

Open-File Report 26-08

Geochemical and Petrogenetic Characteristics of REE-Bearing Carbonatites, Pegmatites and Syenites from the Wet Mountains, South-Central Colorado

By

Mario A. Guzman

Colorado Geological Survey
Colorado School of Mines
Golden, Colorado
2026



COLORADO GEOLOGICAL SURVEY
COLORADO SCHOOL OF MINES

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List of Acronyms

Al ₂ O ₃	Aluminum oxide
Ba	Barium
CaO	Calcium oxide
Cc	Calciocarbonatite
CCMF	molar ratio of CaO/(CaO+MgO+FeO+MnO)
Ce	Cerium
CGS	Colorado Geological Survey
cm	Centimeters
Cr	Chromium
Cs	Cesium
Dy	Dysprosium
EarthMRI	USGS Earth Mapping Resources Initiative
Er	Erbium
Eu	Europium
Fc	Ferrocarnatite
Fcc	Ferruginous carbonatite
FeO	Iron (II) oxide
Fe ₂ O ₃	Iron (III) oxide
g	Grams
Ga	Billion years (giga-annum)
Gd	Gadolinium

HFSE	High-field strength elements
HNO ₃	Nitric acid
Ho	Holmium
HREE	Heavy rare earth elements
ICP	Inductively coupled plasma
K ₂ O	Potassium oxide
km	Kilometers
La	Lanthanum
LILE	Large-ion lithophile elements
LOI	Loss-on-ignition
LREE	Light rare earth elements
Lu	Lutetium
m	Meter
Ma	Million years
Mc	Magnesiocarbonatite
MgO	Magnesium oxide
Mn	Manganese
MnO	Manganese oxide
MS	Mass spectrometry
Na ₂ O	Sodium oxide
Nb	Niobium
Ni	Nickel
Nd	Neodymium
OES	Optical emission spectrometry
ORG	Ocean Ridge Granites
P ₂ O ₅	Phosphorus (V) oxide
Pb	Lead
Pct	Percent
Pm	Promethium
ppm	Parts per million
Pr	Praseodymium
QA/QC	Quality Assurance (QA) and Quality Control (QC)
Rb	Rubidium
REEs	Rare earth elements
Sc	Scandium
SiO ₂	Silicon dioxide
Sm	Samarium
Sr	Strontium
⁸⁷ Sr/ ⁸⁶ Sr	Strontium Isotope Analysis
Syn-COLG	Syn-collisional Granites
Ta	Tantalum
TAS	Total Alkali-Silica
Tb	Terbium
Th	Thorium

Ti	Titanium
TiO ₂	Titanium dioxide
Tm	Thulium
TREE	Total REEs (all the REEs)
U	Uranium
U-Pb	Uranium—lead dating
USGS	U.S. Geological Survey
V	Vanadium
VAG	Volcanic Arc Granites
WDXRF	Wavelength-dispersive X-ray fluorescence
WPG	Within-Plate Granites
wt. %	Weight Percent
Y	Yttrium
Yb	Ytterbium
Zn	Zinc
Zr	Zirconium

Acknowledgments and Notes

This project was funded by the Colorado Geological Survey (CGS), with partial support from the Severance Tax Operational Fund, which is funded through taxes on the production or extraction of metallic minerals, molybdenum, oil and gas, oil shale, and coal, and by the United States Geological Survey (USGS) through Earth MRI grant G20AC00161. Sample analyses were conducted by AGAT Laboratories, Canada, contracted by the USGS. The CGS would like to thank Jay Temple and Peter Barkmann (CGS) for sample collection and Mike O’Keeffe (CGS), Dr. Cody Steven, and Matt Morgan (CGS) for reviewing the report.

Disclaimer

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Abstract

The Colorado Geological Survey (CGS) conducted geologic mapping and geochemical sampling in the Wet Mountains area, a region known for rare earth element (REE) and Th mineralization, to better characterize these deposits and to confirm the occurrence and concentrations of REE and other critical elements at the surface.

Carbonatites are the primary REE host rocks and are characterized by elevated light REEs (LREE: La, Ce, Pr, Nd, Sm, Eu, and Gd), although significant heavy REE (HREE: Tb, Dy, Ho, Er, Tm, Yb, Lu, plus Y) enrichment is also present in some samples. These carbonatites commonly contain high concentrations of Th, Mn, Zr, and Ba. Selected mafic and felsic plutonic rocks and pegmatites within the study area also contain elevated REE concentrations, particularly HREE-rich patterns. These plutonic rocks are characterized by high Mn, Ba, and Th, along with anomalous Cr, Ni, Pb, and Zn.

The new geologic and geochemical dataset supports interpretations derived from the recent U.S. Geological Survey (USGS) airborne magnetic and radiometric survey over the Wet Mountains and constrains the nature of surface and potential subsurface REE-bearing anomalies. A subset of three carbonatite samples contains “ore-grade” LREE concentrations comparable to those in major REE carbonatite deposits such as Elk Creek, Bear Lodge, and Mountain Pass. In addition, some carbonatites and REE-bearing syenites and pegmatites have REE distributions broadly similar to the HREE-enriched Round Top rhyolite deposit in Texas, suggesting multiple mineralization styles and exploration targets within the district.

1. Introduction

The Wet Mountains in south-central Colorado form a northwest-trending exposure of Proterozoic crystalline rocks. The northern half of the range is well known for Th and REE mineralization associated with Ediacaran to Ordovician alkaline intrusions. Three exposed Ediacaran–Cambrian alkaline complexes are recognized: McClure Mountain, Gem Park, and Democrat Creek (Figure 1). These complexes are sequentially cross-cut by Cambrian–Ordovician lamprophyre,

syenite, and carbonatite dikes, as well as mineralized quartz–barite–thorite veins (Armbrustmacher, 1988). Syenite dikes are commonly hydrothermally altered and are interpreted to be temporally associated with the mineralized vein systems (Armbrustmacher, 1988). REE mineralization occurs primarily in carbonatite dikes, quartz–barite–thorite veins, and hydrothermally altered red syenite dikes, in descending order of REE grade (Armbrustmacher, 1988).

Low whole-rock initial $^{87}\text{Sr}/^{86}\text{Sr}$ and trace element systematics suggest the carbonatites are mantle-derived (Armbrustmacher & Hedge, 1982). In context of the established regional geologic setting, Ediacaran-Ordovician magmatism has been attributed to failed intracontinental rifting (Larson et al., 1985; McMillan & McLemore, 2004; Olson et al., 1977). The main alkaline intrusions and associated syenite and lamprophyre dikes yield ages of ca. 551–483 Ma. Geochemical and isotopic studies have been carried out on selected rocks and minerals in the Wet Mountains (Shawe & Parker, 1967; Parker & Sharp, 1970; Armbrustmacher et al., 1979; Armbrustmacher & Hedge, 1982), but with the exception of these focused investigations, the petrogenesis of the Proterozoic granites and associated alkaline complexes have not been systematically evaluated.

The primary objective of this report is to integrate new whole-rock geochemical data collected by the CGS with existing geochronologic constraints to develop an updated petrogenetic framework for magmatic rocks of the Wet Mountains and to assess the distribution and style of REE-bearing carbonatites, pegmatites, and syenites.

2. Geologic Setting

During the Proterozoic, multiple juvenile terranes accreted to the southern margin of the Archean Wyoming Province as part of protracted Laurentian crustal growth (Reed et al., 1993; Whitmeyer & Karlstrom, 2007). The Yavapai Province, composed predominantly of juvenile arc terranes (Bennett & DePaolo, 1987), accreted to Laurentia at 1.78–1.70 Ga along a belt extending from Colorado into Arizona and New Mexico (Jones et al., 2010). The Mazatzal Province, also consisting

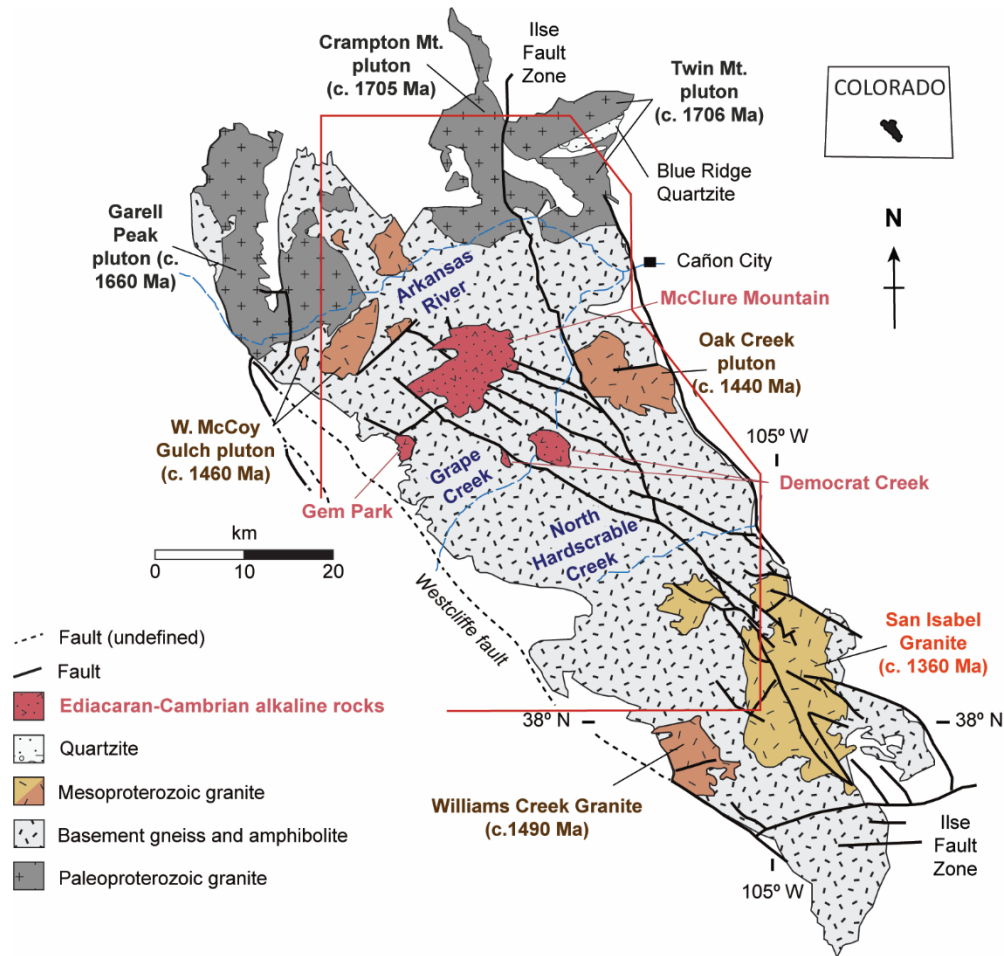


Figure 1: Generalized geologic map of the Wet Mountains area with the major Proterozoic lithostratigraphic units and Ediacaran-Cambrian alkaline rocks. Recent U.S. Geological Survey EarthMRI airborne geophysical survey area outlined by red polygon. Figure modified from Jones et al. (2010) and Palin et al. (2023).

of juvenile arc crust, accreted at 1.66–1.60 Ga along the southern margin of the Yavapai Province (Amato et al., 2008; Bennett & DePaolo, 1987). The Wet Mountains lie within the Yavapai Province and contain a diverse suite of metamorphic and igneous rocks that were deformed and metamorphosed during Mazatzal-age orogenesis.

Regional aeromagnetic data define numerous southwest–northeast-trending lineaments in the subsurface that are consistent with Yavapai–Mazatzal-related structures mapped elsewhere in Colorado (Oshetski & Kucks, 2000). Strong positive gravity anomalies across the Wet Mountains range suggest the presence of voluminous plutonic bodies at shallow crustal levels (Pardo et al., 2008), implying

that Proterozoic magmatism was more extensive than indicated by current surface exposure.

2.1 Early and Middle Proterozoic Metamorphic and Granitic Rocks

Metamorphic grade across the Proterozoic basement increases from northwest to southeast. In the northern Wet Mountains, weakly foliated Paleoproterozoic plutons with gradational contacts into felsic schist and gneiss are exposed (Siddoway et al., 2000). These include the ~1.71 Ga Twin Mountain and Crampton Mountain granites and the ~1.66 Ga Garell Peak granodiorite (Figure 1). Younger Mesoproterozoic granitoids, such as the ~1.46 Ga West McCoy Gulch pluton, exhibit sharper intrusive contacts and limited deformation (Jones et al., 2010).

The central Wet Mountains, between the Arkansas River and North Hardscrabble Creek, are dominated by mid-crustal quartzofeldspathic gneiss (Figure 1). This region also hosts the Oak Creek and West McCoy Gulch two-mica monzogranite plutons, emplaced at ~1.44 Ga (U–Pb zircon; Bickford et al., 1989).

The southern Wet Mountains are lithologically more complex. Siddoway et al. (2000) recognized multiple suites of Mesoproterozoic granitoids, including sheet-like networks of sills and dikes and larger plutons in the southeast part of the range (Figure 1). One of these, the San Isabel intrusion, is a largely undeformed hornblende–biotite monzogranite that crystallized at ~1.36 Ga (Bickford et al., 1989; Cullers et al., 1992). Geochemically, the San Isabel intrusion has an A-type affinity, with a weak Eu anomaly suggesting partial melting of a relatively mafic source (Cullers et al., 1992). It is younger than other Wet Mountains granitoids, including the Williams Creek Granite immediately to the southwest. The Williams Creek Granite is a coarse-grained porphyritic granite with a U–Pb zircon age of ~1.49 Ga (Bickford et al., 1989), overlapping temporally with the Oak Creek and West McCoy Gulch plutons. These intrusions collectively range from syenogranite to granodiorite in composition (Noblett et al., 1987).

2.2 Ediacaran-Ordovician Alkaline Intrusive Complexes

Ediacaran–Ordovician rocks in the Wet Mountains comprise alkaline intrusive complexes, associated dike swarms, and mineralized veins related to a protracted magmatic episode from ca. 551 to 483 Ma (Armbrustmacher, 1988; Olson et al.,

1977; Pivarunas & Meert, 2019). These intrusions are interpreted as partial melts of an enriched mantle source emplaced during regional intracontinental rifting (Larson et al., 1985; McMillan & McLemore, 2004). This magmatic event is closely associated with REE- and Th-rich mineralization of potential economic significance in this area.

The McClure Mountain, Gem Park, and Democrat Creek complexes are composite intrusions consisting largely of mafic–ultramafic cumulates, nepheline syenite, syenite, and quartz syenite (Figure 1; Armbrustmacher, 1988; Christman et al., 1959; Shawe & Parker, 1967). Gem Park includes pyroxenite and gabbro cumulates (Armbrustmacher, 1984; Parker & Sharp, 1970). McClure Mountain can be divided into older mafic–ultramafic cumulates at Iron Mountain to the east and a younger felsic alkaline complex to the west. Democrat Creek is dominated by quartz syenite with local tholeiitic mafic–ultramafic bodies on its margins (Armbrustmacher, 1984; Hanson et al., 2013; Olson et al., 1977).

These complexes are cut by younger Cambrian–Ordovician(?) quartz–barite–thorite veins and swarms of lamprophyre, red syenite, and carbonatite dikes that locally host REE and Th mineralization (Armbrustmacher, 1988; Christman et al., 1954, 1959). Fenite, produced by alkali metasomatism, occurs in rocks adjacent to the alkaline complexes and along carbonatite dikes and quartz–barite–thorite veins, manifesting as K-feldspar– and Fe-rich alteration in felsic rocks and vermiculite replacement in mafic rocks (Armbrustmacher, 1984). Veins are concentrated along fracture zones up to 30 kilometers (km) from the main intrusions (Armbrustmacher, 1988; Christman et al., 1954, 1959; Olson et al., 1977). The mineralized veins and dikes are predominantly northwest-striking, controlled by faults interpreted to be Neoproterozoic or early Paleozoic in age (Christman et al., 1954; Olson et al., 1977).

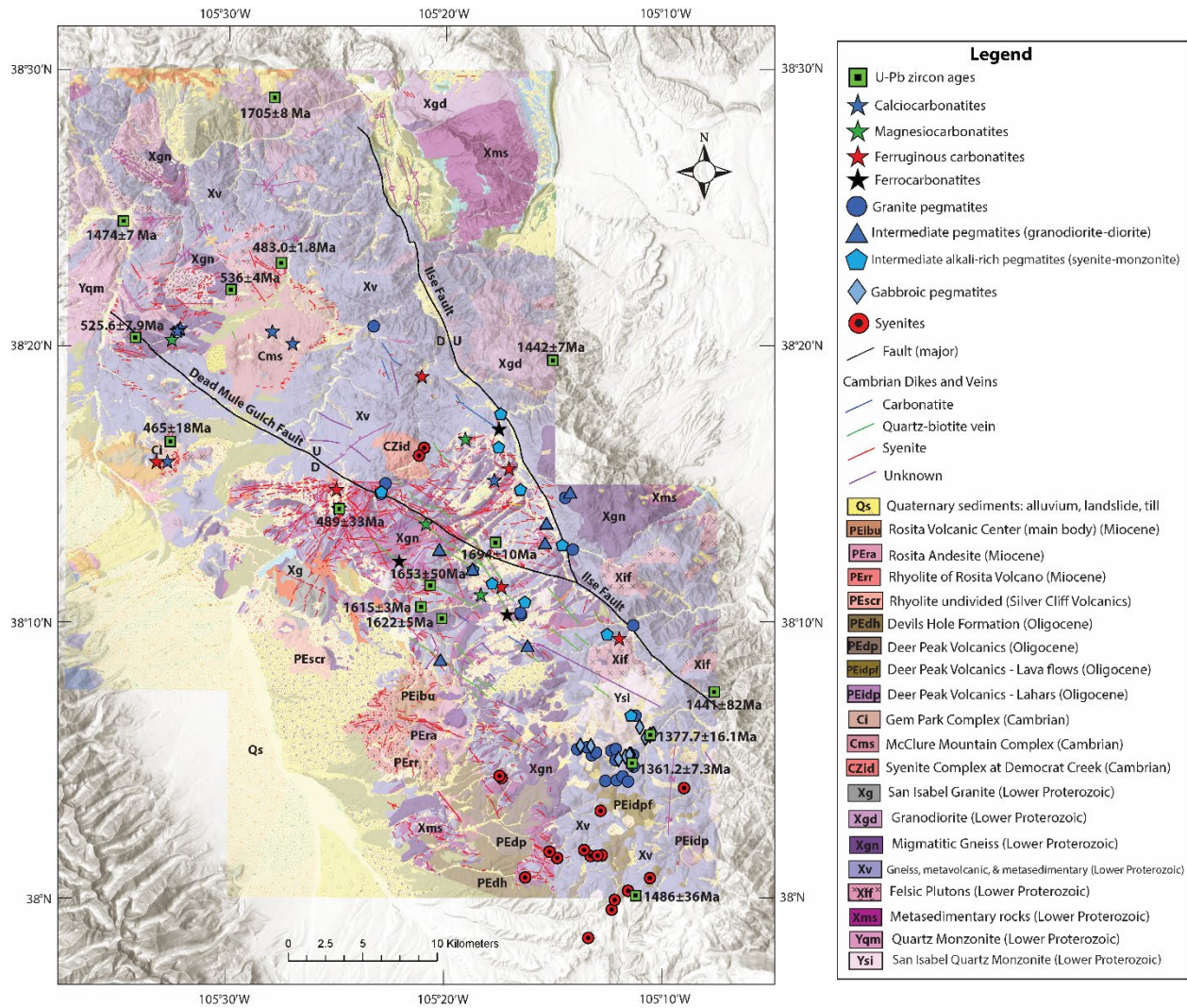


Table 1. Summary of U/Pb zircon ages for plutons and dikes of the Wet Mountains, south-central Colorado. Sample locations are shown in Figure 2.

Lithology (general area)	Geochronology method	Material analyzed	Age (Ma)	Location	Reference
Granodiorite (Crampton Mountain Batholith)	U/Pb	Zircon	1705±8	38.483, -105.467	Bickford et al., 1989
Charnockite (Boneyard Gulch)	U/Pb	Zircon	1694±10	38.215, -105.296	Bickford et al., 1989
Foliated Tonalite (Mt. Tyndall)	U/Pb	Zircon	1653±50	38.189, -105.346	Bickford et al., 1989 ; du Bray et al., 2015
	U/Pb	Zircon	1622±5	38.169, -105.337	Bickford et al., 1989 ; du Bray et al., 2015
Megacrystic Granite (Mt. Tyndall)	U/Pb	Zircon	1615±3	38.176, -105.353	Bickford et al., 1989 ; du Bray et al., 2015
Granite (Williams Creek)	U/Pb	Zircon	1486±36	38.002, -105.188	Bickford et al., 1989
Granite (West McCoy Gulch)	U/Pb	Zircon	1474±7	38.408, -105.583	Bickford et al., 1989
Granite (Oak Creek)	U/Pb	Zircon	1442±7	38.325, -105.241	Bickford et al., 1989
Granite (Hardscrabble Creek)	U/Pb	Zircon	1441±82	38.125, -105.128	Bickford et al., 1989
Orthopyroxenite (Hatchet Complex)	U/Pb	Zircon	1377.7±16.1	38.099, -105.177	Magnin, 2024
Norite (Hatchet Complex)	U/Pb	Zircon	1361.2±7.3	38.082, -105.191	Magnin, 2024
McClure Complex	U/Pb	Zircon	536±4	38.367, -105.5	Bickford et al., 1989
	U/Pb	Zircon	525.6±7.9	38.338, -105.573	Pivarunas & Meert, 2019
Carbonatite dike (Democrat Creek)	U/Pb	Monazite	489±33	38.235, -105.416	Magnin et al., 2023
Lamprophyre dike (McClure Complex)	U/Pb	Zircon	483.0±1.8	38.383, -105.461	Pivarunas & Meert, 2019
Carbonatite dike (Gem Park Complex)	U/Pb	Zircon	465±18	38.275, -105.546	Magnin et al., 2023

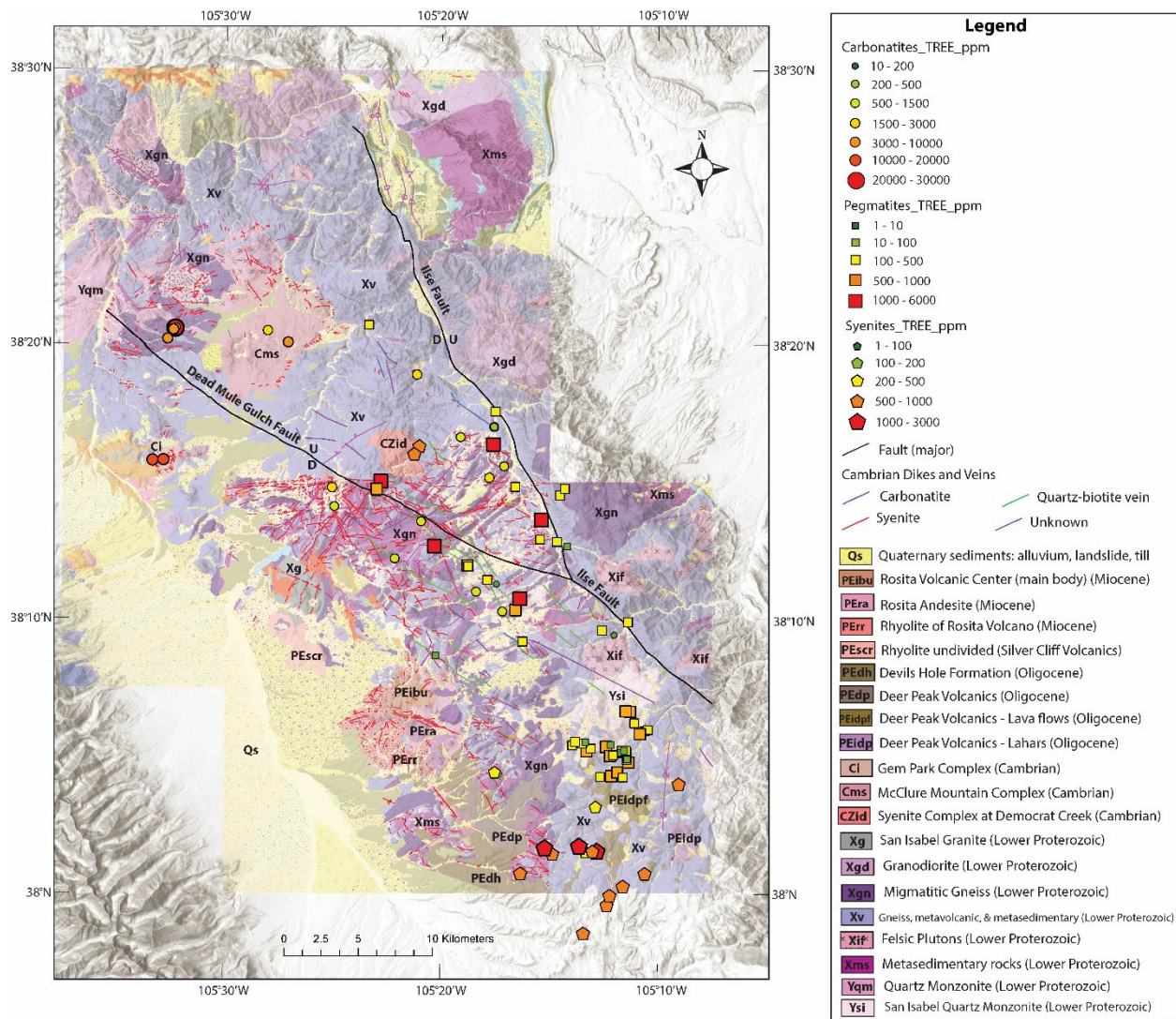


Figure 3: Spatial distribution of total REE (TREE) values for sampled carbonatites (circles), pegmatites (squares) and syenites (pentagons) in the Wet Mountains. Simplified geologic map modified from Temple et al. (2026).

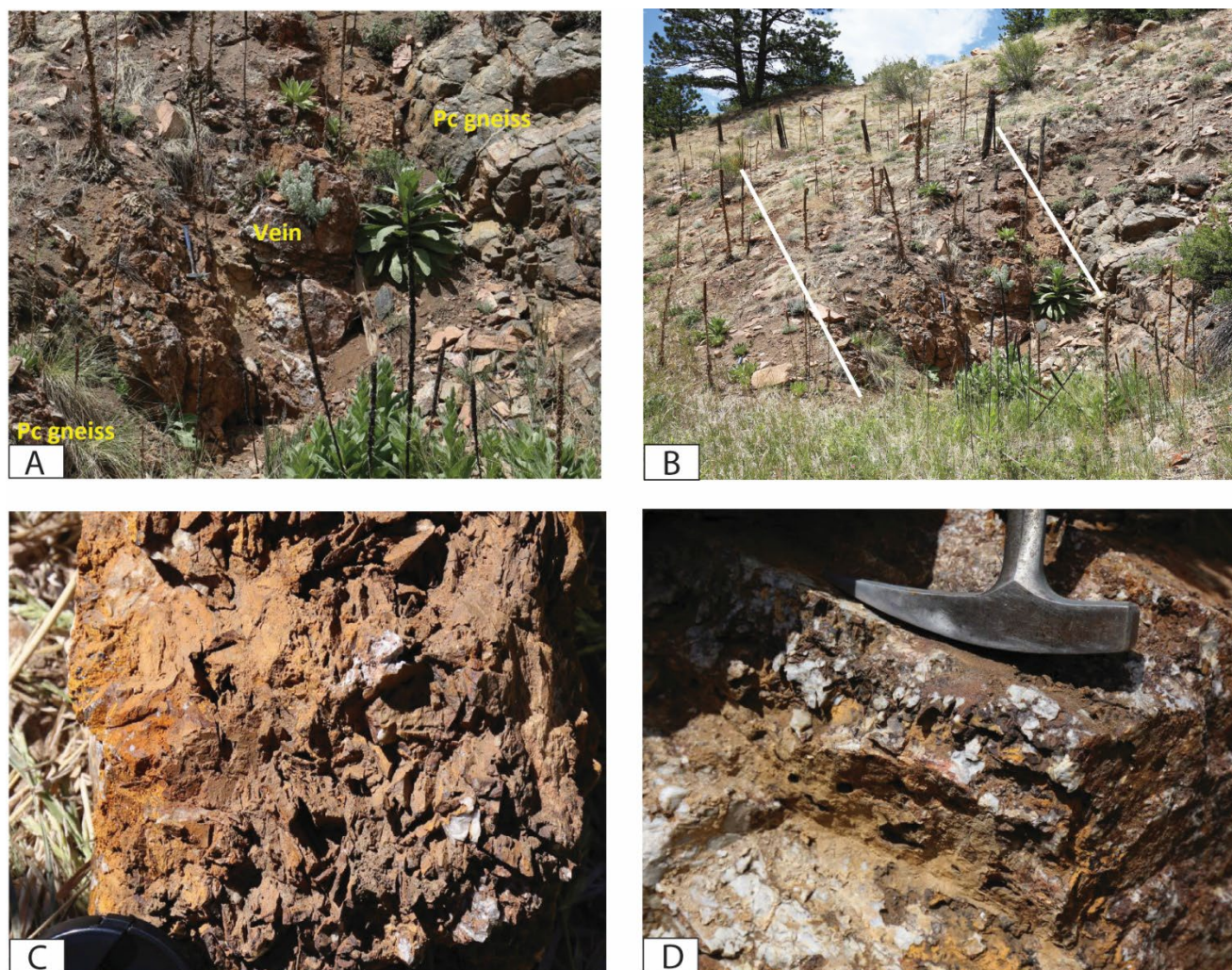


Figure 4: Field images of Precambrian host rock and quartz-barite-thorite veins from the Wet Mountains mapping area. A. Quartz-barite-thorite vein cross-cutting and host in Precambrian (Pc) gneiss. Hammer is ~41 centimeters (cm) long. B. White lines delineate the approximate edge of quartz-barite-thorite vein alteration (~3.7 meters (m) wide). C. Close-up of a quartz-thorite-barite sample and D. Close-up of an outcropping quartz-thorite-barite vein. Hammer head is ~18.5 cm and lens cover is ~8 cm wide. Images from O’Keeffe et al., 2021.

3. Sampling and Methods

Selected samples of pegmatites, syenites, and carbonatites were collected during the 2019-2020 field seasons and analyzed by whole-rock geochemical methods. Precambrian host rocks and quartz-barite-thorite veins were commonly encountered during field work and sample collection (Figure 4). Sample locations and descriptions were recorded. One representative sample from each outcrop was processed for whole-rock major- and trace-element analysis. 25 carbonatites, 52

pegmatites, and 19 syenite samples were subject to geochemical analyses in this study from the Wet Mountains mapping area (Figures 2 and 3).

Carbonatite samples are located around and within the Ediacaran–Ordovician age McClure Mountain, Gem Park, and Democrat Creek alkaline intrusive complexes, as well as in the Mt. Tyndall area, which has plutonic rocks spanning from 1653 to 1615 Ma (Table 1). Pegmatite samples are clustered around the San Isabel quartz monzonite in the southern Wet Mountains and around the foliated plutons of the Mt. Tyndall area in the central Wet Mountains. Syenite samples are focused in the southern Wet Mountains around the Williams Creek granite, with two syenite dike samples from the Democrat Creek complex.

3.1 Whole-rock major- and trace-element analysis

Rock samples were provided to the USGS for analysis by their contract laboratory. The USGS laboratory processed samples and performed quality assurance/quality control (QA/QC) on their contract laboratory. Rocks were pulverized in a ceramic mill. Major and trace element analyses were performed by AGAT Laboratories in Canada. Major elements were determined by wavelength-dispersive X-ray fluorescence (WDXRF), with analytical uncertainties generally <5%. For WDXRF, 2.0 grams (g) of rock powder were fused with a lithium metaborate/lithium tetraborate flux to form a glass disk, which was then analyzed for major oxides (reported in weight percent [wt.%]).

Minor, trace and REE elements, were analyzed by inductively coupled plasma–mass spectrometry (ICP-MS) and inductively coupled plasma–optical emission spectroscopy (ICP-OES) following sodium peroxide fusion digestion at 750 °C and dissolution of the fusion cake in dilute HNO₃. A total of 61 elements were determined, with typical analytical uncertainties <15% of reported values. To monitor analytical accuracy and precision, a USGS certified reference material was submitted with every batch of ten samples and processed as an unknown. Geochemical results are provided in the supplementary zip file (Appendix 1).

4. Results

4.1 REE abundance and spatial distribution

Elevated concentrations of Th, U, REEs, and Nb in the Wet Mountains are dominantly associated with dikes, fracture zones, veins, and irregular intrusive

bodies (Figure 3; Appendix 2). Dike and vein lithologies include carbonatite, red syenite, lamprophyre, and quartz–barite–thorite assemblages. Carbonatites, occurring as dikes and irregular intrusions, are most abundant in and around the Gem Park and McClure Mountain complexes (Armbrustmacher, 1988).

Carbonatites have the highest LREE concentrations (Figure 5) and, together with syenites, contain the highest HREE abundances. Pegmatites are more REE-rich than average upper continental crust but are generally less enriched than carbonatites or syenites. Syenites have the highest Nb, Ta, and Zr contents. All three rock types show strongly elevated Y and Th relative to crustal averages (Figure 5, Table 2).

Table 2. Characteristics of REEs and select strategic and critical metals. Values are medians. Average upper continental crustal values from Yaroshevsky (2006).

Elements	Abundance in the Upper Continental Crust (ppm)	Carbonatites (ppm) N=25	Pegmatites (ppm) N=52	Syenites (ppm) N=19
Rb	110	18.2	118	298
Sr	316	1090	168	47.4
Ba	668	1029	592.5	322
Ti	3117	1600	2800	1700
Mn	527	5970	460.5	842
Th	10.3	87.5	29	71.2
U	2.5	1.92	1.8	8.35
V	53	64	32.0	6
Nb	26	146	28.5	217
Ta	1.5	1	0.9	13.7
Sc	7	13	6.5	<5
Zn	52	201	67.5	94
Zr	237	39	240.5	752
Cr	35	96	17	<10
La	32.3	313	34.5	85.3
Ce	65.7	613	80.1	212
Pr	6.3	64.37	8.7	19.3
Nd	25.9	220	33.2	70.8
Sm	4.7	38.1	7.3	15.2
Eu	0.95	10.64	1.5	2.27
Gd	2.8	34.1	8.2	13.01
Tb	0.5	5.06	1.5	2.31
Dy	2.9	25.91	9.3	13.4
Y	20.7	82.2	52	81.5
Er	2.3	8.12	5.7	9.04
Yb	1.5	8.1	5.8	9.4
Lu	0.27	1.21	0.8	1.33

For all samples, Total REE (TREE) contents range from 48 to 26,821 parts per million (ppm) (average [avg.] 1,536 ppm) (Figure 3). LREEs range from 25 to 26,011 ppm (avg. 1,275 ppm), and HREEs from 12 to 2,017 ppm (avg. 261 ppm). Niobium ranges from <1 to 2,752 ppm (avg. 193 ppm). Strontium ranges from <10 to 6,960 ppm (avg. 668 ppm). Thorium varies from 0.2 to 1940 ppm (avg. 201 ppm), and U from 0.1 to 393 ppm (avg. 9 ppm).

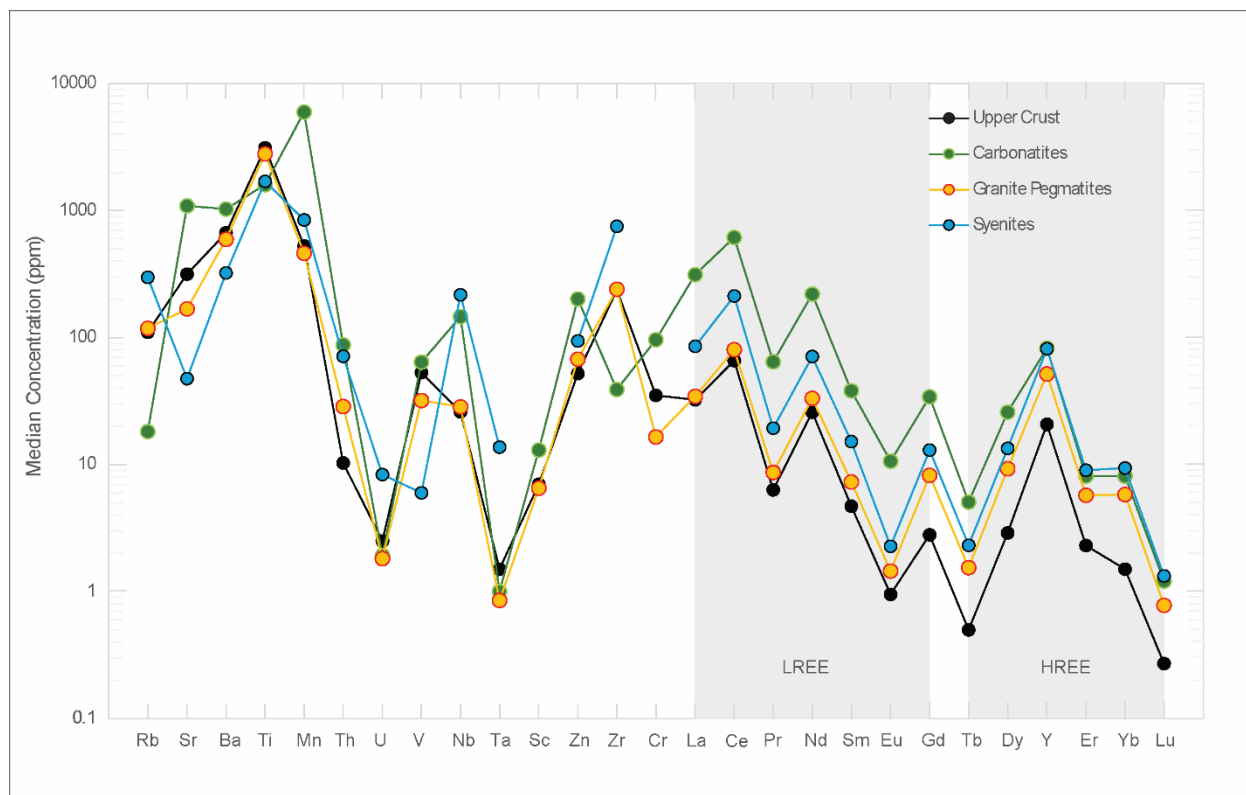


Figure 5: Comparison of median REE and select critical element concentrations to average upper continental crust.

4.2 Carbonatites

The carbonatites of the Wet Mountains have been classified in several ways. Heinrich and Dahlem (1969) recognized three types based largely on modal mineralogy: (1) relatively homogeneous calcitic or dolomitic carbonatites; (2) composite carbonate–K-feldspar bodies that grade into feldspathic Th- and

REE-bearing veins; and (3) carbonatites rich in barite, fluorite, and other accessory minerals.

Compositional classifications are complicated by significant mineralogical variability and gradational contacts between carbonatites and associated silicate rocks. Carbonatites have been further described as primary magmatic or replacement types based on whether igneous textures are preserved (Armbrustmacher, 1979).

4.2.1 Lithologic characterization

Several carbonatite samples lack clear textural or mineralogical criteria for classification as carbonatites. To discriminate magmatic carbonatites from carbonate sedimentary rocks, the [Sr + Ba]–[REE + Y] bivariate diagram of Samoilov (1991) was applied (Figure 6). Samples plotting within the non-carbonatite field and two severely altered samples were excluded from further lithologic and geochemical interpretation.

4.2.2 Major element chemistry

On the carbonatite classification ternary diagram of Gittins & Harmer (1997), most Wet Mountains carbonatites plot in the high-Fe ferrocarbonatite (Fc) field (Figure 7). These samples commonly show evidence of fluid overprinting and are cut by barite–quartz–thorite veinlets. Such alteration is reflected in elevated Fe_2O_3 , MgO , Al_2O_3 , SiO_2 , and TiO_2 contents (Appendix 1). Ba concentrations range from 10,000 to 105,000 ppm, such that, at these concentrations, Ba can be considered a major element.

Due to varying degrees of alteration and oxidation, high-Fe ferrocarbonatites may contain abundant iron oxides, forming what could be considered replacement-type carbonatites as described by Armbrustmacher (1979).

Samples that appear relatively fresh and weakly altered plot in the low-Fe portion of the diagram, including magnesiocarbonatites, ferruginous calciocarbonatites, and calciocarbonatites (Figure 7). Magnesiocarbonatites display elevated MgO and low Al_2O_3 , Fe_2O_3 , K_2O , MnO , Na_2O , and SiO_2 (green symbols) (Appendix 1). Ferruginous calciocarbonatites fall near the CCMF boundary of 0.75, where CCMF is defined as the molar ratio $\text{CaO}/(\text{CaO} + \text{MgO} + \text{FeO} + \text{MnO})$; values above 0.75 indicate carbonatites containing >50% calcite on a molar basis

(red symbols). Calciocarbonatites contain the highest CaO contents (31–52 wt.%; CCMF >0.75) and very low Fe_2O_3 , MgO, and MnO (blue symbols).

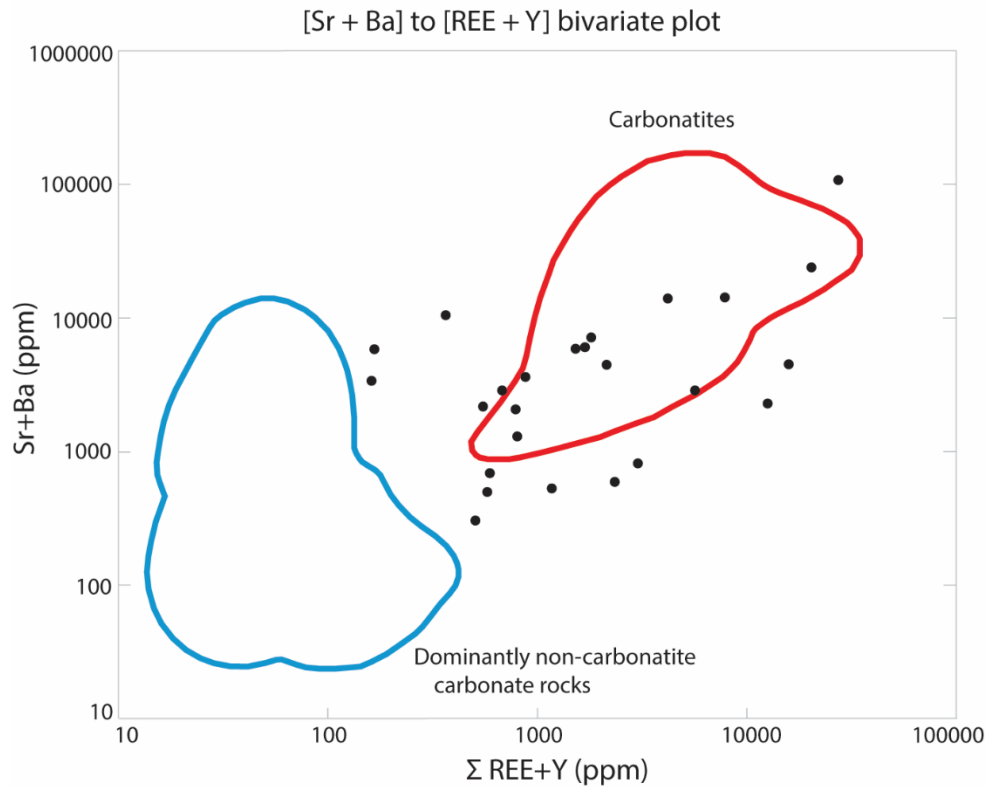


Figure 6: The [Sr + Ba] to [REE + Y] discrimination diagram for Wet Mountains carbonate-bearing rocks. This diagram is used to distinguish magmatic carbonatites from sedimentary carbonates (after Samoilov, 1991).

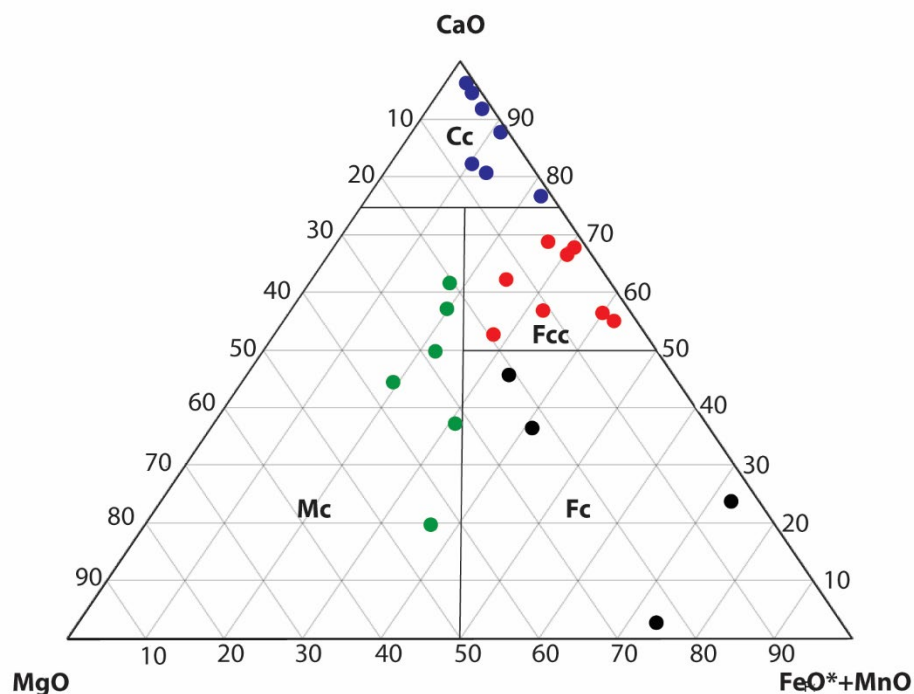


Figure 7: Ternary diagram of Wet Mountain carbonatites plotted as molar proportions. Cc — calcioarbonatites (blue), Mc — magnesiocarbonatites (green), Fcc — ferruginous calcioarbonatites (red), Fc — ferrocarbonatites (black) (after Gittins and Harmer, 1997).

4.2.3 Trace- and minor- element chemistry

Wet Mountains carbonatites are strongly enriched in large-ion lithophile elements (Ba, Sr) and REEs relative to average crust. Ferruginous calcioarbonatites have the greatest variability in REE enrichment (Figure 8). Two ferruginous calcioarbonatites and one calcioarbonatite display pronounced LREE enrichment and steeply negative chondrite-normalized slopes; La and Ce contents in these samples overlap ore-grade ranges for active REE carbonatite deposits such as Mountain Pass, Bayan Obo, and Maoniuping (Fan et al., 2016; Verplanck et al., 2016). This ore-grade subset also contains some of the highest Ba (2,440–105,000 ppm) and Th (66–1,940 ppm) contents, although Ba and Th are not consistently correlated across the broader dataset.

Calcioarbonatites, in general, show the strongest LREE enrichment and steep negative slopes on chondrite-normalized diagrams. A single magnesiocarbonatite sample is LREE-enriched, but most magnesiocarbonatites show only modest LREE enrichment. Samples with La <2,000 ppm have relatively

flat to gently negative patterns. HREE enrichment is limited: a few magnesiocarbonatites have elevated HREE, whereas most carbonatites are generally HREE-poor. Nb ranges from 1 to 1,740 ppm and does not systematically vary among carbonatite types (Appendix 1).

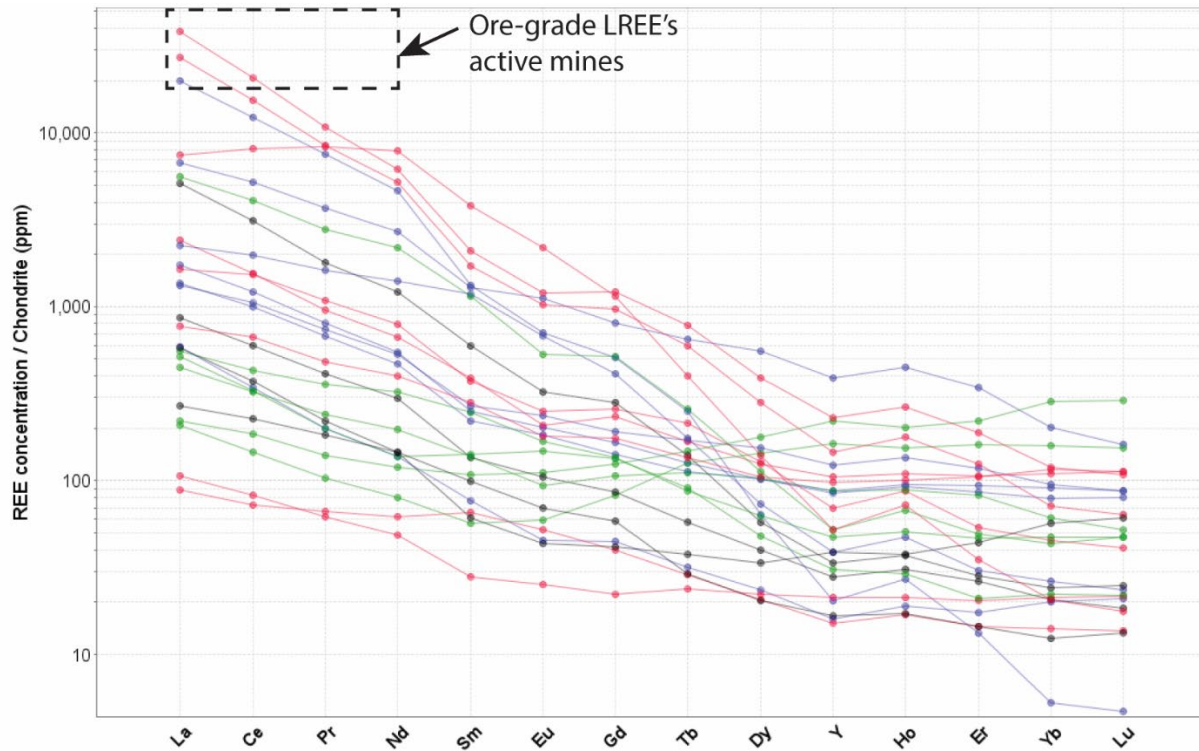


Figure 8: Chondrite normalized REE patterns for Wet Mountains carbonatites. The chart shows ore-grade carbonatite REE patterns from active mines (Fan et al., 2016; Verplanck et al., 2016). Calciocarbonatites (blue), magnesiocarbonatites (green), ferruginous calcicarbonatites (red), ferrocarbonatites (black). Normalization values from Sun & McDonough (1989).

4.3 Pegmatites

The Wet Mountains expose a complex suite of Proterozoic rocks that are predominantly subalkalic to calc-alkaline and marginally metaluminous to peraluminous, with relatively high Fe/Mg ratios (Noblett et al., 1987). Ediacaran–Ordovician intrusions include layered syenite, quartz syenite, nepheline syenite, alkali granite, pyroxenite, and gabbro, which are intruded by pegmatites, carbonatites, and quartz–barite–thorite veins (Armbrustmacher, 1984).

A large set of pegmatite samples contain intense alteration and fenitization of host rocks, leading to ambiguous field classifications. These samples were excluded from geochemical analyses in this study. Because “pegmatite” is a textural rather than compositional term, samples were plotted on a total alkali–silica (TAS) diagram (Middlemost, 1994) to constrain bulk composition and to evaluate relationships between composition and REE enrichment.

4.3.1 Lithologic Characterization and Major-element chemistry

On the TAS diagram (Figure 9), pegmatites span fields corresponding to gabbro (purple), diorite and granodiorite (blue), monzonite and syenite (red), and granite (black). Diorite and granodiorite pegmatites are grouped as intermediate compositions; monzonite and syenite pegmatites are grouped as intermediate, alkali-rich compositions.

Gabbroic pegmatites are characterized by elevated TiO_2 , Fe_2O_3 , MnO , MgO , CaO , and P_2O_5 , low Na_2O and K_2O , and <55 wt.% SiO_2 (Appendix 1). Syenitic and monzonitic pegmatites have high Al_2O_3 , Na_2O , and K_2O , moderately elevated TiO_2 , Fe_2O_3 , and P_2O_5 , relatively low MgO and CaO ; and SiO_2 ranges from 47 to 68 wt.%. Granodiorite and diorite pegmatites have slightly higher SiO_2 (59–71 wt.%), higher Na_2O and lower K_2O relative to syenites, and low MgO , CaO , and MnO . Granite pegmatites show the highest SiO_2 (70–84 wt.%) and K_2O and the lowest TiO_2 , Fe_2O_3 , MnO , MgO , and CaO .

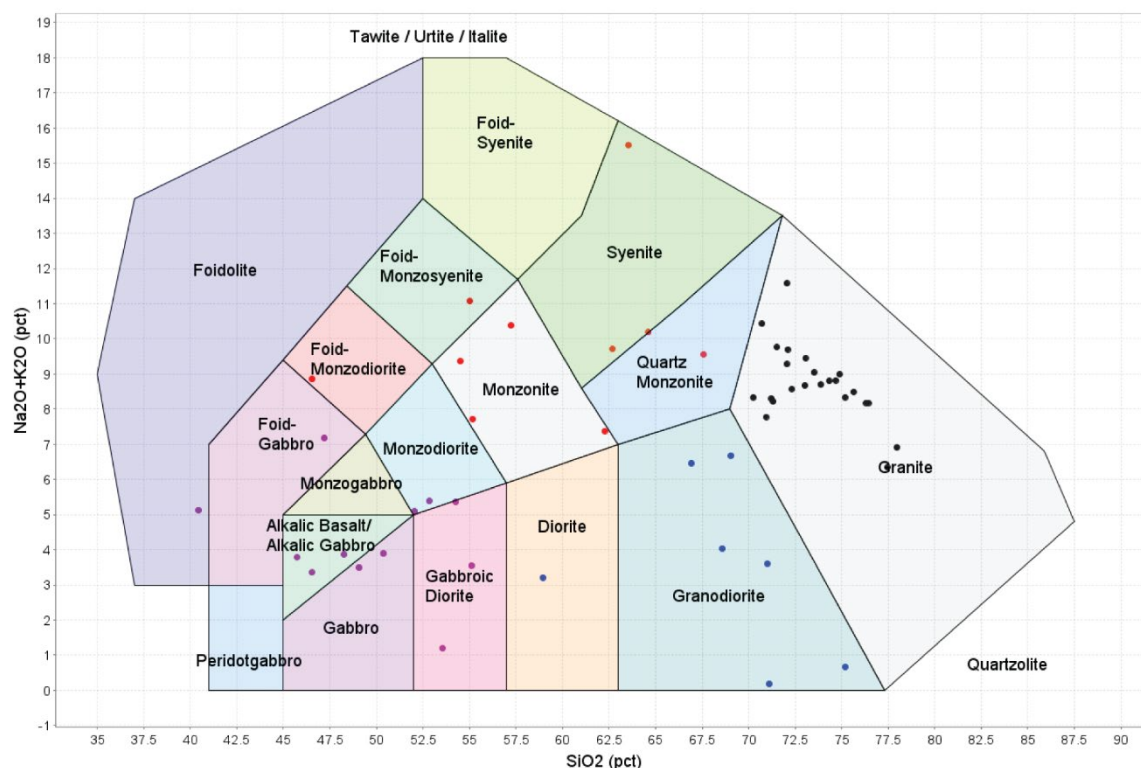


Figure 9: Total alkali-silica (TAS) diagram of pegmatite samples collected from the Wet Mountains. The diagram shows compositional groupings discussed in the text (pct = %). Diagram from Middlemost (1994). Samples with granitic compositions are shown with black circles, intermediate (blue), alkali-rich intermediate compositions (red) and gabbroic compositions (purple).

4.3.2 Trace- and minor- element chemistry

Trace-element compositions of pegmatites cluster in patterns broadly characteristic of their host plutons. Granite pegmatites are distinctly enriched in incompatible trace elements, including REEs, and have LREE-enriched patterns with strong negative Eu anomalies (Figure 10), consistent with derivation from highly fractionated granitic magmas.

The 1.4 Ga “anorogenic” granites of the region are known for high Fe, high K, and elevated abundances of high-field strength element (HFSE). These Proterozoic granites, together with younger alkaline intrusions and associated dikes and veins, are important sources of REEs, Th, U, and Nb. Enrichment of these elements is commonly hosted in accessory minerals such as monazite, zircon, allanite, and brockite, and may be further concentrated by late F-rich fluids. Consequently, elevated large-ion lithophile element (LILE) and HFSE in pegmatites are consistent

with derivation from these evolved magmas but are not diagnostic of a single parental source.

Intermediate pegmatites (granodiorite–diorite field) are enriched in Pb, Zn, Th, Ba, and Zr and elevated in Nb, Ni, Cr, and U, but relatively low in Cs, Hf, and Ta. Their REE patterns are highly variable: some have LREE-enriched, negatively sloping patterns; others have flat patterns, mixed positive and negative Eu anomalies, or an unusual “hump” centered on Sm–Gd (Figure 10). A few samples show modest HREE enrichment.

Intermediate alkali-rich pegmatites (syenite–monzonite field) are enriched in Ba, Sr, Rb, and Zr, slightly elevated in Zn, Th, Cr, Ni, and Nb, and low in Co, U, Ta, Sc, Cs, and Hf. Their REE patterns range from gently sloped LREE-enriched to nearly flat; some have minor HREE enrichment but overall REE concentrations are moderate (<1,000 ppm).

Gabbroic pegmatites are enriched in Cr and Ni and slightly elevated in Mn, Ba, and Sr, but are generally poor in REEs, Sc, Zn, Th, U, and Zr (Appendix 1). Their REE patterns show low LREE enrichment with gentle negative slopes and total REE concentrations typically <300 ppm.

4.4 REE-bearing Syenites in Southern Wet Mountains

Several syenite dike samples were collected from within and adjacent to the ~1.49 Ga Williams Creek and Bear Creek granites in the southwestern Wet Mountains, as well as from the ca. 525–465 Ma Democrat Creek alkaline complex (Olson et al., 1977; Armbrustmacher and Hedge, 1982; Pivarunas & Meert, 2019; Magnin & Kuiper, 2023; Magnin et al., 2023). These brick-red, K-feldspar-rich syenites host anomalous concentrations of REEs (TREE up to 2,326 ppm), U (up to 27.9 ppm), Th (up to ~1,000 ppm), Nb (up to 1,009 ppm), and HREEs (up to ~1,900 ppm). Their composition and alteration style suggest a possible link to the Ediacaran–Cambrian K-metasomatic event that produced fenites, episyenites, and Th–REE ± U mineralization.

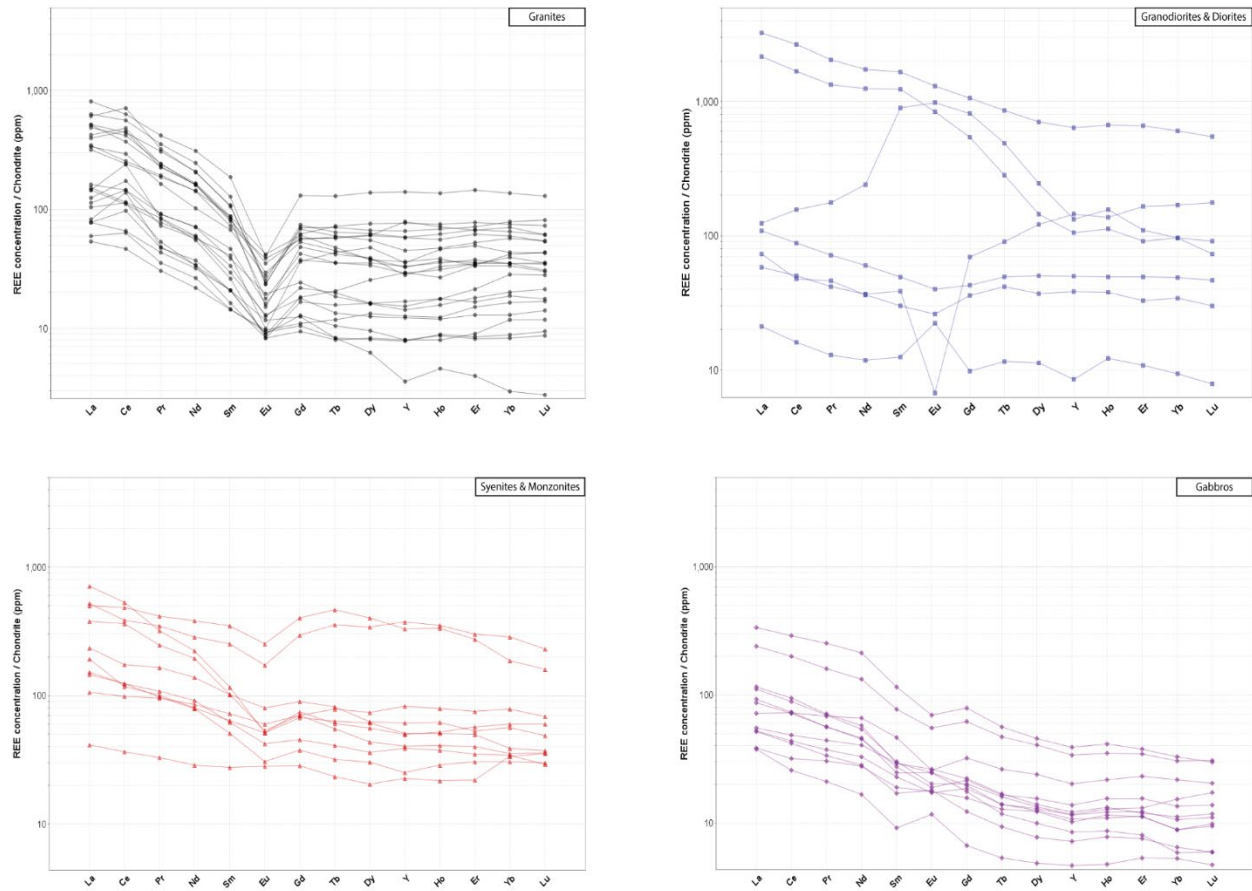


Figure 10: Chondrite normalized REE patterns for pegmatites of different bulk compositions in the Wet Mountains. Granite pegmatites (black) show strong LREE enrichment and pronounced negative Eu anomalies. Intermediate pegmatites (blue) have variable patterns, including flat to gently negative slopes, mixed Eu anomalies, and an Sm–Gd “hump” in one sample. Alkali-rich intermediate pegmatites (red) have generally flat patterns at modest REE levels (<1,000 ppm). Gabbroic pegmatites (purple) have low REE contents and gentle negative slopes. Normalization values from Sun & McDonough (1989).

4.4.1 Lithologic Characterization and Major-element chemistry

On the TAS diagram (Figure 11), syenite samples cluster mainly in the granite quartz monzonite, and syenite fields, with two samples plotting in the monzonite and foid-monzosyenite fields (Figure 11). Most samples have >60 wt.% SiO_2 ; the foid-monzosyenite and monzonite samples have 52.7 and 56.6 wt.% SiO_2 , respectively (Appendix 1).

The two Democrat Creek samples plot in the quartz monzonite field and are relatively low in K_2O (4.92 and 4.74 wt.%) compared with most other samples.

Samples classified as granites have the highest SiO_2 (>70 wt.%) and lowest Fe_2O_3 . Syenite and quartz monzonite compositions are characterized by elevated Al_2O_3 , Fe_2O_3 , K_2O , and TiO_2 . All samples have low MgO and P_2O_5 , consistent with highly evolved, alkali-rich magmas.

4.4.2 Trace- and minor- element chemistry

All syenite samples are variably enriched in incompatible trace elements (LILE and HFSE). They commonly show elevated Rb, Ba, Nb, and Zr and low Cs, Sc, Ni, and Pb (Appendix 1). Granite-composition samples have especially high Zr and Ba; syenite-composition samples are enriched in Rb and Zr and depleted in Ta and Sr; quartz monzonite-composition samples have elevated Th, Zr, Rb, and Ba and low Sr. The foid-monzosyenite and monzonite samples are strongly enriched in Th, TREEs, Ba, Pb, Sr, and Rb and depleted in Ni and Sc.

Democrat Creek samples have moderate TREE contents (595 and 722 ppm) compared with other syenites (>1,000 ppm). Chondrite-normalized REE patterns are variable but typically show negative Eu anomalies (Figure 12). Several samples show pronounced HREE enrichment, with concentrations comparable to or overlapping those of the HREE-enriched Round Top rhyolite in Texas (O'Neill et al., 2017). In contrast, other samples are dominated by LREE enrichment and display steep to gentle negative slopes or nearly flat REE patterns.

Tectonic setting was evaluated using the Rb vs. (Y + Nb) discrimination diagram of Pearce et al. (1984). Wet Mountains syenites and related granitoids plot in the Within-Plate Granite (WPG) field (Figure 13), indicating derivation from an enriched intraplate source in a non-orogenic setting. This supports interpretation of these intrusions as products of continental rifting associated with the Ediacaran–Cambrian alkaline magmatic event.

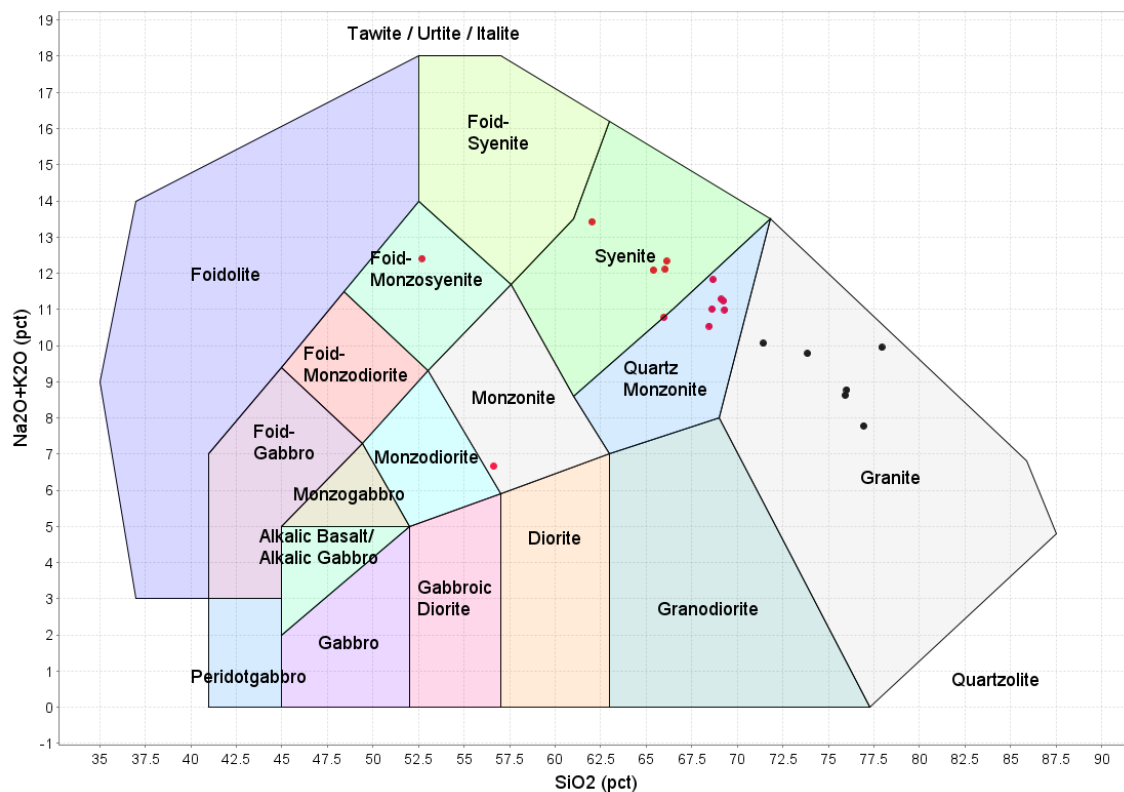


Figure 11: Total alkali-silica (TAS) plutonic diagram of syenite samples collected from the Wet Mountains. The samples primarily cluster in the granite, quartz monzonite and syenite fields with two samples falling in the monzonite and foid-monzosyenite fields. Diagram after Middlemost (1994). Samples with granitic compositions are shown with black circles and alkali-rich intermediate compositions are in red.

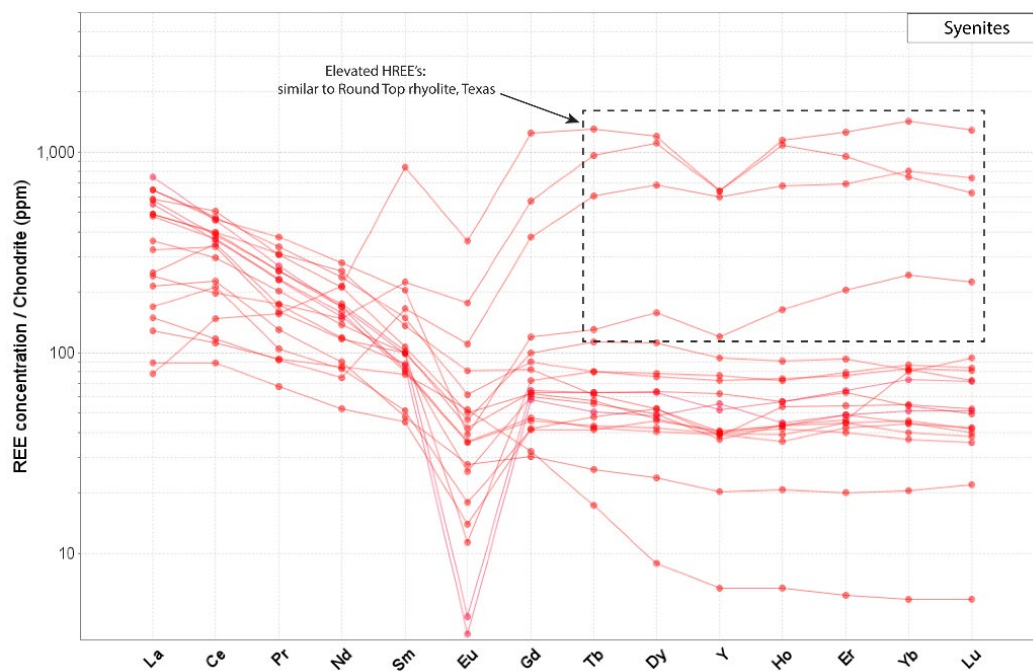


Figure 12: Chondrite normalized REE patterns for REE-bearing syenites in the Wet Mountains. Normalization values from Sun and McDonough (1989). Many samples show LREE-enriched patterns with negative Eu anomalies; some have pronounced HREE enrichment comparable to the Round Top rhyolite field (dotted box; O'Neill et al., 2017).

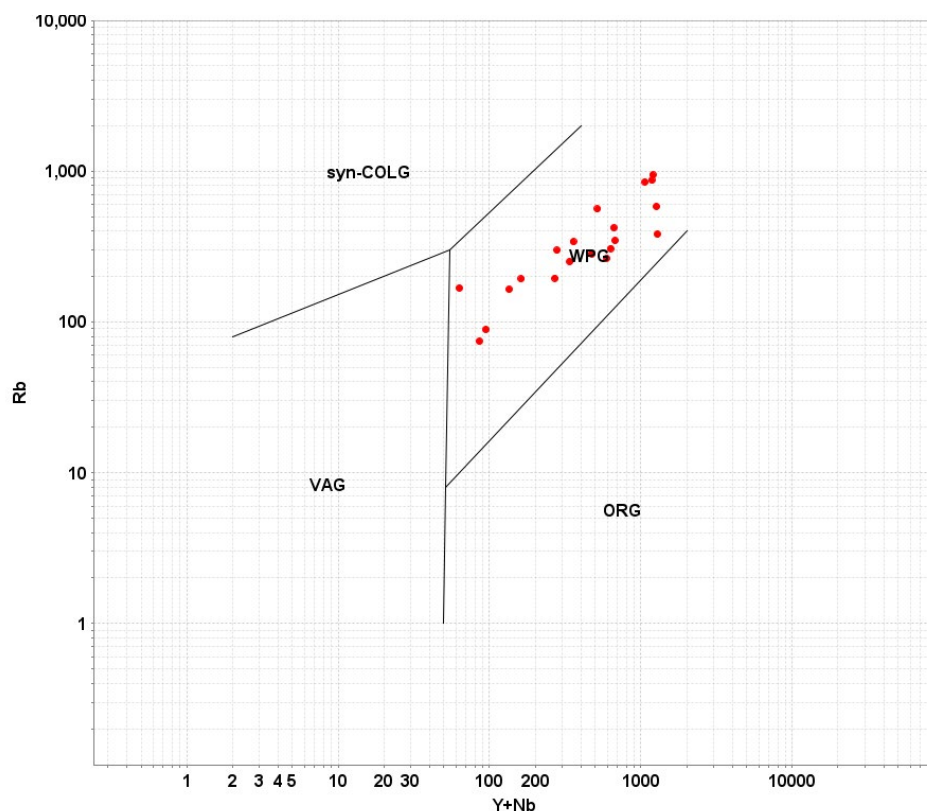


Figure 13: Trace-element, tectonic-setting-discrimination variation diagram. All samples are plotted in the field of Within-Plate Granites (WPG) reflecting magma derived from an enriched source in a non-orogenic setting. syn-COLG — Syn-collisional Granites, VAG — Volcanic Arc Granites, ORG — Ocean Ridge Granites. Tectonic setting-composition boundaries from Pearce et al. (1984).

5. Discussion

The new geochemical dataset indicates that REE-bearing carbonatites, pegmatites, and syenites in the Wet Mountains are related to multiple, distinct magmatic and hydrothermal processes. Integration of whole-rock geochemistry, REE systematics, and correlation analysis provides new constraints on element associations, mineral hosts, and the relative roles of magmatic differentiation and hydrothermal overprinting.

5.1 Relationships Between REE Enrichment and Major and Trace Elements

Correlation analysis was used to evaluate geochemical relationships that may reflect mineralogical controls on REE enrichment. In particular, associations

between REEs and elements such as MnO, Th, Nb, Zr, Ba, and CaO were examined to assess potential mineral hosts and enrichment mechanisms. These relationships provide insight into potential mineralogical controls involving minerals such as monazite, allanite, zircon, pyrochlore, and REE-fluorocarbonates, as well as the effects of magmatic fractionation and hydrothermal overprinting.

In carbonatites, REE enrichment is strongly associated with MnO, Ba, and Th. Total REE (TREE) and LREE show strong positive correlations with MnO ($r = 0.84$), Ba ($r = 0.75$), and Th ($r = 0.73$), whereas CaO, Fe_2O_3 , and K_2O have weak to negative correlations (Table 3). These relationships indicate that REE enrichment is not controlled by bulk carbonate mineralogy but is instead linked to Mn-bearing phases and LILE-rich accessory minerals or fluids. Heavy REEs show only weak correlations with all major and trace elements, suggesting decoupling of HREE from the dominant LREE-enriching processes. This pattern is consistent with typical LREE-dominated carbonatite systems worldwide, where REEs are hosted in minerals such as bastnäsite, monazite, and synchysite and are commonly associated with Ba- and Th-rich phases.

In pegmatites, correlations between REEs and major oxides are generally weak, indicating that bulk composition exerts limited control on REE distribution. In contrast, strong positive correlations exist between REEs and incompatible trace elements, particularly Ba ($r = 0.92$), Th ($r = 0.80$), and Zr ($r = 0.63$ for TREE; $r = 0.67$ for HREE) (Table 4). These relationships suggest that REE enrichment is largely controlled by accessory mineral assemblages, including zircon, monazite, xenotime, and allanite. The similar strength of correlations for both LREE and HREE suggests that pegmatites host mixed REE mineralization styles, reflecting advanced magmatic differentiation and possible fluid-assisted redistribution of incompatible elements.

In syenites, REE enrichment, particularly HREE, is strongly correlated with Fe_2O_3 and K_2O ($r = 0.68$ – 0.75) and with incompatible trace elements such as Rb and Th ($r = 0.73$ – 0.79) (Table 5). These relationships indicate that REEs are concentrated in highly evolved, alkali-rich magmatic systems and are associated with late-stage differentiation processes. The strong coupling between HREE and Fe–K-rich compositions suggests a link to accessory mineral crystallization and melt evolution, whereas LREE show weaker or inconsistent correlations, indicating decoupled behavior and potentially distinct mineral hosts.

Table 3. Correlation coefficients (r) of REEs in carbonatites with major oxide elements (wt%) and trace elements (ppm).

Elements	CaO	Fe₂O₃	K₂O	MnO	Ba	Rb	Th	Nb	Ta	Zr
TREE	0.10	-0.10	-0.36	0.84	0.75	-0.20	0.73	0.10	-0.24	-0.20
LREE	0.10	-0.10	-0.36	0.84	0.75	-0.20	0.73	0.10	-0.24	-0.20
HREE	0.26	-0.37	0.00	0.28	0.40	-0.17	0.39	-0.14	-0.17	0.24

Table 4. Correlation coefficients (r) of REEs in pegmatites with major oxide elements (wt%) and trace elements (ppm).

Elements	CaO	Fe₂O₃	K₂O	MnO	Ba	Rb	Th	Nb	Ta	Zr
TREE	-0.26	0.24	-0.10	0.35	0.92	-0.10	0.80	0.22	0.00	0.63
LREE	-0.26	0.20	-0.10	0.33	0.91	-0.10	0.77	0.14	0.00	0.57
HREE	-0.24	0.30	-0.10	0.33	0.81	-0.10	0.75	0.36	0.10	0.67

Table 5. Correlation coefficients (r) of REEs in syenites with major oxide elements (wt%) and trace elements (ppm).

Elements	CaO	Fe₂O₃	K₂O	MnO	Ba	Rb	Th	Nb	Ta	Zr
TREE	-0.10	0.68	0.71	-0.39	-0.20	0.73	0.76	0.00	-0.10	0.22
LREE	0.10	0.14	0.00	0.22	-0.28	0.24	0.00	0.58	0.45	0.45
HREE	-0.14	0.69	0.75	-0.47	-0.14	0.71	0.79	-0.10	-0.20	0.14

Collectively, these results demonstrate that REE enrichment in the Wet Mountains is controlled by (1) Mn- and LILE-associated processes in carbonatites, (2) accessory mineral crystallization and incompatible element enrichment in pegmatites, and (3) advanced magmatic differentiation in alkali-rich syenites.

5.2 Petrogenesis and Mineralization Processes

The geochemical data support a model in which REE mineralization reflects the superposition of mantle-derived magmatism and crustal differentiation processes.

Carbonatites are interpreted as mantle-derived melts emplaced during the Ediacaran–Ordovician intracontinental rifting event. Their high Sr, Ba, Nb, and strongly LREE-enriched patterns, together with ferrocarbonatite compositions and associated fenite alteration, are consistent with low-degree partial melting of an enriched lithospheric mantle source (Goodenough et al., 2021). Correlation patterns further indicate that REE enrichment was enhanced by late-stage magmatic or hydrothermal processes involving Mn-bearing phases and LILE-rich fluids. Localized hydrothermal overprinting produced replacement-type ferrocarbonatites and barite–quartz–thorite veins. A small subset of samples attains ore-grade LREE concentrations comparable to major carbonatite deposits (e.g., Mountain Pass), indicating that economically significant mineralization is locally developed.

Pegmatites and syenites represent evolved differentiates of Mesoproterozoic and early Paleozoic magmatic systems. In pegmatites, REE enrichment is primarily controlled by crystallization of accessory mineral phases during advanced fractionation, with additional modification by hydrothermal overprinting. In syenites, REE enrichment, particularly of HREE, is linked to highly evolved, alkali-rich melts and incompatible element concentration during late-stage magmatic evolution. The within-plate geochemical signature of syenites supports derivation from enriched intraplate sources associated with rifting.

5.3 Role of Structure and Hydrothermal Processes

Spatial relationships between REE enrichment and airborne radiometric anomalies provide further insight into mineralization processes. USGS EarthMRI radiometric data reveal prominent northwest-trending thorium lineaments that

coincide with areas of elevated TREE values, particularly in intermediate-composition pegmatites in the Mt. Tyndall area (Figure 14).

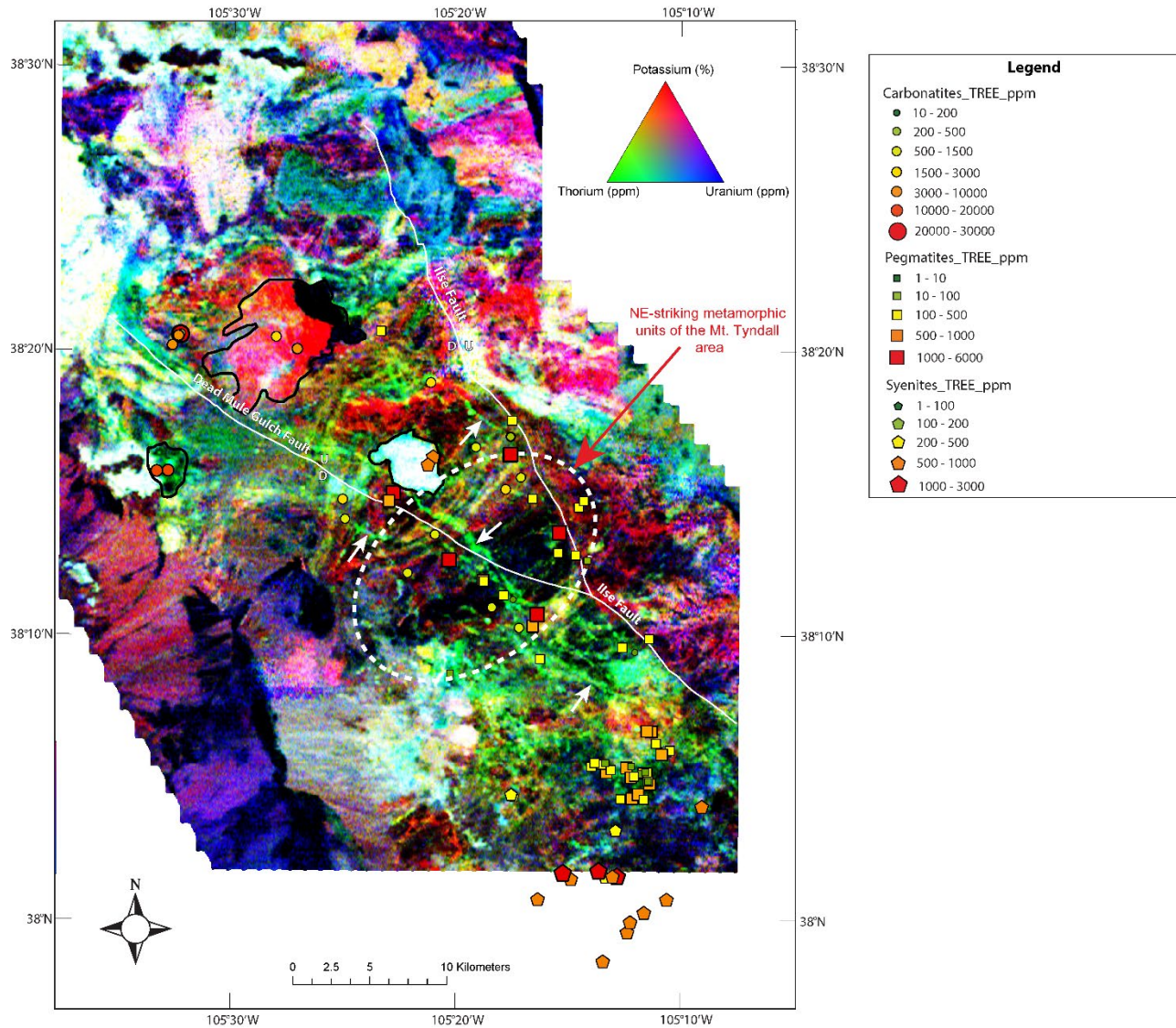


Figure 14: Radiometric ternary map (K-Th-U) showing mapped alkaline complexes with black outlines. Spatial distribution of TREE values for sampled carbonatites (circles), pegmatites (squares) and syenites (pentagons) in the Wet Mountains. The white dotted oval outlines northeast-striking metamorphic units of the Mt Tyndall area. White arrows point to thorium lineaments (green). Airborne radiometric data from Grauch et al., 2023.

These observations suggest that structurally controlled hydrothermal fluids played a significant role in redistributing and concentrating REEs and Th. Two complementary processes are proposed:

1. Primary magmatic enrichment, involving late-stage differentiation and alkali metasomatism associated with Ediacaran–Ordovician alkaline magmatism.
2. Secondary hydrothermal enrichment, in which structurally focused fluids mobilized and reconcentrated REEs along fracture systems, particularly those associated with thorium anomalies.

These processes are not mutually exclusive. Pegmatites and syenites derived from alkaline magmas may have been subsequently overprinted by hydrothermal fluids, resulting in enhanced REE concentrations and complex geochemical signatures.

5.4 Exploration Implications

For exploration, the integrated geochemical and spatial analysis highlights several favorable targets:

1. Carbonatite systems associated with the McClure Mountain, Gem Park, and Democrat Creek complexes, particularly with high MnO, Ba, and Th and strong LREE enrichment.
2. Alkali-rich syenites and episyenites, which locally host significant HREE, Nb, and Th and show strong associations with Fe_2O_3 , K_2O , Rb, and Th.
3. Highly evolved granitic pegmatites, where REEs are concentrated in accessory minerals such as zircon, monazite, allanite, and xenotime.
4. Structurally controlled zones, especially northwest-striking fracture systems defined by thorium-rich lineaments, which likely served as conduits for REE-bearing fluids.

6. Conclusion

The Wet Mountains represent a composite REE mineral system formed through the interaction of mantle-derived carbonatitic magmatism, crustal magmatic differentiation, and hydrothermal fluid activity. Carbonatites host the highest LREE concentrations and locally reach ore-grade levels, whereas pegmatites and syenites provide important hosts for HREE mineralization.

Correlation analysis demonstrates that REE enrichment is controlled by distinct processes in each lithology: Mn- and LILE-associated enrichment in carbonatites, accessory mineral control in pegmatites, and alkali-rich magmatic differentiation in syenites. The strong association of REEs with Th, Ba, and HFSE, together with their spatial correlation with structural lineaments, underscores the importance of both magmatic and hydrothermal processes in concentrating REEs.

Integration of whole rock geochemistry, detailed mapping of dike and vein systems, and follow up mineralogical, petrographic, and isotopic studies will be critical for distinguishing between magmatic and hydrothermal contributions to REE mineralization. Overall, the Wet Mountains constitute a composite magmatic province in which mantle-derived carbonatites and evolved alkaline to peraluminous intrusions provide potential for both LREE- and HREE-dominant resources.

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Appendices

1. Whole rock geochemical data for carbonatites, pegmatites and syenites (Supplementary data included in the zip file.)
2. GIS Files (Supplementary data included in the zip file.)