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Massive ore deposits from microscopic organisms

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Most ore deposits are the result of a sequence of processes that concentrate a compound or element in a small volume that is amenable to recovery. In many cases, copper sulfides precipitate with much more abundant pyrite in massive sulfides that are hydrothermal or volcanogenic in origin. Many of the world's largest and highest quality copper deposits are formed from the secondary concentration of copper from these massive sulfides. These secondary deposits form by oxidation of pyrite through exposure to oxygen, which produces sulfuric acid, insoluble secondary iron oxyhydroxides and occasionally sulfates, and a host of more soluble metals including copper. These metal ions are transported in aqueous solution downward to an anaerobic zone where sulfate reduction creates sulfide, and concentrates (CuS) or chalcocite (Cu_2S) within a cementation zone. Although pyrite oxidation is well known to be catalyzed by microbial species such as *Thiobacillus* spp. (Morse, 1991; Baker and Banfield, 2003; Nordstrom, 2011), the reduction processes resulting in copper sulfide formation have usually been attributed to purely chemical processes. Tornos et al. (2019, p. 143 in this issue of *Geology*,) provide compelling evidence for the direct involvement of microbial processes in the mineralization of these deposits. In doing so, they provide the strongest evidence to date that these large secondary copper deposits are formed by the combination of sulfur redox cycling coupled with transport and provide much-needed clues about the factors that influence the origin of these deposits.

In the study, a combination of imaging, genomic, and metabolic studies were performed to determine the metabolisms that were active within the Las Cruces copper deposit in southwestern Spain, which has undergone secondary mineralization for the past 85 m.y. (Tornos, 2006; Tornos et al., 2017). Of particular note, the authors make use of catalyzed reporter deposition (CARD)-fluorescence *in situ* hybridization (FISH) probes, which are particularly powerful in that they can be used to image specific metabolic functions. Within the cementation zone, CARD-FISH revealed aggregates of sulfate-reducing bacteria, methanogens, and other organisms within exopolysaccharides (EPS) that were concentrated along vein walls, and crystals of copper sulfides were associated intimately with these matrices. Importantly, these veins also contained abundant organic matter and revealed a complex fabric on which the bulk of mineralization occurred. Such architectures are commonplace in biofilms where organisms anchor themselves within a chemical gradient, but seldom directly observed in ore deposits (Sillitoe et al., 1996). In this case, these organisms appear to be organized within a vein to take advantage of abundant sulfate, organic carbon, or hydrogen within the vein. It is likely that this deposit is similar to others, yet the reasons that these structures are only rarely preserved remain unsolved, though most other studies have depended on identifying microbial morphologies in the veins rather than genomic methods of identifying organisms or organism function.

These microorganisms appear to be more than relict structures. Enrichment cultures from mineralization zones released hydrogen gas and consumed sulfate, both indications of viable, or at least potentially active, sulfate reduction. Furthermore, the reported quantities of sulfate consumed are quite high, and viable cell densities appear to be as high as 10^7–10^8 cells/g. For comparison, this cell density is nearly on par with cell densities observed in subsurface soils (Fierer et al., 2003; Rousk et al., 2010) where abundant nutrients and energy sources are available. The abundance of viable organisms is particularly striking given the age of the ore deposit, and begs a series of questions about how these organisms have maintained viability, or if the vein is still actively forming despite its hydrologic isolation. The enrichment culture results suggest that these organisms are capable of efficient metabolisms, and thus potentially much more rapid mineralization than is usually presumed in these deposits. One possible factor that would slow mineralization is that it requires an energy source or electron donor, and this energy source also must be delivered to the microbial community. Hydrogen gas is likely to be the principal electron donor for these microbial communities, and it is probably derived from the thermal decomposition of organic matter within the underlying rocks. The Iberian Belt contains sediment rocks with abundant organic carbon, and this thermogenic (or methanogenic) gas is likely the product of slow diagenesis of those hydrocarbons (Inverno et al., 2015; Puente-Sánchez et al., 2018), producing methane and hydrogen, and the transport of those gases upward to the mineralization zone. If the release of hydrogen was really very slow, however, then presumably the chemical gradients that result from them would also be low, and thus they would likely support relatively lower densities of microbial life than were observed, but more adapted to the chemical environment.

One of the most compelling aspects of the study is the identities of the microorganisms identified in these secondary deposits. While it is tempting to label such an environment "extreme," many of the organisms identified are quite pedestrian, or at least common in nature. Some of the species identified include Crenarchaeota, sulfate-reducing bacteria such as *Desulfosporosinus*, *Desulfitobacterium*, *Desulfotomaculum*, and *Desulfovibrio* sp., and methanogenic archaea of the Methanosarcinales order such as *Methanosarcina*. Many of these bacteria might be encountered in rice paddys similar to where *Desulfovibrio* was isolated originally (Dalsgaard and Bak, 1994) or in other anaerobic soil, an estuary, or groundwater environment. Of these, *Desulfotomaculum* is unique in that it has been identified as a key sulfate reducer found in the deep and warm biosphere typical of low-temperature hydrothermal conditions (~100 °C) thought to be prevalent at the site (Moser et al., 2005; Aüllo et al., 2013).

Cultures also contained less-abundant iron cycling organisms, as well as many other undetermined microorganisms having unknown roles. Given the abundance of iron, this should not be surprising, and it could play an active role in the formation of the ore deposit. There is accumulating evidence that secondary sulfide mineral formation depends on the careful buffering of hydrogen sulfide concentrations. Many metals that

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form insoluble sulfide minerals, including copper, but including other elements like arsenic, also are capable of forming soluble sulfide complexes. As such, the solubility of the metal does not simply decrease as sulfide activities increase, but rather there is a minimum in which the metal is least soluble. In the case of arsenic, this occurs at a sulfide activity of just under 1 μM (Eary, 1992), and in the case of copper, it is complicated by the chemical state of Cu(I)/Cu(II) redox cycling, but also favored at low sulfide activities (Helz et al., 1993; Thompson and Helz, 1994). The separation and enrichment of Cu from other metals is possible only because of the unique stability of each of these sulfide complexes, and it is likely that the redox cycling of iron helps maintain low sulfide concentrations, and thus enhance metal sulfide solubility (Saalfield and Bostick, 2009; Burton et al., 2011). In future work, hopefully the roles of these parallel redox processes can better be constrained.

Overall, microbial sulfate reduction appears to be a key process in the formation of large secondary sulfide deposits in Las Cruces, Spain, and likely in others. There are abundant microorganisms facilitating sulfide reduction, and the reduction of other species including iron can carbon dioxide. Most of those bacteria are relatively commonplace in the environment, and the structures that form in the veins of these deposits appear to be similar to a host of other biofilms, in a variety of geochemical gradients. There is an intriguing and perhaps hidden suggestion from these conventional observations in an unconventional environment; namely, that perhaps an equivalent environmental setting would inherently contain these organisms and minerals, and that they would be using similar metabolisms elsewhere in the world. If so, then it would follow that this study is a reminder that it is the geological setting that supplies the reactants like sulfate and hydrogen gas for sulfate reduction to proceed, and thus controls secondary sulfide deposit formation. The ore deposit is thus rare not because the biological community is rare, but because the habitat these organisms occupy is limited to an uncommon geological setting. Similarly, this ore deposit is large because the geochemical conditions that create microbial substrates, and the transport of them to the mineralization zone, are stable and persistent. As such, understanding the role of biology in shaping ore deposits, and indeed our planet, requires us to examine the physical hydrology, petrology, and geochemistry that controls the formation of biological substrates. Of these factors, we have focused much effort on the geochemistry, but we know much less about how biology couples to transport processes in these ore deposits. Perhaps the isotopic data will be helpful in this regard. In some cases, isotopic fractionation between sulfate and secondary sulfides is negligible (e.g., Enders et al., 2006), indicating that the reduction is either abiotic or complete (the isotopic composition of sulfate are sulfide would be equivalent if it is entirely consumed). In more open systems, the isotopic composition of sulfide should be significantly different from the sulfate because of physical separation between them (Bawden et al., 2003). In either case, there are obvious parallels between the formation of these sulfide deposits and the common coupled redox processes observed in soils and sediments, both of which can only be fully appreciated with a broad geological perspective.

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