

Weathering replacement of limestone by clay+iron oxide at Bloomington, Indiana

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At a unique outcrop uncovered in the excavation for a new building on campus we find that the (vertical) contact between Paleozoic limestone and *terra rossa* consists of a set of metasomatic zones:

A) Fresh, stylonitic Salem Limestone consisting of crinoid and bryozoan fragments, 0.5 to 1 mm across each, well cemented by clear calcite. B) A 1-2-mm-thick band of bleached calcite. C) A one-mm-thick black line of manganese oxides(?). D) A zone 6 cm thick where crinoid fragments can be found in all stages of pseudomorphic replacement by orange clay. And E) The massive clay zone; its peds are bounded by a box work of coarse-crystalline authigenic clay. The zones make up a moving front (Merino et al, 1993).

The orange clay is an aggregate of clay crystals with fairly high birefringence. As the crinoid fragments are pressure-dissolved by the growing clay, they develop a striking outline consisting of identical sharp teeth. The observed replacement warrants adjusting the limestone-to-clay mineral reaction *on volume* (Merino & Dewers, 1998), as $3\text{CaCO}_3(\text{calc}) + 2\text{Al}^{3+} + 2\text{SiO}_2 = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{kaol}) + 3\text{Ca}^{2+} + 3\text{HCO}_3^- + 3\text{H}^+$, where the factor of 3 in front of the calcite formula ensures that the reaction preserves solid volume, as is characteristic of replacement. (Pending accurate identification of the clay and its chemistry we use kaolinite in the reaction above.) In turn the coefficients of the mineral replacement enter into continuity equations as multipliers of the appropriate reaction rates, opening the way for a dynamic modeling of the formation of the *terra rossa* (Wang et al, 1995). The dissolved Al^{3+} and $\text{SiO}_{2(\text{aq})}$ needed to make clay at the moving front probably come from dissolution of dust and loess at the surface, several feet overhead. The H^+ released by the replacement may dissolve some additional calcite, which would account for the dissolution pits represented by the teeth at the calcite surface.

Terra rossa is similar to other laterites (it forms by replacement of parent rock) but presents unique features – the pressure-solution-driven replacement brings about chemical dissolution of calcite at the replacement front.

References

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Hydrologic and kinetic modeling of plagioclase weathering rates in the Rio Vouga Basin (Portugal)

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Chemical weathering rates of plagioclase $W_{i,Pl}$ ($\text{mol m}^{-2} \text{y}^{-1}$) were derived from export rates of major solutes in springs in granites and metasediments in the basin. [1]

$$W_{i,Pl} = (d[\text{PI}]/dt)(V_d/A_{Pl})$$

$(d[\text{PI}]/dt)$ = acquisition of [PI] per unit travel time, V_d = volume of water with concentration [PI] discharged, A_{Pl} = surface area of Pl reacting with aquifer water.

The hydrologic travel times of [PI] were calculated by a finite difference method, the A_{Pl} 's by an earlier described method [2] The V_d 's were derived from base-flows. [3]

The $W_{i,Pl}$'s depend on pH and pollutant concentrations. At pH 5, $n_H (= \log W_{i,Pl}/dpH) = 0.46 \pm 0.12$, at pH 6.5 $n_H = 0.12 \pm 0.04$. An increase of pollutants drops down the $W_{i,Pl}$ values. These features are in keeping with predictions of kinetic modeling, in which dissolution rates depend on $\{\text{H}^+\}$, $\{\text{inhibitors}\}$ and affinity ($f(\Delta G_r)$). [4]

Burch et al. [5] described albite dissolution rates kinetically at pH 8.8 and 80°C, considering the forward and backward reactions. We converted their model parameters to T (15°C) and pH (5 and 6.5) and obtained a couple of model curves in the $W_{i,Pl}$ vs. ΔG_r that fit our data reasonably well. Since the effect of inhibitors was neglected, we fitted our data by a model [6] that specifically takes into account sorption of the network-modifying Na^+ and Ca^{2+} . We could fit our data by introducing a high sorption constant ($K_{Ca} = 10^{6.4} \text{ L mol}^{-1}$) for Ca^{2+} .

References

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