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, stylolitic 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 cemented by clear calcite. B) A 1-2-mm-thick band of high birefringence. As the crinoid fragments are pressure-solution-driven replacement brings about chemical replacement of parent rock) but presents unique features – 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 3CaCO₃(calc) + 2Al³⁺ + 2SiO₂ = Al₂Si₂O₅(OH)₄(kaol) + 3Ca²⁺ + 3HCO₃⁻, 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 flow system.

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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

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

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

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

$V_d = volume of water with concentration [Pl] discharged,$

$A_{Pl} = surface area of Pl reacting with aquifer water.$

The hydrologic travel times of [Pl] 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, $n_H = 0.46±0.12$, at pH 6.5 $n_H = 0.12±0.04$. 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 $\{H^+,\{Ca^2+,\{inhibitors\} and affinity (f(\Delta G_i)). \[4\]

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. $\Delta G_i$ 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 Ca²⁺. We could fit our data by introducing a high sorption constant (K_Ca = 10^{6.4} L mol⁻¹) for Ca²⁺.

References