Research Opportunity: S45. Applying radiogenic isotope geochemistry to enhance geologic framework models

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Research Objectives

- 1. Combine high-precision U-Pb zircon geochronology (chemical abrasion-isotope dilutionthermal ionization mass spectrometry; CA-ID-TIMS) with whole rock radiogenic isotope analyses (Sr, Nd, Pb) of the same samples to trace magma source and compositional changes in the Grizzly Peak magmatic center and White Rock pluton though time.
- 2. Contextualize the Grizzly Peak magmatic system and White Rock pluton with respect to economic and sub-economic magmatic centers in the Colorado Mineral Belt and worldwide, especially in terms of magma sources and magma fluxes.
- 3. Use new geochronologic and isotopic data to evaluate each magmatic center's relationship to important tectonic features. The age of the White Rock pluton bears on the cessation of deformation related to the Laramide Elk Range thrust; the ages and isotopic compositions of late bimodal magmatism in the Grizzly Peak caldera could establish a link to Rio Grande rift extension.
- 4. Test existing hypotheses for the Grizzly Peak caldera's relative chronology and the resurgent cauldron model using absolute timing provided by geochronology and genetic information from radiogenic isotope analyses.
- 5. Assess whether the timing and sources of mineralization-related magmatism in each center differ from main-stage magmatism. In the case of the White Rock pluton, new isotopic and geochronologic data can be used to discern whether Pb-Ag-Zn and Cu-Mo mineralization are distinct from each other in source and time.

Science Strategy

A major aim of the National Cooperative Geologic Mapping Program is to characterize mappable rock units in order to develop a geologic framework. This proposed project will acquire data critical to building out such a framework for Cenozoic magmatism in the Colorado Mineral Belt: high-precision zircon U-Pb geochronology and whole rock Sr, Nd, and Pb isotope geochemistry in two large, adjacent magmatic centers that currently lack such data. Isotope geochemical and geochronology data will allow tracking of magma sources through time within magmatic centers, and permit comparisons between them. The data will contextualize the Grizzly Peak and White Rock magmatic systems within the broader Colorado Mineral Belt, which is the locus of metal mining in Colorado yet has poorly-understood origins. High-precision geochronology will address the timing of tectonic processes in the region, including the transition from Laramide deformation to Rio Grande rifting. Analyses of mineralizing areas in each magmatic center, including some identified by USGS scientists as favorable for undiscovered porphyry Cu deposits (Ludington and Cox, 1996), will also meet U.S. Geological Survey goals to "improve scientific understanding of the origin and occurrence of [...] mineral resource deposits [and] improve the accuracy and reduce the uncertainty of resource assessments" (U.S. Geological Survey, 2007).

Motivation

Some of the chief goals of using geochronology and isotope geochemistry as tools in igneous petrology are to determine the absolute timing of magmatic processes and to track changes in compositions and sources of magmas in time and space. The absolute ages provided by geochronology can establish a chronologic framework of magma assembly from plutons to batholiths (e.g., Chen and Moore, 1982; Wenner and Coleman, 2004), and geochronologic data can elucidate the timing and scale of tectonic processes (e.g., Kylander-Clark et al., 2005; Amato et al., 2017). The combination of isotope geochemistry and geochronology permits evaluation of magma source evolution and crustal growth (e.g., Farmer and Depaolo, 1984; DeCelles et al., 2009). Recent advancements in high-precision zircon U-Pb geochronology, such as chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS; Mattinson, 2005), now allow individual grains to be dated to within $\leq 0.1\%$ of their age (Schoene, 2013). Thus, researchers have progressed from using one or two specimens to determine the history and geochemistry of a magmatic center to a half dozen or more samples (e.g., Frazer et al., 2014; Samperton et al., 2015; Gaynor et al., 2019). Likewise, improvements to instrumentation permit analyses of smaller aliquots, including whole rocks, minerals, and mineral inclusions, for their radiogenic isotopic compositions without sacrificing precision (e.g., Koornneef et al., 2015). These enhancements to geochronology and isotope geochemistry call for re-evaluation of previously studied magmatic centers and regions to better understand their origins, relationships to each other, and significance in larger tectonic frameworks.

It is through this lens that I seek to study magmatism in the Colorado Mineral Belt (CMB; Fig. 1). The CMB is one of the most important U.S. regions of concentrated precious and base metals, including deposits with Ag, Au, Cu, Mo, Pb, and Zn as primary commodities (Wilson and Sims, 2003). Recent recognition that low magmatic fluxes in long-lived magmatic centers are correlated with porphyry development underscore the importance of using geochronology to understand mineralization (Caricchi et al., 2014; Gaynor et al., 2019). However, little work has been done to investigate magma tempos and source evolution within magmatic centers of the CMB. Geochronologic data are generally limited to K-Ar, Rb-Sr, and fission track methods (Obradovich et al., 1969; Cunningham et al., 1994; Bookstrom et al., 1988). These data are imprecise and poorly suited to understanding high-temperature magmatic processes. Likewise, magma sources have been examined in broad isotopic surveys of the CMB's geographic regions and compositional suites (Simmons and Hedge, 1978; Stein, 1985; Stein and Crock, 1990), but such studies may miss variability within magmatic centers and tend to omit sub-economic magmatism. The lack of any isotopic data from many CMB rocks (Fig. 1) makes it difficult to determine whether their magmas were derived mostly from the lower crust (Stein and Crock, 1990) or the mantle (Bailley, 2010).

The west-central CMB, in the Sawatch Range and Elk Mountains (Fig. 1), presents an excellent opportunity to build out a framework of high-quality geochronology and isotope geochemistry to address outstanding questions about the origins of the CMB and variability within it. This area comprises several magmatic centers, including two that each encompass more than 200 km2: the Grizzly Peak caldera and the White Rock pluton. The Grizzly Peak magmatic center is dominated by the rhyolitic super-eruption of the Grizzly Peak Tuff, which is isotopically anomalous relative to other CMB rocks (Fig. 2, 3; Johnson and Fridrich, 1990). The caldera hosts several generations



Figure 1. Generalized geologic map of the northeastern Colorado Mineral Belt (CMB). Inset shows location of CMB (hatched area) relative to volcanic fields. Rio Grande rift sediments, and Precambrian uplifts (dashed lines). Main figure highlights locations of Cenozoic igneous rocks in the CMB. Stars mark locations of major Climax-type porphyry Mo deposits. Colors for plutonic rocks indicate their isotopic compositions: green plutons (including Climax-type Mo deposits) have crustal isotopic compositions as defined by radiogenic 87Sr/86Sri and non-radiogenic ENdi; all other analyzed plutons with either $87Sr/86Sr_i < 0.708$ or $\epsilon Nd_i > -8.0$ are pink. Plutons with no published isotopic data are gray. Note that most plutons with crustal isotopic compositions are located along the central axis of the CMB, and that there are relatively few isotopic data for rocks in the Elk Mountains. Isotopic data from Simmons and Hedge (1978), Stein and Crock (1990), Mills (2012), Frazer (2017), and Rosera (unpub.). Figure after Stein and Crock (1990) and McIntosh and Chapin (2004).

of compositionally-variable resurgent plutons, some of which are associated with low-grade Mo stockwork deposits and polymetallic sulfide veins (Fridrich et al., 1991). The White Rock pluton is located west of the Grizzly Peak caldera in the Elk Mountains. The granodioritic pluton intruded as a laccolith into Paleozoic sedimentary rocks along the Elk Range thrust fault (Fig. 2; Bryant, 1979; Tully, 2009). Sulfide mineralization occurs in both the pluton and hornfels with which it is in contact (Bryant, 1971), and the pluton has been identified as a potential target for Pb-Ag-Zn and porphyry Cu-Mo deposits (Freeman and Weisner, 1984; Ludington and Cox, 1996). There are no geochronologic data to address the magmatic lifespan of either magmatic center, and there are no isotopic data for the White Rock pluton or for pre- and post-caldera rocks of the Grizzly Peak area.

I propose to study the Grizzly Peak magmatic system and White Rock pluton using high-precision U-Pb CA-ID-TIMS geochronology and whole rock radiogenic isotope geochemistry (Sr, Nd, Pb). These data will provide critical information about the chemical isotopic evolution of each and magmatic system, placing them within the existing isotopic database of the CMB (Stein and Crock, 1990) and the Rocky Mountain region (Farmer and Depaolo, 1984). Intriguingly, these magmatic centers may be part of a subregion along the axis of the CMB that has very crust-like radiogenic isotopic compositions and has produced the

CMB's largest Climax-type porphyry Mo deposits (Fig. 1, 3). High-precision U-Pb zircon geochronology will give insight into mineralization, including the timing of intrusions spatially associated with mineralization, and whether the rates at which each magmatic center grew are comparable to productive base metal porphyry deposits worldwide (Caricchi et al., 2014). Tectonic features proximate to each magmatic center can also be evaluated with new geochronology. For



Figure 2. Generalized geologic map of the proposed study area. Locations of notable sulfide mineralization are marked by green stars; blue squares, red triangles, and white square in Grizzly Peak caldera indicate locations of samples analyzed for isotopic compositions by Frazer (2017) (Fig. 3). At Grizzly Peak, there are no age or isotopic data for the pre-caldera rhyolite (Tpc) or late generations of resurgent magmatism (Tlr; Tpr) that are associated with low-grade stockwork Mo deposits. Whereas the Grizzly Peak magmatic center cuts Proterozoic crystalline basement rocks of the Sawatch Range, the White Rock pluton was intruded in laccolith-fashion into Paleozoic sedimentary rocks of the Elk Mountains, exploiting the Elk Range thrust fault as a conduit. There are no isotopic data or modern age data for the White Rock pluton or the nearby Copper Creek sill; thus it is unclear what relation magmatic activity in the Elk Mountains may have had to the Grizzly Peak magmatic center. Figure after Tweto (1979), Fridrich et al. (1998), and Tully (2009).

example, late bimodal resurgent magmatism in the Grizzly Peak caldera could be close in age to the inception of Rio Grande Rift extension in the area (McIntosh and Chapin, 2004; Chapin and Cather, 1994; Zimmerer and McIntosh, 2012). Likewise, the White Rock pluton was intruded into the hanging plate of the Elk Range thrust, part of a deformation front between the North American craton and Colorado Plateau during the Laramide orogeny (Tully, 2009); if the pluton post-dates fault movement, the zircon crystallization age may indicate when deformation waned or ceased (Wawrzyniec et al., 2002).

Background

Grizzly Peak magmatic center

The Grizzly Peak magmatic center hosts one of the best-characterized units in the CMB due to a focus on the super-eruption of the largely rhyolitic 600 km₃ Grizzly Peak Tuff (Fridrich et al., 1991, 1998). The tuff preserves pumice fiamme of a wide variety of compositions (e.g., 57–77 wt% SiO₂; ϵ Nd_i = -13.0 to -11.3; ϵ Sr/ ϵ Sr_i = 0.7099–0.7111; Johnson and Fridrich, 1990), and is isotopically anomalous relative to most of the CMB (Fig. 3; Stein and Crock, 1990). The only CMB rocks with similarly crustal Sr and Nd isotopic compositions come from Climax-type porphyry Mo deposits and small stocks along the central axis of the CMB (Stein and Crock, 1990; Rosera, unpub. data). The Grizzly Peak caldera has a multi-stage history that may fit the classic resurgent cauldron model of Smith and Bailey (1968), comprising pre-caldera rhyolites, the Grizzly Peak Tuff, and several stages of resurgent plutons, some of which are associated with hydrothermal alteration and weak porphyry Mo mineralization (Candee, 1971; Perkins, 1973; Fridrich et al., 1991; 1998). Post-resurgent bimodal stocks and dikes cut all previous stages; some



dikes host granitic xenoliths 2-3 m in diameter initially interpreted as solidified Grizzly Peak magma (Fridrich et al., 1991; 1998).

I recently worked in the Grizzly Peak caldera to test the links between the Grizzly Peak Tuff and the Lincoln Gulch stock (Frazer, 2017). Isotopic data show the Lincoln Gulch stock, which had not been analyzed before, has crustal isotopic more compositions than the tuff (i.e., more radiogenic Sr and less radiogenic Nd; Fig. 3). The isotopic data

Figure 3. Strontium and Nd isotope data for the Grizzly Peak caldera and other Cenozoic igneous rocks in CO. Grizzly Peak Tuff and resurgent plutons of the Lincoln Gulch stock have amongst the most radiogenic Sr and least radiogenic Nd in the CMB. Climax-type porphyry Mo deposits (Climax, Mt. Emmons, Henderson) and several stocks have similar isotopic compositions. Differing isotopic data for the Grizzly Peak Tuff (red triangles) and resurgent plutons (blue squares) do not permit them to have been derived from the same upper crustal magma body (one resurgent sample with ϵ Nd_i = -14.9 plots off the chart with ϵ Sr/ ϵ Sr₁ = 0.732). Data sources given in Frazer (2017).

do not permit the tuff and early resurgent plutons to have been derived from a common magma body in the upper crust, as called for in the resurgent cauldron model (Fridrich et al., 1991). Instead, the isotopic data and high whole rock Th/U ratios suggest the tuff and resurgent plutons could have been derived by partial melting of felsic Proterozoic lower crust (Mills et al., 2018)

New zircon CA-ID-TIMS U-Pb data for the Grizzly Peak Tuff acquired at MIT yield a weighted mean age of 34.776 ± 0.031 Ma (Fig. 4; 2σ analytical uncertainty; n = 5; MSWD = 0.49). This overlaps with published sanidine 40Ar-39Ar data when they are recalculated using an updated 40K decay constant and Fish Canyon sanidine age (Kuiper et al., 2008; Renne et al., 2011; Mercer and Hodges, 2016), giving an 40Ar-39Ar age of 34.75 ± 0.12 Ma (2σ analytical uncertainty; McIntosh and Chapin, 2004). Including standard, tracer, and decay constant uncertainties does not change the relationship of the U-Pb and Ar-Ar data to each other, but does increase their uncertainties to 0.053 Ma and 0.17 Ma, respectively. Additional preliminary U-Pb zircon data from MIT extend the range of magmatism at Grizly Peak, with a ~38 Ma unfoliated granite xenolith hosted in a post-resurgent dike. Coupled with whole rock isotopic data, the granite likely represents a deep remnant of the Twin Lakes pluton exposed mostly east of the caldera (Fig. 3; Feldman, 2010; Frazer, 2017).

White Rock pluton

The White Rock pluton is exposed over an area nearly as large as the Grizzly Peak magmatic center (Fig. 2), yet comparatively little is known about its geochemistry or magmatic history. The pluton is largely biotite or hornblende granodiorite; some aplite and rhyolite porphyry dikes cut the pluton internally (Gaskill et al., 1991). Magma intrusion appears to have largely followed the Elk Range thrust fault (Bryant, 1966, 1971; Wawrzyniec et al., 2002; Tully, 2009). Because the Elk Range thrust is a bedding-plane fault, the White Rock pluton is concordant with bedding in many, but not all, places (Bryant, 1971). Numerous granodiorite dikes emanate from the pluton

into adjacent Paleozoic sedimentary rocks of the Maroon Formation, which has been metamorphosed to hornblende hornfels up to a km from the contact with the pluton (Bryant, 1969, 1971). Disseminated sulfide deposits occur in the granodiorite and its hornfels wallrock (Fig. 2), with some vein samples in the northern part of the pluton containing several thousand ppm Mo and Cu (Bryant, 1971). Productive silverbearing sulfide veins occur in calc-silicate hornfels above plutonic contacts in the southwest part of the White Rock pluton (Gaskill et al., 1991). These types of deposits associated with the pluton (Freeman and Weisner, 1984; Ludington and Cox, 1996).

Obradovich et al. (1969) reported a biotite K-Ar age of 33.9 ± 1.0 Ma for a sample from the east-central part of the White Rock pluton, which Gaskill et al. (1991) recalculated to 34.8 ± 1.0 Ma. Gaskill et al. (1991) also cite an unpublished sericite K-Ar age of 18.7 ± 0.7 Ma for a rhyolite porphyry dike that cuts the southwestern part of the pluton, and suggest that Ag mineralization is younger than the dated dike. Although there are no



Figure 4. Modern geochronologic data for the Grizzly Peak Tuff. Sanidine 40Ar-39Ar weighted mean age of McIntosh and Chapin (2004) recalculated as described in text. Zircon U-Pb CA-ID-TIMS data are corrected for initial 230Th disequilibrium and show individual grain analyses in addition to weighted mean age and uncertainties. Total uncertainties include analytical, standard (40Ar-39Ar), tracer (U-Pb), and decay constant uncertainties.

modern data for the White Rock pluton, the Snowmass pluton, which intruded the Elk Range thrust approximately 15 km northwest of the White Rock pluton (Allen, 1968), has been dated more recently. Garcia (2011) reported a biotite 40Ar-39Ar age of 34.14 ± 0.12 Ma (recalculated using same procedures as detailed for Grizzly Peak 40Ar-39Ar data). Zircon U-Pb data acquired by laser ablation-inductively coupled plasma-mass spectrometry on the same sample yield an age of 33.78 + 0.82/-0.80 Ma, which I re-interpret as 34.41 ± 0.57 Ma (Garcia, 2011). However, the hypothesized links between the Snowmass pluton and White Rock pluton have not been tested geochemically or with modern geochronology.

Proposed Research and Methods

To meet my proposed research objectives, I will collect igneous rock samples from in and around the Grizzly Peak magmatic center and White Rock pluton that capture the spatial, temporal, and compositional breadth of magmatism associated with each center. New U-Pb geochronology data for each magmatic center will measure the lifespan of magmatism exposed and allow calculation of magma accumulation rates, which are particularly important because porphyry Mo and Cu deposits are favored by slower, long-lived intrusive centers (Caricchi et al., 2014). New Sr, Nd, and Pb whole rock isotopic data for the same dated samples will allow me to: 1) track magma source changes with time; 2) assess whether the Grizzly Peak and White Rock magmatic centers share similar sources due to their proximity to each other; 3) evaluate the significance, if any, of the crustal isotopic compositions for rocks in the axial part of the CMB, and whether the White Rock pluton is part of that trend (Fig. 1). I will also use the new geochronologic and isotopic data to test existing hypotheses for the resurgent cauldron cycle at Grizzly Peak (Fridrich et al., 1991).

The new data will also establish the relationship of each magmatic center to important regional events and features in central Colorado: 1) the White Rock pluton exploited the Elk Range thrust during its intrusion, and therefore the pluton's age marks either the waning stages of deformation or postdates deformation (Wawrzyniec et al., 2002); 2) does the bimodal magmatism at Grizzly Peak have a temporal or chemical link to Rio Grande rift extension? New Sr, Nd, and Pb isotopic data will be combined with other recent data in the central CMB (Feldman, 2010; Mills, 2012; Frazer, 2017) to track spatio-temporal magma source variations from ca. 63 Ma through at least 30 Ma in several magmatic centers (Mount Princeton, Twin Lakes, Grizzly Peak, White Rock).

The Grizzly Peak and White Rock field areas are mostly only accessible by 4×4 high-clearance U.S. Forest Service roads, and will only accessible in the summer months due to high elevation. Because this fellowship will likely begin in the winter or spring, I have established a potential collaboration that will allow me to begin immediately working on samples. Dr. Lon Abbott, a University of Colorado researcher who has advised several undergraduate projects in the Elk and West Elk Mountains, has generously agreed to give me access to a vertical transect of samples collected from the southwest White Rock pluton by Mccorkel (2017) for (U-Th)/He analyses. He is also currently working with students on a second vertical transect on the east side of the pluton. These previously-collected samples span the vertical relief of the White Rock pluton and much of its horizontal extent, which are critical to my goal of capturing the maximum temporal and geochemical variability in the pluton. I also have numerous samples of Grizzly Peak Tuff and Lincoln Gulch stock already characterized for whole rock geochemistry that I can begin dating by zircon U-Pb CA-ID-TIMS. These samples will approximate the total time of the tuff's magma assembly and determine how soon resurgent magmatism began after eruption of the tuff.

When snowmelt and weather permit, I will carry out a field campaign in the Grizzly Peak caldera and White Rock pluton, spending approximately 1 week in the field each summer of the fellowship. I will also seek to work with as many collaborators in the field as possible; I have discussed working with Lon Abbott and his students while they collect low-temperature thermochronology samples, and broadly I would welcome the expertise of anyone willing to join me. At Grizzly Peak, I will focus my efforts on collecting pre- and post-caldera rocks that have not been dated or analyzed for their isotope geochemistry before. These samples will be important for spanning the history of the Grizzly Peak system. This includes a pre-caldera rhyolite that is not linked to mineralization, and late-resurgent and post-resurgent stocks and dikes that are spatially associated with alteration and mineralization (Candee, 1971; Cruson, 1973; Holtzclaw, 1973; Perkins, 1973). I also plan to sample mapped ring dikes and intrusions along the eastern margin of the caldera that are associated with stockwork Mo mineralization (Fridrich et al., 1991). For the White Rock pluton, I will collect samples that span the vertical relief and horizontal extent of the intrusion, supplementing the samples of McCorkel (2017). I will also collect aplite and rhyolite porphyry dikes that cut the pluton, rocks associated with mineralization, and extracaldera granodiorite dikes and the Copper Creek sill, which may be part of the same magmatic event (Fig. 2; McCorkel, 2017).

Scientific Facilities

I will carry out this project using the facilities and equipment in the Geosciences and Environmental Change Science Center in Lakewood, CO. I will use standard rock crushing equipment to produce whole rock powders. An aliquot of whole rock powder will be submitted to GGG Analytical Services for measurements of elemental concentrations (major, trace, and rare earth elements). To isolate zircon, I will use density and magnetic separation methods, including methylene iodide and a Frantz magnetic separator, and existing petrographic microscopes to pick grains. Zircons will be placed in quartz crucibles that I will purchase, and then in an existing box furnace for thermal annealing. The remainder of sample preparation will occur in the Geology, Geophysics, and Geochemistry Science Center's modern clean room facilities, using laminar flow hoods, in-house distilled reagents with sub-picogram blanks (A.K. Souders, pers. comm.), ion exchange column chromatography stations, and Class-10 hot plate enclosures. Whole rock Sr, Nd, and Pb isotope geochemistry procedures are already established in the laboratory (e.g., Cosca et al., 2014), and they are similar to those I have used before (Frazer, 2017). However, unlike the basalts of Cosca et al. (2014), my samples will be much more felsic and contain refractory minerals (e.g., zircon), requiring dissolution in acid digestion vessels that I will purchase.

Zircon U-Pb analyses will require implementation of a new accessory mineral U-Pb ID-TIMS pipeline. I will purchase new acid digestion vessels for zircon chemical abrasion and dissolution. I will also build new ion exchange 50 μ L microcolumns for Pb and U separation using existing PTFE heat shrink tubing. Zircon isotopic analyses will be performed on the Isotopx Phoenix thermal ionization mass spectrometer. The motorized Faraday collectors are equipped with 1011 Ω resistors that will be used for static measurement of U isotopes; lead isotopes will be measured by peak-hopping with the Daly ion counting system (e.g., Frazer, 2017). Samples will be loaded on filaments strung with zone-refined Re ribbon (99.999% purity). I would also like to emphasize that the supportive and collaborative nature of the U-Pb ID-TIMS community means that, in addition to the Isotopx service contract, I will be able to get assistance in the form of ideas, experience, and supplies from labs I have worked in (UNC–Chapel Hill, MIT) and those of my colleagues at Princeton, Rochester, Purdue, Boise State, and Geneva. The helpful nature of the U-Pb ID-TIMS community has helped me since I began graduate school, and I plan to continue that tradition at the USGS.

Future Work

This proposed project sets the stage for examining the many under-studied magmatic centers nearby in the Sawatch Range, Elk Mountains, and West Elk Mountains, and building a robust geochronologic and geochemical framework that will contribute to understanding the origins of the CMB. The plutons and sills of the West Elk Mountains, including the Mount Emmons-Redwell Basin Climax-type porphyry Mo deposit, are enticing to study because of their excellent exposures and accessibility; the imminent return of mining claims from Freeport-McMoRan to the U.S. Forest Service should make sample collection simpler. In addition, my collaborators at UNC–Chapel Hill have at least one core sample from within the Mo deposit at Mount Emmons, providing the opportunity to accurately assess the timing and source of porphyry Mo magmatism in the southwest CMB. The detailed characterization of the magmatic histories at Grizzly Peak and White Rock will also support future work on the mineralization in each center, such as the application of zircon relative redox state measurements by TIMS-TEA to understand the approximate oxidation state of Mo-mineralizing magmas.