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IRON INDURATIONS IN SOUTHWEST WISCONSIN: CHEMICAL WEATHERING IN A GROUNDWATER ENVIRONMENT

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ABSTRACT

Iron indurations and locally continuous duricrusts are present in the Saint Peter Sandstone west of Madison, Wisconsin. The indurations are found immediately below the contact of the sandstone with overlying dolomite. The mineralogy, elemental composition and fabric of the indurations are comparable to iron duricrusts evolving by tropical pedogenesis. The frequency of indurations diminishes down dip as the contact becomes separated from the surface by overlying sediments.

The indurations form as iron is released during dolomite solution, moves vertically through the contact, and is immobilized in the sandstone as interstitial cement. The clay mineralogy of the fine fraction associated with the indurations consists of a simple suite of minerals having thermodynamic or kinetic stability in a carbonate electrolyte. Authigenic formation of K-feldspar, evidence of "reverse weathering," has occurred.

The indurations form in a groundwater weathering environment as iron is immobilized at the interface of two dissimilar sediments. The indurations are not directly linked to either surface climates or surface pedogenic processes and are not evidence of paleotropical conditions.

INTRODUCTION

Iron indurated nodules and locally continuous iron duricrust are present in Lower Paleozoic quartzarenites west of Madison, Wisconsin. The indurations consist of quartz sand grains bound together by goethite (FeOOH) and hematite (Fe_2O_3) interstitial cements and pore fillings. The indurations fill joints and cross primary bedding in the sandstone; they are certain post- depositional features. The mineralogy, elemental composition and fabric of the indurations are comparable to iron duricrusts evolving by tropical pedogensis (Dury and Knox 1971, Habermann and Dury 1974, Dury and Haberman 1978). In some localities vertical color changes are suggestive of pallid, mottled and duricrust zones common to deeply weathered tropical soils. The previous workers used this evidence to hypothesize the indurations formed by pedogenesis under Early Tertiary tropical vegetation and climate. In this paper I examine the validity of the proposed paleotropical morphogenesis in view of evidence from the spatial distribution of the indurations and the geochemical environment in which they occur. My work emphasizes the indurations present at the contact of the St. Peter Sandstone with the overlying dolomite of the Platteville Formation.

STUDY AREA AND METHODS

The principal field area encompassed the "Driftless" portion of Dane County, Wisconsin. Exposures of the Saint Peter Sandstone/Platteville Formation contact are common in this area but are blanketed by glacial deposits to the east, have been removed by erosion to the north, and are progressively covered by uneroded Lower Paleozoic sediments to the south and west. Field sites included road cuts and quarries.

Laboratory analysis determined the elemental composition of the indurations and overlying carbonates. Numerical modeling of the groundwater electrolyte was followed by prediction of thermodynamically stable silicate minerals. These predictions are compared to the silicate mineralogy of argillaceous sediments associated with the indurations. Mineral identification in the argillaceous sediment was done by standard X-ray diffraction techniques on K^+, Mg-glycerol, and Na-DMSO solvated samples at room and elevated temperatures.

RESULTS

The iron indurations are restricted to two lithologically similar contacts in the subsurface of Dane County (Figure 1); they are absent from the bulk of the sandstone strata (Figure 2). The carbonate and sandstone bedrock was deposited during cyclic marine transgressions during the Lower Paleozoic (Ostrom 1970). The transitional clayey facies at the Saint Peter Sandstone/Platteville Formation contact are less than 0.5m thick in Dane County but increase rapidly in thickness down dip to the south and west to become the shale of the Glenwood Formation. Iron in the indurations is derived from iron in the dolomite lattice or in sulfide minerals in the Platteville Formation. The iron is released following congruent solution of the parent minerals.

Spatial restriction of the iron indurations to two vertically stacked contacts of similar lithology suggests that the indurations result from the vertical passage of groundwater through the bedrock and that the responsible processes are restricted to the contact zone. The frequency of indurations diminishes rapidly down dip to the west and south; this is concurrent with increasing thickness of shaley sediment at the Saint Peter Sandstone/Platteville Formation constact, increased isolation of the contact from the surface by overlying bedrock, and decreased dissolution of the overlying dolomite. These factors show stratigraphy and structure, rather than surface environment, to be the primary distributional control of the indurations.

Iron indurations are present near the surface and in quarries and valley sidewalls where the contact is separated from the surface by over 20m of intervening carbonates. The geochemical environment at these subsurface contacts differs markedly from surface environments. The groundwater characteristics are dominated by the solution of bedrock carbonate minerals, not surface soil reactions. Electrolyte characteristics at the subsurface contact can be modeled assuming a closed system of carbonate weathering in which chemically reactive soil water equilibrates with the partial pressure of CO_2 in the soil atmosphere and then passes out of contact with the soil and into contact with carbonate rock (Garrels and Christ 1965). This model closely describes the field area where the simple bedrock mineralogy (dolomite, quartz, illite, muscovite) and diffuse groundwater flow allow near-equilibrium to be attained (Dreybrodt 1981). Equilibrium calculations predict the groundwater passing through the carbonates and into the contact will be a calcium-magnesium-bicarbonate solution with high ionic strength and buffered basic pH (pH 7.8-9.9, Melcon 1979).

Silicate minerals are thermodynamically unstable in the acid leaching environment of soils and are altered by complex transformations to a residuum of kaolinite, gibbsite and iron oxhydroxides (Calvert et al 1980). In a non-acid leaching electrolyte, many silicates become thermodynamically stable and "reverse weathering", involving authigenic formation of silicates, is predicted. The qualitative differences in the weathering reactions and resultant mineralogy allow discrimination between soil environments (metastable minerals, reaction kinetics) and groundwater environments (minerals having a wide range of thermodynamic stability). Thermodynamic stability fields for silicates as a function of pK^+, $pSi(OH)_4$, pH, and $pCa^{2+} = pMg^{2+}$ were calculated and are shown in Figure 3 (Melcon 1979). Over the pH range considered, only K-feldspar, illite and kaolinite have stability fields falling within the common concentrations of potassium and silicon in groundwaters; these minerals should be preserved or form authigenically at the contact.

The mineralogy of the clay-sized fraction of Glenwood sediment lying directly above the iron indurations was determined by X-ray diffraction techniques. Three minerals, muscovite, illite, and K-feldspar, are present in significant quantity; vermiculite is a minor constituent; kaolinite is present in trace amount. Muscovite (the high temperature polymorph $2M_1$) is detrital in origin. Although the $2M_1$ polymorph has no thermodynamic stability, muscovite commonly persists in weathering environments because of kinetic limits on its alteration. In a carbonate groundwater these include the lack of acid attack on the Al-hydroxy sheet and the negligible diffusion of K^+ from the interlayer under normal K^+ concentrations (Henderson et al 1976). Illite, a low temperature muscovite polymorph (1M) of variable composition, has a limited thermodynamic stability field at basic pH. It is a common product of diagenesis in sediments (Weaver 1967) and is accorded kinetic stability similar to muscovite. The minor presence of vermiulite, a rapid-forming metastable alteration product of muscovite and illite, reflects low K^+ concentrations in the groundwater (Kittrick 1973).

Two phyllosilicates, chlorite and smectites, have no predicted thermodynamic stability and are absent from the argillaceous sediment. This absence is consistent with the proposed groundwater weathering environment. The trace present of kaolinite reflects authigenic formation similar to that noted by Rex (1966) in the Saint Peter aquifer in Missouri.

The final silicate mineral observed in the clay-sized fraction is K-feldspar. K-feldspar is unstable in the clay-sized fraction of soils and is rapidly weathered (Calvert et al 1980). Its presence suggests that intensive pedogenic weathering has not occurred; the origin is more likely authigenic or detrital.

K-feldspar is, however, thermodynamically stable in a basic Ca-Mg-HCO groundwater. Authigenic K-feldspar has been shown to be present as overgrowths on detrital K-feldspar grains in the Saint Peter Sandstone by Odum et al (1976). X-ray diffraction of volcanic ash laminae in the Platteville Formation of Dane County (this study) and in Northern Illinois (William and Kolata 1978) also confirm the formation of K-feldspar in the subsurface. The presence of non-detrital K-feldspar is evidence that thermodynamic equilibrium has been approached in the buffered groundwater solution. "Reverse weathering," i.e., the authigenic formation of minerals at low temperature and pressure, has occurred (Kastner and Siever 1979).

DISCUSSION AND SUMMARY

The field distribution of the Wisconsin iron indurations is linked to stratigraphic and structural characteristics of the bedrock. The presence of iron indurations in a contact zone separated from the surface by tens of meters of carbonate rock implies that vertically moving groundwater, not the soil reactions of the surface environment, is responsible for their formation. The weathering reactions in a basic carbonate groundwater solution are qualitatively different from those under acid leaching conditions in a surface soil. Thermodynamic equilibrium calculations show two minerals, illite and K-feldspar, to have large stability fields. These minerals dominate the clay-sized fraction of sediments found with the indurations. The presence of K-feldspar demonstrates that reverse weathering has occurred. The clay-sized minerals, and by direct extension, the iron indurations, reflect the low temperature equilibria of a buffered subsurface groundwater environment.

The initial work on this topic involved extensive field work, analysis of the mineralogy of the iron indurations, analysis of the elemental composition of the iron indurations, and description of induration fabrics. The strong physical, chemical and mineralogic similarity with tropical concretions led to a direct analogy being drawn and tropical paleopedogenesis proposed. None of these factors are linked, however, to a unique surface environment. I have demonstrated that the Wisconsin indurations occur in a groundwater environment which includes reverse weathering not characteristic of soils. The occurrence of iron indurations at the Saint Peter Sandstone/Platteville Formation contact is an excellent example of geomorphic convergence

> . . . whereby disparate processes, or different emphases of the same processes, may produce similar results at a particular stage in their operation (Cummingham 1969 pg. 58).

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