Weathering or hydrothermal alteration? Examples from the Rhenish Massif, Germany

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Introduction
The Rhenish Massif is a part of the Variscan mountain belt in central Europe. Lithic arenites, quartzites and shales are the most common rock types in the Massif. Carbonates and volcanic rocks are less abundant. Quartz, feldspars, chlorite, illite and kaolinite are the main rock forming minerals. The dark grey and greenish rocks are locally bleached and weathered and appear in white colors. This alteration, called 'Weiβverwitterung', is caused by the destruction of dark organic material and the kaolinitization of chlorite. It may be an effect of i) descending weathering solutions or ii) ascending mineral waters.

Intensive and long lasting chemical weathering, in Mesozoic and Tertiary time, under warm-humid climatic conditions created a thick weathering mantle (Felix-Henningsen, 1990). Red and grey plastosols (or ferrallitic gleyic acrisols according to the FAO soil map) are relicts of the former soils, which have been eroded during the Upper-Tertiary and Quaternary uplift of the massif. The kaolinite rich saprolites formed the lower parts of the weathering profiles. They have a wider spatial distribution than the plastosols.

A lot of mineral and thermal water springs occur in the Rhenish Massif. Bleaching and kaolinitization of the clastic rocks have been found in the vicinity of these springs too (Spies, 1986). Reactions due to the influence of ascending thermal waters have been claimed to be the cause for the alterations. In some regions both types of weathering products occur together and a distinction between both types was difficult. Estimates about the shape of the paleorelief and the depth of the saprolitization as well as the rare occurrences of dickite give hints to the origin of the saprolitization.

Hydrothermal alteration
In a research project to reveal the genesis of mineral and thermal waters in the Rhenish Massif, rock samples from four mineral water wells, up to 600 m depth, have been analyzed (May, 1994). These wells produce Fe- and CO2-rich Ca-Mg-Na-HCO3-waters. The comparison of altered rocks with stratigraphically equivalent but unaltered rocks allowed to calculate element balances. Water-rock reactions have been calculated with geochemical computer programs.

Lower amounts of chlorite and partly albite and higher contents of kaolinite, in comparison with the unaltered rocks, are usually observed in the cuttings. Dolomite and siderite are common secondary phases; Alunite is a less abundant alteration phase. The main alteration reaction can be described by the following bulk equation:

$\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 5\text{CO}_2 \rightarrow 5\text{FeCO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{H}_2\text{O}$

chlorite + carbon dioxide $\rightarrow$ siderite + kaolinite + quartz + water

The calculation of saturation indices shows, that the waters don't reach equilibrium with the minerals of the aquifers during their underground passage. The waters are undersaturated in respect to chlorite, which is metastable. Its decomposition goes slowly and this is the critical step for the reaction rates. The stability fields for this reaction depend on the temperature and the CO2-partial pressure. The waters contain free CO2 with partial pressures about 1 bar. At this pressure the stability of kaolinite is limited to temperatures below 70°C (Fig. 1). Only one sample from 546 m depth is enriched in chlorite. It probably contains secondary chlorite which may have been formed by the reverse reaction. The aquifer temperatures have been estimated with several hydrochemical kation thermometers. They range from 32 to 62°C. The composition of the precipitated carbonates depends mainly on the temperature and the Ca, Mg and Fe activities of the mineral waters (Woods & Garrels, 1992). Carbon isotopes indicate low temperature equilibria between siderite and dissolved HCO3. The waters at the four sites will precipitate Fe-rich dolomite or Mg-poor siderite. A slight increase of the redox potential will cause the oxidation of siderite to goethite. This happens when oxygen rich groundwaters of shallow origin have access to the reaction sites in the fractured aquifers.
FIG. 1. Stability fields for the hydrothermal kaolinite- 
zation of chlorite.

Weathering

The alteration of chlorite to kaolinite under weathering conditions during Mesozoic-Tertiary time took place at lower pCO₂ and under more oxidizing conditions in the pore fluids. (A reducing environment existed in the lowest horizon of the non bleached and still chlorite bearing saprolite.) Haematite/goethite impregnations, known as 'Hunsruckerze' are widespread in the upper part of the saprolite where chlorite is absent. Iron, liberated during the decomposition of chlorite, was precipitated in the oxidation horizon. The ore has been mined since roman times.

Conclusions

Iron minerals provide an easy tool, even for field use, to distinguish between hydrothermal alteration and deep weathering. Iron which has been liberated during the kaolinitization of chlorite bearing rocks has been precipitated in the altered rocks. According to the different geochemical environment, various iron phases have been formed:

- Siderite and Fe-rich dolomite are characteristic for low temperature hydrothermal alteration in bicarbonate groundwaters.
- Haematite/goethite mineralizations are abundant in the bleached parts of the saprolites of the Mesozoic-Tertiary weathering mantle.

References