.7E+7
EAW9	0.21	4E-3	9.80	5E-2	2.9E-2	3E-4	0.187	9E-4	333	0.0	365	15.5	0.81	3E-3	0.02	1E-3	0.08	5E-3	4.3E+9	2.2E+8
EAW10	0.32	4E-3	9.78	6E-2	2.9E-2	3E-4	0.190	9E-4	296	1.1	32	1.4	0.52	2E-3	0.03	2E-3	0.08	5E-3	3.5E+9	2.6E+8
EAW11	0.21	4E-3	9.79	6E-2	2.9E-2	3E-4	0.193	9E-4	307	1.2	89	3.8	0.52	2E-3	0.03	2E-3	0.04	2E-3	3.6E+9	2.0E+8
EAW12	0.23	3E-3	9.79	6E-2	2.9E-2	3E-4	0.188	9E-4	304	1.2	116	4.6	0.24	8E-3	0.03	1E-3	0.06	3E-3	6.0E+9	2.8E+8

*Data obtained at WHEEL Noble Gas Lab, Ohio State University

Table D.3: Gold Butte (SGH) Olivine Fluid Inclusions He-Ne-Ar Isotope values**

Sample ID	Weight (g)	³ He ccSTP/g	⁴ He ccSTP/g	³ He/ ⁴ He (R/Ra)	²⁰ Ne ccSTP/g	²¹ Ne ccSTP/g	²² Ne ccSTP/g	²⁰ Ne/ ²² Ne ± 1σ	²¹ Ne/ ²² Ne ± 1σ	³⁶ Ar cm ³ STP/g	⁴⁰ Ar cm ³ STP/g	⁴⁰ Ar/ ³⁶ Ar ± 1σ
20GB01-olv	0.04407	5.05E-08	1.47E-06	0.03	2.16E-10	2.38E-12	2.33E-11	9.29 8E-2	1.02E-1 2.33E-3	5.07E-10	3.36E-7	663.3 96.2
20GB05-olv	0.45568	4.56E-08	6.74E-08	0.68	3.91E-11	1.53E-13	3.97E-12	9.85 9E-2	3.84E-2 8.30E-4	1.17E-10	1.16E-7	990.0 17.3

**Data obtained at Woods Hole Oceanographic Institution, MA.

Table D.4: Kevin Dome, northwest Montana USA Bulk Gas Stable Isotope values***

Well Name	Producing Formations	δ ¹³ C ₁ ‰	δDC ₁ ‰	δ ¹³ CO ₂ ‰	δ ¹⁸ CO ₂ ‰	δ ¹⁵ N ‰	Specific Gravity	BTU
<i>Barger 28-34-1</i>	Bow Island, Sunburst	-55.37	-262.0	-11.50	1.62	-0.2	0.626	1054
<i>Fed 28-34-1</i>		-55.04	-265.8	-8.03	0.95	na	0.658	1042
<i>Jones 28-34-1</i>		-56.27	-268.0	-7.71	1.25	na	0.617	1024
<i>Gibler #1</i>	Sunburst	-51.58	-253.2	-11.51	-1.55	0.5	0.695	1092
<i>Bailey 1</i>	Kootenai	-50.48	-229.9	-19.20	-2.07	-0.6	0.628	967
<i>Rogers 5-22</i>	Bow Island, Sunburst, Swift	-51.33	-251.2	-11.76	0.54	0.7	0.618	1011
<i>Wall 4-34</i>		-54.20	-263.1	-16.12	0.37	-0.5	0.619	1028
<i>State 2-21</i>		-52.73	-260.2	-9.29	-0.17	0.5	0.621	1026
<i>Lundin 5-4</i>	Swift	-56.97	-275.5	-16.0	na	-0.5	0.594	1007
<i>Green Well 14-14</i>	Madison	-58.53	-272.2	-3.09	-2.08	na	0.681	981
<i>Arcus 1981/B 18</i>		-55.76	-285.6	1.94	-3.97	-0.1	0.868	1205
<i>Barger 9</i>		-59.41	-277.8	-5.28	-3.02	0.4	0.911	686
<i>Federal 1-6-19</i>		-55.69	-268.2	-10.35	4.49	-0.7	0.609	1015
<i>Flying J #1</i>		-50.62	-245.2	-13.07	-5.68	0.7	0.691	1089
<i>Anderson 14-29</i>	Bakken	-49.46	-257.4	-8.94	6.63	-2.3	0.766	1000
<i>J.P. Johnson 1D</i>	Nisku	-53.27	-244.4	-13.27	1.54	1.6	0.664	1079
<i>Norwood 32-35</i>		-53.12	-243.2	-13.46	9.30	na	0.680	1046
<i>Zimmerman Realty 2</i>		-60.85	-266.3	5.99	1.40	na	0.596	987
<i>Leonard Basher 1</i>		-53.40	-237.8	-13.46	8.86	2.7	0.675	1080

na = not analyzed due to either insufficient sample pressure or concentration for analysis

***Data obtained at ISOTECH Laboratories Inc. IL

Table D.5: Kevin Dome, northwest Montana USA Bulk Gas Molecular Compositional values***

Well Name	Reservoirs	C ₁ (%)	C ₂ (%)	C ₃ (%)	N ₂ (%)	CO ₂ (%)	CO (%)	H ₂ (%)	Ar (%)	O ₂ (%)	He (%)	C ₂ H ₄ (%)	C ₃ H ₆ (%)	iC ₄ (%)	nC ₄ (%)	iC ₅ (%)	nC ₅ (%)	C ₆ + (%)
<i>Barger 28-34-1</i>	Bow Island, Sunburst	91	2.7	1.1	2.4	1.3	nd	0.02	0.02	0.02	0.06	2E-4	8E-4	0.28	0.50	0.24	0.18	0.27
<i>Fed 28-34-1</i>		88	2.2	0.9	2.8	3.4	nd	nd	0.02	0.17	0.06	2E-4	7E-4	0.26	0.43	0.51	0.35	0.54
<i>Jones 28-34-1</i>		91	2.4	0.9	3.0	1.4	nd	0.01	0.03	0.16	0.07	nd	3E-4	0.22	0.36	0.15	0.11	0.14
<i>Gibler #1</i>	Sunburst	86	2.5	1.2	3.7	3.2	nd	nd	0.02	0.01	0.07	6E-4	nd	0.53	0.96	0.74	0.68	0.93
<i>Bailey 1</i>	Kootenai	86	3.4	1.0	8.6	0.5	nd	0.01	0.05	0.25	0.27	1E-4	2E-4	0.15	0.19	0.06	0.03	0.02
<i>Rogers 5-22</i>	Bow Island, Sunburst, Swift	91	2.5	0.9	3.4	1.8	nd	nd	0.02	nd	0.07	nd	2E-4	0.20	0.24	0.10	0.06	0.10
<i>Wall 4-34</i>		90	2.5	1.0	4.1	0.7	nd	0.06	0.03	0.04	0.10	1E-4	5E-4	0.25	0.41	0.20	0.15	0.17
<i>State 2-21</i>		91	2.0	0.6	2.8	1.8	nd	nd	0.02	0.01	0.06	nd	2E-4	0.19	0.29	0.25	0.17	0.28
<i>Lundin 5-4</i>	Swift	92	2.2	0.6	4.0	0.1	nd	0.25	0.03	0.07	0.11	nd	1E-4	0.16	0.14	0.07	0.03	0.06
<i>Green Well 14-14</i>	Madison	82	3.3	1.2	7.3	4.0	nd	0.02	0.06	0.43	0.12	nd	nd	0.43	0.63	0.37	0.13	0.14
<i>Arcus 1981/B 18</i>		64	7.2	7.1	1.3	11.1	nd	2.54	0.02	0.09	0.03	1E-4	2E-4	1.96	3.00	0.97	0.49	0.39
<i>Barger 9</i>		61	0.6	0.4	3.5	32.8	nd	nd	0.02	nd	0.11	nd	nd	0.20	0.27	0.29	0.09	0.21
<i>Federal 1-6-19</i>		91	2.5	1.0	4.6	0.3	nd	0.13	0.03	0.12	0.12	1E-4	3E-4	0.22	0.29	0.11	0.05	0.09
<i>Flying J #1</i>		79	7.0	3.3	7.0	0.9	nd	0.18	0.04	nd	0.23	nd	nd	0.56	0.97	0.27	0.22	0.18
<i>Anderson 14-29</i>	Bakken	71	9.1	3.0	5.3	10.2	nd	nd	0.02	nd	0.18	nd	1E-4	0.22	0.58	0.12	0.13	0.11
<i>J.P. Johnson 1D</i>	Nisku	84	6.8	2.5	4.3	1.4	nd	nd	0.01	0.02	0.12	nd	nd	0.19	0.77	0.10	0.21	0.11
<i>Norwood 32-35</i>		81	6.6	2.4	6.4	2.1	nd	nd	0.03	0.18	0.14	nd	nd	0.19	0.77	0.10	0.21	0.12
<i>Zimmerman Realty 2</i>		93	1.4	0.3	3.4	1.2	nd	0.02	0.03	0.19	0.07	nd	2E-4	0.08	0.12	0.05	0.03	0.03
<i>Leonard Basher 1</i>		83	6.7	2.4	4.3	2.1	nd	nd	0.01	nd	0.12	nd	nd	0.20	0.85	0.12	0.28	0.20

***Data obtained at ISOTECH Laboratories Inc. IL

All gas component carbon isotope values are reported on a scale defined by a two-point calibration of LSVEC and NBS 19. nd = not detected.

Table D.6: Ferguson Field, southern Alberta Canada Bulk Gas Stable Isotope values***

Well Name	Reservoir	$\delta^{13}\text{C}_1$ ‰	δDC_1 ‰	$\delta^{13}\text{CO}_2$ ‰	$\delta^{18}\text{CO}_2$ ‰	$\delta^{15}\text{N}$ ‰	Specific Gravity	BTU
D3EXP 1-20 HZ FERG. 1-22-3-16	Banff Sand	-49.73	-279.3	-9.76	7.66	-1.5	0.945	945
D3EXP 9-27 HZ FERG. 4-30-3-15		-47.03	-280.6	-11.65	6.87	-0.8	0.913	1142
D3EXP 14-21 HZ FERG. 15-23-3-16		-47.56	-274.5	-11.43	8.03	-0.6	1.045	1161
D3EXP 4-26 HZ FERG. 4-27-3-17		-50.22	-296.7	-10.50	6.93	-1.2	1.004	908
D3EXP 8A-14 HZ FERG. 6-18-3-16		-49.43	-280.3	-10.05	7.80	-1.4	0.927	958
D3EXP 15E-18 HZ 1 FERG. 1-24-3-17		-49.43	-282.2	-10.19	5.08	-1.0	1.053	936
6XO 3B – 8HZ FERG. 5-7-3-17		-50.38	-285.5	-9.96	7.22	-1.2	0.969	813
D3EXP 120-8 HZ 1 FERG. 1-14-3-18		-50.89	-309.3	-6.18	7.65	-0.8	1.165	875
6XO 12C – 8HZ FERG. 15-12-3-18		-50.77	-305.9	-6.19	7.89	-0.6	1.094	744

Table D.7: Ferguson Field, southern Alberta Canada Bulk Gas Molecular Compositional values***

Well Name	Reservoir	C ₁ (%)	C ₂ (%)	C ₃ (%)	N ₂ (%)	CO ₂ (%)	CO (%)	H ₂ (%)	Ar (%)	O ₂ (%)	He (%)	C ₂ H ₄ (%)	C ₃ H ₆ (%)	iC ₄ (%)	nC ₄ (%)	iC ₅ (%)	nC ₅ (%)	C ₆ + (%)
D3EXP 1-20 HZ FERG. 1-22-3-16	Banff Sand	54	6.5	5.0	10.0	20.4	nd	nd	0.03	nd	0.22	nd	2E-4	0.75	1.69	0.54	0.50	0.77
D3EXP 9-27 HZ FERG. 4-30-3-15		56	7.9	8.1	12.6	8.9	nd	nd	0.04	0.014	0.15	nd	4E-4	1.22	2.74	0.72	0.68	0.84
D3EXP 14-21 HZ FERG. 15-23-3-16		46	9.4	9.9	7.1	20.0	nd	nd	0.03	nd	0.09	nd	5E-4	1.42	3.48	0.96	0.89	0.84
D3EXP 4-26 HZ FERG. 4-27-3-17		47	7.0	6.0	9.0	26.1	nd	nd	0.03	nd	0.19	nd	1E-4	0.76	1.90	0.52	0.48	0.45
D3EXP 8A-14 HZ FERG. 6-18-3-16		54	6.1	5.2	12.2	17.2	nd	nd	0.04	nd	0.27	nd	2E-4	0.82	1.97	0.61	0.57	0.58
D3EXP 15E-18 HZ 1 FERG. 1-24-3-17		44	7.8	6.7	6.6	29.7	nd	nd	0.02	nd	0.13	nd	2E-4	0.84	2.15	0.61	0.56	0.70
6XO 3B – 8HZ FERG. 5-7-3-17		50	6.8	4.9	8.1	28.4	nd	nd	0.03	nd	0.20	nd	2E-4	0.47	0.98	0.15	0.12	0.08
D3EXP 120-8 HZ 1 FERG. 1-14-3-18		35	6.3	5.9	6.8	39.0	nd	nd	0.02	nd	0.11	nd	nd	0.87	2.42	0.90	0.91	1.54
6XO 12C – 8HZ FERG. 15-12-3-18		40	6.1	4.8	5.9	40.3	nd	nd	0.02	nd	0.10	nd	nd	0.62	1.42	0.38	0.33	0.32

***Data obtained at ISOTECH Laboratories Inc. IL

All gas component carbon isotope values are reported on a scale defined by a two-point calibration of LSVEC and NBS 19. nd = not detected.

Table D.8: Kevin Dome, northwest Montana USA Bulk Gas Noble Gases Isotopic Composition values*

Well Name	Reservoirs	³ He pcc/cc	± 1σ	⁴ He μcc/cc	± 1σ	²⁰ Ne μcc/cc	± 1σ	²¹ Ne μcc/cc	± 1σ	²² Ne μcc/cc	± 1σ	³⁶ Ar μcc/cc	± 1σ	³⁸ Ar μcc/cc	± 1σ	⁴⁰ Ar μcc/cc	± 1σ	⁸⁴ Kr ncc/cc	± 1σ	¹³² Xe ncc/cc	± 1σ
<i>Barger 28-34-1</i>	Bow Island, Sunburst	230	7	751	4	0.37	6E-3	1.1E-3	2E-5	3.7E-2	6E-4	0.36	1E-2	0.07	2E-3	188	2.8	6.8	0.2	0.5	0.02
<i>Fed 28-34-1</i>		161	5	636	6	0.24	4E-3	7.2E-4	1E-5	2.4E-2	4E-4	0.78	2E-2	0.15	4E-3	246	3.9	22.4	0.9	1.4	0.06
<i>Jones 28-34-1</i>		173	5	812	5	0.22	4E-3	6.9E-4	1E-5	2.3E-2	4E-4	0.38	1E-2	0.07	2E-3	187	3.4	11.8	0.4	0.6	0.02
<i>Gibler #1</i>	Sunburst	162	5	771	22	0.68	1E-3	2.1E-3	3E-5	6.9E-2	1E-3	0.36	1E-2	0.07	2E-3	227	3.5	8.4	0.3	0.4	0.02
<i>Bailey 1</i>	Kootenai	739	22	3199	6	0.55	8E-3	1.7E-3	3E-5	5.6E-2	9E-4	0.36	1E-2	0.07	2E-3	413	6.9	8.8	0.3	0.4	0.02
<i>Rogers 5-22</i>	Bow Island, Sunburst, Swift	228	6	800	9	0.25	4E-3	7.5E-4	1E-5	2.5E-2	4E-4	0.49	1E-2	0.09	3E-3	268	3.7	14.0	0.5	0.5	0.02
<i>Wall 4-34</i>		438	14	1294	5	0.56	1E-02	1.7E-3	3E-5	5.7E-2	1E-3	0.50	1E-2	0.09	3E-3	267	4.0	13.5	0.5	0.8	0.03
<i>State 2-21</i>		241	7	719	10	0.22	4E-3	6.5E-4	1E-5	2.2E-2	4E-4	0.38	1E-2	0.07	2E-3	221	3.4	12.6	0.4	0.3	0.01
<i>Lundin 5-4</i>	Swift	309	9	1451	9	0.53	9E-3	1.6E-3	2E-5	5.5E-2	9E-4	0.53	1E-2	0.10	3E-3	268	4.4	15.1	0.5	0.4	0.02
<i>Green Well 14-14</i>	Madison	382	10	1336	2	0.47	8E-3	1.4E-3	3E-5	4.8E-2	8E-4	0.98	3E-2	0.19	5E-3	445	5.9	37.8	1.5	0.3	0.01
<i>Arcus 1981/B 18</i>		62	2	278	13	0.09	1E-3	2.7E-4	8E-5	9.0E-3	2E-4	0.29	8E-3	0.06	2E-3	128	1.6	12.4	0.4	0.3	0.01
<i>Barger 9</i>		496	15	1909	10	0.24	4E-3	7.7E-4	1E-5	2.4E-2	4E-4	0.38	1E-2	0.07	3E-3	244	3.8	12.3	0.4	0.4	0.02
<i>Federal 1-6-19</i>		403	12	1476	19	0.42	7E-3	1.3E-3	2E-5	4.3E-2	7E-4	0.76	3E-2	0.14	5E-3	360	6.1	33.0	1.1	0.6	0.02
<i>Flying J #1</i>		785	25	2812	14	0.39	7E-3	1.3E-3	3E-5	4.0E-2	7E-4	0.90	3E-2	0.17	5E-3	469	7.9	31.9	1.1	2.1	0.08
<i>Anderson 14-29</i>	Bakken	578	17	2038	10	0.24	4E-3	7.5E-4	2E-5	2.4E-2	5E-4	0.12	4E-3	0.02	1E-3	161	2.9	2.6	0.1	0.2	0.00
<i>J.P. Johnson 1D</i>	Nisku	569	17	1491	12	0.23	5E-3	7.2E-4	2E-5	2.4E-2	4E-4	0.08	2E-3	0.02	7E-4	151	2.1	3.0	0.1	0.1	0.04
<i>Norwood 32-35</i>		634	20	1728	5	0.25	6E-3	7.8E-4	2E-5	2.5E-2	7E-4	0.11	3E-3	0.02	9E-4	183	2.9	1.7	0.1	0.1	0.00
<i>Zimmerman Realty 2</i>		245	7	782	10	0.24	5E-3	7.6E-4	2E-5	2.5E-2	5E-4	0.53	2E-02	0.10	5E-3	252	3.8	15.4	0.5	0.3	0.01
<i>Leonard Basher 1</i>		494	14	1463	0	0.19	4E-3	5.9E-4	2E-5	1.9E-2	5E-4	0.07	2E-3	0.01	5E-3	144	2.2	3.0	0.1	0.2	0.01

*Data obtained at WHEEL Noble Gas Lab, Ohio State University

Table D.9: Kevin Dome, northwest Montana USA Bulk Gas Noble Gases Isotope Ratio values*

Well Name	Reservoirs	$\frac{^3\text{He}}{^4\text{He}} \pm 1\sigma$	$\frac{^{20}\text{Ne}}{^{22}\text{Ne}} \pm 1\sigma$	$\frac{^{21}\text{Ne}}{^{22}\text{Ne}} \pm 1\sigma$	$\frac{^{38}\text{Ar}}{^{36}\text{Ar}} \pm 1\sigma$	$\frac{^{40}\text{Ar}}{^{36}\text{Ar}} \pm 1\sigma$	$\frac{^4\text{He}}{^{20}\text{Ne}} \pm 1\sigma$	$\frac{^{20}\text{Ne}}{^{36}\text{Ar}} \pm 1\sigma$	$\frac{^{84}\text{Kr}}{^{36}\text{Ar}} \pm 1\sigma$	$\frac{^{132}\text{Xe}}{^{84}\text{Kr}} \pm 1\sigma$	$\frac{\text{CO}_2}{^3\text{He}} \pm 1\sigma$										
Barger 28-34-1	Bow Island, Sunburst	0.22	9E-3	9.81	0.05	0.03	2E-4	0.189	9E-4	527	2.0	2.1E+3	2E+1	1.02	0.03	0.02	9E-4	0.07	4E-3	6.7E+7	2.3E+6
Fed 28-34-1		0.18	9E-3	9.76	0.05	0.03	2E-4	0.188	9E-4	314	1.2	2.7E+3	3E+1	0.30	0.01	0.03	1E-3	0.06	4E-3	1.7E+8	5.8E+6
Jones 28-34-1		0.15	9E-3	9.80	0.05	0.03	2E-4	0.188	9E-4	499	1.9	3.7E+3	5E+1	0.59	0.02	0.03	1E-3	0.05	3E-3	1.6E+8	5.3E+6
Gibler #1	Sunburst	0.15	9E-3	9.78	0.05	0.03	2E-4	0.189	9E-4	634	2.4	1.1E+3	1E+1	1.89	0.06	0.02	1E-3	0.05	3E-3	4.3E+7	1.6E+6
Bailey 1	Kootenai	0.17	9E-3	9.77	0.05	0.03	2E-4	0.188	9E-4	1160	4.4	5.8E+3	6E+1	1.54	0.05	0.02	1E-3	0.05	3E-3	2.2E+5	7.8E+3
Rogers 5-22	Bow Island, Sunburst, Swift	0.21	9E-3	9.80	0.05	0.03	2E-4	0.187	9E-4	550	2.1	3.2E+3	5E+1	0.51	0.02	0.03	1E-3	0.04	2E-3	7.0E+7	2.4E+6
Wall 4-34		0.24	9E-3	9.71	0.04	0.03	2E-4	0.188	9E-4	529	2.0	2.3E+3	4E+1	1.10	0.03	0.03	1E-3	0.06	3E-3	6.8E+6	2.5E+5
State 2-21		0.24	9E-3	9.78	0.05	0.03	2E-4	0.191	9E-4	579	2.2	3.3E+3	5E+1	0.57	0.02	0.03	1E-3	0.03	1E-3	1.4E+7	4.6E+5
Lundin 5-4	Swift	0.15	9E-3	9.77	0.05	0.03	2E-4	0.186	9E-4	507	1.9	2.7E+3	5E+1	1.01	0.03	0.03	1E-3	0.03	2E-3	3.0E+6	9.8E+4
Green Well 14-14	Madison	0.21	9E-3	9.77	0.05	0.03	2E-4	0.188	9E-4	452	1.7	2.8E+3	4E+1	0.48	0.02	0.04	2E-3	0.01	5E-4	5.2E+7	1.6E+6
Arcus 1981/B 18		0.16	9E-3	9.76	0.05	0.03	2E-4	0.191	9E-4	436	1.6	3.2E+3	4E+1	0.30	0.01	0.04	2E-3	0.03	1E-3	5.5E+8	2.1E+7
Barger 9		0.19	1E-02	9.76	0.05	0.03	2E-4	0.188	9E-4	640	2.4	8.1E+3	9E+1	0.62	0.02	0.03	2E-3	0.04	2E-3	3.1E+8	1.2E+7
Federal 1-6-19		0.20	1E-02	9.79	0.05	0.03	2E-4	0.191	9E-4	476	1.8	3.5E+3	4E+1	0.55	0.02	0.04	2E-3	0.02	9E-4	1.9E+6	6.6E+4
Flying J #1		0.20	9E-3	9.79	0.05	0.03	2E-4	0.189	9E-4	522	2.0	7.2E+3	9E+1	0.43	0.02	0.04	2E-3	0.07	3E-3	1.5E+7	5.9E+5
Anderson 14-29	Bakken	0.20	9E-3	9.76	0.05	0.03	2E-4	0.191	9E-4	1388	5.2	8.6E+3	8E+1	2.05	0.07	0.02	1E-3	0.06	2E-3	1.1E+8	4.2E+6
J.P. Johnson 1D	Nisku	0.28	9E-3	9.79	0.05	0.03	2E-4	0.188	9E-4	1834	6.9	6.4E+3	8E+1	2.83	0.10	0.04	2E-3	0.03	1E-2	1.3E+7	4.6E+5
Norwood 32-35		0.27	9E-3	9.79	0.05	0.03	2E-4	0.187	9E-4	1680	6.3	7.0E+3	8E+0	2.26	0.09	0.02	7E-4	0.06	3E-3	5.3E+6	2.0E+5
Zimmerman Realty 2		0.23	9E-3	9.76	0.05	0.03	2E-4	0.190	9E-4	476	1.8	3.3E+3	4E+1	0.45	0.02	0.03	1E-3	0.02	1E-3	6.7E+6	2.4E+5
Leonard Basher 1		0.24	9E-3	9.81	0.05	0.03	2E-4	0.187	9E-4	1999	7.5	7.9E+3	1E+2	2.57	0.10	0.04	2E-3	0.06	3E-3	1.5E+7	5.4E+5

*Data obtained at WHEEL Noble Gas Lab, Ohio State University.

Table D.10: Ferguson Field, southern Alberta Canada Bulk Gas Noble Gases Isotopic Composition and Ratio values*

Well Name	Reservoir	$\frac{^3\text{He}}{\text{pcc/cc}}$	$\frac{^4\text{He}}{\mu\text{cc/cc}}$	$\frac{^{20}\text{Ne}}{\mu\text{cc/cc}}$	$\frac{^{21}\text{Ne}}{\mu\text{cc/cc}}$	$\frac{^{22}\text{Ne}}{\mu\text{cc/cc}}$	$\frac{^{36}\text{Ar}}{\mu\text{cc/cc}}$	$\frac{^{38}\text{Ar}}{\mu\text{cc/cc}}$	$\frac{^{40}\text{Ar}}{\mu\text{cc/cc}}$	$\frac{^{84}\text{Kr}}{\text{ncc/cc}}$	$\frac{^{132}\text{Xe}}{\text{ncc/cc}}$	$\frac{^3\text{He}}{^4\text{He}}$	$\frac{^{20}\text{Ne}}{^{22}\text{Ne}}$	$\frac{^{21}\text{Ne}}{^{22}\text{Ne}}$	$\frac{^{38}\text{Ar}}{^{36}\text{Ar}}$	$\frac{^{40}\text{Ar}}{^{36}\text{Ar}}$	$\frac{^4\text{He}}{^{20}\text{Ne}}$	$\frac{^{20}\text{Ne}}{^{36}\text{Ar}}$	$\frac{^{84}\text{Kr}}{^{36}\text{Ar}}$	$\frac{^{132}\text{Xe}}{^{84}\text{Kr}}$	$\frac{\text{CO}_2}{^3\text{He}}$
D3EXP 1-20 HZ FERG. 1-22-3-16	Banff Sand	434	1963	0.28	9E-4	0.03	0.55	0.10	348	19.9	2.4	0.16	9.70	0.03	0.180	633	7.0E+3	0.51	0.04	0.12	4.2E+8
D3EXP 9-27 HZ FERG. 4-30-3-15		534	2262	0.29	9E-4	0.03	0.55	0.10	372	19.5	2.1	0.17	9.70	0.03	0.179	679	7.9E+3	0.52	0.04	0.11	2.7E+8
D3EXP 14-21 HZ FERG. 15-23-3-16		329	1530	0.36	1E-3	0.04	0.64	0.12	461	30.7	4.0	0.16	9.75	0.03	0.181	716	4.3E+3	0.55	0.05	0.13	1.5E+8
D3EXP 4-26 HZ FERG. 4-27-3-17		214	956	0.28	9E-4	0.03	0.43	0.09	332	26.9	4.9	0.16	9.75	0.03	0.200	780	3.4E+3	0.66	0.06	0.18	7.1E+8
D3EXP 8A-14 HZ FERG. 6-18-3-16		623	2750	0.25	8E-4	0.03	0.57	0.11	411	18.7	2.0	0.16	9.75	0.03	0.188	723	1.1E+4	0.44	0.03	0.11	1.8E+8
D3EXP 15E-18 HZ 1 FERG. 1-24-3-17		327	1414	0.21	6E-4	0.02	0.35	0.06	258	4.3	0.4	0.17	9.72	0.03	0.179	742	6.9E+3	0.59	0.01	0.09	6.7E+8
6XO 3B – 8HZ FERG. 5-7-3-17		398	1894	0.14	5E-4	0.01	0.38	0.07	266	3.8	0.2	0.15	9.75	0.03	0.178	695	1.3E+4	0.37	0.01	0.05	4.9E+8
D3EXP 120-8 HZ 1 FERG. 1-14-3-18		266	1123	0.72	2E-3	0.07	0.32	0.06	219	7.8	0.9	0.17	9.74	0.03	0.186	674	1.6E+3	2.22	0.02	0.11	1.1E+9
6XO 12C – 8HZ FERG. 15-12-3-18		236	1019	0.19	6E-4	0.02	0.21	0.04	191	6.9	0.8	0.17	9.75	0.03	0.186	891	5.3E+3	0.90	0.03	0.12	1.3E+9

*Data obtained at WHEEL Noble Gas Lab, Ohio State University

SI E: Major gas compositions, stable isotopes, and gas source signatures

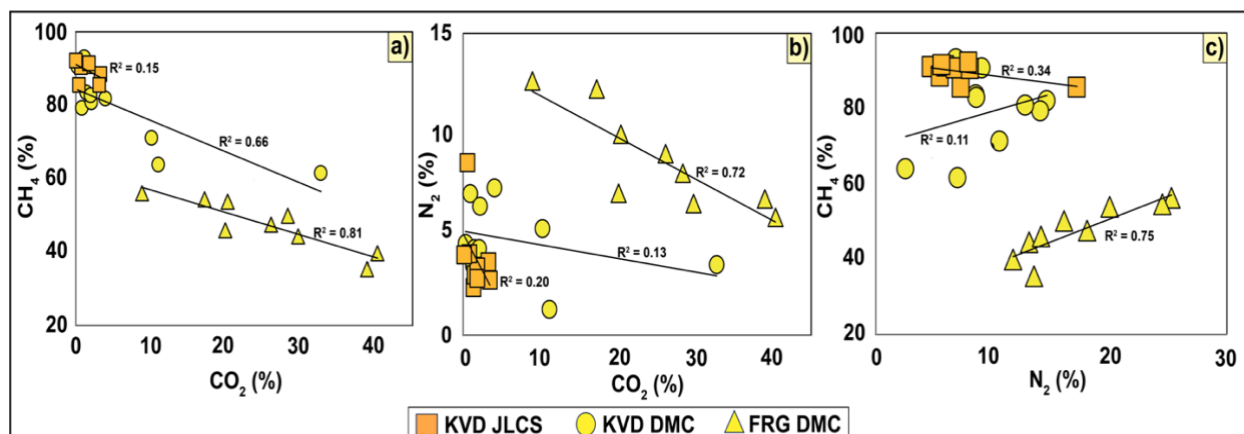


Fig. E.1: Kevin Dome, northwest MT USA and Ferguson Field, southern AB Canada major gas source correlations based on gas compositions (a) CO_2 vs CH_4 , (b) CO_2 vs N_2 and (c) CH_4 vs N_2 . Black line with R^2 values represents correlation trends. **KVD** - Kevin Dome; **FRG** - Ferguson Field; **JLCS** - Jurassic-Lower Cretaceous sandstone and **DMC** - Devonian-Mississippian carbonates reservoirs.

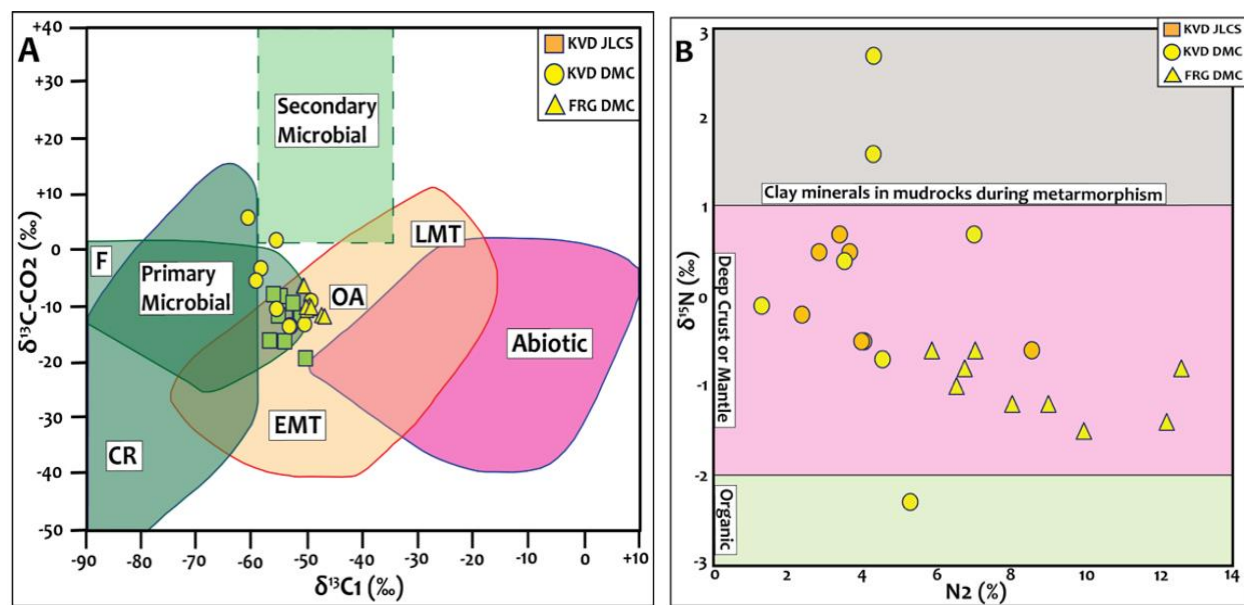


Fig. E.2: Kevin Dome, northwest MT USA and Ferguson Field, southern AB Canada (A) CO_2 origin: Modified CO_2 gas genetic classification scheme (Gutsalo and Plotnikov, 1981; Milkov and Etiope, 2018) (B) N_2 origin: $\delta^{15}\text{N}-\text{N}_2$ against N_2 concentration classification schemes (Zhu et al., 2000). **KVD** - Kevin Dome; **FRG** - Ferguson Field; **JLCS** - Jurassic-Lower Cretaceous Sandstone and **DMC** - Devonian-Mississippian Carbonates reservoirs. CH_4 origin domains: **CR** – CO_2 reduction; **F** – methyl-type fermentation; **SM** – secondary microbial; **EMT** – early mature thermogenic; **OA** – oil-associated thermogenic and **LMT** – late mature thermogenic.

SI F: Rayleigh Fractionation during CO₂ dissolution estimation and reservoir conditions used

Method Summary

The fraction of CO₂ loss by dissolution with changing CO₂/³He and δ¹³C-CO₂ at various pH conditions into surrounding fluids in each reservoir was estimated following Rayleigh fractionation equation and a method described by Gilfillan et al., (2009). Rayleigh equation is based on the relationship:

$$\delta^{13}\text{C-CO}_2 = \delta^{13}\text{C-CO}_{2i} + \epsilon_{\text{DIS}} \ln f \text{ (Eq X).}$$

where δ¹³C-CO₂ and δ¹³C-CO_{2i} are the respective measured and δ¹³C-CO₂ values of the gas, *f* is the fraction of CO₂ remaining in the reservoir.

Known Parameters and Assumptions

The initial δ¹³C-CO_{2i} in system was also set to zero, initial CO₂(%) injected was assumed to be 100% (based on Duperow Formation injected CO₂ purity and measured proportion), thus CO_{2i} = CO₂(%)/100. pH values for each reservoir were assumed and later modeled for accuracy. Borehole Temperature (BHT) was estimated for each assuming on 30°C/km geothermal gradient. Average Salinity (S) for each reservoir was obtained from Operators. ³He (%) was taken from measured values for each sample. ε_{DIS} is the carbon isotope fractionation for dissolution estimated as a function of reservoir temperature (i.e. borehole temperature - BHT), Salinity (S), and pH conditions for CO₂ dissolving to form either H₂CO₃(aq) or HCO₃⁻(aq) (Deines et al., 1974) coupled with Henry's law constants and fractionation factors for CO₂ gas. ε_{DIS} is expressed as:

$$\epsilon_{\text{DIS}} = f_{\text{HCO}_3} * \text{HCO}_3_ \text{CO}_2 + f_{\text{CO}_3} * \text{H}^2\text{CO}_3_ \text{CO}_2 \text{ (Clark and Frits (1997))}$$

The following formulas from Clark and Frits (1997) and Henry's law constants were used to estimate ϵ_{DIS} as follow:

$$H = 10^{(-\text{pH})}$$

$$T \text{ (K)} = \text{BHT} + 273.15$$

$$\text{H}_2\text{CO}_3_{\text{CO}_2} = -0.0000141 * T^2 + 0.0049 * T - 1.18$$

$$\text{HCO}_3_{\text{CO}_2} = 0.00032 * T^2 - 0.124 * T + 10.87$$

$$\text{CO}_{32_{\text{CO}_2}} = 0.00033 * T^2 - 0.083 * T + 8.25$$

$$\text{Equilibrium constants: } K1 = 10^{(0.00009 * \text{BHT}^2 - 0.0167 * \text{BHT} - 1.11)}, K2 = 10^{(-0.00013 * \text{BHT}^2 + 0.0125 * \text{BHT} - 6.58)}, K3 = 10^{(-0.00009 * \text{BHT}^2 + 0.0139 * \text{BHT} - 10.62)}$$

$$\text{CO}_2 \text{ Solubility} = a + b (100/T) + c \ln(T/100) + (d - e (T/100) + f (T/100)^2) * S \text{ (Weiss, 1974)}$$

$$a = -60.2409; b = 93.4517; c = 23.3585; d = 0.023517; e = 0.023656; f = 0.0047036$$

$$\text{Kh}_{\text{CO}_2} = \exp (a + b * (100/T) + c * \log(T/100) + (d - e * (T/100) + f * (T/100)^2) * S)$$

$$\text{CO}_{2_aqi} = \text{CO}_{2i} / 100 * \text{Kh}_{\text{CO}_2}$$

The amount of each dissolved inorganic carbon (DIC) phase dissolved in water were estimated as:

$$m\text{DIC} = \text{CO}_{2_aqi}$$

$$m\text{HCO}_3 = (K2 * m\text{DIC}) / (H + K2)$$

$$m\text{CO}_3 = m\text{DIC} - m\text{HCO}_3$$

$$f\text{HCO}_3 = m\text{HCO}_3 / m\text{DIC}$$

$$f\text{CO}_3 = m\text{CO}_3 / m\text{DIC}$$

$$\epsilon_{\text{DIS}} = f\text{HCO}_3 * \text{HCO}_{3_{\text{CO}_2}} + f\text{CO}_3 * \text{H}_2\text{CO}_{3_{\text{CO}_2}}$$

Once ϵ_{DIS} was obtained for each sample, we rearranged eq. 1 to obtained **f**.

$$\mathbf{f} = \mathbf{EXP}[(\delta^{13}\text{C-CO}_2 - \delta^{13}\text{C-CO}_{2i}) / \epsilon_{\text{DIS}}]$$

Since **f** is the fraction of CO_2 remaining in the reservoir, the fraction of CO_2 dissolved = **1-**

f (Table 1, chapter 3).

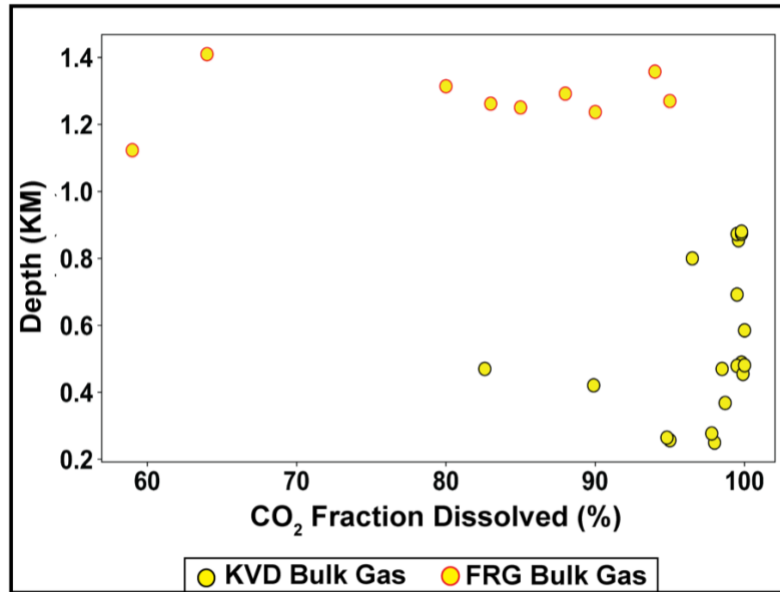


Fig. F.1: Fraction of CO₂ loss by dissolution vs stratigraphic depth of each reservoir at Kevin Dome, northwest MT USA and Ferguson Field, southern AB Canada (described in chapter 3).