

Re-evaluating Genetic Models for Porphyry Mo Mineralization at Questa, New Mexico: Implications for Ore Deposition Following Silicic Ignimbrite Eruption

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Abstract

**JOSHUA M. ROSERA: Re-evaluating Genetic Models for Porphyry Mo
Mineralization at Questa, New Mexico: Implications for Ore Deposition
Following Silicic Ignimbrite Eruption
(Under the direction of Drew Coleman)**

The Questa Mo deposit in New Mexico provides an opportunity to study the relationship between pluton assembly and mineralization. Magmatism along the Questa caldera margin initiated at 25.20 Ma and continued for ~ 770 ka. Emplacement of mineralizing intrusions progressed westward and culminated in the assembly of the Questa Mo deposit between 24.76 and 24.50 Ma. Molybdenite Re-Os ages are integrated with zircon U-Pb and biotite Ar-Ar ages to evaluate the cooling histories within the deposit. These data show that the mineralizing intrusions were generated via rapid melting, separation, and intrusion into the shallow crust without involvement in a long-lived magma chamber. It is proposed that the anomalously high magma flux associated with ignimbrite eruption introduces materials necessary for mineralization. Partial melting and scavenging within a deep-crustal hybridized zone generated Mo-rich magma that formed the Questa deposit. This hypothesis predicts an important connection between caldera-forming systems and porphyry-style mineralization.

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Table of Contents

List of Tables.....	vi
List of Figures.....	vii
1. Introduction.....	1
2. Geological Setting.....	4
3. Methods.....	9
3.1. U-Pb zircon geochronology	9
3.2. Re-Os molybdenite geochronology	10
4. Results	12
4.1. U-Pb zircon geochronology	12
4.2. Re-Os molybdenite geochronology	16
5. Discussion	20
5.1. Intrusive history of the caldera margin plutons	20
5.2. History of mineralization	22
5.3. Re-Os molybdenite: a new thermochronometer	24
5.4. Integrated T-t history of the Questa porphyry system.....	26
5.5. Evaluation of previous genetic models for the Questa Mo deposit	28
5.6. Relationship between caldera formation and mineralization.....	29
6. Conclusions.....	35
References	36

List of Tables

Table 1: U-Pb data for caldera margin rocks from the Latir volcanic field	13
Table2: Re-Os data for molybdenite of the Questa porphyry Mo deposit	17

List of Figures

Figure 1: Geologic Maps of Latir volcanic field and southern caldera margin	5
Figure 2: Cross-section of Southwest zone of the Questa deposit.....	7
Figure 3:Th-corrected $^{206}\text{Pb}/^{238}\text{U}$ results for individual fractions.....	15
Figure 4: Re-Os molybdenite results	18
Figure 5: Summary of geochronology for the Latir volcanic field.....	21
Figure 6: Temperature-time history of the Questa deposit	27
Figure 7: Schematic models for genesis of the Questa deposit	30
Figure 8: Schematic model of ignimbrite-mineralization relationship	32

1. Introduction

In 2010, the United States produced over \$800 million of molybdenum oxide [USGS MCS, 2011], and the demand for Mo as an alloying agent in high-grade steel will likely increase as global economies recover. The majority of the world's Mo reserves are contained within porphyry Cu ($\pm$ Mo) and porphyry Mo ($\pm$ Cu) deposits. Although porphyry Mo deposits are often volumetrically smaller than porphyry Cu systems, they are still a significant source of Mo owing to higher ore grades.

Understanding the timing of mineralization within a magmatic region is important for making accurate regional ore predictions. High-silica granite-related porphyry Mo deposits (Climax-type deposits) are often interpreted to form as magmatic cupolas above larger, more dynamic, magma chambers [Wallace *et al.*, 1968; White *et al.*, 1981; Carten *et al.*, 1988a;b; 1993; Lowenstern, 1994; Burnham, 1997; Klemm *et al.*, 2008]. The depth and size of the magma body, as well as trends in chemical variation, remain a significant topic of debate [Keith *et al.*, 1986; Carten *et al.*, 1993; Audétat, 2010]. Outstanding questions in this debate include: 1) How large is the magma chamber from which mineralizing cupolas originate? 2) At what depth in the crust do these magma bodies exist? 3) What is the mechanism for concentrating Mo in these systems?

In a detailed study of the chemistry, age, and tectonic setting of porphyry Mo deposits, Carten *et al.* [1993] observed that Mo mineralization typically occurs late within the lifespan of long-lived (> 1 Ma) magmatic provinces. For example, at Questa, New Mexico (Fig. 1), mineralizing magmas were emplaced along the southern margin of the Questa caldera and are interpreted to represent cupolas of an extensive late ring intrusion [Lipman, 1988]. Hydrothermal mineralization within or near ring faults is also observed in the Southern Rocky Mountain Volcanic Field in Colorado [Lipman, 2006] as well as at

Round Mountain, Nevada [*Henry et al.*, 1997] and the Borovista caldera in Bulgaria [*Singer and Marchev*, 2000].

Climax-type deposits are thought to form during multiple magmatic-hydrothermal events that occur close in space and time [e.g., *Wallace et al.*, 1968; *White et al.*, 1981; *Carten et al.*, 1988a]. Some models for Mo mineralization rely on over-simplified assumptions about the thermal history of plutons associated with the deposits. For example, *Burnham* [1997] modeled the formation of porphyry ore deposits above plutons intruded as large bodies of mostly liquid magma with relatively simple cooling histories. More recently, *Seedorff and Einaudi* [2004a] analyzed overprinted alteration assemblages along cross-cutting veins to derive a pseudocyclical thermal evolutionary model for the Henderson porphyry Mo deposit in Colorado. These authors note that unidirectional models (simple high- to low-temperature through time, [e.g., *Lowell and Gilbert*, 1970; *Fournier*, 1999]) are of limited use for understanding the complexities observed within these deposits.

The suggestion that thermal cycling is important to development of Climax-type Mo deposits is consistent with recent studies that indicate plutons are assembled episodically and have more complex thermal histories than that of a single intrusion [e.g., *Coleman et al.*, 2004; *Seedorff and Einaudi*, 2004a; *Davis et al.*, 2012]. However, studying the relationship between porphyry-style mineralization and sub-adjacent magma reservoirs is largely inhibited by the lack of exposure of cogenetic rocks. The Questa porphyry Mo system presents an opportunity to study this relationship because numerous intrusions of varying volume and emplacement depths are currently exposed throughout the Latir volcanic field. Additionally, because the system is relatively young, abundant pre-, syn- and (some) post-caldera volcanic rocks [*Lipman et al.*, 1986] are preserved.

Detailed geo-thermochronology allows us to evaluate the link between episodic magmatism and Mo mineralization at Questa. Combining conventional zircon U-Pb and Ar-Ar biotite geochronology with more recently developed molybdenite Re-Os geochronology

allows for full characterization of the temperature-time (T-t) history of the Questa deposit and places the mineralization into the magmatic and thermal history of the system. Applying this approach: 1) lends insight into the timing and duration of magma emplacement relative to Mo mineralization, 2) characterizes how porphyry Mo systems relate to the evolution of a long-lived volcanic field and cogenetic shallow pluton assembly, and 3) evaluates the applicability of Re-Os molybdenite as a new thermochronometer.

2. Geological Setting

The Questa porphyry Mo deposit is located in the New Mexico portion of the Southern Rocky mountain volcanic field. It is part of the composite Latir volcanic field which covers an area of $\sim 1200 \text{ km}^2$ [Fig. 1; *Lipman et al.*, 1986]. Uplift and erosion along the eastern flank of the Rio Grande rift exposed a vertical section of volcanic strata and upper crustal plutons of the Latir field. Volcanism in the field began at 28.5 Ma with the eruption of dominantly andesite with local dacite and rhyolite [*Zimmerer and McIntosh*, 2012] and climaxed with the eruption of the $\sim 500 \text{ km}^3$ Amalia Tuff at $25.52 \pm 0.06 \text{ Ma}$ [*Tappa et al.*, 2011] which resulted in the collapse of the Questa caldera.

A series of plutons was emplaced during and after the eruption of the Amalia Tuff. Exposed plutonic rocks span $\sim 6 \text{ Ma}$ of intrusive history ($\sim 25.6 - 19.1 \text{ Ma}$; *Tappa et al.*, 2011; *Zimmerer and McIntosh*, 2012) and become younger to the south. Caldera margin plutons are intermediate in age among exposed plutonic rocks, and are associated with mineralization [*Meyer and Foland*, 1991; *Zimmerer and McIntosh*, 2012]. From east to west, the caldera margin plutons include the Red River intrusive complex, Sulphur Gulch pluton, Southwest intrusive suite, and the Bear Canyon pluton. The Red River intrusive complex ($\sim 24.96 \text{ Ma}$; *Zimmerer and McIntosh*, 2012) is the most variable in terms of texture and chemistry. It is a rhyolite to aplite porphyry dike complex that cuts granodiorite and fine-grained monzonite [*Lipman*, 1988]. The Sulphur Gulch pluton includes granite porphyry and slightly more mafic biotite-plagioclase porphyry phases ($\sim 24.73 \text{ Ma}$, *Zimmerer and McIntosh*, 2012). At depth, the Sulphur Gulch pluton is in contact with the Southwest intrusive suite, which is a composite of granite, aplite, rhyolite and latite directly associated with, and locally hosting, Mo mineralization [*Ross et al.*, 2002]. The Bear Canyon pluton ($\sim 24.37 \text{ Ma}$, *Zimmerer and McIntosh*, 2012) is compositionally similar to the granitic phase

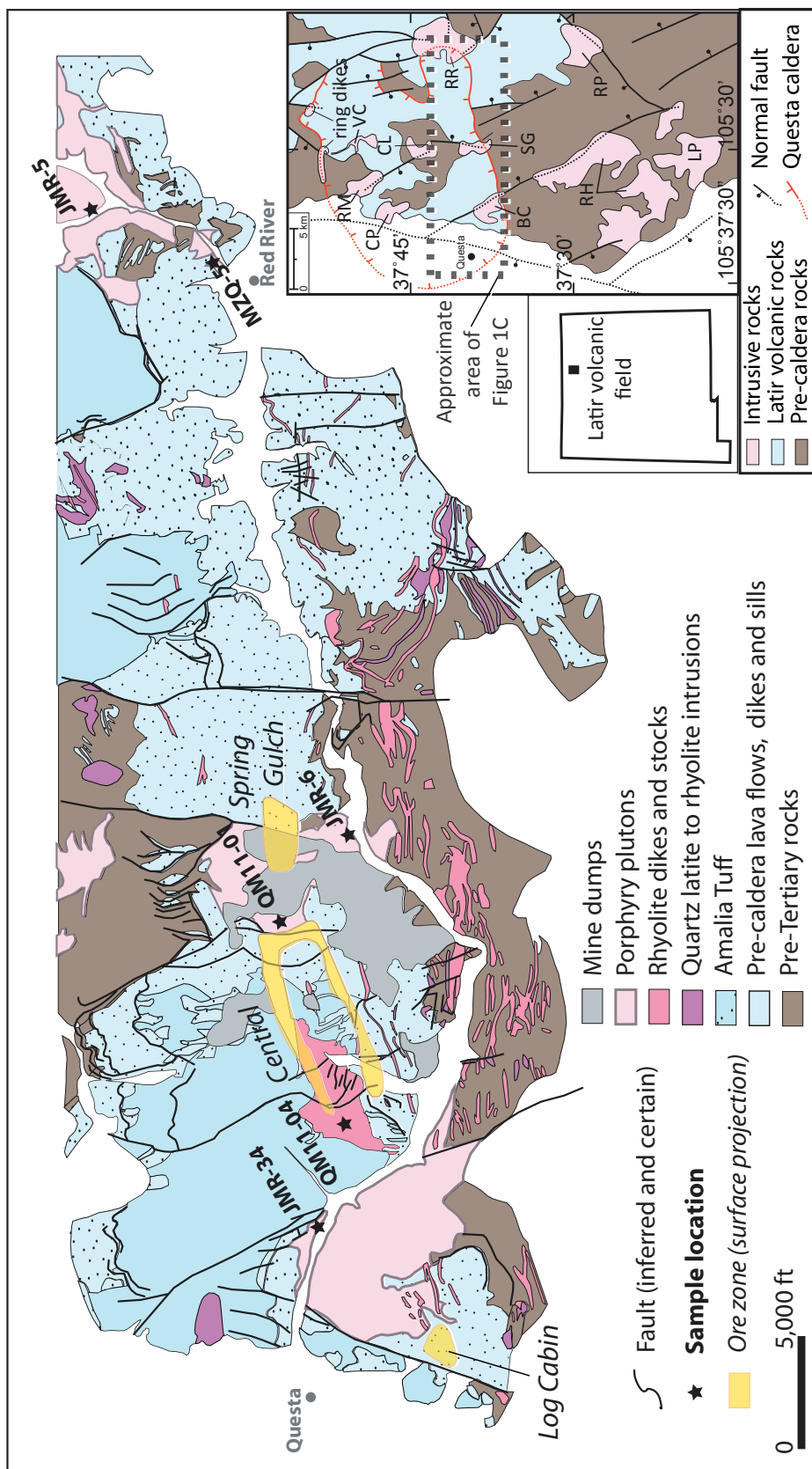


Figure 1. Overview map showing study area location. Simplified geologic map of the Latir volcanic field, after Lipman and Reed (1989). Pluton name abbreviations: CP, Cañada Pinabete; RM, Rito del Medio; VC, Virgin Canyon; CL, Cabresto Lake; BC, Bear Canyon; SG, Sulphur Gulch; RR, Red River; RH; Rio Hondo; RP, Relica Peak. Detailed map of the southern caldera margin showing U/Pb zircon sample locations. Ore zones approximately correspond to 0.2 wt. % MoS₂ contours projected to the surface. After Meyer (1991).

of the Sulphur Gulch pluton and texturally grades from aplite to granite porphyry.

The mineralizing intrusions at Questa dip at a low angle to the north and likely followed a pre-existing anisotropy [Ross *et al.*, 2002]. The structural anisotropy may be related to the low-angle normal faults that are observed throughout the southern caldera margin [Meyer and Foland, 1991]. These faults are believed to have originally formed at high angles and were subsequently rotated to low angles above a batholith that underlies the southern caldera margin [Meyer and Foland, 1991].

The Questa porphyry Mo system is divided into three separate ore deposits: Spring Gulch, Central, and the Log Cabin (Fig. 1). The Central deposit is horseshoe shaped in map view and is the only one that is mined. The most recent mining activity has moved underground along the southwest limb of the horseshoe (“Southwest zone”). Ore bodies are discontinuous along the Southwest zone and subdivided into the Vein zone, D ore body, and the Goat Hill ore body (Fig. 2). The Log Cabin ore body lies near the roof zone of the Bear Canyon pluton, whereas the Spring Gulch deposit lies above the Sulphur Gulch pluton. Major ore bodies at Questa are typically found at the intrusive contact with, or entirely within, pre-caldera volcanic units.

One notable feature of the Questa ore system is that it contains two separate styles of mineralization [Ross *et al.*, 2002]. Both, the Goat Hill and D ore bodies contain significant disseminated molybdenite within the matrix of a magmatic hydrothermal breccia. Superimposed on the hydrothermal breccia bodies are stockwork quartz + molybdenite veins. Ross *et al.* [2002] estimated that 30 to 40% of the molybdenite within the Goat Hill ore body is disseminated within the hydrothermal breccia matrix. Both the breccia and stockwork veins contain similar paragenetic sequences; however, the stockwork veins contain late-stage fluorite, calcite and beryl [Klemm *et al.*, 2008; Rowe, 2012].

Ross *et al.* [2002] subdivided the Goat Hill hydrothermal breccia on the basis of differences in matrix paragenesis, clast alteration, and breccia textures. Consequently, they

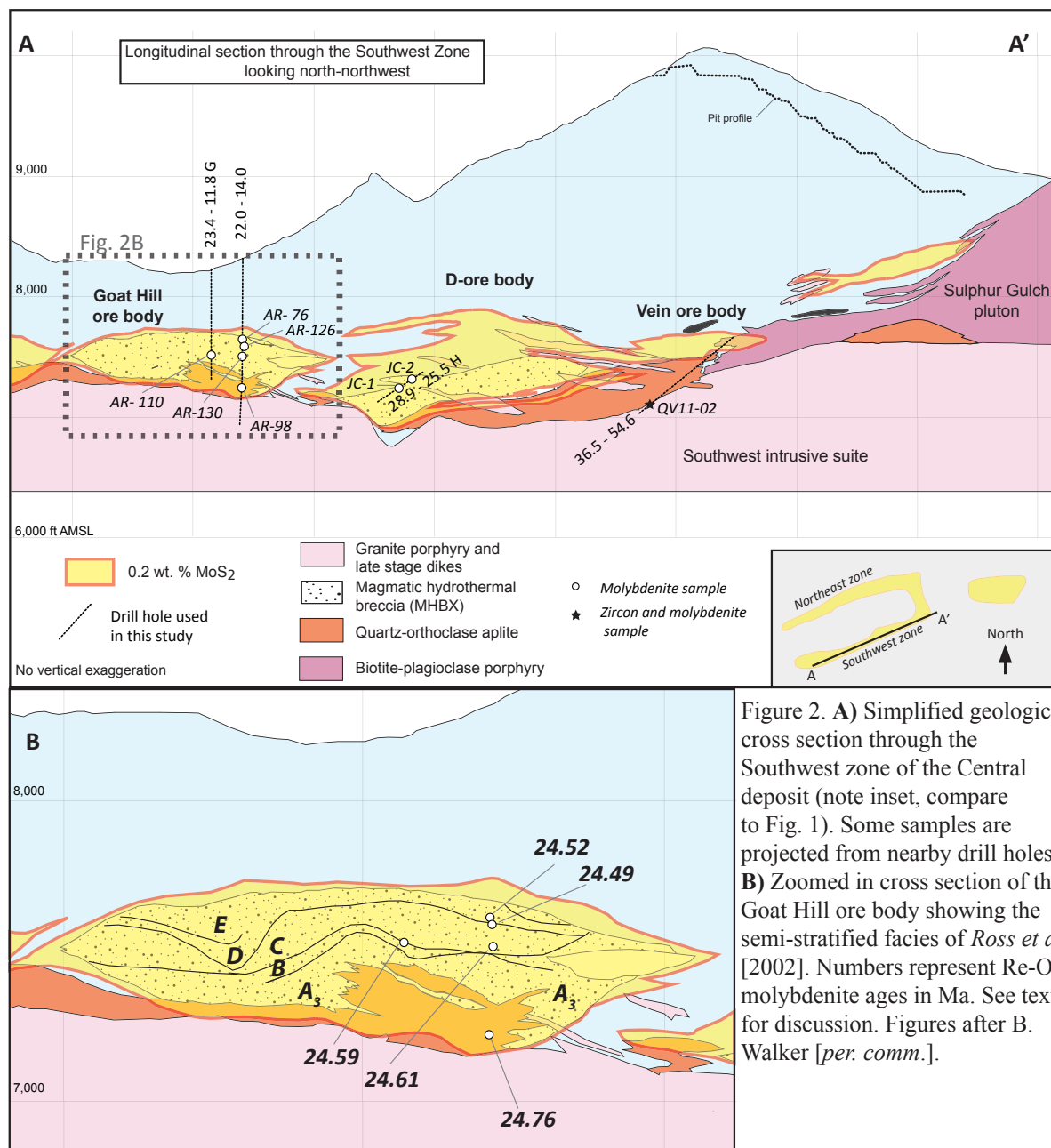


Figure 2. **A)** Simplified geologic cross section through the Southwest zone of the Central deposit (note inset, compare to Fig. 1). Some samples are projected from nearby drill holes. **B)** Zoomed in cross section of the Goat Hill ore body showing the semi-stratified facies of *Ross et al.* [2002]. Numbers represent Re-Os molybdenite ages in Ma. See text for discussion. Figures after B. Walker [per. comm.].

observed five semi-stratified breccia facies (A through E, Fig. 2) and interpreted them to represent evolution of the hydrothermal fluid away from the source aplite. However, fluid inclusion work by *Rowe* [2012] shows that there was little or no correlation between fluid evolution and the breccia facies.

3. Methods

3.1. U-Pb zircon geochronology

Rock samples were collected from units most closely associated with epithermal mineralization (Red River intrusive complex) and the porphyry Mo deposit (the Sulphur Gulch pluton, Southwest intrusive suite, and Bear Canyon pluton; Fig. 1C and 2). Another sample was collected from what is tentatively defined here as the Goat Hill igneous complex (sample QM11-04). Whole-rock samples were broken down with jaw crushers and a disc mill. Samples were either processed on a water table, sieved, or both prior to standard heavy liquid and magnetic mineral separation. Only the least magnetic zircons were analyzed.

Zircons were placed into a 950 °C oven for 48 hours to anneal lattice sites that were damaged due to radiation. Following thermal annealing, the samples were chemically abraded in HF + HNO₃ at 220 °C for 12 hours [Mattinson, 2005]. The abraded zircons were split into fractions, spiked with a ²⁰⁵Pb-²³³U-²³⁶U tracer and equilibrated in HF + HNO₃ for 5 days at 220 °C. Individual fractions contained single or multiple zircon crystals. In some cases, multigrain fractions were analyzed to counter relatively low U concentrations (< 300 ppm) and the young age of these samples. After dissolution, the fractions were dried down to nitrate salts and converted to chlorides by reacting overnight (12 – 16 hours) with HCl at 180 °C. Anion exchange column chromatography was used to separate U from Pb. Uranium was loaded onto 99.98% Re filaments. The majority of the U samples were loaded with 2 – 3 µL of graphite in order to ionize as a metal. However, a few were analyzed without graphite (ionized as UO₂) late in the project in an attempt to raise ionization efficiencies and minimize run variability introduced by concentration gradients in the graphite solution. There are no systematic differences in analyses that could be attributed to how U was measured. Lead

samples were loaded with colloidal Si-gel onto 99.998% Re filaments. Mass analyses were made on the Daly detector of the VG Sector 54 thermal ionization mass spectrometer at the University of North Carolina – Chapel Hill. In-run U fractionations were calculated based on the measured value for $^{233}\text{U}/^{236}\text{U}$ in the spike, and Pb fractionation was assumed to be 0.15 ‰/amu. Analyses in which U was analyzed as an oxide were corrected for oxygen isotope interferences. Raw data were processed and reduced through Tripoli [Bowring *et al.*, 2011] and U-Pb Redux [McLean *et al.*, 2011]. Some analyses had anomalously high total common Pb (>3 pg) that we suspect is derived from inclusions that were not removed during chemical abrasion (e.g., fluorite). Therefore, we assumed a maximum of 3 pg blank Pb and assigned all remaining common Pb to initial sample Pb. The isotopic composition of the sample common Pb was estimated using whole-rock data from Johnson *et al.*, [1990] and Stacey and Kramers [1975] where Pb isotope data were unavailable. All U-Pb ages are Th-corrected weighted mean ^{206}Pb - ^{238}U ages. Correction for Th-disequilibrium was made using published whole-rock data for the plutons [Johnson *et al.*, 1989].

3.2. Re-Os molybdenite geochronology

Molybdenite samples were collected from the Southwest zone of the Central deposit at Questa. We chose to date the five samples of Rowe [2012] and two from Cline and Bodnar [1994] because they determined the mineralization temperatures using fluid inclusion microthermometry for the Goat Hill and D ore bodies, respectively. The granite porphyry host for one of the samples from the Vein zone (QV11-02) was used for U-Pb zircon geochronology.

Molybdenite was physically separated from its host rock with a diamond-tipped drill bit and chemically equilibrated with a mixed ^{185}Re - ^{188}Os - ^{190}Os spike using the *aqua regia* Carius tube method [Shirey and Walker, 1995]. An attempt was made to select samples that did not contain a significant amount of pyrite, although the high Re and radiogenic Os concentrations in molybdenite overwhelm any non-molybdenite Re and Os. After

digestion, Os was selectively extracted into chloroform (CHCl_3) and then back extracted into HBr following the procedure of *Cohen and Waters* [1996]. Further Os purification was completed with micro-distillation [*Birck et al.*, 1997] prior to being loaded onto degassed Pt filaments with $\text{Ba}(\text{OH})_2$ activator. Rhenium was isolated using Cl-based anion exchange column chromatography and loaded onto Pt filaments with $\text{Ba}(\text{NO}_3)_2$. In both cases, the activators permit the sample to run as oxide anions (N-TIMS). Measurements were made at AIRIE (Colorado State University) on a Thermo-Fisher Triton TIMS using simultaneous Faraday cup collectors for Re and stronger intensity Os signals whereas weaker Os signals were collected in peak jumping mode with a secondary electron multiplier. Both Re and Os analyses were corrected for oxygen isotope compositions, and Os was further corrected for: 1) isobaric interferences (W, Re, and Pt); 2) common Os; 3) and mass fractionation based on the measured $^{190}\text{Os}/^{188}\text{Os}$ in the spike [*Markey et al.*, 2003]. During data reduction, Re and Os abundances were also corrected for total analytical blank from reagents and Pt wire although values were negligible compared to molybdenite Re and Os concentrations. Ages are reported in Table 2 with both 2σ analytical errors and the combined analytical + ^{187}Re decay constant uncertainty [*Smoliar et al.*, 1996] errors.

4. Results

4.1. U-Pb zircon geochronology

After Th-correction, all zircon U-Pb ages are concordant within analytical and decay constant uncertainties (Table 1; Fig. 3). Some samples show evidence for minor inheritance (e.g., QV11-02) or Pb-loss (e.g., JMR-34) which are identified where there are at least two outliers. A conservative age estimate was made for two samples from the Sulphur Gulch pluton (QM11-01 and JMR-6) and one from the Red River intrusive complex (MZQ-5) because they revealed a continuum of ages that could be related to inheritance, Pb loss and/or protracted zircon growth.

A granite porphyry (MZQ-5) and equigranular granodiorite (JMR-5) were collected from the southern and central portion of the composite Red River intrusive complex, respectively. Five zircon fractions from the granite porphyry yield a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 25.21 ± 0.055 Ma ($N = 5$; $\text{MSWD} = 5.5$). Four of the five fractions overlap within uncertainty. All four fractions analyzed from the granodiorite phase of the Red River pluton agree within uncertainty and define a weighted mean age that is identical to the granite porphyry (25.20 ± 0.036 ; $\text{MSWD} = 0.79$).

One crystal-rich tuff was collected from the south side of Goat Hill (QM11-04), just below the summit. A preliminary age of 25.13 ± 0.20 Ma was obtained for this sample on the basis of three single-grain zircon analyses.

A sample of the biotite-plagioclase aplite porphyry (sample QM11-01) of the Sulphur Gulch pluton was collected from within the open pit mine in the easternmost portion of the Central deposit. This sample yields a weighted mean age with statistically significant scatter (24.91 ± 0.069 ; $N = 8$; $\text{MSWD} = 14$). The second sample from the Sulphur Gulch pluton is a

Table 1. U-Pb data for caldera margin rocks from the Latir volcanic field

Sample* Fraction (n)		Dates (Ma)		Composition										Isotopic Ratios							
		Th-corrected ^a		± 2σ		± 2σ		± 2σ		± 2σ		± 2σ		± 2σ		± 2σ		± 2σ			
		²⁰⁶ Pb/ ²³⁸ U	abs	²⁰⁷ Pb/ ²³⁵ U ^a	abs	²⁰⁷ Pb/ ²⁰⁶ Pb ^a	abs	corr. coef.	Pb*/ Pbc ^b	Pb*/ (pg) ^c	Pbc (pg) ^d	[U] (ppm)	Th/ U ^e	²⁰⁶ Pb/ ²⁰⁴ Pb ^f	²⁰⁶ Pb/ ²³⁸ U ^g	²⁰⁷ Pb/ ²³⁵ U ^g	²⁰⁶ Pb/ ²⁰⁸ Pb ^g	²⁰⁷ Pb/ ²⁰⁸ Pb ^g			
JMR-5																					
Grandiorite; Red River Intrusive suite (Th/U = 3.3: 464347, 4064398)																					
F-1 (1)		25.26	0.171	26.33	1.71	130.9	146.4	0.542	3.4	7	2.1	149	1.20	195	0.0039161	0.68	0.026268	6.6			
F-2 (1)		25.19	0.040	25.48	0.41	59.2	37.2	0.619	13.8	15	1.1	99	1.29	720	0.0039043	0.15	0.025407	1.6			
F-3 (1)		25.23	0.192	25.82	1.78	87.5	156.5	0.550	2.9	6	2.1	126	1.15	169	0.0039110	0.77	0.025755	7.0			
F-4 (1)		25.26	0.107	25.26	0.98	32.5	89.6	0.516	4.6	13	2.7	133	1.10	259	0.0039146	0.43	0.025191	3.9			
MZQ-5																					
Granite porphyry; Red River Intrusive suite (Th/U = 4.97: 455754, 4701203)																					
F-4 (2)		25.15	0.031	25.44	0.41	61.1	36.6	0.666	12.0	19	1.6	432	0.85	691	0.0038956	0.12	0.025371	1.6			
F-6 (4)		25.23	0.026	25.47	0.23	57.2	20.1	0.615	23.1	44	1.9	1004	0.81	1323	0.0039072	0.10	0.025405	0.9			
F-8 (4)		25.25	0.058	25.62	0.68	68.9	60.4	0.720	4.2	35	8.3	766	0.92	243	0.0039113	0.23	0.025557	2.7			
F-10 (4)		25.27	0.064	26.00	0.92	102.2	80.6	0.700	3.8	39	10.5	406	1.23	207	0.0039146	0.26	0.025940	3.6			
F-12 (2)		25.18	0.048	25.13	0.76	29.1	69.9	0.726	6.7	12	1.7	130	0.92	390	0.0038997	0.19	0.025060	3.1			
QM11-01																					
Biotite-Plagioclase porphyry; Sulphur Gulch pluton (Th/U = 3.8: 454580, 4062090)																					
F-2 (3)		24.78	0.038	24.75	0.21	30.4	19.3	0.553	21.2	59	2.8	230	0.75	1237	0.0038379	0.15	0.024676	0.9			
F-3 (2)		24.85	0.045	25.13	0.45	59.3	40.7	0.546	6.9	41	5.9	101	0.95	393	0.0038498	0.18	0.025054	1.8			
F-4 (1)		24.98	0.035	25.01	0.15	36.9	13.3	0.466	32.8	68	2.1	197	0.77	1896	0.0038688	0.14	0.024942	0.6			
F-6 (2)		24.93	0.031	25.23	0.36	62.6	32.3	0.633	13.7	25	1.8	194	0.79	800	0.0038608	0.12	0.025160	1.4			
F-7 (1)		24.95	0.092	25.63	1.55	98.6	139.4	0.599	1.7	13	7.3	299	0.66	119	0.0038640	0.37	0.025565	6.1			
F-8 (1)		25.03	0.063	25.33	0.97	62.0	88.2	0.759	5.1	9	1.7	202	0.86	307	0.0038765	0.25	0.025256	3.9			
F-9 (1)		24.88	0.052	25.23	0.62	67.0	56.5	0.612	4.8	23	4.8	266	0.87	288	0.0038541	0.21	0.025164	2.5			
F-10 (1)		25.04	0.102	24.87	1.57	15.5	145.6	0.822	3.5	7	1.9	70	1.04	209	0.0038803	0.41	0.024795	6.4			
QV11-02																					
Granite porphyry; Southwest intrusive suite (Th/U = 3.8: Drill hole 36.5 - 54.5, 62)																					
#F-1 (4)		24.59	0.032	24.70	0.16	43.3	14.2	0.498	33.2	42	1.3	334	0.74	1928	0.0038087	0.13	0.024621	0.6			
F-2 (4)		24.50	0.024	24.56	0.11	40.0	9.3	0.614	57.4	71	1.2	351	0.61	3440	0.0037930	0.10	0.024486	0.4			
F-3 (3)		24.53	0.043	24.59	0.14	39.3	12.3	0.497	36.7	69	1.9	427	0.61	2203	0.0037978	0.17	0.024509	0.6			
F-4 (5)		24.51	0.028	24.64	0.20	46.6	18.4	0.544	24.8	36	1.5	296	0.63	1489	0.0037951	0.11	0.024567	0.8			
#F-5 (1)		24.60	0.035	24.64	0.18	37.1	16.2	0.480	19.1	55	2.9	228	0.58	1163	0.0038097	0.14	0.024563	0.7			
F-6 (1)		24.38	0.093	24.77	1.55	71.5	143.6	0.777	3.0	3	1.0	73	0.68	194	0.0037746	0.38	0.024690	6.3			
F-7 (1)		24.47	0.072	24.83	0.70	68.8	64.4	0.522	5.6	13	2.4	164	0.63	353	0.0037887	0.30	0.024755	2.8			
F-8 (2)		24.49	0.090	24.38	1.01	22.5	95.7	0.564	3.3	10	3.1	84	0.61	214	0.0037919	0.37	0.024300	4.2			

JMR-34	Granite porphyry; Bear Canyon pluton (Th/U = 4.0: 450594, 4060825)																			
	F-1 (2)	24.49	0.032	24.67	0.19	50.3	16.9	0.666	9.8	15.0	1.5	179	0.73	584	0.0037927	0.13	0.024589	0.8	0.047020	0.7
	# F-3 (2)	24.29	0.051	24.17	0.55	20.4	53.8	0.429	4.9	9.5	2.	232	0.69	304	0.0037617	0.21	0.024086	2.3	0.046437	2.2
	# F-4 (2)	24.35	0.059	24.16	0.56	14.3	53.	0.626	3.7	22.5	6.1	270	0.74	228	0.0037711	0.24	0.024084	2.3	0.046319	2.2
	F-5 (4)	24.48	0.023	24.47	0.06	32.8	4.6	0.691	60.4	120.4	2.	596	0.60	3629	0.0037899	0.09	0.024392	0.2	0.046677	0.2
	F-6 (4)	24.48	0.024	24.46	0.07	31.5	4.8	0.783	42.6	63.1	1.5	254	0.70	2501	0.0037907	0.10	0.024384	0.3	0.046653	0.2
	F-7 (2)	24.45	0.037	24.56	0.20	43.9	17.8	0.559	10.5	47.4	4.5	388	0.64	628	0.0037859	0.15	0.024480	0.8	0.046895	0.7
	F-8 (4)	24.46	0.041	24.599	0.13	47.2	10.9	0.614	15.7	41.8	2.7	343	0.62	946	0.0037874	0.17	0.024522	0.5	0.046960	0.5
JMR-6	Granite porphyry; Sulphur Gulch pluton (Th/U = 3.8: 455776, 4060997)																			
	F-1 (3)	24.37	0.134	24.11	1.07	7.2	101.1	0.538	2.9	5.4	1.8	129	0.75	185	0.0037740	0.55	0.024032	4.5	0.046184	4.2
	F-2 (2)	24.63	0.096	25.02	0.99	71.7	89.7	0.623	2.6	10.3	4.	246	0.72	164	0.0038136	0.39	0.024948	4.0	0.047446	3.8
	F-3 (4)	24.49	0.055	24.88	0.53	71.6	48.3	0.614	4.6	17.6	3.9	442	0.55	288	0.0037924	0.23	0.024808	2.2	0.047443	2.0
	F-5 (1)	24.57	0.053	25.02	0.76	76.8	69.7	0.736	6.5	6.4	1.	500	0.79	387	0.0038059	0.22	0.024951	3.1	0.047547	2.9
	F-7 (1)	24.46	0.062	24.54	0.22	41.7	20.	0.452	21.1	20.9	1.	528	0.52	1303	0.0037868	0.25	0.024463	0.9	0.046852	0.8
	F-8 (1)	24.25	0.058	24.98	0.78	105.0	70.8	0.749	6.3	5.9	.9	704	0.80	376	0.0037550	0.24	0.024911	3.2	0.048116	3.0
	F-9 (3)	24.39	0.042	24.36	0.18	30.0	15.4	0.643	27.5	54.3	2.	162	0.76	1573	0.0037770	0.17	0.024281	0.7	0.046624	0.6
F-11 (3)	24.44	0.070	24.68	0.70	56.8	64.2	0.679	4.0	14.6	3.6	358	0.64	252	0.0037843	0.29	0.024602	2.9	0.047150	2.7	
	F-12 (3)	24.56	0.184	24.54	0.54	32.6	41.5	0.746	9.8	16.2	1.7	412	0.49	611	0.0038016	0.75	0.024466	2.2	0.046675	1.7

a Isotopic dates calculated using the decay constants $\lambda_{238} = 1.55125\text{E-}10$ and $\lambda_{235} = 9.8485\text{E-}10$ (Jaffey et al. 1971).

b Ratio of radiogenic Pb (including 208Pb) to common Pb.

c Total mass of radiogenic Pb.

d Total mass of common Pb.

e Th contents calculated from radiogenic 208Pb and the 207Pb/206Pb date of the sample, assuming concordance between U-Th and Pb systems.

f Measured ratio corrected for fractionation and spike contribution only.

g Measured ratios corrected for fractionation, tracer, blank and initial common Pb.

Lab blank assumed to be 2 ± 1 pg

Initial Pb for samples QV11-02, QM11-01, and QM11-04 use Stacey and Kramers (1975) at 25 Ma. All others use data from Johnson et al. (1990).

Pb blank ratios: $206/204 = 18.864 \pm 0.25$; $207/204 = 15.630 \pm 0.25$; $208/204 = 38.193 \pm 0.50$ (1-sigma)

excluded from weighted mean age (Fig. 3)

* Locations in NAD 27, UTM Zone 13

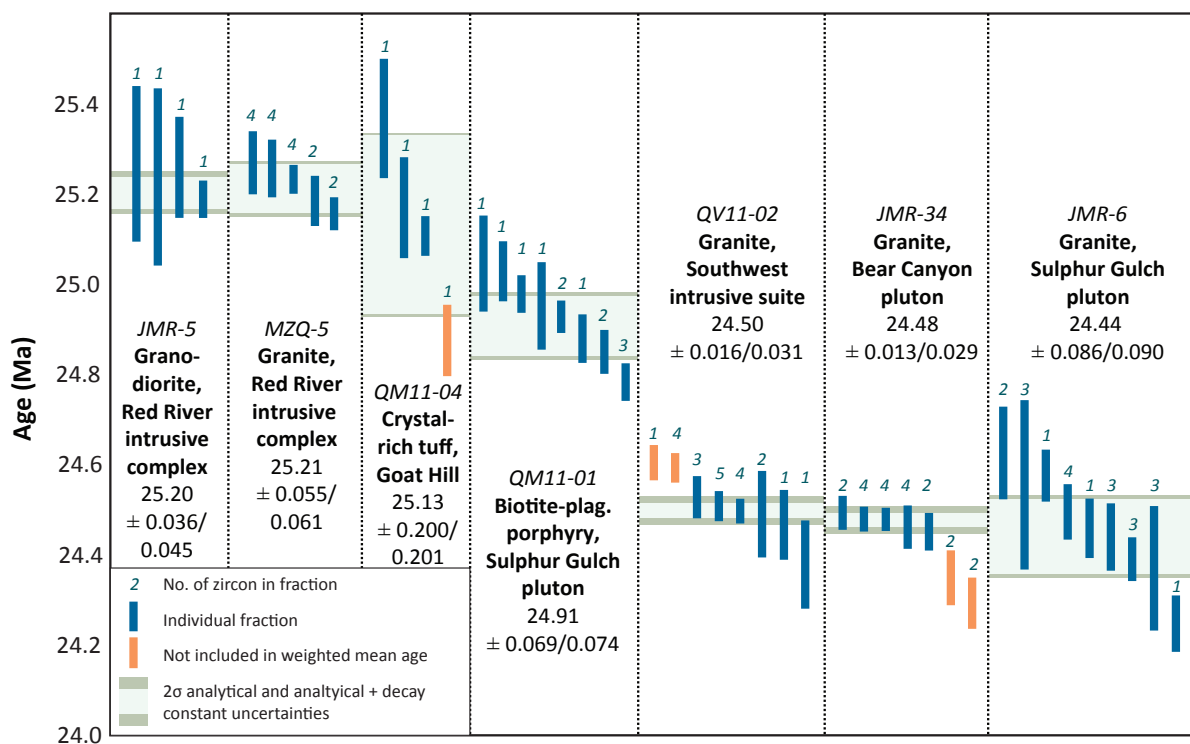


Figure 3. $^{206}\text{Pb}/^{238}\text{U}$ ages for individual analyses. Vertical bars correspond to 2σ analytical uncertainties for individual analyses. Horizontal bars represent the weighted mean age with analytical uncertainty only. Ages in text are in Ma with analytical/analytical + decay constant uncertainties.

granite porphyry (JMR-6) collected near the milling site for the mine. The interpreted age for this sample is 24.44 ± 0.086 Ma (N=9; MSWD = 11).

A granite porphyry with moderate potassic and silicic alteration from the Southwest intrusive suite had five overlapping analyses with a weighted mean age of 24.50 ± 0.016 (MSWD = 2.0). Two fractions not included in the weighted mean age define a slightly older population at 24.60 Ma and are interpreted as antecrysts [Miller *et al.*, 2007].

Sample JMR-34 from the Bear Canyon pluton was the freshest sample collected near the molybdenum mine. Zircon separates from this sample were generally larger and more euhedral than those from more altered samples (e.g. Sulphur Gulch). Two fractions from this sample are significantly younger than the other analyses and probably represent Pb loss. The older population (24.48 ± 0.013 Ma; MSWD = 0.87) is interpreted as the crystallization age. Including the two younger fractions yields a weighted mean age of 24.46 ± 0.050 Ma (MSWD = 11).

4.2. Re-Os molybdenite geochronology

Five vein-hosted and three breccia matrix molybdenite samples were analyzed from three separate ore bodies (Goat Hill, D, and Vein; Table 2, Fig. 4). All samples have moderate Re concentrations less than 70 ppm and there is no correlation of Re concentration with mineralization style or ore body. Errors in this section are analytical only, and quoted at two-sigma.

The oldest molybdenite age obtained in this study is 24.76 ± 0.026 Ma and comes from a thin quartz + molybdenite vein hosted in the aplite beneath the Goat Hill ore body. Two breccia matrix-hosted molybdenite samples yield analytically distinct ages of 24.61 ± 0.028 and 24.49 ± 0.043 Ma. Similarly, two vein-style molybdenite veins from within the same Goat Hill ore body yield ages of 24.59 ± 0.026 and 24.52 ± 0.028 Ma.

Two samples from the D ore body yield ages of 24.61 ± 0.028 and 24.58 ± 0.027 Ma

Table 2. Re-Os data for molybdenite of the Questa porphyry Mo deposit

AIRIE Run #	Sample Name	Drill Hole	Description ^a	Ore body	Re (ppm) ^b	¹⁸⁷ Os (ppb) ^b	Common Os (ppb) ^c	weight (g) ^d	Age (Ma) ^e	$\pm 2\sigma$ abs (analytical) ^f	$\pm 2\sigma$ abs (analytical + λ) ^f
MD-1254	AR-98	22.0 - 14.0	Vein in source aplite facies	Goat Hill	22.2	5.8	0.012	0.0260	24.76	0.026	0.083
MD-1255	AR-110	23.4 - 11.8G	Vein in MHBX facies A ₃	Goat Hill	45.2	11.7	0.041	0.0212	24.59	0.026	0.083
MD-1299	AR-130	22.0 - 14.0	MHBX, C facies	Goat Hill	30.6	7.9	0.000	0.0223	24.61	0.028	0.084
MD-1265	AR-76	22.0 - 14.0	Vein in MHBX facies D	Goat Hill	39.0	10.0	0.000	0.0214	24.52	0.028	0.083
MD-1296	AR-126	22.0 - 14.0	MHBX, D facies	Goat Hill	1.9	0.5	0.000	0.0258	24.49	0.043	0.090
MD-1295	JC-1	28.9 - 25.5HA	Vein	D	6.6	1.7	0.000	0.0331	24.61	0.028	0.084
MD-1298	JC-2	28.9 - 25.5HA	MHBX	D	39.0	10.0	0.016	0.0276	24.58	0.027	0.083
MD-1308	QV11-02	36.5 - 54.5 VN20	Vein	Vein zone	26.4	6.8	0.000	0.0323	24.51	0.032	0.085

a MHBX = Magmatic-hydrothermal breccia; Facies corresponds to those of Ross et al. (2002)

b All data are blank corrected, and Os isotopic measurements are fractionation corrected (using the double Os spike)

c Common Os is insignificant to the age calculation, and essentially zero for all analyzed molybdenites

d Percent molybdenite in separate varies from 20% to 100%, depending on occurrence and availability of molybdenite;

qtz-feldspar-biotite dilutant does not affect Re-Os age calculation

e For AR-98, AR-110, AR-76, Re blank = 24.22 ± 0.15 pg, total Os = 2.00 ± 0.02 pg with $^{187}\text{Os}/^{188}\text{Os} = 0.231 \pm 0.001$

All others, Re blank = 7.85 ± 1.48 pg, total Os = 1.86 ± 0.03 pg with $^{187}\text{Os}/^{188}\text{Os} = 0.322 \pm 0.010$

f Uncertainty on ages shown for both analytical error, and combined analytical and decay constant uncertainty for ^{187}Re errors (0.31%, Smoliar et al. 1996)

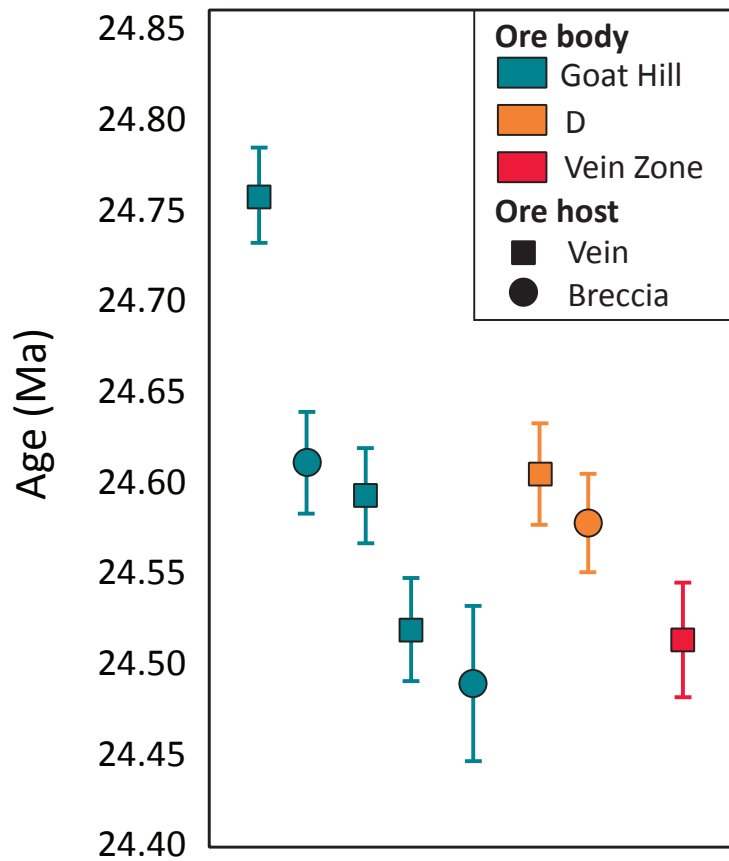


Figure 4. Molybdenite Re-Os ages for various ore bodies. Error bars correspond to 2σ analytical uncertainties. Vein and breccia represent vein- and breccia-matrix hosted mineralization styles, respectively.

for vein and breccia matrix-hosted mineralization styles, respectively. One thin molybdenite vein that cuts granite porphyry within the Vein ore body was selected for both Re-Os molybdenite and U-Pb zircon geochronology. This sample yields a Re-Os age of $24.51 \pm 0.032/0.085$ Ma (uncertainties corresponding to analytical, and analytical with ^{187}Re decay constant error, respectively) which is within uncertainty of the U-Pb zircon age obtained for the host granite (24.50 ± 0.031 Ma).

5. Discussion

Combining U-Pb zircon geochronology of intrusive rocks with Re-Os molybdenite ages from the Questa Mo deposit allows us to characterize the timing and duration of magma emplacement with respect to mineralization. Additionally, most of the samples used for Re-Os geochronology were analyzed for mineralization temperatures in earlier studies [Cline and Bodnar, 1994; Rowe, 2012], thus permitting combination of the new ages with temperature data to evaluate Re-Os as a thermochronometer. All the data can be considered within the framework of the evolution of the host Latir volcanic field to develop a model for porphyry Mo mineralization.

5.1. Intrusive history of the caldera margin plutons

The Red River intrusive complex is the oldest and easternmost of the caldera margin plutons. Equigranular granodiorite exposed in the central portion of the pluton was previously interpreted as the remnant magma chamber of a pre-caldera andesitic volcano [Lipman, 1988; Lipman and Reed, 1989]. However, the geochronologic data presented here indicate that the granodiorite crystallized approximately 300 ka after the eruption of the Amalia Tuff, nearly concurrently with high-silica granitic magma at ~ 25.20 Ma (Fig. 5). However, field relations demonstrate that the Red River granite is part of a dike swarm that crosscuts the granodiorite [Lipman and Reed, 1989]. Therefore, although the units are the same age within uncertainty, the granite is demonstrably younger.

Major and trace element modeling indicate that the granodiorite within the Red River intrusive complex could not be a parental magma for the high silica granite [Johnson *et al.*, 1989], thereby limiting the possibility that these magmas represent a single differentiated intrusion with a simple cooling history. Instead, the Red River pluton appears to have been

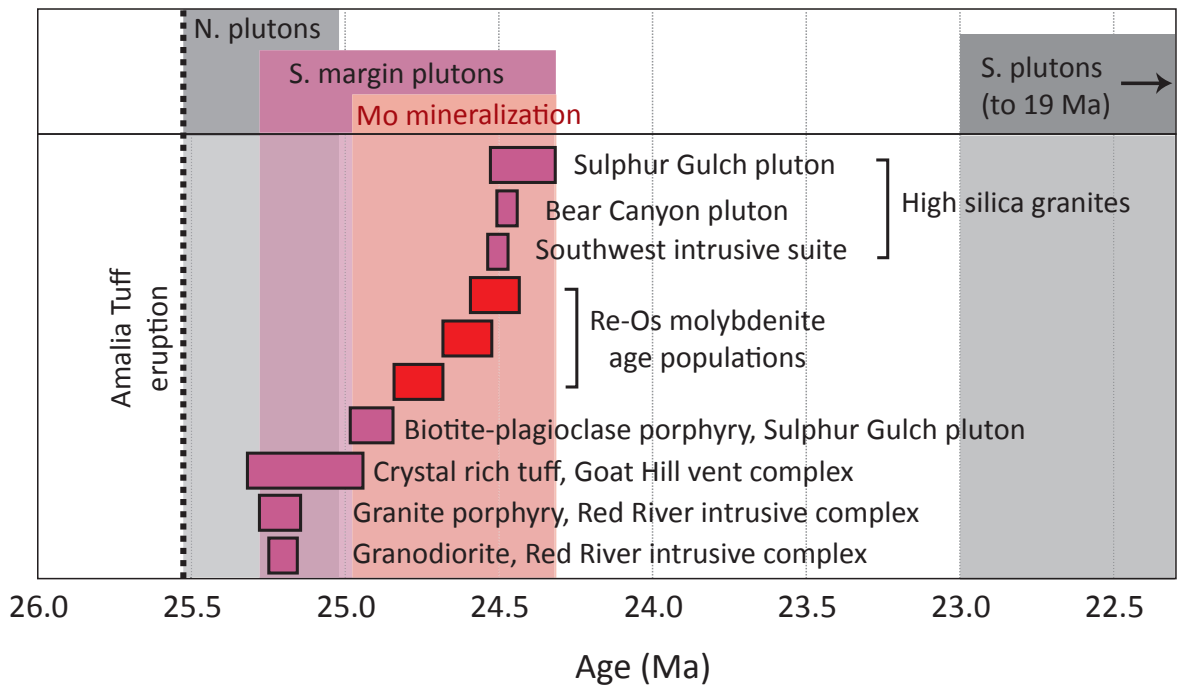


Figure 5. Summary of geochronology for the volcanic and plutonic rocks related to the Questa-Latir volcanic field after the eruption of the Amalia Tuff. Purple and red blocks represent new data from this study. Block width represents 2σ uncertainty, including decay constant uncertainty. N. plutons = northern plutons (Cabresto Lake, Virging Canyon, Cañada Pinabete, and Rito del Medio; Fig. 1B). S. plutons = Southern plutons (Rio Hondo and Lucero Peak; Fig. 1B). Total duration of mineralization includes the approximate emplacement age of the biotite-plagioclase porphyry phase of the Sulphur Gulch pluton, see text for discussion.

assembled rapidly by intrusion of compositionally diverse magma pulses.

Following intrusion of the Red River intrusive complex, magmatism moved westward. New U-Pb zircon ages presented here suggest that the Sulphur Gulch pluton was assembled between 24.91 and 24.44 Ma with the biotite-plagioclase porphyry predating the granitic phase of the pluton. The granitic phases of the Sulphur Gulch pluton, Southwest intrusive suite and Bear Canyon pluton all intruded within uncertainty of each other at ~ 24.50 Ma. These high-silica granites were the primary contributors of metal-rich brines that resulted in breccia matrix-hosted and stockwork-style mineralization [*Cline and Bodnar*, 1994; *Ross et al.*, 2002; *Klemm et al.*, 2008; *Rowe*, 2012].

Field mapping and gravity anomaly data indicate that the southern caldera margin plutons are upper portions of a partial ring intrusion along the caldera margin [*Cordell et al.*, 1985; *Lipman et al.*, 1986; *Meyer*, 1991]. The U-Pb zircon geochronologic data presented here indicate that assembly occurred over ~ 770 ka. This period corresponds to only a small interval of the ~ 6 Ma post-caldera pluton assembly history for the entire region [*Tappa et al.*, 2011; *Zimmerer and McIntosh*, 2012], but brackets the time in which major magmatic hydrothermal systems were active [*McLemore and North*, 1984; *Lipman et al.*, 1986; *Lipman*, 1988; *Meyer and Foland*, 1991; *Ross et al.*, 2002]. These data are consistent with *Zimmerman et al.* [2008], who observed that major porphyry-style mineralization episodes are short-lived relative to their host magmatic districts.

5.2. History of mineralization

Numerous occurrences of epithermal Au-Ag veins are present within the Red River intrusive complex and its wallrocks [*McLemore and North*, 1984]. New ages presented here therefore place a maximum age of 25.20 Ma on the epithermal-style mineralization. A younger age for mineralization cannot be ruled out; however the epizonal textures associated with the pluton [*Lipman*, 1988] suggest that minor epithermal Au-Ag mineralization was synchronous with pluton assembly.

Major molybdenite mineralization at Questa was coeval with the emplacement of the Southwest intrusive suite, and the Sulphur Gulch and Bear Canyon plutons. The earliest mineralizing intrusion identified in this study is the biotite-plagioclase porphyry of the Sulphur Gulch pluton (24.91 ± 0.069 Ma) which is exposed in the open pit, just east of the Central ore body. The open pit mine, which is no longer active, targeted lode-style molybdenum mineralization [Ross *et al.*, 2002] which probably received its metals from this intrusion. Generally, local ore grades are highest sub-parallel to the contact between the biotite-plagioclase porphyry and the pre-caldera andesite. [B. Walker, per. comm.]. These field relationships suggest that this intrusion contributed ore to the system rather than acting as a host for later mineralization events.

Molybdenite Re-Os ages record 250 ka of mineralization in at least three discrete episodes (Fig. 4). These data reflect the minimum duration of molybdenite mineralization because we targeted samples with independent temperature estimates rather than initial and final events. Seven of the eight molybdenite samples have ages between ~ 24.6 to 24.5 Ma, suggesting that major mineralization event occurred over this time interval. During this time period, both breccia matrix- and vein-style ore were deposited within the Goat Hill and D ore bodies [Ross *et al.*, 2002]. These data demonstrate that the two distinct styles of mineralization were coeval in space and time for ~ 100 ka.

The Goat Hill ore body alone was mineralized over a period of 250 ka, and molybdenite Re-Os ages become progressively younger upsection through its semi-stratified facies [Fig. 2B; Ross *et al.*, 2002]. These data could reflect time-progressive fluid evolution away from the source intrusion [Ross *et al.*, 2002], but that requires the hydrothermal system to have been active for hundreds of thousands of years. This is unlikely given the short lifespan predicted by numerical models for an intrusion the size of the source (< 1 km³; Cathles *et al.*, 1997; Ross *et al.*, 2002). It is proposed that initial brecciation created an isotropic zone of weakness that re-fractured episodically during subsequent dike intrusions and fluid exsolution over a prolonged time period. Essentially, the Goat Hill hydrothermal

breccia may have acted as a small trap that was easily shattered, thereby depressurizing small intrusions and favoring magma quenching and fluid exsolution [*Candela, 1997*].

Burnham [1997] suggests that the presence of multiple populations of stockwork veins within porphyry-type systems could be related to the interplay between downward crystallization and repetitious crack-seal events within a single magma chamber. However, the total duration of Re-Os molybdenite ages observed in this study is too long for such a simplified process. It is proposed here that each mineralization stage corresponds to a complete cycle of magma injection, fluid exsolution, circulation, cooling, and mineralization. These data substantiate previous interpretations that Climax-type deposits form via complex multi-phase mineralization [*Wallace et al., 1968; Seedorff and Einaudi, 2004a*].

In all, our data indicate syn-mineralization pluton assembly over a period of about 770 ka with early Au-Ag mineralization followed by at least 250 ka (and perhaps 400 ka if mineralization of the biotite-plagioclase porphyry was synchronous with intrusion) of Mo mineralization. Variable textures throughout caldera margin plutons with discrete intrusive contacts indicate at least a portion of the system was assembled by injection of numerous small and fast-cooling intrusions. These data are consistent with growing body of evidence for incremental pluton assembly [e.g. *Coleman et al., 2004; Matzel et al., 2006; Davis et al., 2012; Tappa et al., 2011; Leuthold et al., 2012*], and links this concept with models for episodic porphyry mineralization [*Wallace et al., 1968; Carten et al., 1988; Makshev et al., 2004; Seedorff and Einaudi, 2004a; Wilson et al., 2007*].

5.3. Re-Os molybdenite: a new thermochronometer

If molybdenum mineralization is demonstrably related to magma emplacement, such as in porphyry ore systems, the mineralization temperature can be used to help construct a system-wide thermal history. Fluid inclusion studies reveal that mineralization within porphyry systems occurs at temperatures between ~ 300 to 500 °C, with modes typically ~ 400 °C [*Cline and Bodnar, 1994; Selby et al., 2000; Klemm et al., 2008*];

Rowe, 2012]. Because thermal modeling [e.g., *Hanson and Glazner*, 1995; *Yoshinobu et al.*, 1998] demonstrates that incrementally assembled plutons “dwell” in the temperature window between hornblende and biotite Ar closure temperatures [~ 525 °C and ~ 325 °C, respectively; *Harrison*, 1981; *Harrison et al.*, 1985], Re-Os molybdenite data can fill an important gap in our understanding of these systems [e.g., *Stein et al.*, 2001; *Markey et al.*, 2003].

Most of the molybdenite separates used in this study are extracted from the same samples that were used in fluid inclusion studies, thereby allowing correlation of microthermometry results and Re-Os molybdenite ages. For the Goat Hill ore body, *Rowe* [2012] determined a primary mineralization stage to occur at 380 °C, with another significant stage at ~ 280 °C. *Rowe* [2012] observed evidence for halite trapping (e.g., multiple halite crystals in one inclusion), and as a result she reported liquid-vapor homogenization temperatures. This is in contrast to the studies from the D ore body [*Cline and Bodnar* 1994; *Klemm et al.* 2008], for which halite homogenization temperatures are reported. Both of these studies determined mineralization temperatures to be > 410 °C for the D ore body. Because halite typically dissolves at a higher temperature than liquid-vapor homogenization in fluid inclusions from porphyry ore systems [e.g. *Becker et al.*, 2008], the difference in temperature estimates between the Goat Hill and D ore bodies is likely minimal. Consequently, we use an intermediate temperature of ~ 400 °C for our discussion.

The dispersion of Re-Os molybdenite ages presented here is interpreted to reflect episodic mineralization events. Therefore chronologically later mineralization episodes with temperatures on the order of 400 °C did not disturb the Re-Os system in molybdenite. This observation is consistent with previous studies where Re-Os molybdenite ages were not reset by high-grade metamorphism [*Stein et al.*, 2001, 2003], and discrete Re-Os molybdenite ages that are concordant with U-Pb zircon ages from associated intrusions [*Selby et al.*, 2007; *Maksaev et al.*, 2004]. These data also support previous work that predicts the closure temperature of the Re-Os system in molybdenite to be > 400 °C [*Suzuki et al.*, 1996]. As a

result, Re-Os molybdenite is considered a useful new thermochronometer in geologic settings where molybdenite is the primary sulfide phase.

5.4. Integrated T-t history of the Questa porphyry system

Combination of new U-Pb and Re-Os dates with published Ar-Ar dates allows evaluation of the T-t history of the caldera margin plutons and mineralization. Uncertainties in ages in this section include propagation of full analytical uncertainties and ^{238}U and ^{187}Re decay constant uncertainties. Individual cycles of magma emplacement, fluid exsolution and mineralization cooled were short-lived from zircon saturation ($\sim 750\text{ }^{\circ}\text{C}$) through molybdenite mineralization ($\sim 400\text{ }^{\circ}\text{C}$). Consider sample QV11-02 from the Vein ore body (Fig. 2; 6A). Zircon crystallization within this sample occurred at $24.50 \pm 0.032\text{ Ma}$ and the pluton is cut by a molybdenite vein, dated at $24.51 \pm 0.085\text{ Ma}$. It is possible that molybdenite from the vein was not sourced from the same intrusive rock that was sampled; regardless, these data limit the duration of time between zircon crystallization and brittle-vein formation to have occurred within uncertainty of the ages, consistent with rapid cooling.

Biotite $^{40}\text{Ar}/^{39}\text{Ar}$ ages for the Southwest intrusive suite and Bear Canyon pluton also agree within uncertainty with U-Pb zircon crystallization ages (Fig. 6). The weighted mean of nine $^{40}\text{Ar}/^{39}\text{Ar}$ biotite ages for the Goat Hill ore body overlaps the emplacement age of the SW intrusive suite ($24.56 \pm 0.06\text{ Ma}$; Rowe *et al.*, [2003]). The close spatial proximity of the Southwest intrusive suite to the Goat Hill ore body and temporal agreement between U-Pb zircon, Re-Os molybdenite and $^{40}\text{Ar}/^{39}\text{Ar}$ biotite chronometers argue strongly for rapid cooling from magma emplacement through biotite closure ($\sim 325\text{ }^{\circ}\text{C}$).

Acknowledging that all analyzed samples advocate rapid cooling rates allows for a general interpretation of thermal cycling within the system (Fig. 6B). Note, however, that our sampling strategy targeted samples where independent determinations of temperature were available and therefore may exclude higher frequency events. Regardless, the combination Re-Os molybdenite and U-Pb zircon geochronology show multiple thermal cycles over a

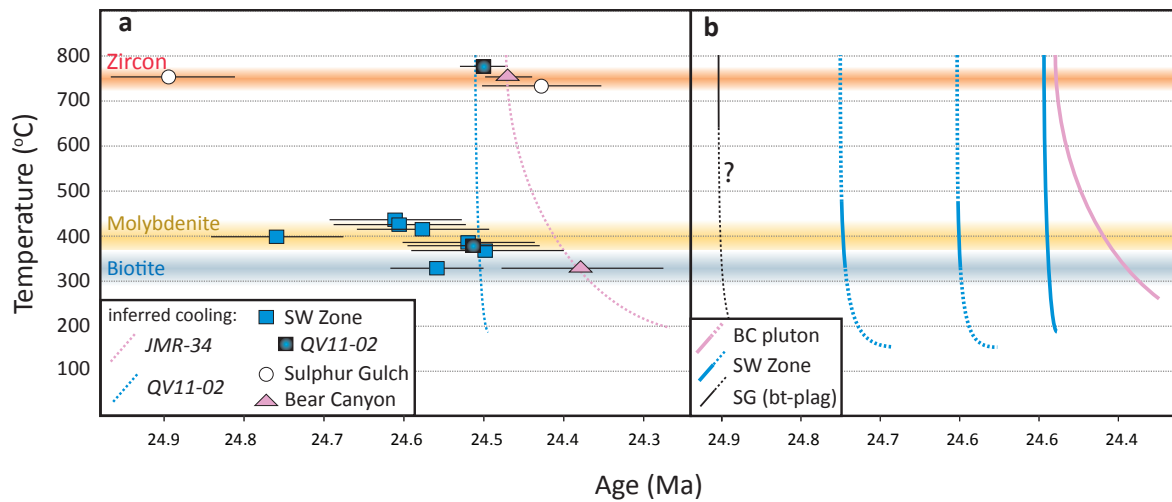


Figure 6. **A)** T-t plot showing crystallization ages of plutons related to molybdenite mineralization within the Questa ore system. Yellow horizontal band corresponds to uncertainties in molybdenite precipitation temperature (see text). Zircon U-Pb saturation temperature was calculated using whole rock data of *Johnson et al.* [1989] and equations of *Watson and Harrison* [1983]. Biotite closure temperature from *Harrison et al.* [1985]. Horizontal error bars represent 2σ uncertainties (including decay constant uncertainties, except for Ar-Ar ages). Note that some samples are offset on the y-axis for clarity and not because of measurable differences in temperature. **B)** Interpreted thermal history based on data in part A. Solid lines represent cooling periods as defined by geochronology where U-Pb zircon data are complemented by a low-T chronometer, whereas dotted lines are inferred. Dotted lines were placed by transposing the rapid cooling rate of the SW and Bear Canyon plutons back in time. Note that three molybdenite populations were identified from Re-Os molybdenite ages without decay constant uncertainties. The added uncertainties only change what intrusion could be paired with the molybdenite age, not their internal differences.

250 ka if it is assumed that each hydrothermal circulation event corresponds to a specific intrusion that cools rapidly [*Cathles et al.*, 1997; blue line, Fig. 6B].

Evidence for rapid cooling from igneous through hydrothermal conditions is consistent with numerical models for shallow magmatic systems such as the one responsible for mineralization at Questa [3 – 5 km at time of emplacement; *Cline and Bodnar*, 1994; *Cathles et al.*, 1997]. These data add to a growing body of evidence that suggest porphyry ore systems are characterized by multiple injections of magma where each pulse creates a hydrothermal circulation cell that remains active for < 100 ka [*Marsh et al.*, 1997; *Maksaev et al.*, 2004; *Lawley et al.*, 2010; *Braxton et al.*, 2012]. However, this study is the first to provide the timing and duration of multiple cycles for a Climax-type porphyry Mo system and we suggest that individual cycles are possibly active for very short times (within uncertainty of the chronometers in this study).

5.5. Evaluation of previous genetic models for the Questa Mo deposit

Previous thought on the origin of the Questa porphyry Mo deposit calls upon 1) chemical differentiation processes (assimilation, crystal fractionation, volatile fluxing) in a long-lived magma chamber within the middle to upper crust [*Johnson et al.*, 1989; *Carten et al.*, 1993] or 2) fractional crystallization in the lower crust [*Klemm et al.*, 2008]. The mineralizing intrusions in these cases are believed to be cupolas that emanate from these long-lived reservoirs. Detailed geo-thermochronology presented here challenges these hypotheses.

Agreement of U-Pb zircon ages with Re-Os molybdenite and Ar-Ar biotite geochronology for the suite of high-silica granites precludes the possibility that these intrusions resided in a long-lived upper crustal magma chamber [e.g. *Johnson et al.*, 1989; *Carten et al.*, 1993]. Any fractionating chamber would have been below zircon saturation temperatures (750° to 780°C) and crystallizing zircon [*Johnson et al.*, 1989]. This predicts a gap between zircon saturation and cooling coincident with intrusion and mineralization

(Fig. 7A). Mafic recharge into the base of the system could reheat it above zircon saturation temperatures [e.g. *Carten et al.*, 1993], however, this requires a significant volume of mafic magma that is unrecognized in surface and subsurface data [*Lipman and Reed*, 1989; *Meyer*, 1991; *Unpub. Consultant Report*].

Alternatively, in situ magma differentiation could take place in the deep crust where ambient temperatures are higher. *Klemm et al.* [2008] suggested that ~ 95% crystallization of a middle to lower crustal magma chamber is required to explain the rapid increase in [Cs] within hydrothermal fluids between breccia matrix-style and vein-style mineralization. However, the Re-Os molybdenite ages in this study clearly show that these mineralization styles were concurrent over a ~ 100 ka period. The data of *Klemm et al.* [2008] suggest a source magma with trace element gradients or the hydrothermal fluids analyzed by these authors exsolved from magmas that were not in communication with one another.

The repetitious intrusion of mineralizing granitic magmas and the synchronicity of high- and low-temperature thermochronometers favors an evolution model in which the magmas are generated, ascend and cool quickly (Fig. 7B). We propose that, like other magmas associated with the Latir field, the origin of the mineralizing magmas was the lower crust [*Johnson et al.*, 1990; *Tappa et al.*, 2011].

5.6. Relationship between caldera formation and mineralization

An intriguing set of observations from the detailed geochronology now available for the Latir volcanic field is that high-silica granites capable of mineralization were emplaced within only 0.25-0.40 Ma of the total 8.5 Ma history of the Latir field (~28.5 to 19.1 Ma; *Zimmerer and McIntosh*, [2012]) and that this short episode of mineralization occurred immediately after the eruption of the caldera-forming Amalia Tuff (~ 25.52 Ma, *Tappa et al.*, 2011). Numerous authors discuss the relationship between large-volume calderas and their control on mineralization [e.g., *Lipman*, 1992; *Rytuba*, 1994; *Henry et al.*, 1997; *Singer and Marchev*, 2000]; however, the majority of the discussion is centered on structural

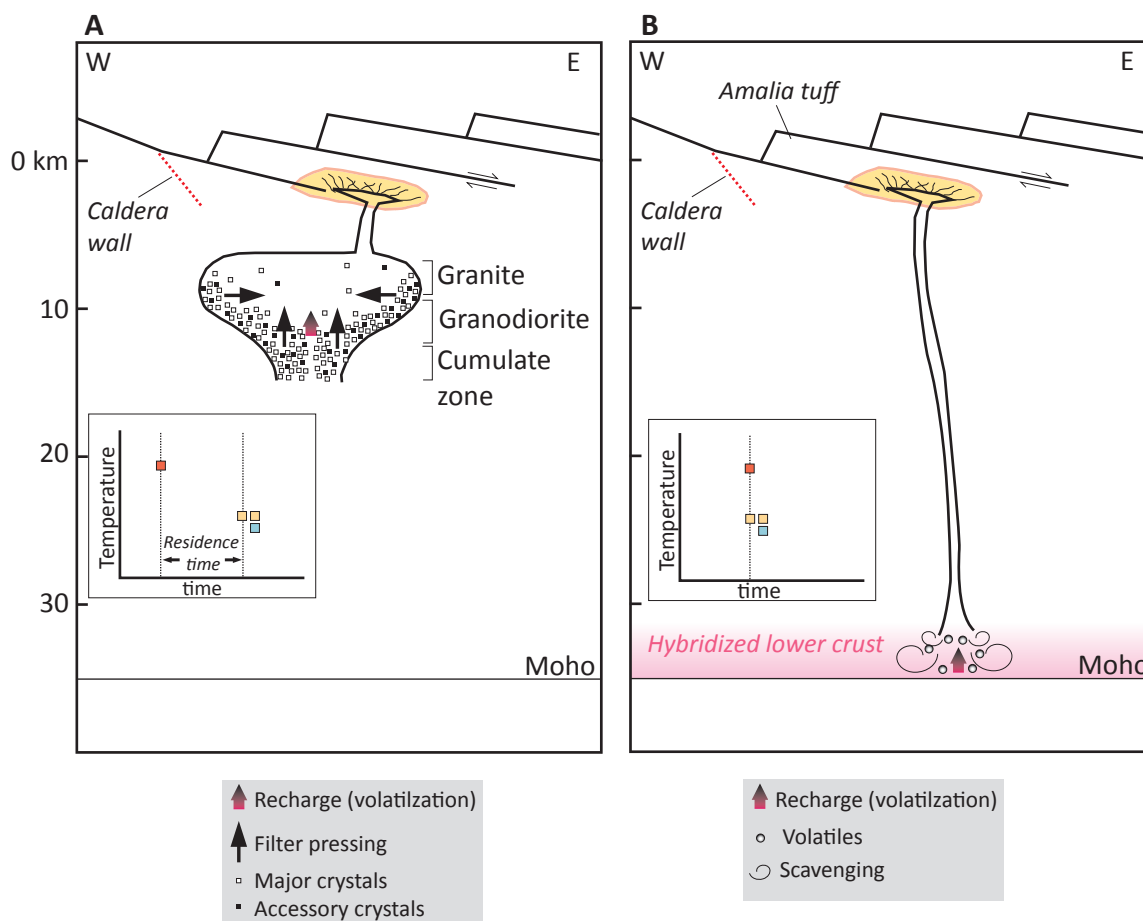


Figure 7. Schematic drawings showing general differences between expected T-t distribution across multiple chronometers (insets) for different magma evolution settings along an E-W cross-section through the southern caldera margin (surface features after Meyer and Foland, 1991). Inset symbols: orange, U-Pb zircon; yellow, Re-Os molybdenite; blue, Ar-Ar biotite. **A**) Crystal fractionation model with variable recharge (modified from Johnson et al., 1989; von Quadt et al., 2011) in a vertically extensive mid- to upper-crust magma chamber. Mineralizing cupolas emanate from the upper crustal reservoir and ultimately crystallize and exsolve hydrothermal fluids in the shallow crust. The presence of a long-lived magma chamber in the upper crust predicts that zircon crystallize at a much earlier time than low-T thermochronometers. **B**) Proposed source model for formation of the Questa porphyry Mo deposit. Scavenging of Mo occurs during a halogen-rich fluxing event in hybridized juvenile lower crust. Upper crustal reservoirs are minimal to absent, and the predicted T-t history crystallizes all zircon within uncertainty of low-T chronometers.

controls related to caldera subsidence (e.g. ring faults) and rarely on the relationship between ignimbrite generation and mineralization.

Recent studies of volcanic-plutonic connections focus on magma flux variations responsible for ignimbrite and non-ignimbrite stages of volcanic field evolution [*Glazner et al.* 2004; *Lipman*, 2007; *Annen et al.*, 2009; *Tappa et al.*, 2011]. Although there are fundamental differences in interpretation among these papers, all agree that an unusually high flux of material (melt, fluid, gas) is required for ignimbrite formation. Most models also focus on the role of a high flux of material from the upper mantle to either remobilize an existing magma body [*Bachmann and Bergantz*, 2003; *Huber et al.*, 2012) or initiate deep crustal melting [*Glazner et al.* 2004; *Tappa et al.* 2011].

It is hypothesized here that the period of high magma flux responsible for generating the Amalia Tuff set the stage for generating mineralizing intrusions at Questa (Fig. 8). A high flux of juvenile mafic rocks may have exsolved hydrothermal fluids during crystallization and created a zone of hybridized crust (juvenile mafic rocks + old lower crust + hydrothermal assemblages). *Stein* [1985] and *Stein and Hannah* [1985] analyzed sulfur isotopes from molybdenite and concluded that all of the sulfur in porphyry Mo systems is derived from the intrusions. Observing the same data, *Pettke et al.* [2010] emphasize that the $\delta^{34}\text{S}$ values are consistent with a mantle source. The high mafic magma flux required for formation of the ignimbrite rapidly transferred unusually high masses of material, including sulfur, into the lower crust as juvenile mafic rocks and hydrothermal fluids. Although mafic underplating throughout the history of the Latir field is hypothesized [*Johnson and Lipman*, 1988; *Johnson et al.*, 1989; 1990] and thus, volatiles were presumably consistently transferred from the mantle to the crust, the unusually high flux necessary for formation of the ignimbrite may have prepared the system for economic mineralization.

Partial melting of the hybridized zone immediately following ignimbrite eruption produced granitic magmas capable of mineralization. Geochemical and experimental studies

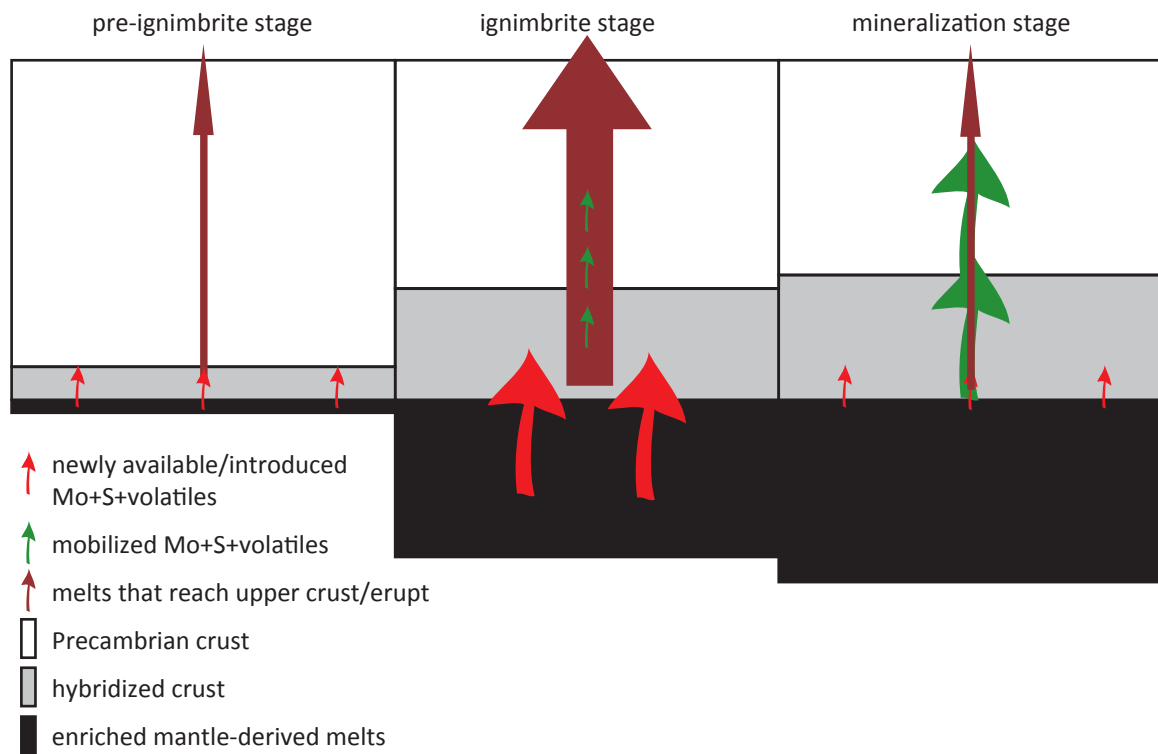


Figure 8. Schematic model showing the relationship between ignimbrite eruption and subsequent mineralization. Thickness of crust and juvenile mantle components are not drawn to scale. Relative size of arrows is proportional to input and output for respective fluxes. See text for discussion.

show that partial melting of hydrous amphibolites (~ lower crust) can create appreciable volumes of granitic magma [Faure and Powell, 1972; Mahood and Halliday, 1988; Ratajeski et al., 2005]. Variable contributions from older lower crust, juvenile mafic rocks, and hydrothermal assemblages may explain slight compositional variations within productive intrusions at Questa (e.g. biotite-plagioclase porphyry –QM11-01 vs. quartz-alkali feldspar porphyry [JMR-6, QV11-02, JMR-34]). Metal endowment within the caldera margin plutons likely comes from a combination of 1) metal-rich lower crust source rocks and 2) scavenging of the hybridized lower crust by volatiles released during crystallization of underplating mafic magmas. According to this model, the halogen-rich volatilization that is typically inferred in porphyry Mo systems occurred during melting, rather than crystallization in an upper crustal magma reservoir [Hildreth, 1981; Keith et al., 1986; Carten et al., 1993; Fig. 7B]. Moreover, this model can account for the observed components of both juvenile mafic rocks and much older (> 1 Ga) lower crust components within porphyry Mo magmas inferred from radiogenic isotope studies [Farmer and DePaolo, 1984; Stein, 1985; Pettke et al., 2010].

This model implies the general possibility that porphyry Mo mineralization follows ignimbrite eruption [e.g. Lipman, 2007]. The world's largest Climax-type deposits in Colorado are located close in space and time to the Eocene-Oligocene flare-up [Chapin, 2012] and the Pine Grove deposit in Utah post-dates regional ignimbrite eruption by ~ 4 Ma [Best et al., 1989; Keith et al., 1986]. Drilling near the western rim of the ~ 1 Ma Valles caldera identified a shallow zone of molybdenum mineralization that is interpreted to be related to Climax-type mineralization at depth [Hulen et al., 1987]. Climax-type mineralization has been inferred from elevated F contents in soils along the partial-ring intrusion of the Bonanza caldera as well [Rose and Pride, 2010]. These observations argue strongly for a genetic relationship between caldera-forming eruptions and Mo mineralization wherein a major hybridization event provides unusually high masses of readily mobile metals and “prepares” the lower crust for subsequent melting events that may produce productive

magmas. Consequently, future exploration models should perhaps target caldera systems where post-ignimbrite intrusions can be identified. Additional detailed geothermochronology such as that presented here should be done to evaluate this hypothesis.

6. Conclusions

New U-Pb zircon geochronology from the Latir volcanic field shows that mineralizing magmas were emplaced along the Questa caldera margin over 770 ka. Epithermal Au-Ag mineralization near the Red River intrusive complex post-dates caldera formation by at least 300 ka. Molybdenite Re-Os ages show that the Questa porphyry Mo deposit was assembled episodically over 250 ka between ~24.76 and 24.50 Ma, and the bulk of the mineralization was synchronous with the emplacement of suite of high-silica granites.

This study demonstrates that Re-Os molybdenite geochronology can be used as a thermochronometer in cases where temperature can be determined independently. These data provide further evidence that the Re-Os chronometer remains closed to diffusion during repeated hydrothermal circulation events with temperatures in excess of ~ 400 °C. These data are used to show the complex thermal history of the incrementally assembled Questa porphyry Mo deposit.

Detailed geo-thermochronology of the Questa Mo deposit is inconsistent with previous genetic models for the system that predict magma residence time in a long-lived system or simple evolution of mineralizing intrusions via fractional crystallization. The fact that Mo mineralization post-dates the eruption of the Amalia Tuff suggests a model wherein anomalously high magma flux mobilizes metals and sulfur from the mantle and lower crust. Scavenging and partial melting of the newly formed hybridized zone is hypothesized to create the magmas responsible for mineralization. This new model suggests that immediate post-ignimbrite plutons within calderas should be considered an important target for mineral exploration.

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