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STABLE ISOTOPES OF HYDROTHERMAL CARBONATE MINERALS IN THE BUTTE PORPHYRY-LODE DEPOSITS, MONTANA

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STABLE ISOTOPES OF HYDROTHERMAL CARBONATE MINERALS IN THE BUTTE PORPHYRY-LODE DEPOSITS, MONTANA

by
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requirements for the degree of

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Abstract

The stable isotopic compositions of over 90 hydrothermal carbonate minerals in the Butte porphyry-lode system were analyzed. These samples came from the underground workings as well as the active Continental Pit area. Most material came from polymetallic “Main Stage” veins which post-date the porphyry Cu-Mo mineralization of Butte. Some samples from late calcite-stellerite veins were also included in the study. Rhodochrosite $\delta^{13}C$ and $\delta^{18}O$ values range from -8.3 to -2.9‰ (average of -6.7±1.0‰) and -1.8 to 12.8‰ (average of 3.6 ±3.4‰) respectively, while calcite $\delta^{13}C$ and $\delta^{18}O$ values range from -9.0 to -2.6‰ (average of -5.4 ± 1.5‰) and -4.4 to 12.3‰ (average of 6.2±2.8‰) respectively. These values are in agreement with the previous work of Garlick and Epstein (1966). Despite the strong ore-mineral zonation of the Main Stage veins of Butte, no systematic changes in stable isotope composition of carbonate minerals are seen across the district, or with depth. Late calcite samples have similar isotopic composition to carbonate minerals from Main Stage mineralization. Some isotopic re-equilibration with a lower temperature fluid may have taken place, with calcite more susceptible to isotopic resetting compared to less soluble and more abundant rhodochrosite. Based on the observed $\delta^{18}O$ values of rhodochrosite, and an inferred temperature of formation of Main Stage veins of 200 to 350°C, the vein forming fluids would have had $\delta^{18}O$ values in the range of -12.6 to 4.1, which suggests mixing of magmatic water with an evolved meteoric water. The stable isotopic composition of vein carbonates from Butte have similar $\delta^{13}C$ but different $\delta^{18}O$ values compared to the vein carbonate minerals from the nearby Coeur d’Alene district, Idaho. Whereas the two world-class silver-base metal mining districts may have inherited a similar carbon source, the much heavier $\delta^{18}O$ values of Coeur d’Alene carbonate suggest involvement of metamorphic fluids, as opposed to the porphyry-meteoric fluids that mineralized the veins of Butte.

Keywords: Butte, porphyry copper, stable isotope, calcite, rhodochrosite, oxygen isotope, carbon isotope

Dedication

To my Dad and Amie, thank you for allowing me to live in your house, its solitude supported many nights of studying. To my Mom, thank you for always allowing me to bug you with Excel questions these last two years, I know there were a lot of them, but your help was always appreciated. Finally, to my fiancée Hannah, thank you for always helping me get a break when studying got to be too much, whether it was going to Philipsburg for pizza and beer or a weekend at Yellowstone in the winter, you helped make grad school that much easier.

Acknowledgements

I’d like to thank my thesis committee, Chris Gammons, Diane Wolfgram, Waleed Alrawashdeh, and Steve Parker. Special thanks to my advisor, Chris Gammons, for guiding my research and helping me through the thesis writing process, along with the countless amounts of edits this took. Thank you to Montana Resources for allowing me to collect samples from the Continental Pit which allowed me coverage of the entire Butte district, as well as covering the cost of sample analysis. In addition, I’d like to thank Steve Czehura for looking over the geology section and providing the updated production data for the Butte district. I would also like to thank Simon Poulson from the University of Nevada – Reno for the additional stable isotope work he provided, as well as Gary Wyss of Montana Tech for allowing me to use his lab equipment and providing me the opportunity to work in his lab whenever I could. I would also like to thank Jon Szarkowski for collecting the XRF data on the mineral samples. Finally, my time at Montana Tech was made much more affordable with the assistance of the Gary L. Grauberger Scholarship and the Geological Engineering Department Scholarship; I am very thankful for these contributions towards my tuition and my career.

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1. Introduction

1.1. Thesis Objectives

The focus of this thesis was to collect the carbonate minerals calcite and rhodochrosite from around the Butte district and analyze the stable isotopic composition of their carbon and oxygen. Similar work had been performed previously and concluded there were no obvious correlations between isotopic values. However, the previous study (Garlick and Epstein, 1966) only looked at 12 samples of carbonate material. This thesis project collected over 90 samples, and it was expected that more stable isotope information might reveal trends that were previously missed.

The stable oxygen and carbon isotopic composition of the carbonate minerals are compared to see if any relationships exist between them. The isotopic values are also compared to depth within the deposit as well as across the district to determine if any relationships exist spatially. Isotopic fractionation factors are applied to the oxygen isotopes of rhodochrosite to estimate the isotopic composition of the fluids that formed the carbonate minerals. Overall, this work adds more information about the carbonate mineralization in Butte. Finally, the results of this study are compared to previous work on carbonate mineral isotopes from the Ag-rich polymetallic vein deposits of the Coeur d'Alene mining district, Idaho.

1.2. Butte Mining History

Mineral exploitation in Butte has gone through several stages, each overlapping the previous. Gold was first noticed in placer gravels in Butte in 1864 and was mined through 1867, with a production value estimated at $1,500,000 (Weed, 1912). The presence of silver had been noted, but had not been thought especially valuable until the discovery of the rich ore shoot of the Travona mine in 1865 (Weed, 1912). Most silver mining ceased around 1892 when the mines were hit hard by the price of silver, though the Lexington produced through 1896 because it also carried veins of copper (Weed, 1912). By 1885 Butte had become a copper mining district, and has remained so to this day.

Mining of the Berkeley Pit commenced in 1955 with the extraction of supergene ore, although underground copper mining continued until the mid-1970's. Mining of the Berkeley halted in 1982 when the smelters would no longer accept the ore due to the amount of arsenic present. Montana Resources commenced mining of the Continental Pit in 1986 by recovering concentrates of copper and molybdenum (Czehura, 2006). Mining has been continuous to the present day, aside from a 3-year hiatus in 2000-2003 due to low metal prices.

Total production from the Butte district over the last 130 years is summarized in Table I (Steve Czehura, pers. communication). Over 24 billion pounds of copper have been produced during operations in Butte. In terms of copper produced and resource remaining, Butte is the largest porphyry copper deposit in the United States (Long et al., 1998).

Table I: Total production in the Butte district through 2014.

Production 1880 - 2004	Butte District	Montana Resources 1986 - 12/31/2014
Copper (lbs.)	22,127,800,000	1,967,700,000
Zinc (lbs.)	4,909,000,000	-
Manganese (lbs.)	3,703,000,000	-
Lead (lbs.)	855,000,000	-
Molybdenum (lbs.)	195,000,000	240,400,00
Silver (oz.)	715,000,000	18,000,000
Gold (oz.)	2,920,000	300

1.3. Regional Geology

The Butte mining district is located in the southern part of the Boulder Batholith, a large igneous intrusive complex located in southwestern Montana. The dominant rock type in the Boulder Batholith is the Butte Granite. This rock, formerly termed the Butte Quartz Monzonite, was renamed by the U.S. Geological Survey (Lund et al., 2002; du Bray et al., 2009) as a granite, based on Streckeisen's (1976) updated classification of igneous rocks which is now accepted by the International Union of Geological Scientists (IUGS). The Butte Granite has been dated to 74.5 ± 0.9 Ma (Lund et al. 2002). Most of the rock is a medium-grained granite containing up to 20% biotite and hornblende, although large masses of aplite and pegmatite are locally present and are believed to be roughly the same age. The Boulder Batholith intruded through the Belt-Purcell Supergroup, a very thick sequence of mid-Proterozoic sediments (Fig. 1). The batholith is overlain by - and in places intrudes into - the Elkhorn Mountains Volcanics, considered to be the extrusive equivalent of the various plutonic rocks in the batholith itself (Fig. 2). To the immediate west and north of the Butte district lie outcrops of the Eocene Lowland Creek Volcanics. These volcanic rocks, mainly rhyolite in composition, post-date and cross-cut the important vein mineralization in Butte.

1.4. Butte Mineralization

The world-class ore bodies of Butte have been extensively researched for over 100 years, and it is beyond the scope of this thesis to review the literature on this topic. Some classic early papers include Weed (1912) and Sales (1914). Reno Sales and Chuck Meyer conducted much of

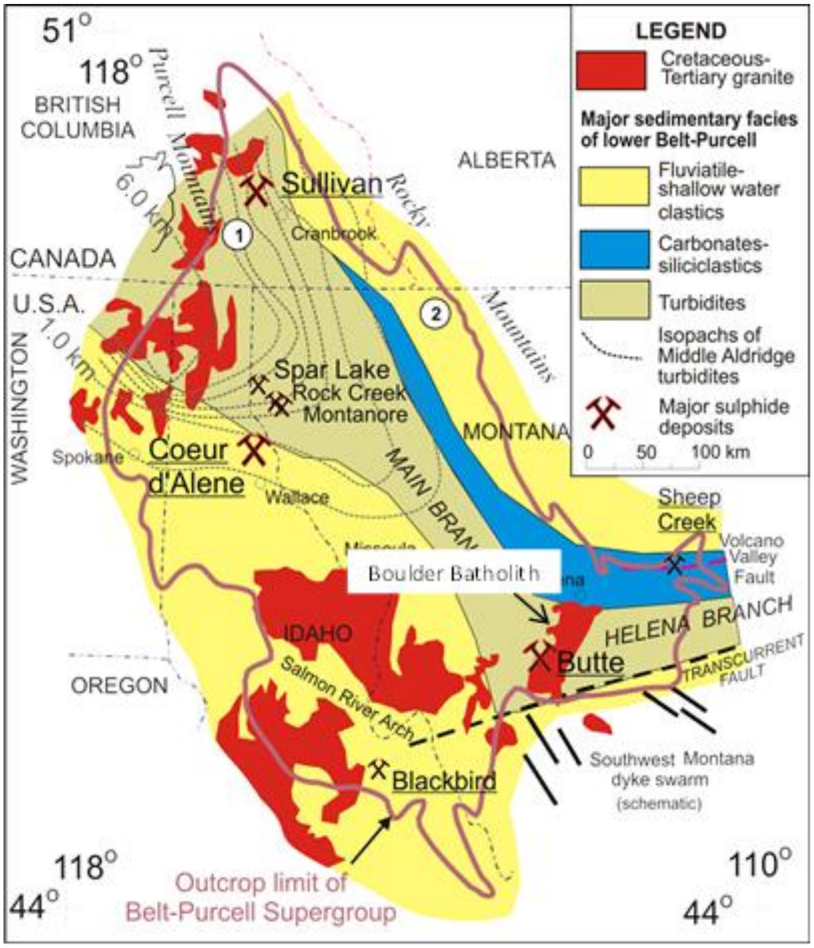

Figure 1: Location of the Boulder Batholith and Butte relative to the Belt-Purcell Supergroup (Modified from Lydon, 2007)

the research on Butte in the mid-1900s, with many landmark papers (e.g., Sales and Meyer, 1948; Meyer et al., 1968). More recent papers on Butte incorporating modern concepts of stable isotopes, ore fluid geochemistry, and fluid inclusion research include Sheppard and Taylor (1974), Brimhall (1977, 1979, 1980), Field et al. (2005), Rusk et al. (2008a, 2008b), Houston and Dilles (2013), and Reed et al. (2013). In modern ore deposit nomenclature, Butte is classified as a porphyry-lode deposit, with low-grade porphyry Cu-Mo mineralization overprinted by much higher-grade, steeply-dipping, “Cordilleran-style” veins and lodes that are strongly zoned with respect to their mineral and metal content. Previous workers refer to the earlier porphyry-style mineralization as the pre-Main Stage event, and the later veins and lodes as the Main Stage event.

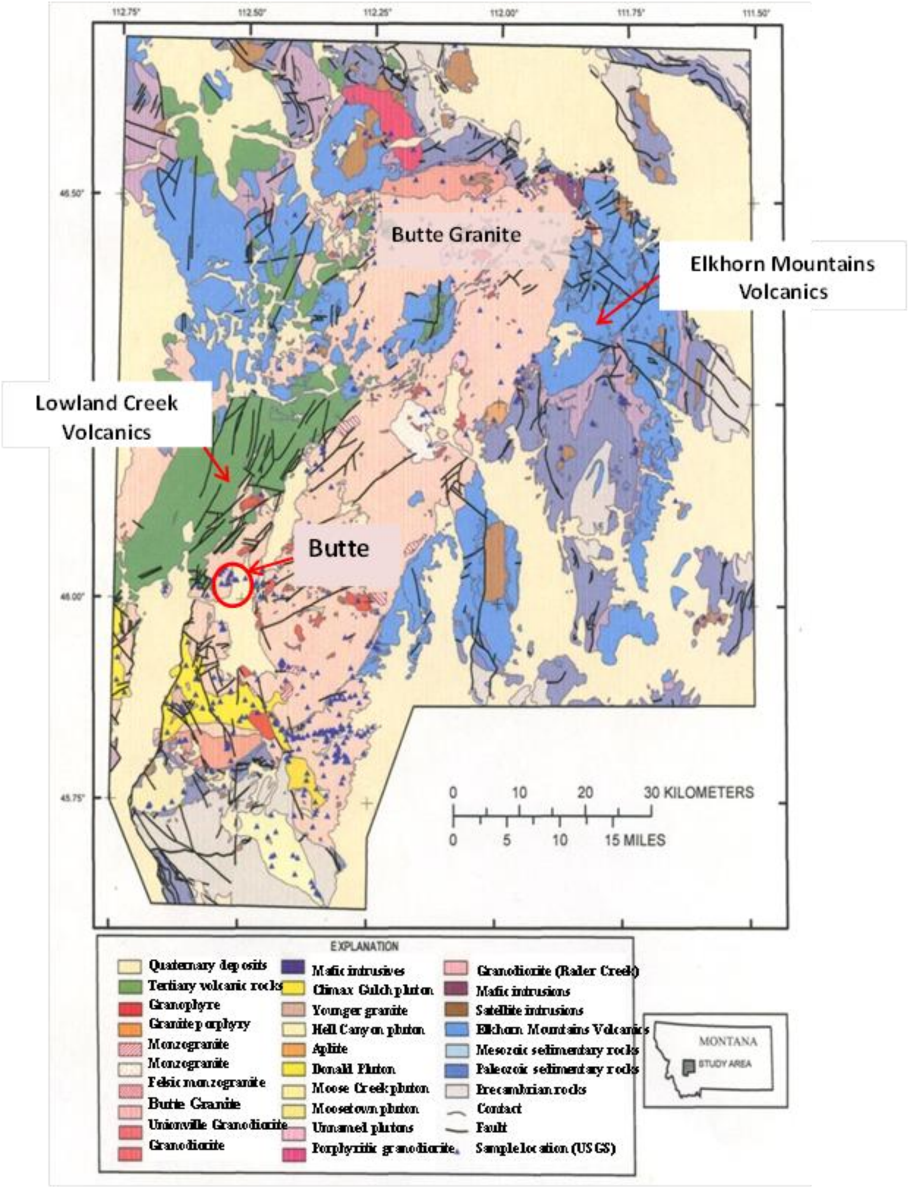

Figure 2:Geologic map showing the extent of the Butte Granite
and other plutons of the Boulder Batholith in relation to the Elkhorn Mountain and Lowland Creek volcanic rocks (du Bray et al., 2009).

The pre-Main Stage veinlets are typically composed of quartz-sulfide and are narrow in size, ranging from a few millimeters to a few centimeters. These veinlets have potassic to sericitic alteration and are similar to porphyry Cu mineralization from other deposits worldwide (Rusk et al., 2008a). The intrusion of numerous quartz porphyry dikes may have created the fractures necessary for the mineralizing fluids to travel along, which resulted in the formation of the pre-Main Stage veinlets (Brimhall, 1977). More importantly, the quartz-porphyry intrusions are thought to be the source of the metal-rich magmatic fluids that mineralized the Butte district (Brimhall, 1977). These quartz-porphyry dikes have been dated to 66 ± 1Ma which places a maximum age for the pre-Main Stage mineralization, and is only 8.5Ma years younger than the Butte Granite (Lund et al., 2002). The porphyry style mineralization forms two broad domes, the Anaconda and Pittsmont Domes (Fig. 3), which are defined by the presence of low-grade copper and molybdenum mineralization and disseminated magnetite (Field et al., 2005). Based on fluid inclusion data, Rusk et al. (2008a) concluded that the pre-Main stage mineralization at Butte occurred at considerable depth (>6km), making Butte one of the deeper porphyry-copper deposits that have been studied extensively.

The Main Stage veins and lodes cut the pre-Main Stage mineralization, and were the result of later hydrothermal fluids that deposited a significant amount of base-metal sulfide. Main Stage veins/lodes are typically large, with some being over 25m wide and spanning up to 3.5km across the district as well as 1.5km deep (Meyer et al., 1968; Rusk et al. 2008a,b). The Main Stage mineralization event displays concentric metal zones, first identified by Sales (1914), termed the central, intermediate, and peripheral zones (Figure 3). The central zone contains a “high sulfidation” (e.g., Einaudi et al., 2003) mineral assemblage rich in Cu-As, including

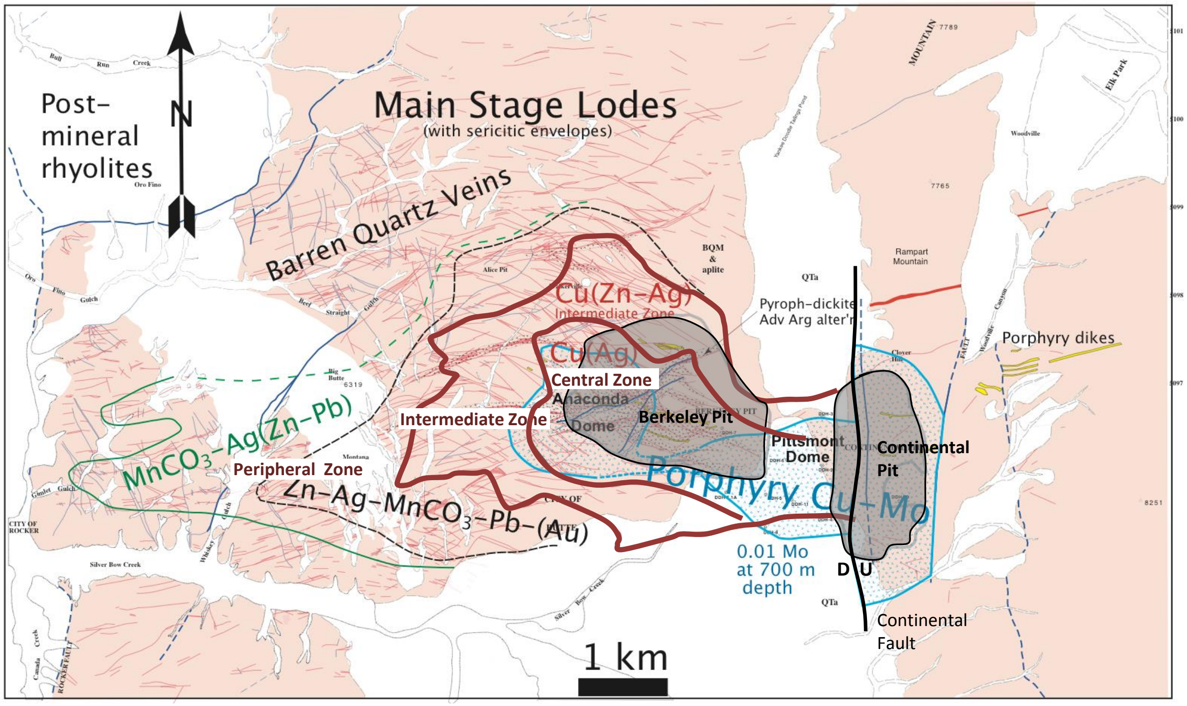

Figure 3: Simplified geologic map of the Butte district
The map (after Dilles, 2004) shows approximate boundaries between the peripheral, intermediate, and central zones (bold brown), and the relationship between Main Stage veins (thin red lines) and earlier porphyry.

enargite, chalcocite, covellite, bornite, and pyrite. The intermediate zone is also rich in copper, but with an “intermediate sulfidation” assemblage (Einaudi et al., 2003) of chalcopyrite, bornite, and tennantite (instead of enargite), as well as sphalerite. The peripheral zone contains very little copper ore, and instead is rich in sphalerite and galena, with minor but economically important quantities of silver-bearing sulfides and sulfosalts. Gangue minerals in the Main Stage veins are also zoned, with quartz being dominant in the central and intermediate zones, and carbonate minerals (especially rhodochrosite, but including calcite and ankerite) being more abundant towards the peripheral zone.

To the east of the Berkeley Pit lies the Continental Pit (Figure 3), another open pit mining complex. The ore of the Continental Pit consists of sulfides (pyrite, chalcopyrite, molybdenite, minor sphalerite) disseminated in weakly altered granite and within vein swarms (Peet, 2010). Main Stage veins with higher concentrations of sphalerite, galena, and Cu-sulfide minerals are present within the Continental Pit but are typically less than 1 m in thickness and are not a major source of ore (Czehura, 2006). Calcite and rhodochrosite are locally present in these Main Stage veins, and calcite also occurs as late veinlets with stellerite (Peet 2010, Lamsma 2012). Lying between the Berkeley and Continental Pit areas is the Continental Fault, dipping to the west at 75 degrees with an offset in excess of 3500 vertical feet (Czehura, 2006). The Continental Fault makes it possible to examine deeper (Continental Pit) and shallower (Berkeley Pit) expressions of porphyry mineralization in close proximity.

1.5. Background: Isotope Geochemistry

Isotopes are atoms of a particular element with the same number of protons but a different number of neutrons. There are two different types of isotopes, radioactive isotopes and stable isotopes. Radioactive isotopes undergo radioactive decay, and have a range of half-lifes, from fractions of a second to billions of years. Stable isotopes are unlike radioactive isotopes in that they do not experience radioactive decay. Because of their difference in mass, stable isotopes of the same element react at different rates in many chemical and physical processes, which results in isotopic fractionation (e.g., Clark and Fritz, 1997). Isotopic fractionation can be an “equilibrium” process or a “kinetic” process, depending on whether the reaction is easily reversible (e.g., exchange of isotopes between dissolved CO_2 and HCO_3^-), or is irreversible (e.g., many redox reactions at low temperature, such as oxidation of methane to CO_2).

The extent of fractionation in stable isotopes is usually very small, with variations in isotopic ratios typically seen in the fourth or fifth decimal place (Clark and Fritz, 1997). For this reason, isotopic ratios are typically reported in “per mil” (‰) or parts per thousand. These ratios, represented by delta (δ), represent the ratio of heavy isotopes to light isotopes in the sample over the same ratio of a standard material.

$$\delta^{18}O_{sample} = \left[\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{standard}} - 1 \right] x\ 1000\ ‰$$

There are two standard materials used for comparison of isotopic ratios in the oxygen and carbon systems, VSMOW and VPDB. VSMOW stands for Vienna Standard Mean Ocean Water and is the isotopic standard used for hydrogen and oxygen in water and in most minerals. VPDB stands for Vienna Pee Dee Belemnite and is a common isotopic standard for carbon. In the isotopic analysis of carbonate minerals, $\delta^{13}C$ and $\delta^{18}O$ are often measured at the same time and are reported relative to the mutual VPDB standard. However, it is common practice to convert measurements in units of $\delta^{18}O$-VPDB to units of $\delta^{18}O$-VSMOW when reporting isotopic data for carbonate minerals (Clark and Fritz, 1997).

1.6. Previous Studies of Stable Isotopes of Hydrothermal Carbonate Minerals

Since the early 1960's, there have been thousands of papers on the application of stable isotopes to the study of hydrothermal ore deposits, of which probably several hundred have looked at either C- or O-isotopes (or both) of carbonate minerals. Despite the importance of the Butte mining district, and in contrast to the large number of papers on S-isotopes of hydrothermal sulfides from Butte (Field et al., 2005, and references therein), there has been little previous work on C- or O-isotopes of the associated carbonate minerals. Garlick and Epstein (1966) conducted the only previous study, and their sample suite was limited to three calcite and nine rhodochrosite specimens from the following mines: Travona, Emma, High Ore, Steward, Badger, and Mountain Con. Their samples represented Main Stage mineralization from the central to peripheral zone as well as depth coverage from the 300 to 4500 (foot) levels. Garlick and Epstein (1966) found no trend in $\delta^{13}C$ or $\delta^{18}O$ of carbonate minerals with respect to depth or location within the district, other than the observation that hydrothermal calcites were, on average, a few per mil heavier than rhodochrosites. Based on this limited data set, few conclusions were drawn by Garlick and Epstein with respect to the origin of the hydrothermal carbonates of Butte.

The following is a short list of published stable isotope studies of carbonate minerals from other hydrothermal mining districts. In contrast to Butte, there have been quite a few detailed studies of stable isotopes of carbonate minerals in the famous Coeur d'Alene district of northern Idaho. Eaton et al. (1995) looked at the $\delta^{18}O$ and $\delta^{13}C$ compositions of siderite ($FeCO_3$) in veins and altered wallrock from the Sunshine Mine. They discovered interesting differences between the isotopic composition of wallrock and vein siderites, and also observed systematic differences across individual veins, but did not see clear differences with depth along a single vein. Rosenberg and Larson (2000) examined variations in the isotopic composition of ankerite ($CaFe(CO_3)_2$) in veins across the entire Couer d'Alene district. Both studies (Eaton et al., 1995; Rosenberg and Larson, 2000) determined that vein carbonates from Couer d'Alene are consistently enriched in $\delta^{18}O$, possibly due to equilibration of hydrothermal ore fluids with Belt-aged meta-sedimentary rocks at temperatures in the range of 300-350°C.

Osaki (1973) and Shikazono (1989) looked at the stable isotopic composition of rhodochrosites and calcites from a number of epithermal vein deposits in Japan. Whereas some of the vein-carbonate minerals appear to have inherited their isotopic signature by interaction with wallrocks, others show trends within individual mines that were attributed to other processes, including fractionation during boiling and loss of CO_2 to the vapor phase (Shikazono, 1989).

Because carbonate minerals are typically absent or scarce in porphyry Cu-Mo mineralization, there have been relatively few studies looking at the isotopic composition of carbonates from these deposits. A recent study of Pass et al. (2014) looked at the stable isotopes of hydrothermal calcites of the Mount Polley porphyry system, in British Columbia, Canada. The Mount Polley complex is a silica-undersaturated, alkalic, breccia-hosted porphyry copper and gold deposit. The stable isotope values in the calcites were enriched and not ratios typically associated with precipitation from a magmatic fluid. The authors concluded that the Mount Polley igneous complex most likely assimilated carbonate material from marine limestones in the country rock, and that this isotopically heavy CO_2 found its way into the later hydrothermal fluids that mineralized the porphyry veins. Interestingly, they were able to correlate areas of the deposit with higher grade Cu-Au-Ag mineralization to local reversals in this trend, that is, to $\delta^{13}C$ depletion in the associated carbonate minerals.

Another recent study by Catchpole et al. (2015) examined stable isotopes in hydrothermal rhodochrosite, calcite, and ankerite from the porphyry-related base-metal lode deposits of Morococha, Peru. This deposit shares many similarities to Butte, including a district-wide zonation from central Cu-rich ore with a high sulfidation mineral assemblage to outer Pb-Zn-Ag ore and abundant carbonates. Among other things, Catchpole et al. (2015) concluded that rhodochrosite from Morococha most likely inherited its CO_2 from a magmatic fluid source, whereas the Ca-rich carbonates appear to have formed by later, lower-temperature circulation of meteoric fluids.

Although the previous summary is just a short introduction to how stable isotopes of carbonate minerals might be used to study hydrothermal metal deposits, it does show the potential of this type of information to lead to new insights into ore-forming processes. This, coupled with the low cost of isotopic analysis with modern instrumentation, was the main motivating factor to undertake the project that became the present study of the isotopic composition of carbonate minerals in Butte.

2. Methods

2.1. Sample Collection

Samples of the carbonate minerals calcite and rhodochrosite from around the Butte district were identified and collected for analysis of their stable isotopic composition. Most of the samples were collected from the Anaconda Mineral Company (AMC) collection or from archived core and surface samples from Montana Resources´ active Continental Pit mine. In addition, a set of 12 samples across a large (50 foot wide) quartz-rhodochrosite-sulfide vein exposed in the Orphan Boy/Orphan Girl mine (100 level) was collected by the author with help from other graduate students.

The AMC collection, housed in a separate building on Montana Tech campus, contains thousands of samples of ore and altered wallrock from the Butte district. Information about each sample, such as the mine name, the depth (level) in the mine, the date and name of the sampler, notes on mineralogy, and the lat-long location, have been compiled and digitized into an Access database that is available on request from the Montana Bureau of Mines and Geology. In this study, it was possible to search for samples in the AMC collection under keywords such as “calcite” and “rhodochrosite”, and then sort the samples by mine or depth. The author then made a list of accession numbers for samples of interest and acquired the samples from the AMC collection warehouse. Most of the samples were photographed and notes were taken as to the ore and gangue mineralogy. After separating out a subsample containing the carbonate minerals of interest, the specimens were returned to the AMC collection.

Figure 4: Example specimens of calcite (left) and rhodochrosite (right).
Both specimens are about two inches across.

Samples acquired from Montana Resources were obtained by examining diamond drill hole core logs for notation of any carbonate minerals and retrieving the core boxes to acquire the samples.

A traverse of a vein rich in rhodochrosite was also performed in the Orphan Girl mine. After accessing the underground workings via the Orphan Boy portal, there is a well exposed Main-Stage vein of quartz, sulfide, and rhodochrosite dipping roughly 40 degrees to the south. A measuring tape was laid down to identify where samples from the vein were obtained. Samples were collected along the vein with hammer and chisel and bagged separately to later separate the carbonate material. Twelve samples in total were collected across the vein.

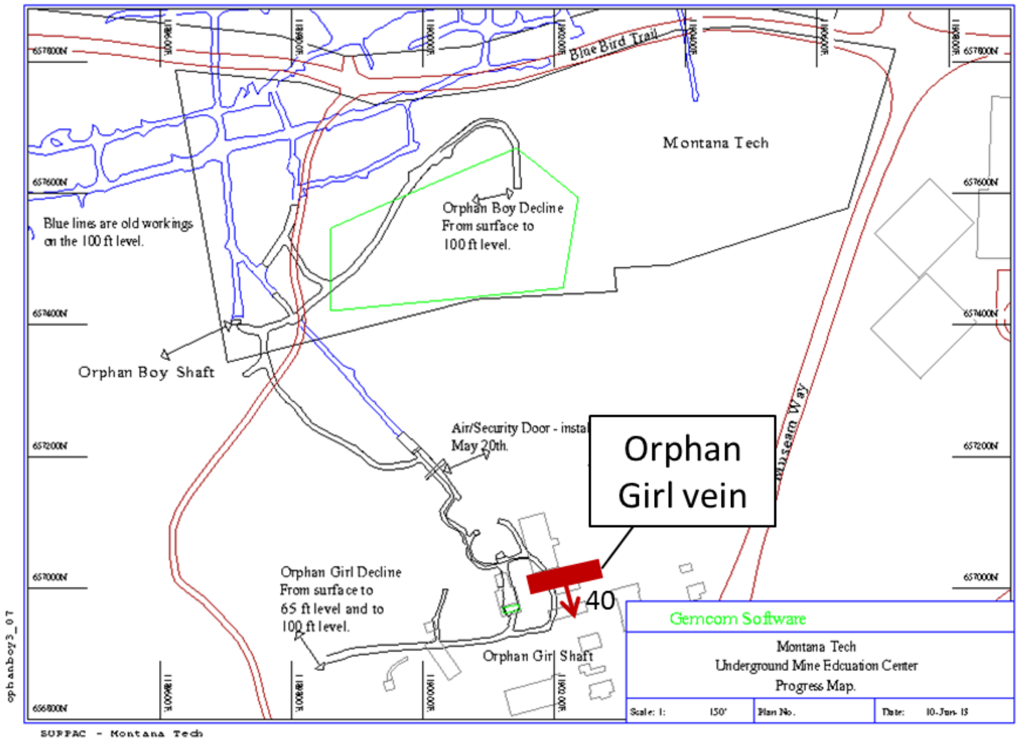

Figure 5: Location of the Orphan Girl vein

Figure 6: Rhodochrosite in the Orphan Girl vein

2.2. Sample Preparation

Mineral samples were ground to a fine, micron-sized powder using a ring and puck pulverizer in the laboratory of the Department of Materials and Metallurgical Engineering at Montana Tech. Several grams of powder for each sample were produced, which was transferred to a small glass vial.

Figure 7: Sample preparation

To confirm the mineralogy and to quantify the existence of impurities (e.g., Si, Al, Mg, Fe), all of the samples were scanned with a Niton portable XRF (X-Ray Fluorescence) meter. The samples were then sent off to one of three analytical laboratories for isotopic analysis.

2.3. Stable Isotope Analysis

A total of 86 unique samples were collected and analyzed for their stable isotopic compositions: 54 from the AMC collection, 20 from the Continental Pit area, and 12 from a traverse of a rhodochrosite vein in the Orphan Girl mine. All of the samples from the AMC collection and Continental Pit were analyzed for $\delta^{13}C$ and $\delta^{18}O$ of mineral carbonate by the Stable Isotope Facility (SIF) at the University of Wyoming, Laramie, WY. This lab was selected because of the low cost of the analyses, bearing in mind that the thesis project was minimally funded. The samples from the Orphan Girl traverse were analyzed for $\delta^{13}C$ using the new Picarro C-isotope analyzer at Montana Tech, which is located in the Montana Bureau of Mines and Geology (MBMG) analytical laboratory. As a cross-check on the accuracy of the SIF results, a subset of samples submitted and returned from the SIF were also analyzed for $\delta^{13}C$ on the Montana Tech Picarro instrument. Because this cross-check raised some questions (see Results section 3.1), the same subset of samples was sent to yet another lab, the stable isotope laboratory of Dr. Simon Poulson at the University of Nevada-Reno. Analytical procedures for each of these laboratories are outlined below. All of the original mineral-powder samples were returned to Montana Tech on request, and are in the possession of Dr. C. Gammons in case further petrographic or isotopic work is warranted.

2.3.1. University of Wyoming

^{13}C and ^{18}O-stable isotope analyses performed at the SIF at the University of Wyoming used a Thermo Gasbench coupled to a Thermo Delta Plus XL Isotope Ratio Mass Spectrometer (IRMS). The following text provides additional details, and was taken verbatim from the SIF website (http://www.uwyo.edu/sif/):

> *"The $^{13}C/^{12}C$ composition of carbonates is determined by acidification of the sample with 99.99% phosphoric acid. The method uses 12 mL headspace vials as the vessel for acidification in conjunction with a gas chromatograph, which is coupled to an isotope ratio mass spectrometer in continuous flow mode. The head space vials containing the samples are flushed with helium. After flushing, 100μL of the phosphoric acid is injected into each vial. The samples are placed on the bench top at room*

> *temperature and allowed to react for 24 hours. After the reaction is complete, a sample of the headspace air is injected onto the gas chromatograph column for gas separation and isotopic analysis. Quality assurance of carbon and oxygen isotope composition of carbonates is based on the standard uncertainty of the known value of the secondary laboratory reference material calculated on multiple analyses. For carbon isotope composition, if the standard uncertainty is greater than 0.15‰, the unknowns are re-analyzed (until the 2-sigma expanded standard uncertainty of the result is better than 0.3‰). The carbon isotopic composition is reported in per mil relative to VPDB scale such that NBS 18 calcite, NBS19 TS-limestone, and LSVEC lithium carbonate, respectively are -5.01‰, +1.95‰, and -46.6‰. For oxygen isotope ratio composition, if the standard uncertainty is greater than 0.2‰, the unknowns are re-*analyzed (until the 2-*sigma expanded standard uncertainty of the result is better than 0.4‰). The oxygen isotopic composition is reported in per mil relative to VPDB scale such that NBS 18 calcite, NBS19 TS-limestone, and LSVEC lithium carbonate, respectively are -23.2‰, -2.2‰, and -26.7‰."*

Figure 8, also taken from the SIF website, gives a schematic of the apparatus used at the SIF for the isotopic determinations.

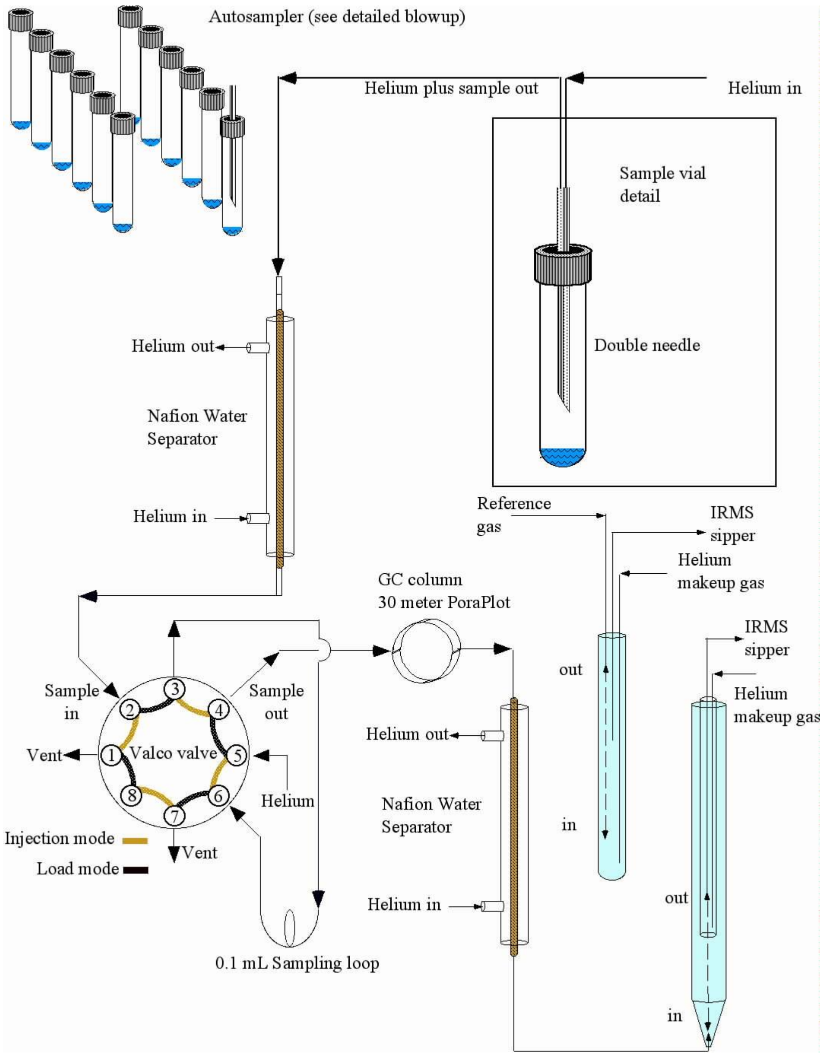

Figure 8: Diagram of sampling technique employed by the GC-IRMS facility at the University of Wyoming (from http://www.uwyo.edu/sif/).

2.3.2. Montana Tech

Carbon stable-isotope analyses of solid samples (e.g., calcite, rhodochrosite) at Montana Tech were performed by Dr. Stephen Parker, and used a Picarro G2131-i CRDS (cavity ring-down spectrometer) analyzer with a Costech combustion module (CM-CRDS).

Figure 9: Carbon isotope analyzer at the MBMG

Between 1 and 4 mg of solid was weighed into a tin (elemental Sn) cup used for the combustion analysis and the cup was crimped closed. The autosampler for the CM instrument drops the sealed tin cup into a reactor chamber at 980ºC in the presence of a stream of O_2. The CO_2 produced by the combustion or decomposition of the solid is carried by a stream of UHP-N_2 into the CRDS cavity for $\delta^{13}C$ determination based on IR absorbance of the CO_2. Carbon isotopic analysis was calibrated using the standards USGS 40 (glutamic acid, $\delta^{13}C$= -26.39), USGS 41 (enriched glutamic acid, $\delta^{13}C$=+37.63), NBS 18 (Calcite, $\delta^{13}C$=-5.014) and CH-6 (sucrose, $\delta^{13}C$=-10.449). Sample analysis includes a standard bracketing every 10 samples. All isotope values were corrected based on a linear relationship between the CRDS reported value and the standard. The slopes for these calibrations were generally close to 1 (e.g., 0.98 to 1.01) with small offset correction (See Figure 10). All isotope values are reported in units of per mil (‰) in the usual δ-notation versus VPDB for carbon. Replicate analyses indicated a relative error of ± 0.05‰ for $\delta^{13}C$ of solid samples.

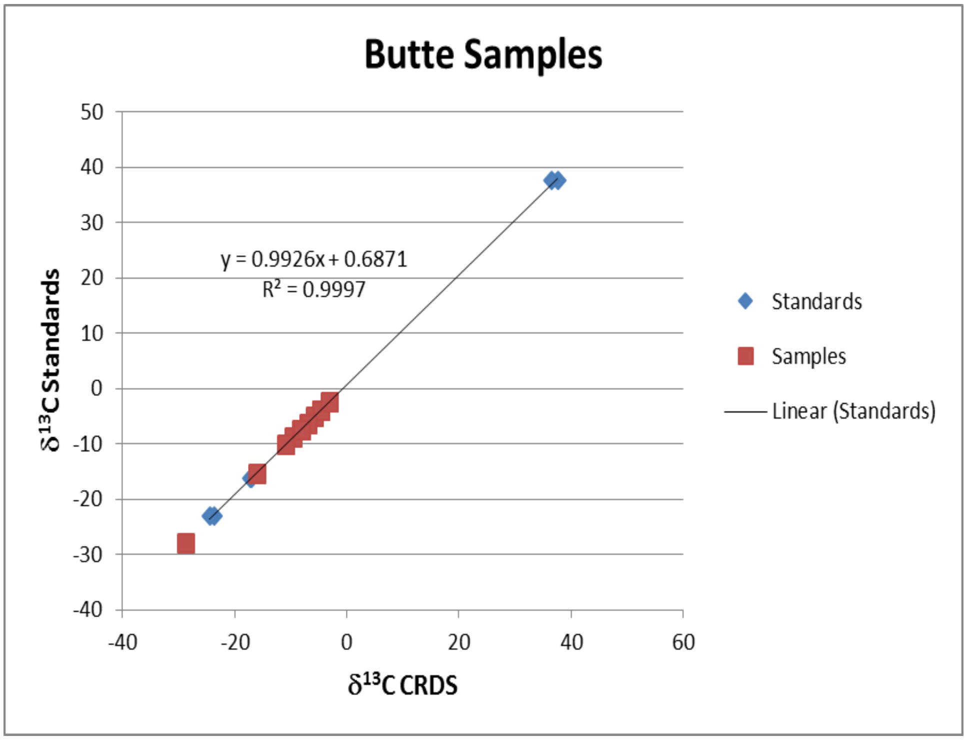

Figure 10: CRDS Standard calibration curve, with samples

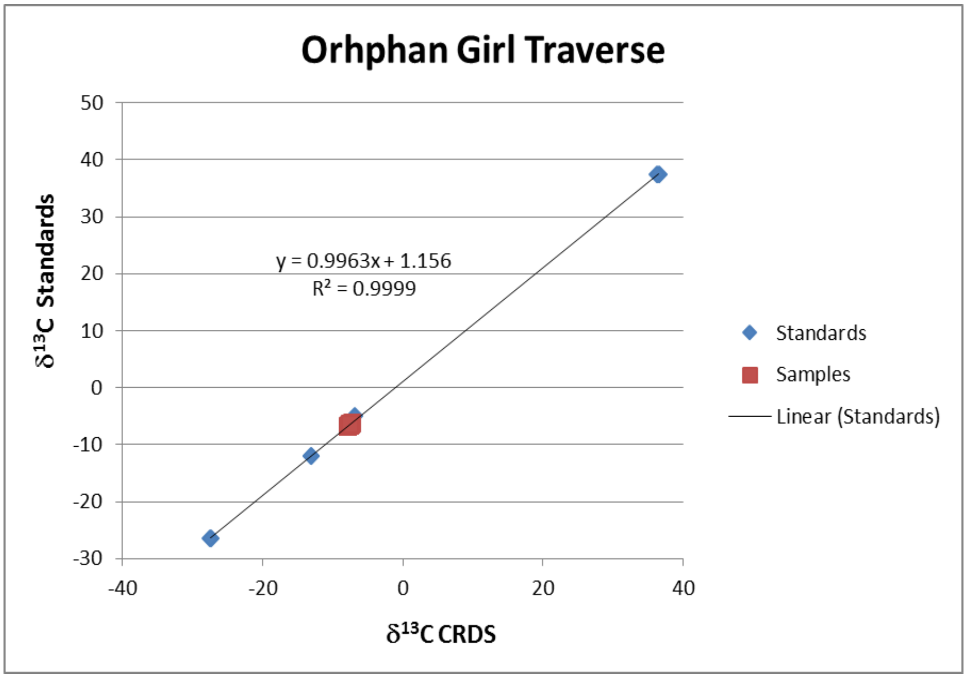

Figure 11: CRDS Standard calibration curve, with Orphan Girl samples

2.3.3. University of Nevada-Reno

Stable isotope analyses of selected samples were performed at the University of Nevada–Reno using a dual inlet Micromass IsoPrime stable isotope ratio mass spectrometer. Sample analyses were performed using the phosphoric acid reaction method of McCrea (1950), except that the reaction was performed at 90°C. Estimated analytical uncertainties are ±0.2‰ for $\delta^{13}C$ and ±0.2‰ for $\delta^{18}O$.

2.4. Unit Conventions and Conversions

All stable C-isotope analyses in this study are reported in the same units as those reported by the labs, i.e., in ‰ relative to the VPDB standard. For $\delta^{18}O$, the data reported in the lab in ‰ relative to VPDB were converted to VSMOW in the following manner: $\delta^{18}O$ (VSMOW) = $\delta^{18}O$ (VPDB) ·1.03091 + 30.91 ‰ (Clark and Fritz 1997).

3. Results

3.1. Results from U-Wyoming SIF lab

Table I summarizes the results for all stable isotope analyses performed at the University of Wyoming Stable Isotope Facility. In Figure 1, the stable isotope results for carbon and oxygen are plotted against each other to see if there are any relationships between values. From the initial comparison of the values, there does not appear to be any obvious trends, other than the observation that calcite is, on average, about 2 ‰ heavier in both $\delta^{18}O$ and $\delta^{13}C$ compared to rhodochrosite. The average and standard deviation in $\delta^{18}O$ and $\delta^{13}C$ for all rhodochrosite samples is 3.6 ± 3.4‰ and -6.7 ± 1.2‰, respectively, and the total range in the same parameters is -1.8 to 12.8‰ and -8.3 to -2.9‰, respectively (see Table II). This compares to an average and standard deviation of 6.2 ± 2.8‰ and -5.4 ± 1.5‰ for $\delta^{18}O$ and $\delta^{13}C$ of calcite, and a total range of -4.4 to 12.3‰ and -9.0 to -2.6‰, respectively. A calcite standard of known $\delta^{13}C$ composition (-16.26‰ VPDB) was analyzed twice at the U-Wyoming lab and returned a value of 16.6‰ VPDB on both occasions.

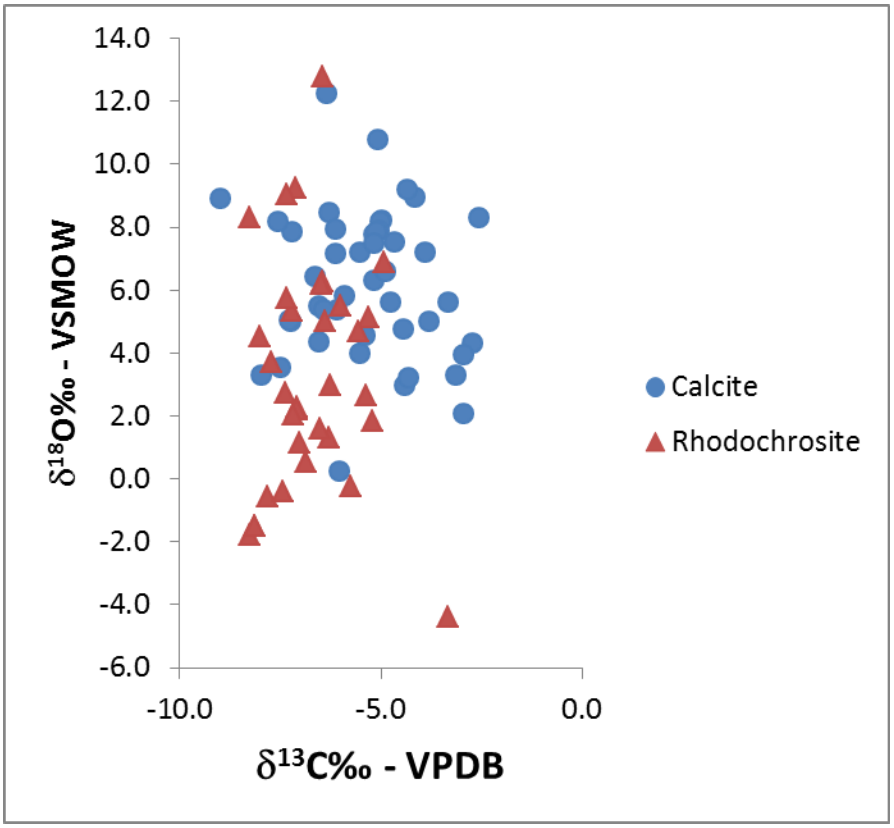

Figure 12: Plot of δ^{13}C vs δ^{18}O for all carbonate mineral samples

Table II: Stable isotope results (U-Wyoming lab)

Mine	Anaconda Accession ID	Mineral	Mine Level	δ^{13}C - VPDB	δ^{18}O - VPDB	δ^{18}O - VSMOW
Anselmo	3087	Calcite	2101	-5.0	-22.0	8.2
	3087	Calcite-dup	2101	-5.0	-22.0	8.2
	975	Rhodochrosite	1247	-7.1	-21.0	9.2
	1814	Rhodochrosite	2100	-8.1	-31.4	-1.5
Badger	990	Calcite	not listed	-8.0	-26.8	3.3
	3091	Calcite	2475	-5.1	-19.5	10.8
	990	Calcite	2802	-7.5	-26.5	3.5
	2040	Calcite	2891	-4.2	-21.3	9.0
	840	Calcite	3059	-6.3	-21.8	8.5
	1601	Calcite	3938	-4.8	-24.5	5.6
	985	Rhodochrosite	3071	-5.2	-28.2	1.8
Belmont	3081	Calcite	not listed	-5.5	-26.1	4.0
	3076	Calcite	3833	-5.5	-23.0	7.2

	868	Rhodochrosite	3559	-7.8	-30.5	-0.6
	1108	Rhodochrosite	3625	-8.0	-25.6	4.5
	669	Rhodochrosite	3813	-5.4	-27.4	2.7
Black Rock	1783	Rhodochrosite	not listed	-7.0	-28.9	1.2
Continental Pit		Calcite	*407	-6.6	-24.7	5.5
		Calcite	*415	-7.2	-22.4	7.9
*samples with asterisks reflect depth in a diamond drill hole		Calcite	*520	-6.4	-24.8	5.4
		Calcite-dup	*520	-6.1	-24.8	5.4
		Calcite	*597	-6.5	-25.8	4.3
		Calcite	*764	-5.2	-23.9	6.3
		Calcite	*806	-5.0	-22.3	7.9
		Calcite	*812	-6.7	-23.7	6.4
		Calcite	*820	-7.2	-25.1	5.0
		Calcite-dup	*820	-7.3	-25.1	5.1
		Calcite	*828	-6.1	-29.8	0.2
		Calcite	*840	-9.0	-21.3	8.9
		Calcite	*981	-5.9	-24.3	5.8
		Calcite	*1145	-4.9	-23.6	6.6
		Calcite	*1217	-2.6	-21.9	8.3
		Calcite	*1225	-6.1	-22.3	7.9
		Calcite	5480 Bench	-6.1	-23.0	7.2
		Calcite	5560 Bench	ND	ND	ND
		Rhodochrosite	*582	-8.3	-21.9	8.3
		Rhodochrosite	*946	-6.3	-28.7	1.3
		Rhodochrosite	5480 Bench	-7.3	-21.2	9.0
		Rhodochrosite	5520 Bench	-6.4	-17.6	12.8
Emma	1003	Rhodochrosite	501	-2.9	-28.0	2.1
	865	Rhodochrosite	1099	-5.2	-22.4	7.8
	702	Rhodochrosite	not listed	-6.5	-28.4	1.6
	1205	Rhodochrosite	492	-7.7	-26.4	3.7
	1003	Rhodochrosite	501	-6.9	-29.5	0.5
	2657	Rhodochrosite	631	-7.2	-24.8	5.3
	860	Rhodochrosite	824	-7.1	-27.8	2.3
	860	Rhodo-dup	824	-7.1	-27.9	2.2
	1434	Rhodochrosite	1000	-7.4	-27.3	2.7
	864	Rhodochrosite	1099	-7.5	-30.4	-0.4
	865	Rhodochrosite	1099	-6.4	-25.1	5.0
Leonard	1371	Calcite	2292	ND	ND	ND
	3176	Calcite	3361	-7.6	-22.0	8.2
	3696	Calcite	3368	-4.7	-22.7	7.5
	1871	Calcite	3381	-5.1	-22.4	7.9

	3707	Calcite	739	-3.3	-34.2	-4.4
Lexington	162	Calcite	272	-6.4	-18.1	12.3
	2473	Calcite	2848	ND	ND	ND
	2510	Rhodochrosite	200	-6.0	-24.6	5.5
Marget Ann	3684	Rhodochrosite	400	-8.3	-31.7	-1.8
Mtn Con	396	Calcite	3017	-5.2	-22.7	7.5
		Calcite	3900	-4.5	-25.4	4.8
	1315	Calcite	4201	-2.7	-25.8	4.3
	4656	Calcite	4219	-3.9	-23.0	7.2
	3793	Calcite	4400	-4.3	-21.0	9.2
	6257	Calcite	4512	-5.4	-25.6	4.6
		Rhodochrosite	3900	-7.3	-24.4	5.8
	6257	Rhodochrosite	4512	-8.1	-31.4	-1.5
Orphan Girl	2245	Calcite	801	-3.3	-24.5	5.6
	1928	Calcite	2802	-3.8	-25.1	5.0
	4906	Rhodochrosite	563	-5.3	-25.0	5.1
	1929	Rhodochrosite	2802	-6.4	-23.9	6.3
	1929	Rhodo-dup	2802	-6.5	-24.0	6.2
Steward	5544	Calcite	4203	-3.0	-26.1	4.0
	5544	Calcite-dup	4203	-3.2	-26.8	3.3
	7154	Calcite	4410	-4.4	-27.1	3.0
	7154	Calcite-dup	4410	-4.3	-26.9	3.2
	3754	Rhodochrosite	3894	-7.2	-28.0	2.1
	1262	Rhodochrosite	4021	-5.7	-30.2	-0.2
Travona	1267	Rhodochrosite	550	-4.9	-23.3	6.9
	1271	Rhodochrosite	550	-5.5	-25.4	4.7
	2597	Rhodochrosite	849	-6.3	-27.1	3.0

*highlighted samples are duplicate samples; ND represents samples where insufficient CO_2 was detected for an isotopic analysis.

Table III: Averages, ranges, and standard deviations for the isotopic measurements of all samples

Mineral	Average $\delta^{13}C$, VPDB	Average $\delta^{18}O$, VSMOW	Range $\delta^{13}C$, VPDB	Range $\delta^{18}O$, VSMOW	Standard Deviation $\delta^{13}C$, VPDB	Standard Deviation $\delta^{18}O$, VSMOW
Calcite	-5.4	6.2	-9.0 to -2.6	-4.4 to 12.3	1.5	2.8
Rhodochrosite	-6.7	3.6	-8.3 to -2.9	-1.8 to 12.8	1.2	3.4

Some samples were split and submitted as separate unknowns. These duplicate samples showed good agreement with each other (Table IV), with a small error between them. The average error was ±0.2 ‰ for both δ^{18}O and δ^{13}C.

Table IV: Average error of field duplicates. Highlighted samples are field duplicates

Mine	Description	Mine Level	δ^{13}C, VPDB	δ^{18}O, VPDB	$\Delta\ \delta^{13}$C	$\Delta\ \delta^{18}$O
Anselmo	Calcite	2101	-5.0	-22.0		
	Duplicate		-5.0	-22.0	0.0	0.0
Continental	Calcite	*520	-6.4	-24.8		
	Duplicate		-6.1	-24.8	0.3	0.0
Continental	Calcite	*820	-6.1	-29.8		
	Duplicate		-6.1	-29.8	0.0	0.0
Emma	Rhodochrosite	824	-7.1	-27.8		
	Duplicate		-7.1	-27.9	0.0	0.1
Orphan Girl	Rhodochrosite	2802	-6.4	-23.9		
	Duplicate		-6.5	-24.0	0.1	0.1
Steward	Calcite	4203	-3.0	-26.1		
	Duplicate		-3.2	-26.8	0.2	0.7
Steward	Calcite	4410	-4.4	-27.1		
	Duplicate		-4.3	-26.9	0.1	0.2
		Average error			±0.2 ‰	±0.2 ‰

Tables V and VI summarize the average and standard deviation values for δ^{13}C and δ^{18}O of calcite and rhodochrosite, respectively, for each mine shaft from which specimens were collected. In some cases only a single specimen was collected from a given mine, in which case the standard deviations could not be computed. The same information is displayed on an aerial photograph of Butte in Figures 12 and 13. The latter figures also include the samples that were collected from the Continental Pit. This gives the reader a better idea of the spatial coverage of sampling in this study. The results are discussed at greater depth in the following chapter.

Table V: Average isotopic values for calcite, organized by mine

Mine	Mineral	N_{samp}	Average δ^{13}C‰, VPDB	Average δ^{18}O‰, VSMOW	StDev δ^{13}C‰, VPDB	StDev δ^{18}O‰, VSMOW
Anselmo	Calcite	2	-5.0	8.2	0.0	0.0
Badger	Calcite	6	-6.0	6.8	1.6	3..1
Belmont	Calcite	2	-5.5	5.6	0.0	2.3
Continental	Calcite	17	-6.2	6.1	1.3	2.0
Emma	Calcite	2	-4.1	4.9	1.6	4.0
Leonard	Calcite	4	-5.8	7.9	1.6	0.3
Lexington	Calcite	2	-6.4	12.3	N/A	N/A
Mtn Con	Calcite	6	-4.3	6.3	1.0	2.0
Orphan Girl	Calcite	2	-3.6	5.3	0.3	0.4
Steward	Calcite	4	-3.7	3.4	0.8	0.4

Table VI: Average isotopic values for rhodochrosite, organized by mine

Mine	Mineral	N_{samp}	Average δ^{13}C‰, VPDB	Average δ^{18}O‰, VSMOW	StDev δ^{13}C‰, VPDB	StDev δ^{18}O‰, VSMOW
Anselmo	Rhodochrosite	2	-7.6	3.9	0.7	7.6
Badger	Rhodochrosite	1	-5.2	1.8	N/A	N/A
Belmont	Rhodochrosite	3	-7.1	2.2	1.5	2.6
Black Rock	Rhodochrosite	1	-7.0	1.2	N/A	N/A
Continental	Rhodochrosite	4	-7.1	7.9	0.9	4.8
Emma	Rhodochrosite	9	-7.1	2.6	0.4	1.9
Leonard	Rhodochrosite	1	-3.3	-4.4	N/A	N/A
Lexington	Rhodochrosite	1	-6.0	5.5	N/A	N/A
Marget Ann	Rhodochrosite	1	-8.3	-1.8	N/A	N/A
Mtn Con	Rhodochrosite	2	-7.7	2.1	0.6	5.1
Orphan Girl	Rhodochrosite	3	-6.1	5.9	0.7	0.7
Steward	Rhodochrosite	2	-6.5	0.9	1.0	1.6
Travona	Rhodochrosite	3	-5.6	4.9	0.7	2.0

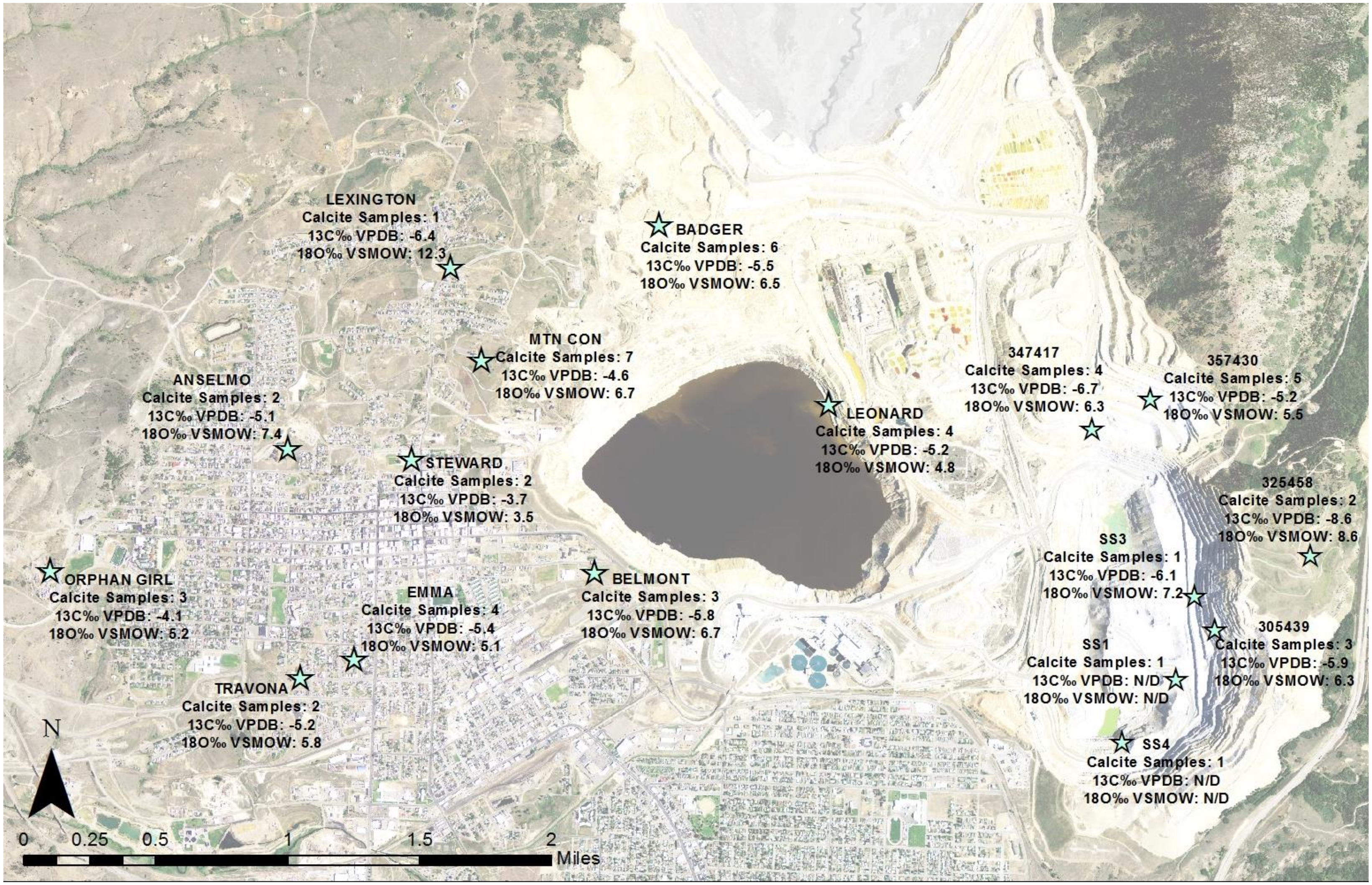

Figure 13: Map of calcite samples, with average isotopic ratios shown

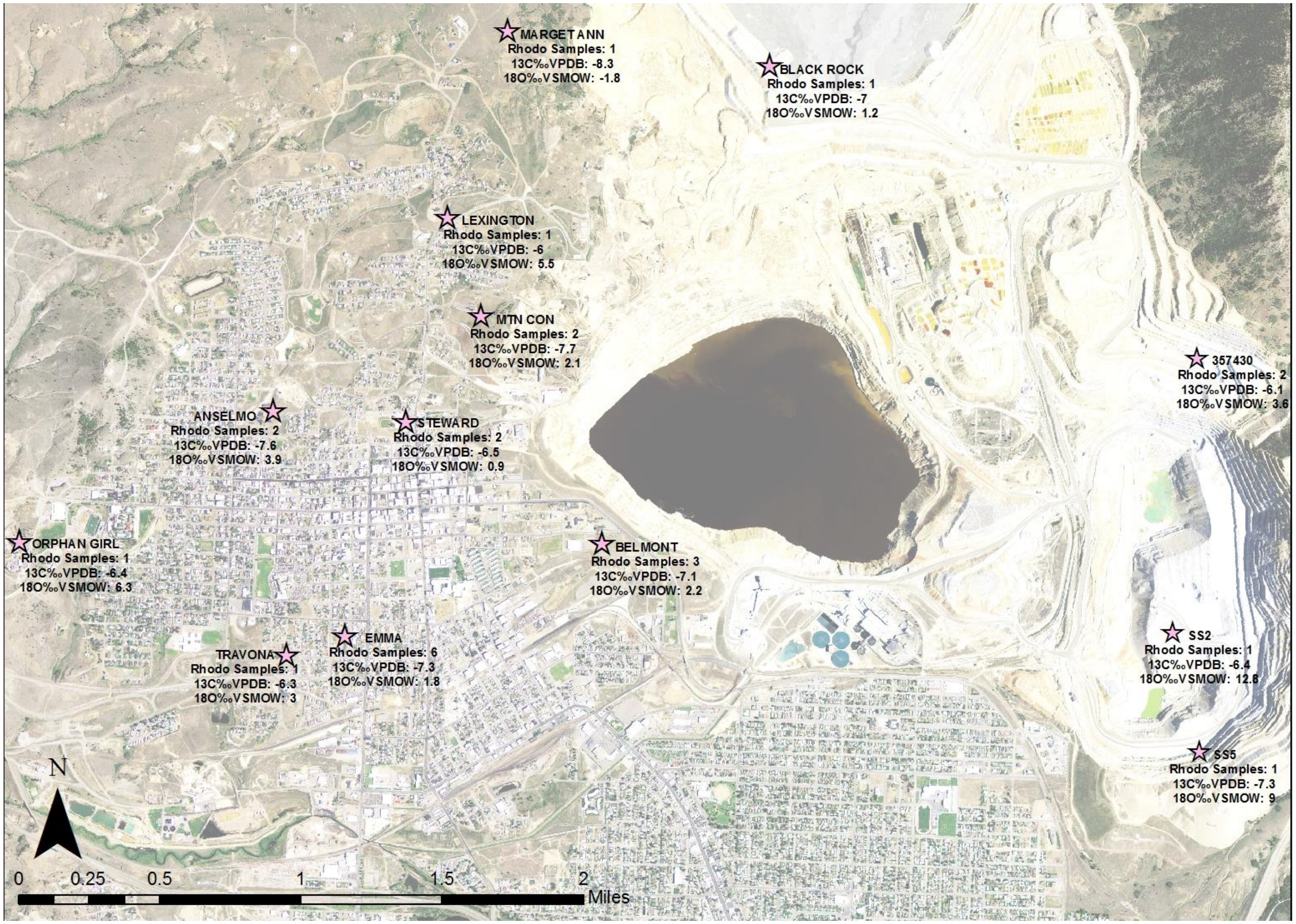

Figure 14: Map of rhodochrosite samples with average isotopic ratios show

3.2. Results from Montana Tech lab

Tables VII and VIII summarize samples run at the Montana Tech lab using the Picarro G2131-i CRDS. This device used a different analysis technique than the other two laboratories which may have volatilized any trace organic carbon present and could have contributed to some of the disagreements between values.

Table VII: C-isotope analyses performed at Montana Tech

Mine	Level	Mineral	δ^{13}C corrected ‰ VPDB
Anselmo	1247	Rhodochrosite	-7.5
Badger	2802	Calcite	(-10.1)*
Belmont	3813	Rhodochrosite	-5.1
Emma	824	Rhodochrosite	-8.8
Lexington	2848	Calcite	(-28.0)*
Mountain Con	4201	Calcite	-4.0
Mountain Con	4201	Calcite	-3.9
Mountain Con	4400	Calcite	-2.4
Continental Pit	5480 Bench	Calcite	(-15.3)*
Continental Pit	5480 Bench	Calcite	-7.3
Continental Pit	5520 Bench	Rhodochrosite	-6.2

*Low CO_2 yield, results may not be accurate

Table VIII: Orphan Girl vein traverse $\delta^{13}C$ values

Mine	Level	Distance from Footwall, feet	$\delta^{13}C$ corrected VPDB ‰
Orphan	100	1	-6.2
Girl	"	5	-6.7
Vein	"	10	-6.4
traverse	"	17	-6.8
	"	20	-6.5
	"	25	-6.3
	"	27	-6.4
	"	30	-6.3
	"	32	-6.4
	"	35	-6.2
	"	38	-6.2
	"	40	-6.4

3.3. Comparison of Data from Different Labs

Several samples were run at three different laboratories, each using different methods, with the data summarized in Table IX. For the two samples that were nearly pure carbonate separates (Anselmo 1247 and Belmont 3813), the agreement between the labs was very good for $\delta^{13}C$ and $\delta^{18}O$, within the analytical errors. However, the agreement in $\delta^{13}C$ between the Montana Tech and UW labs was not good for the other 3 samples. The two samples from Mountain Con had a low % carbonate in the powdered sample, which caused a “below detect” error for the UNR lab, and also a caution from the UW lab. It is likely, then, that the source of error for those two samples was a poor purity of the carbonate mineral separate. The source of error for the Emma 824 sample is not known.

Table IX: Differences between lab $\delta^{13}C$ values, ND indicates no data

Mine	Level	Mineral	MTech $\delta^{13}C$ VPDB	UW $\delta^{13}C$ VPDB	UNR $\delta^{13}C$ VPDB	UW $\delta^{18}O$ VPDB	UNR $\delta^{18}O$ VPDB
Anselmo	1247	Rhodochrosite	-7.5	-7.1	-7.0	-21.0	-20.9
Belmont	3813	Rhodochrosite	-5.1	-5.4	-5.2	-27.4	-27.1
Emma	824	Rhodochrosite	-8.8	-7.1	not run	-27.8	not run
Mtn Con	4201	Calcite	-3.9	-2.7	ND	-25.8	ND
Mtn Con	4400	Calcite	-2.4	-4.3	ND	-21.0	ND

4. DISCUSSION

4.1. Comparison with Previous Work

The first study to look at the stable isotopic composition of carbonate minerals in Butte was that of Garlick and Epstein (1966). Though their sample size was small, 3 calcites and 9 rhodochrosites, they came to the conclusion that there were no obvious correlations between the $\delta^{13}C$ and $\delta^{18}O$ ratios. From Figure 15, it can be see that the data of Garlick and Epstein overlap with the data from this study, and therefore will be included in all of the following figures.

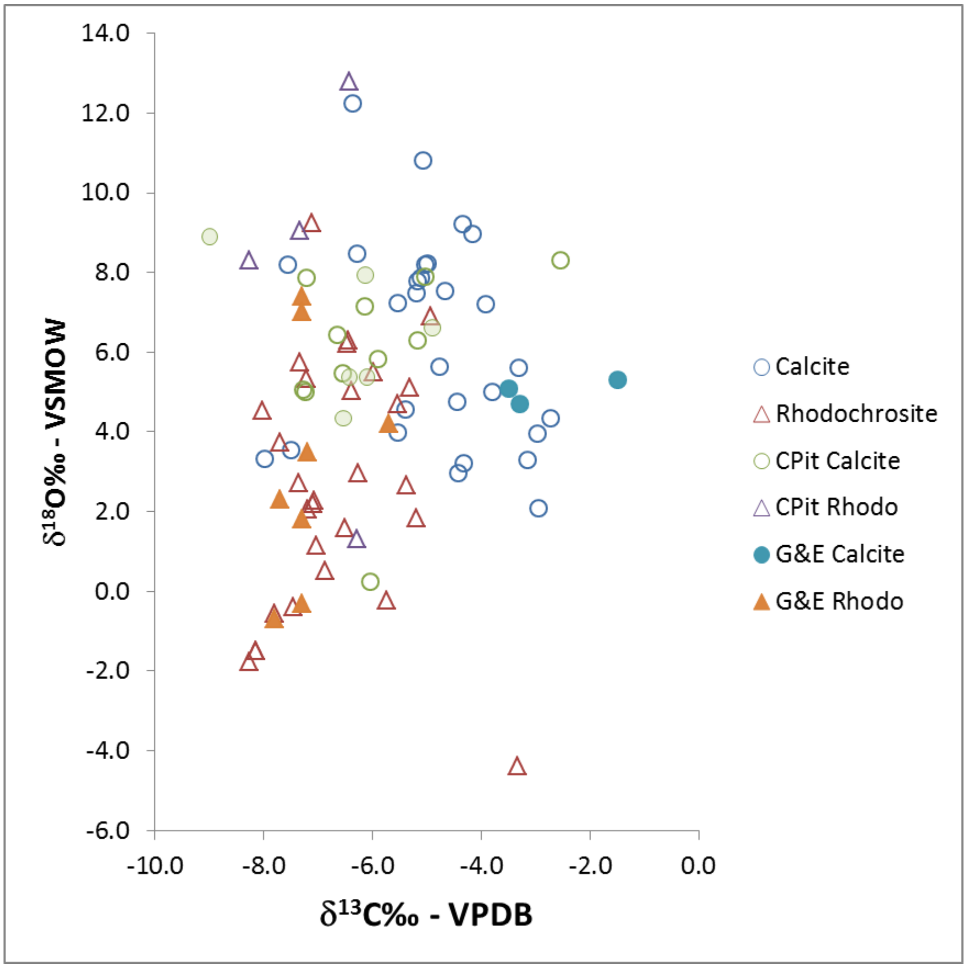

Figure 15: $\delta^{13}C$ vs $\delta^{18}O$ for the Butte district, with data from Garlick and Epstein, shaded Continental Pit calcite markers denote association with stellerite.

4.2. Stable Isotope Trends

4.2.1. Calcite vs. Rhodochrosite

Table X shows that the stable isotope data for the calcite and rhodochrosite has some overlap. To test whether the data for the two carbonate minerals are statistically different, a two-sample t-test was used. This test is based on comparison of the means of the $\delta^{13}C$ and $\delta^{18}O$ values for calcite and for rhodochrosite. When comparing the two sets of data, a "small" P-value indicates a significant difference in the means, where "small" is typically $P < 0.05$, the smaller the P-value the stronger the evidence of a statistical difference.

Table X: Summary of T-test results for calcite vs. rhodochrosite

Carbon	N_{samp}	Mean	Standard Deviation	t Stat	P-value
$\delta^{13}C$-Calcite	45	-5.37	1.5	4.79	3×10^{-6}
$\delta^{13}C$-Rhodochrosite	45	-6.64	1.0		

Oxygen	N_{samp}	Mean	Standard Deviation	t Stat	P-value
$\delta^{18}O$-Calcite	45	6.22	2.4	4.21	3×10^{-5}
$\delta^{18}O$-Rhodochrosite	33	3.31	3.7		

As shown in the last column of the table above, the P-values based on both carbon and oxygen in calcite and rhodochrosite are small enough to be considered significant and confirm that they are statistically different.

4.2.2. Isotopic Differences Between Mines

An examination of the data in Tables VIII and IX and Figures 12 and 13 (Results) shows no systematic differences between the average C- and O-isotopic compositions between each mine, nor with respect to x-y location within the district. This is surprising considering the size of the district as well as the large differences in depth at which each sample was collected. The Continental Pit area, which is an expression of a deeper area of the porphyry system due to 3500 feet of offset from the Continental Fault, was expected to show some difference from the rest of the Butte complex. However, the isotopic values for calcite samples collected in the Continental Pit show no real deviation from the average values in the Butte mine shafts. Rhodochrosite $\delta^{18}O$ values from small Main Stage veins in the Continental Pit are on average heavier than the rest of the Butte area, though this could be an artifact of the small number of samples.

Several calcite samples from the Continental Pit were collected from late veins and veinlets that contained stellerite ($CaAl_2Si_7O_{18}\cdot 7H_2O$), a low temperature hydrothermal mineral which is considered to be late in the paragenetic sequence (Peet, 2010). The coexistence of stellerite with calcite implies that the two minerals formed at similar times and temperatures. However, the isotopic compositions of calcite in the stellerite veins were similar to those collected elsewhere in the Continental Pit. The average values of $\delta^{18}O$ and $\delta^{13}C$ for stellerite-calcite veins were 6.4 ± 1.7 ‰ and -6.5 ± 1.3 ‰, respectively (errors denote 1 standard deviation), which compare with 6.0 ± 2.2 ‰ and -6.0 ± 1.4 ‰, respectively, for the rest of the samples from the Continental Pit. The small differences in the isotopic values between the different stages of calcite fall well within the standard deviations of each data set.

4.2.3. Isotopic Differences With Depth

To examine isotopic trends with depth, the $\delta^{13}C$ and $\delta^{18}O$ values were plotted against the elevation above sea level of each sample. To calculate the elevations for samples from the AMC collection, the reported mine level for each sample was adjusted to the known surface elevation of the top of the shaft, based on a Butte mine database that is available from the MBMG (Ted Duaime, pers. communication). Both $\delta^{13}C$ values for calcite and rhodochrosite appear to have no obvious correlation with depth. The same can be said for $\delta^{18}O$ values as there appears to be no trend with depth.

Boiling that occurs in hydrothermal systems imparts different isotopic signatures based on which fluid the carbonate mineral formed from, such as the trends attributed to boiling in Shikazono (1989). The lack of any trends in the Butte deposit with depth imply that boiling did not occur during the formation of the Main Stage Veins. If boiling were taking place, the values for $\delta^{13}C$ and $\delta^{18}O$ would be heavier towards the surface. The CO_2 that partitions into vapor phase during boiling is depleted in $\delta^{13}C$ and $\delta^{18}O$ and the remaining DIC in the fluid becomes heavier. As the fluid rises, any carbonate minerals precipitated will be heavier in $\delta^{13}C$ and $\delta^{18}O$. If the Butte deposit did experience boiling it is likely that a trend would be apparent with depth in calcite or rhodochrosite. Since there are no trends with depth, it is unlikely that Butte ever experienced boiling. This agrees with the previously published idea that Butte was a deep porphyry-lode deposit that did not undergo large-scale liquid-vapor phase separation (Rusk, 2008a, 2008b).

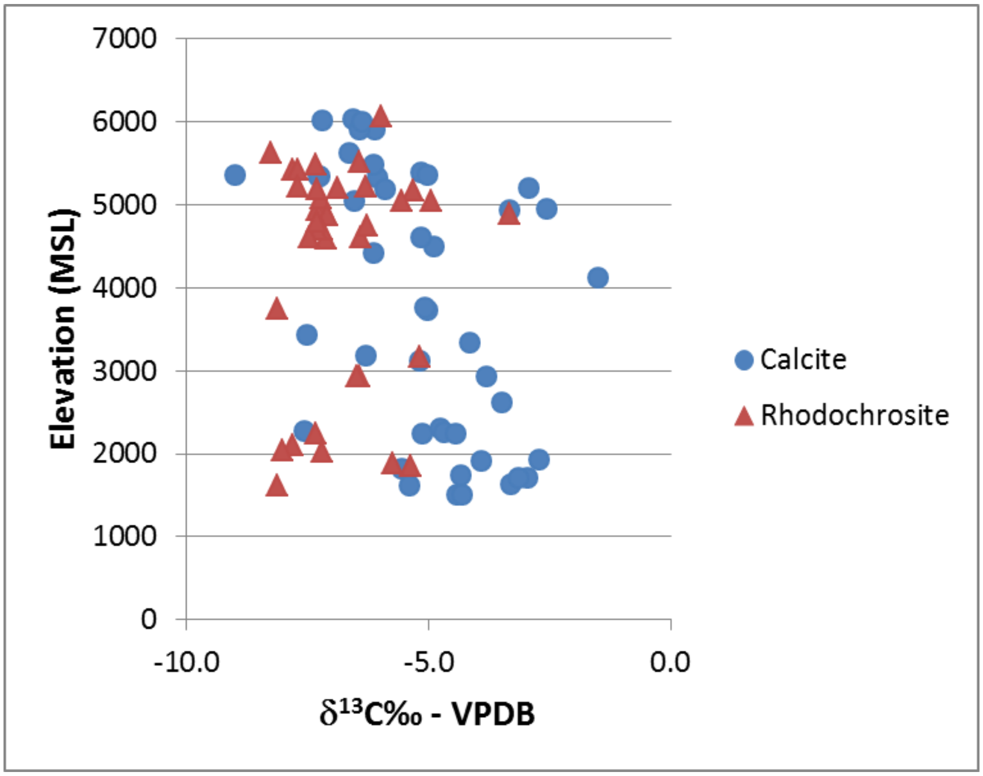

Figure 16: Carbon isotope values vs. elevation

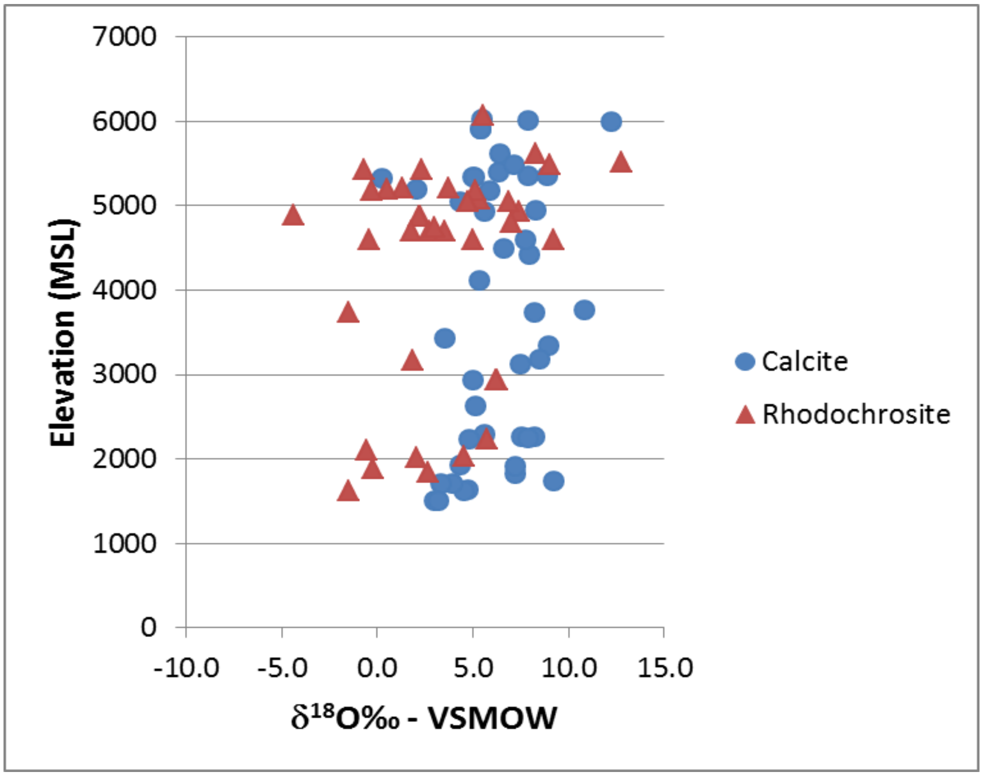

Figure 17: Oxygen isotope values vs. elevation

4.2.4. Isotopic Differences Across a Single Vein

The Orphan Girl mine is located on the western margin of the Butte deposit and is located in the peripheral zone. The 12 samples from the traverse of the Orphan Girl vein (lode) are very similar. Samples closer to the hanging-wall of the vein were more similar in composition while samples near the foot-wall were less similar in composition. Unlike the study of Eaton et al. (1995), which showed systematic differences in δ^{13}C of siderite across a large vein in the Coeur d'Alene district, Idaho, there are no systematic differences in the δ^{13}C composition of rhodochrosite across the Orphan Girl vein.

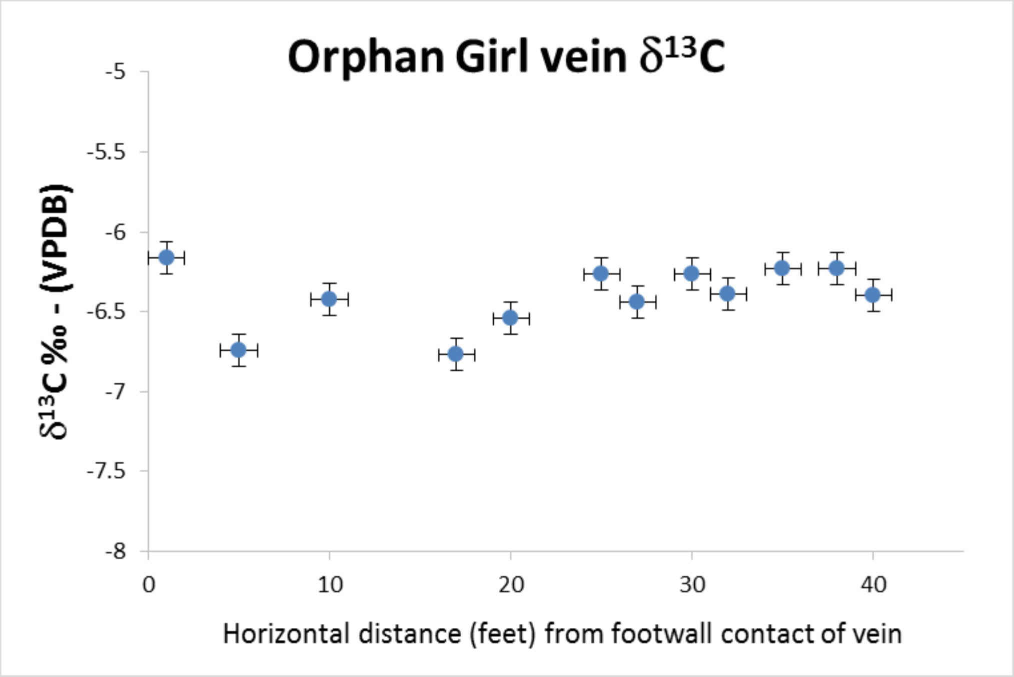

Figure 18: δ^{13}C vs. distance across a large vein in the Orphan Girl mine

4.2.5. Relationship Between Isotopes and Cu/Mo Grades

Continental Pit samples that came from core drilling also had copper and molybdenum grades for the five-foot intervals that the samples came from. The study of Pass et al. (2014) had success correlating high grade mineralization with depletion of δ^{13}C values, so the Continental Pit sample values were plotted against the reported grade for their respective intervals to see if any trends emerged. Samples associated with late veins of stellerite are not included as their formation was not related to any deposition of economic minerals. Grade values cluster near the average value of δ^{13}C and δ^{18}O of the Continental deposit. There appear to be no trends with Cu/Mo grades and the isotopic ratios.

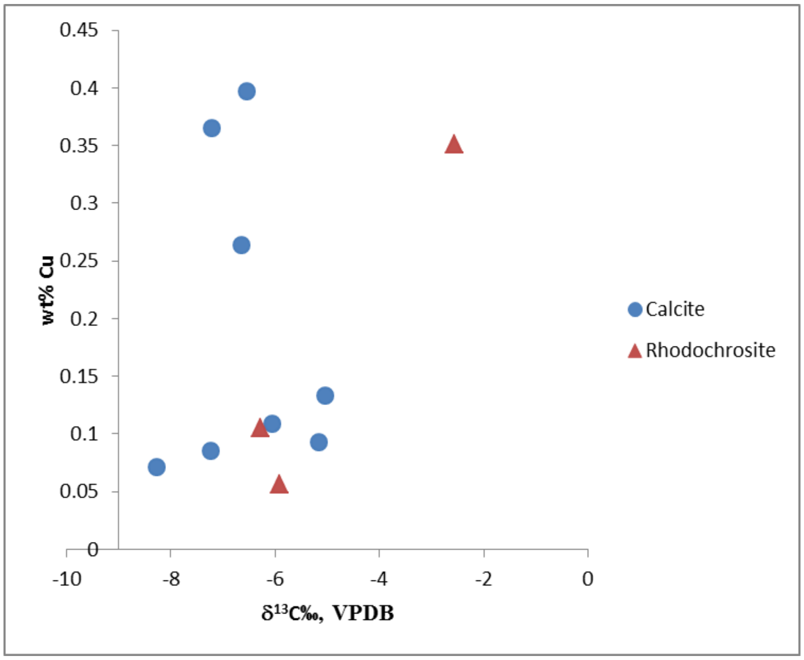

Figure 19: δ^{13}C vs. wt% Cu

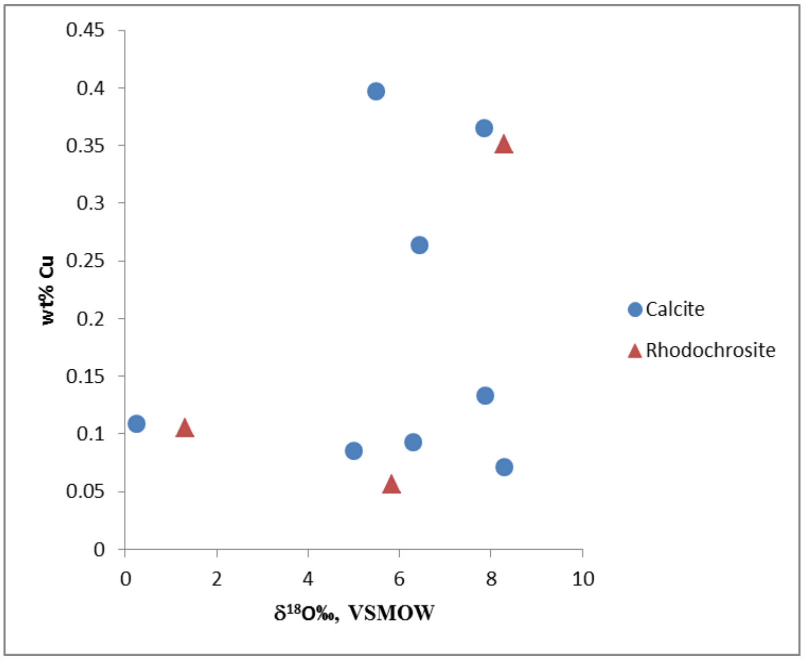

Figure 20: δ^{18}O vs. wt% Cu

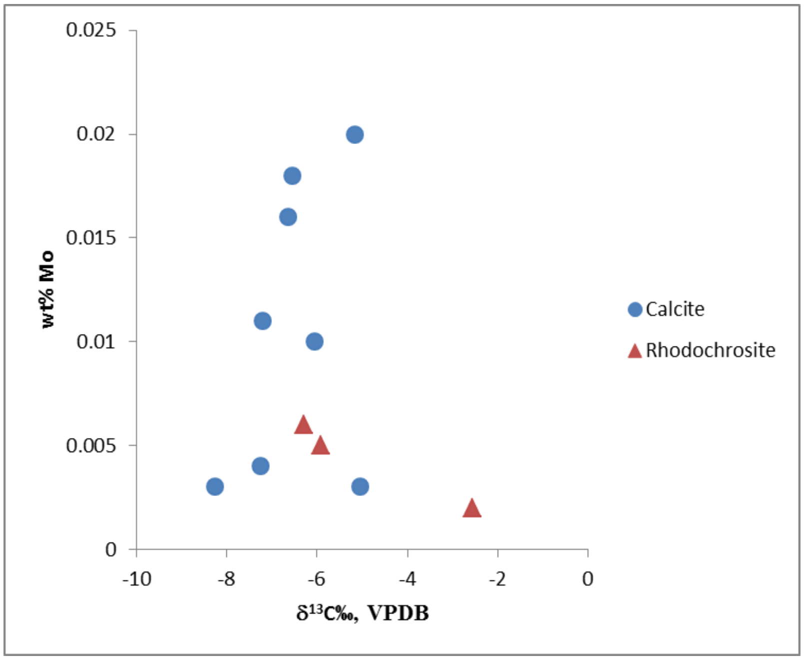

Figure 21: δ^{13}C vs. wt% Mo

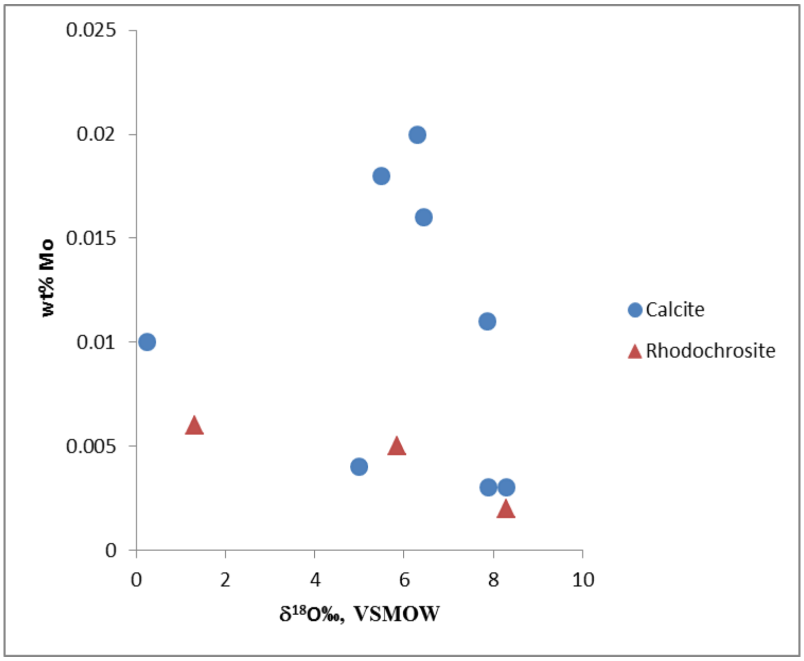

Figure 22: δ^{18}O vs. wt% Mo

4.3. Constraints on Conditions of Ore Formation

4.3.1. Previous Estimates of the Temperature of Main Stage Mineralization at Butte

Rusk et al. (2008b) measured fluid inclusion homogenization temperatures of 220 to 340°C for Main Stage veins from Butte, with higher T_h values in the central zone (near the Berkeley Pit) and lower temperatures in the intermediate and peripheral zones. After applying a 50°C pressure correction, they concluded that Main Stage vein quartz formed in the 250 to 350°C temperature range. These results are in line with S-isotope geothermometry performed by Lange and Cheney (1971), who obtained a range of 260° to 350°C for co-existing pyrite-sphalerite pairs from three samples taken from veins in the peripheral zone. The estimated temperatures are also in agreement with the study of Sheppard and Taylor (1974), who adopted a temperature of 300°C for all Main Stage mineralization, referencing previous work of Meyer et al. (1968) and Lange and Cheney (1971).

4.3.2. Speciation of Dissolved Inorganic Carbon at High Temperature

Figure 23 (adapted from Barnes, 1979), shows the relationship between temperature and pH for several reactions that have relevance to this study. The two dash-dot lines plot the boundary between (muscovite + quartz) and K-feldspar, for two different total dissolved K concentrations. The ore-forming fluids that precipitated Cu-Ag-Pb-Zn were probably weakly acidic (muscovite-stable) to strongly acidic (adv. argillic alteration) (e.g., Meyer et al., 1968). The area shaded yellow shows the possible range of pH and temperature for these fluids, assuming the temperature range of 250 to 350°C of Rusk et al. (2008b). If the carbonates formed at the same time and temperature as the quartz, then this implies a similar pH range, which means that CO_2(aq) would have been the dominant form of dissolved inorganic carbon. It is also possible that some of the carbonates formed at a later time from higher pH fluids. However, the lack of any significant K-spar associated with carbonates suggests that the pH values were still below the Kspar/muscovite limits. Given these temperature and pH considerations it is concluded that the probable form of dissolved carbon in the system was $CO_2(aq)$.

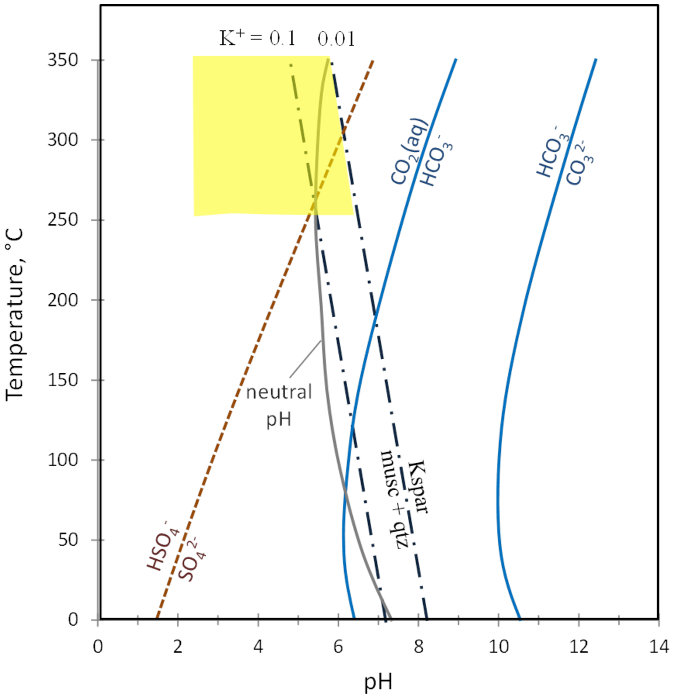

Figure 23: Diagram showing the temperature dependence of several hydrothermal reactions (modified after Barnes, 1979).

4.3.3. Compilation of High-Temperature Isotope Fractionation Factors

Fractionation factors are known isotopic separations between various phases and forms of compounds which vary by temperature. In this study, isotopic fractionations factors at high temperature are used to determine the isotopic composition of the the possible sources of carbon in the Butte district as well as the ore forming fluids. Tables XI and XII, along with Figure 24, summarize the equilibrium fractionation factors (1000 ln α) for isotopic exchange between calcite, rhodochrosite, CO_2, and water, at 25° to 350°C. The sources of data are Zheng (1999), Deines (2004), and Ohmoto and Rye (1979). In the following tables, if a value is (+) and is written "calcite-CO_2", it means that calcite is isotopically heavier than CO_2 and if a value is (-) and is written "calcite-CO_2", it means that calcite is isotopically lighter than CO_2.

Table XI: Oxygen isotopic exchange values at high temperature

T,C	T,K	CO_2-calcite	CO_2-rhodochrosite	calcite-rhodochrosite	calcite-H_2O	rhodochrosite-H_2O
10	283.15	10.6	8.1	2.5	35.3	37.8
25	298.15	10.9	8.6	2.3	31.2	33.5
50	323.15	11.2	9.2	2.0	25.7	27.6
100	373.15	11.1	9.6	1.5	18.0	19.5
150	423.15	10.7	9.5	1.2	13.1	14.3
200	473.15	10.1	9.1	1.0	9.8	10.7
250	523.15	9.4	8.6	0.8	7.5	8.3
300	573.15	8.8	8.1	0.7	5.8	6.5
350	623.15	8.2	7.6	0.6	4.6	5.1

Source of data: Zheng (1999)

Table XII: Carbon isotopic exchange values at high temperature

T,C	T,K	rhodochrosite-CO_2	calcite-rhodochrosite	calcite-CO_2
25	298.15	8.6	1.6	10.2
50	323.15	6.3	1.4	7.8
100	373.15	2.8	1.2	4
150	423.15	0.5	1	1.5
200	473.15	-1	0.9	-0.2
250	523.15	-2	0.8	-1.3
300	573.15	-3	0.7	-2
350	623.15	-3	0.6	-2.4
ref		*b,c*	*b*	*c*

Sources of data: b) Deines 2004 c) Ohmoto and Rye 1979

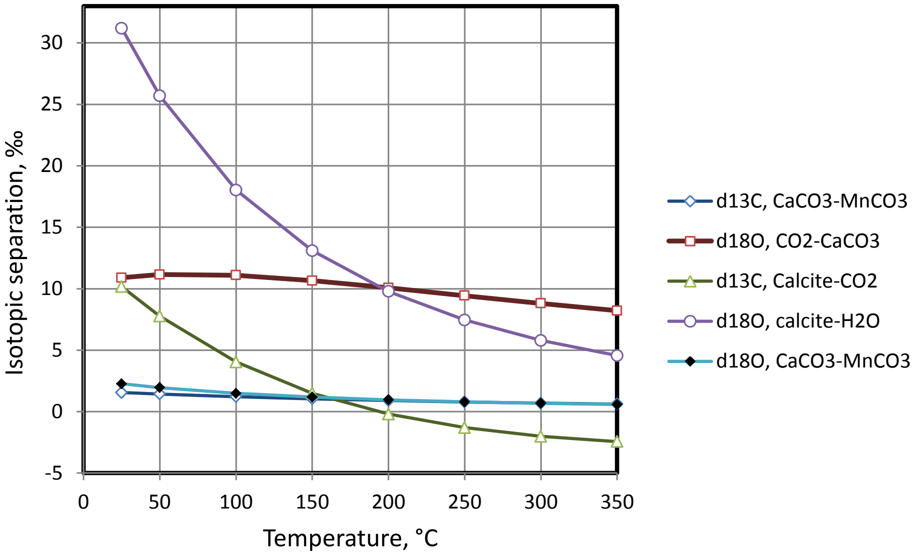

Figure 24: Temperature dependence of isotopic fractionation factors for various reactions. The data come from Tables XI and XII.

4.3.4. Geothermometry Based on the Results of this Study

The consistent 1 to 3‰ isotopic enrichment of $\delta^{18}O$ and $\delta^{13}C$ of calcite relative to rhodochrosite in the veins and lodes of Butte could theoretically be used to estimate the temperature of formation of these minerals. This type of approach is only valid if: 1) the two minerals formed at the same time from the same fluid; 2) isotopic equilibrium was attained during mineral precipitation; and 3) the isotopic compositions were not affected by low-temperature water-rock interaction after the vein formed. In this study, only two specimens were found that had both calcite and rhodochrosite in the same hand sample, coexisting in a way that is consistent with simultaneous precipitation in a vein. These two samples were both from the Mountain Con mine and the isotopic data are summarized in the following table:

Table XIII: Calculated temperatures based on isotope geothermometry

	$\delta^{18}O$, calcite	$\delta^{18}O$, rhodo.	Calculated temperature	$\delta^{13}C$, calcite	$\delta^{13}C$, rhodo.	Calculated temperature
Mtn Con 3900	4.8	5.8	Out of range	-4.5	-7.3	Out of range
Mtn Con 4512	4.6	-1.5	Out of range	-5.4	-8.1	Out of range

To get the "calculated temperature" values in the above table, the data in Tables XI and XII were rearranged to create polynomials that can be solved for temperature, based on the isotopic separation between calcite and rhodochrosite (Figure 25, below).

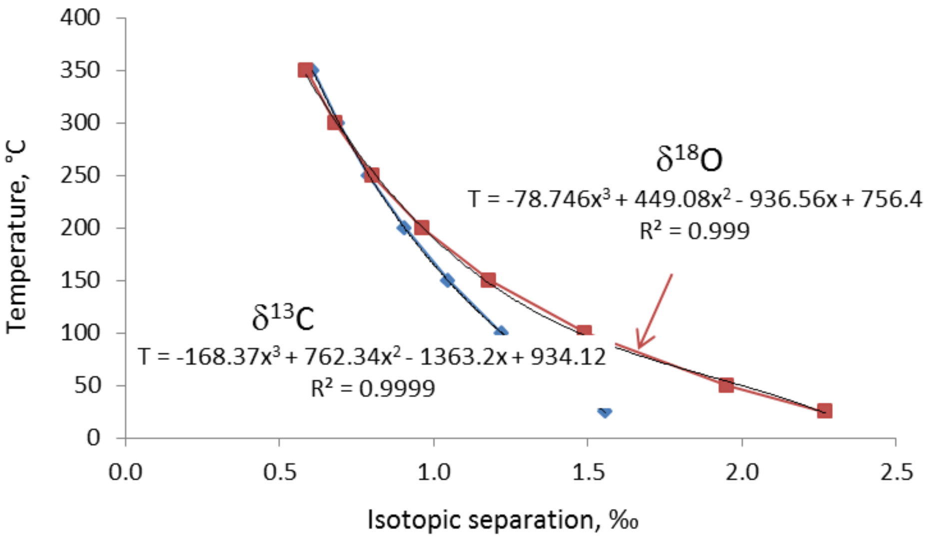

Figure 25: Polynomials used to estimate temperature from the observed isotopic separation values

However, when the polynomial equations in Figure 25 are applied to the actual data from the Mountain Con samples, the estimated temperatures are well out of the range of the equations. Clearly this approach cannot be used to accurately estimate the temperatures of formation of the carbonate minerals. Either the minerals did not form at equilibrium at the same time from the same fluid, or one or both of the minerals were affected by low-temperature isotopic exchange during retrograde fluid-rock interaction.

4.3.5. Isotopic Re-Equilibration at Low Temperature

Previous workers (e.g., Kerrich, 1990) have suggested that hydrothermal carbonate minerals, especially calcite, may have their C- and O- isotopic signatures partly or completely reset by interaction with lower temperature (retrograde) fluids. This is because the kinetics of equilibrium isotope exchange between calcite-O and water-O, or calcite-C and dissolved inorganic carbon, are fairly rapid, even at low temperature (e.g., Clark and Fritz, 1997). The question then becomes whether or not ALL of the minerals in this thesis have been isotopically reset, and whether or not any inferences can be made as to the sources of C or sources of water based on the isotopic data.

The extent of low-temperature isotopic exchange between water (e.g., groundwater) and a given mineral is dependent on temperature, the relative mass of an element (e.g., C, O) in the aqueous and solid phase, and also the solubility and kinetics of dissolution of the mineral into the aqueous phase. For example, because quartz is so insoluble in water and takes > 1000 years to reach equilibrium solubility at low temperature (Brady and Walther, 1990), the O-isotopic composition of hydrothermal quartz cannot be reset by interaction with low temperature waters, even over millions of years. This is not the case for the carbonate minerals of this study, especially for calcite which is much more soluble than rhodochrosite. Based on data in Drever (1997), the solubility products of calcite and rhodochrosite (log scale) at 25°C are -8.48 and -11.43, respectively. In other words, at the same pH and temperature conditions, calcite is about 1000 times more soluble than rhodochrosite. Also, the kinetics of dissolution and precipitation of calcite are faster than those of most other common carbonate minerals, such as dolomite, siderite, or rhodochrosite (Morse and Arvidson, 2002; Pokrovsky and Schott, 2002). Thus, it is likely that any isotopic re-equilibration at low temperature would proceed at a faster rate for calcite vs. rhodochrosite.

Isotopic re-equilibration also depends on the relative masses of C and O in the solids as compared to the groundwater that circulates through the rock. The mineralized rock in Butte contains a huge mass of carbon in the form of rhodochrosite (as well as lesser amounts of calcite) in the Main Stage veins, especially in the Mn-rich veins of the peripheral zone (e.g., Emma, Travona, Orphan Girl) where the lodes of rhodochrosite were up to 10 m thick. In contrast, the groundwaters of Butte contain relatively low concentrations of DIC, typically less than 100 mg/L (< 10 mmol/L) (e.g., Gammons et al., 2009). For this reason, if isotopic exchange occurs between groundwater and rock, it is more likely that the groundwater will see its isotopic signature of DIC adjust to become closer to equilibrium with the rhodochrosite in the veins, and not the other way around. This was one of the conclusions in the study of Gammons et al. (2009), who investigated the geochemistry and stable isotopic composition of dissolved inorganic carbon in the flooded mine workings of Butte.

In the case of oxygen, it is no longer true that the concentration (e.g., moles per unit volume) of O in the rock is much greater than in the water. This is because water is mostly oxygen (by mass). Also, isotopic exchange of O between H_2O and CO_2 is fairly rapid, even at low temperature (Clark and Fritz, 1997). Over 1000’s to millions of years, it is possible that water moving through cracks and veins in the mineralized bedrock could partly reset the O-isotopic composition of the carbonate gangue minerals. Modern day groundwater in Butte has a $\delta^{18}O$ composition of around -18‰ (Gammons et al., 2006). If calcite in veins equilibrated with water of this composition at a temperature near 10°C (the temperature of many groundwaters in the Butte area), the calcite would have a $\delta^{18}O$ value that is about 35‰ heavier, or close to +18‰. Rhodochrosite would be even heavier, at roughly +20.5‰. None of the carbonate minerals in this study had $\delta^{18}O$ over +13‰, suggesting that none of the minerals had their O-isotopic composition completely reset to low temperature values. However, it is possible that the carbonates were *partly* reset by recent groundwater, or by any intermediate-temperature paleowater that passed through the veins in the time between when the veins formed and the present day.

In summary, the likelihood of isotopic re-equilibration is higher for calcite vs. rhodochrosite, based on the fact that calcite is much more soluble than rhodochrosite, and also has faster kinetics of dissolution and precipitation. If either mineral partly re-equilibrated with water at low temperature, its $\delta^{18}O$ value would be shifted to more positive values. This may explain the fact that Butte calcite consistently has heavier $\delta^{18}O$ compared to Butte rhodochrosite. On the other hand, because of the much greater mass of solid carbonate in the veins and lodes compared to DIC in the water, it is less likely that re-equilibration could have shifted the C-isotope signature of the minerals. This is especially true for rhodochrosite, which is both relatively insoluble and extremely abundant in the veins and lodes of Butte. This helps to explain the fact that the total range in $\delta^{13}C$ of the carbonate minerals is much less than the total range in $\delta^{18}O$, and that the range in $\delta^{13}C$-rhodochrosite is less than the range in $\delta^{13}C$-calcite (see Figure 15).

4.3.6. Sources of Carbon for the Carbonate Minerals

Since it is less likely that the $\delta^{13}C$ values have been reset due to re-equilibration, we can speculate what the potential sources of carbon may have been. The average $\delta^{13}C$ values for calcite and rhodochrosite in the Butte deposit are -5.4‰ for calcite and -6.6‰ for rhodochrosite.

Referring to Figure 26, the carbonate minerals from Butte have $\delta^{13}C$ values that overlap with several possible fields.

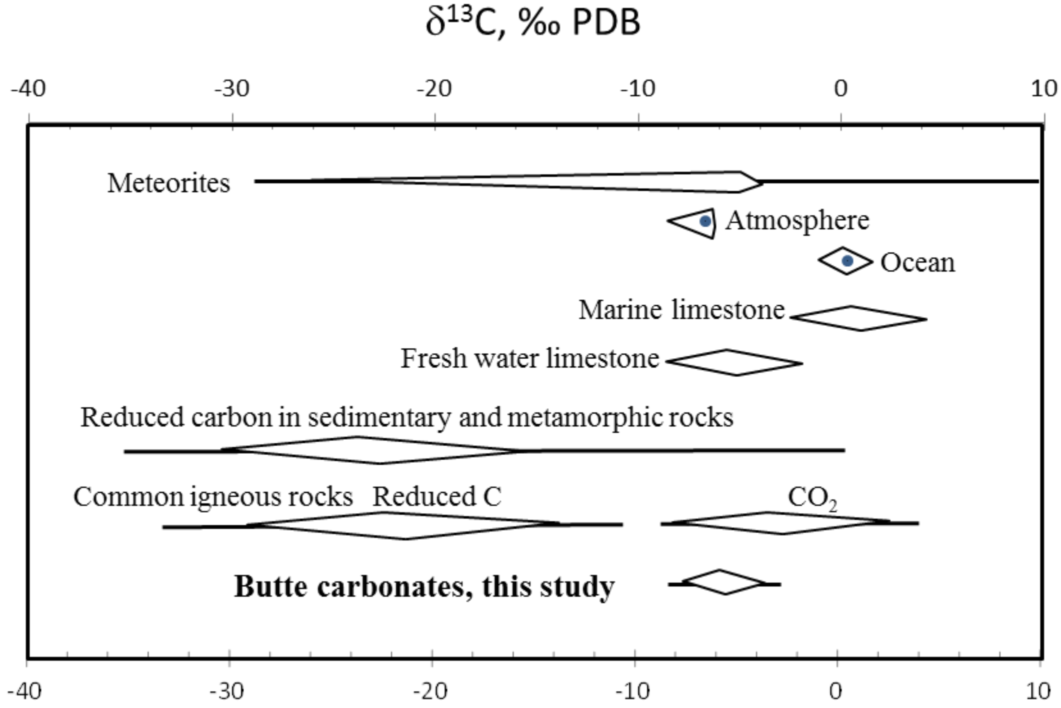

Figure 26: Approximate ranges of C-isotopic composition of different carbon reservoirs on Earth (modified from Ohmoto and Rye, 1979).

The study of Catchpole et al. (2015) concluded that the rhodochrosites in the Morococha district, Peru, inherited their carbon from magmatic CO_2, whereas the more isotopically-enriched calcites in the district may have formed by later, lower temperature meteoric fluids. The $\delta^{13}C$ values for the rhodochrosites in Butte display a much tighter distribution compared to the calcites (Figure 14) which were consistently heavier in $\delta^{13}C$. Although the isotopic composition of dissolved inorganic carbon (DIC) in meteoric water is sensitive to many variables, most groundwaters tend to have $\delta^{13}C$-DIC around -12 ± 5‰ (Clark and Fritz, 1997).

If the fractionation factors from Zheng (1999) are applied to the average values for calcite and rhodochrosite, an estimate of the isotopic composition of the fluids is obtained. From Table

XII we can see the isotopic ranges for low to high temperature fluids. These values relate to many possible sources of carbon; however the most likely source of carbon is from magmatic CO_2. A fluid leached out of igneous rocks is also plausible since the Butte deposit is completely surrounded by igneous rock. The study of Field et al. (2005) concluded that the sulfur in Butte was enriched due to magmatic assimilation of isotopically enriched sulfate from Belt metasediment evaporites. It is possible that the magmatic CO_2 value seen in this study represents isotope ratios of carbon that was assimilated from the carbonate units found in the Belt Supergroup, this enrichment could have even extended to the huge metal content found in the Main Stage veins. Since there are many possible sources of carbon that formed the carbonate minerals, including magmatic CO_2, groundwater DIC, or perhaps even assimilated sedimentary carbon from the Belt Basin group that is a mix of marine limestone ($\delta^{13}C$ near zero) and reduced organic matter (graphite, $\delta^{13}C < -10‰$), determining a singular source of carbon seems unlikely.

Table XIV: Isotopic composition of DIC in fluid at various temperatures

Avg Calc, incl G&E		Avg Rhod, incl G&E	
C	O	C	O
-5.4	6.2	-6.6	3.3
CO_2			
C	O	C	O
-15.6	-4.7	-15.2	-5.3
-13.2	-5	-12.9	-5.9
-9.4	-4.9	-9.4	-6.3
-6.9	-4.5	-7.1	-6.2
-5.2	-3.9	-5.5	-5.8
-4.1	-3.2	-4.5	-5.3
-3.4	-2.6	-3.9	-4.8
-3	-2	-3.6	-4.3

4.3.7. Sources of Hydrothermal Fluid for the Carbonate Minerals

Since partial re-equilibration is more likely to have happened to the calcites than the rhodochrosites, the isotopic values for rhodochrosite seem like a far better indicator of what the isotopic composition of the original fluids would have been. Fractionation factors from Zheng (1999) have been applied to the minimum and maximum values for rhodochrosite throughout the district. When these factors are applied to the stable isotope data for a mineral, an estimate of the original fluid O-isotopic composition is made. The result is the range of $\delta^{18}O$ values that the fluid could have been at various temperatures.

Table XV: $\delta^{18}O$ composition of fluids 25°C to 350°C using minimum and maximum rhodochrosite $\delta^{18}O$ values

Rhodochrosite (Minimum)			Rhodochrosite (Maximum)		
	O			O	
		-1.8			12.8
H2O	O			O	
25		-35.3	to		-20.7
50		-29.4	to		-14.8
100		-21.3	to		-6.7
150		-16.1	to		-1.5
200		-12.5	to		2.1
250		-10.1	to		4.5
300		-8.3	to		6.3
350		-6.9	to		7.7

Sheppard and Taylor (1974) estimated the $\delta^{18}O$ of the hydrothermal fluids of Butte by first determining the isotopic composition of the hydrothermal quartz in Main Stage and pre-Main stage veins. They then assumed equilibrium with a fluid at 300°C for Main Stage veins and 600°C for pre-Main Stage veins and used equilibrium fractionation factors to determine the isotopic composition of the fluids (Table XVI). We can compare these values with those computed for this study and find that the values for Sheppard and Taylor overlap with the values of rhodochrosite for their assumed temperature of formation at 300°C of the Main Stage veins.

Table XVI: Results of Sheppard and Taylor

Mineralization Stage	T°C	^{18}O Mineral	^{18}O Water
Pre Main Stage	600	+3 to +5	+6 to +9
Main Stage Central	300	-9 to +12	-12 to +8
Main Stage Intermediate	300	-4 to +7	-7 to +4
Main Stage Peripheral	300	-2 to +4	-5 to +1

The study of Gammons et al. (2006) determined the local meteoric water line for the Butte area and found that the average composition of the water contributing to flooded mine recharge had a δ^{18}O of -18‰. If the carbonate minerals re-equilibrated with a water that had a δ^{18}O of -18‰, then the computed temperature of re-equilibration lies between 100°C and 150°C (Table XIII). Although it is possible that some late-stage calcites and rhodochrosites could have equilibrated with warm meteoric water in this temperature range, it seems unlikely that the bulk of the carbonate minerals in the veins and lodes could have been reset.

Figure 27 shows the δ^{18}O values of the carbonate minerals compared to the values obtained from Sheppard and Taylor (1974) and the common values associated with magmatic and meteoric water. Sheppard and Taylor concluded that pre-Main Stage Cu-Mo mineralization formed from magmatic fluids, whereas later Main Stage veins formed from a mixture of magmatic and meteoric waters. During the formation of the Butte deposit local meteoric water probably had a different isotopic composition since Montana was at lower latitude than it is currently and δ^{18}O values have been shown to differ by latitude (Clark and Fritz 1997). Since isotope values for meteoric water can vary by location, the “meteoric water” end-member is not a single value. There is a possible range of values imparted by the uncertainty of the “meteoric water” that could have been present and influencing the system. Ultimately, the results of this study show very similar results to that of Sheppard and Taylor with the bulk of the rhodochrosites overlapping with their results for Main Stage vein quartz.

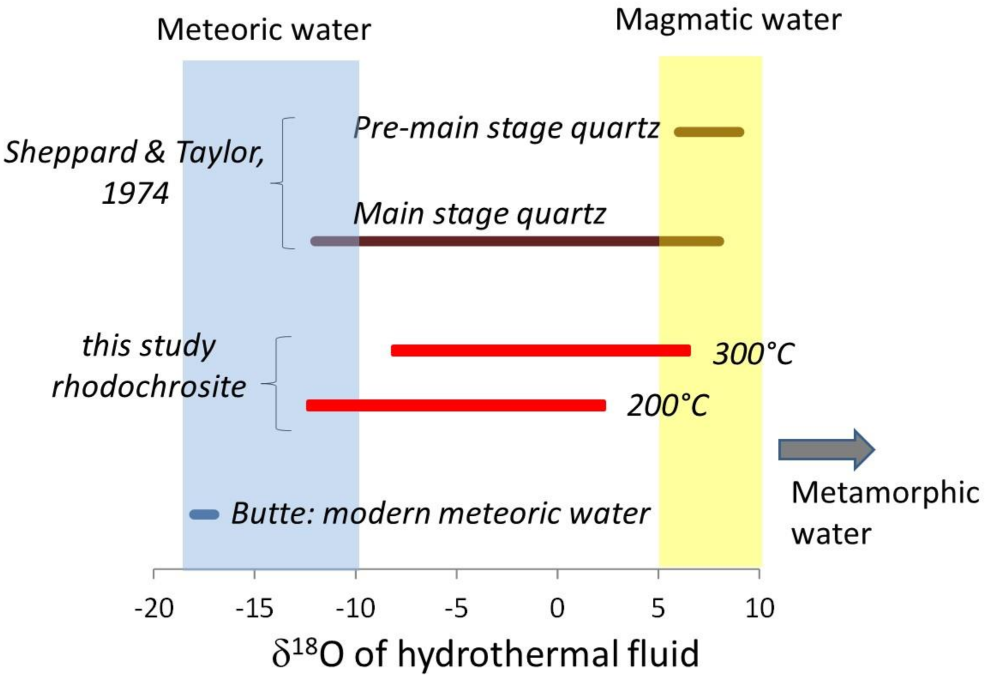

Figure 27: δ^{18}O values of different fluids

4.4. Comparison of Butte Carbonates and Couer d’Alene Carbonates

An interesting comparison that can be made is that between the Butte porphyry-lode system and the base metal cordilleran-type veins of the Coeur d’Alene district. There are several reasons for making this comparison. The Butte and Coeur d’Alene systems both contain large Ag-base metal veins and lodes that are persistent along strike and dip for large distances (>1km). These deposits are also ranked as the two biggest producers of silver in the United States (Long et al., 1998). Though the age of mineralization of the Coeur d’Alene deposit remains contentious, it is possible that they both formed during the late Cretaceous (Eaton et al., 1995). The deposits are rich in carbonate minerals, Butte with rhodochrosite and Coeur d'Alene with ankerite and siderite (Eaton et al., 1995, Rosenberg and Larson, 2000). Metals in the Coeur d'Alene deposit may have even been similarly sourced from the Belt metasediments (Leach et al., 1988) as the sulfur (and possibly metals) in the Butte deposit (Field et al., 2005). Due to the nature of these similarities it is important to compare the two districts to see if isotopic trends are equally similar.

When the two are plotted with each other (Fig. 28), we see the different trends between two deposits. While the Butte deposit shows a wide range in both carbon and oxygen isotopes, the Coeur d'Alene district has the same range of carbon isotopes while exhibiting a narrow range in oxygen isotopes. This difference in oxygen isotopes can be attributed to the different fluids that formed the minerals. The Coeur d'Alene district was formed by metamorphic fluids (Leach et al., 1988), where the water has come out of the minerals as the area underwent prograde metamorphism. The Butte deposit is associated with magmatic fluids (Rusk et al., 2008a; Reed, 2013), or a combination of magmatic and meteoric fluids (Sheppard & Taylor, 1974; this study). Re-equilibration with lower temperature fluids may also have shifted some of the $\delta^{18}O$ values in this study, resulting in the wider range of values displayed at Butte. Overall, the stable isotope data in this thesis do not support the theory that the Main Stage veins had a common origin to the veins of the Coeur d'Alene district in Idaho.

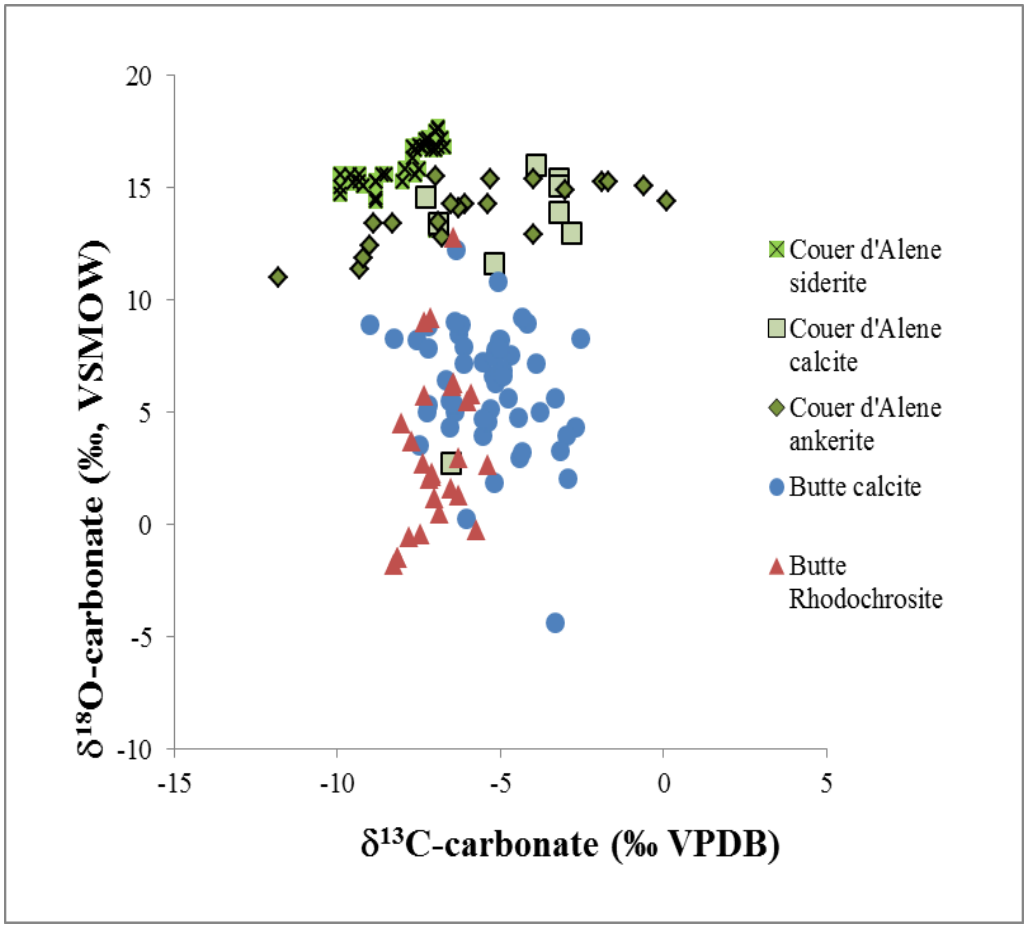

Figure 28: Carbon and oxygen isotopes of Butte and Coeur d'Alene carbonates

5. Conclusions and Recommendations

5.1. Conclusions

- 96 samples of hydrothermal rhodochrosite and calcite from Butte have been analyzed for their O and C isotopic composition. These samples include most of the major underground mines as well as a set of samples from the active Continental Pit.
- Rhodochrosite has $\delta^{13}C$ values in the range of -8.3 to -2.9 ‰ (average of -6.7 ± 1.2‰) and $\delta^{18}O$ ranging from -1.8 to 12.8 ‰ (average of 3.6 ± 3.4‰).
- Calcite has $\delta^{13}C$ values in the range of -9.0 to -2.6 ‰ (average of -5.4 ± 1.5‰) and $\delta^{18}O$ ranging from -4.4 to 12.3‰ (average of 6.2 ± 2.8‰).
- The above findings are in agreement with the early study of Garlick and Epstein (1966).
- On average, Butte calcite is about 1.3 ‰ heavier in $\delta^{13}C$ and about 2.6 ‰ heavier in $\delta^{18}O$ compared to Butte rhodochrosite. These differences cannot be explained by equilibrium isotopic fractionation between calcite and rhodochrosite, and are probably due to partial re-equilibration of calcite with lower temperature fluids.
- This study found no systematic variations in $\delta^{13}C$ or $\delta^{18}O$ of carbonate minerals with respect to location or depth within the Butte district. Likewise, a traverse across a 50 foot wide Main Stage vein in the Orphan Girl mine found no change in isotopic composition of rhodochrosite between the center and edges of the vein.
- For the Continental Pit samples, no relationships could be found between the isotopic composition of carbonate minerals and the concentrations of Cu or Mo in the associated drill core.

- Although there are many possible sources of carbon with similar isotopic signature that could have led to the carbonate minerals of Butte, the most likely source is magmatic CO_2.
- Based on the measured $\delta^{18}O$ values of rhodochrosite, and assuming a temperature of formation of 200 to 350ºC, the possible range of $\delta^{18}O$ of the hydrothermal fluids at Butte is computed to be –12.6 to +6.3‰. This range lies midway between present-day meteoric water in Butte (-17 to -18‰) and primary magmatic water (+5 to +10 ‰), and is similar to what was proposed in the earlier study of Sheppard and Taylor (1974).
- Although their C-isotopes overlap, the O-isotopic compositions of rhodochrosite and calcite from the Ag-rich base metal veins in Butte are distinct from those of siderite and ankerite from the Couer d'Alene district, Idaho. This reflects the difference in ore deposit type: whereas Butte is a classic porphyry-lode deposit, the veins of the Couer d'Alene district are thought to have formed from metamorphic fluids in a much deeper (orogenic) setting.

5.2. Recommendations

- Better relationships between the isotopic composition of carbonate minerals and associated Ag- and base metal mineralization may come to light if a more detailed study focusing on the paragenesis of carbonate mineralization in conjunction with economic mineralization is conducted. The present study used a very broad approach and looked at the entire Butte district, rather than examining a single vein or vein system in detail. A more detailed paragenetic study of rhodochrosites might reveal trends with depth, or along strike on a single vein. Such a study could be combined with new information using cathodoluminescence, trace metal concentrations in carbonate minerals, and/or fluid inclusions. Calcite would be a lower priority in such a study because it is more likely to have re-equilibrated at lower temperature.

- Although the isotopic results from the three labs used in this study were similar, the disagreement for some replicate samples was outside the quoted lab uncertainty. This problem was worse for samples that were impure, and had a relatively low carbonate content compared to quartz. Any future study needs to pay close attention to how the mineral separate samples are collected, processed, and analyzed. Some isotope labs use acid digestion to liberate CO_2 from carbonates, whereas others use pyrolysis. Rhodochrosite is slower to react with acid and this could be one reason for disagreement between the various labs. Sample crushing and homogenization is also critical.

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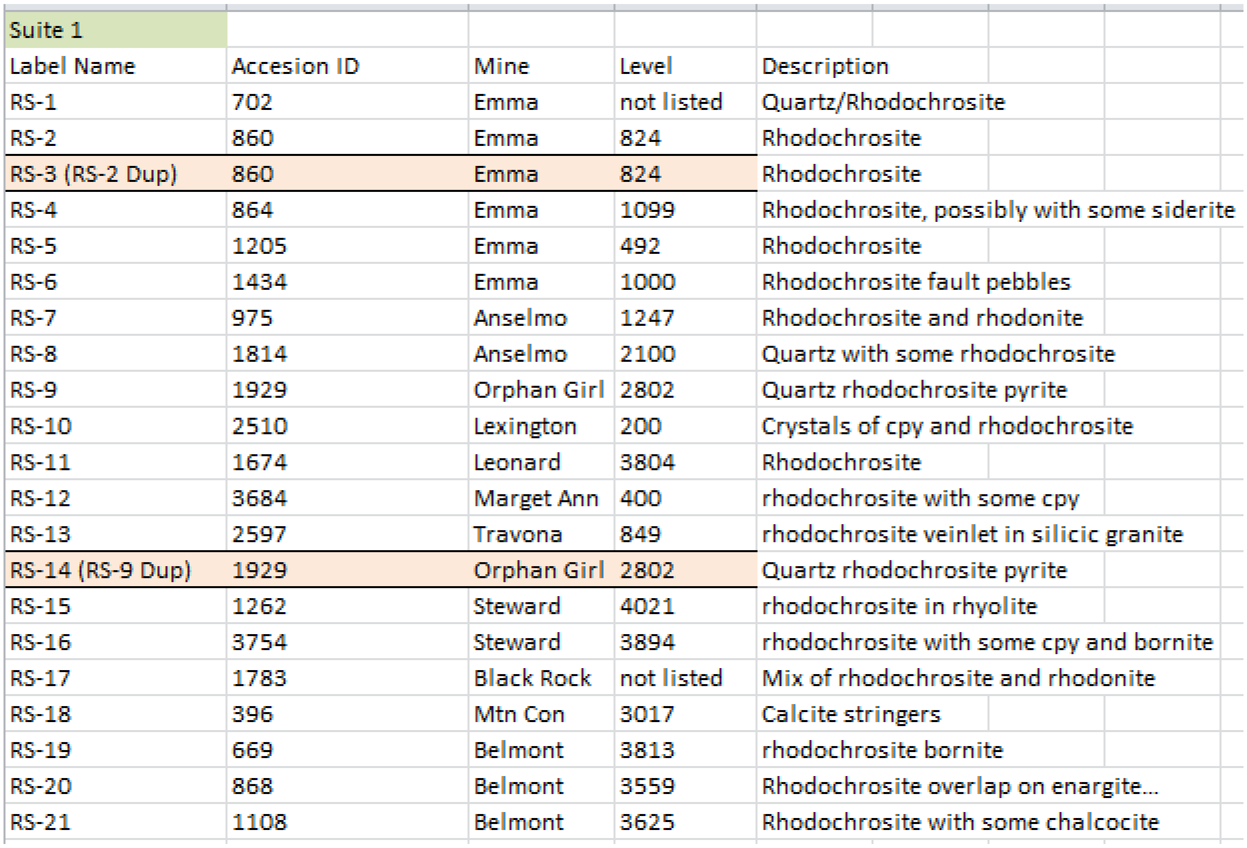
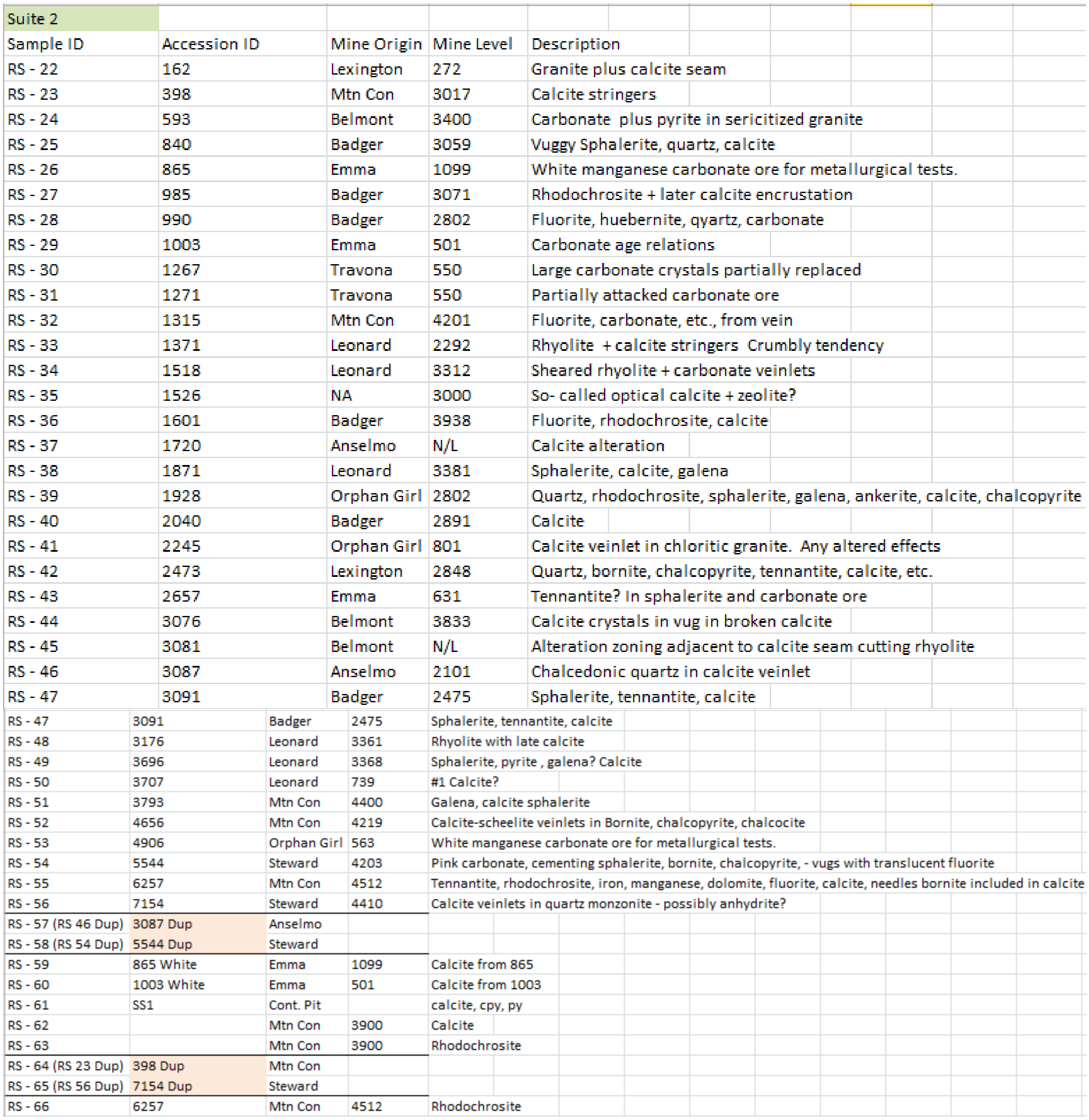
Appendix A: Sample Identification

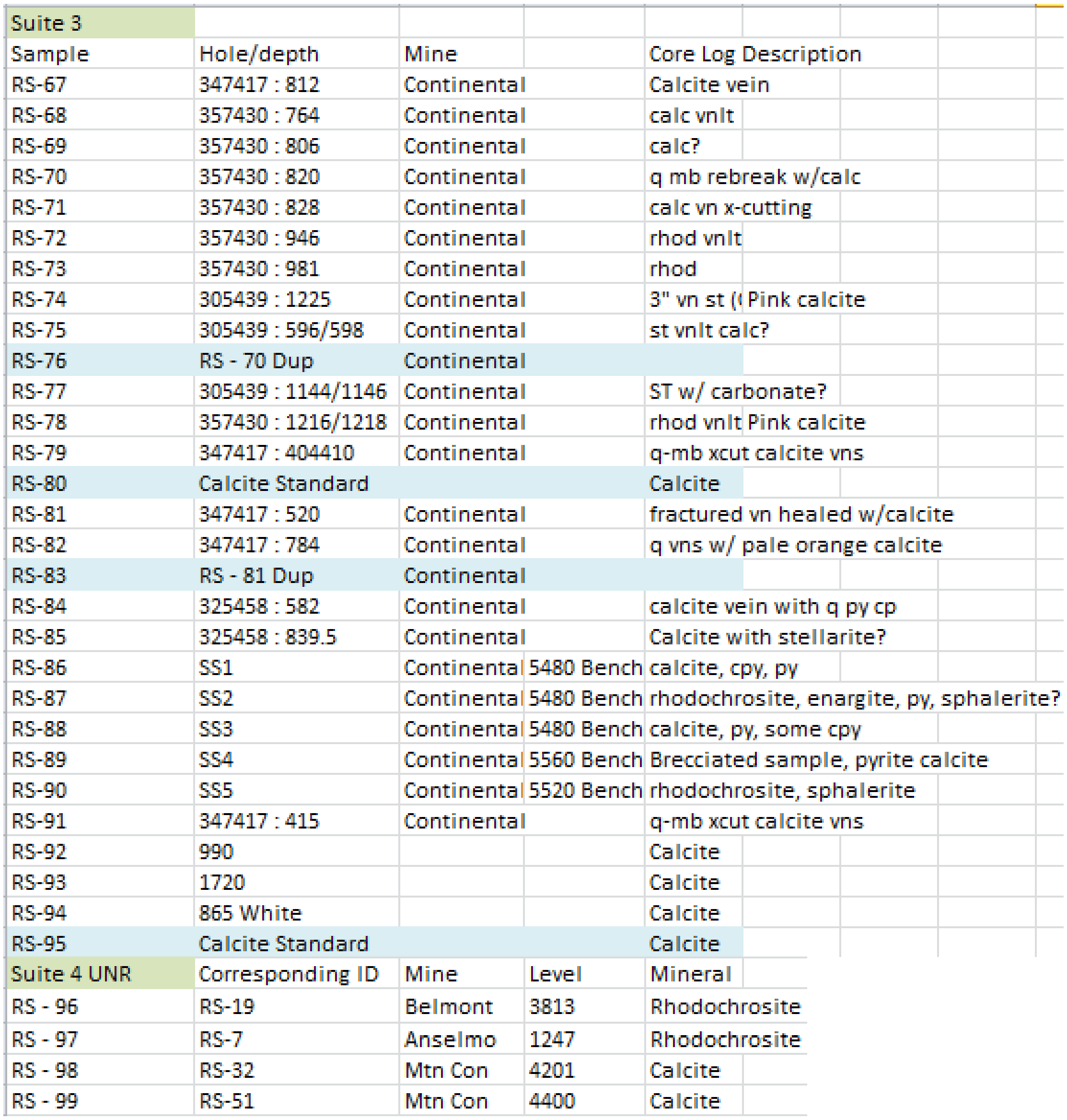


Suite 1				
Label Name	Accesion ID	Mine	Level	Description
RS-1	702	Emma	not listed	Quartz/Rhodochrosite
RS-2	860	Emma	824	Rhodochrosite
RS-3 (RS-2 Dup)	860	Emma	824	Rhodochrosite
RS-4	864	Emma	1099	Rhodochrosite, possibly with some siderite
RS-5	1205	Emma	492	Rhodochrosite
RS-6	1434	Emma	1000	Rhodochrosite fault pebbles
RS-7	975	Anselmo	1247	Rhodochrosite and rhodonite
RS-8	1814	Anselmo	2100	Quartz with some rhodochrosite
RS-9	1929	Orphan Girl	2802	Quartz rhodochrosite pyrite
RS-10	2510	Lexington	200	Crystals of cpy and rhodochrosite
RS-11	1674	Leonard	3804	Rhodochrosite
RS-12	3684	Marget Ann	400	rhodochrosite with some cpy
RS-13	2597	Travona	849	rhodochrosite veinlet in silicic granite
RS-14 (RS-9 Dup)	1929	Orphan Girl	2802	Quartz rhodochrosite pyrite
RS-15	1262	Steward	4021	rhodochrosite in rhyolite
RS-16	3754	Steward	3894	rhodochrosite with some cpy and bornite
RS-17	1783	Black Rock	not listed	Mix of rhodochrosite and rhodonite
RS-18	396	Mtn Con	3017	Calcite stringers
RS-19	669	Belmont	3813	rhodochrosite bornite
RS-20	868	Belmont	3559	Rhodochrosite overlap on enargite...
RS-21	1108	Belmont	3625	Rhodochrosite with some chalcocite



Suite 2

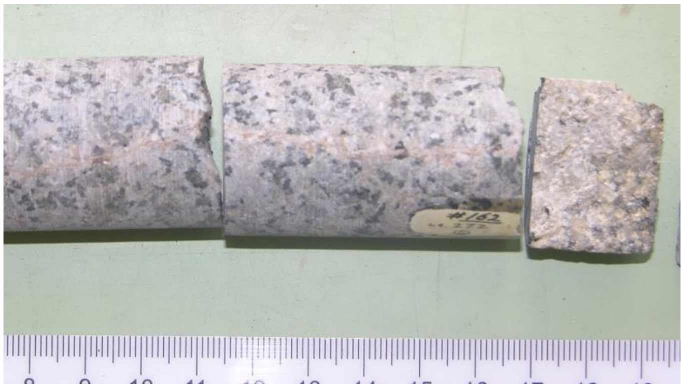
Sample ID	Accession ID	Mine Origin	Mine Level	Description
RS - 22	162	Lexington	272	Granite plus calcite seam
RS - 23	398	Mtn Con	3017	Calcite stringers
RS - 24	593	Belmont	3400	Carbonate plus pyrite in sericitized granite
RS - 25	840	Badger	3059	Vuggy Sphalerite, quartz, calcite
RS - 26	865	Emma	1099	White manganese carbonate ore for metallurgical tests.
RS - 27	985	Badger	3071	Rhodochrosite + later calcite encrustation
RS - 28	990	Badger	2802	Fluorite, huebernite, qyartz, carbonate
RS - 29	1003	Emma	501	Carbonate age relations
RS - 30	1267	Travona	550	Large carbonate crystals partially replaced
RS - 31	1271	Travona	550	Partially attacked carbonate ore
RS - 32	1315	Mtn Con	4201	Fluorite, carbonate, etc., from vein
RS - 33	1371	Leonard	2292	Rhyolite + calcite stringers Crumbly tendency
RS - 34	1518	Leonard	3312	Sheared rhyolite + carbonate veinlets
RS - 35	1526	NA	3000	So- called optical calcite + zeolite?
RS - 36	1601	Badger	3938	Fluorite, rhodochrosite, calcite
RS - 37	1720	Anselmo	N/L	Calcite alteration
RS - 38	1871	Leonard	3381	Sphalerite, calcite, galena
RS - 39	1928	Orphan Girl	2802	Quartz, rhodochrosite, sphalerite, galena, ankerite, calcite, chalcopyrite
RS - 40	2040	Badger	2891	Calcite
RS - 41	2245	Orphan Girl	801	Calcite veinlet in chloritic granite. Any altered effects
RS - 42	2473	Lexington	2848	Quartz, bornite, chalcopyrite, tennantite, calcite, etc.
RS - 43	2657	Emma	631	Tennantite? In sphalerite and carbonate ore
RS - 44	3076	Belmont	3833	Calcite crystals in vug in broken calcite
RS - 45	3081	Belmont	N/L	Alteration zoning adjacent to calcite seam cutting rhyolite
RS - 46	3087	Anselmo	2101	Chalcedonic quartz in calcite veinlet
RS - 47	3091	Badger	2475	Sphalerite, tennantite, calcite
RS - 47	3091	Badger	2475	Sphalerite, tennantite, calcite
RS - 48	3176	Leonard	3361	Rhyolite with late calcite
RS - 49	3696	Leonard	3368	Sphalerite, pyrite , galena? Calcite
RS - 50	3707	Leonard	739	#1 Calcite?
RS - 51	3793	Mtn Con	4400	Galena, calcite sphalerite
RS - 52	4656	Mtn Con	4219	Calcite-scheelite veinlets in Bornite, chalcopyrite, chalcocite
RS - 53	4906	Orphan Girl	563	White manganese carbonate ore for metallurgical tests.
RS - 54	5544	Steward	4203	Pink carbonate, cementing sphalerite, bornite, chalcopyrite, - vugs with translucent fluorite
RS - 55	6257	Mtn Con	4512	Tennantite, rhodochrosite, iron, manganese, dolomite, fluorite, calcite, needles bornite included in calcite
RS - 56	7154	Steward	4410	Calcite veinlets in quartz monzonite - possibly anhydrite?
RS - 57 (RS 46 Dup)	3087 Dup	Anselmo		
RS - 58 (RS 54 Dup)	5544 Dup	Steward		
RS - 59	865 White	Emma	1099	Calcite from 865
RS - 60	1003 White	Emma	501	Calcite from 1003
RS - 61	SS1	Cont. Pit		calcite, cpy, py
RS - 62		Mtn Con	3900	Calcite
RS - 63		Mtn Con	3900	Rhodochrosite
RS - 64 (RS 23 Dup)	398 Dup	Mtn Con		
RS - 65 (RS 56 Dup)	7154 Dup	Steward		
RS - 66	6257	Mtn Con	4512	Rhodochrosite



Suite 3					
Sample	Hole/depth	Mine		Core Log Description	
RS-67	347417 : 812	Continental		Calcite vein	
RS-68	357430 : 764	Continental		calc vnlt	
RS-69	357430 : 806	Continental		calc?	
RS-70	357430 : 820	Continental		q mb rebreak w/calc	
RS-71	357430 : 828	Continental		calc vn x-cutting	
RS-72	357430 : 946	Continental		rhod vnlt	
RS-73	357430 : 981	Continental		rhod	
RS-74	305439 : 1225	Continental		3" vn st (	Pink calcite
RS-75	305439 : 596/598	Continental		st vnlt calc?	
RS-76	RS - 70 Dup	Continental			
RS-77	305439 : 1144/1146	Continental		ST w/ carbonate?	
RS-78	357430 : 1216/1218	Continental		rhod vnlt	Pink calcite
RS-79	347417 : 404410	Continental		q-mb xcut calcite vns	
RS-80	Calcite Standard			Calcite	
RS-81	347417 : 520	Continental		fractured vn healed w/calcite	
RS-82	347417 : 784	Continental		q vns w/ pale orange calcite	
RS-83	RS - 81 Dup	Continental			
RS-84	325458 : 582	Continental		calcite vein with q py cp	
RS-85	325458 : 839.5	Continental		Calcite with stellarite?	
RS-86	SS1	Continental	5480 Bench	calcite, cpy, py	
RS-87	SS2	Continental	5480 Bench	rhodochrosite, enargite, py, sphalerite?	
RS-88	SS3	Continental	5480 Bench	calcite, py, some cpy	
RS-89	SS4	Continental	5560 Bench	Brecciated sample, pyrite calcite	
RS-90	SS5	Continental	5520 Bench	rhodochrosite, sphalerite	
RS-91	347417 : 415	Continental		q-mb xcut calcite vns	
RS-92	990			Calcite	
RS-93	1720			Calcite	
RS-94	865 White			Calcite	
RS-95	Calcite Standard			Calcite	
Suite 4 UNR	Corresponding ID	Mine	Level	Mineral	
RS - 96	RS-19	Belmont	3813	Rhodochrosite	
RS - 97	RS-7	Anselmo	1247	Rhodochrosite	
RS - 98	RS-32	Mtn Con	4201	Calcite	
RS - 99	RS-51	Mtn Con	4400	Calcite	

Appendix B: Photographs of samples from the Anaconda Collection

The scale is in mm (larger ticks in cm). Numbers refer to the AMC Accession Numbers, which can be used to relocate a given sample. (All samples were returned after removing a small piece of carbonate vein material.)



AMC #162

AMC #396

AMC #398

AMC #593

AMC #669

AMC #702

AMC #706

AMC #840

AMC #860

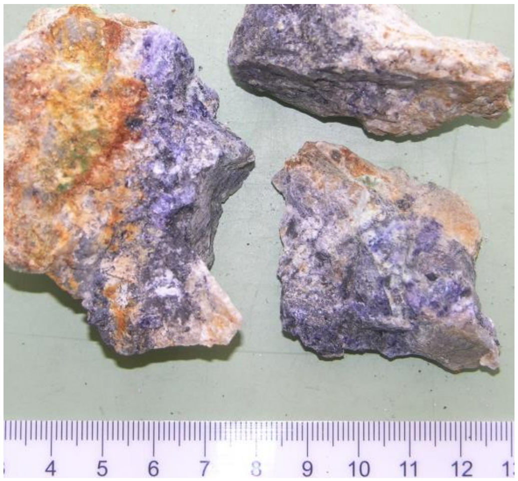
AMC #864

AMC #865

#868

AMC #975

AMC #985



AMC #990

AMC #1003

AMC #1108

AMC #1262

AMC #1267

AMC#1271

AMC #1315

AMC #1371

AMC #1434

AMC#1518

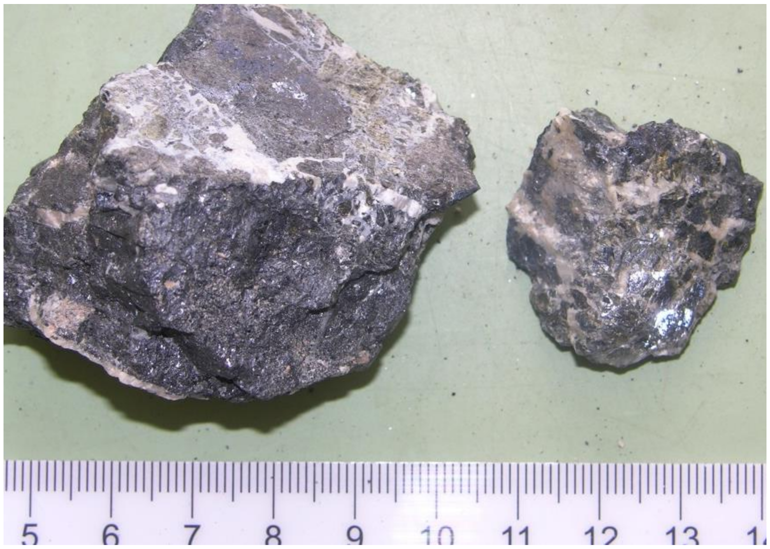
AMC #1526

AMC #1601

AMC#1783

AMC #1720

AMC #1814



AMC #1871

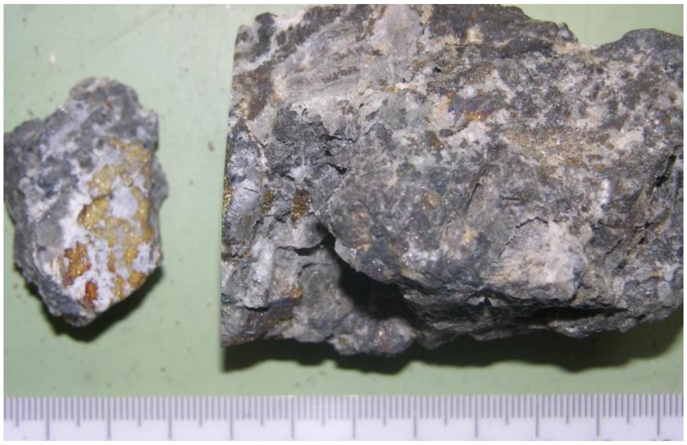
AMC #1928


AMC #1929


AMC #1998


AMC #2040


#2245


AMC #2473


AMC #2597


AMC #2657

AMC #3076

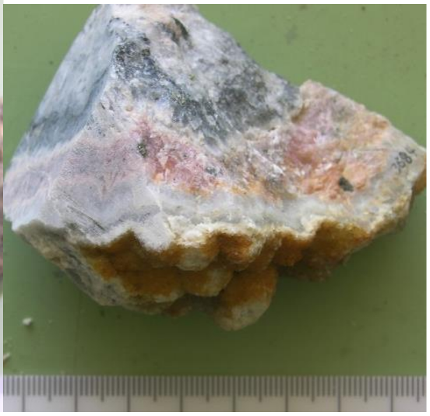
AMC #3081

AMC #3087

AMC #3091

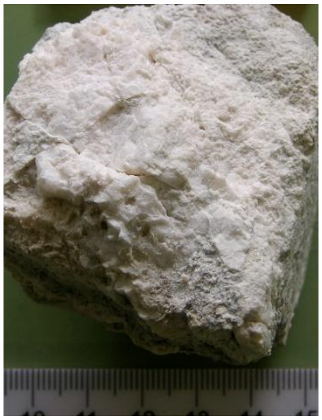
AMC #3176

AMC #3510



AMC #3684


AMC #3696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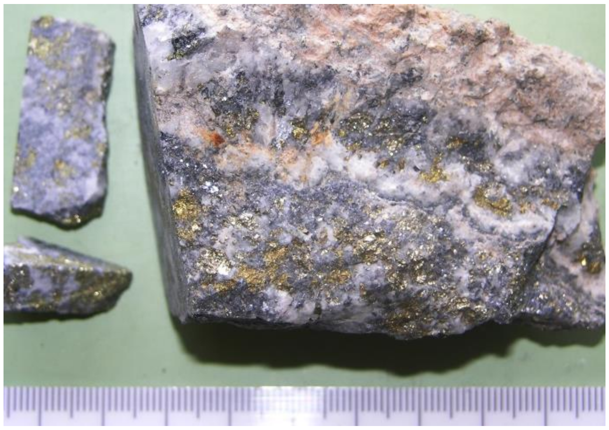
AMC #3754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AMC #3793


AMC # 4316

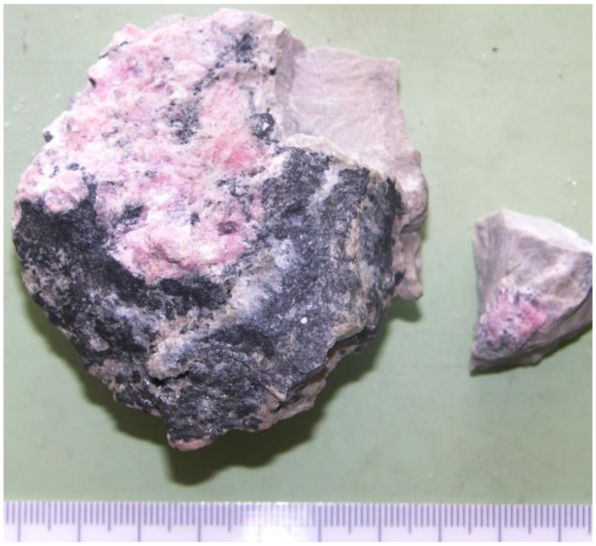

AMC #4596

AMC #4656

AMC #4906

AMC #5060

AMC #5584



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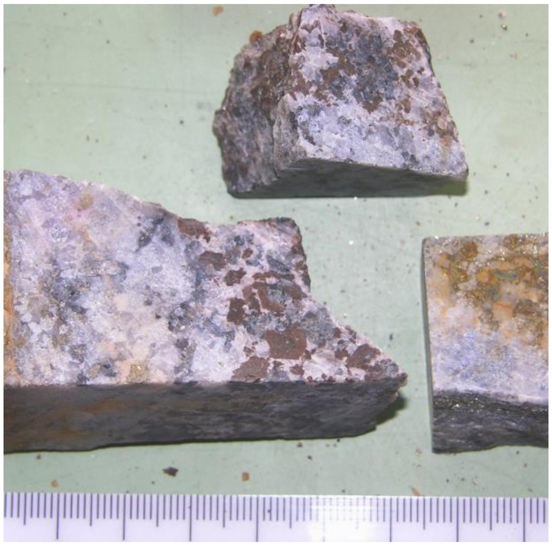
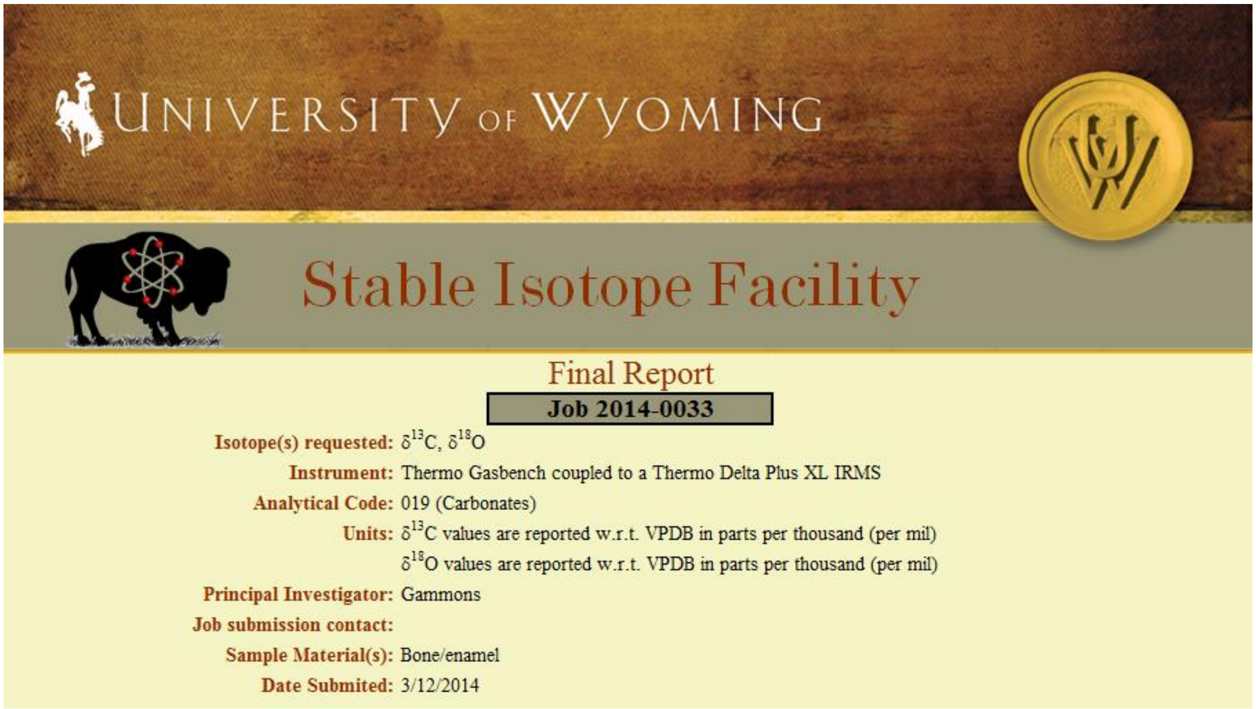


AMC #7154

Appendix C: University of Wyoming Stable Isotope Facility Data



UNIVERSITY OF WYOMING

Stable Isotope Facility

Final Report

Job 2014-0033

Isotope(s) requested: $\delta^{13}C$, $\delta^{18}O$

Instrument: Thermo Gasbench coupled to a Thermo Delta Plus XL IRMS

Analytical Code: 019 (Carbonates)

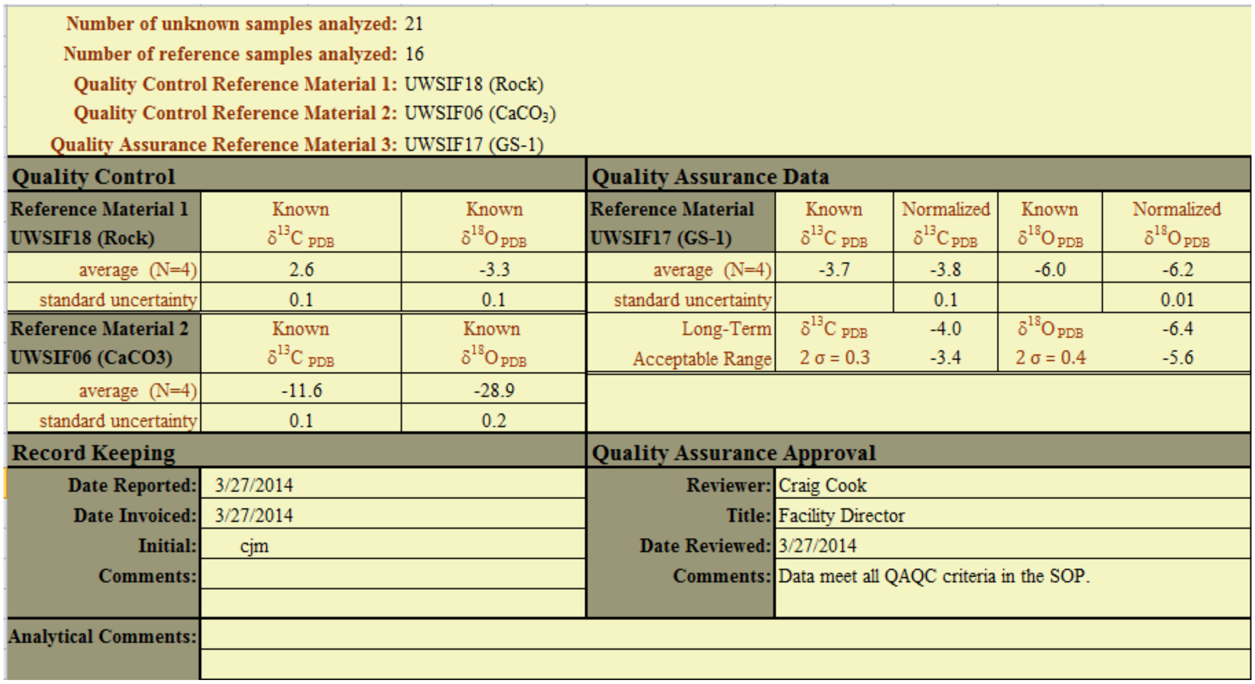
Units: $\delta^{13}C$ values are reported w.r.t. VPDB in parts per thousand (per mil)
$\delta^{18}O$ values are reported w.r.t. VPDB in parts per thousand (per mil)

Principal Investigator: Gammons

Job submission contact:

Sample Material(s): Bone/enamel

Date Submited: 3/12/2014



Number of unknown samples analyzed: 21

Number of reference samples analyzed: 16

Quality Control Reference Material 1: UWSIF18 (Rock)

Quality Control Reference Material 2: UWSIF06 ($CaCO_3$)

Quality Assurance Reference Material 3: UWSIF17 (GS-1)

Quality Control

Reference Material 1 UWSIF18 (Rock)	Known $\delta^{13}C_{PDB}$	Known $\delta^{18}O_{PDB}$
average (N=4)	2.6	-3.3
standard uncertainty	0.1	0.1
Reference Material 2 UWSIF06 (CaCO3)	Known $\delta^{13}C_{PDB}$	Known $\delta^{18}O_{PDB}$
average (N=4)	-11.6	-28.9
standard uncertainty	0.1	0.2

Quality Assurance Data

Reference Material UWSIF17 (GS-1)	Known $\delta^{13}C_{PDB}$	Normalized $\delta^{13}C_{PDB}$	Known $\delta^{18}O_{PDB}$	Normalized $\delta^{18}O_{PDB}$
average (N=4)	-3.7	-3.8	-6.0	-6.2
standard uncertainty		0.1		0.01
Long-Term Acceptable Range	$\delta^{13}C_{PDB}$ $2\sigma = 0.3$	-4.0 -3.4	$\delta^{18}O_{PDB}$ $2\sigma = 0.4$	-6.4 -5.6

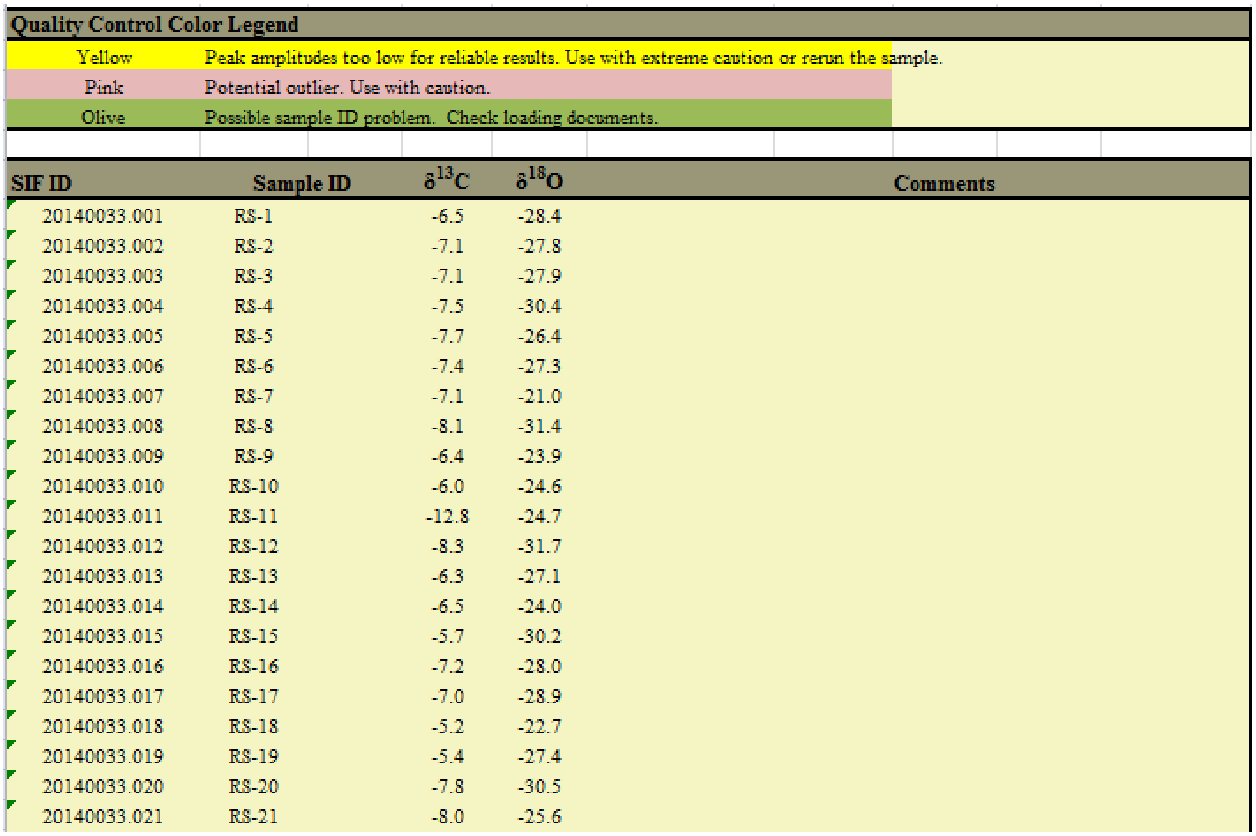
Record Keeping

Date Reported: 3/27/2014
Date Invoiced: 3/27/2014
Initial: cjm
Comments:

Quality Assurance Approval

Reviewer: Craig Cook
Title: Facility Director
Date Reviewed: 3/27/2014
Comments: Data meet all QAQC criteria in the SOP.

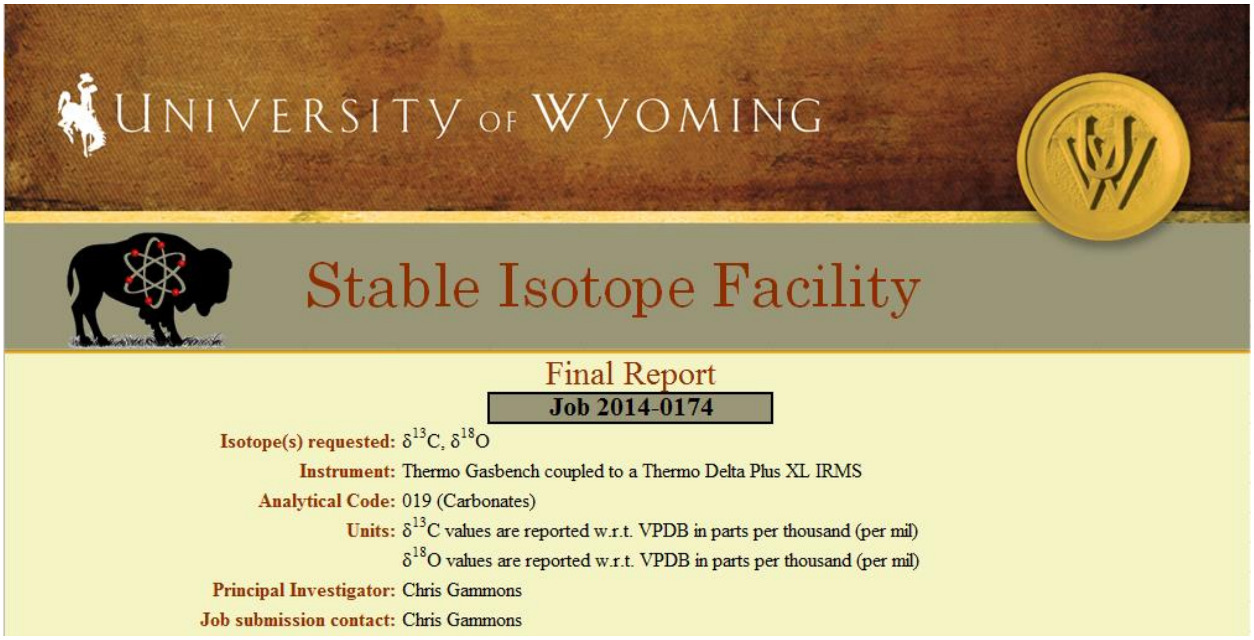
Analytical Comments:



Quality Control Color Legend

Yellow	Peak amplitudes too low for reliable results. Use with extreme caution or rerun the sample.
Pink	Potential outlier. Use with caution.
Olive	Possible sample ID problem. Check loading documents.

SIF ID	Sample ID	$\delta^{13}C$	$\delta^{18}O$	Comments
20140033.001	RS-1	-6.5	-28.4	
20140033.002	RS-2	-7.1	-27.8	
20140033.003	RS-3	-7.1	-27.9	
20140033.004	RS-4	-7.5	-30.4	
20140033.005	RS-5	-7.7	-26.4	
20140033.006	RS-6	-7.4	-27.3	
20140033.007	RS-7	-7.1	-21.0	
20140033.008	RS-8	-8.1	-31.4	
20140033.009	RS-9	-6.4	-23.9	
20140033.010	RS-10	-6.0	-24.6	
20140033.011	RS-11	-12.8	-24.7	
20140033.012	RS-12	-8.3	-31.7	
20140033.013	RS-13	-6.3	-27.1	
20140033.014	RS-14	-6.5	-24.0	
20140033.015	RS-15	-5.7	-30.2	
20140033.016	RS-16	-7.2	-28.0	
20140033.017	RS-17	-7.0	-28.9	
20140033.018	RS-18	-5.2	-22.7	
20140033.019	RS-19	-5.4	-27.4	
20140033.020	RS-20	-7.8	-30.5	
20140033.021	RS-21	-8.0	-25.6	



UNIVERSITY OF WYOMING

Stable Isotope Facility

Final Report

Job 2014-0174

Isotope(s) requested: $\delta^{13}C$, $\delta^{18}O$

Instrument: Thermo Gasbench coupled to a Thermo Delta Plus XL IRMS

Analytical Code: 019 (Carbonates)

Units: $\delta^{13}C$ values are reported w.r.t. VPDB in parts per thousand (per mil)

$\delta^{18}O$ values are reported w.r.t. VPDB in parts per thousand (per mil)

Principal Investigator: Chris Gammons

Job submission contact: Chris Gammons

Sample Material(s): Calcite and rhodochrosite
Date Submited: 10/2/2014
Number of unknown samples analyzed: 45
Number of reference samples analyzed: 27
Quality Control Reference Material 1: UWSIF18 (Rock)
Quality Control Reference Material 2: UWSIF06 ($CaCO_3$)
Quality Assessment Reference Material 3: UWSIF17 (GS-1)

Quality Control

Reference Material 1 UWSIF18 (Rock)	Known $\delta^{13}C_{VPDB}$	Known $\delta^{18}O_{VPDB}$
average (N=9)	2.6	-3.3
standard uncertainty	0.1	0.2
Reference Material 2 UWSIF06 (CaCO3)	Known $\delta^{13}C_{VPDB}$	Known $\delta^{18}O_{VPDB}$
average (N=10)	-11.6	-28.9
standard uncertainty	0.2	0.1

Quality Assessment Data

Reference Material UWSIF17 (GS-1)	Known $\delta^{13}C_{VPDB}$	Normalized $\delta^{13}C_{VPDB}$	Known $\delta^{18}O_{VPDB}$	Normalized $\delta^{18}O_{VPDB}$
average (N=8)	-3.7	-3.7	-6.0	-6.1
standard uncertainty		0.1		0.2
Long-Term Acceptable Range	$\delta^{13}C_{VPDB}$ 2 σ = 0.3	-4.0 -3.4	$\delta^{18}O_{VPDB}$ 2 σ = 0.4	-6.4 -5.6

Record Keeping

Date Reported: 12/23/2014
Date Invoiced: 12/23/2014
Initial: cjm
Comments:

Quality Assurance Approval

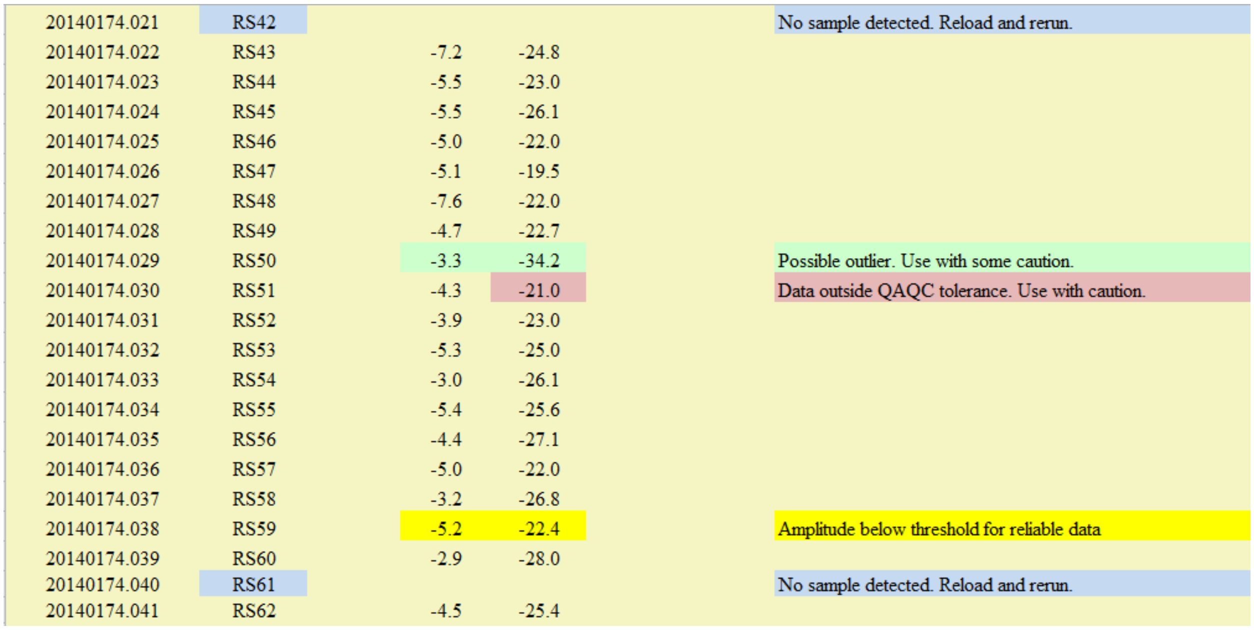
Reviewer: Craig Cook
Title: Facility Director
Date Reviewed: 12/22/2014
Comments: Data meet all QAQC criteria in the SOP

Analytical Comments

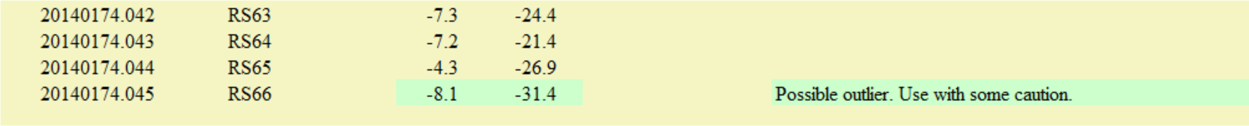
Quality Control Color Legend

Yellow	Peak amplitudes too low for reliable results. Use with extreme caution or rerun the sample.
Blue	No sample detected. Reload and rerun.
Green	Possible outlier. Use with some caution.
Pink	Data outside QAQC tolerance. Use with caution.
Olive	Possible sample ID problem. Check loading documents.

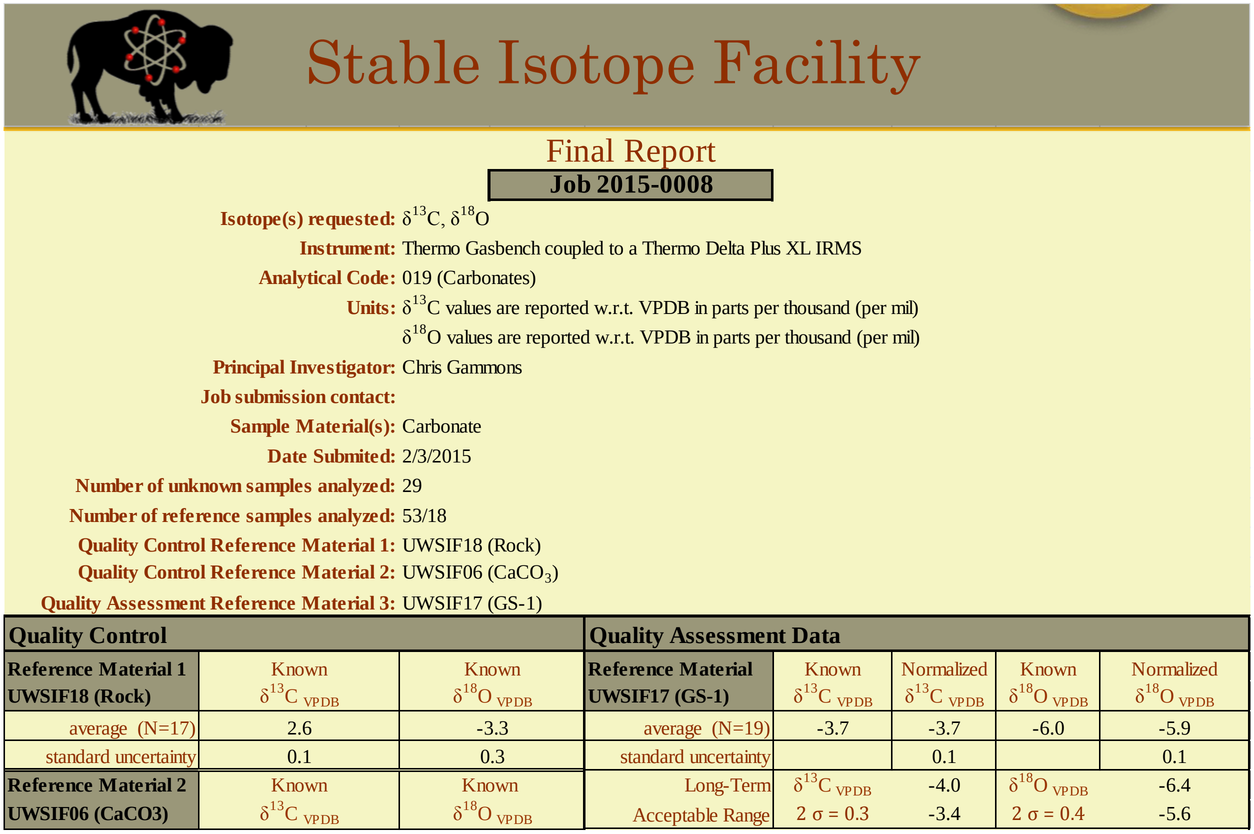
SIF ID	**Sample ID**	**$\delta^{13}C$**	**$\delta^{18}O$**	**Comments**
20140174.001	RS22	-6.4	-18.1	
20140174.002	RS23	-6.4	-21.2	
20140174.003	RS24	-6.2	-21.3	
20140174.004	RS25	-6.3	-21.8	
20140174.005	RS26	-6.4	-25.1	
20140174.006	RS27	-5.2	-28.2	
20140174.007	RS28	-7.5	-26.5	Amplitude below threshold for reliable data
20140174.008	RS29	-6.9	-29.5	
20140174.009	RS30	-4.9	-23.3	
20140174.010	RS31	-5.5	-25.4	
20140174.011	RS32	-2.7	-25.8	
20140174.012	RS33			No sample detected. Reload and rerun.
20140174.013	RS34			No sample detected. Reload and rerun.
20140174.014	RS35	-13.2	-29.2	Possible outlier. Use with some caution.
20140174.015	RS36	-4.8	-24.5	
20140174.016	RS37	-5.2	-23.6	Amplitude below threshold for reliable data
20140174.017	RS38	-5.1	-22.4	
20140174.018	RS39	-3.8	-25.1	
20140174.019	RS40	-4.2	-21.3	
20140174.020	RS41	-3.3	-24.5	



20140174.021	RS42			No sample detected. Reload and rerun.
20140174.022	RS43	-7.2	-24.8	
20140174.023	RS44	-5.5	-23.0	
20140174.024	RS45	-5.5	-26.1	
20140174.025	RS46	-5.0	-22.0	
20140174.026	RS47	-5.1	-19.5	
20140174.027	RS48	-7.6	-22.0	
20140174.028	RS49	-4.7	-22.7	
20140174.029	RS50	-3.3	-34.2	Possible outlier. Use with some caution.
20140174.030	RS51	-4.3	-21.0	Data outside QAQC tolerance. Use with caution.
20140174.031	RS52	-3.9	-23.0	
20140174.032	RS53	-5.3	-25.0	
20140174.033	RS54	-3.0	-26.1	
20140174.034	RS55	-5.4	-25.6	
20140174.035	RS56	-4.4	-27.1	
20140174.036	RS57	-5.0	-22.0	
20140174.037	RS58	-3.2	-26.8	
20140174.038	RS59	-5.2	-22.4	Amplitude below threshold for reliable data
20140174.039	RS60	-2.9	-28.0	
20140174.040	RS61			No sample detected. Reload and rerun.
20140174.041	RS62	-4.5	-25.4	



20140174.042	RS63	-7.3	-24.4	
20140174.043	RS64	-7.2	-21.4	
20140174.044	RS65	-4.3	-26.9	
20140174.045	RS66	-8.1	-31.4	Possible outlier. Use with some caution.



Stable Isotope Facility

Final Report

Job 2015-0008

Isotope(s) requested: $\delta^{13}C$, $\delta^{18}O$
Instrument: Thermo Gasbench coupled to a Thermo Delta Plus XL IRMS
Analytical Code: 019 (Carbonates)
Units: $\delta^{13}C$ values are reported w.r.t. VPDB in parts per thousand (per mil)
$\delta^{18}O$ values are reported w.r.t. VPDB in parts per thousand (per mil)
Principal Investigator: Chris Gammons
Job submission contact:
Sample Material(s): Carbonate
Date Submited: 2/3/2015
Number of unknown samples analyzed: 29
Number of reference samples analyzed: 53/18
Quality Control Reference Material 1: UWSIF18 (Rock)
Quality Control Reference Material 2: UWSIF06 ($CaCO_3$)
Quality Assessment Reference Material 3: UWSIF17 (GS-1)

Quality Control			Quality Assessment Data				
Reference Material 1 UWSIF18 (Rock)	Known $\delta^{13}C_{VPDB}$	Known $\delta^{18}O_{VPDB}$	**Reference Material UWSIF17 (GS-1)**	Known $\delta^{13}C_{VPDB}$	Normalized $\delta^{13}C_{VPDB}$	Known $\delta^{18}O_{VPDB}$	Normalized $\delta^{18}O_{VPDB}$
average (N=17)	2.6	-3.3	average (N=19)	-3.7	-3.7	-6.0	-5.9
standard uncertainty	0.1	0.3	standard uncertainty		0.1		0.1
Reference Material 2 UWSIF06 (CaCO3)	Known $\delta^{13}C_{VPDB}$	Known $\delta^{18}O_{VPDB}$	Long-Term Acceptable Range	$\delta^{13}C_{VPDB}$ $2\sigma = 0.3$	-4.0 -3.4	$\delta^{18}O_{VPDB}$ $2\sigma = 0.4$	-6.4 -5.6

average (N=19)	-11.6	-28.9
standard uncertainty	0.1	0.2

Record Keeping

Date Reported:	6/30/2015
Date Invoiced:	6/30/2015
Initial:	cjm
Comments:	

Quality Assurance Approval

Reviewer:	Craig Cook
Title:	Facility Director
Date Reviewed:	7/1/2015
Comments:	Data meet all QAQC criteria in the SOP.

Analytical Comments:

Quality Control Color Legend

Yellow	Peak amplitudes too low for reliable results. Use with extreme caution or rerun the sample.
Pink	Potential outlier. Use with caution.
Olive	Possible sample ID problem. Check loading documents.

SIF ID	Sample ID	$\delta^{13}C$	$\delta^{18}O$	Comments
20150008.001	RS-67	-6.7	-23.7	
20150008.002	RS-68	-5.2	-23.9	
20150008.003	RS-69	-5.0	-22.3	
20150008.004	RS-70	-7.2	-25.1	
20150008.005	RS-71	-6.1	-29.8	
20150008.006	RS-72	-6.3	-28.7	
20150008.007	RS-73	-5.9	-24.3	
20150008.008	RS-74	-6.1	-22.3	
20150008.009	RS-75	-6.5	-25.8	
20150008.010	RS-76	-7.3	-25.1	
20150008.011	RS-77	-4.9	-23.6	
20150008.012	RS-78	-2.6	-21.9	
20150008.013	RS-79	-6.6	-24.7	
20150008.014	RS-80	-16.6	-20.3	
20150008.015	RS-81	-6.4	-24.8	
20150008.016	RS-82	-5.3	-22.5	Amplitude below threshold for reliable data
20150008.017	RS-83	-6.1	-24.8	
20150008.018	RS-84	-8.3	-21.9	
20150008.019	RS-85	-9.0	-21.3	
20150008.020	RS-86	-7.6	-22.0	
20150008.021	RS-87	-6.4	-17.6	
20150008.022	RS-88	-6.1	-23.0	
20150008.023	RS-89	-4.9	-24.6	Amplitude below threshold for reliable data
20150008.024	RS-90	-7.3	-21.2	
20150008.025	RS-91	-7.2	-22.4	
20150008.026	RS-92	-8.0	-26.8	
20150008.027	RS-93	-3.8	-17.9	Amplitude below threshold for reliable data
20150008.028	RS-94	-4.8	-24.8	Amplitude below threshold for reliable data
20150008.029	RS-95	-16.6	-20.3	

Appendix D: XRF Analysis (all data in mg/kg)

ID	Anaconda Accession	Initial Min ID	XRF Min ID	Ca	Ca Error	Fe	Fe Error	Mn	Mn Error	Sr	Sr Error	Zn	Zn Error	Cu	Cu Error	S	S Error	Bal	Bal Error
RS-1	702	Rhodochrosite	rhodo (low Zn)	11110.87	524.22	9494.48	903.68	254720.4	3078.28	< LOD	4.63	35.16	20.97	113.53	36.93	2148.43	898.62	735603.3	2983.45
RS-2	860	Rhodochrosite	rhodo	4312.32	290.6	10498.39	300.74	200599.4	1423.08	13.27	2.19	646.83	28.72	197.73	23.44	2335.29	706.48	783744.7	1391.57
RS-3	860	Rhodochrosite	rhodo	4598.78	309.83	11090.18	261.11	150815.6	1027.16	8.48	1.67	526.15	22.53	126.92	17.2	2098.66	713.05	834002.8	977.2
RS-4	864	Rhodochrosite	rhodo (low Zn)	3590.92	291.61	9932.39	763.92	336044.7	2661.97	< LOD	3.23	128.33	19.51	< LOD	33.84	< LOD	815.87	657289.4	2596.66
RS-5	1205	Rhodochrosite	rhodo	5810.57	403.62	5853.83	416.23	231083.5	1532.12	< LOD	1.99	118.52	13.41	< LOD	20.07	< LOD	1080.5	762922.7	1453.56
RS-6	1434	Rhodochrosite	rhodo	3059.89	284.26	5695.11	567.97	279757.2	2057.89	< LOD	2.9	740.07	35.66	115.46	24.97	1287.4	702.57	713686.8	1987.58
RS-7	975	Rhodochrosite	rhodo	4724.96	319.3	13656.39	428.16	213882.5	1431.04	< LOD	2.32	810.55	30.52	28.95	16.7	2790.77	801.49	772793.5	1389.19
RS-8	1814	Rhodochrosite	rhodo	3428.3	196.73	6889.28	150.06	56510.8	470.87	4.78	1.14	192.47	11.79	< LOD	13.37	568.99	342.99	932932.8	370.9
RS-9	1929	Rhodochrosite	rhodo	12633.16	1001.83	18876.38	311.86	141726.4	1033.06	8.18	1.76	2922.11	54.01	< LOD	22.18	1279.93	586.1	823114.6	1092.95
RS-10	2510	Rhodochrosite	rhodo (hi Zn)	5209.1	299.95	35777.63	469.93	215523.4	1663.48	< LOD	2.7	6290.71	99.99	4170.36	94.18	12452.11	1293.52	735369.9	1892.05
RS-11	1674	Rhodochrosite	NOT rhodo NOT calcite	508.18	97.44	18059.66	223.62	< LOD	45.78	146.15	3.66	121.04	9.49	30.37	9.75	12339.43	716.42	966991.6	199.36
RS-12	3684	Rhodochrosite	rhodo	5901.33	248.68	10346.72	334.17	163867.1	1134.46	2.27	1.42	394.59	20.61	< LOD	19.41	895.21	376.64	824131.2	1070.1
RS-13	2597	Rhodochrosite	rhodo	12816.94	381.31	14671.59	247.02	91724.6	691.85	202.63	5	299.35	15.51	94.23	14.1	2865.89	598.26	876110.1	714.3
RS-14	1929	Rhodochrosite	rhodo (hi Zn)	17709.17	1118.99	23175.01	359.54	184841.3	1331.29	13.08	2.16	4377.35	71.78	< LOD	23.87	2978.6	935.6	769141.4	1475.21
RS-15	1262	Rhodochrosite	??	31924.26	1233.31	12978.94	233.21	86781.7	660.89	9.48	1.47	346.24	16.04	< LOD	15.52	< LOD	663.87	867051.9	746.53
RS-16	3754	Rhodochrosite	rhodo (low Zn)	16272.92	1048.88	10840.01	369.24	290928.4	2306.68	5.54	2.25	138.33	23.52	5583.06	114.42	2848.54	874.83	676378.3	2424.36
RS-17	1783	Rhodochrosite	rhodo (low Zn)	9007.26	365.47	4113.44	301.54	162158.5	1149.29	3.08	1.49	81.9	12.46	< LOD	21.35	941.93	522.65	828302.1	1067.16
RS-18	396	Calcite	calcite	83094.38	1652.74	24048.59	284.54	15748.1	272.55	18.73	1.76	883.3	25.14	98.97	14.06	1537.78	498.35	873934.6	717.84
RS-19	669	Rhodochrosite	rhodo	35335.01	1372.1	14907.29	254.14	111018.9	786.91	10.63	1.59	162.94	13.68	1775.6	42.8	2041.23	748.51	835971.8	916.72
RS-20	868	Rhodochrosite	rhodo	1999.96	276.11	590.1	351.89	344970.4	2691.93	< LOD	300000	< LOD	300000	1681.03	71.48	< LOD	1176.74	650684.2	2623.72
RS-21	1108	Rhodochrosite	rhodo	1770.83	204.61	14051.82	356.74	168176.6	1110.39	< LOD	2.09	309	21.49	6124.87	88.01	3328.93	780.61	814607.8	1093.07
RS-22	162	Calcite	calcite	45093.52	828.71	6396.32	122.11	1231.96	72.97	250.48	5.36	19.87	6.45	< LOD	16.75			931299.4	429.59
RS-22	162	Calcite	calcite	47402.96	893.88	16151.07	200.99	676.17	51.3	75.39	2.18	212.71	11.34	< LOD	12.51			921755.4	422.91
RS-23	398	Calcite	Ankerite?	8262.89	458.89	19333.5	260.11	1275.65	78.34	11.5	1.64	306.8	16.21	413.76	22.57			938644.3	385.72
RS-24	593	Calcite	Ankerite?	5531.39	156.58	17439.15	255.76	369	52.95	78.45	3.23	60.91	9.28	837.78	29.85	3522.32	329.18	943858.6	377.1
RS-25	840	Calcite	Sph, galena, calcite?	4497.47	336.54	3374.8	124.34	336.65	85.95	14.36	3.34	48473.81	457.63	84.36	21.88			930080.3	590.44
RS-26	865	Calcite	rhodochrosite low Zn	3236.61	215.74	3847.36	414.83	221825.1	1553.06	4.57	1.79	54.13	11.24	42.28	18.02	< LOD	661.93	773951.8	1458.49
RS-27	985	Calcite	rhodochrosite hi Zn	6994.62	421.32	1169.71	179.46	82360.22	720.67	12.04	1.88	2465.77	48.57	< LOD	23.73			906414.8	615.72
RS-28	990	Calcite	calcite	31708.64	646.55	1985.28	77.18	2910.95	105.61	35.12	2.29	62.59	10.9	1332.52	36.39	1924.05	207.2	955279.3	309.71
RS-29	1003	Rhodochrosite	rhodochrosite low Zn	11207.05	763.89	5915.92	459.1	245984.7	1619.94	9.68	2.06	50.39	11.56	94.46	20.38			738837.8	1593.07
RS-30	1267	Calcite	rhodochrosite hi Zn	1856.98	258.28	5770.41	319.34	140028.5	1015.17	7.91	1.93	10720.01	112.22	< LOD	27.28			843701.3	983.36
RS-31	1271	Calcite	rhodochrosite	2968.25	133.22	5265.93	258.39	125671.2	945.92	8.53	1.73	338.44	18.91	< LOD	20.97	808.18	254.17	865831.4	844.6
RS-32	1315	Calcite	calcite	63396.89	2486.1	2176.23	75.22	687.93	59.74	56.38	2.75	32.69	7.43	116.97	14.69			926514.1	2711.49
RS-33	1371	Calcite	calcite	8061.5	333.35	5667.22	140.96	261.84	46.3	54.68	2.15	35.66	7.1	< LOD	15.72			968851.6	213.23
RS-34	1518	Calcite	ankerite? Siderite?	791.82	49.87	2077.26	72.54	111.05	39.91	15.18	1.69	26.07	6.64	< LOD	16.72	230.62	84.03	986119.4	100.81
RS-35	1526	Calcite	calcite	171754.1	5480.63	478.28	42.63	250.79	46.33	7.99	1.45	10.34	5.79	< LOD	16.25			827179.1	5363.07
RS-36	1601	Calcite	calcite	161472.3	1589.19	1625.78	78.48	5056.88	140.52	28.87	2.19	41.06	8.07	229.43	18.77	1200.29	362	818477.9	1068.67
RS-37	1720	Calcite	ankerite? Siderite?	2141.34	61.24	5615.46	128.2	206.65	50.22	106.15	4.04	35.15	8.28	< LOD	20.07	303.4	79.02	979792.7	167.65
RS-38	1871	Calcite	calcite high sulfide	64570.32	1191.66	1350.33	99.48	1959.36	148.19	24.32	3.27	70639.69	740.31	456.18	36.65	18127.95	672.87	860279.3	1225.03
RS-39	1928	Calcite	calcite + rhodo	81855.38	1335.95	19413.06	299.21	42672.65	515	50.11	2.96	3142.3	52.67	< LOD	20.8	3720.7	466.55	849565.4	962.65
RS-40	2040	Calcite	calcite	214403.5	7485.74	1531.81	74.5	1489.98	87.93	56.7	3.05	45.38	8.78	< LOD	20.18			780919.9	7519.76

RS-41	2245	Calcite	calcite	210059.5	1845.18	804.67	59.01	2286.47	100.47	113.79	3.97	10.6	6.31	< LOD	17.56	< LOD	554.23	784853.4	1240.25
RS-42	2473	Calcite	calcite high sulfide	13776.66	611.58	49447.6	493.63	< LOD	106.05	5.41	1.46	375.52	36.61	40190.73	410.56	27152.38	935.46	890519.3	854.25
RS-43	2657	Rhodochrosite	rhodochrosite	791.07	72.71	10133.3	261.21	95159.59	817.55	5.52	1.83	2241.97	49.77	3730.14	72.8	6285.57	493.53	885729.5	760.79
RS-44	3076	Calcite	calcite	193148.4	1725.16	2031.61	79.42	1712.69	88.28	50.14	2.75	22.77	7.05	< LOD	18.58	< LOD	481.15	797621.4	1177.83
RS-45	3081	Calcite	calcite	22507.2	556.89	2867.75	84.74	167.83	43.35	72.41	3.08	18.79	6.4	< LOD	16.85	175.75	111.86	956227.6	315.19
RS-46	3087	Calcite	calcite	90793.8	1220.66	11697.31	232.08	2360.85	107.34	116.81	4.22	80.79	10.29	< LOD	20.74	445.25	180.91	891122.9	748.52
RS-47	3091	Calcite	sph, cpy, calcite?	910.61	163.05	4976.19	145.17	128.97	71.59	3	1.4	65677.69	632.1	10678.87	151.27			915019.8	735.48
RS-48	3176	Calcite	calcite	8869.35	537.97	3525.76	94.9	240.17	46.51	181.14	4.77	17.39	6.52	< LOD	16.89			973170	1170.16
RS-49	3696	Calcite	calcite high S and Zn	91285.69	1378.99	1571.7	104.67	2691.74	146.12	15.24	2.5	53760.64	531.34	1241.4	53.47	15717.09	677.57	848547.1	1168.93
RS-50	3707	Calcite	calcite some rhodo	105972.8	1372.17	1826.76	118.24	35356.66	463.69	118.74	4.14	1738.75	37.69	< LOD	19.24	1638.04	354.15	853150.9	912.23
RS-51	3793	Calcite	calcite high S and Zn	56135.77	1104.88	8188.28	200.19	3630.26	174.02	5.62	1.83	31779.93	327.24	593.02	35.08	10590.96	494.96	891623.1	858.74
RS-52	4656	Calcite	calcite or ankerite, high Cu	45508.6	1071.03	36999.13	394.8	1064.71	109.62	27.66	2.95	553.84	40.35	51557.58	482.04			861296.4	1016.93
RS-53	4906	Rhodochrosite	rhodochrosite some calcite	23138.88	658.62	4615.39	188.36	66252.95	676.11	11.13	1.83	112.04	12.16	< LOD	22.02	632.26	151.39	902607.2	687.92
RS-54	5544	Calcite	calcite	163082.2	1696.7	5152.34	128.26	3237.5	123.91	39.55	2.69	6530.06	75.25	1481.76	42.97	3435.8	418.44	816783.8	1133.24
RS-55	6257	Calcite	calcite	131328.6	1438.36	942.62	76.84	6442.64	171.45	38.51	2.67	16.57	7.52	260.42	21.98	341.87	185.88	856684.9	958.56
RS-56	7154	Calcite	calcite	20854.28	644.4	12763.31	244.01	309.56	55.57	39.96	2.68	21.78	8.01	29.58	14.66	2859.33	216.22	947299.2	409.36
RS-57	3087 Dup	Calcite	calcite	67975.91	1054.47	10664.47	231.39	1961.16	103.09	99.65	4.07	84.44	10.95	< LOD	21.5	243.1	121.22	915663.1	629.54
RS-58	5544 Dup	Calcite	calcite	138198.5	1578.23	4426.37	132.48	2784.83	128.29	32.88	2.77	5414.49	76.03	1454.66	47.6	2103.47	252.46	844069.2	1103.44
RS-59	865 White	Calcite	sphalerite?	84.41	20.46	3304.45	110.41	1761.48	101.45	6.76	1.7	23502.21	230.61	288.87	25.26	7949.32	362.01	969675	234.96
RS-60	1003 White	Calcite	calcite some rhodo	135348.3	1536.46	5129.13	139.25	23137.87	382.51	86.87	3.58	34.33	8.13	127.05	16.65	560.55	317.06	834156.3	1024.64
RS-61	SS1	Calcite	siderite?	1468.42	85.4	45334.37	468.11	110.09	54.15	7.36	1.64	38.25	10.13	1167.23	39.33	17747.26	629.15	931208.1	501.55
RS-62	Mtn Con 390	Calcite	calcite some rhodo	124477	1719.53	37118.98	443.18	13479.05	304.8	43.62	3.13	< LOD	32.09	17269.42	213.22	26302.5	994.3	806620.7	1314.64
RS-63	Mtn Con 390	Rhodochrosite	rhodochrosite ankerite?	2420.57	109.05	64496.94	613.01	47997.43	574.54	5.14	1.43	< LOD	300000	22035.02	281.14	35499.46	1120.18	859654.3	1036.68
RS-64	398 Dup	Calcite	ankerite? Siderite? Cc + pyrite?	2244.63	72.05	11720.34	231.45	890.32	73.18	10.52	1.71	209.6	14.82	250.34	21.02	818.71	124.71	964188.8	282.84
RS-65	7154 Dup	Calcite	calcite	14868.97	592.51	8905.26	228.59	< LOD	300000	20.01	1.88	< LOD	300000	< LOD	300000	1442.29	144.09	962131.9	343.88
RS-66	6257	Rhodochrosite	rhodochrosite	6523.89	482.92	938.6	223.23	138637.5	1054.02	4.46	1.23	1710.4	46.44	2066.65	59.42			849145.3	987.61
RS-67	347417 : 812	Calcite	Calcite	26974.66	715.23	15389.79	228.49	334.06	47.96	134.63	3.92	94.43	9.98	851.4	28.66	1881.05	254.48	918963	513.99
RS-68	357430 : 764	Calcite	calcite	79446.23	1065.64	15803.7	203.13	1213.64	64.51	47.27	1.79	156.31	10.2	42.4	10.26			887134.1	590.24
RS-69	357430 : 806	Calcite	calcite	169415.6	1616.74	12012.29	195.57	3852.06	109.72	80.85	2.95	101.72	9	22.94	10.3	1348.9	473.94	809759	975.49
RS-70	357430 : 820	Calcite	calcite	42350.67	793.7	11013.81	171.21	978.25	59.33	19.03	1.62	72.57	7.94	166.97	14.01			920455.2	412.74
RS-71	357430 : 828	Calcite	calcite	120362.6	1646.62	14347.01	238.22	11168.91	254.72	75.66	3.21	59.54	9.47	914.1	31.52	3346.93	510.04	835413.1	977.28
RS-72	357430 : 946	Rhodochrosite	rhodochrosite	5360.17	191.15	6859.11	131.19	24009.73	323.8	9.29	1.34	1481.05	29.55	43.54	10.99	1532.22	320.88	947067.9	321.9
RS-73	357430 : 981	Rhodochrosite	calcite	14152.82	589.41	18800.42	243.18	490.77	50.31	60.39	2.61	66.72	7.9	129.24	13.63	3356.14	359.72	942352.6	350.83
RS-74	305439 : 122	Calcite	calcite	54405.98	965.53	5142.58	97.56	< LOD	46.55	60.12	2.49	72.2	7.92	415.78	19.27	1386.6	281.17	929470.1	418.82
RS-75	305439 : 597	Calcite	calcite	26428.33	724.97	16022.29	213.02	159.64	37	84.65	2.87	112.73	9.22	512.57	20.68	3543.36	395.71	939689.3	359.54
RS-76	RS - 70 Dup	Calcite	calcite	36818.06	834.49	13114.52	198.08	842.17	57.42	18.14	1.62	139.27	10.07	135.42	13.22	5859.89	538.44	926921.3	438.05
RS-77	305439 : 114	Calcite	calcite	82956.26	1365.2	18382.57	233.94	< LOD	51.14	481.34	6.73	226.91	12.14	< LOD	13.31	6236.07	659.39	892913.4	598.19
RS-78	357430 : 121	Rhodochrosite	calcite	60312.43	1338.03	22698.65	298.81	2421.65	102.89	20.69	1.96	1378.81	33.87	4225.38	65.5	10148.55	683.39	894690.9	641.27
RS-81	347417 : 520	Calcite	calcite	16670.13	736.44	17796.03	231.09	235.37	41.66	94.84	3.13	158.11	11.3	1191.08	31.06	3593.16	453.87	936897.6	385.64
RS-82	347417 : 784	Calcite	ankerite?	4159.04	177.24	16220.63	226.65	< LOD	49.54	28.87	1.97	175.96	11.99	1147.82	31.52	4669.64	440.52	936705.3	397.68
RS-83	RS - 81 Dup	Calcite	calcite	15520.6	668.21	18458.54	248.3	339.19	47.67	111.65	3.55	140.52	11.49	1268.12	33.73	3659.7	394.21	939510.4	378.17
RS-84	325458 : 582	Calcite	calcite	40524.08	941.54	14199.83	220.74	73.01	37	16.33	1.66	73.51	8.59	135.26	14.64	6165.53	452.35	925512.6	477.99
RS-85	325458 : 840	Calcite	calcite	38283.72	893.03	10147.88	165.49	< LOD	44.5	60.46	2.37	137.92	9.21	70.77	10.5	1108.73	312.91	941902.3	326.91
RS-87	5480 Bench	Rhodochrosite	rhodochrosite high Zn	15531.07	1199.9	10582.36	345.06	216953.1	1708.15	4.18	1.71	28373.81	383.8	9847.29	182.07	15597.72	1636.7	711598.8	2210.97
RS-88	5480 Bench	Calcite	calcite	113557.2	2123.3	78724.42	694.33	514.37	75.67	5.12	1.57	288.82	18.37	307.93	24.14	44894.01	1849.25	805140.4	1233.22
RS-89	5560 Bench	Calcite	no carbonate? High Zn	714.83	405.1	8998.84	232.28	957.12	120.71	< LOD	2.39	138466	1754.34	2049.19	79.3	< LOD	1.5	828318.5	1976.21
RS-90	5520 Bench	Rhodochrosite	rhodochrosite + sulfides	14281.39	1479.69	33502.14	634.8	207045.4	2178.4	16.52	4.78	24983.9	523.09	136009	2465.53	< LOD	1.5	533179.3	6292.18
RS-92	990	Calcite	calcite	37364.34	913.36	4782.5	101.14	3878.17	108.12	26.16	1.85	165.49	12.9	1501.49	34.59	3723.5	443.17	943186.6	330.53
RS-93	1720	Calcite	calcite	7712.53	195.2	19281.71	241.98	155.28	39.12	154.8	3.94	152.15	10.38	< LOD	13.35	483.3	202.51	959959.1	254.35
RS-94	865	Calcite	ZnCO3?? No carbonate?	< LOD	34.64	6427.1	139.01	1881.74	97.28	2.11	1.34	25405.21	228.66	315.43	24.13	12066.4	607.03	964432.3	243.54
RS-95	Calcite Stan	Calcite	calcite	200069.4	1878.41	5232.38	91.84	< LOD	33.86	9.09	1.2	241.21	11.33	< LOD	11.18	< LOD	1121.08	792244.9	939.69

SIGNATURE PAGE

This is to certify that the thesis prepared by Ryan Alexander Stevenson entitled "Stable Isotopes of Hydrothermal Carbonate Minerals in the Butte Porphyry-Lode Deposits, Montana" has been examined and approved for acceptance by the Department of Geological Engineering, Montana Tech of The University of Montana, on this 10th day of August, 2015.

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