How do bacteria dissolve metal sulfides?

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A holistic perspective on the role of bacteria in metal sulfide dissolution processes is presented. Metal sulfides comprise on the one hand iron sulfides such as pyrite or pyrrhotite, which generate sulfuric acid by their oxidative dissolution. This can be either beneficial for metal recovery via leaching or detrimental as acid mine/rock drainage. On the other hand, metal sulfides comprise important minerals for base metal mining such as e.g. copper, zinc or lead. During the oxidative dissolution of metal sulfides various sulfur compounds with an intermediate oxidation state between sulfide (-2) and sulfate (+6) occur. Ferric iron as well as molecular oxygen have been described as chemical oxidants for the metal sulfides as well as for the intermediate sulfur compounds. Iron- and sulfur-oxidizing bacteria and archaea enzymatically accelerate most of these chemical oxidation reactions, which is described as indirect bioleaching for acidophiles thriving at low pH < 3. The indirect thiosulfate und polysulfide pathways described for metal sulfide oxidation are equal for suspended cells (non-contact) and those attached to the mineral surface (contact). But likely the reaction kinetics should be higher for attached cells with a high iron content in their extracellular polymeric substances (EPS) serving as a "glue" between cells and the mineral. The oxidation products have distinct signatures of stable isotopes, which may allow to differentiate between chemical and biological reactions by different isotope fractionation. Published isotope data support the indirect oxidation pathways. In the older literature, an iron-free direct oxidation of metal sulfides by acidophiles has been proposed. This would require cells attached to the mineral surface and a direct electron transfer from the metal sulfide surface to electron shuttling biochemical compounds in the cell wall or nanowires, which both have been described for ferric iron reducing neutrophilic bacteria. However, neither an iron-free cultivation of acidophiles nor nanowires have been demonstrated for acidophiles, thus bioleaching is likely only an indirect process. At circumneutral pH, also nitrate has been described as electron acceptor for microbial metal sulfide oxidation, however in contrast to several reports pyrite can likely not be oxidized by this process according to recent findings.