CRITICAL MINERALS

BELOW NORTH DAKOTA'S ANCIENT SUBTROPICAL SOILS

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MINERAL SUPPLIES AS CRITICAL AS EVER

As discussed in Part I (Moxness, 2023), the pressure on the United States to secure reliable sources of critical minerals is a product of several converging factors. American imports are subject to geopolitical tensions with countries that produce the world's supply of minerals. Even if the threats to restrict exports to the U.S. are never implemented, the lack of domestic production weakens the U.S. position in trade negotiations and undermines foreign policy. Reshoring U.S. manufacturing, one of the few consistent bipartisan priorities in recent years, does little to fix the overall strategic vulnerability if the raw materials needed are still mostly sourced from adversarial foreign countries. In 2020, China announced sanctions on U.S. defense contractors Lockheed Martin and Raytheon to restrict their access to rare earth elements over tensions regarding arms sales to Taiwan, which Chinese state-affiliated media would later credit for delays in F-35 fighter jet production (Asia Times, 2022).

The latest critical mineral chess pieces involve gallium and germanium, which are used in the manufacture of semiconductors, vital components in most high-performance technology. China announced export restrictions on these two elements in July of 2023, likely as retaliation for the US CHIPS and Science Act of 2022, which limited the export of microchips and advanced technology to China. The United States imports all of its gallium and most of its germanium, and more than half of each was sourced from China last year (USGS, 2023). As for the rare earth elements, despite what is now several years of scrambling to develop more domestic production, the United States' only major commercial source remains Mountain Pass Mine in California. Minor additional production of rare earths from monazite in heavy mineral sands in the southeastern U.S. has done little to reduce the reliance on imports, which were up nearly 40% between 2021 and 2022, 74% of which overall were from China (USGS, 2023).

The fact that the U.S. needed to import more rare earths last year, despite its own production climbing, illustrates the other force driving the recent wave of critical mineral exploration - demand is outpacing supply. Even if tensions between the U.S. and China ease, some estimates forecast a global undersupply of magnetic rare earths (neodymium, praseodymium, dysprosium, terbium) of nearly 62,000 metric tons annually by 2030 and over 246,000 tons by 2040, as it will be difficult for new mines to meet an estimated 7% annual demand growth (Mining.com, 2023). In the near future, countries could limit exports to the U.S. not because of geopolitical posturing, but to prioritize short supplies for their own industries.

SEMI-RARE ELEMENTS WITH VERY RARE ORES

The United States is fortunate to have a world-class rare earth deposit at Mountain Pass mine, which hosts an ore with an average total rare earth oxide grade of 8.9% (Liu et al., 2023). Additional promising resources like Round Top (Texas), Bear Lodge (Wyoming), Elk Creek (Nebraska), and Bokan Mountain (Alaska) are at varying stages in the long road from resource assessment to realized production. Even with the identification of these new traditional hard rock deposits, the U.S. Department of Energy (DOE) has been steadily investing in characterizing the critical mineral contents of U.S. coal and developing extraction technologies for coal-hosted minerals. It has used 300 parts per million (ppm) rare earth elements as a rough threshold for potentially promising concentrations in coal. Why would the DOE propose 300 ppm as a promising concentration in coal when an American mine is actively excavating a hard rock ore containing 250 times that?

Coal has some advantages over hard rocks as a mineral ore. Not all ores of the same overall grade are created equal, since different ores contain different proportions of each element and certain rare earths are 1,000 times more valuable than others. Cerium and lanthanum are two of the "least rare" rare earths (Table 1), and market prices reflect that. Oxides of these two elements are worth less than a dollar per pound and make up over 83% of the total rare earth content of Mountain Pass carbonatite, which is effectively economic solely on its neodymium and praseodymium production. These four elements, along with samarium and europium, represent the light (by atomic weight) rare earth elements. The more valuable, "rarer", heavy rare earths make up just 0.49% of the total rare earth element content at Mountain Pass and are not even currently economically recoverable using existing processing techniques. By contrast, the average North Dakota lignite with rare earth concentrations of 300 ppm or greater can be as much as 50% heavy rare earths and scandium (a highly valuable rare earth not traditionally grouped with the light or heavy elements as it does not occur in hard rock ores), with an average of 29%.

HOW ORE TYPE INFLUENCES ECONOMICS

Rare earths and other critical mineral commodities can best be thought of as elements locked inside of minerals locked inside of rocks. To get these elements out of the ground and into a smartphone, wind turbine, electric car, or nuclear submarine requires mining, beneficiation, leaching, separation, refining, alloying, and manufacturing. Mining rock is a relatively straightforward process, although it is marginally more costly to mine veins of hard rock in the mountains than it is to mine a flat-lying lignite just below the surface on the plains, especially if that lignite is already economically mined to supply a thermal power plant. The most cost savings are to be found as the elements are extracted from the minerals. Monazite, xenotime, bastnäsite, and other REE-bearing minerals found in hard rock are expensive to break down. This can involve high temperature roasting and acid digestion after ultra-fine grinding and gravity or magnetic separation. As you leach the rare earth elements from these minerals, alongside them are radioactive contaminants uranium, thorium, and all the associated costs of handling radioactive waste. Coal may be far less enriched in rare earth elements than these traditional ores, but it is also typically less enriched in the contaminants, making it far easier to avoid indirectly concentrating uranium and thorium above strict regulatory thresholds.

Since most of the cost to produce rare earths from traditional ores involves the mechanical breakdown of rock, followed by acid leaching of the primary minerals to release the elements, it's more economic to find a setting where nature has already done most of the work. Placer deposits of heavy mineral sands can be economic where they concentrate rare earth-bearing mineral grains, but the mineral grains themselves still need to be broken down. The most economic deposit, which supplies almost all of the world's heavy rare earth supplies, are ionic clays in South China and Myanmar. Granites in this subtropical climate have been subjected to weakly acidic meteoric waters which become more acidic upon percolation through humus-rich topsoil. The granites break down into primary mineral grains which in turn chemically weather and release rare earth cations into the acidic groundwater percolating downward through the soil profile. The deposits are characterized by the clay mineral kaolinite,

TABLE 1.
The average abundance of elements in the Earth's crust.

Group	Rank	Element (criticals in bold)	Crustal Abundance	Unit
Major Elements	1.	Oxygen	46.1	weight percent (%)
	2.	Silicon	28.2	
	3.	**Aluminum**	8.23	
	4.	Iron	5.63	
	5.	Calcium	4.15	
	6.	Sodium	2.36	
	7.	**Magnesium**	2.33	
	8.	Potassium	2.09	
	9.	**Titanium**	0.56	
	10.	Hydrogen	0.14	
	11.	Phosphorus	0.11	
Minor Elements	12.	**Manganese**	950	parts per million (ppm)
	13.	Fluorine	585	
	14.	**Barium**	425	
	15.	Strontium	370	
	16.	Sulfur	350	
	17.	Carbon	200	
	18.	**Zirconium**	165	
	19.	Chlorine	145	
	20.	**Vanadium**	120	
	21.	**Chromium**	102	
Trace Elements	22.	**Rubidium**	90	
	23.	**Nickel**	84	
	24.	**Zinc**	70	
	25.	**Cerium** (Rare Earth Element)	66.5	
	26.	Copper	60	
	27.	**Neodymium** (Rare Earth Element)	41.5	
	28.	**Lanthanum** (Rare Earth Element)	39	
	29.	**Yttrium** (Rare Earth Element)	33	
	30.	**Cobalt**	25	
	31.	**Scandium** (Rare Earth Element)	22	
	32.	**Lithium**	20	
	33.	**Niobium**	20	
	34.	Nitrogen	19	
	35.	**Gallium**	19	
	36.	Lead	14	
	37.	Boron	10	
	38.	Thorium	9.6	
	39.	**Praseodymium** (Rare Earth Element)	9.2	
	40.	**Samarium** (Rare Earth Element)	7.05	
	41.	**Gadolinium** (Rare Earth Element)	6.2	
	42.	**Dysprosium** (Rare Earth Element)	5.2	
	43.	Argon	3.5	
	44.	**Erbium** (Rare Earth Element)	3.5	
	45.	**Ytterbium** (Rare Earth Element)	3.2	
	46.	**Cesium**	3	
	47.	**Hafnium**	3.0	
	48.	**Beryllium**	2.8	
	49.	Uranium	2.7	
	50.	Bromine	2.4	
	51.	**Tin**	2.3	
	52.	**Europium** (Rare Earth Element)	2.0	
	53.	**Tantalum**	2.0	
	54.	**Arsenic**	1.8	
	55.	**Germanium**	1.5	
	56.	**Holmium** (Rare Earth Element)	1.3	
	57.	**Tungsten**	1.25	
	58.	Molybdenum	1.2	
	59.	**Terbium** (Rare Earth Element)	1.2	
	60.	Thallium	850	parts per billion (ppb)
	61.	**Lutetium** (Rare Earth Element)	800	
	62.	**Thulium** (Rare Earth Element)	520	
	63.	Iodide	450	
	64.	**Indium**	250	
	65.	**Antimony**	200	
	66.	Cadmium	150	
	67.	Mercury	85	
	68.	Silver	75	
	69.	Selenium	50	
	70.	**Palladium**	15	
	71.	**Bismuth**	8.5	
	72.	Helium	8	
	73.	Neon	5	
	74.	**Platinum**	5	
	75.	Gold	4	
	76.	Osmium	1.5	

77-118. Others under 1 ppb (Source: CRC, 2008) a byproduct of weathering aluminosilicate minerals like feldspar. The positively charged rare earth cations, 50% or more of which are the heavy elements, stick to the negatively charged surfaces of the clays but are easy to wash back into solution, which is why this deposit is economic at grades as low as 500 ppm (Bao and Zhao, 2008).

Organic matter can also "catch" rare earths and other elements from descending groundwater. Coal, in particular low rank "brown coal" like lignite, contains oxygen function groups and sites for bonding cations as they infiltrate through. Coal can also contain rare earths in the form of tiny grains of primary minerals from clay and silt that washed or blew into the swamp, but it's the organically bound elements that are easiest to extract. Leaching experiments on rare earth-enriched North Dakota lignite at the University of North Dakota College of Engineering & Mines Research Institute (CEMRI) shows that the elements are indeed mostly organically associated and therefore weakly held within the coal and simple (cheap) to extract (Laudal et al., 2018). Gallium and germanium are two other top candidates that could one day be commercially produced alongside rare earths from lignite in the U.S. Gallium, germanium, and the rare earths dysprosium, terbium, and scandium are some of the highest value commodities on the critical minerals list, with market prices in the range of $100 to $500 per pound.

The case for critical mineral production from lignite is simple: easy extraction of high value trace elements. They just need to be found in slightly elevated concentrations, or produced as a byproduct where mining costs are already covered. What does "slightly elevated" look like? The DOE's 300 ppm figure is probably less than twice the rare earth concentrations in the dirt below your feet right now, as the average abundance of rare earths in upper continental crust (rocks and sediment near the Earth's surface) is 182 ppm (McLennan, 2001). The important distinction is most of that is locked up in those resistant primary mineral grains, while in coal it is weakly bound to the organics. With the latest research showing how easy rare earths are removed from lignite, and the added value of gallium and germanium, CEMRI has evaluated that critical mineral extraction from lignite at an existing mine could be economic far below the 300 ppm rare earth element concentrations initially proposed by the DOE. To open a new mine or reopen an abandoned mine, concentrations might need to be somewhat higher. Double the "average" upper crustal abundance is a good place to start, with anything over 364 ppm considered enriched (Dai et al, 2015).

CONDITIONS FOR ENRICHMENT IN NORTH DAKOTA

While granitic bedrock in South China has been weathering into the world's foremost heavy rare earth deposit, the sandstones, siltstones, mudstones, and claystones near the surface of southwestern North Dakota have also been leaching their rare earth elements. Part I described the phenomena where lignites near the tops of buttes often contain elevated rare earth element concentrations. Although spot concentrations of lignites in these settings can exceed 1,000 ppm rare earths, on par with the clay deposits in South China, the zones of enrichment are only a few inches thick; far thinner than the clay deposits mined overseas, which can be over 30 feet thick. Part of the discrepancy is due to the parent materials. The clays in South China formed as concentrated weathering products from granites that contained roughly 200 to 300 ppm rare earth elements (Li et al., 2017), while clastic sedimentary rocks in North Dakota are likely much closer to average upper continental crust (182 ppm). The more important factor is the climate.

Rare earths and other critical elements are mobilized by acidic waters, and the most acidic soils are found under lush vegetation where the climate is warm and wet. Long-term landscapes subjected to subtropical climates are required to naturally break down the plethora of different rare earth bearing mineral grains and concentrate them in coals or ionic clays below. Some uplands in southwestern North Dakota could have been weathering for hundreds of thousands, if not millions of years, but the climate has been anything but subtropical during that period. Glaciers may have been visible on the northeastern horizon at points during the Quaternary, which includes the last ice age starting 2.58 million years ago. A much warmer and wetter climate would be required to weather large volumes of sediment intensely enough to produce thicker zones of significant rare earth enrichment. Fortunately, the climate of North Dakota's more distant past was far less temperate.

THE BEAR DEN AND RHAME BED WEATHERING PROFILES

Exposures across the central part of western North Dakota preserve the record of one of the warmest and wettest climate events in Earth history, the Paleocene-Eocene thermal maximum, which occurred approximately 56 million years ago. The acidic waters that percolated through the soil profile during this period intensely weathered the feldspar and smectite-rich sediments to form a thick sequence of kaolinite, which primarily appears today as a bright white bed with orange iron staining that is easily traced across Dunn, Stark, and adjacent portions of the surrounding counties (fig. 1). Another thick interval of bright, kaolinized sediment called the Rhame bed occurs 1,000 feet lower in the stratigraphic column. It represents the uppermost portion of Slope Formation, marking the contact with the overlying Bullion Creek Formation. This weathering zone is older, having formed around 62 million years ago, outcropping today across Golden Valley, Slope, Bowman, Hettinger, Grant, and Morton counties.

The two weathering profiles are broadly analogous; both typically vary from 15 to 30 feet thick, are brightly colored due to leaching (figs. 2 and 3), rich in kaolinite, and often contain pedogenic silcretes. The Bear Den has been formalized as a member of the Golden Valley Formation (Hickey, 1977), but the Rhame has been referred to as a bed (Wehrfritz, 1978) despite it often containing multiple beds of sandstone, siltstone, mudstone, claystone, or lignite within it. It is probably more appropriate to consider the Rhame a zone, although it is thick, widespread, and consistent enough that we are considering it for elevation to member status.

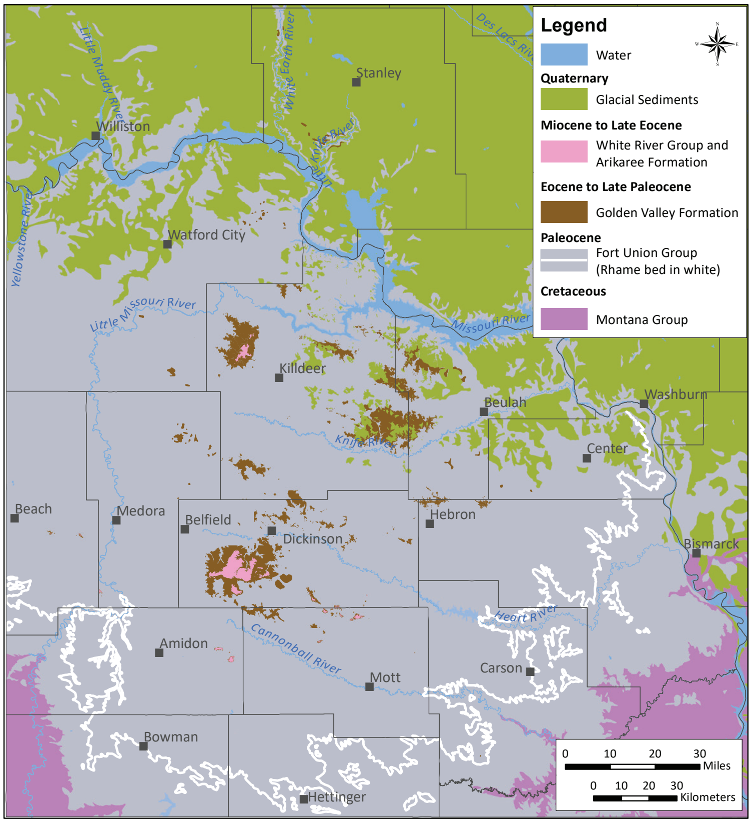

FIGURE 1.
The generalized surface geology of western North Dakota. The Bear Den Member occurs at the base of the Golden Valley Formation along the contact with the underlying Fort Union Group. Geology modified from Clayton and others (1980), with additional data from the NDGS 24K surface geology map series.

FIGURE 2.
The Bear Den Member of the Golden Valley Formation outcrops in southwestern Dunn County.

FIGURE 3.
The Rhame bed outcrops in north-central Slope County.

The Bear Den Member has been well studied as it represents one of the most detailed records of one of Earth's most significant climate events (Harrington et al., 2005; Clechenko et al., 2007). Large injections of carbon into the atmosphere, likely from volcanism in the North Atlantic, caused abrupt warming across the globe. Temperatures within the interior U.S. were already much warmer than today but rose another 5°C (9°F) for a period of up to 200,000 years (Wing et al., 2005; Murphy et al., 2010). The Rhame bed has been studied in less detail, but there is no known global thermal event known to have occurred between 61 and 63 million years ago, suggesting instead that it represents an extended pause in deposition. The relatively short, high intensity weathering of the Bear Den verses the longer, more moderate weathering of the Rhame bed produced remarkably similar profiles.

Both weathering zones have historically been the subject of mineral exploration, but for the clay itself, and not the critical minerals below. Kaolinite is commonly known as "pottery clay," and both the Bear Den Member and Rhame bed have been utilized in the state for the manufacture of ceramics (Murphy, 1995). A brick and tile plant operated just to the north of the town of Hettinger from the late 1930s through the mid-1960s that likely utilized the Rhame bed, and the Hebron Brick plant still mines the Bear Den Member today. The Fargodome and many other brick structures in the state are built with clays from fossil soils formed during a far more tropical, ancient North Dakota.

THE NDGS INVESTIGATES (PART II)

The North Dakota Geological Survey examined these weathering zones in the early 2010s, this time for their alumina contents. Aluminum is an immobile element that is concentrated as other elements are leached away by weathering. Murphy (2013) evaluated both horizons to determine the suitability of manufacturing ceramic proppant from these kaolinite-rich units, finding individual samples contained up to 34% alumina in the Bear Den Member and 27% in the Rhame bed. He also used X-ray diffraction to collect data on many other elements which a few years later would be classified as critical to the national security of the United States. Murphy reported enrichment in arsenic, cobalt, hafnium, magnesium, nickel, and titanium in some clay samples. Also included in this report were analyses of one rare earth element, yttrium, which were generally low (around 15 ppm), but Murphy targeted the most intensely weathered sediment which contained the most residual aluminum and had little reason to look lower in the profile for where the other mobile trace elements leached to. By 2015, rare earth production from coal had become a topic of national interest, and the NDGS began its broad-based characterization study of North Dakota lignites (Kruger, 2015).

Five years and over 1,000 lignite samples later, the NDGS had found some promising rare earth concentrations scattered across the southwestern part of the state, but a cohesive exploration model was still elusive. It seemed apparent that long-term, low-intensity weathering of stable uplands could produce slight, thin enrichment in the coals below, but this model could not explain the seemingly random, higher-grade enrichment seen in some coals that were not associated with uplands. An 18-inch-thick lignite in the Logging Camp Ranch area of Slope County was especially perplexing, as two or three thick coals (the Harmon, Hanson, and H lignites) occurred above it and were not enriched. Outcrops of the Bear Den and Rhame bed had been investigated, but early sites didn't contain well developed lignites and the organic-rich mudstones sampled were only slightly enriched.

In August of 2021, the NDGS was looking to round out the stratigraphic and geographic distribution of our lignite sampling and visited outcrops in Dunn and Stark counties, two of which contained lignites within the Bear Den Member. Samples from these two outcrops, representing the same interval over 50 miles apart, collected within a few hours of each other, were some of the highest rare earth concentrations seen in seven years of sampling (fig. 4). This included the first sample of significantly enriched coal during the project (defined as ten times the average concentrations of the upper continental crust, or over 1,820 ppm rare earth elements). 2022 was marked by visits to another 15 outcrops where the Bear Den was exposed. By combining all of the sample results from these locations on a composite stratigraphic column (fig. 5), a clear picture emerges: maximum enrichment near the base of the weathering zone, consistent with what would be expected in a model involving critical element mobilization within an ancient weathering profile. More significantly enriched samples were found, as high as 2,570 ppm rare earths at the Hebron Brick Company pit (Murphy et al., 2023).

These elevated concentrations also prompted more intense investigation of the Rhame bed. Although several previous mappers had suggested it was not exposed in the Logging Camp Ranch area, the NDGS was able to correlate it northeastward where it is often very subtle in appearance. It was found that the Rhame bed directly overlies the enriched lignite in that area, explaining how it could have become so enriched while the coals above it (deposited after the Rhame bed weathered) were not. Extensive lateral sampling of this lignite produced 15 enriched samples (over 910 ppm rare earth elements) and three significantly enriched samples, as high as 2,792 ppm in the same relative position as the enriched Bear Den samples, ie., at the base of the weathering profile.

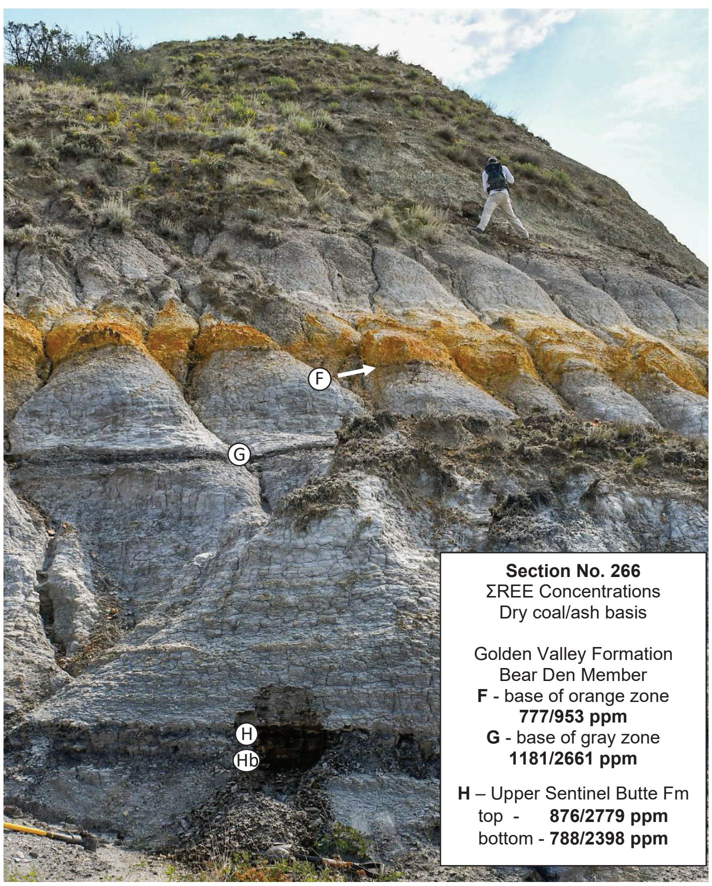

FIGURE 4.
Sampling the Bear Den Member and uppermost Sentinel Butte Formation in southwestern Dunn County in August 2021. Four samples from three thin lignites in the lower part of the weathering profile contained total rare earth element (ΣREE) concentrations averaging 903 ppm, nearly 5 times higher than average rocks and sediment near the Earth's surface.

WHAT TO DO WITH AN EXPLORATION MODEL

The 1,706 NDGS samples analyzed so far would only be a tiny fraction of what would be required to characterize the rare earth contents of North Dakota's lignites via randomized sampling. Now that we have a somewhat cohesive explanation for the rare earth element distribution in the Williston Basin, we are able to narrow down exploration within the 1,800 feet of lignite-bearing rock to two 30-foot intervals that should contain the most enrichment. This is still a very large area. The Bear Den Member, despite being mostly eroded away, is still present over approximately 340 square miles of the state, often within 100 feet or less of the surface and easily explored through drilling. The Rhame bed is more difficult to quantify, but its area is likely several times more than that of the Bear Den Member. It underlies most of the western half of the state and is well exposed and well-developed along the southern rim of the basin, but it is buried by several hundred feet of younger sedimentary rock in middle portions of the basin and obscured by glacial cover where it would outcrop along the northern rim. Despite this, there are hundreds, likely thousands, of yet unexplored outcrops of these two horizons and certainly thousands of fields and pastures where they are present just below the surface.

The expansive nature of these weathered rocks is important if the underlying lignites are ever to one day be commercial targets for critical mineral production. Over much of that area there will be no lignites present below the weathered horizon to uptake the critical minerals as they infiltrated the profile. In other areas lignites will be present but in positions too low for the critical mineral-bearing acidic waters to have reached them, or they were too high and leached away themselves. The most promising possible outcome of exploration is to find a thick, well-developed lignite in the perfect position, just below the base of a strongly weathered profile. Just how much rare earth content should such a coal accommodate? That question remains unanswered, but a nearly optimal example in southeastern Golden Valley County provides some clues. A 17-inch-thick lignite is fairly well-developed below 12 feet of brightly-colored claystone, mudstone, and siltstone, representing the Rhame bed weathering zone (fig. 6). The upper 6.5 inches of lignite are significantly enriched in rare earth elements, and the bottom of the bed is still 653 ppm, 10 times higher than the average U.S. coal (66 ppm; Finkelman, 1993).

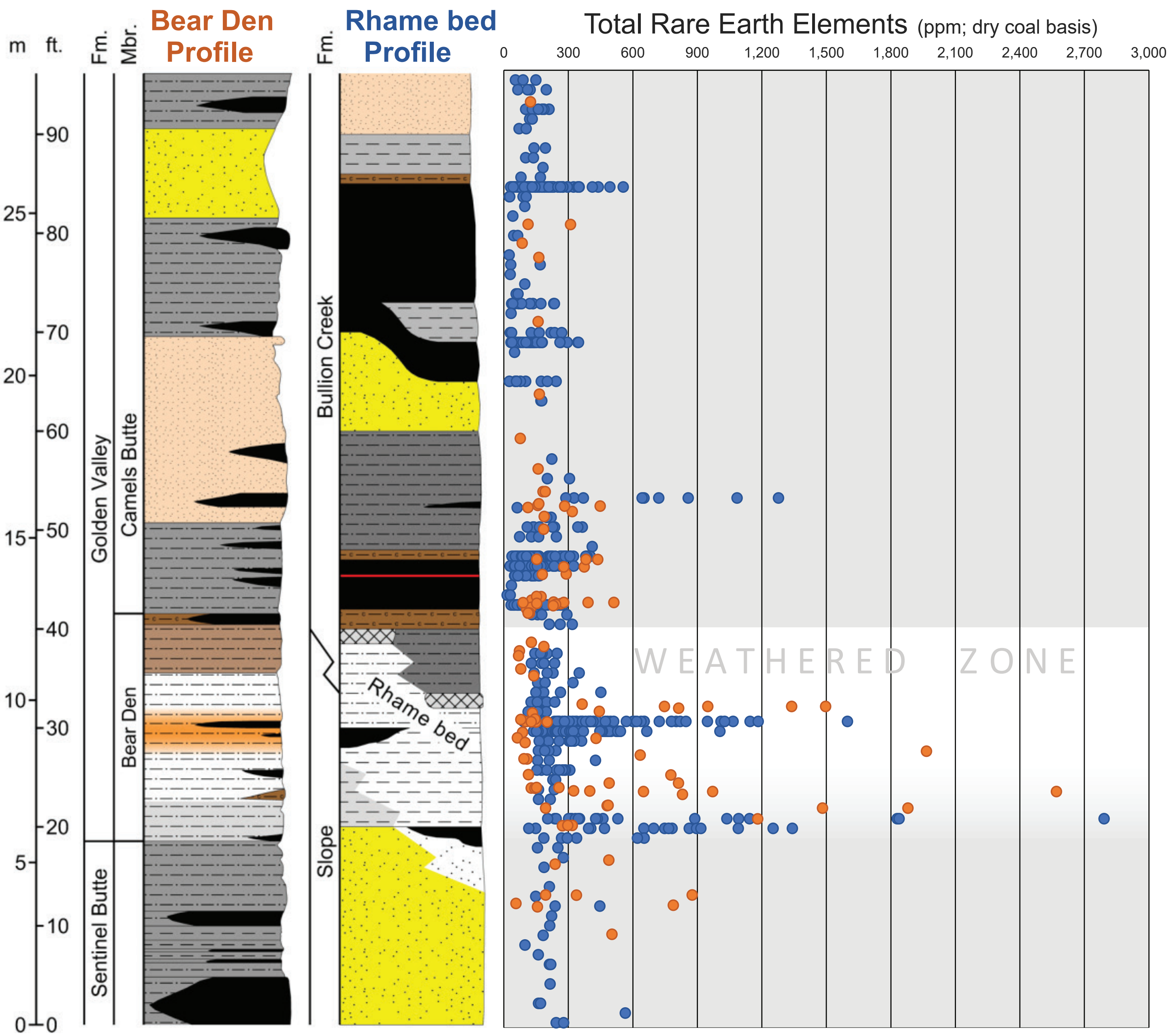

FIGURE 5.

Generic stratigraphic columns of the lower Golden Valley and upper Sentinel Butte Formations (left) and lower Bullion Creek and upper Slope Formations (right). Samples from over 100 sites across southwestern North Dakota are plotted with their rare earth element concentrations, showing enrichment in lignites positioned below the weathered portion of these two profiles. Samples from the Bear Den and Rhame bed profiles are represented by orange and blue dots, respectively (modified from Murphy et al., 2023 and Moxness et al., 2023).

Does the enrichment all the way through the lignite imply some of the weathered rare earths continued downward and dispersed through the underlying profile? If the lignite had been thicker, it would have been enriched at two feet? Three feet? The NDGS continues its exploration to find thicker coals in these settings, as it's difficult to imagine mining a bed only 17 inches thick, especially in rugged badlands terrain, even if it contains some of the highest concentrations reported in the nation. Still, coal 17 inches thick averaging 1,150 ppm contains more rare earth content than five feet of coal at 300 ppm, with less material handling.

The specifics of exactly how thick and how enriched a coal would need to be in order to be developed solely for its critical mineral contents is still speculative, as no one has commercially produced rare earths from lignite before. The U.S. DOE continues its effort to realize critical mineral production from coal-based feedstocks, and there is real potential for an extraction plant to be built in North Dakota in the coming years (Grand Forks Herald, 2023). It makes the most sense to scale this technology at North Dakota's existing lignite mines, where low concentrations are offset by low mining costs, but once the extraction technology is commercialized, the economics of highly-enriched lignites nearby will become much less cloudy, and we will better understand the prospects for these unique coal seams to contribute to the national security of the United States.

FIGURE 6. Sampling a 17-inch-thick lignite below the Rhame bed in southeastern Golden Valley County. Sample locations and total rare earth element (REE) concentrations plotted on the right.

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