

Caliche Dissolution and Calcite Biomineralization by the Endolithic Lichen *Verrucaria rubrocincta* Breuss in the Sonoran Desert

Laurence A. J. Garvie¹, Frank Bungartz², Thomas H. Nash² & L. Paul Knauth¹

¹ Department of Geology, Arizona State University, Tempe, 85287-1404, Arizona, USA

² Department of Plant Biology, Arizona State University, Tempe, 85287-1601, Arizona, USA

Verrucaria rubrocincta is an endolithic lichen that inhabits exposed caliche in southwestern Arizona, and has developed a survival strategy against the high photon fluxes, aridity, and temperature extremes of the Sonoran Desert. The lichen occurs within the surface of flat caliche plates weathered from basaltic and rhyolitic rocks. *Verrucaria*-inhabited caliche is evident by the abundance of reddish-black perithecia protruding through the caliche surface. Old perithecia may fall out leaving empty pits. Only the surfaces of smaller <10 cm, caliche plates are completely inhabited by the lichen, whereas larger decimeter-sized plates are only partially covered, mostly around the edges. The lichen invades the rock from the edges, penetrating the rock surface.

Light and scanning electron microscopy of thin sections reveal the anatomy of the endolithic growth, and show five zones: (1) A 50 to 150 μm surface layer of fine-grained calcite (micrite), with few hyphae. The perithecial neck protrudes through this layer. (2) Just below the micrite surface a ca. 120 μm thick upper medulla is developed. It is characterized by an abundance of algal cells; the perithecial cavity is embedded within this layer. (3) A <400 μm thick lower medulla that is mostly devoid of algal cells. Here the fungal hyphae abundantly penetrate the caliche. (4) In a transitional zone only few hyphae grow above (5) unaffected caliche. Fungal hyphae penetrate up to 1 cm into the caliche. The micrite layer on the surface can be flaked off revealing the algal cells below.

By powder x-ray diffraction the micrite layer is dominated by calcite with minor quantities of weddellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), and

detrital quartz. The calcite grains in the micrite layer are anhedral and typically <2 μm diameter. Larger quantities of weddellite and minor amounts of whewellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), occur within the lower medulla. Ca-oxalates are absent in the unaltered caliche. The Ca-oxalates presumably arise through the reaction of oxalic acid excreted by the hyphae with the calcite from the caliche in the lower medulla.

The stable isotope results show that the micrite is enriched in ^{13}C ($\delta^{13}\text{C} = 8.1$) relative to the underlying caliche ($\delta^{13}\text{C} = 0.0$). The micrite layer is therefore ca. 5 per mil enriched in ^{13}C relative to calcite in isotopic equilibrium with atmospheric CO_2 , indicating that the light carbon is fractionated into organic material hence leaving heavy CO_2 to form carbonate. The heavy ^{13}C enrichment suggests that the micrite layer is not *sensu stricto* a biological precipitate but a biologically-induced fractionation with light CO_2 extracted from the organism leaving a residual heavy CO_2 to form the micrite.

Our observations suggest that the endolithic growth of the lichen results from two different processes: 1) dissolution and mechanical weathering of the caliche from the fungal hyphae of the lower medulla, and 2) precipitation of a protective surface layer of micrite. The lichen thus simultaneously dissolves the caliche substrate and biomineralizes a micrite surface. Our field observations suggest the *Verrucaria*-inhabited substrate weathers at a similar rate as uninhabited caliche.