Supplementary Material for:

FLUORINE-RICH MAFIC LOWER CRUST IN THE SOUTHERN ROCKY MOUNTAINS: THE ROLE OF PRE-ENRICHMENT IN GENERATING FLUORINE-RICH SILICIC MAGMAS AND PORPHYRY MO DEPOSIT

Joshua M. Rosera[1,2], Ryan E. Frazer[3,2], Ryan D. Mills[2], Kristin Jacob[4], Sean P. Gaynor[5,2], Drew S. Coleman[2], and G. Lang Farmer[4]

[1]U.S. Geological Survey, Geology, Energy, and Minerals Science Center, Reston, VA, USA

[2]Department of Geological Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC, USA

[3]U.S. Geological Survey, Geosciences and Environmental Change Science Center, Denver, CO, USA

[4]Department of Geological Sciences, University of Colorado, Boulder, CO, USA

[5]Department of Earth Sciences, University of Geneva, Geneva, Switzerland

SUPPLEMENTARY MATERIAL CONTENTS

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SUPPLEMENTARY TEXT S1: WHOLE ROCK SAMPLES USED IN THIS STUDY

This following overview of whole rock samples used in this study is organized based on the tectono-magmatic suites introduced in the main text.

Laramide compressional suite

We analyzed 24 whole rock samples of igneous rocks that intruded the Colorado Mineral Belt between approximately 66 to 38.7 Ma (Table S3). The samples come from three intrusive centers, from southwest to the northeast, these include: the Twin Lakes pluton; Breckenridge, Alma, and Leadville mining districts; and the Montezuma mining district (Fig. 1, main text).

The Twin Lakes pluton (66 to 57 Ma and 43 to 40 Ma; Feldman, 2010) is an equigranular to porphyritic granodiorite with alkali feldspar megacrysts up to 15 cm long. The main body grades into leucocratic and mafic compositions in the southwestern portion of the pluton. The pluton is cut by numerous aplite dikes and also contains modally layered zones that were interpreted to have resulted from shear segregation processes (Fridrich et al., 1998). The southwestern portion of the pluton is cut by the 35 Ma Grizzly Peak caldera, and Twin Lakes intrusions were incorporated into a megabreccia within the caldera (Fridrich et al., 1998). We collected multiple samples of the main pluton, as well as two aplite samples, a modally layered sample, and two samples from the megabreccia in the Grizzly Peak caldera.

Shallow intrusions ranging in age from approximately 66 to 39.7 Ma occur throughout the Breckenridge, Alma, and Leadville mining districts (Fig. 1a; Bookstrom, 1990; Rosera et al., 2021). A quartz monzonite porphyry with 2-3 cm alkali feldspar megacrysts from the Leadville area (LV17-17). Fine-grained granodiorite porphyry samples near the Leadville district were also collected, including one that was a xenolith entrained in the 26.3 Ma Chalk Mountain rhyolite (Fig. 1a; Rosera et al., 2021). One of these samples (NC16-02) was previously dated with U-Pb zircon geochronology and yielded a crystallization age of 43.5 Ma (Rosera et al., 2021). Samples collected from the historic Alma mining district include: 1) a granodiorite (to dacite) porphyry a fine-grained groundmass and plagioclase, amphibole, biotite, and sparse quartz phenocrysts; 2) a latite porphyry with a fine grained, dark ground mass and plagioclase phenocrysts was also collected nearby; and 3) two samples of light gray rhyolite dikes that contain sparse quartz phenocrysts (39.7 Ma; Rosera et al., 2021). Two samples of the Swan Mountain sill complex near Breckenridge were also collected (Fig. 1a). These two samples are quartz monzonite porphyries that have a fine-grained groundmass and abundant quartz, plagioclase, alkali feldspar, biotite, and amphibole phenocrysts.

Six whole rock samples from the historical Montezuma mining district were collected. The largest feature of the mining district is the 38.8 Ma Montezuma pluton (Rosera et al., 2021), which is broadly transitional from inequigranular quartz monzonite in the west to porphyritic quartz monzonite with distinct 1 to 2 cm K-feldspar phenocrysts in the east. The pluton is cut by numerous aplite and trachyandesite dikes. The trachyandesite dikes have a dark gray to green, fine-grained groundmass with plagioclase, biotite, and clinopyroxene phenocrysts. The south and eastern part of the pluton intrude along a Proterozoic shear zone. Numerous small volcanic plugs and breccia occur within the shear zone. We also collected a sample of the 38.8 Ma Webster Pass porphyry (Rosera et al., 2021), which is a fine-grained porphyry with abundant (>25 modal%) phenocrysts, including white plagioclase and anhedral (and fragmented) quartz phenocrysts, and is slightly altered by sericite and pyrite throughout the outcrop.

Transitional suite

Twenty-two igneous whole rock samples from the post-Laramide transitional suite (approximately 38.7 Ma to 31 Ma) were selected for analysis. All of the samples are from the Sawatch range in the central Colorado Mineral Belt, except for two regional ignimbrite samples (Badger Creek and Wall Mountain tuff) that were collected on the east side of Arkansas Valley (Fig. 1c). Six samples from the Mount Princeton – Mount Aetna igneous complex were collected, ranging from quartz monzonites of the Mount Princeton batholith (35.8 to 35.4 Ma) to porphyritic quartz monzonite from Mount Aetna caldera complex (35.0 to 34.6 Ma; Table S3; Mills and Coleman, 2013).

Eleven samples from the 35 Ma Grizzly Peak caldera complex were also collected, including three samples of the Grizzly Peak Tuff. Several plutons are interpreted as resurgent into the caldera. The largest plutons in the northern part of the caldera are generally zoned from felsic granodiorite near their margins to mafic granodiorite at their cores (Fridrich et al., 1998). Seven samples of resurgent plutons were analyzed in this study, including one mafic enclave (GP-08) from one of the oldest resurgent plutons. Preliminary U-Pb zircon geochronology indicates that the resurgent plutons were emplaced approximately 500 ka after formation of the Grizzly Peak caldera (Frazer, 2017). We also sampled a pink, medium-grained granite xenolith that was entrained in a post-caldera dike. U-Pb zircon analyses from this sample yielded an age of approximately 38 Ma (Frazer, 2017).

Three silicic porphyries related to magmatic-hydrothermal alteration and/or mineralization along the Sawatch Range were also selected for whole rock analysis. These include samples related to Mo-F porphyry prospects at Middle Mountain (36.4 Ma) and Turquoise Lake (35.8 Ma; Rosera et al., 2021). Both of these samples have fine-grained groundmasses and contain mainly quartz, feldspar, and trace biotite phenocrysts, and both are associated with quartz-sericite-pyrite alteration. Sample TL18-01 was collected from a north-south trending, 34.0 Ma granodiorite dike with abundant feldspar phenocrysts, some of which are megacrystic (up to 5 cm long), as well as fragmented smokey quartz phenocrysts. This dike is located east of the Middle Mountain Mo prospect, and associated with sericite-pyrite (now mostly Fe-oxides) alteration.

Extensional suite

A total of 10 whole rock samples related to 31 to 24 Ma Rio Grande Rift extension were analyzed. Three samples of the Mount Antero leucogranite were analyzed (31.3 to 30.3 Ma, Zimmerer and McIntosh, 2012; Table S3). We also analyzed the 26.3 Ma Chalk Mountain topaz rhyolite, which is a porphyritic rock with smokey quartz, feldspar, and biotite phenocrysts (Audétat, 2015; Rosera et al., 2021). The Chalk Mountain rhyolite is an eruptive equivalent to mineralizing intrusions from the nearby

Climax Mo porphyry deposit (Bookstrom et al., 1987).Pumice from a red-weathered basaltic-andesite flow preserved along the west side of Arkansas Valley was also collected (24 Ma; Table S3).

Five new whole rock samples from the Never Summer batholith were selected for whole rock analyses. These include two silicic dikes from the northern end of the batholith. These dikes yielded a U-Pb zircon age of 29.2 Ma (Rosera et al., 2021) and intruded before the Mount Richthofen granodiorite (approximately 29.0 to 28.7 Ma). The dikes have a fine-grained groundmass, and phenocrysts of quartz, K-feldspar, and plagioclase. Biotite and amphibole phenocrysts are largely altered to chlorite. A third silicic dike was collected in the historical Teller mining district along Jack Creek, west of the Never Summer mountains (Fig. 1). This dike has not been dated and has coarse phenocrysts of quartz and K-feldspar. The feldspars are variably altered in this sample; plagioclase is replaced by white to greenish clays, and cores of alkali feldspar phenocrysts are altered to Fe-oxides. Although altered, we included this sample in our dataset given the scarcity of data from the Teller district. Two new samples of the 28.2 Ma Mount Cumulus pluton were analyzed in this study, including one samples collected from the western phase of the pluton (NS17-05; Fig. S2), and another from the center of the pluton.

SUPPLEMENTARY TEXT S2: ANALYTICAL METHODS

Electron microprobe analyses

Electron microprobe analyses were performed on the JEOL JXA-8600 located at the University of Colorado Boulder. All wavelength dispersion analyses were performed with an accelerating voltage of 15 kV, a beam current of 10 nA, and 2 μm spot size. The analysis measured Cl and F first in the sequence and intensities were corrected for time-dependent intensity. The 99% confidence of Cl and F were ~ 0.012 and 0.14 wt.%, respectively. The molar proportions of ferric and ferrous iron in amphibole were estimated after the methodology of Locock (2014; 13- and 15-cation schemes).

Whole-rock geochemistry

Whole-rock samples were initially broken in the field prior to being brought to the lab and passed through a jaw crusher. Samples were then pulverized to fine powder with an alumina-ceramic SPEX 8530 shatterbox and sent to Actlabs (Ontario, Canada) for major and trace element analysis. Samples were dissolved by fusion in a lithium metaborate/tetraborate mixture; major elements and Ba, Sr, Y, Zr, Sc, Be, and V were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES), with remaining trace elements and REE analyzed by ICP-MS. Uncertainties are dependent on the abundances of the oxides and elements analyzed and for these samples are approximately: major elements uncertainties are less than 2% (±2σ relative) for all oxides except MgO (3%), MnO (5%), and P_2O_5 (16%). Trace elements analyzed at Actlabs that are reproducible (±2σ relative) at better than 2 ppm include Ag, Be, Cs, Ge, Hf, Sb, Sn, Ta, Th, Tl, U, and W. Other elements are reproducible within 3 ppm (Co, Mo, Nb, Sc), 4 ppm (Ga, Y) and others have higher uncertainties (Pb, Cu, Rb, Zr, V, Ni, Sr, and Ba between 9 to 30 ppm; Ba, Zn, and Cr between 31 to 49 ppm). Rare earth elements reproducibility (±2σ absolute) is generally < 0.2 ppm for Eu, Ho, Lu, Tb, and Tm; REE reproducibility for La, Ce, Pr Nd, Sm, Gd, Dy, Er, and Yb are generally between 0.2 to 2 ppm.

Isotopic analyses used aliquots of whole-rock powder that were dissolved in high-pressure Teflon (Parr) vessels with $HF+HNO_3$ at 180°C for 72 – 120 hours. The solution was then dried down and fluxed in 6M HCl for 2 hours at 180°C on a hot plate and subsequently aliquoted for Sr, Pb, and Nd separation. Lead was purified by double-passing aliquots through anion exchange column chemistry following an HBr-based technique modified after Parrish and Krogh (1987). Purified Pb was loaded onto Re filaments with Si gel and analyzed as a metal in static multi-collector mode on either the VG Sector 54 or Phoenix thermal ionization mass spectrometer (TIMS) at the University of North Carolina at Chapel Hill. Lead analyses were corrected for mass fractionation based on replicate analysis of 20 ng loads of NBS-981 standard (see Table S5 for Pb mass fractionation values). Strontium was isolated using Sr-spec cation exchange resin following the method of (Lundblad 1994). Samples were dried down on single Re filaments with a TaF_5 activator and analyzed on the VG Sector 54 TIMS at the University of North Carolina at Chapel Hill. Strontium analyses used a dynamic multicollector method and mass fractionation was corrected by using an exponential law and normalization to $^{86}Sr/^{84}Sr$ = 0.1194. Measured $^{87}Sr/^{86}Sr$ were normalized again based on replicate analyses of Sr standard NBS-987 (normalized to $^{87}Sr/^{86}Sr_{NBS-987}$ = 0.710150). Replicate analyses of NBS-987 from 2018 to 2020 yielded $^{87}Sr/^{86}Sr$ = 0.710260 ± 0.000024 (2σ, n = 128) and are representative of values and uncertainties used to correct older data (Mills 2012; Frazer 2017). Neodymium aliquots were separated by a three-stage column method modified after either Pin and Zalduegui (1997) or Harvey and Baxter (2009). Neodymium was analyzed in dynamic multicollector mode on either the VG Sector 54 or Phoenix TIMS at the University of North Carolina at Chapel Hill. All Nd analyses were corrected to $^{146}Nd/^{144}Nd = 0.7219$ and normalized against Nd standard JNdi ($^{143}Nd/^{144}Nd_{JNdi} = 0.512115$). Replicate analysis of JNdi standard from 2019 to 2020 yielded $^{143}Nd/^{144}Nd = 0.512111 \pm 0.000016$ (2σ, n = 12) and are representative of values and uncertainties used to correct older data (Mills 2012; Frazer 2017). All isotopic data were corrected to initial values using ages listed in Table S3. Neodymium is presented in ε units relative to CHUR ($^{143}Nd/^{144}Nd_{present} = 0.512638$; $^{147}Sm/^{144}Nd = 0.1967$).

SUPPLEMENTAL FIGURE CAPTIONS

Figure S1. Photomicrographs of garnet-free mafic granulite samples used in this study. All panels are in cross-polarized light. **(a)** SD2-LC76 **(b)** NX4-LC2 **(c)** SD2-LC38. Note plagioclase altered to sericite in this sample. **(d)** SD2-LC78**.** amph – amphibole, cpx – clinopyroxene, opx – orthopyroxene, pl – plagioclase.

Figure S2. Photomicrographs from the Mount Cumulus leucogranite **(a)** Sample 10-KJ-MC-91 (central portion of the pluton) in cross-polarized light **(b)** Sample NS17-05 (western portion of pluton) in cross-polarized light. **(c)** Backscattered electron image from 10-KJ-MC-91 showing biotite associated with fluorite and zircon **(d)** Backscattered electron image from sample NS17-05 showing Fe-Ti oxide cluster rimmed by quartz and biotite. bt – biotite, fl – fluorite, mag – magnetite, qtz – quartz, rt – rutile, zrc – zircon.

Figure S3. Fluorine concentration versus modal abundance of amphibole in State Line granulite xenolith samples. Modal abundance data from Bradley (1985) and this study (SD2-LC76 only).