

Isotopic tools of dating paleoweathering in Europe

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Introduction

Direct dating of paleosurfaces and associated paleoweathering phenomena is one of the great challenges in geochronology, as the neoformation of minerals suitable for isotope dating in these environments is rather the exception than the rule. Hydrolysis reactions often cause a depletion of elements with suitable radiogenic isotope systems (e.g., K, Rb or U), and some other elements, such as Sm, Lu, La or Th, are usually immobile and their isotope systems do not fractionate during weathering.

I will present a review of geochronological methods using radiogenic isotope systems, mainly K-Ar, $^{40}\text{Ar}-^{39}\text{Ar}$, and Rb-Sr, as well as indirect dating methods using stable isotopes (O, H) and their application to paleoweathering phenomena ranging from Mesozoic to Quaternary in Europe. The potentials and limitations of the U series and U-Th-He method for dating continental weathering are shortly discussed. This review, however, does not include terrestrial cosmogenic nuclide or surface exposure dating (e.g., Cerling and Craig, 1994; Gosse and Phillips, 2001), as these methods have only very rarely been applied to pre-Pliocene continental weathering phenomena. Poorly constrained production rates of cosmogenic nuclides in the past are another problem for accurate dating with these methods.

Direct dating using the K-Ar, $^{40}\text{Ar}-^{39}\text{Ar}$ and Rb-Sr systems

There are three major groups of minerals that can form during continental weathering and that are suitable for dating with the K-Ar, $^{40}\text{Ar}-^{39}\text{Ar}$ or Rb-Sr method: manganese oxides, aluminum (\pm iron) phosphate sulfate (APS) minerals and authigenic clay minerals. The recent developments in geochronology using these supergene minerals were summarized by Clauer and Chaudhuri (1995) and Vasconcelos (1999a,b). A careful mineralogical characterization of the samples is of utmost importance to avoid (or possibly correct for) contamination with older, detrital phases or minerals with a low retentivity of K and Ar, such as birnessite, vernadite and todorokite in complex

K-bearing Mn oxide samples. Other potential, but significant problems are the presence of excess ^{40}Ar and Ar loss due to the thermal history of the sample. The step-heating $^{40}\text{Ar}-^{39}\text{Ar}$ technique is clearly the preferential method for dating K-Mn oxides and also alunite group minerals, as it provides informations about K and Ar retention, hypogene contaminants, ^{39}Ar recoil during irradiation and can be applied to small single crystals ($>0.1\mu\text{g}$) (Vasconcelos, 1999a,b). Geochronological data on European supergene K-Mn oxides are very sparse (Hautmann and Lippolt, 2000). The K-Mn oxide samples in that study (hollandite, cryptomelane and romanechite) derive mainly from the Schwarzwald, Odenwald, Spessart, Rheinisches Schiefergebirge, Harz, Erzgebirge, Thüringer Wald, and Massif Central. They yielded ages spanning from 25 to 1 Ma, but most samples have Late Miocene formation ages.

The K-Ar method is useful for dating K-rich APS minerals, such as alunite or jarosite. Gilg and Frei (1997) reported on Eocene K-Ar data (~ 45 to 41 Ma) of supergene alunite from the St. Yrieix kaolin deposit, Massif Central. The alunite formed during kaolinization of Carboniferous pegmatite dikes that intruded sulfide-bearing amphibolites and micaschists. The timing of alunite formation can be correlated with regionally widespread Eocene ferricretes and kaolinite-rich alterites ("Siderolithique"). Supergene pseudocubic alunites at the Rodalquilar Au alunite deposit, Spain, yielded Pliocene ages (4-3 Ma), whereas hydrothermal platy alunites from the same deposit formed during the Late Miocene (11-10 Ma) (Arribas *et al.*, 1995). Sr-rich supergene APS minerals (goyazite, svanbergite, kemmlitzite) are sometimes found in saprolites and paleosols (Dill, 2001). They form during weathering of feldspars, carbonates, phosphates and/or sulfides. New Rb-Sr data of goyazite-rich clays, feldspars and primary phosphates from the Hirschau kaolin deposit, Germany, yield formations ages of ~ 100 to 150 Ma for the supergene Sr-rich APS minerals and thus kaolinization. The pre-Cenomanian age is consistent with stable isotope and geological data (Gilg, 2000).

The confirmation of a supergene (and not detrital or hydrothermal) origin of K-bearing clay minerals (illite,

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illite-smectite, celadonite) in saprolites is very problematic (e.g., Gilg and Frei, 1997). A combination of radiogenic and stable isotope and fluid inclusion data can be useful in this respect. The ^{40}Ar - ^{39}Ar method is usually not suitable for dating very fine-grained clay minerals due to ^{39}Ar recoil during irradiation (e.g., Clauer and Chaudhuri, 1995). Both the K-Ar and Rb-Sr methods are appropriate for dating clay minerals. Combined K-Ar and Rb-Sr data of illite-rich illite-smectite mixed layer minerals (I-S) in kaolins formed by weathering of glass-rich Carboniferous volcanic rocks in the Meissen area, Saxony, yielded consistent Lower Cretaceous ages (Gilg *et al.*, 2003). Even older Rb-Sr ages of I-S (Triassic to Jurassic) were found at the Kemmlitz kaolin deposit, Saxony (Gilg *et al.*, 2003). The significance of the latter geochronological data still have to be substantiated by further studies.

Direct dating using U disequilibrium and U-Th-He systems

The U series or disequilibrium methods, e.g. ^{230}Th - ^{234}U - ^{238}U , are principally restricted to Quaternary samples due to the short half times of the involved radioactive nuclides. These geochronological techniques have been applied to pedogenic carbonates (calcretes), opal (e.g. Neymark *et al.*, 2002; Ludwig and Paces, 2002), hematite, goethite (Short *et al.*, 1989) and Fe-oxide-bearing clays (Dequincey *et al.*, 1999). Dating of Upper Miocene to Pleistocene pedogenic opal and chalcedony was achieved by using the $^{207}\text{Pb}/^{235}\text{U}$ technique at Yucca mountain, USA (Neymark *et al.*, 2002). Secondary uranium minerals, such as torbernite or carnotite, formed by supergene remobilization of primary U mineralization have been dated using the U series methods (e.g., Wendt and Carl, 1985; Kaufmann and Ku, 1989; Hofmann and Eikenberg, 1992). All these methods can be very useful in arid regions. They cannot be considered "standard" techniques and are very problematic in non-arid regions due to continuous remobilization of uranium.

The potentials of U-Th-He dating of K-Mn oxides (hollandite, cryptomelane) have been illustrated by Lippolt and Hautmann (1995). However, no U-Th-He studies on supergene Mn oxides have yet been published. As these minerals can also be dated by the ^{40}Ar - ^{39}Ar technique, further systematic studies using both independent geochronological methods are necessary.

Indirect dating using stable isotope systems (H, O)

The use of stable isotope ratios of weathering clays in geochronology was demonstrated by Bird and Chivas (1988) and Gilg (2000). The D/H and $^{18}\text{O}/^{16}\text{O}$ values of

supergene clay minerals reflect (1) temperatures of crystallization and (2) the isotope compositions of ground waters with which they equilibrate. If the isotope compositions of local meteoric waters change systematically with time due to paleoclimatic and/or paleogeographic variations, if this isotope change can be calibrated and if the clay minerals retain their initial isotopic compositions, then stable isotopes of clay minerals can be applied to date paleoweathering. Gilg (2000) presented evidence that D/H ratios of sedimentary kaolinitic clays in NE Bavaria change systematically from Late Triassic to Miocene and are not in equilibrium with present-day ground waters. Stable isotope data from two large residual kaolin deposits in NE Bavaria (Tirschenreuth, Hirschau) have been used in combination with additional geological evidences to constrain the timing of surficial alteration. A late Early Cretaceous kaolinization age is suggested for the Triassic sandstone-hosted deposits near Hirschau and a Late Oligocene to Mid-Miocene age for Carboniferous granite-hosted Tirschenreuth deposit. New stable isotope data indicate a Cretaceous and Miocene age for two chemically and mineralogically distinct kaolinitic clays in the Degelhof deposit near Schmidtmühlen, Bavaria.

Other supergene oxygen and/or hydrogen-bearing minerals can also potentially be used for indirect dating using their stable isotope ratios if the isotope fractionation factors between mineral and water are well established. At present, iron oxihydroxides (goethite) and the APS minerals alunite and jarosite are the best candidates for this application. Hydrogen isotope data of weathering goethites and alunite from Central Europe and their geochronological implications will be presented.

Conclusions

Precise dating of pre-Pliocene paleoweathering phenomena using radiogenic isotope systems is presently restricted mainly to oxidation products of manganese-, sulfide- or uranium-bearing rocks. K-rich clay minerals (illite, I-S, or celadonite) are potentially very useful for weathering geochronology. However, a supergene, authigenic origin of these clay minerals seems to be a rare case and contamination with detrital components is very critical. The U series methods are favoured for dating Quaternary surficial alteration minerals. The use of stable isotope ratios (D/H and $^{18}\text{O}/^{16}\text{O}$) of supergene minerals holds great potentials for indirect dating of paleoweathering despite its low precision. The currently available isotope geochronological data indicate significant continental weathering in Europe during Lower Cretaceous, Eocene, Miocene and Pliocene times. Further systematic geochronological studies are clearly needed to decide whether these data represent a more or less continuous process or distinct weathering episodes.

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