### 4.5.P09

# Ages and lateritic weathering rate in northern Brazil deduced from cryptomelane 40Ar/39Ar geochronology

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The <sup>40</sup>Ar/<sup>39</sup>Ar dating of 50 cryptomelane grains (K-Mn oxides) has been applied to the geochronological study of the stepped landscape supergene Mn-rich deposit of the Serra do Navio manganese deposit from North Brazil.

First we have carried out a detailed petrological study of the oxidized ores developed from the weathering of manganiferous garnet and rhdocrosite-rich protores. Different generations of cryptomelanes have been distinguished by ttheir structure, texture and potassium contents. The dating of the various generations of cryptomelanes suggests that the oxidation front didn't always continuously propagate with time. The average rate of the weathering front propagation is about 2.5 m/Ma. The datings confirm the development of different generations of cryptomelanes associated to successive weathering main periods: 25-18 Ma and 15-13 Ma; 6.2-4.6 Ma; 2.6-2.3 Ma; 0.5-0.2 Ma). <sup>40</sup>Ar/<sup>39</sup>Ar age for Oligocene and late Miocene periods are not recorded, implying, for those periods, intense regional erosion processes in relation to planation surface development, comparable with those of the Guiana shield. Then, beyond the fact that our study confirms that the <sup>40</sup>Ar/<sup>39</sup>Ar dating of the cryptomelanes is an effective tool to study morphoclimatic events of lateritic landscapes, in agreement with previous study [1,2,3], we propose two scenarios related to the geomorphology regional path compared to west African lateritic landscapes:

(1)-The upper surface would be a lowered relict of the Cretaceous-Eocene bauxite (surface II). The lower surface would correspond then to Oligo-Miocene surface III, equivalent to the African intermediate surface.

(2) The upper and lower surfaces would be respectively from Oligocene and late Miocene periods (surface III and IV) and their African equivalents would be the intermediate surface and the "haut-glacis" lateritic surface.

#### References

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## 4.5.P10

# Impact of cyclic freezing on precipitation of silica in Me-SiO<sub>2</sub>-H<sub>2</sub>O systems and geochemical implications for cryosoils and -sediments

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In natural surroundings inorganic precipitation of silica is mostly induced by cooling of thermal water or by evaporation. However, in polar regions freezing of soil solutions may cause deposition of silica in specific soil horizons, glacial streams are often milky with suspended silica, and a formation of e.g. chabazite may be induced by repeated cycles of freezing and thawing.

Precipitation of silica by cyclic freezing was studied with and without dissolved chlorides (0.01 mol L<sup>-1</sup> of Me). The temperature was continuously shifted from 20 to -20 °C and vice versa within 24 hours in a climatic exposure test cabinet at reproducible conditions. It was ensured that the solutions totally defrosted within the respective time intervals. The treated solutions were filtrated (0.45µm) and analysed at various standby times.

The experimental results show that cyclic freezing of aqueous solutions may cause a significant precipitation of amorphous silica, where about 90 mol% of the primary dissolved silicic acid can be fixed. In analogy to evaporation  $H_2O$  molecules are separated from aqueous solutions by freezing and supersaturation with respect to amorphous silica is reached. Cyclic freezing induces a self accelerative process as silica precipitation by freezing is strongly stimulated by low concentrations of Si(OH)<sub>4</sub> and increasing numbers of freeze-thaw cycles.

Additionally dissolved metal ions (Me) favour the formation of amorphous silica in the sequence of Na<sup>+</sup> < Mg<sup>2+</sup> < Ca<sup>2+</sup> < K<sup>+</sup> < Li<sup>+</sup> < Sr<sup>2+</sup> < Ba<sup>2+</sup>. This may be mostly related to amorphous silica solubility in the respective remaining solutions. Co-precipitation yields Me/Si ratios of the depositions between 1 and 4. Such solids are suitable for a neo-formation of silicates in particular with regard to an incomplete re-dissolution.

If the results are applied to natural systems, cyclic freezing can significantly reduce the geochemical and ecological availability of silica. The induced silica precipitation stimulates the alteration of minerals and rocks. As secondary authigenic silicates like zeolites are formed, their occurrence and exposure in cryosoils and -sediments may be used as a proxy indicator of past climate.