Master's Thesis♣

Petrology of Saprolites in Central Hesse

Oluwatobiloba Odukoya

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University of Freiburg
Geology - Institute of Mineralogy and Petrology
Faculty of Environment and Natural Resources

Author Oluwatobiloba Odukoya,
Matriculation Number: 5364725

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Examiners Dr. Lukas Gegg,
Department of Sedimentary Geology and Quaternary Research
Department of Geology

Supervior Prof. David Dolejs,
Institute of Mineralogy and Petrology
Department of Geology

Declaration

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Abstract

The comprehensive analysis of saprolites from various lithologies endemic to Central Hesse has provided valuable insights into the weathering processes and products of Tertiary Europe. Through the integration of petrology, micromorphology, grain size analysis, and geochemistry, a detailed picture of formation conditions has emerged. Geochemical analyses reveal a consistent enrichment of immobile elements and depletion of alkali components, highlighting the intensity of chemical weathering. Secondary mineralizations of hematite, goethite, and siderite further confirm the transformative effects of weathering on the original rock compositions. Petrographic observations complement these findings, showcasing fine-grained textures, clay coatings, and flow structures indicative of fluid activity. Collectively, these features point to weathering as the dominant alteration mechanism, with little evidence of hydrothermal interference.

The observed alteration patterns provide valuable insights into past climatic conditions, suggesting a history of intense weathering regimes. These results have broader implications for reconstructing paleoenvironments and understanding the mobility of elements during weathering. Additionally, the study highlights the need for methodological advancements in grain size analysis, particularly for fine-grained materials, to improve measurement accuracy. By integrating multidisciplinary approaches, this research contributes to unraveling the complexities of weathering processes and their implications for geological and environmental sciences.

In conclusion, this study underscores the transformative impact of weathering on saprolites, driven by a combination of chemical, physical, and mineralogical processes. Past climatic conditions have facilitated intense chemical weathering, aided by fluid transport, resulting in highly altered mineral assemblages enriched in immobile elements, some of which hold economic significance. These findings enhance our understanding of weathering dynamics and provide a foundation for future investigations into the interplay between geology, climate, and surface processes.

Zusammenfassung

Die umfassende Analyse von Saproliten aus verschiedenen in Mittelhessen vorkommenden Lithologien hat wertvolle Einblicke in die Verwitterungsprozesse und -produkte des tertiären Europas geliefert. Durch die Integration von Petrologie, Mikromorphologie, Korngrößenanalyse und Geochemie ist ein detailliertes Bild der Bildungsbedingungen entstanden. Geochemische Analysen zeigen eine konsistente Anreicherung von immobilen Elementen und eine Verarmung von Alkalibestandteilen, was die Intensität der chemischen Verwitterung verdeutlicht. Sekundäre Mineralisierungen von Hämatit, Goethit und Siderit bestätigen die transformativen Auswirkungen der Verwitterung auf die ursprüngliche Gesteinszusammensetzung. Petrographische Beobachtungen ergänzen diese Ergebnisse und zeigen feinkörnige Texturen, Tonüberzüge und Fließstrukturen, die auf flüssige Aktivitäten hinweisen. Insgesamt deuten diese Merkmale auf Verwitterung als vorherrschenden Alterationsmechanismus hin, wobei es kaum Anzeichen für hydrothermale Störungen gibt.

Die beobachteten Alterationsmuster bieten wertvolle Einblicke in die klimatischen Bedingungen der Vergangenheit und lassen auf eine Geschichte intensiver Verwitterungsregime schließen. Diese Ergebnisse haben weitreichende Auswirkungen auf die Rekonstruktion von Paläoumgebungen und das Verständnis der Mobilität von Elementen während der Verwitterung. Darüber hinaus unterstreicht die Studie den Bedarf an methodischen Fortschritten bei der Korngrößenanalyse, insbesondere bei feinkörnigem Material, um die Messgenauigkeit zu verbessern. Durch die Integration multidisziplinärer Ansätze trägt diese Studie dazu bei, die Komplexität von Verwitterungsprozessen und ihre Auswirkungen auf die Geologie und die Umweltwissenschaften zu entschlüsseln.

Zusammenfassend unterstreicht diese Studie die transformativen Auswirkungen der Verwitterung auf Saprolite, die durch eine Kombination von chemischen, physikalischen und mineralogischen Prozessen angetrieben werden. Die klimatis-

chen Bedingungen der Vergangenheit haben eine intensive chemische Verwitterung begünstigt, die durch den Flüssigkeitstransport unterstützt wurde und zu einer stark veränderten Mineralzusammensetzung führte, die mit immobilen Elementen angereichert ist, von denen einige wirtschaftliche Bedeutung haben. Diese Ergebnisse verbessern unser Verständnis der Verwitterungsdynamik und bieten eine Grundlage für künftige Untersuchungen des Zusammenspiels zwischen Geologie, Klima und Oberflächenprozessen.

Acknowledgments

I am deeply grateful to my supervisor, Prof Dolejs, for his invaluable guidance, support, and encouragement throughout this research. His expertise and dedication have been instrumental in shaping the direction and success of this work.

To my classmates, especially Nico Nöthen and Edwin Wambicho, I appreciate your camaraderie and insightful discussions, which made this journey both intellectually stimulating and enjoyable. To the wonderful staff at the department that lent me their wisdom, expertise and precious time.

On a personal note, I owe a heartfelt thanks to my family for their unwavering support, patience, and encouragement. Your belief in me has been my greatest source of strength.

Finally, I dedicate this work to Alethea Harrison, my muse and my inspiration.

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Chapter 1

Introduction

Saprolites, which are also known as "Weathering mantles" or "Grus" (especially concerning weathering granites), are a widespread feature of landscapes on every continent, occurring at or near the earth's surface. They are most prominent in tropical to subtropical regions where they regularly exceed depths of 50 m Stoops, Marcelino, and Mees (2018), however, saprolites are not restricted to these locations as they can be as small as a few millimetres thick in temperate regions. In Europe, the distribution of saprolites is varied but is of significant quantities as they are present in central, western, and northern Europe. Locations where the presence of saprolites is well documented include the Iberian Peninsula, the Massif Central in France, parts of the Rhenish Massif in Germany (our study area), the British Isles, the Scandinavian Mountains, and the Fennoscandian Shield Migoń and Lidmar-Bergström (2001); Vazquez (1981).

The word "Saprolite" was coined from the Greek for "rotten rock" (*/sapros lithos/*) by G.F. Becker (1895) to describe bedrock still in the process of pedogenesis and delineate it from the layers further down the line of decomposition. They are the weathering remains of preexisting rocks exposed to atmospheric conditions such as precipitation, diurnal temperature changes, microbial activity, and high oxygen fugacity. They are the product of mineral transformations driven by thermodynamics, as the formation conditions at depth significantly differ from the conditions they encounter after their host rocks are exhumed. Saprolites differ from other weathering products because they remain in situ, meaning they develop as a covering, lying directly on top of the unweathered rock, like an outer skin. Due to this lack of mobilization, they also retain their rock fabric, even though the degree to which the fabric preservation varies with depth. The exact rate of weathering and thickness of the weathering mantle depends on the time spent at or close to the surface, the climate, and the rock type Ehlen (2005).

Saprolites frequently constitute a part of a more extensive stratigraphic sequence and usually only serve as a subordinate layer within the weathered profile. The weathered profile or regolith, as a whole, is an aggregate of layers of rock pieces in various stages of disintegration and originating from multiple sources. The A-B-C scheme was first introduced by Orth (1873, 1875) and later evolved by Dokuchaev, Vasily (1879a, 1879b). Improvements by Fowler (1925) brought the scheme to what is recognized today as the most widely accepted approach to the description of soil profiles Tandarich, Darmody, Follmer, and Johnson (2002). However, even though there is a unification of the scheme, there is no unification of the terms within the scheme, and the components are modified by authors to represent a variety of features studied, as evidenced by the review of Tandarich Tandarich et al. (2002).

The German soil classification scheme, as defined in the KA5 Eckelmann et al. (2006), begins the weathered profile with a layer littered with organic material that has just begun to humify and is known as the "O Horizon." Below this layer is a completely disaggregated and unstructured layer which has lost all structure due to some varying combinations of biological and environmental processes and is known as the "A Horizon" or topsoil. The next layer, called the "E Horizon," is where acids formed during humification of the organic matter in the previous layers, strip elements from the minerals in its layer and precipitates them further down, in a process called podzolization. Next is the "B Horizon," which is structurally similar to the A Horizon but includes precipitates formed from the leaching processes in the layers above and less organic material. After that is the "C Horizon," which has begun to weather but still preserves the structure of the bedrock below it. This layer corresponds to the titular saprolites and can be characterized as being the closest in density to the unaltered bedrock and the least affected by soil-forming processes of all the horizons.

Saprolites are studied by geochemists, civil engineers, hydrologists, geomorphologists, soil scientists, and exploration geoscientists for different purposes. They can serve as aquifers from which groundwater can be tapped or may form hosts for economic deposits through secondary or supergene enrichment for resources such as gypsum, clays, aluminium, manganese, nickel, copper, uranium, iron, gold, and other heavy minerals. Saprolites also serve as a window to the past, through which the events that led to their formation can be observed. Therefore, their study is important to understanding and predicting the effects of current geo-climatic processes.

Chapter 2

Geological Setting

The study was carried out in localities in and around Central Hesse. The localities range from Weickartshain in eastern Giessen (central Hesse) to Liebenscheid in southern Siegen (North-Rhine Westphalia) and Wasenbach in north-eastern Rhein-Lahn-Kreis (Rhineland Palatinate). A general triangulation of the area is shown in Figure 2.1 and shows that the samples come from an area encompassing a total of 1,432 km^2.

Figure 2.1: Showing study area dimensions (maps.google.com)

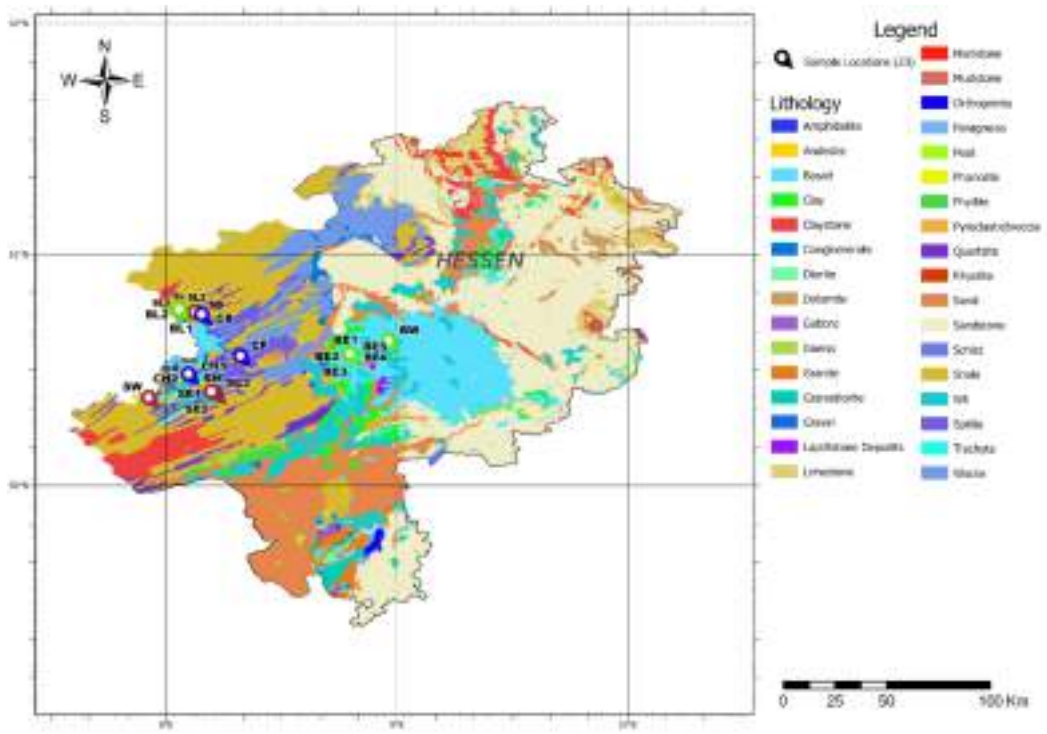

Figure 4.1: Geological map of study area showing sample location and the geology that underlay them (modified from BGR (2018)

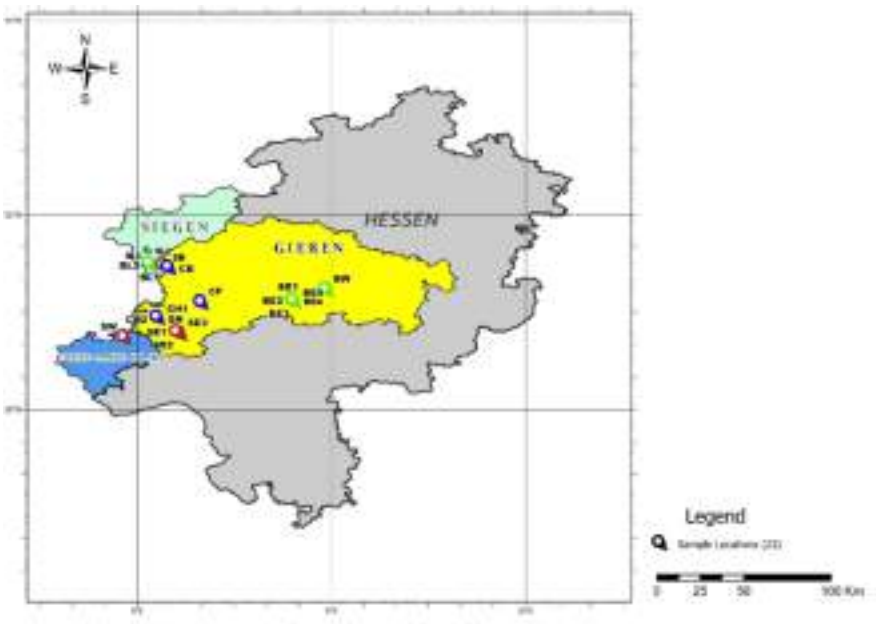

Figure 2.2: Sample locations relative to their position on a map of Hesse

The regional geology of the study area varies greatly in formation time and lithologyThe area is chiefly underlain by metasedimentary rocks from the late Palaeozoic era that are crosscut in various locations by Cenozoic volcanics. There are also various sedimentary units stretching geochronologically between the Palaeozoic and the Cenozoic. The units belong to geological provinces of the Rhenish Massif or Rhenish Slate Mountains ("Rheinisches Schiefergebirge" in German) and the Hessian Depression ("Hessische Senke" in German), both of which have been affected by the tectonics of the Tertiary period. The Rhenish massif is a made up of smaller geological units and the units which were sampled are the Taunus and Westerwald, located in the southern eastern portion of the province. The Hessian Depression also hosts a number geological units and the unit of interest to our study is the Vogelsberg volcanic field. The three significant units are shown in Figure 2.3 and would be discussed individually for the rest of the chapter.

Figure 2.3: Regional Geology of Study Area Modified from (BGR, 2018)

2.1 Taunus

Taunus is the name given to a NW-SE striking mountain range located between Lorch am Rhein and Bad Nauheim with a length of about 75 km Toussaint (2024). It has a shared formation history with the adjacent Hunsrück hills, which are located on the other side of the Rhine river, as both resulted from orogenic events. The mountains are characterized by rugged ridges, deeply incised river valleys and broad plateaus. Together with the Hunsrück hills, they form the southern base of the Rhenish massif.

The Taunus as a geologic structural unit began as series of sedimentary facies that underwent tectonic compression between the Devonian and the Carboniferous periods Doublier, Potel, Franke, and Roache (2012). This was followed by episodic uplift from the Oligocene through to the Quaternary (low rates in the present day) and volcanism that formed two of the largest volcanics in Germany (Vogelsberg and Westerwald) from the Oligocene to the Quaternary El-Kelani, Jentzsch, and Schreiber (1998); Felix-Henningsen (2018); Haase, Goldschmidt, and Garbe-Schönberg (2004); Todt and Lippolt (1980). According to (Felix-Henningsen, 1994a, 2003, 2018) weathering began in the Rhenish massif in a tropical to subtropical paleoclimate during the Upper Mesozoic. This series of events resulted

Chapter 3

Analytical Methods

A total of twenty-three samples were selected to be investigated using the analytical methods discussed in this chapter. After the samples were collected from the field, they were air-dried in open plastic sampling bags between March 2024 and August 2024. A brief overview of the samples selected for each method is given in Figure 3.1. Following this is a detailed description of the procedures for each method.

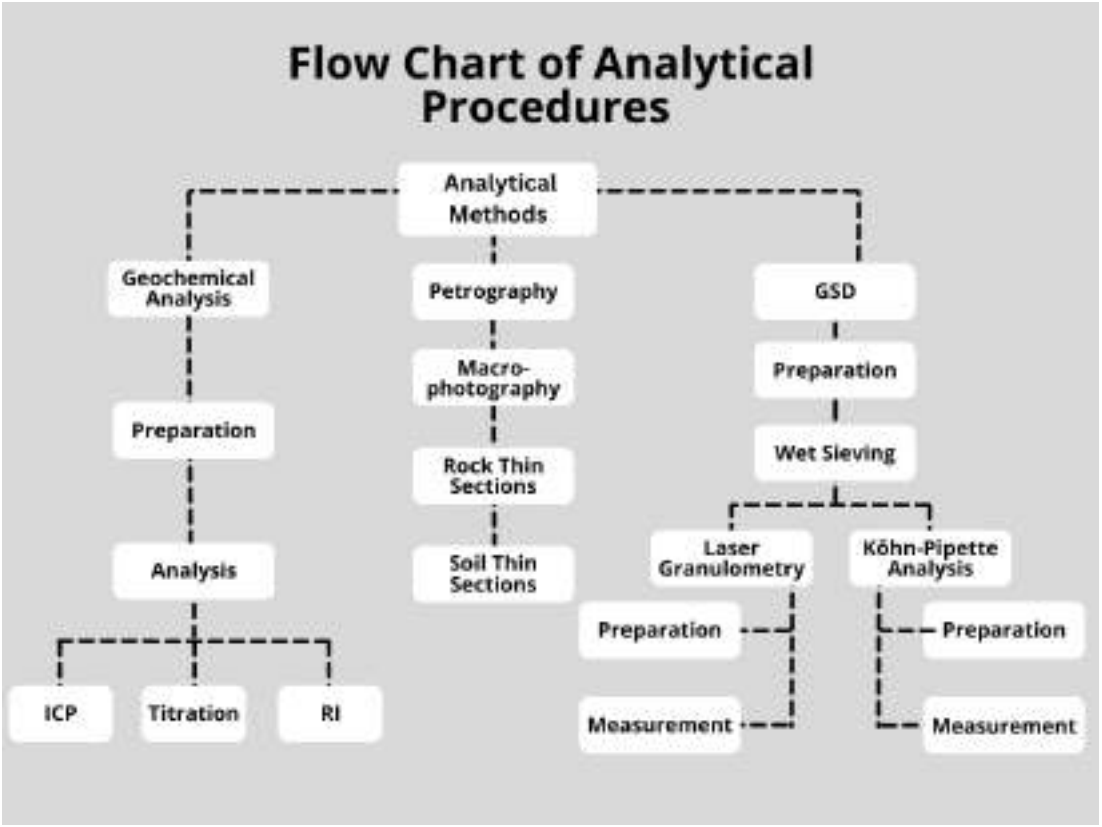

Figure 3.1: Flow Chart of Analytical Procedures

Table 3.1: Table 3.1: The Schedule of Analytical Methods

No.	Samples	Methods					
		WR-GCH	**Microphotography**		**Macro-photog-raphy**	**Grain Size Distribution**	
			Rock Sect	Soil sect		Sedimat	Mastersizer
Slate saprolites							
1	SB	✓				✓	✓
2	SE1	✓			✓		
3	SE2	✓			✓	✓	✓
4	SE3	✓		✓	✓	✓	✓
5	SH	✓			✓	✓	✓
6	SL	✓				✓	✓
7	SL2		✓✓[a]		✓		
8	SW	✓		✓	✓	✓	✓
Carbonate saprolites							
9	CB	✓	✓✓[a]		✓		
10	CF		✓✓[a]		✓		
11	CH1	✓		✓	✓	✓	✓
12	CH2	✓		✓	✓	✓	✓
13	CH3			✓	✓	✓	✓
14	CH4			✓	✓		
Basalt saprolites							
15	BE1	✓	✓		✓	✓	✓
16	BE2	✓	✓		✓	✓	✓
17	BE3	✓	✓		✓	✓	✓
18	BE4	✓	✓		✓		
19	BE5		✓		✓		
20	BL1	✓	✓		✓		
21	BL2	✓	✓		✓		
22	BL3	✓			✓		
23	BW			✓	✓		

a double tickmarks indicate that there are two samples for these lithologies

4.4.4 Classification and Discrimination Diagrams

The data above is presented in this final section as mineral classification and geotectonic classification plots to help classify the saprolites and also to observe how much they deviate from their ideal chemistry.

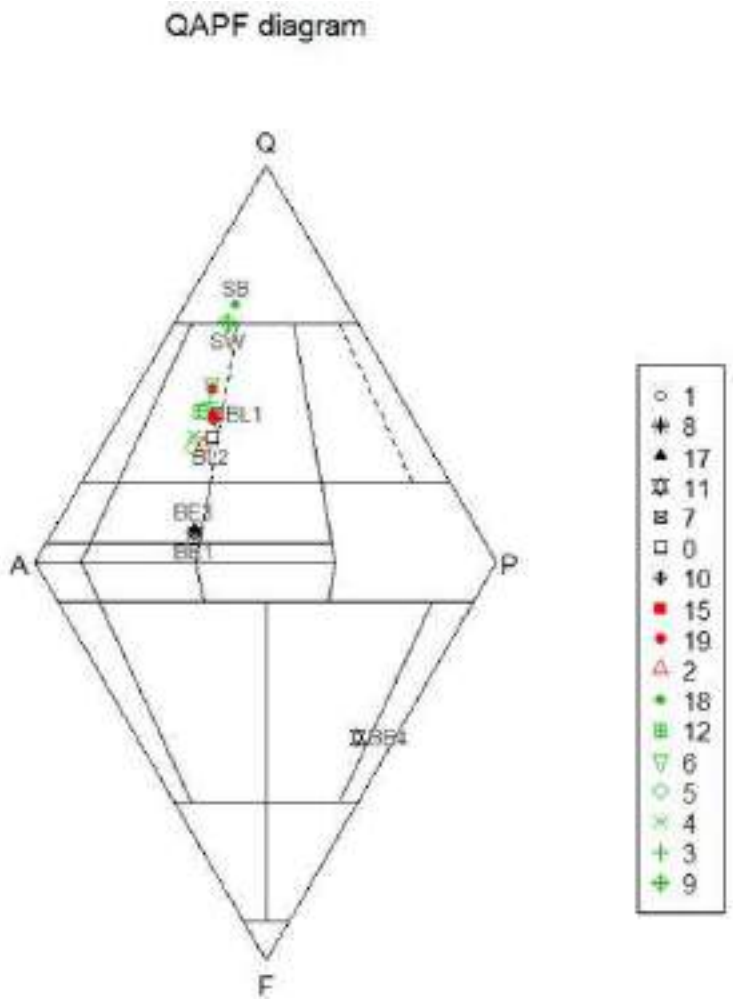

Figure 4.17: Quartz-Alkali-Plagioclase-Feldspathoid Classification Diagram from CIPW-norm data (Streckeisen, 1976) (BE1=1, BE2=8, BE3=17, BE4=11, BL1=7, BL2=0, BL3=10, CB=15, CH1=19, CH2=2, SB=18, SE1=12, SE2=6, SE3=5, SH=4, SL=3, SW=9)

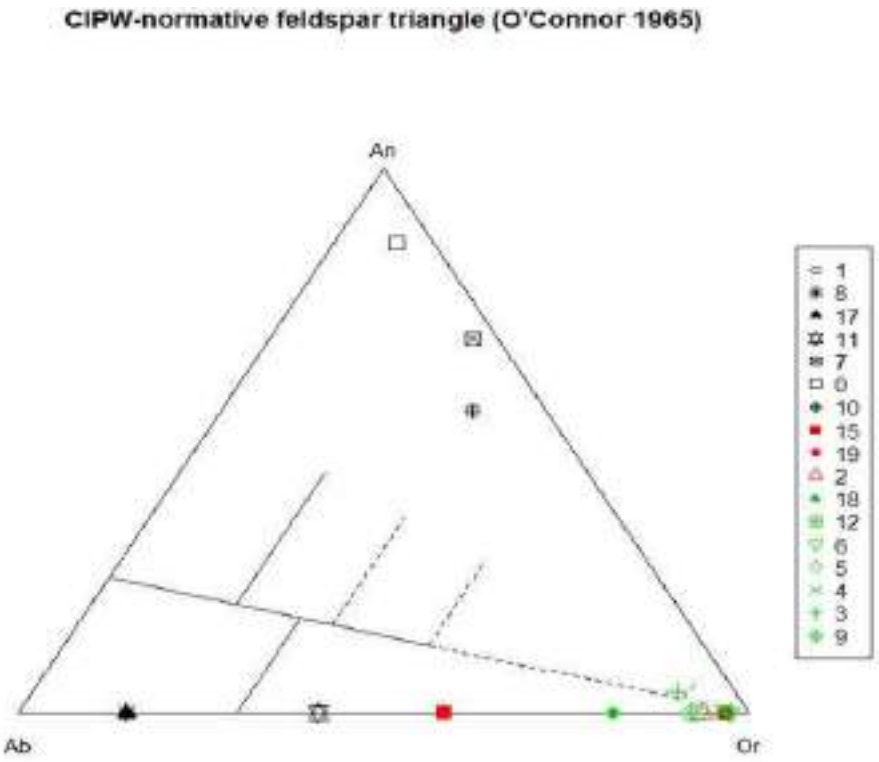

Figure 4.18: Albite-Anorthite-Orthoclase Classification (O'Connor 1965) (BE1=1, BE2=8, BE3=17, BE4=11, BL1=7, BL2=0, BL3=10, CB=15, CH1=19, CH2=2, SB=18, SE1=12, SE2=6, SE3=5, SH=4, SL=3, SW=9)

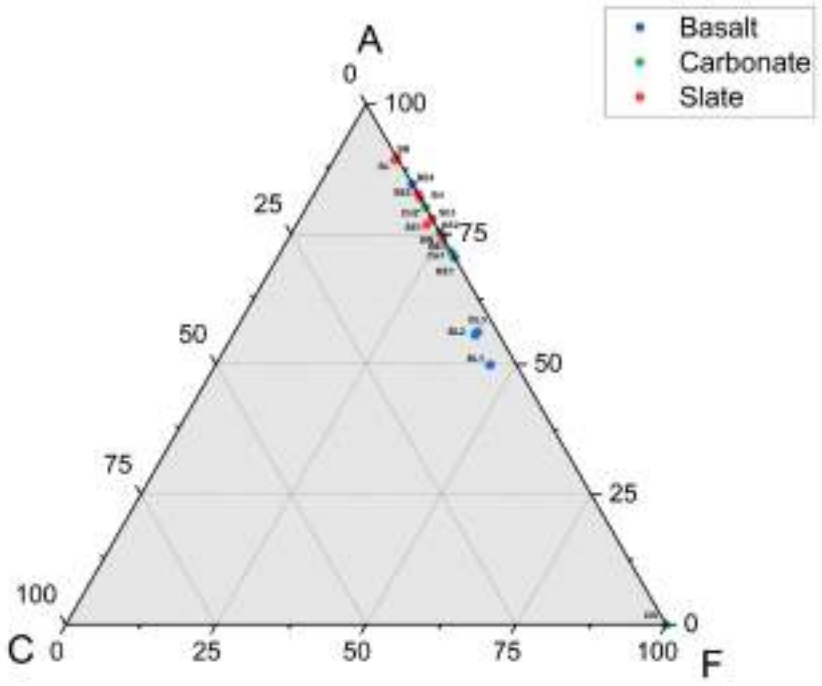

Figure 4.19: Al_2O_3-CaO-FeO/MgO Discrimination Diagram

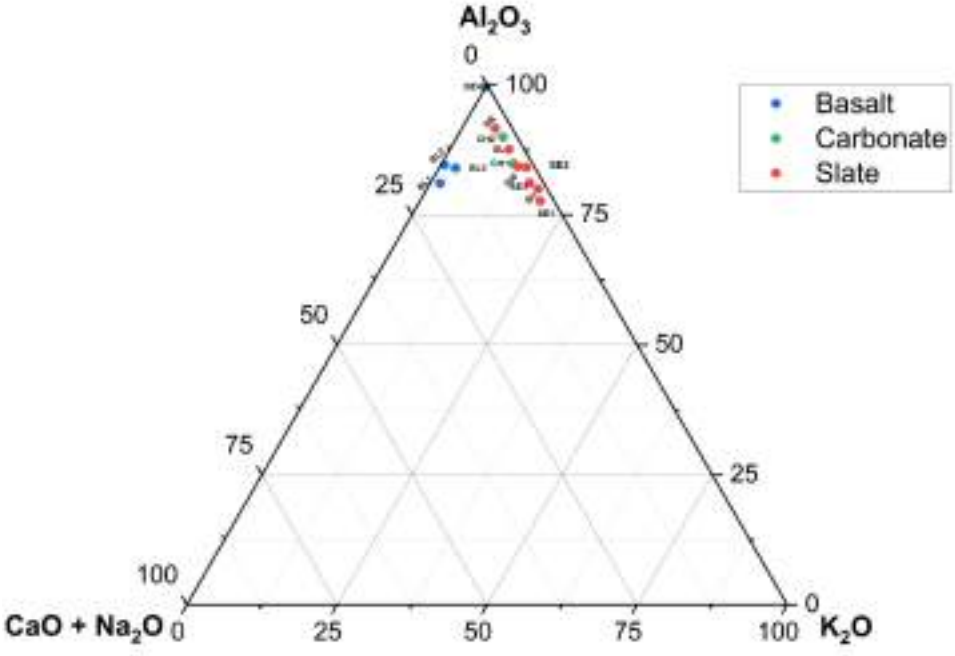

Figure 4.20: Al_2O_3-CaONa_2O-K_2O Discrimination Diagram

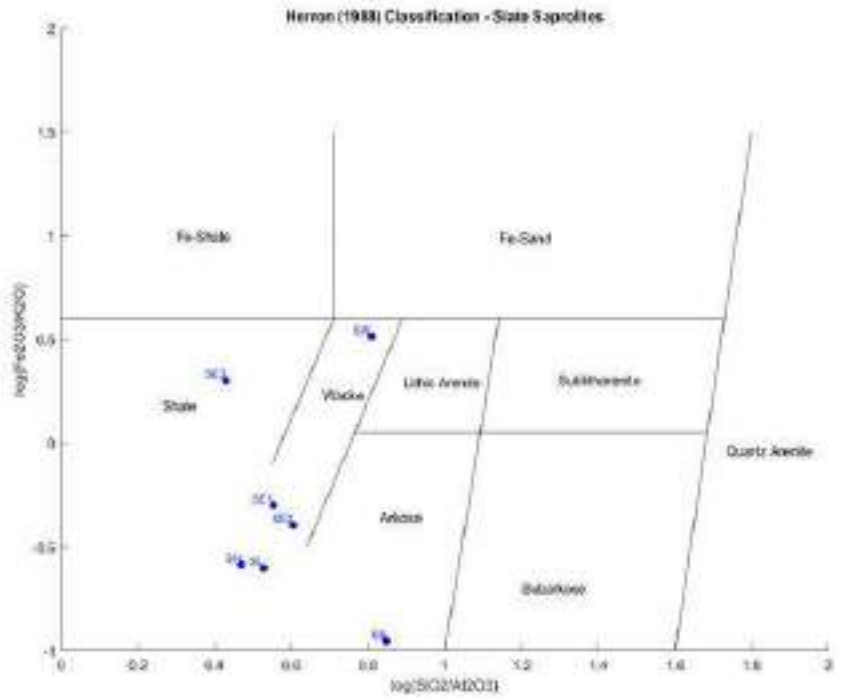

Figure 4.21: Classification diagram of Herron (1988) for Discriminating Sediment Types

Chapter 5

Discussion

Discussion This chapter discusses the results obtained from the analysis of the saprolites from three precursor rock types. The results are brought to life by comparing the findings with those from other studies in the region, as well as distant localities with similar settings. The results from the grain size determination are also examined, as the results of the two methods defer quantitatively.

The results in the previous chapter confirm the alteration of the samples from the various precursor rocks analysed. The premise for the study was established, as the extent of alteration observed is not commensurate with the current climatic conditions. The evidences that support the alteration to be by weathering are first discussed here. The weathering indices show that there is significant alteration in all saprolite precursors. From the petrography and geochemistry, it can be seen that all lithologies are significantly enriched in oxides of iron, titanium and aluminium. This increase was seen to coincide with a depletion in alkali oxides, which was especially observable in the carbonate samples which had unexpectedly low Cao values. The low CaO values were coupled with unexpectedly low CO2 values which indicate that they had been hitherto lost. The basalt saprolites were also observed to have high LOI values of up to 25 % (wt). In Addition to all these, the petrography revealed an abundance of flow structures left behind by the action of fluids. These evidences however prove that the precursor rocks are altered but doesn't point us in the direction of weathering or hydrothermal alteration.

To differentiate between these two types of alterations, we first look at the mineral assemblages. Petrographically, the secondary mineral products of hematite, goethite and siderite along with the opaque oxides in the groundmass and clay coatings on crystals suggest the mineralization was achieved at temperatures closer to surface temperature. There are also no assemblages that indicate

hydrothermal, such as the absence of barite and fluorite that usually occurs with the formation of siderite in carbonate (Xie et al., 2023). Geochemically, the high concentration of Al oxides over the alkali oxides suggests that there was significant leaching of the alkali components or enrichment of Al oxides, both of which are only possibilities in places with intensive weathering regimes. Qualitatively, the two methods for grain size analysis confirm the abundance of fine-grained particles which have also been petrographically observed. While the formation of fine grains is not unique to the weathering process, it is sufficient to suggest that the adjacent kaolinite zones observed in the field could be genetically linked to the rocks sampled and profiles can be analysed in the future to trace the movement of the mobile elements.

In the Hunsrück area, which is about 30 km west of the general study area, the same weathering phenomena have been observed (Felix-Henningsen, 1994b; Felix-Henningsen & Spies, 1986; Sauer & Felix-Henningsen, 2006). Geochemical studies in the Ardennes Massif of Luxembourg by Moragues-Quiroga et al. (2017), are comparable to the results of our slate saprolites. The SiO2 and Al2O3 values fit with that of the slates in our study, but when comparing the alkali component, our slates appear to be significantly depleted. Conversely, the iron content is higher in the slates from our study area, which signifies that the measured samples were more weathered than that chosen in the study of Moragues-Quiroga et al. (2017).

5.1 Comparison of Grain Size Determinations: Mechanical vs. Diffraction Methods

Grain size distribution is an important parameter of lithologies as they are one of the building blocks for the physical properties used for their identification. The study of the size distribution is typically most emphasized for sedimentary lithologies and thus, the methods have been optimized for this type of lithologies, especially quartzofeldspathic lithologies which are richer in coarser grains due to the resistance of quartz and feldspar to abrasion. This emphasis has resulted in the lack of innovation in the methods for the measurement of fine-grained materials which are usually of alternate mineralogy.

In this study, the Koehn method and the laser diffraction method have both been applied to ensure the accuracy of the results. However, while they are equally qualitative, they did not produce quantitative results that matched one

another. Results from both methods have been recast to cumulative frequencies and are presented in Figures 5.1 to 5.3. In the plots for the basalt and carbonate saprolites (Figures 5.1 and 5.2), a clear partition is seen between the two datasets belonging to the two methods. There is also a difference in the shapes of the curve profiles, which is significant because the gradient of the curves depict the rate of change of grain sizes which is a function of grain size sorting. The slate saprolites do not appear to have the same gap between the data sets and therefore the two sets of data roughly have the same shapes overall. The datasets for each method still differ by up to 20 % for the same data points, causing the significant underestimation or overestimation of significant classes necessary for the classification of the grain size distribution.

The problem is seen to arise due to the deviation from sphericity of clay minerals. Both methods make their measurements with the assumption that the particles being measured are spherical. In addition to this assumption of sphericity, the laser diffraction method also assumes a uniform density of materials being measured. Increasing abundances of clay minerals in samples propagates measurement uncertainty and increases errors in both methods.

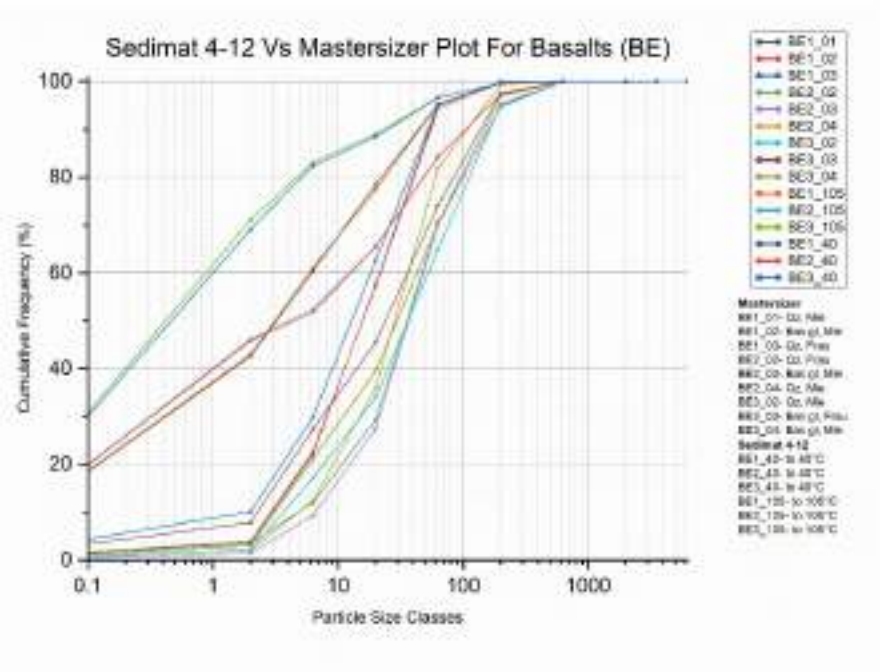

Figure 5.1: Comparison of Grain Size Distribution Results from Sedimat 4-12 and Mastersizer 3000 for Basalts

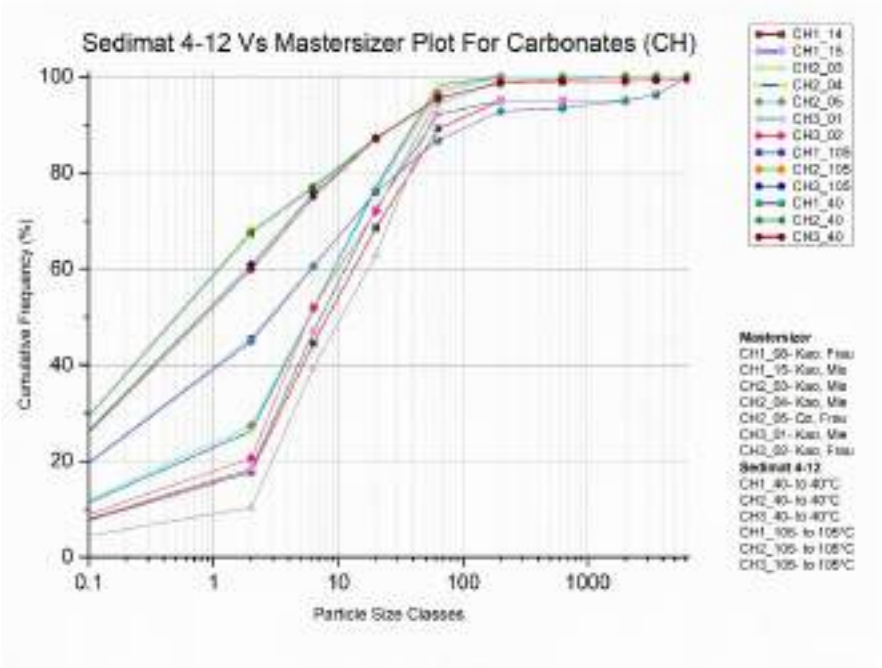

Figure 5.2: Comparison of Grain Size Distribution Results from Sedimat 4-12 and Mastersizer 3000 for Carbonates

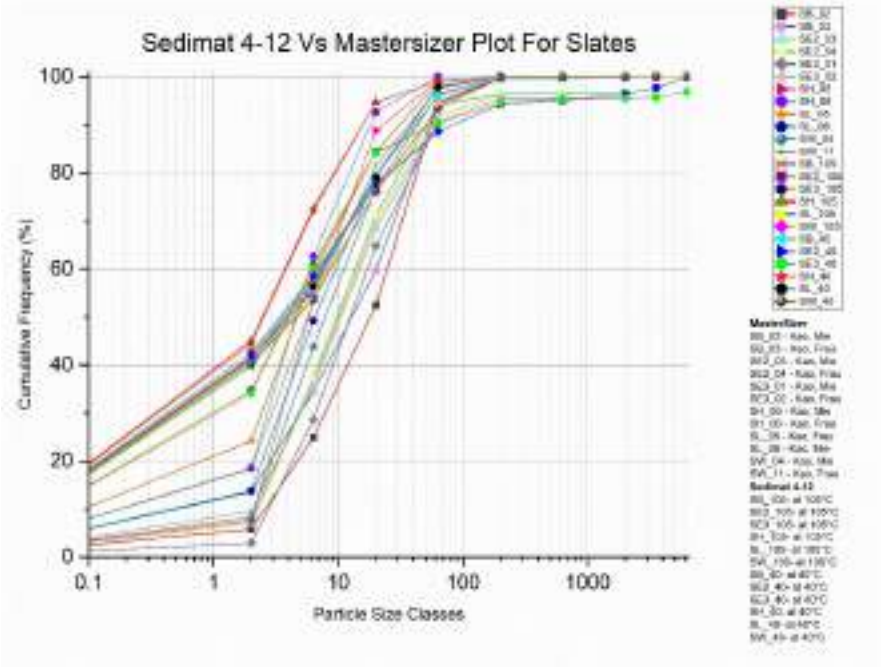

Figure 5.3: Comparison of Grain Size Distribution Results from Sedimat 4-12 and Mastersizer 3000 for Slates

5.2 Interpretation of Weathering Processes

The weathering process in these saprolites can be summarized as a system exhibiting high chemical activity, significantly enhanced by water as a transporting medium.. Chemical weathering leads to the breakdown of primary minerals, leaching of mobile elements, and formation of secondary minerals. This is evidenced by the geochemical trends and the petrographic observations of mineral replacements.This seems to have been consistenly followed by redistribution by fluids, presumably exposing fresh surfaces for chemical weathering to re-intensify. This can be seen especially in the carbonate and slate samples with their relict water pathways.

Weathering intensity varies across samples, with some retaining more of their original characteristics (BE2 and BE5) while others show advanced alteration (BE3, BE4 and BL3). This variability likely reflects differences in local environmental conditions, exposure time, and inherent rock properties. The formation of secondary minerals, such as clays and iron oxides, plays a crucial role in the weathering process. These minerals not only contribute to the observed color changes but also influence the physical properties of the saprolite, such as porosity and permeability.

In conclusion, past climatic conditions has led to a suite of rocks that underwent intense chemical weathering aided by fluid transport. This has led to the formation of assemblages that are mineralogically highly altered to the state of enrichment in immobile elements which are economically significan in some cases.

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