A multi-proxy study of red clays from the Carpathian Basin: implications for provenance, sedimentary processes and age, and late Cenozoic climate and environmental changes

Final report

The goals of this research were to gain insights into the quantitative estimates of paleoclimatic variabilities through the purpose to reveal connections between paleosol (red clay) genesis and paleoclimatology. There are climofunctions or mathematical relationships between climate and soil characteristics (elemental compositions). This feature is thought to be important as the goethite–hematite (G/H) ratio of paleosols can be used, based on a recently developed climate transfer function, for reconstructing quantitative mean annual precipitation (MAP) estimates in the Cenozoic. Red clay/paleosol chronology using (U-Th)/He dating of pedogenic goethite and an extensive dataset of heavy minerals is established for provenance from the various red clays, also considering the stratigraphy and ages of red clay sedimentation.

The project was successful in all aspects. As a result of the complex mineralogical, petrological, geochemical, and age estimation investigations we (1) have clearly demonstrated that two types of red clay can be distinguished, (2) an integrated interpretation of the stable isotope-geochemical results have shown that these data are in good agreement with the climatic evaluations of the paleontological stable isotope data of the primate tooth enamel, (3) demonstrated by particle size distribution studies that some of the red clay (especially in the Pleistocene), like the loess, was deposited from wind-blown dust, (4) have delimited the dominant source area of the red clay, (5) the goethite pisolites formed in the clay provides a lot of information on the paleoenvironment, the genetics of the clay/silt sediment, (6) provided new data for the age determination of red clays using the goethite (U-Th)/He dating method, (7) discovered microcrystals of wavellite, crandallite, and cacoxenite in cracks of some iron pisolites, (8) have pointed out that the red clay/paleosol of the lower red clay in the Paks Loess Formation and the red clay of the Kerecsend Red Clay Formation are mineralogically quite similar to the Tengelic Red Clay Fm.

The most significant results have been published in the leading journals of geosciences, mineralogy, and paleoenvironments such as Quaternary Science Reviews, Palaeo3, Frontiers in Earth Science, and Mineralogy, they were reported in a book chapter. The cumulative impact factor for the published papers is 17.805. A Ph.D. dissertation and a BSc thesis which received the second prize at the OTDK conference were completed based on the project. The participants reported their results at national and international conferences, including a session topic in INQUA convened by the P.I. “Plio-Pleistocene transition”, which was organized among others to disseminate the findings of this project.
(https://virtual.oxfordabstracts.com/#/event/public/574/session/4676)

Major results

1. *Clay mineralogical investigations*

Clay mineralogical investigations and the findings interpreted from them support, and in part compliment, our knowledge of red clays. Although these investigations have not brought any ground-breaking new information, they have provided new insights into the paleoenvironmental conclusions that can be drawn from the clays. This information complemented and confirmed the paleoenvironmental interpretation based on geochemical studies. The mineralogical analyses clearly demonstrated that two types of red clay can be distinguished within the red clays; one is the younger (Pleistocene) red clay (reddish clay) with a high illite-montmorillonite (smectite) content, and the other is the older (Pliocene) red clay, in which the dominant minerals of the clay fraction are kaolinite with minor illite and smectite, as well as gibbsite which is also present in some samples. The weathering product of a warm (subtropical)-humid climate is kaolinite-halloysite, which is characteristic of Pliocene red clays. Smectite dominant weathering, at similarly high temperatures but with lower precipitation, occurs in a dry Mediterranean climate, which is characteristic of Pleistocene red clays. These two different mineral parageneses mark two different mineral facies in the Pannonian Basin. Our findings show that in the wider Carpathian Basin, Slovak, Croatian, Serbian, and Romanian red clay deposits are predominantly Pleistocene in age. This lower rainfall, and dry Mediterranean climate, which played a role in the formation of the Pleistocene red clays, is also evidenced by the clay minerals. Our measurements have confirmed that the dominant minerals in these deposits are illites and smectites.

2. *Geochemical data and interpretation*

Geochemical data were used to support the mineralogical results. Also, during the weathering processes, a higher and a lower weathering grade clay group can be distinguished. We applied the geochemical climate equations to the red clay sediments of the Carpathian Basin. These provided sufficiently accurate data to determine paleotemperature and paleoprecipitation. Based on the mineralogical-geochemical findings and partly on an integrated interpretation of the stable isotope-geochemical results of the co-authors, we have shown that these data are in good agreement with the climatic evaluations of the paleontological stable isotope data of fossil tooth enamel. We have also determined the past pH of paleosols using a so-called FeCa pedotransfer equation. Knowledge of soil pH is essential for understanding weathering processes, nutrient availability, and bio-edaphic relationships. This approach uses pH-dependent mineralogical transformations based on paleosol B horizon geochemical data and derived proxies to calculate paleosol pH. We found that the obtained pH values (5.4-5.9) support the formation-acidic chemistry of red paleosols. Furthermore, we used the stable isotope data to support the vegetation cover (paleoflora) types already described by paleobotanists, which during the Pliocene - Early Pleistocene could have been mainly forested steppe and mesic steppe.

3. Granulometry

We have clearly shown by the particle size distribution studies that some of the red clay (especially in the Pleistocene), like the loess, was deposited from wind-blown dust. We have pointed out that some of the red clays, like the loess, were wind-blown to their present location and weathered to clay. We have also recognized the eolian transposition of some red paleosols. This implies that the forearc areas required a dry, windy climate during certain periods. Such paleoenvironments may have been present during the dry periods of the Late Miocene and Early Pliocene and Pleistocene. We have supported the eolian genetics using several methods, including micromorphological analysis of quartz grains and heavy minerals, both RADIUS and other statistical techniques.

4. Heavy minerals analyses - provenance

We have delimited the dominant source area of red clays based on the heavy mineral analyses. The probable proximal source area is the deep igneous and metamorphic sedimentary deposits of the central mountain ranges of the Northwestern Carpathians and the Neogene calc-alkaline volcanic rocks. The distal source material is the sedimentary material of the Alps and the Bohemian Massif. Local sources may have been the lower mountainous areas of the basin (Bakony, Mórágy Hills). In addition, dust deposited from the ash fall of Miocene-Pliocene volcanic activity (andesitic, basaltic) may have been a contributor to the formation of the red clay.

5. Age determination

This work package has brought the most novelty and professional interest in the research of red clays. We have found that goethite pisolites formed in the clay provide a lot of information about the paleoenvironment and the genetics of the clay/aleuritic sediment. We have provided new data in determining the age of red clays using the goethite (U-Th)/He dating method. The older, weathering crust-originated red clays (e.g., the Kabhegy RC Member) were also formed in the early Pliocene (K/Ar method: 5.2-3.9 million years). The also older Tengelic RC. Fm. "Beremend-type" red clays were also of Pliocene age [(U-Th)/He method: 3.88-2.78 million years], similar to the red clay sediments of the Vienna Basin (cosmogenic ^{10}Be and ^{26}Al method: 3.8 Ma). The younger red clays of Tengelic RC. Fm. "Tengelic-type" red clays [(U-Th)/He method: 2.12-1.89 million years; ^{10}Be/^{26}Al method: 2.3 Ma]. The red clays in the loess-paleosol sequence and the reddish paleosols in the horizons of the loess-paleosol sequence are the youngest red-clay formations [(U-Th)/He method: 1.8-0.43 million years].

6. Mineralogical discoveries

In sedimentary rocks, Fe-Al phosphate minerals occur in different rocks and depositional environments. We found microcrystals of wavellite, crandallite, and cacoxenite from pedogenic goethite pisoliths and nodules. Pisoliths and nodules are generally dominated by Fe oxides and oxihydroxides. Frequently, pisoliths and nodules demonstrate high phosphatization and a substantial contribution of allogenic detritus. We describe the geochemistry and mineralogy of the pisoliths and try to interpret the possible paragenesis of the minerals. The studied red paleosols are weathered in a tropical/subtropical climate. In such conditions, fersiallisation and ferruginisation are the most important processes during the diagenesis of the pisoliths and nodules. The goethite pisoliths and nodules buried in paleosol have a homogeneous structure with mottled and syneresis fabrics. The newly formed precipitation products, namely wavellite, crandallite, and cacoxenite, accumulated into syneresis cracks and cavities during the weathering of apatite minerals. The phosphate availability is influenced by the distribution of phosphate at the goethite-water interface. Moreover, the phosphate distribution during goethite-water interaction is dependent on the solution composition, pH, and ionic strength. During the mineral paragenesis of wavellite, crandallite, and cacoxenite, pH conditions in the range 4–6 are supposed to have occurred. Such pH values may be expected under normal tropical/subtropical weathering conditions. Well-crystalized goethite associated with Fe-Al phosphates evolved under near-ambient conditions (buried in paleosol). This mineral assemblage formed and concentrated by chemical weathering reactions at the earth's surface is a typical residual mineral deposit.

7. Mössbauer and DR spectroscopic analyses of red clays

The aim of this analysis is to determine the goethite/hematite ratio in the red clays. This topic within the research theme failed the first time but re-tried with another lab and now we have very good results. Twenty samples were investigated by Mössbauer spectroscopy at room temperature and 80 K to obtain information about the various Fe oxides present. Diffuse reflectance spectroscopy (DRS) of the red clays. With this technique is possible to obtain rapid and quantitative estimates of the absolute concentration of hematite and goethite in the red clay samples. It is an additional method for controlling and validating the Mössbauer results, giving more detailed information on the hematite and goethite ratio. We have great preliminary data from this measurement; therefore, we have submitted 20 samples for DRS analyses. We are preparing a new research paper based on the new results from these analyses.

Future perspectives

The P.I. is invited as an expert in a Hungarian-Spanish-Swiss project. The aim of the campaign is to analyze the Paleocene-Eocene-Thermal-Maximum (PETM) succession in the Esplugafreda area (Tremp-Graus Basin), which consists of upper Palaeocene floodplain deposits with intercalated coarse sandstones and clast-supported conglomerates filling isolated single- and multi-storey ribbon fluvial channels. Levels of gypsum, ubiquitous *microcodium* remains, abundant carbonate nodule horizons, and reddish paleosols indicate deposition in generally semi-arid alluvial plains. As an expert in reddish paleosols, the P.I. would work with the team in the field and compare the PETM paleosols of the Esplugafreda Formation with the mid-Pliocene Warm Period (MPWP) paleosols of the Tengelic Redclay Formation in the Carpathian Basin. This field campaign will help all participants to improve their knowledge on sedimentary basins and will be a good opportunity to exchange information with academic geologists coming from different fields of expertise.

Use of the project results

Our new results are of fundamental interest for understanding the eolian sedimentary process alongside chemical weathering in basin environment. The findings are relevant for getting insights into the structure and formation mechanisms of red clays. Paleosols – soils incorporated into the stratigraphic record – have received increasing attention in geological research over the past several decades. As a result, paleosols are an important resource for terrestrial environmental and climatic reconstructions. The project provides some major advances in late Neogene–Quaternary geochronology, paleoclimatology, and peleoenvironmental reconstruction.

The P.I. of the project submitted his application and thesis for the “Doctor of the Academy” title to the Hungarian Academy of Sciences in 2020. Although he received three independent reviews with supportive expert opinions, he still failed his doctoral defense.