ABSTRACT

GOLD FROM THE TYPE 4 ORE OF ROUND MOUNTAIN, NEVADA: A TEXTURAL AND MINERALOGICAL STUDY OF MACROCRYSTALLINE GOLD VS. DISSEMINATED GOLD

by Mackenzie C. Taylor

New knowledge regarding epithermal gold from Round Mountain Gold Mine (RMGM) aims to add to what is known about gold mineralization and ore formation. The Type 4 gold ore (RMGM nomenclature) is unusual in that it contains both disseminated gold (nm-μm) and macrocrystalline gold. Unmodified samples of macrocrystalline gold and disseminated gold within bulk ore were acquired from the Type 4 and determined to be texturally and mineralogically distinct. Detailed investigation using field emission scanning electron microscopy (FESEM), coupled with energy dispersive x-ray spectroscopy (EDXS), concluded that gold mineralization began as two-dimensional nucleation following nanoparticle aggregation. The dominant mechanism for mineralization then shifted to adhesive growth, as gold in solution reached increased levels of supersaturation. Results further indicate two distinct sequences for gold mineralization occurred where only macrocrystalline gold contained paragenetic apatite, goethite, and gold telluride, while pyrite and chlorite were associated strictly with bulk ore. Minerals such as pyrite, goethite, and chlorite may have significant implications for extraction efficiency using conventional cyanide heap leaching. U-Pb dating of Type 4 apatite was also conducted in an attempt to further constrain the deposit’s complex mineralization history, but was determined to be inaccurate in determining an age date due to sample restrictions.
GOLD FROM THE TYPE 4 ORE OF ROUND MOUNTAIN, NEVADA: A
TEXTURAL AND MINERALOGICAL STUDY OF MACROCRYSTALLINE GOLD
VS. DISSEMINATED GOLD

A Thesis
Submitted to the
Faculty of Miami University
in partial fulfillment of
the requirements for the degree of
Master of Science
Department of Geology and Environmental Earth Science
by Mackenzie C. Taylor
Miami University
Oxford, Ohio
2017

Advisor _________________________
Dr. Mark P.S. Krekeler

Reader ___________________________
Dr. John Rakovan

Reader ___________________________
Dr. Claire McLeod

©2017 Mackenzie C. Taylor
# Table of Contents

List of Figures .............................................................................................................. iv  
Acknowledgements ....................................................................................................... v  
1. Introduction .............................................................................................................. 1  
   1.1 Gold .................................................................................................................... 1  
   1.2 Round Mountain Gold Mine .............................................................................. 1  
       1.2.1 Location and Mining History ...................................................................... 1  
       1.2.2 Geologic Setting. ...................................................................................... 2  
       1.2.3 Deposition ................................................................................................. 3  
   1.3 Low Sulfidation Epithermal Deposits ................................................................. 4  
2. Hypotheses .............................................................................................................. 5  
3. Materials and Methods .......................................................................................... 6  
   3.1 Samples .............................................................................................................. 6  
   3.2 Sample Preparation ........................................................................................... 7  
   3.3 Scanning Electron Microscopy .......................................................................... 7  
   3.4 Liberation of Nanoparticles by Partial Bulk Ore Dissolution ......................... 7  
   3.5 U-Pb Geochronology of Apatite ...................................................................... 8  
4. Results .................................................................................................................... 9  
   4.1 FESEM Results ................................................................................................. 9  
       4.1.1 Textural and Chemical Analysis of Gold .................................................. 9  
       4.1.2 Textural and Chemical Analysis of Paragenetic Mineralogy .................... 11  
       4.1.2.1 Macrocristalline Gold ........................................................................... 11  
       4.1.2.2 Bulk Ore ............................................................................................... 14  
   4.2 U-Pb Dating of Apatite ...................................................................................... 16  
5. Discussion ............................................................................................................... 17  
   5.1 FESEM Growth Textures and Composition of Gold ......................................... 17  
   5.2 Associated Paragenetic Mineralogy .................................................................. 19  
   5.3 Nanoparticle Gold and Silver ........................................................................... 23  
   5.4 Gold Processing ................................................................................................. 25  
       5.4.1 Implications for Cyanide Heap Leaching .................................................. 25  
       5.4.2 Implications for Cyanide Heap Leaching Alternatives .............................. 26
5.5 Apatite Geochronology ................................................................. 27
5.6 Sequence of Mineralization .......................................................... 29
6. Conclusions .................................................................................... 31
7. References ..................................................................................... 33
8. Figures ........................................................................................... 39
9. Appendices ..................................................................................... 66
  9.1 Review in Silver ......................................................................... 66
  9.2 Detrital Minerals Found (Chromite and Zircon) ......................... 67
  9.3 Supplementary FESEM Micrographs ........................................... 68
List of Figures

Figure 1: The Open Pit at Round Mountain Gold Mine............................................. 39
Figure 2: Round Mountain Gold Mine Location......................................................... 40
Figure 3: Geologic Map of the Round Mountain Gold Mine...................................... 41
Figure 4: Sampling Location....................................................................................... 42
Figure 5: Sample Images............................................................................................ 43
Figure 6: Rough Gold Growth...................................................................................... 44
Figure 7: Step Texture in Gold..................................................................................... 45
Figure 8: Hexagonal Cavities in Gold.......................................................................... 46
Figure 9: Flaky Gold.................................................................................................... 47
Figure 10: Gold Spheres.............................................................................................. 48
Figure 11: Macrocryalline Gold in Bulk Ore............................................................... 49
Figure 12: Gold and Silver Concentration of Electrum in Type 4................................. 50
Figure 13: Gold and Silver Concentrations in Nanoparticles...................................... 51
Figure 14: Nanoparticles of Electrum in Macrocryalline Samples.............................. 52
Figure 15: Nanoparticles of Electrum in Bulk Ore Samples......................................... 53
Figure 16: Quartz........................................................................................................ 54
Figure 17: Adularia..................................................................................................... 55
Figure 18: Clay Minerals (Illite-Smectite).................................................................. 56
Figure 19: Apatite........................................................................................................ 57
Figure 20: Stellated Iron-bearing Mineral (Goethite).................................................... 58
Figure 21: Clay Mineral (Palygorskite)....................................................................... 59
Figure 22: Chlorite....................................................................................................... 60
Figure 23: Pyrite.......................................................................................................... 61
Figure 24: Carbonates............................................................................................... 62
Figure 25: U-Pb Dating of Apatite............................................................................ 63
Figure 26: Sequence of Mineralization: Macrocryalline vs. Bulk Ore..................... 64
Acknowledgements

I would like to acknowledge Matt Duley and Dr. Richard Edelmann of Miami University’s Center for Advanced Microscopy and Imaging for their training and assistance with analytical techniques and imaging of samples, Terry Jennings and Dave Emmons for loaning samples, Michelle Burke for bulk sample collection and project guidance, Mark Pecha and others at the Arizona LaserChron Center responsible for analyses of samples sent, and Dr. Jonathan Levy, Dr. Amy Wolfe, Dr. Kelly McHugh, Alex Kugler, and Wladyslaw Betkowski for assistance in sample preparation and data interpretation.

I would also like to acknowledge the Department of Geology and Environmental Earth Science at Miami University and the Lipman Foundation (Lipman Research Award), by way of the Geological Society of America, for supporting this work.

I want to thank my advisor Dr. Mark Krekeler for agreeing to work with me and for supervising research conducted. Thank you to my committee members Dr. John Rakovan and Dr. Claire McLeod for their guidance from project start to finish. And I want to thank my parents, family, friends, and girlfriend Jennifer Bjelac for their constant support and encouragement.

Finally, I would like to honor and thank my dear friend and undergraduate advisor Dr. Michael R. Hudson (1954 – 2016) for his unwavering support and constructive feedback.
1. Introduction

1.1 Gold

Long prized for its luster, resistance to corrosion, conductivity, and malleability, gold is primarily used as a medium of exchange in the form of jewelry and bullion (Butt & Hough, 2009). However, applications for gold are numerous and increasing in variety as gold is also used in several advanced technologies; many of which require nanoparticles (Cobley & Xia, 2009; Corti et al., 2002; Pustovalov & Babenko, 2004). Gold nanoparticles are becoming increasingly important in the medical industry, where they are used in various ways including tumor detection and use as a drug carrier (Cai, 2008).

The worldwide gold industry totaled approximately $83.1 billion in 2013, and $171.6 billion when indirect employment is considered (Britton, 2015). Historically, the highest ever gold price peaked on September 5th 2011 at 1895 USD/ozt. Today, gold is valued between ~1250 and 1350 USD/ozt, yet it remains the second most valuable metal. High modern gold prices are encouraging new exploration, as well as mining of low grade ores (<5 ppm), and refining knowledge regarding gold mineralization and associated mineral paragenesis has never been more important. Due to the extensive economic importance of gold, fundamental work in understanding the nature of gold, and its applications, is critical for global economic growth.

Although gold is found as a native metal, it commonly exists as an alloy with Ag, Cu, Fe, Sn, and Te (Ridley, 2013; Walshe & Cleverley, 2009). While auric gold (Au\(^{3+}\)) forms and complexes with Cl\(^{-}\) under highly oxidizing conditions, aurose gold (Au\(^{+}\)) is far more common and tends to complex with the soft ligands S\(_2\)O\(_3\)^{2-}\) (oxidizing conditions), CN\(^{-}\), SCN\(^{-}\), and HS\(^{-}\) (reducing conditions) (Williams-Jones et al. 2009). Gold is usually considered an economic resource at concentrations of 5-10 ppm, which is 1250 to 2500 times higher than its bulk crustal abundance of 0.004 ppm (Ridley, 2013).

1.2 Round Mountain Gold Mine

1.2.1 Location and Mining History

In 2016, the United States produced 209 metric tons of gold, comprising 7% of global gold production (~3100 metric tons), and was the fourth largest producing country behind Russia (8%), Australia (9%), and China (15%) (George, 2016). In the United States, Nevada produces 3 times as much gold as all other U.S. states combined, and in Nevada the Round Mountain Gold
Corporation (RMGC) has served as a major producer for close to 30 years. The RMGC and the mine itself are located in the town of Round Mountain in Nye County, about 55 miles north of Tonopah and approximately 250 miles NNW of Las Vegas. The mine operates as a large open pit approximately 8200 feet long oriented in the north-west to south-east direction and is 5000 feet wide with 35-foot benches (Hanson, 2006)(Figure 1).

Between 1906 and 1969 approximately 350,000 ounces of gold were produced (Hanson, 2006). The Copper Range Company, Felmont Oil Company, and Case Pomeroy Company formed the Smoky Valley Common Operation (SVCO) in 1975, and in 1977 took ownership of RMGM (50%, 25%, and 25% respectively between the three companies) and began commercial production. In 1984 25% of the mine ownership was taken over by the Homestake Mining Company, and in 1985 50% of the mine became owned by Echo Bay Mines Incorporated. Then in 2000 the Homestake Mining Company increased ownership to 50%. In 2001 Homestake merged with the Barrick Gold Corporation, and in 2003 Echo Bay merged with Kinross Gold Corporation (Hanson, 2006). From 2003 to early 2016 the mine was owned 50-50 by Kinross and Barrick, with Kinross serving as the operating partner. At the beginning of 2016 Kinross Gold Corp. took over as the sole owner and operator of RMGM.

Between the years 1989 and 1999, the RMGM produced between 300,000 and 550,000 ounces of gold a year with an average recovery of 75-80%. (Emmons, 2008). Years 2000 to 2006 Round Mountain produced at least 600,000 ounces a year with the mine’s peak production year in 2003 producing 785,300 oz (Emmons, 2008). Between 2007 and 2013 the mine produced again between 300,000 and 550,000 ounces each year, and then 169,839 oz., 197,818 oz., and 378,264 oz. in 2014, 2015, and 2016 respectively (Emmons, 2008; Kinross Gold Corporation, 2017). Since 1977 RMGM has produced 14,533,196 ounces of gold (Emmons, 2008; Kinross Gold Corporation, 2017).

1.2.2 Geologic Setting

The RMGM sits in the Big Smoky Valley which runs between the Toiyabe and Toquima Mountain Ranges (Figure 2). The valley and two ranges are products of Basin and Range extension which was followed by plutonic intrusions (~95 Ma) and volcanism (~27 Ma) (Shawe et al., 1986). Highly deformed, Paleozoic meta-sedimentary rocks comprise the material that underlies the deposit, and these rocks include limestone, dolomite, siltstone, argillite, quartzite,
phyllite, and schist (Hanson, 2006). Stacked as a series of thrust sheets, these units underwent deformation beginning in the late Paleozoic and continued into the Mesozoic. Several Cretaceous age granitic plutons then intruded the sedimentary rocks, subjecting them to significant degrees of metamorphism. The now meta-sedimentary rocks were then overlain by rhyolitic ash flow tuffs Oligocene to Miocene in age. Ash flow tuffs are the result of several caldera eruptions from the two ranges. The main caldera in the Big Smoky Valley in which these tuffs are found is the Round Mountain Caldera, which was eventually buried by alluvium and continued extension. The margin of the Round Mountain Caldera, and fractures from Basin and Range extension, provided pathways for gold bearing hydrothermal fluids to migrate closer to the surface. The majority of gold is hosted in the volcanic tuff as disseminated electrum, but mineralization within the Paleozoic meta-sedimentary rocks did occur (Hanson, 2006).

1.2.3 Deposition

The Round Mountain gold deposit is developed in a complex low sulfidation epithermal system primarily hosted in altered rhyolitic tuff. Gold mineralization occurs as electrum of variable Au-Ag concentrations. Associated with electrum mineralization are primarily quartz, potassium feldspar (adularia), pyrite, illite-smectite and iron oxides. These minerals are primarily found in the paleozoic bedrock, but do occur in various quantities in the tuff.

At RMGM several specific different lithologies are used in the RMGC mining nomenclature (Figure 3). Partially underlying the deposit, and exposed to the east wall of the caldera, is the Cretaceous age Round Mountain granitic pluton; known as the Type 8. In the base of the mine resides the Type 4 ore which is comprised of Paleozoic meta-sedimentary rocks broken down into the Mayflower Schist, the Gold Hill Formation, and the Zanzibar Limestone (Hanson, 2006). The Type 4 is unique because it contains both disseminated gold, and macrocrystalline gold found in high-grade quartz veins. Also residing low in the mine is the Type 3 which is a moderately welded, lithic-rich tuff which serves as a moderate source of gold. On top of the Type 3 and 4 units is the primary ore source known as the Type 2. The Type 2 is a non-welded to poorly-welded, pumice-rich tuff where disseminated gold occurs in high grade. Above the Type 2 is a thinner, transitional unit between the Type 2 and Type 1 known as the Type 9, which is a moderately-welded rhyolitic tuff of minor ore grade. The Type 1, at the top is a densely-welded rhyolite tuff with some fracture controlled gold mineralization. This unit served
as the cap rock for upwelling hydrothermal fluid. The three remaining units once covered what is now the RMGM and can be observed at the perimeter of the open pit. The Stebbins Hill unit, Type 33, sits directly on top of the Type 1 and is composed of volcanlastic rocks, ash flows, lake sediments, and breccias. Volcanlastic dominated gravels that accumulated during the late Tertiary sit on top of the Type 33 and are known as the Type 52. The Type 52 once contained minor amounts of placer gold which was virtually depleted due to heavy mining prior to 1962 (Hanson, 2006). Granitic alluvium of Quaternary age comprises the Type 51 and is considered a non-producing unit.

1.3 Low Sulfidation Epithermal Deposits

Low sulfidation epithermal deposits, often referred to as adularia-sericite or quartz-adularia type deposits, are a common type of gold deposit and have been extensively studied (e.g., Pohl, 2011; Ridley, 2013; Sillitoe, 1993; Tosdal et al., 2009; White & Hedenquist, 1995). These deposits are thought to occur primarily in volcanic dome fields where rifting due to extension has permitted shallow magmatic intrusions. Rifting and pluton emplacement create structural pathways for deep circulating meteoric waters and magma to interact forming hydrothermal fluids. Hydrothermal fluids can then travel along these pathways promoting mineralization. Fluid interaction with wall rock creates near neutral pH of chloride-dominated waters and reduced conditions, allowing for $\text{H}_2\text{S}$ to exist. The $\text{H}_2\text{S}$ serves as an important ligand for gold to complex with, and can then be transported through hydrothermal fluids. The primary complex for gold transportation in these environments is typically $\text{Au(HS)}_2^-$, but transportation mechanism may vary with deposits. As fluids boil during ascent, sulfide deposition occurs and decreasing pressures and temperatures allow for mineralization of gold, quartz, adularia, and calcite. Boiling of fluids volatilizes dissolved $\text{CO}_2$ and $\text{H}_2\text{S}$, and fractures surrounding rock, creating new pathways for hydrothermal fluids and mineralization (Kesler, 2005; Tosdal et al., 2009). Mineralization occurs at depths of 1-2 km and temperatures of 200°C-300°C. The majority of mineralization takes place in veins formed from recent fracturing. This can lead to crystallization of gold macrocrystals, as well as disseminated mineralization if host lithology porosity permits. Deposits most often occur directly above magmatic centers, or within 2-10 km of a magmatic source. Vapor $\text{CO}_2$ and $\text{H}_2\text{S}$ migrate towards the surface eventually interacting with cool ground water forming $\text{H}_2\text{SO}_4$. Sulfuric acid lowers the pH of meteoric groundwater.
altering minerals in surrounding rocks typically forming minerals such as illite, opal, alunite, kaolinite, and pyrite.

Colloidal gold present may nucleate and lead to nanoparticle formation (J. A. Saunders, 1990; J. A. Saunders & Schoenly, 1995; J. Saunders & Burke, 2017; Shuster & Southam, 2015). Formation of nanoparticles may then aggregate to form larger crystals of gold. Chemical and physical properties of colloidal and nanoparticle gold have been studied as advancements in industry, requiring nanoparticle gold, have been perpetuated (e.g., Burke et al., 2017; Cobley & Xia, 2009; Hough et al. 2009; Williams-Jones et al., 2009). Physical aggregation is likely the predominant mechanism for nanoparticle aggregation (Saunders & Schoenly, 1995; Williams-Jones et al., 2009). Microorganism facilitation of gold nanoparticles by reducing and/or oxidizing bacteria, archaea, and fungi has been known to occur (Shuster & Southam, 2015; Southam et al., 2009). Colloidal gold nucleation in epithermal deposits seems to require accompaniment by colloidal silica in order to keep colloids stable at temperatures of 200°-300°C (Frondel, 1938; J. A. Saunders, 1990). Studies have shown that silica may occur as an amorphous gel precursor to crystalline quartz, and this silica gel is what protects gold colloids at higher temperatures of up to 300°C-350°C (Saunders, 1990). It is clear that gold colloids and nanoparticles play a very important role in the formation of gold in epithermal deposits. However, the details of how these particles relate to macrocrystalline gold, and the paragenetic mineralization sequence of ores of different types, are poorly understood.

2. Hypotheses

The paragenetic mineralization of gold in the Type 4 ore from Round Mountain is currently poorly constrained. The objective of this project is to gain new insight into gold mineralization in order to build upon what is previously known regarding mechanisms of mineralization in epithermal deposits. Careful analysis of the interface between gold and associated paragenetic minerals can help determine whether or not the two types of gold, macrocrystalline and disseminated gold in the bulk ore, formed from a single mineralization event or from multiple events. Understanding the paragenetic mineralogy of the deposit could aid exploration and refinery processes at Round Mountain, as well as around the world. The objective of the project tests 2 hypotheses:
(1) A complex paragenetic mineralization sequence exists in both Type 4 Macr
cystalline gold and bulk ore that has not been recognized.

If supported, this hypothesis includes: (a) paragenetic sequence will have consequence
for a refined understanding of the geologic history of the deposit, (b) minerals observed will
potentially be useful for understanding lower or variable extraction efficiency, and new
knowledge may aid in improving extraction efficiency, and (c) a well-constrained mineralization
sequence for the Type 4 may provide useful for exploration. If the hypothesis is not supported,
the simple existing model for mineralization stands.

(2) Further geochronological study of the paragenetic minerals closely associated with
gold will provide a better understanding of the timing of gold mineralization.

Implications for this hypothesis relate to extant geochronology from adularia from the
tuff of the Type 2 ore, and this primary igneous mineral is only presumed to be nearly coeval
with gold mineralization. However gold mineralization could be significantly younger. If so,
younger age gold mineralization may impact exploration in the region.

3. Materials and Methods

3.1 Samples

Samples of both macrocrystalline gold and disseminated gold within bulk ore were
acquired from the Type 4 deposit at RMGM that are known to be unmodified. Samples were
provided by Terry Jennings and the staff from RMGM, Dave Emmons, or collected by Mark
Krekeler and Michelle Burke, all of which were obtained during an April 2015 trip to Round
Mountain. Several bulk ore samples were collected from Round Mountain by Mark Krekeler and
Michelle Burke during the same site visit (Figure 4). The macrocrystalline samples came from
Terry Jennings who donated a 2.5 cm elongate gold crystal of a habit common to spinel twins
with partially hopered surfaces, and Dave Emmons who loaned a high-grade ore sample
containing a quartz-adularia vein bearing macrocrystalline gold (Figure 5). All samples came
directly from the Type 4 gold deposit from RMGM and no samples were cleaned with acid prior
to microscope analysis.
3.2 Sample Preparation

Samples were made to fit aluminum SEM sample stubs and were mounted using carbon sticky tabs and carbon tape. The carbon sticky tabs were utilized to stick the sample to the stub while the carbon tape was wrapped around the sides, undersides, and then one strip over the top of the sample to ensure the best ground possible.

3.3 Scanning Electron Microscopy

The primary instrument used in this study was a Zeiss Supra 35 VP field emission scanning electron microscope (FESEM). Textural analyses of the samples were conducted using a secondary electron detector in secondary electron mode (SE2) and variable pressure mode (VPSE). Variable pressure mode utilizes N₂ as a compensating gas which is injected into the microscope sample chamber to reduce charging in uncoated, nonconductive samples. Backscatter detection (BSD) was used to identify and differentiate between paragenetic mineral phases, and to locate gold and silver nanoparticles. An EDAX Genesis 2000 energy dispersive spectroscopy (EDXS) detector was used to collect qualitative data regarding the chemical composition of areas of interest. The identity of minerals was determined using a combination of textural analyses as well as EDXS.

3.4 Liberation of Nanoparticles by Partial Bulk Ore Dissolution

In order to better locate and analyze nanoparticles in bulk ore samples, a single sample was initially chosen to partially dissolve after initial FESEM analysis was concluded. A sample ~1 mm in diameter was placed in a 1.5 ml Eppendorf tube and submerged in ~1 ml of 1 N HCl. The sample was left in the acid for ~3 hours, was then drained, and then re-submerged in ~1 ml of concentrated HCl (~36%) and placed on a hot plate at 80° C. The sample was left for ~15 hours, then drained, rinsed with deionized water and allowed to dry. After completely drying, the sample was mounted on an SEM stub, according to the steps explained in section 3.2, and analyzed using BSD in the FESEM. The sample was later removed from the stub and, along with two other bulk ore samples (~0.5 mm and ~1 mm in diameter) that had already been analyzed by FESEM, was partially dissolved in acid further. All three samples were placed in 15 ml glass sample jars and submerged in approximately 4 ml of 8 N room temperature nitric acid. Samples were left in the acid for ~28 hours, the solution was then drained and replaced with ~ 8 ml of
concentrated room temperature nitric acid (68%). The three samples were left in the acid for ~23 hours, rinsed with deionized water, dried, and mounted on SEM stubs and analyzed. In every step where an acid solution was removed from a vile or jar the solution was placed on a hot plate at 80°C to be evaporated leaving behind any particles that had been removed from the sample during dissolution.

3.5 U-Pb Geochronology of Apatite

Over sixty apatite crystals were collected from the 2.5 cm macrocrystalline gold sample. Apatite crystals (20 µm to 115 µm in diameter), were collected using a high powered light microscope and micrometer size glass sampler needles. As the majority of crystals collected were <50 µm, only a total of 5 crystals were determined to be large enough for U-Pb geochronological analyses (ranging from about 60 µm across to about 115 µm). These crystals were sent to the Arizona Laserchron Center to be dated using U-Pb laser ablation multiple collector inductively coupled plasma mass spectrometry (U-Pb LA-MC-ICPMS). The Arizona Laserchron Center uses a Nu Plasma multicollector with an attached short-pulse 193 nm excimer laser for analyses. The samples were prepared at Arizona by first polishing the crystals to remove clay. As Arizona typically uses no smaller than a ~60 µm spot size, only 1 spot analysis was possible per crystal. Drilling depth of the laser was 15 µm/µm²/s. Well characterized standards, correction of concordia-intercept age-errors due to decay constant errors and lead loss, as well as largest possible spot size help to ensure accurate data collection (Ludwig, 2000; Schoene, 2013; Thomson et al., 2012). Arizona uses two apatite standards, the Durango apatite from the Cerro de Mercado iron mine in Mexico and apatite from Madagascar. Five standards are run before analysis, two standards are run between every 4 to 5 unknowns, and three standards are run at the end. The U-Pb isotopic data collected from the analyses can be plotted on concordia and used to calculate an age for the apatite crystals. The ages for the apatite crystals were determined by plotting $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ on a concordia diagram. Data that does not fall on the concordia line defines a line of discordia with the intercepts interpreted as the point of lead loss (upper intercept) and the age of the crystals (lower intercept).
4. Results

4.1 FESEM Results

4.1.1 Textural and Chemical Analysis of Gold

The dominant texture observed for the surface of macrocrystalline gold samples is (~55%) rough growth that typically varies from lightly striated to pitted (Figure 6). This texture is present in both positive and negative portions of the crystals’ surface macrotopography. Striations often transition into large deep crevices that are occasionally lined with a saw-tooth texture. Rough growth is also found where gold has a ropy texture. Finally, there are several areas exhibiting smeared or irregular growth, like that observed in Figure 6C.

The second most pervasive texture (~40%) is a step texture (Figure 7). The steps are found linking high terraces and low valleys. Step widths vary <0.5 µm to approximately 25 µm, while the step height remains fairly uniform at no greater than ~0.5 µm. Regions exhibiting steps are found varying from a few steps to upwards of 100 steps extending from a low topographic area to a high terrace.

An unusual surface feature on one of the samples (~4% of surface area) is the presence of hexagonal cavities which often have prismatic islands in their centers (Figure 8). These vary from small features where the length of each side varies from 20 to 40 µm to large hexagons with 50 to >100 µm sides. The angles vary between each side and can be near perfect 120° angles or appear to vary between approximately 100° and 140°. When an island occurs inside the cavity, the distance between the island and edge of the hexagon varies from 10 µm to about 100 µm. This distance can vary within individual cavities by up to 40 µm. Gold outside of the cavity is of equal height as the gold island within, and the texture of the gold is typically rough with small striations. Gold on the inside of the cavity does not maintain the general hexagonal shape as that outside of the cavity. Surfaces from the edge of the cavities into the bottom can be gradual with step texture, or steep. The hexagonal cavities are filled in with paragenetic minerals preventing the bottom of the cavities from being observed, however, depth of the cavities is estimated to be approximately 15 µm to 30 µm.

Other features identified on macrocrystalline gold (<1%) are areas of flake gold and gold-rich spheres. Only a few aggregates of flake gold occur. Gold flake widths vary from <1 µm to about 5 µm, and lengths are commonly <1 µm up to about 15 µm (Figure 9). Flake thickness is fairly uniform at approximately 60 nm. Gold spheres occur sparingly and vary from
approximately 1 µm to about 3.5 µm in diameter (Figure 10). Identified using EDXS, one gold sphere contains a significant amount of tellurium suggesting a gold telluride.

Although the overwhelming majority of gold and silver present in the bulk ore exists as nanoparticles, there are some rare examples of macrocrystalline gold of micrometer scale present in the Type 4 ore. These crystals vary from approximately 1 µm x 2 µm x 0.5 µm thick to 5.5 µm x 8.5 µm x 1 µm thick, and are entirely rough (Figure 11).

Concentrations of gold and silver in electrum differed from macrocrystalline samples to bulk ore samples. Normalized mass percentages of only gold and silver were collected from EDXS analysis (Figure 12). Gold concentrations in macrocrystalline samples vary from 47% to 76% and averaged 61%. Silver concentrations in these samples vary from 24% to 53% with an average concentration of 39%. The majority of Au-Ag minerals in the bulk ore are nanoparticles, and almost all of them contained little to no gold. Therefore, gold concentrations in bulk ore samples vary from 0% to 61% with an average concentration of 8.0%. Silver concentrations vary from 39% to 100% and average 92%. Standard deviation (1 σ) of both gold and silver in macrocrystalline samples was calculated to be 7.9 and the variance was 62. Standard deviation (1 σ) of both gold and silver in bulk ore samples was found to be 18 and variances were calculated to be 320 (Figure 12). Two different t-tests were calculated for the data to determine if the concentrations of gold and silver differ between macrocrystalline samples and bulk ore samples. A two-sample t-Test assuming unequal variance was calculated for gold and silver concentrations between macrocrystalline and bulk samples, and both p-values were calculated to be 1.5x10⁻⁷. The p-value using the Wilcoxon test was also calculated for both gold and silver concentrations in the two sample types, and the value for both was found to be 4.2x10⁻⁷. Both tests conclude that gold and silver concentrations differ significantly between macrocrystalline samples and bulk ore samples.

Nanoparticles of electrum, with varied amounts of gold and silver, are found with both macrocrystalline and bulk ore samples. Aggregates of nanoparticles occur where the diameter of nanoparticles varies from 10 nm to 200 nm in each aggregate. Aggregate sizes vary ~1.5 µm to about 150 µm in diameter with an average diameter of ~6 µm. Size of nanoparticles and nanoparticle aggregates for both macrocrystalline samples and bulk ore samples were very similar. Normalized mass percentages, of only gold and silver concentrations in nanoparticle aggregates, were also collected from EDXS analysis (Figure 13). Gold concentrations in
nanoparticles associated with macrocrystalline samples vary from 47% to 67% with an average concentration of 56% (Figure 14). Silver concentrations in the same particles vary from 33% to 53% with an average concentration of 44%. Nanoparticles associated with bulk ore samples (Figure 15) were primarily void of gold and have compositions dominated by silver, sulfur, and chlorine. Including sulfur and chlorine into the normalized mass percentages, variable gold concentrations from 0% to 16% were observed with an average of 3.0%. Silver concentrations vary 84% to 100% with an average of 97%. Standard deviation (1 σ) of both gold and silver in macrocrystalline samples was calculated to be 10 and the variance was 110. Standard deviation (1 σ) of both gold and silver in bulk ore samples was found to be 6.0 and variances were calculated to be 39 (Figure 13). The same two different t-Tests were calculated for the data regarding nanoparticles as with all electrum, and both tests concluded that gold and silver concentrations differ significantly between macrocrystalline samples and bulk ore samples. The two-sample t-Test assuming unequal variance had a calculated p-value of 1.4x10^{-2} for gold and silver concentrations between the two sample types, and the p-value for both gold and silver between macro and bulk samples for the Wilcoxon test was 7.9x10^{-4}. This conclusion was not as significant with nanoparticles as it was regarding all electrum analyzed, however, the results still indicate a variation in concentrations of gold and silver in macrocrystalline samples and bulk ore samples.

4.1.2 Textural and Chemical Analysis of Paragenetic Mineralogy

4.1.2.1 Macrcrystalline Gold

Macrocristalline gold samples typically form in quartz and adularia veins, making these minerals common paragenetic species. Other paragenetic minerals associated with macrocrystalline gold samples are, illite-smectite, apatite, and presumed crystals of iron-oxyhydroxides. All associated mineralogy is present only on the surface of macrocrystalline gold, or on the surface of other paragenetic minerals on gold.

A common morphology of quartz associated with macrocrystalline gold is characterized by massive anhedral crystals (Figure 16). These crystals vary from 30 µm x 60 µm x 15 µm thick to 80 µm x 110 µm x 30 µm thick. Another common morphology of quartz is characterized by euhedral hexagonal prisms with pyramidal terminations. Prisms vary from 5 µm to 20 µm in diameter and approximately 30 µm to 120 µm in length. EDXS analysis of quartz aided textural
analysis in identifying the mineral. The spectrum shown in Figure 16F shows the presence of only 2 characteristic x-ray lines for elements silicon and oxygen; which support the identification as quartz.

The given EDXS spectrum (Figure 17F) shows the presence of only potassium, sodium, aluminum, silicon, and oxygen supporting the textural analysis that adularia is present. Adularia associated with macrocrystalline samples also occurs in two general morphologies. Crystals of adularia can occur as large as 180 µm x 260 µm x 50 µm thick. These massive crystals vary from anhedral to euhedral and often contain linear gaps that originate and terminate within a crystal face and extend throughout the entire crystal. Occasionally linear gaps in feldspar extend beyond crystal edges, opening the crystal interior up on 3 faces. Adularia also exists as euhedral blocks as small as 30 µm x 40 µm x 10 µm thick and as large as about 70 µm x 90 µm x 20 µm thick. Euhedral crystals occasionally appear to have Carlsbad type twinning. Both massive and euhedral crystals of adularia may contain hopper growth that is either diamond or triangular in shape (Figure 17). Diamond shaped hopper growth tends to be larger reaching up to 15 µm across and about 30 µm long with 1 µm high steps. Triangle shaped hopper growth is considerably smaller averaging about 3 µm across with steps around 0.2 µm deep.

Illite-smectite (I-S) is identified by minor potassium in EDXS spectra combined with textural analysis of characteristic lamellar aggregates. I-S is abundant with the Type 4 deposit macrocrystalline gold and coats much of the surface of gold crystals in a smooth film, or concentrated as lamellar aggregates (Figure 18). Included in Figure 18D is a representative EDXS spectrum of I-S observed showing characteristic X-ray lines of potassium, iron, calcium, magnesium, aluminum, silicon, and oxygen.

Apatite is common as a paragenetic mineral associated with macrocrystalline gold samples. Apatite is exclusive to macrocrystalline gold and no examples are observed in the bulk ore. EDXS analysis indicates these crystals are fluorapatite, Ca$_5$(PO$_4$)$_3$F, due to the presence of calcium, phosphorous, oxygen, and fluorine (Figure 19F). Apatite morphology is characterized by euhedral hexagonal prisms and pseudo-hexagonal tabular crystals. Tabular crystals comprise 80% of the apatite present and vary from 50 µm across and 10 µm thick to 120 µm across and 20 µm thick (Figure 19). These crystals are euhedral, but not always hexagonal. The crystals often have a mosaic surface texture on faces parallel to the c axis. Many of the tabular crystals are intergrown as aggregates of 2 to approximately 100 crystals. The hexagonal prisms comprise
20% of the apatites, and are all euhedral and very uniform averaging 2 µm across and 2 µm in length. Hexagonal prisms are typically concentrated together in areas of lower topography on the surface of gold crystals. Some isolated hexagonal prisms can be found across gold samples.

A possible iron-oxyhydroxide mineral interpreted as goethite (FeO(OH)), based on morphology, (e.g., Cornell, R.M., Schwertmann, 2000, 2003) was observed as a paragenetic mineral associated with macrocrystalline gold. This mineral is only associated with macrocrystalline gold and is not found in bulk ore samples. The mineral is pseudo-hexagonal and stellated, and is concentrated with other similar crystals in low crevices on top of clay minerals on the surface of the gold (Figure 20). Stellated crystals are almost acicular with a layered morphology and vary from 0.5 to 1 µm across and average approximately 0.2 µm thick. At high magnification the crystals appear to be layered and almost platy, consistent with those observed from laboratory experiments of Cornell and Schwertmann (2000) (Figure 20B). EDXS analysis of the crystals shows the presence of X-ray lines of Al, Mg, Si, Au and Ag which are interpreted as originating from the underlying substrate (Figure 20C). The prominent iron and oxygen peaks in conjunction with the morphology of the crystals, suggests that the minerals may be iron-oxyhydroxides interpreted as goethite.

Quartz, adularia, and illite-smectite minerals are found in direct contact with each other, as well as gold. Quartz crystals are on top of, as well as beneath, adularia crystals. When in contact, illite-smectite minerals are present strictly on the surface of quartz and adularia, and never beneath the two. Apatite growth is intermixed with illite-smectite growth. Goethite is only present on top of clay minerals lining crevices in gold. Goethite is not in contact with any other paragenetic minerals other than clay and is never in contact with gold.

If an average of 60% of the surface of macrocrystalline gold samples is visible gold, the remaining 40% of the surface of the sample is covered in paragenetic minerals. Of that 40%, the modal abundance of quartz and adularia is about 10% each. The stellated iron-oxyhydroxide crystals comprise about 5% of that 40%, and apatite is approximately 25%. Visible aggregates of nanoparticles of electrum constitute <1% of the surface of crystals. The remaining 50% of the paragenetic minerals present on macrocrystalline samples are illite-smectite crystals.
4.1.2.2 Bulk Ore

Most of the gold mined at Round Mountain is disseminated throughout various lithologies. The Type 4 bulk ore is hosted in Paleozoic meta-sedimentary rocks, carbonates and siliciclastics, and contains disseminated electrum and silver on micrometer and mainly nanometer scales. An abundance of paragenetic quartz, adularia, calcite, pyrite and clay minerals are identified. The clay minerals identified were illite-smectite minerals, palygorskite, and chlorite.

The variety of morphologies of quartz increases from macrocrystalline gold to bulk ore samples. Quartz exists as massive and prismatic crystals of similar size to that of macrocrystalline samples, but also exists as platy pseudo-hexagonal pseudo-prisms as well as sections of groundmass. Platy quartz, or parallel lattice bladed quartz, varies from mostly prismatic with minor plate-like morphology to completely micaceous-like morphology (Figure 16C and D). These quartz crystals are mostly hexagonal and vary from 80 µm to 350 µm across and 165 µm to 300 µm long. Quartz also exists as large sections of groundmass covered in clay minerals and other paragenetic minerals. Macroscopic and microscopic vugs occur where quartz prisms radiate from the surface protruding towards the center of the vug. The crystals are hexagonal and have pyramidal terminations. For microscopic vugs, the average size of these crystals is 20 µm in diameter and they typically extend no more than about 50 µm from the surface into the opening.

Adularia present in the bulk is very similar to that of macrocrystalline samples. Both euhedral block crystals as well as massive crystals of feldspar occur in bulk ore samples, and are of similar dimensions to those in macrocrystalline samples. Hopper growth and twinning of feldspar is also prevalent in bulk ore. Tabular crystals of adularia and euhedral prisms also exist (Figure 17). Tabular crystals can be greater than 200 µm x 200 µm x up to 6 µm thick. Some crystals exhibit a saw-tooth texture that can comprise entire crystal faces. Hopper growth is also present with tabular feldspars. Large euhedral hexagonal prisms of feldspar exist among massive crystals.

Illite-smectite minerals are about as abundant in bulk ore samples as they are with macrocrystalline samples. There is little to no variations in morphology of these clays comparing macrocrystalline gold to bulk ore samples, except perhaps a slight reduction in the amount of lamellar aggregates in the bulk ore (Figure 18). Slight chemical variations occur as different I-S
aggregates are analyzed, and variations also occur when analysis is focused on different sections within a single clay aggregate. These variations are expected and are likely due to the difficulty in differentiating between the interlayering of illite and smectite species.

Palygorskite occurs as acicular crystals typically on illite-smectite and other paragenetic minerals (Figure 21). These crystals vary in length from about 1 µm to 8 µm and the average length is 4 µm. The width of palygorskite crystals is approximately 100 to 300 nm. Acicular crystals are typically isolated, but can overlap at all angles. Crystals of palygorskite are often observed as an aggregate in the same orientation and ends of the needles appear feathered. This texture is consistent with alteration or transformation textures of Krekeler et al. (2005) and bundle texture observed in Krekeler et al. (2004). There are also some aggregates of palygorskite where acicular crystals radiate from a center point, but these are uncommon (Figure 21C). A representative EDXS spectrum of palygorskite is given in Figure 21D and shows the presence of magnesium, aluminum, silicon, and oxygen which are all constituents of palygorskite \((\text{Mg, Al})_5(\text{Al, Si})_8\text{O}_{20}(\text{OH})_2\cdot8\text{H}_2\text{O}\). These compositions are consistent with EDXS work by Krekeler et al. (2004) and Krekeler (2004).

A micaceous mineral presumed to be chlorite is abundant in Type 4 bulk ore samples. It exists as very platy coatings of subhedral to euhedral crystals covering large sections of the surface of samples, as well as rosette aggregates (Figure 22). These textures are interpreted as authigenic and not detrital or deformed detrital in origin. In the representative EDXS spectrum for chlorite Mg, Al, Fe, Si and O are all present and this composition is consistent with ripidolite \((\text{Mg,Al,Fe})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8\) (Figure 22D).

Pyrite exists primarily as two different morphologies which likely formed at different times. Pyrite occurs as euhedral cubes and small spheres (Figure 23). Cubes vary from near perfect cubes to perfect cubes which have faces varying from 15 µm to 300 µm across. Pyrite cubes are often intergrown and found throughout the bulk ore. Spheres are much smaller averaging about 4 µm in diameter and vary from 1 to 8 µm in diameter. Both morphologies often contain striations along the crystal faces. EDXS analysis of the minerals is conclusive that crystals are composed of iron and sulfur (Figure 23F). This analysis supports the identification of pyrite.

Calcite is an abundant phase in the bulk ore. EDXS analysis yielded data concluding that Ca, Fe, Mg, and Mn were all present in carbonate minerals (Figure 24D). The calcite is
interpreted to be a low magnesium calcite with some solid solution with siderite and rhodochrosite components. Carbon and oxygen were also present on the EDXS spectrum, along with residual aluminum and silicon X-rays collected from adjacent clays. Calcite crystals vary in size from approximately 100 µm to greater than 1 cm (Figure 24).

Carbonate minerals comprise 70% of the groundmass with quartz making up the remaining 30%. Non-groundmass quartz can be found both on top of, as well as beneath, adularia crystals. Clay minerals, chlorite, and pyrite can all be found on top of quartz, adularia, and carbonates. Often embedded in the bulk ore groundmass are euhedral crystals of cubic pyrite. These pyrite crystals are often partially covered in carbonate minerals, quartz, and various clays. Chlorite is on quartz, adularia, cubic pyrite, and carbonate minerals. Secondary carbonate can be seen growing into chlorite in Figure 23C. This carbonate is secondary growth after the primary carbonate that constitutes the host lithology. Illite-smectite, palygorskite, and spherule pyrite can also be found on top of chlorite. Palygorskite was found on top of illite-smectite minerals, but never beneath them. Spherule pyrite was found on top of all other paragenetic minerals, and only ever had very minor amounts of illite-smectite on the crystal surfaces. Nanoparticles of electrum and silver were typically found clustered on top of clays, chlorite, and groundmass, but never on top of pyrite.

Excluding groundmass mineralogy, chlorite was the most abundant paragenetic mineral phase comprising 25% of the surface of bulk ore samples. Secondary carbonate crystals made up 15% of the paragenesis mineralogy and clay minerals illite-smectite and palygorskite constituted 20% and 10% respectively. Cubic pyrite comprised 10% of the paragenetic make-up while spherule pyrite attributed 5%. Adularia was also 5% and quartz comprised 8% of the surface of bulk ore samples. Detrital minerals and electrum/silver nanoparticles comprised 1% each totaling 2%. As only a few micrometer size macrocrystals of electrum were found in the bulk ore, these crystals contributed <1% of the paragenetic make-up.

4.2 U-Pb Dating of Apatite

The measured concentrations of uranium and lead for 4 of 5 crystals analyzed were plotted on a Tera-Wasserburg diagram (Figure 25). The isotopic values for each of the crystals are plotted on the diagram as an ellipse illustrating measurement error calculated during ablation. As the ellipses do not fall on the concordant line, the data is discordant and the intercepts of the
discordant line generated can be used to determine the crystals’ age. The upper intercept for the line was determined to be 4930.5±3.8 Ma and the lower intercept is 60±32 Ma. The mean squared weighted deviation (MSWD) for the concordia is 0.046 and the probability of fit for the data is 0.95.

5. Discussion

5.1 FESEM Growth Textures and Composition of Gold

Based on morphology and surface texture analysis, the predominant mechanism for gold growth in macrocrystalline gold within the Type 4 is consistent with adhesive type, where growth occurs at high degrees of supersaturation (Burke et al., 2017). Adhesive type growth occurs during extreme supersaturation and is characterized by rough growth texture along crystal faces (Sunagawa, 1999). Rough growth with a high kink density is the most common texture associated with Type 4 gold, and the second most common is step texture. Step texture occurs when growth is dominated by two-dimensional nucleation at levels of supersaturation in which smooth growth layers are preferentially generated near edges and corners (Berg, 1938; Sunagawa, 1999). Other gold textures found on the surface of these crystals, such as flake gold and gold spheres, are also thought to be products of adhesive type growth. Spherulitic and fractal growth, like that of gold flake, are thought to only occur during increased levels of fluid supersaturation relative to two-dimensional nucleation (Sunagawa, 1999). Also characteristic of the surface texture of macrocrystalline gold were hexagonal cavities in the surface. Some of the cavities had a cylindrical island in the middle completely isolated from the outside of the cavity. These cavities are presumed to either be the result of competitive growth where gold grew against another phase, or they are molds of remnant mineral phases that crystallized around the same time of gold mineralization, but were then dissolved. Given the hexagonal shape, it is likely that the remnant mineral was quartz. The cause for island formation within the cavities may be due to competitive growth between the remnant phase, gold, and paragenetic phases described, or partial dissolution of the remnant phase allowing for mineralization of paragenetic minerals and secondary gold growth; however, both hypotheses are highly speculative.

Gold textures observed are comparable to that of Burke et al. (2017), and primarily differ in modal abundance. In that study, macrocrystalline gold samples were collected from the Type 4 ore deposit from RMGM and were analyzed using FESEM and transmission electron
microscopy (TEM). Results from the data collected were that ~60% of macrocrystalline gold texture was characterized by steps and terraces, ~30% was rough growth, ~3% hopper growth, and ~7% vein like features (Burke et al., 2017). No hexagonal cavities were found in Burke’s samples, and definitive microscopic hopper growth in gold, nor vein like features, were identified in Type 4 samples from this study. Although hopper growth was not identified on the microscopic scale, partially hoppered surfaces were identified at the macroscopic scale for the spinel twinned sample. Also dissimilar to Burke et al. (2017) there were no distinct topographic highs and lows (islands and depressions), and the majority of the step texture is located as a disconnected network across the surface of macrocrystalline samples; instead of being as pervasive (~60% of crystals’ texture) as Burke observed. Nanoparticles of electrum and silver were found in both studies and varied in abundance and composition. Burke et al. (2017) emphasized the role of nanoparticle assembly in macrocrystalline gold via orthokinetic aggregation and this is an important process in the formation of macrocrystalline gold. Burke et al. (2017) indicates that two-dimensional nucleation and growth mechanism is dominant and nanotextural evidence suggests that nanoparticulate gold was the first stage of growth in the formation of these macrocrystalline samples that grew rapidly at high degrees.

The current model for gold deposition at Round Mountain suggests that as hydrothermal fluids migrated towards the surface and mixed with groundwater, post faulting and jointing of country rock, they were cooled and gold was rapidly reduced (Henry et al., 1997; Sander & Einaudi, 1990). The reduction of gold caused destabilization of gold-transporting complexes leading to fluid supersaturation of gold and then deposition (Sander & Einaudi, 1990). It is thought that as fluids migrated towards the surface, levels of gold in solution reached supersaturation initially yielding two-dimensional nucleation. Then gold concentrations quickly surpassed supersaturation leading to the primary mechanism for the majority of mineralization as adhesive growth. Specific locations for the samples reported in Burke et al. (2017) are not known, however, the contrasts in morphology between the two studies are potentially due to differences in depth of formation within the Type 4 or perhaps a concentration gradient within the deposit.

Average concentrations of gold and silver differ between macrocrystalline samples and bulk ore samples. Gold constitutes a higher proportion of the chemistry of electrum in macrocrystalline samples, and then severely decreases in concentration within the bulk. The
average concentrations of gold and silver in macrocrystalline samples are 61% and 39% respectively, and for bulk samples 8.0% and 92% respectively. The decrease in gold from macrocrystalline samples to bulk samples becomes even more severe in the context of nanoparticles. In nanoparticles the average concentrations of gold and silver in macrocrystalline samples are 56% and 44% respectively, and in the bulk ore 3.0% and 97% respectively. The decrease in gold from macrocrystalline samples to bulk ore samples could be explained by late stage dissolution. It is possible that silver could have been remobilized from gold crystals hosted in quartz veins, and then reprecipitated as disseminated and aggregated silver nanoparticles within the porous bulk ore. The idea of late stage dissolution-reprecipitation in the Type 4 ore is consistent with Burke et al. (2017), and the idea of silver mobility is consistent with the findings of Krupp and Weiser (1992). Although not detected using EDXS, macrocrystalline gold from the Type 4 has been observed using scanning transmission electron microscopy (STEM) elemental mapping as being in solid solution with copper, as well as silver (Burke et al., 2017). Although copper was not detected, high silver content in the Type 4 suggests a late stage silver overprint, confirms observations of Burke et al. (2017) and points to complexity in mineralization of the Type 4 not previously recognized. The analysis of copper in the Type 4 gold was a new discovery and was suggested to be the result of changes in fluid composition from a more Ag-rich solution to more Cu-rich (Burke et al., 2017).

5.2 Associated Paragenetic Mineralogy

Understanding mineral paragenesis for an ore deposit can be extremely important in regards to the overall success of a mine. Characterization of unmodified samples, samples analyzed directly after being mined without cleaning, has given new detailed insight on the associated mineralogy of the Type 4 gold deposit. Former studies of the deposit, like that of Burke et al. (2017), have used samples rinsed in acid to study gold morphology. Rinsing samples in acid modifies them removing most of the paragenetic mineralogy, leaving behind only those that withstand dissolution. This is why the only paragenetic minerals observed by Burke et al. (2017) during investigation were quartz, adularia, illite-sericite and Ti-oxide. Quartz and adularia were both observed in macrocrystalline and bulk ore samples, as well as several other phases.

Quartz is a common, and typically highly abundant, paragenetic mineral associated with epithermal deposits, and is crucial to furthering understanding of the conditions associated with
the mineralization of ore deposits (Moncada et al., 2012; Rusk et al., 2011; Rusk & Reed, 2002). Textures of quartz such as colloform, moss, and pseudoacicular are thought to be indicators of the former presence of a silica gel precursor (Dong et al., 1995). These textures are formed from very slow rates of precipitation relative to typical prismatic quartz, at temperatures as low as 100°C and high fluid supersaturation levels relative to amorphous silica (Fournier, 1985; Dong et al., 1995; Rimstidt & Barnes, 1980). Colloidal silica precipitating amorphous gel can have great implications on the stability of colloidal gold aggregation and gold growth (Frondel, 1938). Although textural analysis of the Type 4 ore suggests that colloidal gold aggregation led to macrocrystalline gold growth, the presence of quartz textures indicative of amorphous silica were not detected. Massive quartz in the bulk ore and prismatic quartz in veins are primary growth textures of quartz. Lattice bladed quartz crystals are interpreted as former intergrowths of quartz and calcite. These minerals are common in epithermal deposits and often occur as intergrowths of lattice bladed crystals (Moncada et al., 2012). The lattice bladed crystals in the Type 4 are entirely quartz and void of calcite. It likely that lattice bladed calcite intergrown with quartz was dissolved away leaving just the quartz behind. Lattice bladed calcite is thought to be the product of rapid growth due to loss of carbon dioxide to vapor during boiling (Simmons & Christenson, 1994). Quartz has also been known to completely replace calcite in these environments yielding a transition from lattice bladed calcite to lattice bladed quartz, and it is possible that partial quartz replacement of calcite could have occurred in the Type 4 (Moncada et al., 2012).

Adularia is a potassium feldspar (KAlSi$_3$O$_8$) that is characteristic of low sulfidation epithermal deposits and is often thought of as a disordered microcline or a more ordered orthoclase (Deer et al., 1992). The identification of adularia can also be aided by the presence of sodium, which it often incorporates. Minor amounts of sodium, relative to potassium, were observed in the majority of EDXS analyses of adularia. There are four common textures of adularia that occur in epithermal deposits: sub-rhombic, rhombic, tabular, and pseudo-acicular, and the presence of these textures, as well as the composition and degree of alteration, can reveal growth conditions for adularia and other minerals like gold (G. Dong & Morrison, 1995). The two common textures of adularia in the Type 4 are small sub-rhombic crystals and small tabular crystals. Sub-rhombic crystals are most often anhedral to subhedral, and have relatively ordered Al/Si distribution (G. Dong & Morrison, 1995). Boiling of deep hydrothermal fluids slightly
supersaturated in adularia and quartz in low permeable rock, followed by slow crystallization, will yield sub-rhombic adularia and coarse-grained quartz (Dong & Morrison, 1995). Violently boiling fluids in more permeable rock, yield more disordered adularia in tabular form (Dong & Morrison, 1995). The presence of these two morphologies in the Type 4 indicates either distinct changes in hydrothermal fluid conditions during upwelling, or that different fluids were migrating through at different times. Linear gaps in adularia crystals are interpreted as former intergrowths of bladed, or platy, calcite crystals that have been dissolved away. Therefore, changes in hydrothermal fluid conditions, or multiple fluid introductions, could also explain the dissolution of calcite as well as differing morphologies in mineral phases.

Clay minerals are also abundant in epithermal deposits and tend to precipitate following quartz and adularia. Clay minerals observed in the Type 4 are illite-smectite, palygorskite, and chlorite. Illite-smectite minerals are often associated with these deposits and can also reveal details about growth conditions and mineralization in hydrothermal systems (White & Hedenquist, 1995). Morphology of smectite can be used to help determine hydration-dehydration conditions undergone by the mineral, and this can help to constrain the amount of hydraulic and differential pressures that a system was subjected to (Colten-Bradley, 1987). As pressures decrease and dehydration persists, these minerals will contract and appear as wrinkly aggregates also known as cornflake-lamallae aggregates. The precise identification of I-S is challenging as insufficient material is available for powder X-ray diffraction analysis. Potassium observed in EDXS is consistent with R0 or R1 illite-smectite (Dong et al., 1997). The morphologies observed are consistent with R0 or R1 illite-smectite, and no hexagonal plates or laths are observed as interpreted by Flett et al. (2016) as illite or sericite in the Type 2. The interstratified minerals were able to be identified by their morphology and combined chemistry. Illite has a chemical formula of $K_{0.65}Al_2[Al_{0.65}Si_{3.35}O_{10}](OH)_2$ and smectite has the general formula of $A_{0.3}D_{2.3}[T_4O_{10}]Z_{2\cdot n}H_2O$ where calcium, aluminum, and magnesium often fill the A and D sites, silicon fills the T site, and hydroxide fills the Z site. Elements identified during EDXS analysis: potassium, calcium, magnesium, aluminum, silicon, and oxygen, indicate that lamellar aggregates are in fact illite-smectite.

Palygorskite is also observed in association with illite-smectite minerals, and occurs as fibrous needles; a common morphology (Galan, 1996; Krekeler et al., 2005). Palygorskite has a modulated 2:1 layered structure with open channels containing high amounts of water and
exchangeable Na\(^+\), K\(^+\), and Ca\(^{2+}\) (Krekeler & Guggenheim, 2008). All chemical constituents of the chemical formula for palygorskite \(((\text{Mg,Al})_5(\text{Si,Al})_8\text{O}_{20}(\text{OH})_2 \cdot 8\text{H}_2\text{O})\) were identified using EDXS. Illite-smectite and palygorskite are precipitates and a shift occurs from illite-smectite to palygorskite. The stability diagram of Hojati et al. (2012) shows a transformation of illite-smectite to palygorskite, due to dissolution in alkaline conditions. Analysis of the Type 4 bulk ore supports this shift as palygorskite is present on top of illite-smectite and most other minerals, and is suspected to be the last phase mineralizing in the deposit. The final clay mineral, chlorite, is suspected of being the product of partially metamorphosed bulk rock during hydrothermal alteration.

Although apatite is a common accessory mineral in most rocks, it was previously thought to be less characteristic of epithermal gold deposits. However, studies have shown that apatite is more common in gold deposits than prior knowledge would suggest and when present, it can prove as a very useful tool (Carillo Rosua et al., 2005; Cline et al., 2005; Hickey et al., 2014; Mao et al., 2016; Márton et al., 2010). Apatite can be used as a geochronometer in U-Pb dating in order to put geologic dates to deposit orogenesis. The phosphate mineral can also be used to constrain changes in chemistry of hydrothermal fluids as it incorporates a wide variety of trace elements such as REE, Y, Sr, Mn, and U and Pb. Understanding the partitioning of trace elements between apatite, co-existing minerals, and the co-existing melt, can help reveal information regarding fluid evolution from the magmatic source, to metal precipitation, and finally hydrothermal alteration. For example, the presence of late stage fluorine in the Type 4 produces fluorapatite.

Pyrite is ubiquitous and highly abundant in epithermal deposits. The mineral’s presence in hydrothermal systems has been highly studied as it is one of the most common minerals associated with gold rich ores (Craig et al., 1998; Muntean et al., 2011; White & Hedenquist, 1995). Although pyrite varies in habit and texture, pyrite is primarily found as euhedral cubes especially in low temperatures between 150°-250° C, but occurs initially as framboids (Craig et al., 1998). It is possible that with appropriate fluid conditions during Type 4 mineralization associated with gold deposition, pyrite initially formed as framboids and then aggregated completely to form the spherule observed. Striations on the pyrite spherules in the Type 4 show signs of two-dimensional nucleation that, had mineralization continued, could have led to formation of cubes. Even when not initially the dominant morphology of pyrite, low-grade
metamorphism can cause recrystallization of cubes. Later hydrothermal activity is likely the cause of secondary pyrite in the form of spheres, and this is why two generations of pyrite exist. The iron sulfide mineral is known to often contain variable amounts of cobalt, arsenic, and nickel in the crystal lattice, and may also contain variable amounts of gold adsorbed on the crystal faces (Craig et al., 1998; Muntean et al., 2011). The interface between pyrite and gold in the Type 4 has been studied (Hanson, 2006), but new findings suggest that this is not as common and is rarely seen in Type 4 samples.

One hypothesis presented by Kinross staff is that there is gold on the surface of pyrite based on the behaviors of cyanide leach tests. Although details could not be provided, the behavior is described as a very brief initial pulse of gold followed by no significant yield. The data do not support this interpretation and there appears to be little to no gold on or associated with the surface of Type 4 pyrite. Thus any beneficiation to concentrate pyrite would not be effective.

The observation of the stellated pseudo-hexagonal, acicular mineral presumed to be goethite may have significant implications for the Type 4 ore regarding epithermal conditions. Acicular goethite has been studied and used in laboratory experiments to constrain conditions of formation in significant depth (e.g. Cornell, R.M., Schwertmann, 2000, 2003; Cornell & Giovanoli, 1985; Ford et al., 1997). In order for acicular goethite to mineralize, it has been suggested that the system must have low levels of aluminum (Ford et al., 1997) and a pH of >12.2 (Cornell & Giovanoli, 1985). This is concerning for gold deposition at Round Mountain because it is a low sulfidation epithermal deposit which are thought to occur at near neutral pH, and the hydrothermal fluids that deposited minerals present were Al-rich. It is possible that goethite mineralization occurred at greater depths and was brought to the Type 4, or that conditions of goethite mineralization in the Type 4 differ from previous studies.

Secondary calcite mineralization is thought to be due to continued hydrothermal activity, which could have dissolved bulk carbonate from Type 4 bedrock allowing it to recrystallize as secondary calcite and other minerals.

### 5.3 Nanoparticle Gold and Silver

Nanoparticles of electrum and silver sulfide/chloride were found during FESEM investigation, and are known to be common in the Type 4 ore. Although not widely studied in
low sulfidation epithermal gold deposits, it has been proposed that increased kinetic energy due to boiling causes aggregation of gold nanoparticles (Burke et al., 2017; J. Saunders & Burke, 2017). Growth of nanoparticles and their behaviors have been studied in other ore metals and were found to be characterized by depth of occurrence as well as pressure and temperature conditions (Adushkin et al., 2006). Analysis of both macrocrystalline gold samples, as well as bulk ore samples, from the Type 4 deposit at Round Mountain indicate that aggregation of gold and silver nanoparticles does occur, and that the constrained geologic setting and temperature conditions support theories regarding nanoparticle aggregation leading to macrocrystalline gold growth. Nanoparticles are observed under FESEM investigation on the surfaces of both macrocrystalline gold and bulk ore samples. Rarely seen isolated, nanoparticles are almost solely observed in clusters or aggregates where overlapping of particles is typical. These aggregates are observed at the surface of samples and were common occurrence across the entire surface. Nanoparticles were observed almost exclusively associated with quartz, adularia, and clay minerals, but were found sparingly in contact with other phases. No nanoparticles of electrum or silver were directly observed as embedded in other mineral phases, and could only be identified as surficial. However, observation of many aggregates of nanoparticles following partial rock dissolution suggests that nanoparticles are partially embedded or covered by other phases.

Just as concentrations of gold and silver seemed to be very different between macrocrystalline samples and bulk ore samples, so are the nanoparticles associated with the two sample types. Nanoparticles associated with macrocrystalline samples were exclusively electrum with average normalized Au-Ag concentrations of 56% and 44% respectively. Average normalized Au-Ag concentrations associated with bulk ore samples are quite different at 3.0% Au and 97% Ag. Other nanoparticles associated with bulk were almost exclusively void of gold and entirely silver sulfide/chloride. However, some aggregates of nanoparticles did occur where gold was present, but in concentrations between 8% and 15%.

Chlorine was found to be associated with both Au-Ag nanoparticles as well as Ag nanoparticles void of gold, while sulfur was only observed in Ag nanoparticles and not Au-Ag nanoparticles. Chlorine was only observed with nanoparticles within bulk ore and was not found associated with either nanoparticles, or any other mineral, associated with macrocrystalline gold. Chlorine was observed in bulk ore nanoparticles in all 3 samples partially dissolved, and is therefore interpreted as being authigenic and not sample prep in origin. The majority of
nanoparticle aggregates in bulk ore samples were observed under backscatter detection in the FESEM following partial rock dissolution. Partial dissolution allowed for liberation of nanoparticles making them easier to locate and characterize. The surficial location of nanoparticles in both macrocrystalline and bulk ore samples might explain why the RMGM reports getting a pulse of gold from Type 4 bulk ore upon initial cyanide processing, and then little to no metal shortly after cyanide leaching begins. Nanoparticles are likely only exposed at the surface of the bulk ore and the cyanide solution does not permeate the interior of the ore owing to low porosity.

5.4 Gold Processing

5.4.1 Implications for Cyanide Heap Leaching

Information from Kinross USA indicates that the extraction efficiency of the Type 4 ore using conventional cyanide heap leaching is variable. The causes of this behavior are not understood, however the paragenetic mineral analysis provides some explanation.

Extraction of gold using cyanide heap leach has a low startup cost, low cost of operation, and is mostly efficient (Bartlett, 1997; Marsden & House, 2006), but several mineral phases and the overall texture of the Type 4 bulk ore may have a significant impact on the extraction efficiency of gold using this method. Although occasionally characterized as having coarse macrocrystals of differing composition, the majority of the surface of Type 4 bulk ore is comprised of small, tightly-cemented siliciclastics and carbonate minerals with a considerable amount of clay minerals. This inhibits the cyanide solution from penetrating the bulk to reach disseminated gold. This is especially the case when un-milled ore is processed with cyanide. Breaking ore down into smaller particles creates enhanced pathways through which cyanide can more efficiently to better reach the gold in the ore, and increases surface area decreasing time needed to dissolve the gold. The RMGM only mills what is deemed high grade ore (>10 ppm) and doing so they report ~85% recovery (Hanson, 2006). The low grade ore (<5 ppm) is left to be processed by cyanide heap leaching and recovery efficiencies drop severely to about 16% (Hanson, 2006). It is likely that the bulk ore textures observed have significant impacts on decreasing extraction efficiency, but it is more likely that associated mineral phases have a greater impact on extraction.
Iron is known to compete with gold for complexing with cyanide (Lopez et al., 2014; Marsden & House, 2006). This competition reduces extraction efficiency by increasing the amount of cyanide, and amount of interaction time, needed to maximize gold recovery. Increases in cyanide use, as well as time extensions needed for processing, and overall increases in extraction costs, decrease efficiency and can lead to mine closure. The abundance of iron bearing minerals pyrite, goethite, chlorite and calcite in the Type 4 ore poses a significant threat to decreasing gold recovery efficiencies, especially owing to the small crystal size, high surface area and high Fe content.

Gold spheres containing Au, Ag, Te, and S were observed amongst macrocrystalline gold samples. It is likely that these spheres are aggregates of more than one mineral. Gold tellurides are a common form of gold and minerals such as sylvanite (AuAgTe₄), calaverite (Au₀.₈₅Ag₀.₁₅Te₂), and krennerite (Au₀.₇₅Ag₀.₂₅Te₂) are known to occur. Gold tellurides have a decreased rate of dissolution in cyanide solution relative to native gold or electrum (Marsden & House, 2006). Therefore, gold telluride has the potential to play a role in the variable extraction efficiency.

Copper also is known to compete with gold for complexing with cyanide (Lopez et al., 2014; Marsden & House, 2006). Although no copper was found during FESEM investigation of Type 4 samples, Burke et al. (2017) did identify zonation of silver, gold, and copper at the macrocrystalline gold crystal interface. Copper may be of concern for remnant macrocrystalline gold extraction; however Cu is likely not a major concern for competing with gold in the Type 4 bulk ore matrix.

### 5.4.2 Implications for Cyanide Heap Leaching Alternatives

Cyanide is toxic to both humans and other animals when 0.05 mg CN⁻/kg/day is ingested over an intermediate duration, and 4.6-15 mg CN⁻/kg is ingested acutely (Eisler & Wiemeyer, 2004; U.S. Department of Health and Human Services PHS, 2006). Accidental spills and cyanide attenuation in old mine tailings can serve as agents for introducing the toxin into the environment which can be detrimental on surrounding organisms including human beings (Rao & Reddy, 2006; Zagury et al., 2004) Finding alternative, more environmentally sound extraction approaches to replace cyanide extraction are sought (Guo et al., 2017; Kuzmina et al., 2017; Whitehead et al., 2004; Whitehead et al., 2007). These “green chemistry” approaches however
are more complex and a refined understanding of the causes for variation in extraction efficiency is not yet at hand. The occurrence of both illite-smectite and palygorskite have the potential to impact extraction efficiency if the mine chose to switch to more green chemistry extraction approaches. Thiourea can be used in extraction of gold (Guo et al., 2017; Whitehead et al., 2004) but this compound can also be absorbed in the interlayer by montmorillonite (Ngassa et al., 2014; Ngassa Piegang et al., 2016). Thus thiourea would be expected to be absorbed by smectite layers in illite-smectite and therefore reduce extraction efficiency. Ionic liquid extraction approaches have also been demonstrated as an alternative, most commonly utilizing imidazolium and ethylammonium cations (Kuzmina et al., 2017; Whitehead et al., 2007) and sometimes in combination with thiourea (Whitehead et al., 2004). The presence of illite-smectite may reduce extraction efficiency of imidazolium based approaches as Matzke et al. (2009) demonstrated that smectite was a strong absorbant for imidazolium. De Lima et al. (2017) investigated rheological properties of sepiolite by addition of 1-methyl-3-butylimidazolium and found that the sepiolite retained 5 weight percent of the compound. Sepiolite and palygorskite are closely related structurally and chemically (Guggenheim & Krekeler, 2011) and thus by analogy palygorskite would reduce extraction efficiency by adsorbing imidazolium molecules. Finally, the use of thiosulfate has shown great potential as a lixiviant for gold that is environmentally sound, but is utilized very little in comparison to conventional cyanide (Hilson & Monhemius, 2006; Muir & Aylmore, 2004). The benefits are that rates of gold dissolution using thiosulfate can be faster than cyanide, there are decreased risks of interference from competing cations, and yields are generally high (Muir & Aylmore, 2004). Difficult chemistry regarding maintaining proper leach solution conditions and the need for large quantities of solution (Muir & Aylmore, 2004), currently leave cyanide easier to use and more economic.

5.5 Apatite Geochronology

Hydrothermal activity that formed the gold deposit at Round Mountain was previously dated using $^{40}$Ar/$^{39}$Ar of nine adularia samples from tuff comprising the Type 1; of which 5 are the result of potassic alteration yielding adularia replacement of sanidine (Henry et al., 1997). The analyses yielded an age of 26.03±0.08 Ma for potassium feldspar within tuff hosting the Type 1, 2, and 3 ore deposits. Hydrothermal activity is thought to have lasted only about 0.1 Myrs. It was proposed by Henry et al. (1997) that hydrothermal mineralization could have lasted
as short as 0.05 Myrs. or as long as 0.5 Myrs. Using the youngest and oldest possible ages calculated for the feldspars and the longest projected duration of 0.5 Myrs. for hydrothermal activity, Henry et al. (1997) suggest mineralization could be as young as 25.35 Ma and as old as 26.75 Ma. This would be the case if there were only one hydrothermal event mineralizing all throughout the deposit. It is likely that there were multiple mineralization events, and dating other phases from other lithologies, such as apatite in the Type 4 ore, could help better constrain these mineralization ages. Dating other phases that turn out to be significantly younger or older than the feldspars from the tuff would suggest that multiple mineralization events occurred.

Apatite is common, and almost ubiquitous as an accessory phase, in both felsic and mafic igneous, clastic sedimentary, and metamorphic rocks. The phosphate mineral has the potential to serve as a robust geochronometer because it is so common and can incorporate almost half of the naturally occurring elements, and does so where variations in concentrations are large (Chew & Donelick, 2012). Dating apatite of hydrothermal origin using U-Pb is beneficial due to the moderate closure temperature of 350°C-550°C and its sensitivity to changes in magmatic fluid conditions (Chew & Spikings, 2015; Chew et al., 2011).

Apatite crystals were collected from macrocrystalline gold and analyzed using U-Pb LA-MC-ICPMS. These crystals were analyzed at the Arizona LaserChron Center where the minimum crystal size is typically set so that 2-3 spot analyses, of minimum 50 µm in diameter, can be conducted per crystal. Spot sizes as small as 30 µm have been used for U-Pb LA-MC-ICPMS of apatite before, but larger spot sizes of at least 50 µm are preferred (Thomson et al., 2012). Larger spot sizes allow for increased quantities of U to be measured, which is crucial when analyzing apatite as it is typically very deficient in U (partitioning coefficient of U into apatite for peraluminous granite is 43.7) and therefore deficient in radiogenic Pb (Bea et al., 1994). Apatite is also generally concentrated with common Pb, and this too makes having the largest possible spot size more efficient. Due to the majority of crystals collected from macrocrystalline gold samples being <50 µm in diameter, only 5 crystals were determined to be large enough to obtain even just one spot analysis on. Only 4 of the 5 apatite crystals analyzed could be used to calculate an age due to low $^{238}$U concentrations relative to $^{206}$Pb concentrations in one of the crystals. Low concentrations of U, accompanied by high concentrations of common Pb, attributed to decreased analytical precision of measurements made during ablation. Large errors in isotopic ratio measurements are evident of this decreased precision, and yielded large
ellipses on the concordia around each data point. Concentrations of common Pb are even higher in apatite crystals from Round Mountain not only because they are found in association with large quantities of clay and adularia, but primarily because they are so young. If mineralization did occur around 26.0 Ma and this is the approximate age of the apatite crystals, Pb-bearing minerals would all have very high levels of common Pb (Stacey & Kramers, 1975).

The well-characterized Madagascar and Durango apatite standards and maximum spot sizes allowed by crystal diameter were used in order to increase analytical precision and accuracy. Ultimately, the 4 crystals analyzed were used and data from analyses were plotted on a concordia which yielded intercepts at 4930.5±3.8 Ma and 60±32 Ma. The lower intercept is taken to be the age of the crystals, and when error is taken into account this data suggests the apatites could be as young as 28 Ma or as old as 92 Ma. The extremely large spread between the intercepts and the >50% error associated with the calculated age indicates poor precision, and suggests a low accuracy for the results. It is likely that the concentrations of U and radiogenic Pb were too low relative to common Pb, the crystals were too small, and that not enough crystals were analyzed to produce a precise discordant line to calculate an accurate age. Even when a discordant line anchor point of 0.83757 for $^{207}\text{Pb}/^{206}\text{Pb}$ was determined by Stacey and Kramers (1975) for terrestrial Pb isotope concentrations at 26.0 Ma, the errors were too extreme (ranging from 55% of the calculated age to 300%) and calculated ages surpassed 135 Ma.

5.6 **Sequence of Mineralization**

Considerable variation exists for the mineralization sequences of macrocrystalline gold samples and bulk ore samples from the Type 4 ore, and these sequences are distinct and complex. Mineralization is hosted in primarily siliciclastic and carbonate rock. Detrital minerals and large cubic pyrite crystals exist in the host rock, and are likely from the Paleozoic diagenetic history. In both sample types, quartz and adularia precede gold mineralization. This is consistent with the concept that colloidal silica formed beneath the deposit (Herrington & Wilkinson, 1993; Saunders, 1990; Saunders & Schoenly, 1995) served as a precursor in the form of amorphous silica that may crystallize into quartz (Dong et al., 1995; Saunders, 1994). Similar to the findings of Burke et al. (2017), no evidence was detected for an amorphous silica precursor. Although gold deposition is thought to be largely coeval with quartz and adularia crystallization (Figure 26), initial mineralization of these two gangue minerals did precede gold and may therefore have
served as a nucleation surface. The presence of gold nanoparticles in macrocrystalline samples and bulk ore samples serves as evidence for aggregation of colloidal gold. This aggregation is produced by near-instantaneous metallic bonds that form during collision of nanoparticles during boiling (Saunders, 1994; Weitz & Oliveria, 1984). As aggregation of gold nanoparticles persists and gold in solution reaches increased degrees of supersaturation, two-dimensional nucleation and macrocrystalline gold growth can occur. Two-dimensional nucleation is evident from the observed step texture in macrocrystalline samples, and this gold growth allows for new nucleation surfaces for nanoparticles leading to increased aggregation and growth. As levels of gold increased further to higher degrees of supersaturation, adhesive growth evidenced by rough growth texture, becomes the dominant mechanism for gold mineralization.

Macocrystalline gold is almost exclusively found in quartz and adularia veins within the Type 4, and therefore the mineralization sequence differs significantly from the bulk ore. Lamellar aggregates of illite-smectite were observed as a pervasive mineral phase on the surface of gold crystals. Coeval with illite-smectite are apatite crystals which are often observed directly on top of clay minerals, and occasionally covered by them. The last mineral associated with macrocrystalline samples is goethite, which is only in direct contact with illite-smectite and always on top of the clay. These are the only paragenetic minerals observed with macrocrystalline samples, and apatite and goethite were only detected with macro crystals and not bulk ore samples. The mineralization sequence for macrocrystalline samples is presented in Figure 26A, and the mineralization sequence for bulk ore samples is presented in Figure 26B.

FESEM analysis indicates that alteration of minerals in the host rock, due to low-grade metamorphism during hydrothermal activity, produced chlorite which mineralized on top of quartz, adularia, and the carbonate host within the bulk ore. Following chlorite mineralization is crystallization of secondary carbonate, primarily calcite, which was observed intergrown between chlorite crystals. Mineralizing after secondary calcite was significant amounts of illite-smectite which shifts to palygorskite, however, chlorite was the dominant clay mineral associated with bulk ore samples. Mineralization of gold nanoparticles and the few examples of micrometer size gold begins early when quartz and adularia crystallize, and then continues to be deposited until almost all other mineralization ceases. The presence of nanoparticles on the surface of macrocrystals of gold, and various phases in the bulk argue for this interpretation. Late stage dissolution leads to silver leaching in gold and later precipitated nanoparticles of silver.
dominated electrum and silver. Finally, the last mineral to begin to crystallize in the bulk ore is spherule pyrite which was observed during textural analysis as always being on top of all of the other mineral phases. Mineralization appears to begin in veins and then permeates throughout the host rock leading to other new phases. These phases crystallize after hydrothermal fluids introduce new dissolved species to the host rock leading to the formation of clays and pyrite.

The two distinct and different mineralization sequences for macrocrystalline gold and bulk ore indicate that multiple mineralization events or styles occurred in the Type 4 ore. Combining the two sequences for macrocrystalline gold and bulk ore establishes an overall mineralization sequence for the Type 4 (Figure 26C). This well-constrained mineralization sequence for the Type 4 should aid in exploration of gold within sections of the Type 4 ore, as well as other potential sources of gold, by providing the associated phases to search for. Knowing the phases present can also greatly help increase extraction efficiency, should changes to processing procedures be made to account for challenging paragenetic minerals like pyrite, goethite, chlorite, and gold telluride.

6. Conclusions

Results from FESEM analysis suggest that gold mineralization in the Type 4 ore begins with aggregation of nanoparticle or colloidal gold, as collision and bonding of particles is induced from boiling and a higher energy environment. As levels of gold in solution reach increased supersaturation, two-dimensional nucleation and growth of gold begins. The data further suggests that gold concentrations within upwelling hydrothermal fluids increased to higher degrees of supersaturation leading to the dominant mechanism of mineralization for macrocrystalline gold which is adhesive or rough growth. Nanoparticles continued to be deposited and aggregate even after macrocrystalline gold crystallization ceased. Late stage dissolution led to leaching of silver from mineralized gold which was then recrystallized within bulk ore as silver nanoparticles and nanoparticles of electrum with >85% silver concentrations.

The mineralization history for the Type 4 ore from RMGM is distinct and far more complex than previously thought. Detailed investigation using FESEM of unmodified samples provided new insight into the paragenetic minerals associated with the deposit. The results indicate different mineralization sequences for macrocrystalline gold from quartz-adularia veins and bulk ore. Both sample types are associated with quartz, adularia, and illite-smectite minerals.
Apatite and the stellated pseudo-hexagonal mineral, presumed to be goethite, are unique to macrocrystalline gold, while chlorite, palygorskite, 2 forms of pyrite, and carbonate minerals are only found in Type 4 bulk ore. The two distinct sequences suggest that more than one mineralization event occurred even though hydrothermal activity is thought to have lasted no more than 0.5 Myrs. The Type 4 gold deposit is electrum and averages 61% Au and 39% Ag when macrocrystalline, and averages 8.0% Au and 92% Ag in bulk ore. However, nanoparticles of electrum were observed in both macrocrystalline gold as well as bulk ore, and aggregates of silver nanoparticles void of gold were also identified in the bulk ore. Results show that gold concentrations decrease, while silver concentrations increase, going from macrocrystalline gold in veins to being disseminated in bulk ore. Mineralization is proposed to have originated in veins and then spread throughout the bulk carbonates and siliciclastics. This detailed mineralization sequence for the Type 4 ore should aid in exploration efforts, and greatly improve extraction efficiencies due to a better constrained understanding of mineral paragenesis. Knowing that Fe-bearing minerals such as pyrite, goethite, and chlorite are present within the deposit can have important implications for the efficiency of cyanide heap leaching. The presence of newly discovered gold telluride also may be decreasing extraction efficiency, as it requires more time for dissolution over electrum. Altering refinery processes to account for these phases may prove useful in increasing total yields and overall efficiency. Although several alternatives to conventional cyanide heap leach processing have been proposed, cyanide remains more economical regardless of environmental impacts.

Attempts at dating gold mineralization by conducting U-Pb age analysis of apatite proved imprecise and overall inaccurate. The inability to locate enough apatite crystals of sufficient size, as well as inherent problems with U-Pb dating of young apatite (low U and high common Pb), yielded data with severe errors and unreliable ages. Although geochronology data collected is unusable, further analysis of the deposit and attempts to date apatite, as well as other viable mineral phases within the Type 4, could be beneficial to thoroughly understanding mineralization history.
7. References


Letters, 1(10), 516–520.


8. Figures

Figure 1- The Open Pit at Round Mountain Gold Mine

*Figure 1*) Photograph of the Round Mountain Gold Mine open pit with the Toquima Range in the background. The photograph was taken by Michelle Burke (2015). The red star at the base of the mine marks the location where Type 4 bulk ore samples were collected by Michelle Burke and Mark Krekeler.
Figure 2- Round Mountain Gold Mine Location

Figure 2) Aerial photograph of the Round Mountain Gold Mine at the base of the Toquima Range, adjacent to the Toiyabe Range. The inset map shows the location of the mine which resides in Tonopah of Nye County, Nevada. The map was created by Burke (2015) in ESRI’s ArcGIS using the World Imagery basemap. Sources: Esri, DigitalGlobe, Earthstar Geographics, CNES/Airbus DS, GeoEye, USDA FSA, USGS, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.
Figure 3) Geologic map of the Round Mountain Gold Mine open pit showing the various ore types. The main ore body is the Type 2 ore, a non-welded, rhyolite tuff which contains disseminated gold, and is shown in orange. The Type 4 ore is shown in lavender and is comprised of Paleozoic sedimentary rocks and contains both disseminated and macrocrystalline gold.
Figure 4) Photograph of a representative sampling location in the base of the mine where Type 4 bulk ore samples were collected by Mark Krekeler in 2015. Stakes mark the location where samples were collected. This particular area marks the boundary between the Type 4 (on the left) and Type 3 (on the right). The Type 4 host lithology is comprised of Paleozoic siliciclastics and carbonates, and the Type 3 host is comprised of moderately welded, lithic-rich tuff breccias containing minor amounts of Paleozoic rocks.
Figure 5- Sample Images

A) High grade ore sample with gold bearing quartz and adularia vein as well as a quartz lined vug. Macrocristalline gold can be seen in the vein and macrocrystalline pyrite can be identified throughout the bulk. Sample was obtained from Dave Emmons.

B) High magnification photo of sample in A showing macrocrystalline gold, quartz and adularia.

C) Macrocristalline gold crystal obtained from Terry Jennings.

D) Representative bulk ore sample collected by Mark Krekeler and Michelle Burke in 2015.

E) Bulk ore sample mounted on SEM stub showing macrocrystalline calcite as well as pyrite inclusions within the bulk material.

F) Bulk ore sample mounted on SEM stub post acid dissolution.
Figure 6- Rough Gold Growth

**Figure 6**) SEM micrographs showing rough gold growth of macrocrystalline gold. A) Pervasive rough gold growth composing much of visible gold in low magnification. B) Paragenetic minerals on surface of gold filling in topologic lows. C) Rough growth smeared over top of gold.
Figure 7- Step Texture in Gold

**Figure 7**) SEM micrographs showing smooth gold growth of macrocrystalline gold represented by step texture. **A)** Step texture is pervasive in micrograph, but is less common for macrocrystalline samples than image suggests. **B)** Steps are smooth with clear edges when step width is less than about 4 µm. Steps then transition into rough growth as width increases. **C)** Two-dimensional layered steps are largely uniform and start/terminate at varied points on the surface. Steps provide points for paragenetic minerals to cling to.
Figure 8- Hexagonal Cavities in Gold

Figure 8) SEM micrographs of hexagonal cavities in gold that have all been filled in with paragenetic minerals. A) Backscatter image of cluster of 5 hexagonal cavities where 3 of the cavities are rimmed around an apparent island that is the same topologic height as the surrounding surface. The other 2 cavities are without islands and are filled in with paragenetic minerals. B) Higher magnification backscatter image showing contrast between gold and paragenetic minerals. The gold has a rough texture surrounding the cavity as well as the island in the middle. C) Secondary electron image of hexagonal cavity showing morphology of rough gold growth surrounding the cavity as well as the surface of the island. Morphology of the paragenetic minerals filling in the cavity can also be seen. Paragenetic minerals consist of tabular apatite crystals and clay minerals. D) Backscatter image of hexagonal cavity without an island that is filled in with other minerals. Gold transitions from rough growth to step texture leading into the cavity, and step texture can be seen away from the cavity.
Figure 9- Flaky Gold

Figure 9) SEM micrographs of a gold flake aggregate on a fungal hyphae on macrocrystalline gold. A) Entire aggregate is shown sitting on top of rough gold growth with clay mineral coating. B) Higher magnification image of gold flake shown anchored around hyphae.
**Figure 10- Gold Spheres**

**Figure 10** Two SEM micrographs of gold spheres and one EDXS spectrum. 

A) A 1.5 µm diameter gold sphere nestled into clay on top of rough gold. 

B) A 3 µm diameter gold-telluride sphere on top of clay minerals on macrocrystalline gold. 

C) EDXS analysis of the gold-telluride sphere in Figure 10B showing the presence of gold, silver, and tellurium. Other chemical constituents are present in the spectrum due to surrounding clay.
Figure 11- Macrocrystalline Gold in Bulk Ore

Figure 11) SEM micrographs of micron size gold particles from bulk ore Type 4 samples. A) Backscatter image of a gold particle measuring approximately 2 µm x 1 µm on top of a cubic pyrite crystal. B) Backscatter image of a gold particle measuring about 5 µm x 3 µm nestled in clay and adularia.
Figure 12- Gold and Silver Concentrations of Electrum in Type 4

The data was collected using EDXS analysis, and then the concentrations were normalized to just include gold and silver. A) Distribution of concentrations measured in macrocrystalline samples versus bulk ore samples. B) Minimum, maximum, and average concentrations of gold and silver are given along with gold and silver standard deviations and variances for the two sample types. C) Both standard t-Tests and t-Tests using the Wilcoxon method were calculated comparing the gold and silver concentrations in macro and bulk samples. The pvalues for these tests are given in the table. The very small pvalues support what the graph shows visually, that the concentrations of gold and silver in macrocrystalline electrum differs from that in the bulk ore.

<table>
<thead>
<tr>
<th>B</th>
<th>Min. Au (%)</th>
<th>Max. Au (%)</th>
<th>Min. Ag (%)</th>
<th>Max. Ag (%)</th>
<th>Avg. Au (%)</th>
<th>Avg. Ag (%)</th>
<th>Au St. Dev.</th>
<th>Ag St. Dev.</th>
<th>Au Variance</th>
<th>Ag Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro</td>
<td>47</td>
<td>76</td>
<td>24</td>
<td>53</td>
<td>61</td>
<td>39</td>
<td>7.9</td>
<td>7.9</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>Bulk</td>
<td>0.0</td>
<td>61</td>
<td>39</td>
<td>100</td>
<td>8.0</td>
<td>92</td>
<td>18</td>
<td>18</td>
<td>320</td>
<td>320</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>t-Test Au: pvalue Macro to Bulk</th>
<th>t-Test Ag: pvalue Macro to Bulk</th>
<th>Wilcoxon Test Au: pvalue Macro to Bulk</th>
<th>Wilcoxon Test Ag: pvalue Macro to Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.5 \times 10^{-7}$</td>
<td>$1.5 \times 10^{-7}$</td>
<td>$4.2 \times 10^{-7}$</td>
<td>$4.2 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
**Figure 13- Gold and Silver Concentrations in Nanoparticles**

![Graph showing normalized gold and silver concentrations in nanoparticle samples](image)

**Table B**

<table>
<thead>
<tr>
<th></th>
<th>Min. Au (%)</th>
<th>Max. Au (%)</th>
<th>Min. Ag (%)</th>
<th>Max. Ag (%)</th>
<th>Avg. Au (%)</th>
<th>Avg. Ag (%)</th>
<th>Au St. Dev.</th>
<th>Ag St. Dev.</th>
<th>Au Variance</th>
<th>Ag Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro</td>
<td>47</td>
<td>67</td>
<td>33</td>
<td>53</td>
<td>44</td>
<td>10</td>
<td>10</td>
<td>110</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Bulk</td>
<td>0.0</td>
<td>16</td>
<td>84</td>
<td>100</td>
<td>97</td>
<td>6.0</td>
<td>6.0</td>
<td>39</td>
<td>39</td>
<td></td>
</tr>
</tbody>
</table>

**Table C**

<table>
<thead>
<tr>
<th></th>
<th>t-Test Au: pvalue Macro to Bulk</th>
<th>t-Test Ag: pvalue Macro to Bulk</th>
<th>Wilcoxon Test Au: pvalue Macro to Bulk</th>
<th>Wilcoxon Test Ag: pvalue Macro to Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.4x10^{-2}</td>
<td>1.4x10^{-2}</td>
<td>7.9x10^{-4}</td>
<td>7.9x10^{-4}</td>
</tr>
</tbody>
</table>

**Figure 13** Gold and silver concentrations in nanoparticles, in normalized percentages, from macrocrystalline and bulk ore samples. The data was collected using EDXS analysis, and then the concentrations were normalized to just include gold and silver. 

A) Distribution of concentrations measured in macrocrystalline samples versus bulk ore samples.  
B) Minimum, maximum, and average concentrations of gold and silver are given along with gold and silver standard deviations and variances for the two sample types.  
C) Both standard t-Tests and t-Tests using the Wilcoxon method were calculated comparing the gold and silver concentrations in macro and bulk samples. The pvalues for these tests are reported in the table. The very small p values support what the graph shows visually, that the concentrations of gold and silver in nanoparticles differs from that in the bulk ore.
Figure 14) SEM micrographs of nanoparticles of electrum observed in macrocrystalline samples. A and B) Variable pressure secondary electron images of nanoparticle aggregates of electrum. Nanoparticles vary in size from 25 nm to 200 nm. C) Backscatter image of nanoparticles embedded in clay minerals adjacent to rough gold growth. D) Representative EDXS spectrum of electrum nanoparticles from macrocrystalline gold samples showing the presence of both gold and silver.
Figure 15- Nanoparticles of Electrum in Bulk Ore Samples

A and B) Backscatter images of aggregates of silver nanoparticles seemingly void of gold where nanoparticles vary from 25 nm to 200 nm in size. C) Representative EDXS spectrum of silver nanoparticles showing the presence of silver, sulfur, and chlorine, and is void of gold. D) Backscatter image of large aggregate of electrum. E) Higher magnification backscatter image of aggregate in Figure 15E better illustrating nanoparticle size and distribution. F) EDXS spectrum of electrum in Figure 15E showing presence of both gold and silver.
Figure 16- Quartz

Figure 16) SEM micrographs of quartz crystals and an EDXS spectrum of quartz from both bulk ore and macrocrystalline gold samples. A) Quartz prisms lining vug in bulk ore sample. Quartz comprises the bulk groundmass in image, and clay minerals can be seen filling in the vug. B) Bulk ore sample with cubic pyrite crystal on top of quartz groundmass covered in clay. C) Bulk ore sample with pseudo-hexagonal quartz prism, likely formerly intergrown with calcite that has been dissolved. Clay minerals and spherical pyrite are also present in image. D) Pseudo-hexagonal quartz crystal with platy texture imaged from a bulk ore sample. E) Diverging hexagonal quartz prisms covered in clay minerals from a macrocrystalline sample. F) Representative EDXS spectrum of quartz showing the presence of silicon and oxygen.
Figure 17- Adularia

Figure 17) SEM micrographs and an EDXS spectrum of adularia from both bulk ore and macrocrystalline gold samples. A) Euhedral adularia crystal coated in clay minerals on a macrocrystalline sample of gold. B) Blocky adularia from macrocrystalline gold sample containing gaps presumed to once contain calcite. C) Diamond shaped hopper growth in adularia from macrocrystalline gold sample. Surrounding crystal face exhibits saw-tooth texture that is common for adularia of this deposit. D) Euhedral crystals of adularia from bulk ore sample. E) Layered tabular adularia crystals exhibiting both saw-tooth texture as well as the beginnings of hopper growth. F) Representative EDXS spectrum for adularia showing potassium, sodium, aluminum, silicon, and oxygen.
Figure 18) SEM micrographs and an EDXS spectrum of illite-smectite clay minerals from both bulk ore and macrocrystalline gold samples. A) Illite-smectite enveloping macrocrystalline gold. B) Cornflake-lamallae aggregation of illite-smectite on top of macrocrystalline gold. C) Cross-section of illite-smectite crystal from bulk ore showing internal structure. D) Representative EDXS spectrum of illite-smectite showing potassium, calcium, magnesium, aluminum, silicon, and oxygen.
Figure 19- Apatite

Figure 19) SEM micrographs and an EDXS spectrum of apatite from macrocrystalline samples. A) High magnification image of several tabular apatite crystals all showing etching parallel to the c axis. Cornflake lamellae aggregates of illite-smectite minerals can also be seen in the image surrounding apatite crystals. B) Tabular apatite crystals with etching and clay minerals lining a crevice on the surface of a macrocrystalline gold sample. Apatite crystals present have clay minerals on the surface, and can be seen on top of the clay. C) Cluster of small, euhedral hexagonal apatite prisms with cogenetic clay minerals on the surface of macrocrystalline gold. D) Isolated, intergrown apatite crystals with etching. Clay minerals can be seen on top of the crystals. E) Isolated, euhedral hexagonal apatite crystal approximately 115 µm across. F) Representative EDXS spectrum of apatite showing the presence of calcium, phosphorous, oxygen, and fluorine. Fluorine present indicates that the species of apatite is fluorapatite.
Figure 20- Stellated Iron-bearing Mineral (Goethite)

Figure 20) SEM micrographs and an EDXS spectrum of presumed goethite from macrocrystalline samples. A) Stellated, pseudo-hexagonal crystals of goethite on top of clay minerals lining a crevice on a macrocrystalline gold sample. B) High magnification image of single stellated goethite showing detailed layered morphology. Crystal is sitting on top of clay. C) EDXS spectrum of crystal in Figure 20B. Iron and oxygen present in spectrum support possible identification of goethite. Other chemical constituents present, magnesium, aluminum, silicon, gold, and silver, are due to surrounding clays and electrum.
Figure 21- Clay Mineral (Palygorskite)

Figure 21) SEM micrographs and an EDXS spectrum of palygorskite from bulk ore samples. **A and B)** Pervasive acicular palygorskite crystals on top of illite-smectite minerals. **C)** High magnification image of birds nest cluster of palygorskite needles on top of illite-smectite minerals. **D)** Representative EDXS spectrum of palygorskite showing presence of magnesium, aluminum, silicon, and oxygen.
Figure 22- Chlorite

A) Rosette clusters of euhedral chlorite from a bulk ore sample. B) Chlorite crystals comprising the majority of the field of view with minor palygorskite on top of the chlorite. C) Chlorite minerals comprising majority of image from left to right with presence of illite-smectite grown over chlorite in the upper right corner of micrograph. Palygorskite crystals can be seen on top of illite-smectite. D) Representative EDXS spectrum of chlorite showing magnesium, aluminum, iron, silicon, and oxygen.
Figure 23- Pyrite

A) Lower magnification image of Figure 16B showing euhedral cubic pyrite crystal embedded in quartz and clay minerals.  B) High magnification image of euhedral pyrite cube corner with illite-smectite minerals directly on the surface.  C) Corner of intergrown pyrite cube sticking out of the face of another pyrite cube.  Both crystals contain surficial clay minerals.  D) Two adjacent cubic pyrite crystals enveloped in illite-smectite minerals.  Small spherule pyrite crystals can be seen both on top of the cubic pyrite crystals as well as the clay minerals.  E) High magnification image of spherical pyrite with clay minerals at the surface.  Pyrite crystals have step texture that is characteristic of all faces of spherule pyrite crystals identified.  F) Representative EDXS spectrum of pyrite showing only iron and sulfur.
Figure 24) SEM micrographs and an EDXS spectrum of carbonate minerals from bulk ore samples. A) Calcium carbonate groundmass of bulk ore sample covered in clay minerals. B) Cleavage planes in calcite crystal with surficial clay minerals. C) Secondary calcium carbonate grown into chlorite crystals. D) Representative EDXS spectrum of carbonate minerals showing calcium and oxygen. Aluminum and silicon present are likely due to surrounding clays, and manganese could either be a component of the clay minerals or carbonates. Iron is not present in spectrum, but was identified in multiple calcite crystals.
Figure 25- U-Pb Dating of Apatite

Figure 25) Tera-Wasserburg diagram with data representing 4 spot analyses each from a separate apatite crystal. Analyses were conducted using LA-MC-ICPMS and the data plotted shows the ratio between $^{238}\text{U}$ and $^{206}\text{Pb}$ concentrations versus $^{207}\text{Pb}$ and $^{206}\text{Pb}$ concentrations. Each analysis is represented as a red ellipsis and can be seen on a discordant line which intercepts the concordia at 4930.5±3.8 Ma and 60±32 Ma. The MSWD is 0.046 and the probability of fit is 0.95.
Figure 26 - Sequence of Mineralization: Macroparametric vs. Bulk Ore
Figure 26) Three figures shown represent the mineralization sequences for minerals associated with macrocrystalline gold deposition and bulk ore formation. Arrows and hashed lines show approximate duration of mineralization, relative to other phases. The left of each figure marks the start of crystallization and then mineralization continues to late stage growth as the figure progresses from left to right. Hashed lines indicate a less definitive start or end in mineral formation than arrows; except in the case of palygorskite which appears to be the last mineral to finish crystallizing. A) Mineralization sequence associated with macrocrystalline gold deposition. Each mineral has its own color. Mineralization can be seen starting with quartz and adularia and ending with gold and silver nanoparticles crystallizing. B) Mineralization sequence for bulk ore samples where each phase again has its own color. Carbonate minerals and cubic pyrite are the first minerals to grow and nanoparticles of electrum and palygorskite are the last. C) Composite sequence of both macrocrystalline gold minerals and bulk ore minerals. Minerals are color coated where purple is the starting material, blue represents minerals only found with macrocrystalline gold, green is for bulk ore minerals only, and orange represents minerals found in both types of deposits.
9. Appendices

9.1 Review in Silver

Silver may not be as valuable as gold but it has just as many, if not more, uses and applications. Prized for many of the same reasons that gold is, the majority of silver is used in electrical applications followed by coin making. Some other major uses are in photography, jewelry, pharmaceuticals, soldering, automotives, and photovoltaic solar cells (Butterman & Hilliard, 2005). Silver is often found as electrum as well as in its native state. Although there are several silver bearing minerals, common minerals are acanthite (Ag$_2$S), proustite (Ag$_3$AsS$_3$), pyrargyrite (Ag$_3$SbS$_3$), and minerals consisting of silver bonded to a halogen (Butterman & Hilliard, 2005; Ridley, 2013). Silver (I) is more common than other oxidation states of the metal, and the most common complexes are CN$^-$, NH$_3^{2+}$, S$_2$O$_3^{2-}$, and halides (Butterman & Hilliard, 2005). Silver is an economic source when the concentration reaches about 100 ppm. With a crustal abundance of approximately 0.07 ppm, silver must be concentrated ~1000 times in order to be economical to extract and process (Ridley, 2013). The silver industry is worth considerably less than the gold industry, as in 2013 it totaled approximately $19.6 billion (“Silver Supply & Demand,” 2017). Silver has dropped in value since 2013, when the average price was 23.70 USD/ozt, today the price of silver varies between 16 and 18 USD/ozt (“Silver Supply & Demand,” 2017). Silver is projected to increase in value over the next year.
9.2 Detrital Minerals Found (Chromite and Zircon)

Appendix 9.2) SEM micrographs, and two EDXS spectra, of minerals from bulk ore samples that are interpreted as detrital. A) Backscatter image of anhedral chromite crystals on top of clay minerals. Chromite is grooved and striated. B) Representative EDXS spectrum of chromite showing the presence of iron, chromium, and oxygen. Silicon present is likely due to surrounding paragenetic mineral C) Backscatter image of a fractured zircon crystal embedded in clay minerals. Only 2 zircon crystals were found during FESEM analysis. D) Representative EDXS spectrum of zircon showing zirconium, silicon, and oxygen.
9.3 Supplementary FESEM Micrographs

Appendix 9.3) A) Secondary electron image of now solitary quartz crystal showing morphology consistent with a former intergrowth of calcite that had been dissolved away leaving behind only quartz. Quartz crystal analyzed from a bulk ore sample. B) Secondary electron image of adularia from a macrocrystalline gold sample with linear gaps and triangular shaped hopper growth on the crystal face. C) Macrystalline gold mineralization overlapping adularia illustrating sequence of mineralization. The overlapping of gold in this image, as well as the euhedral shape of adularia, indicates that adularia crystallized first and gold grew over top. This micrograph was imaged using variable pressure secondary electron detection. D) Secondary electron image of numerous crystals of both spherical and cubic pyrite. Cubic pyrite can be seen embedded, and partially enveloped, by clay minerals and other phases while pyrite spherules are primarily surficial.