Rare Earth Element Enrichment in the Weathering Profile of the Bull Hill Carbonatite at Bear Lodge, Wyoming, USA

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Abstract

Bull Hill is a carbonatite diatreme within the Paleogene Bear Lodge Carbonatite Complex in Wyoming, USA. Rare earth element (REE)-bearing carbonate, fluorocarbonate, phosphate, and oxide minerals occur within near-vertical carbonatite dikes on the western margin of Bull Hill. Changes in mineralogy and REE concentrations with depth are ascribed mainly to late-stage magmatic-hydrothermal and supergene alteration. Approximately 35 m of drill core from Bull Hill was analyzed and encompasses least altered, weakly weathered, and moderately weathered carbonatite. The least altered carbonatite contains magmatic burbankite, typically as inclusions within Mn-rich calcite (stage I). Secondary REE-bearing minerals, which pseudomorphically replaced unidentified hexagonal phenocrysts, include ancylite, bastnäsite with synchysite-parisite, and an unidentified Sr-Ca-REE-phosphate (stage II). These replacive minerals generated small amounts of incipient porosity (~7–8%) and are largely stable in the lower portion of the weathering profile. Progressive weathering (stages III and IV) of the carbonatite involved the oxidation of pyrite to iron oxides and iron hydroxides, dissolution of calcite and strontianite, and the replacement of Mn-rich calcite by manganese oxides. These mineralogical changes resulted in an ~40% porosity gain in the core studied here. The volumetric concentration of weathering resistant REE-bearing minerals resulted in REE enrichment from an average of 5.4 wt % in the least weathered carbonatite to an average of 12.6 wt % in moderately weathered carbonatite, and to an overall increase in REE ore tenor of two to three times compared to the least altered carbonatite. Isocon plots confirm the increased concentration of REEs in the weathered carbonatite and demonstrate that REEs, along with TiO2, Ta, Nb, Zr, and Hf, were conserved in the lower weathered zone.

Introduction

The economics of mineral deposit production depend on many factors including location, commodity, mineralogy, size, and grade. All things considered, mineral deposits with higher tonnages and grades typically have better mining and economic outlooks. Unsurprisingly, late-magmatic and postmagmatic enrichment processes (i.e., hydrothermal alteration and supergene enrichment) can play an important role in the economics for rare earth element (REE)-bearing carbonate deposits (Verplanck et al., 2016).

The first stages of enrichment in carbonatite systems typically occur through fractional crystallization, resulting in late-magmatic fluids/melts greatly enriched in REEs. These REE-bearing fluids may precipitate REE-rich minerals and/or redistribute REEs via hydrothermal fluids, modifying existing carbonatite minerals (Mariano, 1989; Gieré, 1996; Williams-Jones et al., 2012, Verplanck et al., 2016). Additional enrichment can occur through in situ weathering, either through dissolution and remobilization of REEs or through removal of gangue materials (Morteani and Preinfalk, 1996). During the former, minerals such as REE-fluorocarbonates are broken down, releasing REEs, which are reprecipitated as rhabdophane, gorceixite, or other minerals under meteoric conditions (Lottermoser, 1990; Morteani and Preinfalk, 1996; Chakhmouradian and Wall, 2012; Slezak et al., 2021). Under the latter conditions, minerals such as gangue carbonates are dissolved and removed from the rock, generating porosity and increasing the concentration of REEs (Morteani and Preinfalk, 1996; Mitchell, 2015; Slezak et al., 2021).

The Bear Lodge carbonatite is a dike-hosted REE deposit, located in northeastern Wyoming (USA). It is one of the largest REE deposits in the United States, with a measured and indicated resource of ~16.3 million tonnes (Mt) at a grade of 3.05% total rare earth oxide (TREO) (Long et al., 2010; Noble, 2014). Bull Hill marks the central portion of the Bear Lodge deposit and is particularly enriched in light rare earth elements (LREEs). The REE-bearing minerals are concentrated within dominantly NW-trending, steeply dipping carbonatite dikes that cut heterolithic diatreme breccias. These carbonatite dikes have undergone variable degrees of late- and postmagmatic alteration and weathering (Noble, 2014), which have caused an increase in ore grade within the deposit. Previous work has focused on either the primary mineral compositions of the Bear Lodge Carbonatite Complex (Moore et al., 2015; Andersen et al., 2017; Chakhmouradian et al., 2017) or the intensely weathered (i.e., saprolitic) REE mineralogy (Andersen et al., 2017; Van Rythoven et al., 2020). This study focuses on a single drill hole (RES09-17) intercept of continuous carbonatite at Bull Hill and investigates the evolution of the carbonatite from the primary (stage I), magmatic-hydrothermally altered (stage II), and weathered (stages III-V) mineral assemblages. It identifies porosity generation as marking the start of weathering and demonstrates the mechanisms and environmental conditions that contributed to the mineralogy and REE grades observed in Bull Hill. This study illustrates the importance of supergene processes in increasing the REE grade of carbonatite rare metal deposits.

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ISSN 0361-0128; doi:10.5382/econgeo.4900; 19 p.
Digital appendices are available in the online Supplements section.
Geologic Setting

The Bear Lodge Mountains are the northwestern expression of the Black Hills domal uplift, which is a result of the Late Cretaceous–Paleogene Laramide orogeny. Alkaline igneous intrusions in the Bear Lodge Mountains are associated with the Black Hills Paleogene magmatic belt that extends approximately 110 km in a northwesterly (N70°–80°W) trend from Bear Butte in western South Dakota to the Missouri Buttes in northeastern Wyoming (Staatz, 1983; Jenner, 1984; Duke, 2009). Intrusions within this belt range in age from 58 to 46 Ma and generally decrease in age to the northwest (Duke, 2009).

The central Bear Lodge dome consists of an alkaline igneous core flanked by Paleozoic and Mesozoic sedimentary rocks (Fig. 1; Staatz, 1983; Jenner, 1984; Felsman, 2009). Crosscutting relationships indicate three major stages of Paleogene magmatism:

1. The initial alkaline silicate stage that includes the emplacement of syenite, microsyenite, porphyritic trachyte, and megacrystic sanidine trachyte porphyry as well as lesser latite, quartz latite, phonolite, and diatreme breccias (Duke, 2009; Felsman, 2009);
2. A second episode resulting in the emplacement of calcicarbonatite and silicocarbonatite dike swarms, which intrude older alkaline silicate rocks; and
3. A late phase of alkaline silicate magmatism including phonolite intrusions, lamprophyre dikes, and volcanic breccias (Jenner, 1984; Duke, 2009; Felsman, 2009).

The early alkaline silicate rocks were pervasively altered by potassic metasomatism. Late alkaline silicate rocks appear to lack this alteration, indicating that potassic metasomatism was likely associated with the second magmatic episode and is a form of potassic fenitization. Dating via 40Ar/39Ar analyses of biotite and K-feldspar yielded carbonatite ages of 52–51 Ma (Andersen et al., 2013).

Three main intrusive diatreme breccia bodies (Bull Hill, Whitetail Ridge, and Carbon Hill) occur within the north lobe of the Bear Lodge dome (Fig. 1). Carbonatite dikes and surrounding stockworks form a swarm cutting the three diatremes. The dikes are steeply dipping, strike north-northwest, and range from ≤0.3 up to 80 m wide (Noble, 2014; Hutchinson, 2016). They are predominantly calcite carbonatites and lesser silicocarbonatites that display strong Mn, REE, and Sr enrichment.

The depth of weathering at Bear Lodge is variable. In the Bull Hill area, strongly weathered carbonatite contains no residual calcite and comprises the Upper Weathering zone (i.e., stage V; Fig. 2). This material is underlain by granular, calcite-bearing oxide material (Noble, 2013, 2014) that composes the
moderately weathered carbonatite investigated in this study (i.e., stage IV). In the Bull Hill area, the boundary between the calcite-bearing and calcite-poor weathered rocks generally occurs 91–152 m below the surface and marks the boundary between the Upper Weathering zone and Lower Weathering zone (Fig. 2). The transition between the calcite-bearing and the overlying calcite-absent zones is gradual and generally coincides with a shift from anecylite-dominant rare earth mineralogy to bastnäsite group-dominant rare earth mineralogy (Noble, 2013, 2014; Moore et al., 2015). The basal portion of the Lower Weathering zone is characterized by weakly weathered carbonatite (i.e., stage III) that typically occurs between 152 and 183 m below the surface (Fig. 2; Noble, 2013, 2014). Below the Lower Weathering zone is the least weathered carbonatite, which comprises more primary magmatic-hydrothermal compositions (i.e., stages I and II).

**REE-Bearing Minerals at Bear Lodge**

Rare earth elements are concentrated within calcite carbonatite and silicocarbonatite dikes and associated stockwork veins (Fig. 2). REE mineral assemblages vary with depth in the calcite carbonatites. A summary of REE-bearing minerals and their compositions can be found in Table 1. Ancylite is the main REE-bearing mineral in unweathered carbonatite, occurring with minor burbankite and carbocernaite (Moore et al., 2015; Chakhmouradian et al., 2017). Also present, but in lesser amounts, are synchysite/pariste, bastnäsite, and burbankite (Noble, 2014; Hutchison, 2016). In addition, an unknown Sr-Ca-REE-phosphate (SCRp) phase was observed. This mineral may be Sr- and Ca-bearing monazite and/or rhabdophane. Minor REE-bearing minerals in the Lower Weathering zone include REE-fluorocarbonates, monazite, SCRp, and cerianite. Rare earth fluorocarbonates, especially bastnäsite, are dominant in the Upper Weathering zone and are often commonly accompanied by lesser monazite, cerianite, and very minor rare earth aluminum phosphates (Noble, 2014; Van Rijthoven et al., 2020).

**Methods**

Diamond drill hole RES09-17 from the western slope of Bull Hill was logged in detail (Hutchison, 2016). The samples that best represent the different degrees of alteration and the various textures observed while logging were acquired for further analyses (see below).

**Table 1. Summary of Minerals and Their Formulas Found in Carbonatites and Discussed in This Study**

| Mineral         | Formula                                      |
|-----------------|----------------------------------------------|
| Carbocernaite   | (Ca,Na)(Sr,Ce,Ba)(CO₃)₂                      |
| Burbankite      | (Na,Ca)(Sr,Ba,REE)(CO₃)₅                     |
| Stromatolite    | SrCO₃                                        |
| Ancyline        | (REE, Sr)(CO₃)OH- H₂O                       |
| Bastnäsite      | (REE)CO₃F                                   |
| Daqingshanite   | (Sr,Ca, Ba)(REE)(PO₄)(CO₃)₃+x(OH,F)          |
| Monazite        | (REE,Th)PO₄                                  |
| Rhabdophane     | (REE,Th)PO₄-H₂O                              |
| Pariste         | Ca(REE)(CO₃)F                               |
| Synchysite      | Ca(REE)(CO₃)F                               |
| Cerianite       | (Ca,Ce,Th)O₃                                |
| Florencite      | REEAl₃(PO₄)₃(OH)₃ H₂O                       |
| Goyazite        | SrAl₃(PO₄)₃(OH)₃H                          |

REE = rare earth element
Microscopy

Forty-five polished thin sections were utilized for transmitted- and reflected-light petrographic analysis. Thin sections, nopoxy grain mounts of granular weathered carbonatite samples, and epoxy mounts of intact and granular moderately weathered carbonatite samples were analyzed on three different scanning electron microscopes: an FEI Quanta 600, a JEOL JSM-5800LV, and a JEOL JSM540-A. Mineral analyses reported in this paper were obtained by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). Optical cathodoluminescence (CL) microscopy was performed on four least weathered carbonatite samples to document the zoning in Mn-rich calcite and calcite. The CL microscopy was conducted using an HCS-LM hot-cathode CL microscope from Lumic Special Microscopes, operated at 14 kV with a current density of 10 μA mm⁻².

Sixteen samples underwent compositional and textural analysis using SEM-based automated mineral technology at the Colorado School of Mines. These analyses were completed with an FEI QEMSCAN system and the control program iDiscover to acquire spectra. The mineral phase assignment was made based on comparison of acquired EDS spectra and backscattered electron (BSE) values with those in a reference mineral library. Results included mineral maps and modes. Scans were completed at resolutions ranging from 2 to 40 μm. The porosities of least weathered and moderately weathered carbonatites were also measured at 2-μm resolution, following the method of Jobe (2013).

Porosity measurements

Porosity was quantified using QEMSCAN for three of the least weathered carbonatite samples and three moderately weathered samples from the upper portion of the Lower Weathering zone (Table 2). Analysis was performed on thick sections of the least weathered carbonatite and epoxy pucks of the more solid and intact pieces within the moderately weathered carbonatite. The details for porosity determination by QEMSCAN are in Jobe (2013).

Whole-rock geochemistry

Seventeen quarter core samples and eight quality control samples were submitted to Analytical Laboratory Services (ALS) in Reno, Nevada. The results can be found in the Appendix. The samples were analyzed for the major elements—C, Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Sr, and Ba as oxides (including Fe₂O₃ and FeO)—and the trace elements—Rh, Y, Zr, Nb, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th, and U. Samples were prepared as lithium metaborate/lithium tetraborate fused discs. Major element oxides were determined using inductively coupled plasma-atomic emission spectrometry. Iron (III) concentration was determined by titration with a potassium dichromate solution on samples prepared with a four-acid digestion (HCl-HNO₃-H₂SO₄-HF), ammonium hydroxide Fe precipitation, and SnCl₂ Fe reduction. Loss on ignition was determined by heating samples to 1,000°C for 1 h. Trace element concentrations, including REE concentrations, were determined using inductively coupled plasma-mass spectrometry. Total S and total C were determined on samples using the Leco method.

Results

Least weathered carbonatite

Within the Bear Lodge dome, carbonatite dikes are generally white to light gray in color, are fine to coarse grained in texture, and contain dark biotite books, Ti oxide clusters, brassy sulfide mineral clusters, and light pink-tan hexagonal pseudomorphs. The primary carbonate assemblage typically consists of Mn-rich calcite and calcite with minor amounts of strontianite, dolomite, and ankerite. Accessory phases include potassium feldspar, biotite, aegirine-augite with minor barite, fluorapatite, and sulfides. The last includes marcasite, pyrite, pyrrhotite, chalcopryite, galena, sphalerite, and rare molybdenite. Minor oxides such as ilmenite, pyrophanite, and TiO₂ polymorphs are also present. The REE phases occur in variable amounts as ancylate, synchysite/parisite, bastnäsite, burlankite, carbonarite, daqingshanite, and an unidentified SCRp (see Table 1 for chemical formulas; Noble, 2013, 2014; Hutchinson, 2016). The primary carbonate assemblage typically consists of Mn-rich calcite and calcite with minor amounts of strontianite, dolomite, and ankerite. Accessory phases include potassium feldspar, biotite, aegirine-augite with minor barite, fluorapatite, and sulfides. The last includes marcasite, pyrite, pyrrhotite, chalcopryite, galena, sphalerite, and rare molybdenite. Minor oxides such as ilmenite, pyrophanite, and TiO₂ polymorphs are also present. The REE phases occur in variable amounts as ancylate, synchysite/parisite, bastnäsite, burlankite, carbonarite, daqingshanite, and an unidentified SCRp (see Table 1 for chemical formulas; Noble, 2013, 2014; Hutchinson, 2016). Trace Fe and Mn oxides, which are only visible microscopically, infill voids within REE-bearing minerals.

The least weathered carbonatite dikes in this study display minimal supergene alteration and correspond to Noble’s (2014) sulfide zone and Moore et al.’s (2015) oxidized zone (Table 3). Textures observed in thin sections from the Bull Hill least altered carbonatite indicate two main hypogene stages of REE mineral growth compared to the five stages suggested in other studies. This may be related to the samples coming from a single drill hole in a different area compared to previous

| Sample type       | Sample   | Porosity (%) | Mineral (%) | Total (%) |
|-------------------|----------|--------------|-------------|-----------|
| Least weathered    | RBL11-42B| 6.2          | 93.8        | 100       |
| carbonatite        | RBL11-45A| 8.6          | 91.4        | 100       |
|                    | RBL11-45B| 8.7          | 91.4        | 100       |
| Average            | 7.8      | 92.2         | 100         |           |
| Moderately         | RBL11-25Q| 41.4         | 58.6        | 100       |
| weathered          | RBL11-27Q1| 61.2        | 38.8        | 100       |
| carbonatite        | RBL11-27Q2| 47.5        | 52.5        | 100       |
| Average            | 50.1     | 49.9         | 100         |           |
works. However, we believe the general nature of categorization in this study is more widely applicable throughout the complex. The hypogene REE growth stages are referred to herein as stage I and stage II. Details of the mineralogy from various stages, including weathering, from this study as well as previous studies are summarized in Table 3.

**Stage I mineralogy:** The carbonatite displays early magmatic crystallization textures of Mn-rich calcite with phenocrysts and microphenocrysts of biotite, aegirine-augite, and plagioclase, and a completely replaced hexagonal mineral, likely burbankite. Potassium feldspar crystals are also present and are moderately to strongly embayed and exhibit resorption textures and alteration rims, suggesting they are xenocrysts.

Manganese-rich calcite has grain sizes ranging from 0.02 to 5 mm and typically displays a bimodal size distribution. Smaller grains are anhedral and contain few inclusions, mainly burbankite (Fig. 3A). Larger grains are also anhedral with a conertal texture (i.e., grains with irregular, interlocking margins) and contain inclusions of burbankite and fluorite as well as abundant one- and two-phase fluid inclusions. Manganese-rich calcite contains up to 8 wt % Mn and up to 1.5 wt % Fe. Small grains exhibit zoning, which is expressed as quenching, dark cores with bright red rims, in BSE images (Fig. 3A) and in CL. Larger, conertal grains exhibit quenching luminescence (Fig. 3B) and may encapsulate relic smaller grains.

Potassium feldspar occurs as large (up to 4 cm) subhedral crystals that display a strongly resorbed and partially embayed texture with Mn-rich calcite and REE minerals infilling the interstices. Crystal rims contain up to 1.5 wt % Ba.

The composition of biotite mainly forms part of the phlogopite-anthophyllite series with some grains occurring as tetraferriphlogopite or tetraferrrianthophyllite (Hutchinson, 2016). Because of its compositional variability, this mica will hereafter be referred to as “biotite.” Biotite is Ti bearing and commonly intergrown with potassium feldspar xenocrysts and, in some places, appears to be replaced by potassium feldspar. Biotite commonly exhibits multiple resorption and renewed growth events, as indicated by varying degrees of complex compositional zoning (Fig. 3D, E), suggesting open-system processes, possibly magma mixing or reaction with the potassium feldspar xenocrysts.

Aegirine-augite is observed as subparallel to slightly radiating clusters of euhedral prismatic crystals (Fig. 3F) and is intergrown with calcite and biotite. Rarely, aegirine-augite appears to be intergrown with the REE minerals synchysite/parasite and SCRp.

Ilmenite contains up to 16.6 wt % Mn and is, therefore, an ilmenite-pyrophanite solid solution. It is generally anhedral and commonly displays partially resorbed edges with discontinuous rims of Nb-bearing TiO2 polymorphs (Fig. 4A). Ilmenite also occurs as rims on burbankite pseudomorphs together with biotite (Fig. 4D) and, rarely, can be intergrown with galena, chalcopyrite, and pyrite. Minor fluorapatite, with up to 1.7 wt % Na and up to 1.6 wt % Sr, occurs as single crystals and clusters of anhedral to subhedral grains intergrown with biotite, Mn-rich calcite, and biotite.

Hexagonally shaped, stage I crystals are likely burbankite (Olender, 2012; Moore et al., 2015; Hutchinson, 2016). The burbankite crystals (Fig. 4C, D; now replaced), constitute about 10 vol % of the primary magmatic mineralogy that consisted of a polymineralic assemblage dominated by REE-bearing minerals (see stage II; Fig. 4E, F). The pseudomorphed burbankite crystals range in diameter from 1 mm to 1 cm (Fig. 4C-E) with rare examples up to 2 cm. The pseudomorphs contain rare relics of burbankite cores and/or inclusions (Moore et al., 2015).

**Stage II mineralogy:** Magmatic mineral assemblages were replaced by a mineral suite formed during late magmatic and/or hydrothermal processes. The term REE-fluorocarbonate (RfC) is used to denote the grouping of synchysite/parasite and bastnäsite when the compositions of these minerals cannot be separated.

Early magmatic hexagonal phenocrysts (formerly burbankite) were pseudomorphically replaced with a multimineral assemblage consisting of prismatic to anhedral REE-bearing minerals, strontianite, and barite surrounded by interstitial calcite (Fig. 5A, B). The REE-bearing mineral
Fig. 3. Magmatic mineral textures and relationships in carbonatite. A) Backscattered electron (BSE) image of fine-grained, Mn-rich calcite exhibiting compositional zoning and small burbankite inclusions. B) Cathodoluminescence (CL) image of carbonatite showing zoning in fine-grained calcite and quenching in coarse-grained calcite. The edge of a rare earth element (REE)-bearing pseudomorph is outlined at the top of the image. C) Photomicrograph under crossed-polarized light (cpl) of the image in (B). D) Photomicrograph in plane-polarized light (ppl) of biotite displaying complex zoning and multiple resorption and regrowth boundaries, surrounded by REE-bearing minerals and calcite. E) Biotite displaying weak zoning and alteration in a matrix of Mn-bearing calcite (ppl). F) Weakly zoned biotite intergrown with aegirine-augite (dark to pale green; ppl). Abbreviations: aeg-aug = aegirine-augite, anc = ancylite, bt = biotite, bur = burbankite, Mn-cal = Mn-rich calcite, Ti-bt = Ti-rich biotite.
Fig. 4. Textural relationships of hexagonal burbankite pseudomorphs and magmatic ilmenite. A) Backscattered electron (BSE) image of ilmenite phenocryst replaced by TiO₂ polymorphs, surrounded by secondary assemblage. B) BSE image of ilmenite exhibiting resorbed edges and secondary TiO₂ polymorphs. C) Photomicrograph (plane-polarized light; ppl) of hexagonal phenocrysts (outlined with dashed red lines) that are replaced by strontianite, ancylite, calcite, and rare earth element (REE)-fluorocarbonates and rimmed by ilmenite, biotite, and TiO₂ polymorphs. D) False-color mineral map from automated mineral analyses of the same area as shown in (C). E) Hexagonal pseudomorph surrounded by magmatic Mn-rich calcite (ppl). Creamy orange blebs are epoxy-filled voids. F) Photomicrograph (ppl) of pseudomorph surrounded by magmatic Mn-rich calcite and replaced mainly by ancylite and barite. Abbreviations: anc = ancylite, brt = barite, bt = biotite, ilm = ilmenite, Mn-cal = Mn-rich calcite, Rfc = rare earth fluorocarbonate, str = strontianite, Ti-ox = TiO₂ polymorph, vd = void.
assemblage consists of ancylite, REE-fluorocarbonates (synchysite/parisite, rarely with bastnäsite cores), SCRp, and daqingshanite (Figs. 6, 7). Ancylite and strontianite are the main constituents (Fig. 4E, F), each accounting for 5–30 vol % of the total pseudomorphic assemblage, along with up to 20–30 vol % calcite, and up to 5 vol % each of barite and REE-fluorocarbonates. The unidentified Ca-Sr-REE-phosphate and daqingshanite make up less than 2 vol % of the pseudomorph assemblage.

The pseudomorphed burbankite contains a secondary porosity that, rarely, can account for up to 40 vol % of the original mineral. While some of this open space may arise from grain loss during core extraction and sample preparation, core logging and petrographic observations in this study (Fig. 4F) and by others (see Olinger, 2012; Moore et al., 2015; Hutchinson, 2016) suggest that much of the porosity originated during replacement of the original hexagonal mineral.

Ancylite is the principal rare earth mineral in the least weathered carbonatite. It is intergrown with or replaced by an unidentified SCRp phase. Ancylite commonly occurs as chains of individual linked euhedral to subhedral crystals (Fig. 5A, C). Sprays of goethite are generally associated with ancylite grains (Fig. 5D). Ancylite compositions contain significant Ce, La, Nd, and Pr and may incorporate up to 0.7 wt % Th and 2 wt % Ca.

Synchysite and parisite are grouped together as synchysite/parisite because of potential intergrowths of the two compositions on a finer scale than is recognizable with the methods used. Synchysite/parisite forms euhedral radiating sprays 0.01–0.2 mm in length that locally contain anhedral bastnäsite cores (Fig. 6A). Synchysite/parisite is commonly intergrown with ancylite and barite (Fig. 6B) and more rarely with TiO₂ polymorphs, pyrite, and calcite (Fig. 6C, D), suggesting some were formed during hypogene hydrothermal alteration. Synchysite/parisite has variable Th contents ranging up to 1.3 wt % Th.

Strontianite is 0.01–1.0 mm in size and typically displays a platy morphology. It is generally locally intergrown with ancylite, barite, and REE-fluorocarbonates but replaces those minerals (Fig. 7A). Barite occurs as subhedral to anhedral, 0.03- to 1.5-mm grains that are commonly intergrown with ancylite, strontianite, and synchysite/parisite (Figs. 5A, B, 6A, B).
Rare earth element-phosphates appear to have formed late in the replacive sequence. Daqingshanite occurs in trace amounts as subhedral grains with ancyelite and strontianite (Fig. 7B). It is locally replaced by the anhedral SCRp phase (Fig. 7B), which also occurs as small inclusions within strontianite and replacing ancyelite (Fig. 7B, C) and as euhedral wedge-shaped crystals (Fig. 7D). The SCRp phase contains around 55 wt % LREEs and up to 4.5 wt % combined Ca and Sr and can be compositionally zoned (Fig. 7C, D), with subtle variations in REEs and P compared to Ca and Sr.

Pyrite occurs as medium to coarse, subhedral, and commonly skeletal grains intergrown with calcite or enclosing potassium feldspar, calcite, biotite, and REE-bearing minerals (Fig. 6D). It may also replace biotite and chlorite. Fine- to very fine grained pyrite forms intergrowths with magnetite, and locally pyrrhotite, at the edge of large, subhedral pyrite grains. Other sulfides present include galena, chalcopyrite, and sphalerite.

Niobium-bearing TiO₂ polymorph grains are subhedral to anhedral and appear to have crystallized contemporaneously with the pseudomorph assemblage. The TiO₂ polymorphs generally contain less than 2.0 wt % Nb and commonly replace ilmenite-pyrophanite along cleavage planes and edges (Fig. 4A, B). It is also intergrown with synchysite/parisite, ancyelite, and calcite.

Weathered carbonatite (stages III-V)
Weathering intensity within the drill core ranges from relatively unweathered (i.e., least weathered) to weakly weathered to moderately weathered (Fig. 8). Weakly weathered...
carbonatite forms an irregular interval 146.3–147.8 m above least weathered carbonatite and corresponds to the bottom of the Lower Weathering zone (Fig. 2). Above this, the carbonatite is moderately weathered to the top of the carbonatite interval at 132.9 m. Highly weathered carbonatite that lacks remnant carbonate minerals is not present in the drill core studied but is present at surface (Fig. 8) as described by Noble (2013, 2014) and Van Rythoven et al. (2020).

Progressive weathering of carbonatite resulted in a change from white-gray holocrystalline rock to brown-black, highly porous, and saprolite material. Weathering involved partial to complete dissolution of calcite and strontianite, replacement of magmatic Mn-rich calcite by Mn oxides, and the oxidation of sulfides to Fe oxides and Fe hydroxides (Fig. 9). Potassium feldspar was variably replaced by clay minerals at shallow depths. The REE mineralogy of moderately weathered carbonatite is dominated by ancylite in the lower weathered zone, with bastnaesite becoming dominant in the upper weathered zone (Fig. 8). Secondary cerianite, monazite, and REE-Al-phosphate abundances increase with increasing weathering (Fig. 8), outlining paragenetic stages III and IV.

**Weakly weathered mineralogy (stage III):** The most apparent visual effect of the onset of weathering is the oxidation of Fe-bearing minerals and the formation of hematite, which can constitute up to 4 vol % of the rock. Iron sulfides such as pyrite and marcasite are moderately to strongly oxidized, primarily to hematite. Other sulfides are less affected by weathering; both chalcopyrite and galena commonly display only partial to complete hematite rims. Biotite proximal to oxidized iron sulfides exhibits a strong red color, probably the result of either higher titanium or iron content (Lalonde and Bernard, 1993). Hematite also rims or replaces ilmenite and TiO₂ polymorphs. Hematite and goethite partially infill pores within the pseudomorphed hexagonal phase and infill fractures in potassium feldspar.

**Moderately weathered mineralogy (stage IV):** Moderately weathered carbonatite exhibits textural and mineralogical progressions ranging from a rock with Mn-rich calcite in which original igneous textures are still discernable to dark-brown, granular material with up to 50 vol % Mn and Fe oxides (Fig. 9A). Minor calcite is commonly preserved within the rare earth pseudomorphs, although most pseudomorphs exhibit increased porosity, as calcite was dissolved during weathering. Ilmenite, potassium feldspar, fluorapatite, and barite are generally resistant to weathering in the moderately weathered samples.
Manganese oxides initially replaced the cores of granular Mn-rich calcite (Fig. 9A) grains as well as larger interstitial Mn-rich calcite grains. The Mn oxides have variable crystal habits and exhibit bladed, sheet-like, or botryoidal textures (Fig. 9B, C). Manganese oxides contain up to 2.7 wt % Na, 5.5 wt % Ca, 1.9 wt % Si, 4.0 wt % Ba, 12.0 wt % Pb, and 7.5 wt % Fe. Iron sulfides were progressively replaced by hematite and goethite (Fig. 9D). Iron oxides contain up to 5.5 wt % Si, 4.4 wt % Na, 3.0 wt % Zn, and minor Mn, Al, and Ca. Biotite exhibits variable alteration to Fe oxides.

Ancylite makes up 6–40 vol % of moderately weathered carbonatite. With progressive weathering, ancylite occurs as loosely bound, subhedral to euhedral grains (Fig. 10A) that can exhibit etched crystal faces. Ancylite is intergrown with or replaced by Sr-Ca-REE phosphate, and it is also commonly encapsulated by Fe and/or Mn oxides (Fig. 10). Ancylite contains up to 5.5 wt % Si, 4.4 wt % Na, 3.0 wt % Zn, and minor Mn, Al, and Ca. Biotite exhibits variable alteration to Fe oxides.

Strongly weathered mineralogy (stage V): Stage V consists of the most advanced stages of weathering resulting in lateritic soil conditions. It was not directly investigated as a part of this study. The mineralogical details of this advanced weathering can be found in Andersen et al. (2017) and Van Rythoven et al. (2020). In summary, stage V consists of very fine to fine-grained hydrous Al phosphates goyazite and florencite. Also present are botryoidal Fe and Mn oxides as well as oxidized REE phases such as cerianite and hydrous REE-bearing minerals such as rhabdophane (Table 1; Andersen et al., 2017; Van Rythoven et al., 2020). The normalized REE contents are variable in the strongly weathered carbonatites, especially concerning the heavy REEs (HREEs; Fig. 11).

Geochemical changes due to weathering

Mineral reactions during weathering, most importantly the loss of calcite and strontianite at the Bull Hill carbonatite, resulted in increased porosity and concentration of weathering-resistant minerals. Rock chemical compositions change correspondingly, as shown for major and minor elements (App.). The least weathered carbonatite contains, on average, 27.9 wt % CaO and 7.68 wt % SrO, while moderately weathered carbonatite contains, on average, 2.57 wt % CaO and 4.55 wt % SrO.
12

HUTCHINSON ET AL.

% SrO (App.), demonstrating open-system dissolution and loss of calcite and strontianite. Carbon concentrations also decrease, from an average of 8.37 wt % in the least weathered carbonatite to an average of 4.59 wt % in the moderately weathered samples. Manganese, on the other hand, is progressively concentrated in residual Mn oxides during weathering and increases from an average of 2.62 wt % in the least weathered carbonatite to an average of 7.13 wt % MnO in moderately weathered carbonatite (App.), an increase of 172%. The average sulfur concentration in carbonatite decreases from 6.63 wt % in the least weathered, which contains sulfides, to 0.49 wt % in the low-carbonate-bearing, moderately weathered carbonatite, suggesting that most sulfur was transported out of the local system during weathering. The remaining sulfur is hosted by barite, which remained stable in the weathering environment. Iron (III) averages 3.24 wt % in the least weathered carbonatite but is below detection (using EDS) in the most moderately weathered carbonatite. Iron (III), however, increases from 1.86 wt % in the least weathered carbonatite to 13.70 wt % in the low-carbonate, moderately weathered zone. Concentrations of high field strength elements (HFSEs) such as Hf, Nb, Ti, and Zr increased with increasing weathering (App.) because of their preferred residence in weathering-resistant minerals (MacLean and Kranidiotis, 1987). REE contents in carbonatite increase with progressive weathering (Fig. 11).

Porosity generation and isocon analysis

Porosity generation was first observed in minor amounts in stage II where burbankite was replaced by other minerals such as ancylite and parasite/synchesite (Fig. 4C-F). This incipient porosity generation contributes to approximately 7–8% porosity measured in the least weathered carbonatites (Fig. 12A, B). In addition to the geochemical changes related to weathering, petrographic observations document an additional increase in porosity during weathering of the carbon-

Fig. 9. Backscattered electron images of replacive textures of Mn and Fe oxide minerals in moderately weathered carbonatite. A) Mn oxide replaced cores of Mn-bearing calcite, with secondary interstitial Pb-bearing Mn oxide from 143 m. B) Lead-bearing Mn oxide with amorphous, slightly crustiform texture. The Mn oxide replaces Mn-rich calcite and occurs interstitial to Mn-rich calcite grains. C) Sheet-like and botryoidal Mn oxide from 135 m. D) Iron oxide replacing cubic pyrite and spreading beyond the pyrite boundary (144 m). Abbreviations: anc = ancylite, Fe-ox = iron oxide, Mn-cal = Mn-rich calcite, Mn-ox = manganese oxide, Mn-ox (Pb) = lead-bearing Mn oxide.
REE ENRICHMENT, BEAR LODGE, WYOMING

atite due to the dissolution of calcite and strontianite as well as the replacement of Mn-rich calcite by Mn oxides (Fig. 9). The moderately weathered carbonatite has an average porosity of approximately 50% (Fig. 12C, D). The weathered samples are more consolidated (i.e., less granular) than most of the material in the zone sampled and, therefore, provide minimum porosity values (i.e., more granular samples have higher porosity).

Mass balance calculations and diagrams are used to define and illustrate element redistribution in altered rocks (Gresen, 1966; Grant, 1986). Isocon studies (e.g., Grant, 2005; Guo et al., 2009; Hilchie et al., 2018) use element concentrations of least altered and altered material to better visualize data and to circumvent the need for volume measurements (e.g., Gresen, 1966). However, this study uses QEMSCAN to measure the observed porosity in weathered samples (see Figs. 4, 9, 12) to calculate concentration factors and to clarify element redistribution in carbonatite during weathering (Fig. 13). Using the average porosity measurements (Table 2), a hypothetical concentration of a conserved element—one that has not been removed from a reference volume during alteration—can be calculated with the following equations:

\[ C_1 \times V_1 = C_2 \times V_2 \]  
\[ C_1 \times 92\% = mC_1 \times 50\% \]

(1)
(2)

where \( C_1 \) and \( C_2 \) denote the concentration of the conserved element in the least and moderately weathered carbonatite, respectively. The numeric values \( V_1 \) and \( V_2 \) represent the total rock volume percent in the mildly porous, least weathered carbonatite (92%; Fig. 12A, B) and the average rock volume percent of the highly porous, moderately weathered carbonatite (50%; Fig. 12C, D), respectively. Lastly, \( m \) is the factor by which the original concentration of a conserved element increases due to weathering. Higher porosity in more weathered carbonatite would yield a higher concentration factor. For example, a weathered carbonatite porosity of 70% would result in a conserved element concentration factor \( m = 3.1 \).

The isocon plots (Fig. 13) are therefore shown with two trend lines, \( m = 1.8 \) and \( m = 3.1 \), to account for the expected lower and upper limits of porosity variation at Bear Lodge as determined by the QEMSCAN porosity measurements (e.g., Fig. 12). The observed conservative elements best fit line has a slope of \( m = 1.7 \) (Fig. 13). This line is a best fit for the HFSEs: Hf, Zr, Nb, Ta, and TiO₂, which are expected to behave conservatively during weathering (Grant, 1986; MacLean and Kranidiotis, 1987; Lottermoser, 1990; Morteani and Preinfalk, 1996).

![Fig. 10. Textures of ancy late and the SCRp mineral in moderately weathered carbonatite. A) Backscattered electron image of subhedral ancy late that is loosely bound to other minerals and contains iron oxide growing on mineral facets (at 133-m depth). B) Ancy late intergrown with and partially replaced by SCRp. SCRp is strongly stained by and replaced with Fe oxide (cross-polarized light). C) Fe and Mn oxide minerals replace ancy late and SCRp (automated mineral analysis image). Abbreviations: anc = ancy late, Fe-ox = iron oxide, Mn-ox = manganese oxide; SCRp = Sr-Ca-rare earth element (REE)-phosphate mineral.](http://pubs.geoscienceworld.org/segweb/economicgeology/article-pdf/doi/10.5382/econgeo.4900/5543695/4900_hutchinson_et_al.pdf)
Element and oxide concentrations plotting near or within the bounds of the conservative element (i.e., $m = 1.7$) and $m = 3.1$ trends are likely to have increased in concentration because of rock volume loss (Fig. 13). Elements plotting below the line $m = 1.7$ (e.g., SrO, C, S, CaO, and MgO) are constituents that were variably removed from the system during weathering (Fig. 13A), while those plotting above the $m = 3.1$ trend line (e.g., $\text{Fe}_2\text{O}_3$, Th, $\text{P}_2\text{O}_5$, $\text{SiO}_2$, and $\text{BaO}$) are components concentrated by weathering (Fig. 13A).

Although Al$_2$O$_3$ and K$_2$O plot above the $m = 3.1$ line (Fig. 13A), their error bars are large, and heterogeneous distributions of phases containing both components (i.e., K-feldspar) are likely responsible for this variability. Similarly, SiO$_2$ is mobile in this system, as evidenced by the silification of weathered carbonatite in northern areas of the Bear Lodge dome. The moderately weathered zone is depleted in iron (III), while $\text{Fe}_2\text{O}_3$ increases well above the $m = 3.1$ trend, suggesting that oxidation of Fe$^{2+}$ to Fe$^{3+}$ during sulfide alteration resulted in fixing of iron as Fe$^{3+}$ oxide. Phosphorus also shows a strong increase with weathering and was concentrated in the unidentified SCRp and, to a lesser degree, apatite. Petrographic estimates and automated mineral analyses show that the average abundance of the SCRp phase increases from approximately 1.0 wt % in the least weathered carbonatite to about 2.4 wt % in the moderately weathered carbonatite, while apatite shows a similar percentage increase.

Although thorium is traditionally grouped with the HFSEs, it does not appear to have behaved conservatively during weathering of the Bear Lodge carbonatite, plotting above the $m = 3.1$ line (Fig. 13B). Similarly, the large increase in BaO concentration from the least weathered to the low-carbonate, moderately weathered carbonatite indicates potential barium supergene enrichment. Alternatively, it could indicate spatial variability in hypogene barium distribution.

Fig. 12. False-color porosity maps of the least weathered carbonatite and moderately weathered carbonatite. Samples RBL11-42B (A) and RBL11-45A (B) exhibit lower porosity (shown in blue and green) than the moderately weathered samples RBL11-25Q2 (C) and RBL11-27Q1 (D).

Fig. 11. Rare earth element + Y (REY) chondrite-normalized (McDonough and Sun, 1995) plot of the least, weakly, and moderately weathered carbonatite samples. Saprolitic (i.e., most weathered) carbonatite data is from Van Rythoven et al. (2020).
Rare earth elements plot within the conserved element field (Fig. 13B), with the middle rare earth elements (MREEs), including Sm, Eu, Gd, Tb, and Dy, showing the greatest enrichment. Europium and Gd plot directly on the $m = 3.1$ trend line (Fig. 13B). Other than the slight increase in MREE concentration, the geochemical data do not indicate differential mobilization of LREEs versus HREEs between the least altered carbonatite (stages I and II) and moderately weathered carbonatite (stage IV; Fig. 11). However, the spread in normalized REE concentrations in the saprolitic (i.e., most weathered) carbonatite are hugely variably, especially concerning the HREEs. The increase in HREE contents in some samples (Fig. 11) indicates a shift in REE mobilization processes, which has been documented as HREE fractionation by Andersen et al. (2017) and Van Rythoven et al. (2020).

**Discussion**

**REE enrichment during preweathering hypogene alteration**

Economic REE occurrences commonly result from late-magmatic, postmagmatic, and/or hydrothermal enrichment of originally REE-rich igneous material (Mariano, 1989; Gicré, 1996; Chakhmouradian and Wall, 2012; Williams-Jones et al., 2012). The Bear Lodge carbonatite is no exception, as evidenced by the late magmatic/hydrothermal transformation of burbankite to a multimineralic REE-bearing assemblage (Fig. 14).

Burbankite is a common early crystallizing phase in many carbonatites (Zaitsev et al., 2002; Belovitskaya and Pekov, 2004), including Bear Lodge (Fig. 14), where it is observed as small anhedral inclusions within migmatic Mn-rich calcite. In carbonatites from the Kola Peninsula, burbankite commonly displays pseudomorphic replacement by strontianite, ancyline, and barite (Zaitsev et al., 2015), similar to that observed in the hexagonal pseudomorphs at Bear Lodge. Replacement of burbankite by these minerals (Fig. 14) has been interpreted to result from open-system, late-magmatic, or magmatic-related hydrothermal events (Zaitsev et al., 2002, 2015; Belovitskaya and Pekov, 2004).

At Bear Lodge, burbankite may have become unstable because of decreasing alkalinity in the melt or because of alteration resulting from the influx of late magmatic or hydrothermal fluids (Belovitskaya and Pekov, 2004; Fig. 14). The replacement of migmatic burbankite at Bear Lodge by the ancyline, strontianite, barite, and synchysite/parasite assemblage (Figs. 4, 14) appears to have occurred prior to weathering, generating early, incipient pore space (~7–8% porosity; Table 2) in the least altered carbonatite. These initial spaces contain microscopic Fe and Mn oxides, and ancyline shows microscopic Fe oxide growths in these voids (Fig. 10), demonstrating the beginnings of weathering on early pore spaces. We propose that this early pore space may have facilitated the infiltration of meteoric fluids in the higher levels of the carbonatite system, leading to greater porosity generation and overall REE enrichment throughout the weathering process (Figs. 11, 14).

**REE enrichment from weathering**

Rare earth element enrichment of carbonatites due to weathering typically occurs through the breakdown of less stable REE-bearing phases, mainly REE-fluorocarbonates. After mineral decomposition in the meteoric environment, the REEs are mobilized, redistributed, and reprecipitated as REE-bearing oxyhydroxides and incorporated into Al phosphates and/or plombogummite (Lottermoser, 1990; Morteani and Preinfalk, 1996). Under meteoric conditions, the LREEs...
may fractionate from the HREEs, and Ce anomalies appear in REE profiles due to the oxidation of Ce$^{3+}$ to Ce$^{4+}$ (Lottermoser, 1990; Andersen et al., 2017). Cerianite is stable under conditions with pH 4–12; however, cerianite stability is highly dependent on redox conditions (Pan and Stauffer, 2000; Loges et al., 2012). Cerianite appears to be stable in an alkaline environment with reduced conditions. As the environment becomes more acidic, it must also become more oxidizing for cerianite to remain stable. Cerianite appears to be less abundant in the Lower Weathering zone of this study than what is reported for the Upper Weathering zone (J. Clark, pers. commun., 2016; Van Rythoven et al., 2020). Thus, the Lower Weathering zone at Bull Hill could have progressed from reduced and alkaline to oxidized and acidic conditions during weathering.

In instances where the REE-bearing phases are less mobile (e.g., phosphates), REE enrichment typically occurs through the dissolution and removal of more soluble gangue minerals like calcite and strontianite in the Bear Lodge carbonatite. The Bull Hill zone demonstrates an initial increase in REEs in the weakly and moderately weathered carbonatites (stages III and IV; Fig. 11) through carbonate dissolution (Fig. 9) and sulfide oxidation. This resulted in generation of significant porosity (Fig. 12C, D; Table 2) and passively increased the REE concentrations by approximately two to three times (Figs. 11, 13A). The MREEs show the greatest variability in concentration (Fig. 12B), which cannot completely be accounted for by the breakdown of burbankite, which is dominated by the LREEs (Moore et al., 2015). Burbankite constitutes approximately 10 vol % of the least weathered carbonatite and would have a REE grade of about 0.53−1.7 wt %, based on the REE content (5.3−17 wt %) of magmatic burbankite inclusions within calcite. This grade is less than that measured in the least weathered carbonatite (5.38 wt %). Additional REEs may have been contributed by dissolution of magmatic calcite, which Olinger (2012) has determined to contain up to 1,000 ppm REEs at northwestern Bull Hill. It is also possible that the difference in grade is related to mineralogical heterogeneity in the carbonatite.

In the most weathered carbonatite zones (stage V), the LREEs start to fractionate from the HREEs, as demonstrated by the variability of REE concentrations and the noticeable increase in HREEs in some samples from the saprolitic (i.e., most weathered) carbonatite samples (Fig. 11; Andersen et al., 2017; Van Rythoven et al., 2020). The upper weathering profile at Bull Hill was not examined during this study but has been documented to be dominated by bastnäsite group minerals with lesser monazite, cerianite, and Al phosphates (Andersen et al., 2017; Van Rythoven et al., 2020). The upper weathering profile at Bull Hill was not examined during this study but has been documented to be dominated by bastnäsite group minerals with lesser monazite, cerianite, and Al phosphates (Andersen et al., 2017; Van Rythoven et al., 2020). However, the precipitation of carbonates, such as bastnäsite, is problematic in a lateritic environment that involves low-pH groundwater (Mariano, 1989). Weathered carbonatite REE deposits in lateritic environments, such as Mount Weld and Gifford Creek (Australia) contain REE-phosphates as the main REE phas-
Enrichment of REEs in carbonatite systems by in situ weathering has been demonstrated at Mount Weld and Gifford Creek (Australia) as well as Catalão I (Brazil) (Lottermoser, 1990; Morteani and Preinfalk, 1996; Mitchell, 2015; Slezak et al., 2021). The ore endowment of these deposits was significantly increased through laterization caused by extended periods of exposure to humid, tropical environments during the Paleogene (Oliveira and Rosely, 1998; Pillans, 2007). Similarly, the Bear Lodge carbonatite in northeastern Wyoming has undergone subaerial exposure resulting in a deep weathering profile, which when combined with late magmatic-hydrothermal processes (Fig. 14), has enhanced the grade of REE mineralization in the deposit (Figs. 11, 13).

Environmental conditions for weathering at Bear Lodge

Environmental conditions in the Bear Lodge Mountains at the precise time of early alkaline silicate and carbonatite magmatism (early to middle Eocene) are uncertain. However, the laterite cap at Mount Weld (Australia) contains late-stage carbonate and silica, like that observed at Bull Hill. This mineral assemblage may indicate a transition from a tropical, humid to a more arid climate (e.g., Fig. 15; Lottermoser and England, 1988; Lottermoser, 1990). Nearby areas of southwestern, central, and much of northern Wyoming contain extensive lacustrine deposits (Snake, 1993), suggesting that the Bear Lodge area was subaerially exposed. Furthermore, Lillegraven (1993) suggests that this portion of Wyoming experienced widespread and intense erosion between 42 and 37 Ma (Fig. 15), which is partially contemporaneous with the late alkaline magmatic activity (40–38 Ma) in the Bear Lodge region (Fig. 15; Duke, 2005). The unconformity between the late Eocene-Oligocene White River Formation and the underlying Paleogene intrusive rocks and pre-Cenozoic rocks, including the Spearfish Formation, the Minnelusa Sandstone, and the Sundance Formation, indicates that these rocks were exposed at the surface prior to deposition of the White River Formation (Staatz, 1983; Lillegraven, 1993). Thus, the late Eocene to Oligocene transition probably represents the first period of significant weathering that could have affected the carbonatites (Fig. 15).

In addition, the Oligocene Ogallala Formation is preserved in a graben adjacent to the Bull Hill diatreme and contains clasts of igneous rocks potentially derived from the deposit area (Staatz, 1983). This further indicates subaerial exposure and active erosion and suggests the rocks at Bull Hill have been exposed since the Oligocene and potentially weathered for at least the last 12 m.y. (Fig. 15).

Of note is that Moore et al. (2015) reported high $\delta^{18}$O$_{V-SMOW}$ values (~18‰; Vienna-standard mean ocean water) from the Bull Hill carbonatite samples that support the mixing of meteoric water with late magmatic-hydrothermal fluids during emplacement of the carbonatite. Weathering at Bear Lodge from groundwater infiltration likely occurred between the late Eocene and the Holocene, resulting in an increased ore.

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**Fig. 15.** Regional and local geomorphological and climatic events and affecting the Black Hills, Wyoming.
tenor through the removal of easily dissolvable carbonate gangue minerals. Continued weathering in a potentially more semiarid environment, at least episodically since the Oligocene, likely created a stable environment for the formation of supergene REE-fluorocarbonate minerals (e.g., bastnasite) at Bull Hill/Bear Lodge.

Conclusions

Investigations of the textural, mineralogical, and geochemical changes within a continuous drill core interval of carbonatite suggest that late magmatic-hydrothermal porosity generation and in situ weathering led to supergene REE enrichment of approximately two to three times at Bull Hill. Aneidine is the dominant REE-bearing mineral throughout the drill core interval, occurring in the least weathered carbonatite, where it appears to replace magmatic barytinite, as well as in the moderately weathered intervals of carbonatite. The least altered carbonatite displays low porosity (~7–8%) with only trace oxidation of sulfides and minor precipitation of Fe oxides. As weathering intensity increases, carbonatite exhibits stronger sulfide oxidation, manganese oxide replacement of Mn-rich calcite, and partial dissolution of calcite. REE concentrations increased primarily because of volume loss from carbonate mineral dissolution. The most weathered occurrences of carbonatite in the core interval studied lack primary igneous carbonate minerals and consist largely of Fe and Mn oxides with other rare earth minerals (e.g., cerianite and REE-fluorocarbonates), suggesting subaerial exposure to oxidizing, meteoric fluids.

Acknowledgments

Support for this research was provided by Rare Element Resources, the Society of Exploration Geologists, the Department of Geology and Geological Engineering at Colorado School of Mines, and a Science Foundation Ireland Research Professor grant to Murray Hitzman. Thomas Meoneck and James Clark are both thanked for their reviews and contributions throughout the duration of this project. A special thanks to Jock Harmer, whose discussions and insights improved this work. We also thank the associate editors, Paul Spyry and Anton Chakhmoradian, Jaroslav Dostal, and two anonymous reviewers for their comments and reviews, which enhanced the quality of this manuscript.

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