# Clay mineral and geochemical composition of Cenozoic paleosol in the Eastern Alps (Austria)

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## Abstract

Red clays from Cenozoic palaeosols of the Eastern Alps record periods of stagnating uplift and decrease of relief. Tropical to sub-tropical weathering of a crystalline substratum formed dominant or abundant kaolinite, reflecting Paleogene and Early Miocene conditions, respectively. Abundant illite and chlorite, but a lack of kaolinite in red clays on the plateaus of the Northern Calcareous Alps reflects feldspar-poor compositions of the Cenozoic siliciclastic cover. The presence of high Ba/Sr and Rb/Sr ratios and vermiculite in these red clays indicates high precipitation and temperate weathering conditions, respectively, during the Late Miocene and Early Pliocene on the uplifting plateaus of the Northern Calcareous Alps.

Rote Tone aus känozoischen Paläoböden der Ostalpen belegen Perioden stagnierender Hebung bzw. abnehmenden Reliefs. Tropisch-subtropische Verwitterung des kristallinen Untergrundes führte zur dominierenden oder häufigen Bildung von Kaolinit im Paläogen bzw. Unter-Miozän. Häufiges Vorkommen von Illit und Chlorit bei gleichzeitigem Fehlen von Kaolinit in roten Tonen auf den Plateaus der Nördlichen Kalkalpen spiegelt eine feldspatarme Zusammensetzung der känozoischen siliziklastischen Auflage wider. Das Vorhandensein von hohen Ba/Sr- bzw. Rb/Sr-Verhältnissen bzw. von Vermiculit in diesen roten Tonen weist auf hohe Niederschläge und gemäßigte Verwitterungsbedingungen auf den sich hebenden Kalkalpen-Plateaus im Obermiozän und Unterpliozän hin.

## 1. Introduction

Paleosols in mid-latitude regions of temperate climates may readily be detected by their distinct colouration. In the Eastern Alps of Europe, relics of plastic paleosols are red-coloured or altered to yellow colours, whereas Holocene soils are brown or black-coloured, depending on the local bedrock. These red paleosols do not appear to have formed under present-day or Holocene interglacial climatic conditions but represent pre-Pleistocene remnants of lateritic soils, potentially formed under subtropical climatic conditions (Thiedig, 1970). Due to their similar macroscopic characteristics, the regional literature uses the general term "Cenozoic red clays" or "red loams" for soils formed on Palaeozoic and crystalline bedrocks (e.g,, Winkler-Hermaden, 1957; Thiedig, 1970), consequently assuming a Miocene age of formation. Locally, a Late Paleocene or Early Eocene period of red clay formation has also been assumed (van Hinte, 1963, and references therein), but not always accepted (e.g., Thiedig, 1970). Nevertheless, similar plastic red clays found on the plateaus of the Northern Calcareous Alps (NCA) are believed to have formed after Miocene times (Louis, 1968) or even in warm Pleistocene periods (Solar, 1964).

The assumption of a uniform time of formation for the red clays appears unlikely, since a differential pattern of subsidence and uplift of crustal blocks in the Eastern Alps after Eocene nappe stacking is evident (Frisch et al., 1998, 1999; Dunkl et al. 2005).

Evidence for a change from tropical climatic conditions du-ring the Early Eocene to temperate conditions during the Oligocene, short-term warming in the Early-Middle Miocene and degrading conditions since then in the Alpine realm has been confirmed from studies on regional (Schwarz, 1997; Bruch, 1998; Janz and Vennemann, 2005; Tütken et al., 2006), continental (Zubakov and Berzenkova, 1990), and global scales (e.g. Zachos et al., 1999). Since the Late Miocene, additional local cooling was related to the uplift of the Eastern Alpine tectonic blocks (Frisch et al., 2000). Hence, the geochemical compositions of the red clays may reflect local climatic conditions and might constrain their time of formation.

The clay mineral composition of paleosols is sensitive to the prevailing environmental conditions, varying between tropical and temperate conditions, and the seasonality and amount of precipitation. Intense tropical weathering under humid to semihumid conditions would produce kaolinite or allite minerals (bauxite and laterite). Stronger seasonal dryness may be indicated by palygorskite (Foucault and Melieres, 2000). A temperate and humid environment would favour the formation of illite.

Oxygen and hydrogen isotope compositions of clay minerals have been determined in order to evaluate the relative effects of changes in paleoclimate, expressed by changes in the stable isotope composition of meteoric water. Such changes could also have been related to local surface uplift which would have resulted in local cooling of the surface. The isotopic compo-

sition of meteoric precipitation gets increasingly depleted in heavy isotopes with increasing altitude of condensation, increasing distance and hence "rain-out" of the moisture source, and decreasing temperature (Rozanski et al., 1993). An important condition for using this approach to paleoclimatic interpretations is the *in-situ* weathering to form the clay minerals, equilibrium conditions of clay mineral – water fractionation at the time of first formation of the clay and the preservation of these compositions. These conditions are met by smectite forming *in-situ* on volcanic material, such as airborne tuffs (Kent-Corson, 2006), as well as by most Cenozoic clays found in weathering profiles in similar tectonic settings as those of this study (Chamberlain et al., 1999; Chamberlain and Poage, 1999; Mulch et al., 2004). Apparent systematic changes of the isotopic composition of a mixture of clay minerals in the molasse foreland-basin during the Miocene would support the hypothesis that the signal might reflect environmental changes and may be traced from the sediment sink to the source.

The scope of this paper is to evaluate the geochemical and geological records relevant to the development of the paleosols in terms of likely changes in the regional climate.

## 2. Regional setting

The red plastic paleosol relics very rarely include so-called *in situ* soil profiles (e.g., Solar, 1964), but typically consist of locally reworked red clays.

Red clays have been found in the eastern part of the Eastern Alps (1) in Cenozoic basins, (2) on top of paleosurfaces (Fig. 1) and (3) locally in Permian red beds. The latter cases are beyond the scope of this study, but some red clays situated on exposed Permian red-beds have been misinterpreted as Cenozoic red clays in the local literature (see Thiedig, 1960).

(1) Cenozoic basins within the Eastern Alps include (a) Late Cretaceous to Paleocene ("Gosau"-type) basins, (b) late Early Miocene to Middle Miocene, and (c) Middle to Late Miocene basins.

(a) "Gosau"-type basins typically experienced rapid subsidence during the Late Cretaceous, forming deep-marine basins, whereas the topmost Late Paleocene and Early Eocene sedimentary columns are represented by shallow water limestones in the central-Alpine region (e.g. Wagreich and Faupl, 1994). In the Krappfeld Gosau section, Cretaceous flysch depo-

sits are overlain by several metres of flamed, intensely red and yellow to white fire clay (van Hinte, 1963). The subsequent 4 m thick succession of well-sorted, sulphide- and organic matter-rich fluvial sandstone and intercalated clayey siltstone contains a tropical palynoflora (pers. comm. R. Zetter, Vienna, 1998). The terrestrial succession is succeeded by Early Eocene shallow-water limestones. The fire clay represents a regional reference sample for fully tropical weathering conditions. When sampled, this section was well-exposed and its stratigraphic continuity within the Paleocene succession was obvious.

(b) Numerous small pull-apart basins formed along prominent faults during late Early Miocene to Middle Miocene times. These deposits formed during lateral extrusion of the Eastern Alps (Ratschbacher et al. 1991), which led to crustal extension, subsidence and fragmentation of the upper crustal blocks. Although basal breccias or thin regoliths are typical for the base of the basin fill, red clays are also frequently found. These soil remnants are of late Early Miocene age, according to the dated overlying sediments (Weber and Weiss, 1983).

(c) Middle to Late Miocene basin formation is restricted to the southeastern part of the Eastern Alps, due to continued minor SE-directed extension and strike-slip movements (Fodor
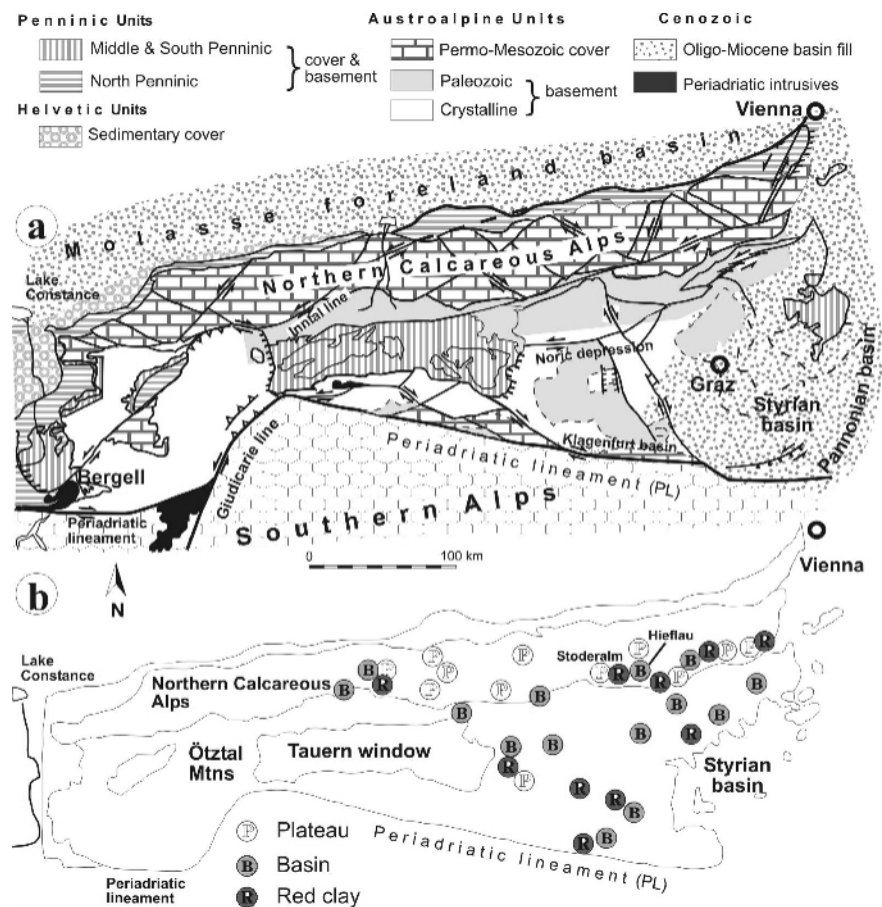


**Figure 1:** (a) Geological sketch of the Eastern Alps showing the major tectonostratigraphic units. (b) Locations of major elevated paleosurfaces, Cenozoic extensional basins, and occurrences of Cenozoic red clays (for references, see text).

et al., 1998; Márton et al. 2000). Red soils are rarely found at the base of these formations.

(2) Paleosurfaces with scattered thin residuals of red clays are widely preserved in the eastern Eastern Alps (Fig. 1).

(a) Paleosurfaces in the central part of the eastern Eastern Alps occur in areas of low grade-metamorphism and crystalline rocks at altitudes that are today typically below 1600 m a.s.l.. They are tilted at variable but low angles. In some cases, these paleosurfaces are covered by latest Early Miocene to Middle Miocene deposits (Exner, 1949; Zeilinger et al., 1999). The thermal history of the bedrock suggests that these terrains have experienced erosion and decreasing relief in a period of tectonic quiescence in the Early Miocene (Frisch et al., 1998, 1999).

(b) Paleosurfaces extending over 300 km in an E-W direction occur in the central and eastern Northern Calcareous Alps (NCA) on top of kilometre-thick, flat-lying or tilted Middle or Upper Triassic platform carbonates (Louis, 1968). There is an ongoing discussion on the increasingly younger formation age of paleosurfaces at decreasing elevation levels. Here, we refer to the highest (and oldest) paleosurface level, which was termed the "Dachstein paleosurface" by Frisch et al. (2001) with respect to the best preserved example in the NCA. Today, this paleosurface has been dissected and differentially uplifted to altitudes of between 1400 and 2800 m a.s.l.. The frequent presence of quartz sand and micro-pebbles indicates that most, if not all occurrences were associated with and formed by weathering of the Early Oligocene to probably Early Miocene siliciclastic Augenstein Formation (see also Solar, 1964). The material was derived from low grade metamorphic rocks exposed south of the drowning NCA (Frisch et al., 2001). Thus, red clays of the NCA are in fact Cenozoic basin remnants (Kuhlemann et al., 2001; Kuhlemann and Kempf, 2002). The Dachstein paleosurface is probably of Late Eocene age and was re-exhumed after the Early Miocene (Frisch et al., 2001). A sudden increase of Upper Triassic limestone pebbles in the largest foreland fan (Paleo-Inn) indicates that by 10 Ma the Inn River had started to incise the Late Eocene paleosurface of the central NCA, whereas the siliciclastic cover was reworked and redeposited in the North Alpine Foreland Basin in earlier times (Frisch et al., 1998). Due to increasing karstification of the progressively exposed limestone plateaus after 10 Ma, the siliciclastic relics were protected from fluvial erosion and were subjected to in situ weathering during the latest Miocene and Pliocene. These relics represent the oldest deposits of the formerly up to 1.3-2 km thick pile of Augenstein Formation (Frisch et al. 2001).

## 3. Material

All material was unstratified with a red colour of variable intensity, often partly altered to yellow or brownish-red colours by subsequent reduction of the formerly oxidized clays. The material is typically plastic. At least few sand-sized quartz grains were found in all samples. Many samples, particularly from the NCA plateaus, contained small quartz pebbles or limonite nodules (Pichler, 1962). Periglacial processes during the Late Pliocene and Pleistocene may have modified most, if not all soil profiles.

## 4. Methods

Paleosols were wet sieved to extract > 5 grams of the < 63 µm fraction. In a standard preparation procedure for clay mineral analysis, portions of 10-20 mg of <2 µm sample material were dispersed in 50 ml of distilled water with ultrasound waves after washing and removal of carbonates by acetic acid. This was followed by several rinse and centrifugation cycles with distilled water. After dispersion and settling for 12 h, the still suspended <2 µm fraction was pipetted and transferred for further preparation. The suspension was loaded with 5 - 10 ml 0.5m $SrCl_2$ for 12 h at 50 -60 ˚C. The settled clay fraction was taken up in ca. 10 ml of distilled water and pipetted onto glass. After drying, the preparates were X-rayed using a Siemens D 501 (Cu-anode) X-ray diffractometer (wave length 1,5406 Å). All preparates were measured also with ethylenglycol to identify expandable mineral phases. 4 samples were also measured after heating to 300°C to identify vermiculite and chlorite.

The major element composition of clay minerals is sensitive to moisture conditions in the soil. High or moderate regular precipitation rates would favour depletion of mobile elements, such as Mg and K. Normalized to Ti, the index value is indicative of relative differences within a set of locations. The minor element composition of clay minerals would similarly indicate relative precipitation rates. Less mobile elements such as Ba and Rb are normalized to Sr as a highly mobile element.

Quantitative analysis of major and trace elements has been performed by wavelength-dispersive X-ray fluorescence (XRF) analysis (Hahn-Weinheimer et al., 1984) with a Siemens SRS 300 spectrometer. Samples were pulverized in an agate mill and heated at 1000º C for 1 h. Weight loss of $H_2O$, $CO_2$ and $Fe^{2+/3+}$ reactions are calculated as $H_2O$. Homogeneous preparates were formed by mixing of 1.5 g of sample and 7.5 g Spectromelt flux (Merck A12, di-lithiumtetraborate / lithiummetaborate 66:34) and flame heating at 1200ºC in an OxiFlux-System of CBR Analysis Service.

The hydrogen isotope compositions of the clay minerals were measured following the methods outlined in Vennemann and O'Neil (1993), using both an in-house kaolinite and NBS-30 biotite (δD = -65‰) as standards for calibration purposes and to evaluate the reproducibility (± 2‰) of the method. Oxygen isotope measurements on clays were made on samples previously dried in a vacuum dessicator using phosphorous-pentoxide as drying agent for 24 hours and subsequent measurements of the dried samples in a conventional silicate line using $BrF_5$ as reagent (e.g. Vennemann and Smith, 1990). Analyses were calibrated using NBS-28 quartz as reference material (δ$^{18}$O = 9.64). δD and δ$^{18}$O values are given relative to the VSMOW standard in the conventional δ-notation in parts per thousand (‰).

| sample code | location | clay [%] | silt [%] | sand [%] | elevation [m] a.s.l. | clay min. composition | formation age | bedrock type |
|---|---|---|---|---|---|---|---|---|
| R-11 | Klein St. Paul | 52 | 40 | 8 | 1000 | kao>>il | E. Eocene | limestone |
| R-13 | Griffen 1 (17 Ma) | 31 | 38 | 31 | 1000 | kao>il | E. Miocene | basement |
| R-14 | Griffen 1 | 29 | 65 | 6 | 600 | il>kao>cl | E. Miocene | marble |
| R-17 | Rax | 78 | 21 | 1 | 1700 | cl>il>>ver | E. Miocene | limestone |

TABLE 1: Soil parameters and setting of selected samples. Clay minerals: ver = vermiculite, cl = chlorite, il = ilite, kao = kaolinite, smec = smectite.

| region | n | MgO/ TiO$_2$ | K2O/ TiO$_2$ | Ba/ Sr | Rb/ Sr | formation age |
|---|---|---|---|---|---|---|
| Kaisergebirge | 3 | 0.8 - 1.6 | 1.3 - 1.9 | 3.2 - 4.3 | 0.8 - 1.9 | L. Miocene |
| Dachstein | 4 | 0.8 - 1.4 | 1.3 - 2.7 | 3.3 - 7.4 | 1.3 - 2.1 | L. Miocene |
| Hochschwab | 2 | 1.9 - 2.8 | 2.6- 3.8 | 5.8 - 11.9 | 1.7 - 2.8 | L. Miocene |
| Oberwölz | 1 | 0.55 | 0.86 | 1.32 | 0.40 | E. Miocene |
| Swiss Jura | 1 | 0.11 | 0.11 | 1.58 | 0.38 | Eocene? |
| Swabian Alb | 1 | 0.11 | 0.14 | 0.97 | 0.28 | Eocene? |

TABLE 2: Main elements normalized to TiO$_2$ (low mobility) and minor elements normalized to Sr (high mobility) for three samples from this work and three reference samples for comparison.

## 5. Results

Some samples have been tested for grain size distribution and pH in order to characterize the material (Table 1). The content of the sand fraction is low except for sample R-13, from a paleosol on crystalline basement at the base of a conglomerate succession. The pH of the paleosols is moderately acidic, even if resting on limestone bedrock.

### 5.1. Major and trace element composition

XRF analysis of major elements of the red clays from the NCA plateaus partly reflects the high Mg and K contents (normalized to immobile TiO$_2$, Table 2) of the weathered substrate and the authigenic clay minerals, as compared to the reference samples. The minor element compositions have high Ba/Sr and Rb/Sr ratios with respect to the reference samples, indicating stronger leaching of Sr due to enhanced precipitation.

The Fe-enrichment in the reference samples, in turn, reflects less leaching and enhanced oxidation.

### 5.2 Clay mineral composition

Red clays from the central-eastern part of the Eastern Alpine medium- to high-grade metamorphic crystalline substrate are dominated by kaolinite, in particular for two of the samples. Illite and chlorite are always present, but mainly in concentrations subordinate to those of kaolinite. One kaolinite-rich sample is represented by a Paleogene reference sample (R-11, Klein St. Paul; Fig. 2 and appendix), and presumably formed under fully tropical weathering conditions. Sample R-2 (Maria Hilf, Fig.2) is of similar kaolinite-rich composition. It is located on a crystalline substrate, a few km from the Paleogene reference sample, and its formation age in the local context is ambiguous. It is, therefore, suggested that this clay also formed during the Paleogene and was sealed, possibly by Eocene marine deposits and subsequently by latest Early Miocene conglomerates. Red clays found at the base of such conglomerates are composed equally of kaolinite and illite. This composition is interpreted in terms of less intense, subtropical weathering. The relative importance of kaolinite appears to result from weathering of the feldspar-rich substrate. Smectite is present in very minor quantities except one sample, in which the dominance of smectite is probably related to in-situ weathering of Middle Miocene ash from the Styrian volcanic province.
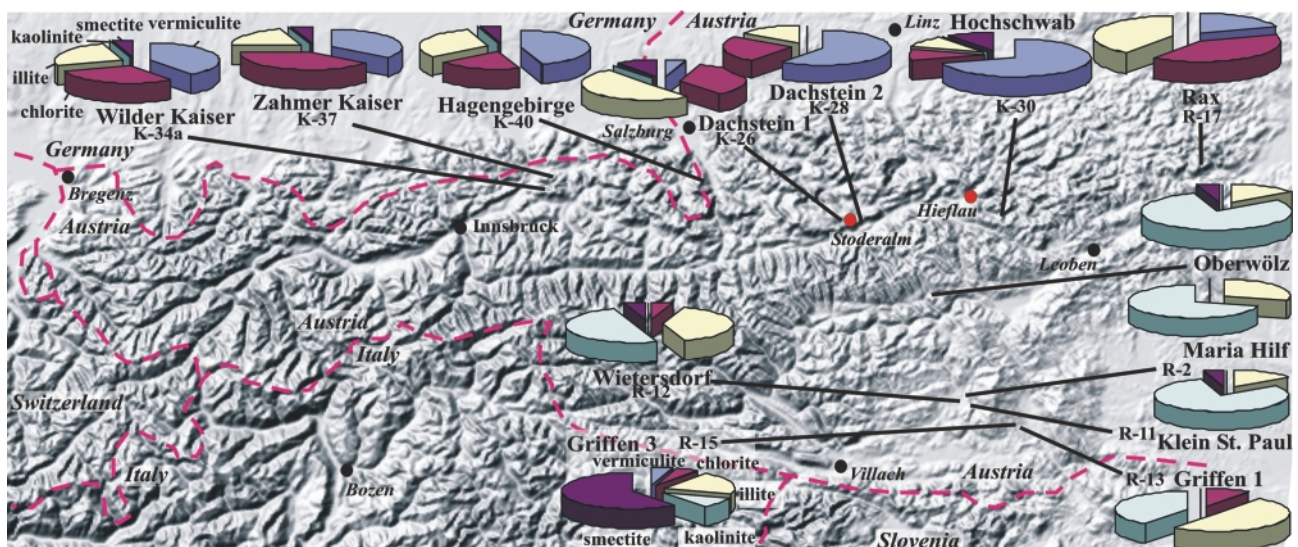


FIGURE 2: Clay mineral distribution of red paleosols in the Eastern Alps (shaded digital elevation model). Note that the percentage of the composition is semi-quantitative – the plots shall provide a regional overview (see also Appendix A).

The clay mineral compositions of red clays from the NCA are dominated by vermiculite, illite and chlorite, with rare kaolinite and smectite mixed-layer minerals. These clay minerals are derived from weathering of the Augenstein Formation. The deposits are composed of low-grade metamorphic material, comprising quartz pebbles, quartzite, meta-siltstone, meta-greywacke, slate, meta-tuff and chlorite schist. Dominant mineral constituents are quartz, sericite, highly ordered illite, chlorite and some plagioclase. Chlorite and part of the illite in the clay mineral fraction of the red clays represent residuals of the metamorphic substrate. Vermiculite is assumed to have been derived from the degradation and hydratisation of chlorite under wet and temperate climatic conditions. Poorly ordered illite typically forms under humid temperate climatic conditions from weathering or degradation of sheet silicate minerals, represented by sericite and highly ordered illite. According to the geodynamic evolution of the NCA, the red clay probably formed after 10 Ma and before the onset of glaciations at 2.7 Ma. Clays altered to a yellow to brown colour turn out to have quite similar clay mineral compositions as degraded Negene red clays.

### 5.3. Oxygen and deuterium isotopes

The oxygen and hydrogen isotope compositions of clay minerals from the Eastern Alpine paleosols do not differ systematically when related to the chemical compositions of the clays, their mineralogy, or their estimated age of formation (Table 3). There is also no direct correlation with their present altitude. This latter would be expected if all clays were formed at their present altitudes through equilibration with meteoric water, as calibrations for recent systems have indicated that there is a correlation between the isotopic composition of meteoric water and decreasing temperature with increasing altitude. In addition, the isotopic composition of precipitation at any one locality is a function of the distance of transport or, more precisely, the loss of water from the air mass while it is being transported from the tropical-subtropical source of moisture to the place of precipitation and clay formation. All of these factors will, of course, also change as a function of the prevailing climate. As such, the range in isotopic compositions measured and its lack of correlation neither with present-day altitude nor with the global climate expected for the estimated time of formation is not surprising given the uncertainty of the ages and their temperature and altitude of formation. However, the fact that the clay minerals do not correlate with the present altitude can also be taken to suggest that the clays have preserved their original isotopic compositions and have not been reset. Given a fractionation factor ($\alpha$) of about 0.968

for hydrogen isotope exchange between kaolinite and water at about 25°C of Gilg and Sheppard (1996), the $\delta D$ value of water in equilibrium with the kaolinite-rich samples would be between -46‰ and -57‰. For the smectite-rich sample with a lower $\delta D$ value of -111‰, but a larger smectite-water fractionation factor (critically dependant on the Fe-content of the smectite; Sheppard and Gilg, 1996) of 0.951, the $\delta D$ value of water in equilibrium would have a value of about -65‰. In general, such values are higher than those for average annual present-day meteoric water in Vienna (Table 3) and much lower than those expected for water at higher altitudes. Hence, these values do support subtropical to tropical conditions of clay formation. In terms of the oxygen isotope compositions, fractionation factors at low temperatures between clay minerals and water are even less well constrained as compared to those for hydrogen. In addition, the oxygen isotope compositions can, in part, be inherited from precursor substrate minerals such as feldspars.

### 6. Discussion

The geochemistry of red clays in the Eastern Alps has been investigated by Bezvodova et al. (1990) in the NCA with the basic conclusion that the main element composition reflects weathering of a siliciclastic substrate rather than residuals of carbonate dissolution. All plateaus of the central and eastern NCA were covered by the siliciclastic Augenstein Formation, which was shed from low-grade metamorphic terrains exposed in the central Eastern Alps during the Oligocene (Kuhlemann et al., 2001). After and during reworking of most of these deposits and redeposition in the foreland basin during the Early Miocene, subtropical weathering in the late Early Miocene caused local bauxite formation in low-elevation sites of the eastern Dachstein plateau (Stoderalm; see Fig.1b,2) and the eastern Enns valley depression at Hieflau, prior to Ottnangian/Karpatian sedimentation (Wagreich et al., 1997). Incision of rivers into the underlying Triassic platform carbonates since ~10 Ma in the course of strong uplift enabled karstification and preservation of local Augenstein occurrences in karst depressions (Frisch et al., 2001). Protected from

| sample code | location | weight % H₂O | δ¹⁸O [‰] | δD [‰] | elevation [m] a.s.l. | clay min. composition | bedrock type |
|---|---|---|---|---|---|---|---|
| K-13 | Steinernes Meer | 11.9 | -105 | -14.9 | 800 | n.d. | limestone |
| K-26 | Dachstein | 8.5 | -98 | -15.9 | 2000 | ver>cl>il | limestone |
| K-27 | Dachstein | 7.8 | -76 | -19.2 | 1950 | n.d. | limestone |
| K-30 | Hochschwab | 6.4 | -103 | -19.9 | 2000 | ver>>cl>il | limestone |
| K-34 | Wilder Kaiser | 7.8 | -76 | -17.9 | 1900 | ver>>cl>il | limestone |
| K-40 | Hagengebirge | 8.3 | -91 | -18.6 | 2200 | n.d. | limestone |
| R-11 | Klein St. Paul | 11.6 | -77 | -17.4 | 1000 | kao>>il | limestone |
| R-13 | Griffen 1 (17 Ma) | 10.3 | -88 | -15.5 | 1000 | kao>il | basement |
| R-15 | Griffen 2 | 8.9 | -111 | -17.0 | 600 | smec>>kao/il | Miocene tuff |
| R-17 | Rax | 12.8 | -100 | -18.6 | 1700 | cl>il>>ver | limestone |

**Table 3:** Oxygen and hydrogen isotope compositions of clay minerals of Eastern Alpine paleosols expressed in ‰ relative to VSMOW. Clay minerals: see Tab. 1 (n.d. = not determined). Molasse sediments (for reference) give -62 to -97 ‰ δD and -16.3 to -20.9 ‰ δ¹⁸O.

further fluvial erosion, these remnants were subjected to slow weathering under increasingly wetter, temperate conditions, as indicated by progressive leaching of major and minor mobile elements. This probably resulted from cooling on top of the uprising plateaus and orographically triggered precipitation. Regional climate change in the Middle and Late Miocene were characterized by a decline of winter temperatures, whereas precipitation was quite variable and encompassed periods of strongly increased precipitation (Fig.3; Bruch, 1998; Böhme et al., 2006).

Kaolinite-rich red clays found on the paleorelief relics of the central Eastern Alps, e.g., the Gurktal Alps, reflect lateritic weathering of the feldspar-rich bedrock. Similar geochemical composition of paleosols buried by latest Early Miocene siliciclastic deposits of the East Alpine intramontane basins suggests that these paleosols were formed in the Early Miocene (Fig. 3). During this period of tectonic quiescence, the central Eastern Alpine paleorelief was formed (Frisch et al., 2000). During the Middle Miocene the paleorelief of the eastern part of the Eastern Alps was partly covered by orogenic debris. Re-exhumation probably started in the Late Miocene and accelerated from the Pliocene onwards (Kuhlemann, 2000, 2007). Exposure of paleosols to temperate weathering conditions may, therefore, have been fairly short, possibly in the range

of a few million years, a time that is considered as being too short to modify the mineralogy and chemical composition of previously formed clay minerals.

Karst plateaus in Mesozoic carbonates with infills of bauxites and lateritic red clays are characteristic features of the peri-Pannonian region (Mindszenty, 1984). They occur at different elevations in the Western Carpathians (Aggtelek karst and Slovakian karst; Less, 1998; Zacharov and Thuroczy, 1986), Apuseni Mountains (Bleahu, 1989), Dolomites (Bosellini, 1989), the Bakony Mountains in Hungary (Dunkl, 1990) and in the Dinarides (Mijatovic, 1984). The age of formation of these plateaus and the paleosols preserved on them is not well constrained. An estimate can be achieved mainly by the help of stratigraphic, tectonic, and climatic data and analogies with the surrounding areas (Jakucs, 1971; Beck and Borger, 1999). Part of these bauxites contain early Eocene volcanic zircons and are covered by late Eocene sediments (Dunkl, 1992).

Lateritic bauxites in central Germany were formed by weathering of well-dated basalts of late Early to early Middle Miocene age (Schwarz, 1997). The clay mineral composition of kaolinite and the bauxite mineral gibbsite indicates intense, almost tropical weathering conditions during the early Middle Miocene climatic optimum (Fig. 3). The degree of weathering
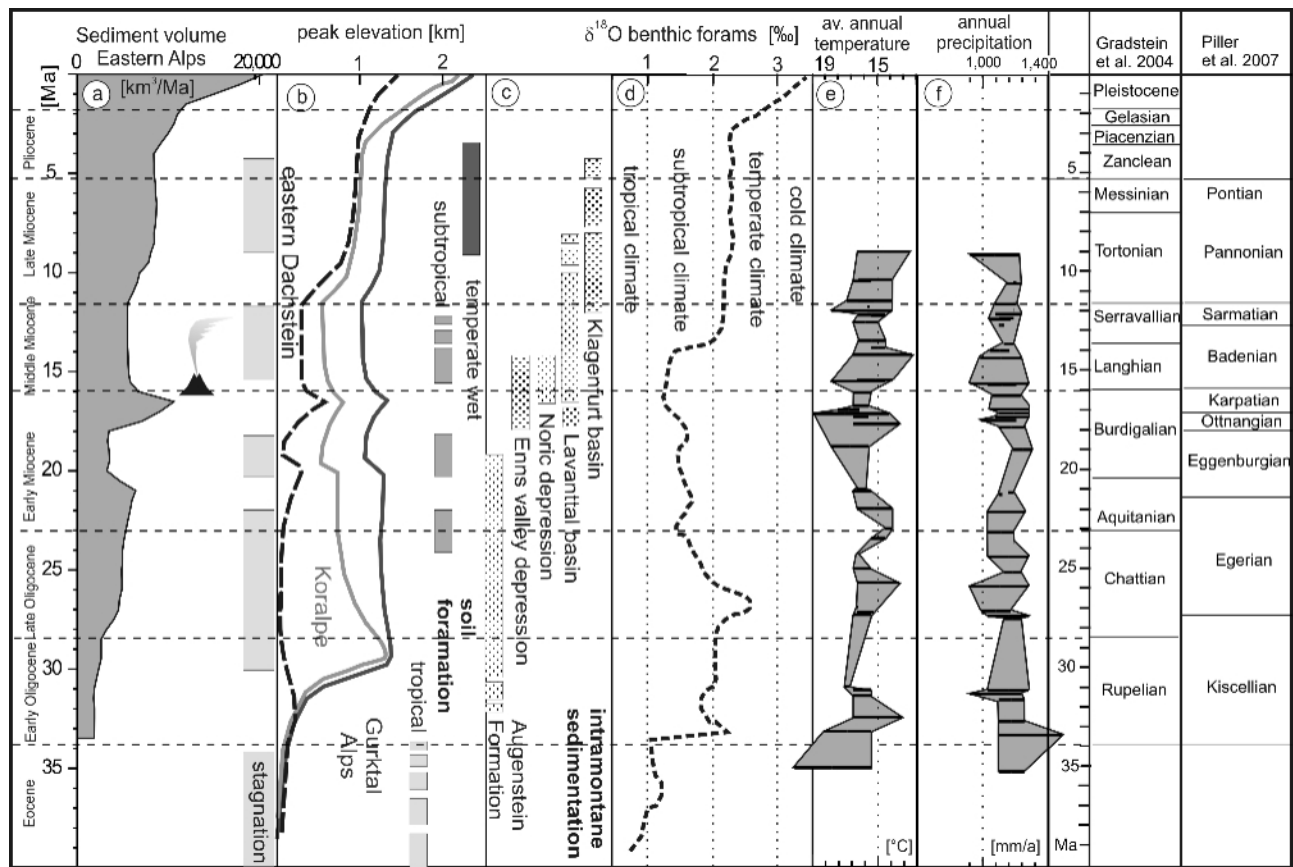


**FIGURE 3:** Stratigraphic column of parts of the Cenozoic with (a) volume of eroded material from the Eastern Alps (Kuhlemann et al., 2002) and periods of stagnation, (b) estimate of peak elevation (Kuhlemann, 2007) and inferred time of soil formation, (c) periods of intramontane basin formation and sediment deposition, (d) global climate change data from the ocean record (Pearson and Palmer, 2000) with a rough estimate of climate conditions in the working area, (e-f) regional temperature and precipitation changes (Bruch, 1998).

in this region appears to have been higher than in the Eastern Alps during the Early Miocene, which may have been related to the sensitivity of fresh basalts to subtropical weathering.

The oxygen and hydrogen isotope compositions of the clay minerals may also have preserved the isotopic compositions of the water during their first formation. Systematic trends in isotopic composition related to paleo-elevation and temperature change during the Cenozoic are difficult to evaluate as the clay mineralogy changes for the different localities and with that the mineral-water fractionation factors. Moreover, estimates of paleo-elevation and the age of clay mineral formation are very difficult to constrain. For the central part of the Alps, it is evident that high mountainous relief already existed in the late Early Miocene (Kocsis et al., 2007), but this can be ruled out for the plateau relics in the eastern parts of the Eastern Alps (Kuhlemann, 2007).

The values estimated for water in equilibrium with the clay minerals are generally more positive compared to present-day average annual meteoric precipitation in the region (Rozanski et al., 1993), which would indicate more subtropical to tropical conditions of formation. The low δD values for some smectite-rich samples may be related to the high Fe-contents in these samples and the associated higher mineral-water fractionation factors (Sheppard and Gilg, 1996). The calculated δD values for possible meteoric water in equilibrium with the clay minerals of -46 to -65‰ would, however, still suggest that the localities lay well within the interior of the continent, as they do not correspond to values typical for coastal stations. Elevation hardly played a role, since the smectite-rich samples are derived from locations presently located below 1000 m a.s.l.. In the Neogene, these sites have, similar to the eastern part of the Eastern Alps, always been situated at lower elevations than at present (Fig. 3; Kuhlemann, 2007). Periods of stagnation of uplift and erosion, as indicated by sediment export to the adjacent basins (Fig. 3a,b) are proposed as periods of deep-seated weathering and soil formation. Depending on the global climate (Fig. 3d), weathering conditions changed from tropical (Eocene) to subtropical (Early and Middle Miocene) to temperate wet (Late Miocene-Pliocene) conditions. Despite global and regional cooling and ongoing uplift, the oxygen and deuterium isotope ratios do not reflect these environmental changes, but instead may have been controlled by low fluid-rock ratios and buffering of their isotope ratios through the substratum. Hence, the clay minerals kaolinite, vermiculite, and illite are of limited use for reconstructions of paleo-elevation in the present case.

## 7. Conclusions

Red clays found in the Eastern Alps formed at different times during the Cenozoic. Whereas the dominance or abundance of kaolinite in the red clays on the crystalline substrate reflects Paleogene tropical or Early Miocene subtropical weathering, respectively, its absence in red clays on the already uplifted plateaus in the Northern Calcareous Alps reflects the feldspar-poor composition of the substrate and temperate weathering

conditions in the Late Miocene and early Pliocene. The presence of vermiculite and high Ba/Sr and Rb/Sr ratios indicates high precipitation and wet conditions in the paleosols. The oxygen and hydrogen isotope compositions of the clays are compatible with warmer climates as compared to the present-day conditions. However, given the changes in clay mineralogy and uncertainty in age and altitude of formation, direct correlations with climate and changes in topography are difficult to make.

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## Appendix

XRD diagrams of red clays of the Eastern Alps. For locations, see Fig. 2.