Geochemical Atlas of North Carolina Web-Experience: Supplemental Documentation with Analyte Concentration Maps and Histograms

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ABSTRACT

In 1991, the North Carolina Geological Survey (NCGS) first published (revised in 1993) a paperbound geochemical atlas of North Carolina based on the National Uranium Resource Evaluation (NURE) program's stream sediment sample data. Since that time, interactive web services have made the distribution of information to an end-user in digital media more readily accessible and available. Also, since that time the U.S. Geological Survey (USGS), as the NURE database custodian, has made corrections to the database. The NCGS has made the NURE stream sediment data available via an interactive web platform. In addition to the analyte first-order statistics, the NURE program data for each tested analyte at all sample points in the state are available to the internet-based user. Also available are descriptions for each analyte, describing the analytes relevance to North Carolina, to help guide the users' understanding of the sample data. As with all large databases, decisions were made to best manage the distribution of the information. Explanations behind some of those decisions are documented herein. The appendix of this document contains analyte concentration map figures, using a blend of symbologies (graduated colors and proportional symbol sizes) for each of the available analytes, based on the NURE sample data.

PART 1: NURE STREAM SEDIMENT PROJECT AND THE GEOCHEMICAL ATLAS OF NORTH CAROLINA WEB-EXPERIENCE

I. INTRODUCTION

NCGS Bulletin 93

In 1991, Dr. Jeffery C. Reid produced A Geochemical Atlas of North Carolina (revised in 1993), NCGS Bulletin 93 (Reid, 1993), in paper-copy. The <u>Geochemical Atlas of North Carolina Web-Experience</u> is a value-added effort to NCGS Bulletin 93. It has an updated emphasis with respect to two essential considerations: (1) digital technology advances in information distribution since the early 1990s allowing for a more interactive experience for the end-user and (2) modifications and re-processing of the NURE program database for corrections of the original entries that have occurred since original publication. Additionally, updated analyte concentration maps and histogram distributions have been created for each of the available analytes. These maps and graphs aid in trend visualizations that the web-experience alone does not provide.

NURE/HSSR Background

The NURE program provided North Carolina with a regional database from the Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) survey. The NURE program was established in 1974 and terminated in 1984. It was administered by the Grand Junction (Colorado) Office of the U.S. Atomic Energy Commission and succeeding agencies, the U.S. Energy and Development Administration and the U.S. Department of Energy (DOE). The main purposes of the NURE program were to provide the assessment of the nation's uranium resources and to identify areas favorable for uranium mineralization. Although the NURE program was intended to aid in evaluation of potential uranium resources, much of the geochemical data can be used to assess areas for other types of mineral resources and to identify regional geologic and geochemical features. The objective of the NURE program was to define uranium provinces by collecting and analyzing samples of various types of sediments and waters; additional elements were used as pathfinders. The program was intended to outline general regions favorable for uranium mineralization; it was not designed to delineate specific orebodies. Sampling and analytical procedures were optimized for uranium analyses and for rapid, inexpensive determination of pathfinder elements. Except for uranium, analytical precision was sacrificed in favor of analytical speed. Unusual patterns, or anomalies, are difficult to interpret unambiguously. An unusually high concentration of an element surrounded by samples with a more normal concentration can be interpreted many ways without other, more constraining, data, such as regional geologic features (Smith, 2006).

The NURE data are applicable to mineral exploration, agriculture, health, and environmental studies. Applications in state government include resource surveys to assist mineral exploration by identifying geochemical pathways and areas of potential mineralization. Plant growth conditions, disease, and crop productivity are areas where agronomists search for favorable

parameters. Certain trace elements must be present within narrow ranges in soils for optimum plant growth and productivity. Trace elements as a contributing factor to disease are of concern to health professionals. Industry can use pH and conductivity data from stream water samples to site facilities which require specific water quality standards (Reid, 1993).

II. THE DATABASE

Sampling of North Carolina's 126,100 km² (48,688 mi²) of land area was completed and stream sediments at 6,668 sample sites were analyzed before the NURE program was terminated. Sample density averages one sample site per 18.6 km² (7.2 mi²) of land area (Reid, 1993). The database for North Carolina contains 9,240 samples from the 6,668 sites. Sampling was performed by established geochemical exploration procedures as explained in standard texts (Rose and others, 1979), and by Sargent and others (1982). The Savannah River Laboratory prepared the North Carolina samples and analyzed an original group of elements by automated neutron activation analyses. This group includes U, Th, Hf, Ce, Fe, Mn, Na, Sc, Ti, V, Al, Dy, Eu, La, Sm, Yb, and Lu. Contractors analyzed additional elements by atomic absorption and other methods (Sargent and others, 1982). In their report, Fay and Cook (1982) included previously unreported neutron-activation analyses of gold in sediment samples determined at the Savannah Research Laboratory (SRL). In the data used herein, samples in which gold was detected by neutron activation analysis are reported (Reid, 1993).

Sampling and analytical procedures were described by Sargent and others (1982) and are summarized here. Conductivity and pH were measured at each of the stream sampling sites. A minimum of five sediment subsamples were composited from each stream site. Approximately 400 grams of sediment passing a 400 μ m screen (U.S. standard 40 mesh) were collected at each sampling site. Sediment samples were dried at 105°C, sieved to <149 μ m (100 mesh), blended, coned, and quartered. One and one-half gram aliquots of the <149 μ m material were packed into ultrapure polyethylene capsules for analyses. The encapsulated samples, in batches of 25, including one standard, and one blank, were loaded into the NAA pneumatic system. Transport into the irradiation assembly and counting stations and the collection and processing of data were computer-controlled (Sargent and others, 1982; Reid, 1993).

In addition to pH and conductance, the complete list of analytes measured in North Carolina include (from increasing atomic number, or Z value): lithium [Li], beryllium [Be], fluorine [F], sodium [Na], magnesium [Mg], aluminum [Al], phosphorus [P], potassium [K], calcium [Ca], scandium [Sc], titanium [Ti], vanadium [V], chromium [Cr], manganese [Mn], iron [Fe], cobalt [Co], nickel [Ni], copper [Cu], zinc [Zn], arsenic [As], selenium [Se], strontium [Sr], yttrium [Y], niobium [Nb], molybdenum [Mo], silver [Ag], tin [Sn], cesium [Cs], barium [Ba], lanthanum [La], cerium [Ce], samarium [Sm], europium [Eu], terbium [Tb], dysprosium [Dy], ytterbium [Yb], lutetium [Lu], hafnium [Hf], tantalum [Ta], tungsten [W], gold [Au], lead [Pb], thorium [Th], and uranium [U].

Sargent and others (1982) explained some limitations of the data. The survey objectives dictated sample coverage over a wide area and determination of many variables on each sample. Although rigorous sampling and analytical procedures were employed, the scale of the project,

the diverse nature of personnel and analytical procedures, and the length of time over which these activities were conducted, all combine to introduce variations within the database that at times can inhibit direct comparisons. A major limitation is that large areas of the state are not included in the supplemental analyses (Smith, 2006; Reid, 1993). For instance, data extents are commonly limited by county-level political boundaries.

III. NURE PARAMETERS AND CONSIDERATIONS

The NURE HSSR data were originally generated by four Department of Energy (DOE) Laboratories (Lawrence Livermore Laboratory, Los Alamos Scientific Laboratory, Oak Ridge Gaseous Diffusion Plant, and Savannah River Laboratory) and at least one unspecified subcontractor laboratory (Smith, 2006). From the DOE laboratories, the data from North Carolina were analyzed at the Savannah River Laboratory. In 1985, the responsibility for the NURE HSSR data was transferred from the Department of Energy to the U.S. Geological Survey. In 1994, and after the publication of NCGS Bulletin 93, use of a recently compiled version of the NURE HSSR database revealed several inconsistencies, some introduced systematic errors, duplicated records, and missing data. Beginning that year, efforts to use large amounts of NURE HSSR data from the state of Montana led to a decision to recompile the dataset from the original files. The success of this task led to a larger project with the goal of reformatting the entire database. At this time, the decision was also made to separate the water data and the sediment data to create two distinct datasets (Smith, 2006).

The samples in the dataset were chemically analyzed by several laboratories using a variety of techniques that changed over time. The accuracy of the geochemical data varies with the particular laboratory instrumentation and techniques, the analytical methodology employed, the analyte being examined, the concentration of the analyte, and the mixture of elements present within a given sample. Values that were less than the lower detection limits of an analytical method were reported as a negative number (Smith, 2006). Also, it was later discovered that some field samplers had changed the negative values to zeros in the database. No one sample necessarily contains data in all the analyte data fields; and no analyte data field is completely populated within the dataset. The amount of data in elemental fields varies with the responsible DOE laboratory and with the analytical methods used (Smith, 2006). It should also be noted that all sediment analyte concentrations are reported in either parts per million (ppm) or as a percentage (%), depending on the individual analyte, while electrical conductance of the water from the stream where the sediment sample was collected is reported in microsiemens per centimeter (μ mhos/cm).

IV. CRITICAL MINERALS VITAL TO U.S. ECONOMIC INTERESTS

In 2022, the USGS released an Action Notice highlighting a series of 50 minerals that researchers have determined are vital to the economic interests of the United States for the foreseeable future (Applegate, 2022). With the critical minerals defined, the effort to locate the minerals for exploitation has been developed in the Earth Mapping Resources Initiative (Earth

MRI). Earth MRI is planned as a partnership between the USGS, the Association of American State Geologists (AASG), and other federal, state, and private-sector organizations (Day, 2019).

The 2022 Final List of Critical Minerals

(* Denotes material sampled for as analytes in the NURE stream sediment program)

*Aluminum	*Dysprosium	Indium	Palladium	*Terbium
Antimony	Erbium	Iridium	Platinum	Thulium
*Arsenic	*Europium	*Lanthanum	Praseodymium	*Tin
Barite	Fluorspar	*Lithium	Rhodium	*Titanium
*Beryllium	Gadolinium	*Lutetium	Rubidium	*Tungsten
Bismuth	Gallium	*Magnesium	Ruthenium	*Vanadium
*Cerium	Germanium	*Manganese	*Samarium	*Ytterbium
*Cesium	Graphite	Neodymium	*Scandium	*Yttrium
*Chromium	*Hafnium	*Nickel	*Tantalum	*Zinc
*Cobalt	Holmium	*Niobium	Tellurium	Zirconium

V. ADDITIONAL HELPFUL REFERENCES

North Carolina Geological Survey Interactive Geologic Maps

The North Carolina Geological Survey has a number of interactive geologic maps, which can be found at the following location (<u>Interactive Geologic Maps | NC DEQ</u>). These are helpful references as you read through the following analyte information, which highlight, among other things, locations in our state where these elements and their associated ore minerals are known to occur. These maps provide geologic context in terms of major terranes, features, and units that help explain the origins of these elements and minerals.

The Mineral Resources Data System (MRDS)

The MRDS is a collection of mineral resource reports worldwide, maintained by the USGS and developed by the USGS with the assistance of the state geological surveys and other organizations. This resource may also be useful to the end-user for broader mineral analyses - MRDS interactive map (USGS, 2011).

Topical Index of Downloadable Spatial Data

A virtual clearinghouse of data is also available through the US Geologic Survey's (USGS) link below, which provides a periodic table of elements that is searchable by element. Additionally,

many related links to topics such as natural resources, earth science, environmental issues, and more can be readily accessed from the following site <u>Mineral Resources On-Line Spatial Data:</u> <u>Topical index</u> (USGS, 2023)

VI. THE ANALYTES

By increasing Z-value (atomic number):

Lithium [Li], Z=3, is a soft and silvery, highly reactive, alkali metal and is the lightest of all solid elements on Earth. Along with hydrogen and helium, it was one of the only elements produced in significant quantities upon the creation of the universe. It is ubiquitous around the globe, although only concentrated enough for commercial production from a few deposit types and areas. Worldwide, lithium is most often produced from continental brines in the shallow subsurface and further concentrated in man-made evaporation ponds. A significant additional source is from lithium-bearing minerals within coarse-grained crystalline rocks (Bradley, 2017). Historically, lithium has been mined in North Carolina from spodumene (LiAl(SiO₃)₂) ore found in unique pegmatites of the Kings Mountain district (Horton, 1981). Spodumene mining continued for several decades in this area, ceasing production in the 1990's. The Tin-Spodumene Belt of the Kings Mountain District was at one time considered the largest spodumene pegmatite deposit in the world (Swanson, 2013). Lithium as a commodity is valuable in the production of batteries, ceramics, glass, and numerous other applications. The rising utilization of lithium in many rechargeable battery applications (electric vehicles, smartphones, etc.) has created a strong surge in demand. Global consumption is substantially on the rise at the time of this report (USGS, 2022). Lithium is listed as a "Critical Mineral" by the US Department of Interior, which has presented a final list of 50 critical mineral commodities that are vital to the nation's security and economic prosperity (Burton, 2022).

Beryllium [Be], Z=4, is the lightest of the alkaline earth elements. Because of its small size, it is not easily displaced and occurs most frequently within distinct minerals. The two most common beryllium ore minerals are bertrandite (Be₄Si₂O₇(OH)₂) and beryl (Be₃Al₂Si₆O₁₈), both of which are found in association with igneous rocks. Bertrandite is the principal ore mineral being mined globally for beryllium. It occurs in moderate to low pressure regimes in near-surface volcanogenic and carbonate-hosted rocks (Foley, 2017). Beryl, on the other hand, is most often found in veins or pegmatites; the latter of which are rocks that contain the last minerals to crystallize from the highly enriched residual fluids of large igneous intrusions. Only specific pegmatites named 'rare-metal granitic pegmatites' contain enough beryl to warrant mining for beryllium (Foley, 2017). In North Carolina, beryl occurs in pegmatites in several counties in western North Carolina, most notably Avery, Mitchell, and Yancey (Stuckey, 1965). More significant ore deposits are found in the Kings Mountain area, which hosts a rare-metal granitic pegmatite that has co-produced several minerals, including those containing beryllium and lithium. Beryllium as an alloy with copper accounted for approximately 75% of the total used in 2018 in the U.S. Much of the remaining consumption was in the form of purified beryllium metal (Jaskula, 2021). Beryllium has unique chemical characteristics of strength, hardness, high

electrical and heat conductivity, as well as high resistance to corrosion and fatigue. These traits make beryllium and its alloys well suited for various aerospace, computer, defense, and other high technology applications (Foley, 2017). Beryl can also be a gemstone-quality mineral, principally as aquamarine and emerald. Beryllium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Fluorine [F], Z=9, is a pale-yellow gas within the halogen group on the periodic table of elements. It is the most electronegative (i.e., it strongly attracts electrons) element and therefore is highly reactive. It reacts with every element except neon and helium. Interestingly, the gemstone topaz (Al2SiO4(F,OH)2) contains on average over 10% fluorine by weight. The most common ore mineral of fluorine is fluorite (CaF2), which is also commonly termed commercially as fluorspar. The term fluorescence gets its name from this mineral, though it is believed that common impurities within fluorite permit the quality of fluorescence. Fluorine is known to be an "incompatible" element within igneous melts. Consequently, it becomes concentrated in the latter stages of magma differentiation (Hayes, 2017). Fluorite is most often mined from the associated hydrothermal deposits, though it also commonly occurs in sedimentary deposits of phosphorites. Although not actively produced in North Carolina, fluorine-containing minerals can be found in the Quaternary age phosphorite deposits (as fluorapatite) of the coastal plain as well as certain formations within the Hot Springs Window in Madison County (as fluorite). Fluorspar has a host of applications, including as a fluxing material in ceramic, steel and glass making. It is also commonly used as feedstock for fluorine chemicals generated principally after the production of hydrofluoric acid (Hayes, 2017). Fluorine is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Sodium [Na], Z=11, when separated from naturally occurring compounds, is a soft, silverywhite metal. However, because it is so highly reactive and water-soluble, it does not occur as a free metal in nature. Plagioclase feldspar, halite and soda ash are examples of ore minerals containing the sodium cation in abundance. Common ore minerals mined elsewhere around the globe for sodium-containing compounds include halite (NaCl or "rock salt") and soda ash (Na₂CO₃-10H₂O), which are both formed primarily as chemical sedimentary rocks in evaporative basins within arid regions. In North Carolina, feldspars (including sodium-rich varieties NaAlSi₃O₈) have been mined in several locations where these intrusive igneous rocks are found. North Carolina was the top feldspar producer in the nation in 2021, and along with four other states, accounted for approximately 60% of US feldspar production (Ghalayini, 2020). Feldspar mining, commonly from pegmatites and associated rocks, has a long history in western North Carolina that continues today most prominently in deposits of the Spruce Pine Mining District (Tugaloo Terrane, west of the Brevard fault zone) in Yancey, Mitchell, and Avery Counties. Additionally, in the Kings Mountain area, feldspar has been recovered in the process of extracting spodumene for its lithium content (Carpenter, 1995). Feldspars are most often utilized today in the formulation of glass and ceramics (USGS, 2022).

Magnesium [Mg], Z=12, is an alkaline earth metal and the third most abundant element in seawater (Kramer, 2001). Common ore minerals include magnesite, olivine, dolomite, brucite

and carnallite. North Carolina hosts magnesite (MgCO₃) and olivine (($\underline{Mg}^{2+}, \underline{Fe}^{2+})_{2}\underline{SiO}_{4}$) deposits mostly in the western part of the state where ultramafics (naturally dark-colored igneous rocks with high amounts of magnesium and iron) occur. These deposits have been mined historically for decades in the state. In fact, North Carolina once led the nation in the production of olivine (Carpenter, 1995); although no current production exists as of 2022. Elsewhere in the US and around the world, seawater and brines are extracted for their magnesium in the form of magnesium oxides and other compounds (Bray, 2021). These extraction methods accounted for most of the domestic production of various magnesium compounds in 2021 (USGS, 2022). Magnesium compounds are used primarily in the environmental and agricultural industries. As a primary metal, magnesium is used commonly as an alloy with aluminum (chiefly in castings made for the automotive industry) and for the removal of sulfur from iron and steel (USGS, 2022). Magnesium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Aluminum [Al], Z=13, is one of the basic metals and is the second most abundant metallic element in the Earth's crust after silicon. The sedimentary rock bauxite contains the primary aluminum ore mineral named gibbsite (Al(OH)₃). Bauxite is formed primarily in tropical regions within lateritic (formed through intense chemical weathering) soils having excellent drainage and intense wet/dry cycles. It requires an extraction process to produce alumina (aluminum oxide) before smelting is performed to create pure aluminum (Bray, 2021). Bauxite is utilized widely across many common applications and industries, including transportation, packaging, construction, and many others. Pyrophyllite, a hydrous aluminum silicate with approximately 28% aluminum content, has been an intermittently significant economic product in North Carolina since 1855, when it was first mined. Pyrophyllite mainly occurs in economic quantities along the east side of the Carolina Terrane (also known as the Carolina Slate Belt), with the more significant mining activity occurring in Moore, Randolph, Alamance, Orange, and Granville counties (Stuckey, 1965). The applications of pyrophyllite have varied over time, with modern uses including as an additive in clays, bricks, and insecticides. Many industrial abrasives involve aluminum in the form of the mineral corundum (Al₂O₃), which was also formerly mined in North Carolina, primarily in Jackson and Macon Counties. Aluminum is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Phosphorus [P], **Z=15**, is not found naturally in its elemental form, as it is highly reactive with oxygen. This reaction generates a faint glow termed chemiluminescence, a unique property of some phosphorus-containing rocks. (Phosphorescence is a separate process whereby upon exposure to shorter-wavelength light (radiation), those substances absorb and slowly re-emit longer wavelength light.) Phosphate rocks (containing the PO_4^{3-} ion) provide the principal ore mineral source for phosphorus. The mineral apatite (the name for a group of phosphate minerals) is a common accessory in igneous and metamorphic rocks, where it is sometimes mined directly from these source rocks. Most phosphorus is mined from sedimentary phosphorites (containing up to 80% apatite minerals in cryptocrystalline form) deposited in shallow, near-shore marine settings. The Miocene age Pungo River Formation on the North Carolina coast hosts phosphate ores that have been actively mined in our state for several decades. The Aurora Mine in Richland

Township makes North Carolina a leading producer in the nation for phosphorus-containing compounds. Agricultural uses account for over 95% of the phosphorus consumption in the US (USGS, 2022).

Potassium [K], **Z=19**, is a soft, silvery-white, alkali metal. When processed into its elemental form, a strong combustion reaction quickly ensues in the presence of air or especially water. Potassium is similar in nature to sodium in that it occurs often as ionic salts originally deposited within intense, evaporitic basins. Potash, being a mixture of various potassium salts, is a primary ore rock involving this element. Marine and lacustrine evaporite depositional settings are the most common environments where potash is mined in the US, although mining also occurs in certain lithocap (broadly stratabound and laterally extensive alteration domains) deposits in the uppermost portions of igneous porphyry systems (Hammerstrom, 2022). Potassium also features in plutonic rocks within the feldspar mineral orthoclase (KAISi₃Q₈). In fact, North Carolina is one of the leading states in the nation for feldspar production, with historic and present mining activity most concentrated in Yancey, Mitchell, and Avery counties in the western part of the state (Stuckey, 1965). Approximately 85% of US potash sales were for the fertilizer industry (USGS, 2022).

Calcium [Ca], **Z=20**, is found in a wide array of compounds and is the fifth most common element on Earth. The primary ore mineral of calcium is calcite (CaCO₃), which is the principal mineral found in limestone and marble (metamorphosed limestone). Gypsum (CaSO₄·2H₂O), fluorite (CaF₂) and apatite (a group of phosphate minerals) are also important ore minerals for calcium. Calcium also occurs abundantly within many other minerals, including anorthite (<u>CaAl₂Si₂O₈</u>) as the end-member of the plagioclase mineral series. Sedimentary calcite is often formed in-situ as a precipitate from relatively warm, shallow, calm, marine settings. These sources can be directly from seawater (chemical) or from the accumulated remains of organisms (biological). Marble, being metamorphosed limestone (as well as dolomite (CaMg(CO₃)₂)), has been periodically mined in Cherokee county in far western North Carolina for dimension stone (Carpenter, 1983). A few of the many uses of calcium-containing rocks and minerals include in the production of cement and mortar, as an additive in certain foods and pharmaceuticals, and as a reduction agent in the production of other metals.

Scandium [Sc], Z=21, is the lightest of the rare earth metals. It is a soft, silvery metal that is relatively common in the Earth's crust, but rarely concentrated in commercial quantities. Along with yttrium, scandium is classed with the chemically similar group of rare earth elements termed the lanthanides, which are mostly non-radioactive (in contrast to the other rare earth element group named the actinides). Ore minerals for scandium are quite rare and are produced exclusively as a byproduct of a variety of other ores (USGS, 2022). Over 245 minerals from which rare earth elements are found have been identified (Van Gosen, 2017). Scandium is most often used in alloys with aluminum in aerospace, military, and other applications. Scandium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Titanium [Ti], **Z=22**, is found in nature only as an oxide. Ilmenite (FeTiO₃) and rutile (TiO₂) are the two most common ore minerals. These minerals occur in a wide variety of deposit types. In North Carolina, sedimentary placer deposits are found in the "heavy minerals" of the coastal plain. Recent mining has occurred in Virginia along a linear belt named the Fall Zone, which extends into North Carolina as the contact zone between crystalline rocks of the Piedmont and the sedimentary cover of the Coastal Plain. Based on sample analyses and other research, similar areas in North Carolina are also considered prospective for commercial titanium mining (Van Gosen, 2018). Additionally, certain crystalline rocks of metamorphic origin in and near the mountains contain noted occurrences (as lenses and associated residuum) of titanium-bearing minerals (Stuckey, 1965). Most usage of titanium ore minerals is as a white pigment in paints, plastics, papers, and other items. Titanium metal is also utilized in metal alloys to increase the strength-to-weight ratio and corrosion resistance of components for the aerospace industry and other applications (Woodruff, 2017). Titanium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Vanadium [V], Z=23, is a widely distributed trace element found in a variety of minerals and deposit types. 80 to 85% of the world's Vanadium is from orebodies (either mined directly or produced from a resulting steelmaking slag) of certain mafic and ultramafic rocks also having ilmenite and magnetite (Kelly, 2017). Among the lesser but emerging sources of vanadium are as a byproduct of petroleum products, especially from heavy crude oils. An estimated 10% of the world's vanadium supply is derived from fossil fuels. Most vanadium is utilized in steelmaking applications to greatly increase strength. In fact, vanadium-titanium alloys have the highest strength-to-weight ratio of any engineered material to date (Kelly, 2017). Vanadium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Chromium [Cr], Z=24, is the third hardest naturally occurring element on Earth. The primary ore mineral is the oxide Chromite (FeCr₂O₄), which is concentrated in certain mafic and ultramafic igneous bodies as an orthocumulate. Orthocumulates are rocks formed from the fractionation of a cooling magma chamber via settling or flotation (USGS, 2022). Various mines, mostly in western North Carolina have produced modest amounts of chromite ore in the past (Stuckey, 1965). Chromium is most significantly used in an alloy with iron to increase strength and greatly enhance corrosion resistance in "stainless" steel. Chromium metal has a high polish and is synonymously known as "chrome," where it is commonly used as a metal plating in numerous applications (Papp, 2001). Chromium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Manganese [Mn], Z=25, is another transition metal often found in combination with iron. Manganese ore minerals are concentrated through various processes that occur most frequently in the world's oceans. Consequently, most manganese deposits are found amongst ancient marine sedimentary rocks that were long ago emplaced on land where commercial mining could occur. Ferromanganese nodules and crusts occur throughout the world's seabeds and, if proven commercially, would open a tremendous additional supply of this vital element. Additionally, supergene deposition (secondary enrichment) is an important deposit type, especially in more tropical regions (Cannon, 2017). Across the various deposit types, some of the more common ore minerals for manganese are rhodochrosite (MnCO₃), braunite ($Mn^{2+}Mn^{3+}_{6}(SiO_4)O_8$), manganite (MnO(OH)), and pyrolusite (MnO₂). No significant manganese mining occurs in the United States today, but there are numerous occurrences in North Carolina, including in the Battleground Formation schist in the Kings Mountain area; as well as several scattered localities in western North Carolina (Stuckey, 1965). Manganese is a ferrous metal vital to modern industrial economies and used primarily as an alloy to create steel. In fact, manganese is currently an irreplaceable element in the conversion of iron ore to steel. It is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Iron [Fe], **Z=26**, is the fourth most common element in the Earth's crust and the most common element by mass, just ahead of oxygen. It is considered one of the seven metals of antiquity due to its lengthy and significant historical usage. Along with nickel, iron comprises the majority of our planet's inner and outer cores. There are many iron ore minerals, but a few of the most common include: hematite (Fe_2O_3), magnetite ($Fe^{24}Fe^{3+}_2O_4$), siderite ($FeCO_3$) and goethite (α -<u>FeO(OH</u>)). Magnetite and hematite are the most common iron ore minerals in the United States (Tuck, 2021). Numerous small historic mines with some iron ore production have existed in many regions of North Carolina going back to colonial days. During the main iron production period of the early 1900's, two areas produced the most iron ore in the state: the Cherokee County limonite deposits, and the Cranberry Mine magnetite deposits of Avery County (Stuckey, 1965). The vast majority (estimated at 98%) of iron ores at present are utilized to produce iron and steel. Iron and steel are of course key ingredients to most building and infrastructure, as well as transportation and numerous other economic sectors in the modern, industrialized world.

Cobalt [Co], **Z=27**, is a silvery gray metal not found in nature in its pure, free form. It does have a similar ionic radius to various other metallic cations, and so substitution readily occurs to create numerous cobalt-containing compounds and minerals. Deposit types are primary or secondary (supergene enrichment from surficial weathering). Ultramafic rocks contain the highest natural proportions of cobalt (Slack, 2017). Among the primary deposit types, cobalt is most often recovered from sulfide, arsenide and sulfarsenide mineral ores. Most of the world's cobalt is from stratiform (formed parallel to the bedding planes of the surrounding rock), lateritic, or magmatic sulfide deposits. It is most often produced as a byproduct of copper mining in stratiform deposits. North Carolina has seen trace cobalt occurrences in a small number of historic mines and prospects in the mountains region, as well as potentially higher-grade deposits in Wake, Gaston, and Lincoln Counties (Stuckey, 1965). The uses of cobalt are increasingly important and with few if any substitutes. The primary applications include as cathode materials in rechargeable batteries and as a component in superalloys for jet engines and other high-end technologies (Slack, 2017). It is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Nickel [Ni], Z=28, is another transition metal that in its pure form is silvery gray with a slight gold tint. It has unique characteristics of hardness and ductility. Importantly, it also has the quality of ferromagnetism, which only cobalt, iron and rare earth metals also have. Nickel, like

iron, is most concentrated in the inner and outer cores of Earth. There are a couple of depositional systems from which nickel is extracted today. Magmatic sulfide deposits provide around 40% of global nickel resources. The main ore mineral from these deposits is pentlandite (Ni,Fe)₉S₈. The intense weathering of ultramafic igneous rocks can produce laterite deposits, which are host to ~60% of the world's produced nickel. Nickeliferous limonite (Fe,Ni)O(OH) and garnierite (an informal name consisting of various Ni-Mg hydrous silicate minerals) are the primary ore minerals in these deposit systems. An emerging prospective region for nickel mining is the deep-sea floor, where various heavy metals accumulate as nodules or crust (Boland, 2012). In North Carolina, nickel occurrences have been noted in several areas known to have ultramafic rocks in the western part of the state (Stuckey, 1965). Nickel has long been used as an alloy with iron to help impart corrosion resistance, heat tolerance and hardness to the resulting material. These alloys are often utilized in intense environments like jet engines and power generation facilities where these material qualities are important. Nickel is also increasingly being utilized in rechargeable batteries for a wide variety of applications. It is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Copper [Cu], **Z=29**, is one of the few metals that can occur in nature in its pure form. This fact helped lead to copper becoming one of the "seven metals of antiquity" as it has been utilized in raw and readily alloyed forms for many hundreds of years. In its pure form, it is reddish-orange, soft and malleable with a high thermal and electrical conductivity. Commercially minable quantities are found predominantly in one of two depositional systems. In both systems, replacement is the dominant mechanism of formation. Porphyry copper accounts for ~75% of global production. It is formed from hydrothermal fluids originating from underlying magma deep below. The remaining ~25% is found in sedimentary rock-hosted stratabound (isolated within a particular bed of sedimentary strata) deposits. These deposits are concentrated and precipitated through supergene processes (those occurring via deposition or enrichment of mineral deposits by solutions moving downward through rocks (Doebrich, 2009). There are a large variety of copper ore minerals in both depositional systems, but a few of the primary ones include: chalcopyrite (CuFeS₂), chalcocite (Cu₂S) and bornite (Cu₅FeS₄). While no copper mining occurs today in North Carolina, we do have a long history with copper production from numerous mines. A number of these historic copper mines were originally gold mines that had appreciable amounts of copper as well (Stuckey, 1965). Those deposits are concentrated in three areas across our state: west of the Brevard zone in the Blue Ridge Mountains and in two areas of the Piedmont province – a zone along the eastside of the Charlotte terrane, and a zone along the westside of the Carolina terrane. Importantly, each of these areas of activity broadly trends NE-SW. This is a first-order feature of North Carolina geology in that large-scale terrane features trend in similar orientations. Less significant mining activity has occurred in/near Chatham County as well (Stuckey, 1965).

Zinc [**Zn**], **Z=30**, is a bluish-white, transition metal with diamagnetic (having properties of repulsion from an external magnetic field) and anti-corrosion properties. The primary ore mineral for zinc is sphalerite ((Zn,Fe)S), which is nearly always found in association with sulfides of copper, lead and iron. Three primary zinc ore deposit types exist: 1) Mississippi

Valley Type (MVT) deposits where low temperature hydrothermal solutions precipitated zinc, lead and other metals in often stratabound deposits, 2) Sedimentary Exhalative (SedEx) deposits where metal-rich fluids are released into a body of water, dispersed and reconcentrated in basin floor sediments, and 3) Volcanogenic Massive Sulfide (VMS) deposits where submarine vents release geothermally-heated waters that precipitate high concentrations of metals like zinc into stratiform accumulations (Kropschot, 2011). Most North Carolina production of zinc was prior to 1900 and as a byproduct of historic gold, silver, copper and lead mining (Stuckey, 1965). That said, zinc is widely used today and is the fourth most utilized metal in the world. Zinc's strong anti-corrosion properties make it desirable for alloying with other metals (for example, combining with copper to make brass) and galvanizing (coating other materials with thin layers of zinc). Zinc oxide is an opaque, water-insoluble compound used for skin protection from sun and wind exposure (Kropschot, 2011). Zinc is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Arsenic [As], **Z=33**, is a semi-metal that is most often grey with a metallic luster when utilized in industrial applications. Arsenopyrite (FeAsS), orpiment (As_2S_3), and realgar (As_4S_4) are the most common arsenic-bearing minerals. Arsenopyrite is the primary ore mineral for arsenic and is often formed as a high-temperature precipitate from hydrothermal, vein-filling fluids. It is often associated with gold, copper, iron, lead, and other metallic deposits of similar origin. In North Carolina, arsenic has been noted in trace amounts in a few historic mines as a byproduct of gold and other mining efforts. Applications for arsenic have historically been limited to lumber and agricultural biocide treatments, given the well-known toxicity of arsenic in the environment. A recent application for pure arsenic metal includes the formation of gallium arsenide semiconductors useful in solar cells, smartphones, and other technological equipment (Bedinger, 2014). Arsenic is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Selenium [Se], **Z=34**, is a nonmetal that is a trace element in the earth's crust and rarely found in its pure form in nature. It is a chalcophile element (i.e., having an affinity for the sulfide phase) where it will sometimes substitute for sulfur given their similar ionic radii. Consequently, the predominant ores where selenium is recovered are copper sulfides. As a byproduct of copper refinement, selenium is collected from the anode slimes developed during copper electrolysis (Stillings, 2017). Its practical applications include uses in glass manufacturing, electronic and photocopier components, among others. More recent uses take advantage of some unique properties. Selenium is both photovoltaic (light sensitive) and photoconductive (electrically conductive upon light exposure). These qualities have led to increased utility in photovoltaic cells and solar panels. Alloys of copper-indium-gallium-selenium (CIGS) show markedly increased conversion efficiency over first-generation silicon-based, thin film photovoltaics (Stillings, 2017).

Strontium [Sr], **Z=38**, is a soft, alkaline earth metal with a silvery-white, yellowish color. It is highly reactive in the environment and consequently not found in nature in its pure form. Strontium has intermediate properties between calcium and barium and substitutes for those

cations in some cases. The primary ore mineral is celestine (SrSO₄), which occurs more frequently in sufficient quantities than strontianite (SrCO₃), which otherwise would make a valuable candidate ore mineral for strontium. While also recognized in hydrothermal veins and some pegmatites, celestine is most often found in sedimentary basins with other evaporite deposits. Strontium minerals and compounds are utilized in several applications today, including as a drilling mud additive (as a replacement for barite), and in the ceramics, glass, medical and pyrotechnics industries (Singerling, 2021). Interestingly, finely ground strontium metal is pyrophoric, causing it to spontaneously combust and impart a bright red color to the flames when exposed to the atmosphere.

Yttrium [Y], **Z=39**, is another silvery-white colored transitional metal. Like scandium, it is sometimes grouped in with the chemically similar rare earth element group named the lanthanides. Rare earth elements are widespread in nature, just at very low concentrations. Yttrium is classified with the heavy rare earth elements (HREEs), which are a subset of the REEs that are chemically and physically similar, and rarer and more expensive (Van Gosen, 2019). In the rare cases of concentrated deposition, the most common mineral ores for yttrium are monazite (a phosphate mineral) and bastnaesite (a fluorocarbonate). Deposit types are numerous, but alkaline igneous complexes and heavy mineral placers are two of the primary systems in which rare earth elements are found (USGS, 2022). In North Carolina, monazite, allanite, and other yttrium-containing minerals have most often been noted in placer systems both along the Fall Zone (linear belt of erosion between crystalline rocks and coastal plain sediments), as well as just below the Blue Ridge escarpment (Stuckey, 1965). Most of these placer mines in western North Carolina produced both gold and a variety of rare earth elements. Modern day uses for yttrium are most often as yttrium oxides and include glass additives, dental ceramics, laser technologies, and as a phosphor in luminescence applications (Van Gosen, 2017).

Niobium [Nb], Z=41, is a light grey, ductile transition metal formerly known as "columbium." It is commonly found with tantalum (see description of Tantalum, Z=73) due to their high degree of chemical similarity. Like tantalum, niobium is not found in nature in its pure elemental form, but rather as oxides, hydroxides and in a few rare silicate minerals. The most common ore mineral for niobium is the pyrochlore group (Na,Ca)₂Nb₂O₆(OH,F), which itself is primarily associated with the metasomatic (chemical alteration by hydrothermal and other fluids) end stages of alkaline igneous complexes (Schulz, 2017). North Carolina has deposits of niobium that have been produced only as a byproduct of feldspar and mica mining mainly in the Spruce Pine and Kings Mountain mining districts, with occurrences elsewhere in the mountains and piedmont provinces (Stuckey, 1965). The primary application of niobium is as a high-strength, low-alloy steel for pipelines, transportation, and structural applications. Many of its applications are specialized, including in superconducting magnets and in high-temperature conditions. It can also be substituted for nickel as a non-allergenic component in jewelry (Schulz, 2014). Niobium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Molybdenum [Mo], **Z=42**, is a silver to grey transition metal with a high melting point. It does not occur as a free element in nature, but rather in combination with sulfur, oxygen, and other

metals. The primary ore mineral is molybdenite (MoS₂), which has historically been confused with graphite due to superficial similarities or low hardness (close to that of talc) and a greasy feel. Molybdenum mining occurs predominantly in two deposit types: greisen (formed by endogenous alteration of certain granites) and porphyry (formed by large scale hydrothermal systems within intrusive igneous rocks) deposits (Ridgley, 2020). It is sometimes mined as a primary product, but even more of the production volume comes by way of co-production with copper and gold mining. Aside from a few scattered occurrences in our state, a concentration of historical molybdenum prospects and occurrences exist in Halifax County within intrusive rocks of the eastern piedmont (Stuckey, 1965). The principal applications for molybdenum are as an alloying element in steel and other metals. Key benefits of molybdenum in metallic alloy are its added strength, anti-corrosion qualities, and high resistance to heat (Kropschot, 2010).

Silver [Ag], Z=47, is one of only a few metals commonly found as a native element in the environment. The name is synonymous with the lustrous, white metallic color exhibited by this highly ductile and malleable transition metal. Silver is one of the "seven metals of antiquity," given its known usage during prehistoric times. Most production of silver comes as a byproduct of mining sulfide-rich deposits (e.g., lead, copper, gold, and zinc) related to igneous activity. Less often, silver is mined as a native element, where it occurs as a hydrothermal deposit, often in veins and cavity fill (Goonan, 2014). Most of the silver production in North Carolina came as a byproduct of copper and gold mining. A few locations however were mined principally for lead, zinc, and silver. Galena (PbS), from which lead is often mined, consistently contains some amount of silver and has thus been a particularly important ore mineral (Stuckey, 1965). The applications of silver are plentiful given its unique characteristics. It has the highest electrical and heat conductivity of all the metals. These properties make it useful in electronics and solar energy technologies. Additionally, its photosensitivity, high-temperature strength, and malleability are important properties leading to numerous industrial applications. Silver also can have germicidal capabilities leading to applications such as high-end silverware and nano silver inclusions in textiles and water supplies for example (Goonan, 2014). Lastly, silver has been used since antiquity as coinage. At times, silver's value has exceeded that of gold.

Tin [Sn], **Z=50**, is a post-transition metal that is relatively soft and malleable. It occurs in two main allotropes (or forms): one is silvery-white with a metallic luster at room temperature, while the other is nonmetallic with a dull grey appearance and stable below room temperature. The primary ore mineral of tin is cassiterite (SnO₂). Tin also occurs as an element in numerous sulfide minerals. Approximately 20% of the identified global resource of tin is found as lodes (hard-rock veins of metallic ores) within certain continental granites. The remaining 80% is found in placer settings (river, valley, sea bottoms) (Kamilli, 2017). Due to the high specific gravity (ratio of density of a substance to that of water) of tin, weathered cassiterite grains will preferentially concentrate by deposition along boundaries where water velocity drops suddenly. In North Carolina, tin has been produced in modest volumes (frequently with lithium, which later became the primary element of interest) in a linear trend within the Kings Mountain area named the tin-spodumene belt. Here tin is found sporadically in the various pegmatites in the area (Horton, 2008). Numerous occurrences also have been noted in southern Cleveland and

Rutherford counties as placer deposits (Stuckey, 1965). Tin is almost always utilized as an alloy with other metals. As another one of the "seven metals of antiquity," tin is famously alloyed with copper to make bronze. Tin is also a key alloy in the making of pewter. Most tin today is utilized in container, construction, and transportation materials, as well as a solder material. A recent application of tin is as an indium-tin oxide, which makes a clear and electrically conductive glass especially useful for modern touch screens (Kamilli, 2017). Tin is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Cesium [Cs], Z=55, is an alkali metal that is silvery-gold in color. It is one of only five elemental metals that occurs as a liquid at/near room temperature. In fact, of the stable, elemental metals, only mercury has a lower melting point. Importantly, cesium is the most electropositive of all the metals and is thus considered the most reactive (Butterman, 2005). The primary ore mineral of cesium is pollucite, which is in the class of minerals known as zeolites. Zeolites are microporous aluminosilicates formed when volcanic rock and ash react with alkaline groundwaters. Pollucite is often found in association with petalite and lepidolite, which themselves are important ore minerals for the sometimes associated element, lithium. Pollucite has been noted as a rare occurrence in at least one mica mine in western North Carolina in Yancey County, although no production is recorded. There are only a few applications for cesium at present, although research and development uses are under investigation. Cesium isotope 133, with its highly consistent electron emission frequency when bathed in microwave radiation, is used for official timekeeping in the U.S. In fact, cesium electron emissions are used for international time and frequency standards to officially measure both the second and the meter. These properties make cesium valuable to many technologies requiring exact time and position identification, like GPS, internet, and cellphones. Most cesium however is used as a component in drilling muds for high-pressure/high-temperature applications (USGS, 2022). Cesium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Barium [Ba], **Z=56**, is a soft and dense alkaline earth element that is highly chemically reactive. Barite (BaSO4) and witherite (BaCO3) are ore minerals involving barium. Barite is by far the most common ore mineral. Several deposit types exist for barite. Bedded-sedimentary is the term for the most commonly mined deposit type since it is often the most simple and efficient to mine. These deposits form in marine environments as fluids circulate through the subsurface and rise towards the surface near basin edges, where the barium that is scavenged from organic matter combines with sulfates in the seawater to later precipitate out as barite (Johnson, 2017). Other deposit types exist, including those found in North Carolina. In our state, barite has been prospected or mined in three locations: Orange County, the Hot Springs area of Madison County, and the Battleground formation of the Kings Mountain area. The Hot Springs deposits owe their origin to infilling of cavities and veins with pods and stringers, as well as some mineral replacement in mylonitized zones (Stuckey, 1965). Approximately 90% of barite globally is used as a weighting agent in drilling fluids for oil and gas production (USGS, 2022). The high specific gravity (~4.5 g/cc) helps maintain hole integrity and convey drill cuttings out of the hole and to the surface. Barium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Rare Earth Elements (REE), Z=57-71: A few elements amongst this chemically similar group were tested for in the subject NURE study, including the following: lanthanum (La), cerium (Ce), samarium (Sm), europium (Eu), terbium (Tb), dysprosium (Dy), ytterbium (Yb) and lutetium (Lu). A brief description with some distinguishing characteristics and important uses of each will follow this broader discussion of REEs.

These elements are named 'rare' because, although not actually rare on Earth, they are generally found in only very low concentrations. They are named 'earths' because they were first found as components within oxides and similar rocks, which were all termed as 'earths' in the past. A total of 15 elements, termed the lanthanide series after the prototype lanthanum, make up most of the rare earth elements because they are somewhat chemically similar. Scandium and yttrium are sometimes also included due to some chemical similarities with REEs (Van Gosen, 2017). This group of elements is commonly divided between light (LREE) and heavy (HREE) on the variable of atomic number. Terbium (Tb) is often noted as the first in the HREE group. A further division into just light, medium, and heavy is also sometimes employed. In general, with greater atomic weight these elements are rarer, have smaller markets and are more difficult and expensive to produce. Consequently, the HREEs are a more pressing supply concern domestically as they are also particularly important to emerging technologies in key realms of defense, "clean energy" alternatives, and electronics (Hammarstrom, 2019). Numerous ore minerals and deposit types exist amongst all REEs. Elements of this group are generally considered as incompatible elements within an igneous melt because of unique chemical properties that tend to prevent ligand bonding until the later stages of crystal fractionation (Van Gosen, 2017). Particular deposit types commonly have their own unique, constituent primary ore minerals. Carbonatites (igneous rocks having greater than 50% carbonate, as opposed to the more common silica-rich magmas) are associated with many of the world's REE deposits. Bastnaesite (a carbonate-fluoride mineral) is considered one of the most important REE minerals given it is the primary ore mineral at the world's two largest REE deposits (in California and China). Other deposit types, including peralkaline magmas, certain mafic gneisses, ionadsorption clays, iron oxide-apatite (IOA) deposits, placer deposition, and others can concentrate commercial quantities of REEs as well. In the case of placer deposition, monazite (a phosphate mineral) is the most common REE ore mineral, owing to its high specific gravity and resistance to chemical weathering. It is found along, and east of, the Fall Zone in several southeastern states, where it occurs with other "heavy minerals" like ilmenite, zircon, and xenotime, which can all be co-produced. In fact, quite often multiple REEs are mined concurrently and separated later during processing. North Carolina has only ever been a small producer of REEs, mostly from counties in the mountains and inner piedmont, although numerous other deposits do exist (Stuckey, 1965).

Lanthanum [La], Z=57, is a soft, silvery-white, ductile element that is the largest of the rare earth elements (REE). It is the first (i.e., smallest atomic number) of the rare earth elements and

has the largest atomic size. That large atomic radius makes lanthanum the most reactive of the REEs. It often is found in conjunction with cerium, and other REEs. Many of the unique applications for lanthanum and other REEs rely on their unusual magnetic and optical properties. Among numerous specialty applications, lanthanum is used in some camera lenses and other optical glasses. Importantly, it is also utilized as a catalyst in many petroleum refineries (Van Gosen, 2017). Lanthanum is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Cerium [Ce], **Z=58**, is second in the lanthanide series and its most common constituent. It is a soft, ductile, and silvery-white metal. Cerium is the most abundant of all the lanthanide elements in the Earth's crust and is surprisingly even more abundant than the ubiquitous element copper. Along with iron, cerium is the only other metal to generate a spark if you strike it. As with many of the lighter REEs, it is used in many high-tech glass applications, for example, cerium oxides help achieve a precision polish in flat panel display screens. Cerium is also a catalyst component in many automotive catalytic converters. (Van Gosen, 2017). Cerium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Samarium [Sm], **Z=62**, is a moderately hard, silvery metal. Interestingly, it was named after the mineral samarskite, from which the element was first isolated. Samarskite is found in usually small amounts at several mica mine locations in western North Carolina (Stuckey, 1965). One of the main applications of this element is as samarium-cobalt magnets. These are very powerful and permanent magnets with a high tolerance to heat stress (Van Gosen, 2017). Samarium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Europium [Eu], **Z=63**, is a silvery-white metal in its pure form and is the softest and most reactive of all the rare earth elements. It is often considered the last (i.e., highest atomic number) of the light rare earth elements. As an oxide, it is used as a red phosphor in older cathode ray televisions and flat panel display screens. Many of the REEs exhibit some degree of phosphorescence, but europium is particularly efficient at producing a bright red color. It is also utilized as a dopant (or doping agent) in various optical devices for a wide range of specific purposes (Van Gosen, 2017). Europium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Terbium [Tb], **Z=65**, is the ninth member of the Lanthanide series. It is yet another silverywhite rare earth metal. It is malleable and ductile, and soft enough to cut with a knife. Sometimes considered the first of the heavy rare earth elements, terbium is stable in air, when compared to the lanthanides of lower atomic number. Terbium provides the green phosphor that complements the europium (red) and yttrium (blue) that make up the red-green-blue phosphor combination used in many light bulbs, panels, and television screens (Van Gosen, 2014). Another interesting application of terbium is in an alloy named Terfenol D. This alloy expands and contracts in response to a magnetic field more than any other metal, leading to numerous important uses as actuators and other sensors. Terbium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022). **Dysprosium [Dy]**, **Z=66**, is a silvery lustrous metal of the lanthanide series. Like all the other REEs, it is rarely if ever found in nature in its elemental form. It is a well-known neutron absorber for use in temperature control of nuclear fuel rods. As with terbium, it is also highly magnetorestrictive (a quality where shape or dimension changes when exposed to a magnetic field) and utilized in similar applications that take advantage of this unique trait. Also, dysprosium is utilized in small amounts to improve heat and demagnetization resistance in some of the most powerful magnets on earth (neodymium-iron-boron magnets). Dysprosium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Ytterbium [Yb], **Z=70**, is a heavy rare earth metal element that is soft, silvery, and lustrous. It is one of four elements named after the town of Ytterby, Sweden where gadolinite ((Ce,La,Nd,Y)₂FeBe₂Si₂O₁₀) is found. Detailed studies of this mineral led to the discovery of four new elements (yttrium, terbium, erbium, and ytterbium). Uses for ytterbium are mostly niche applications, including as a dopant in phosphors and ceramic capacitors. It also has a quality of changing from a conductor to a semiconductor at very high pressures. This quality permits its utility as a pressure sensor in extreme environments for various phenomena, including earthquakes and high-powered explosions. Ytterbium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Lutetium [Lu], Z=71, is the final lanthanide in the series, as it has the highest atomic number (i.e., number of protons in the atomic nucleus). Consequently, lutetium is the hardest and most dense of the group. It owes these qualities to the phenomenon of "lanthanide contraction," whereby, opposite to the normal progression, lanthanide atoms become progressively smaller in size with higher atomic number (Van Gosen, 2017). Lutetium has at present just a few niche uses, including in the creation of synthetic garnets of lutetium and aluminum for LED lighting, in radioactive isotopes for medical uses, and in conjunction with hafnium it is helpful for age-dating certain meteorites. Lutetium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Hafnium [**Hf**], **Z=72**, is a silver-colored, corrosion-resistant, and ductile metal. Due to the lanthanide-contraction in atomic radii, hafnium is very close in size to the element zirconium, which has only atomic number 40 (that is, 32 fewer protons in the nucleus). This size similarity helps explain the reason why zircon (ZrSiO4) is the primary ore mineral for hafnium. Hafnium nearly always exists as a minor constituent in zircon and is never found as a free element in nature. The primary deposit type is in alkaline igneous rocks, which account for roughly 1% of all igneous rocks by volume. These types of rocks host many of the rare earth elements, as well as numerous other critical minerals. However, igneous deposits are often in such low concentrations of hafnium and zirconium that they are not economic to mine. Consequently, secondary deposits, including modern and paleoplacers in coastal and alluvial/fluvial environments, provide most of the world's production. Sedimentary processes accumulate and concentrate these minerals so well due to zircon's high specific gravity, hardness, and excellent chemical stability. Even so, zircon is often mined as a by-product of heavy mineral mining for

titanium minerals (ilmenite and rutile) due to the often-low relative abundance even when concentrated and the comparative economics (Jones, 2017). In North Carolina, zircon (with its attendant hafnium) was briefly mined up until the early 1900's in areas of Henderson County in the western part of the state. Here there is a pegmatite source vein with some related placer weathering products downstream (Stuckey, 1965). Occurrences in our state also concentrate along the Fall Zone (i.e., the transition from crystalline piedmont rocks to the coastal plain sediments). Hafnium has relatively few applications primarily because zirconium is far more abundant and so chemically similar that it fulfills most of what hafnium could provide. That said, hafnium is still used as a neutron absorber for nuclear fuel rods. Also, isotopes of the lutetiumhafnium decay series are used to age date certain meteorites. Hafnium is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Tantalum [Ta], **Z=73**, is a dark blue-grey transition metal. It is often associated with niobium (see description of niobium, Z=41), as both metals are chemically similar and have low probabilities of substituting for common rock-forming cations. The primary ore mineral for tantalum is tantalite ((Fe,Mn)(Ta,Nb)₂O₆), which is most often found as an accessory mineral in rare-metal granites – in particular, lithium-cesium-tantalum (LCT) enriched pegmatite zones (Schulz, 2017). As with niobium, tantalum also occurs in modest amounts in the mountains and piedmont physiographic provinces of North Carolina. The Kings Mountain area has abundant LCT pegmatites, although tantalum has not been a primary production objective. Tantalum has unique properties, including resistance to corrosion by acidity and excellent heat and electrical conductivity, that make it vital to many technologies today. Most uses today are in electronics, commonly as tiny capacitors in mobile phones and computers. It is also used in medical applications (e.g., support stents, suture clips) and in the chemicals industry where its anti-corrosion properties make it useful for lining storage and transmission equipment (Schulz, 2014). Tantalum is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Tungsten [W], Z=74, is a steel-grey transition metal with a density comparable to that of gold. It also has the highest boiling and melting points of all other elements (except carbon, which sublimates at very high temperatures, bypassing the liquid phase entirely). Never found in its pure elemental form, tungsten is most often mined from the ore minerals scheelite (CaWO₄) and wolframite ((Fe,Mn)WO₄). Various deposit types exist, with the most common from a mining standpoint being vein/stockworks, skarns, porphyries, and strata-bound deposits (Werner, 2014). In North Carolina, sporadic occurrences in the mountains, as well as in Cabarrus County, have been noted. However, the Hamme Tungsten mining district in Vance County has been the only producer of tungsten in the state. Although not currently active, this area was the largest single producer of tungsten in the nation during much of the 1950's (Stuckey, 1965). Tungsten has important uses owing to some of its unique properties mentioned earlier. As an alloy with carbon, tungsten carbide is utilized for its exceptional hardness in machining and cutting tools and applications, as well as some military ammunitions. Its ability to tolerate extreme temperatures has supported its use as filament in incandescent lightbulbs for many years. Tungsten is listed as a "Critical Mineral" by the US Department of Interior (Burton, 2022).

Gold [Au], Z=79, is known as a precious metal due to its high value and relative scarcity. It is a distinctive lustrous, orange-yellow colored transition metal. It is malleable, ductile, dense, soft, and one of the least reactive of all the chemical elements. Often found in its pure, elemental form, gold is famously one of the seven metals of antiquity. Several of these metals, like gold, have such a long history of human use owing to their common occurrence in native form as well as their relative ease in heating, mixing, isolating, and shaping. Gold also forms in solid solution series with silver, copper, nickel, platinum, and palladium. Native gold and alloys like electrum (silver and gold) are the primary ore minerals. Of the few other minerals containing gold, many involve tellurium, and a few are of economic importance, such as calaverite (AuTe₂), sylvanite (Ag,Au) Te₂, and petzite (Ag₃AuTe₂) (Butterman, 2005). Gold mining occurs as either lode or placer mining. Lode involves all non-placer mining and includes, among many other systems, gold found disseminated through base metal, sulfide-rich systems or concentrated by hydrothermal vein systems. Placer mining involves reworked gold-bearing sedimentary detritus along rivers and ocean coasts (present or ancient). North Carolina has a famous history with gold, as ours is the first state to have documented discovery of gold when a 17-pound nugget was found in Cabarrus County in 1799. Once gold mining began around 1802, North Carolina was the only gold-producing state until 1828. Gold production continued and many different lode and placer mines were opened in several areas of the state, including numerous counties surrounding the original discovery and others to the northeast among the metavolcanic rocks of the Carolina Terrane; the Kings Mountain area; as well as the South Mountains area in the western Piedmont (Stuckey, 1965; Carpenter, 1993). Of special note, there are long abandoned mine workings hidden or buried under downtown Charlotte and elsewhere. Charlotte even briefly had an official branch of the United States Mint during peak gold production activity in the early 1800's (Knapp & Glass, 1999). The uses of gold range from ornamentation to coinage and investment to high technology. Most technological uses today involve the electronics industry where the high conductivity and resistance to oxidation and corrosion that gold provides is vital.

Lead [Pb], Z=82, is a dense, soft, malleable, post-transition metal with a blue-gray luster. It is the heaviest element having stable, natural isotopes. Isotopes of lead are the end products of three major decay chains involving radioactive elements of the actinide series, including thorium and uranium. Lead is another of the seven major metals of antiquity, as its very low melting point allowed for it to be isolated from ore minerals and utilized readily. The primary ore mineral of lead is galena (PbS). Lead is often found in association with varying amounts of silver, gold, copper, and zinc. There are three primary depositional environments where lead is found (SedEx - sedimentary exhalative, MVT - Mississippi Valley Type, and VMS - Volcanogenic Massive Sulfides), and all of these involve hydrothermal fluid circulation and precipitation of metallic ores. North Carolina has never been a major producer of lead, but it has been co-produced and produced as a by-product of more economically valuable metals like silver, gold, and copper. Lead occurrences have been located sporadically in several counties in the mountains, including some minor historical mining in Haywood County. Many of the same areas as mentioned earlier for gold are also where lead occurs or has been mined in modest quantities in the past (Stuckey, 1965). The uses of lead of course relate to its physical properties mentioned earlier, as well as its chemical properties (very low melting point, low conductivity, and high corrosion resistance).

Since lead became well-recognized as a neurotoxin in the environment, its usage has dramatically declined. Formerly, lead was used in many items like gasoline, paints, and water pipes. Most of the lead mined today goes into lead-acid batteries, with a smaller amount utilized in ammunition and as oxides in making ceramics and glass (Kropschot, 2011).

Thorium [**Th**], **Z=90**, is a dense, ductile, bright silver, highly radioactive metal. It is a member of the actinide group, a radioactive series of elements comprising actinium through lawrencium on the periodic table. Along with uranium, thorium is the only actinide member that occurs naturally in the environment above trace quantities. The primary ore mineral for thorium is monazite (a phosphate mineral that also contains rare earth elements). Monazite and its depositional environments were briefly discussed in the rare earth elements section of this compendium. As elsewhere in the world, economic concentrations of monazite are most often found via placer mining of transported deposits downstream of primary monazite source areas. Abrupt changes in slope gradients downstream can help to concentrate the heavier minerals like monazite. In North Carolina, there are monazite placer concentrations where some historic mining has occurred in the South Mountains area (McDowell, Burke, Rutherford Counties) as well as one location in Madison County (Stuckey, 1965). Monazite also occurs elsewhere in the state, including importantly along the Fall Zone in eastern North Carolina. Most monazite mining has rare earth elements as the primary objective, while only rarely is thorium isolated and produced. This infrequent production is due to the health hazards inherent with high levels of radioactivity in thorium. As such, over time, substitutes have been developed to help bypass the need for thorium in materials. Some current uses of thorium include some high-temperature applications like ceramics, aircraft engines, and light bulbs. Thorium has one of the highest melting points of any metal. A few radiometric age-dating techniques involve thorium; and numerous countries are exploring the feasibility of new nuclear technologies involving thorium instead of uranium (USGS, 2022).

Uranium [U], **Z=92**, is a naturally occurring, metallic, silver-gray, highly dense, and weakly radioactive element of the actinide group. The most common ore rock of uranium is pitchblende, a mostly amorphous form of the mineral uraninite (UO₂), although many other minor varieties of uranium-bearing minerals exist. These minerals are distributed widely across the globe in mostly very low concentrations. Uranium is often associated with other metallic elements such as copper, gold, and silver. Uranium deposits can be found in a wide variety of settings, including as primary deposits (formed directly from the Earth's mantle) and as secondary deposits (formed through the alteration of primary deposits). Uranium is considered an incompatible element in an igneous melt and thus can become concentrated in fractionated portions during latter stages of crystallization. Uranium also is readily soluble in the environment and can be dissolved, transported and reprecipitated based on subtle changes in reduction-oxidation (redox) conditions. This process generates secondary deposits of uranium. An example of secondary deposition occurs at certain Proterozoic unconformities where highly fractured and brecciated Proterozoic age rock lies below relatively undeformed Paleozoic strata (World Nuclear Association, May 2020). North Carolina does have numerous uranium occurrences across the state, with concentrations in/near the Spruce Pine Mining District and associated pegmatites, as well as

associations with phosphorite deposits in Quaternary sediments in/near Beaufort County on the coast. Interestingly, there are confirmed high uranium concentrations in the metasomatite deposits of Coles Hill, Virginia. A recent study (Hall, 2022) provides an updated depositional model for this area. Uranium deposits here reside along the western fault boundary of the Dan River Triassic age basin and could be a model for additional deposits in North Carolina, where the same and similarly situated Triassic basins exist. Uranium has several important and controversial uses in society. Most of these take advantage of uranium radioactivity and consider uranium to be an "energy mineral." U²³⁸ is the most abundant isotope of uranium, while U²³⁵ is one of the most high-energy radioactive isotopes. Most uranium comes with only small percentages of U²³⁵, which must be enriched to higher levels well beyond the typical 0.7% to be used as a fuel for nuclear power plants or weapons. A handful of other applications involve depleted uranium (DU), where much of the U²³⁵ has been removed. Because DU is very dense (~70% more than lead), it is sometimes used for radiation shielding, ballasts, and counterweights, for example (World Nuclear Association, November 2020).

PART 2: ANALYTE CONCENTRATION MAPS AND HISTOGRAMS

Symbolization Methods

In the creation of the analyte concentration maps, each analyte was first filtered for only those sampled values within North Carolina. A dual-symbology method of illustrating the variance in analyte concentrations is employed. First, a consistent, graduated color scheme was utilized for each analyte. A set of five discrete colors (yellow to red, with increasing concentration size) was initially used and the data distributed according to a Natural Breaks (Jenks) classification method. If an analyte had negative values, those were grouped separately and assigned a grey color.

As discussed earlier, negative values are meaningful and an important part of the dataset. Consequently, all values, including negatives, are represented in the maps. Negative values indicate only that the readings for that particular analyte were not determinable given factors including inherent instrument detection resolution and interference from other analytes within the sample.

Secondly, a proportional size symbology was blended with the graduated colors to better illustrate the variance in analyte concentrations. Symbol size ranges will vary across the many analytes and are particular to each analyte being examined. The sample locations for each analyte are variable in both geographic extent and density. The data for each analyte are also highly variable in statistical terms as well, including manner of distribution and overall value range. Negative values, if present in each dataset, are represented by the smallest size symbols.

Data Analysis

Following each analyte concentration map, a simplified histogram chart is included. Histograms visually summarize the distribution of a continuous numeric variable by measuring the frequency at which certain values appear in the dataset. The x-axis in the histogram is a number line of analyte concentration values that has been split into number ranges or bins. To be as consistent as possible, while accommodating such a large variable dataset, the number of bins for each analyte is set to a base-10 logarithmic scale. One example of histogram utility is that an end user can quickly evaluate where their concentration values of interest fall within the statewide frequency distribution for a given analyte.

Negative values are not included within the histogram data, to maintain consistency among charts and to aid in understanding. The USGS notes there are detailed methods for handling negative data values, including deriving statistics (see Helsel, 2005). The user is encouraged to explore such methods if a more rigorous data analysis is desired.

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APPENDIX – ANALYTE CONCENTRATION MAPS AND HISTOGRAMS

The following figures contain an analyte concentration map and a histogram chart for each analyte listed in Part 1, Section II of this document. These figures are arranged by the analytes' increasing atomic numbers (Z-values).

Map Parameters:

- All maps were created with Esri ArcGIS[®] Pro, version 3.1.1 software.
- Each analyte value is represented with a blend of two symbologies: 1) graduated colors, and 2) proportional sizes.
- A modified natural breaks (Jenks) classification method is employed for the graduated color scheme. Five classes are created and coded by discrete colors ranging from pale yellow to deep red, with increasing analyte concentrations. Negative values, if present, are colored grey and replace the lowest end color (pale yellow).
- Proportional symbol sizes are further utilized to highlight data variations. Each analyte has a unique symbol size range to account for the large variance between analyte datasets. Negative values, where present, are represented by the smallest symbol sizes.
- The largest symbol sizes have transparency settings of 30% to aid in visualization when points are clustered around high values.
- Each map is set to 1:2,084,627 resolution.

Histogram Parameters:

- Histograms were created using Microsoft PowerBI[®] software. Data was downloaded directly from the USGS NURE HSSR sediment data website (<u>Geochemistry of sediments</u> <u>in the US from the NURE-HSSR database https://mrdata.usgs.gov/nure/sediment/</u> (<u>usgs.gov</u>)) as a single csv file restricted to the state of North Carolina geographic boundary.
- The count data (y-axis) is on a linear scale, while the sample values data (x-axis) is on a logarithmic (base-10) scale for clarity in visualizing the range of value information. Note: count refers to the number of samples registering a particular value.
- Negative values actually have meaning and are termed "nondetects," which is defined as concentration values registering below the determination limit of the particular instrumentation utilized for a given analyte. In the context of this report, such values are not shown in the histograms for clarity of visualization. Because of these nondetects, it is advised that users view these histograms as an approximate guide to data distribution only. If more precision is desired, users are advised to access the raw data directly and analyze according to their preferences.
Lithium [Li]





Beryllium [Be]

Z=4





Fluorine [F]





Sodium [Na]





Magnesium [Mg]





Aluminum [Al]





Phosphorus [P]





Potassium [K]





Calcium [Ca]





Scandium [Sc]





Titanium [Ti]





Vanadium [V]





Chromium [Cr]





Manganese [Mn]





Iron [Fe]







Cobalt [Co]





Nickel [Ni]







Copper [Cu]




Zinc [Zn]





Arsenic [As]





Selenium [Se]





Strontium [Sr]





Yttrium [Y]





Niobium [Nb]







Molybdenum [Mo]

Z=42





Silver [Ag]







Tin [Sn]







Cesium [Cs]





Barium [Ba]





Lanthanum [La]





Cerium [Ce]





Samarium [Sm]





Europium [Eu]





Terbium [Tb]





Dysprosium [Dy]





Ytterbium [Yb]




Lutetium [Lu]





Hafnium [Hf]





Tantalum [Ta]





Tungsten [W]





Gold [Au]





Lead [Pb]







Thorium [Th]





Uranium [U]







TERMS OF USE FOR NCGS PRODUCTS

The use of information contained on the <u>Geochemical Atlas of North Carolina Web-Experience</u> platform, as well as the maps and histograms, is encouraged for any persons or entities, with emphasis on industry professionals, county and municipal governments, and other state government agencies working within North Carolina. As part of our mission states, the NCGS examines, surveys, and maps the geology, mineral resources, and topography of the state to encourage the wise conservation and use of these resources by industry, commerce, agriculture, and government agencies for the general welfare of the citizens of North Carolina. The NCGS conducts basic and applied research projects in environmental geology, mineral resource exploration, hazards mapping, and systematic geologic mapping. Services include identifying rock and mineral samples submitted by citizens and providing consulting services and specially prepared reports to agencies that require geological information.

In addition to newer digital means of distribution, such as the <u>Geochemical Atlas of North Carolina Web-Experience</u>, the Geological Survey Section publishes Bulletins, Information Circulars, Open-file Reports and Maps, Field Trip Guidebooks, Geologic Map Series, and Special Publications that can be ordered from the <u>NCGS publications ordering page</u>.

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IN MEMORIAM

Project inspired by the previous efforts of former NCGS colleague, Dr. Jeffrey C. Reid (1948 - 2019).