

THE MYSTERY OF ANTIBACTERIAL CLAYS: A STORY OF MUD, METALS AND METABOLIC MALFUNCTION

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In 2002, Line Brunet de Courssou, a philanthropist working in Cote d'Ivoire, Africa, observed that French Green clays killed Buruli ulcer. This infection by *Mycobacterium ulcerans*, is a flesh-eating disease that attacks the subcutaneous lipids causing flesh removal over large areas of the body. It is most common in swampy regions where people forage for food and may be transmitted by a water bug that is common in the roots of swamp vegetation. Courssou had presented to the World Health Organization (WHO), photo-documentation of her treatment of over a hundred women and children (food gatherers) with the disease. Using daily applications of the green clay poultice (mud), she healed infections that did not respond to any known antibiotic, and normally required excision or amputation. The WHO, could not fund treatment until a scientific basis for the antibacterial effect was recognized. Her question was simply, "What makes clay antibacterial?"

A decade of research on clays that kill human pathogens, including antibiotic resistant strains such as methicillin resistant *S. aureus* (MRSA), has documented their common characteristics. Having tested dozens of clays worldwide, similar to the French green clay, about 10% have shown antibacterial effects on model Gram positive and Gram negative pathogens. Common among the antibacterial clays are that they each contain phases with reduced metals (e.g., pyrite, magnetite, jarosite) and phyllosilicates including dominantly illite-smectite, typical of assemblages found in the alteration zones of massive sulfide deposits. However, the mineralogy alone does not define antibacterial clay. Another common characteristic is the dominance of nanometric particle sizes. Testing various size fractions of clay has shown that the finest fraction ($<0.1\mu\text{m}$) is antibacterial, while the coarser fractions are not. Furthermore, oxidation of the clay removes the antibacterial effect.

Critically important is the role of the clay mineral surface in buffering the water pH to conditions <4 or >10 , where Al and Fe dissolve from various minerals in the clay. Because of the enormous surface area of expandable clays (smectites), metals adsorb to their interlayer surfaces. When the clays are taken out of their natural environment and mixed with de-ionized water for a medicinal poultice, cation exchange and mineral dissolution releases reduced metals that become oxidized, generating hydroxyl radicals that damage organic compounds in the bacterial cell and cause metabolic malfunction in the bacteria. Different modes of action have been documented for different clay mineralogies, but in each case the role of the clay is either to flood pathogens with toxic metals (e.g., Fe, Al), or to rob bacteria of essential nutrients (Ca, Mg, P). Lessons learned will drive the design of new treatments for antibiotic resistant bacteria. The cumulative knowledge from studies of antibacterial minerals may lead to the recognition of natural antibacterial deposits



near massive sulfides (e.g., argillic alteration zones), developing new economic prospects.