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MECHANISMS OF BACTERIAL OXIDATION OF THE
COPPER SULPHIDE MINERAL, COVELLITE

by

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ABSTRACT

The aim of this work was to determine whether a mechanism exists for bacterial oxidation of covellite (CuS) other than that involving cyclic reduction and oxidation of soluble iron, and to describe any such mechanism. It was thought likely that mechanisms of bacterial attack on CuS would also apply to other metal sulphides.

High purity covellite was synthesized by the thermal reaction of sulphur and copper. Thiobacillus cultures were obtained from other workers and from the natural environment, and enriched for sulphide oxidizing capability.

Oxygen consumption was monitored polarographically. Soluble copper, sulphate and total iron were assayed by Atomic Absorption Spectrophotometry while ferrous ion was determined spectrophotometrically as a complex with ortho-phenanthroline.

By rapid specific inhibition of biological activity during sulphide oxidation, the contribution of bacteria to the stoichiometry of oxidation was determined. At pH 2.5 the product of either biological (Thiobacillus ferrooxidans) or non-biological oxidation was CuSO_4 , the biological rate exceeding the non-biological rate about a hundredfold. At pH 4.5 T. thiooparus was incapable of oxidizing CuS itself but catalysed attack by oxygen (about fivefold) by oxidizing a sulphur passivation film which formed by reaction of CuS with oxygen. The nett result was again CuSO_4 production.

At pH 2.5 three strains of T. ferrooxidans oxidized CuS itself without the aid of ferric ion; a fourth strain

(BJR-V-1) was completely dependent on ferric ion or dissolved oxygen to oxidize CuS to sulphur.

In situations where dissolved oxygen initiated the oxidation of CuS, the oxidation rate was approximately first order with respect to dissolved oxygen, while zero order kinetics were observed when other mechanisms predominated.

In dilution experiments designed to demonstrate the dependence of sulphide oxidation (to sulphate) on physical contact between bacteria and mineral surfaces, no dependence was observed. It was concluded that water soluble intermediates were involved in CuS oxidation by T. ferrooxidans and in sulphur transport to the cells of T. ferrooxidans and T. thioparus. Arguments were advanced suggesting that the intermediates were inorganic and the concentration of intermediates was estimated from experimental results and the theory of diffusion.

The process of CuS passivation was studied; consumption of oxygen and acid, and production of cupric ion and sulphate were measured, the results indicating that passivation resulted from the accumulation of approximately 30 micro-mole of elemental sulphur per square metre of CuS. Oxygen consumed during depassivation by thiobacilli supported this conclusion. Assuming an even distribution of sulphur over the surface, the film was calculated to be one or two atoms thick.

From consideration of the results of this study it was proposed that polythionates may be involved both in CuS oxidation by bacteria and in transport of sulphur into bacterial cells.

The role of iron was investigated. Chemically synthesized ferric ion was less effective in CuS oxidation than was ferric ion produced by T. ferrooxidans strain BJR-V-1 through oxidation of ferrous ion.

The half saturation ferrous ion concentration with respect to oxidation by each of the T. ferrooxidans strains was approximately 10^{-5} molar, in contrast to values of 10^{-2} molar reported by others. Further ferrous oxidation kinetic experiments with strain BJR-V-1 indicated that the major substrate for the rate limiting reaction in ferrous oxidation was a ferrous phosphate complex; a sulphate complex also played a part.

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Abbreviations

This list includes only those abbreviations which may require definition and are not defined in the text.

Units:

mol = mole	Pa = pascal = newton metre ⁻²
M = mole litre ⁻¹	atm.= atmosphere (pressure)
m = metre	J = joule
sec.= second	°K = Kelvin temperature
l = litre (liquid measure)	°C = Celsius temperature
g = gram	V = volt
<i>g</i> = gravitational acceleration (9.8 m/sec ⁻²)	F = farad
Å = Ångstrom unit =10 ⁻¹⁰ m)	μ = micron = 10 ⁻⁶ m

Prefixes:

p = pico = 10 ⁻¹²
n = nano = 10 ⁻⁹
μ = micro = 10 ⁻⁶
m = milli = 10 ⁻³
c = centi = 10 ⁻²
d = deci = 10 ⁻¹
k = kilo = 10 ³

Others:

ΔG^0 = standard free energy change of reaction (usually at 25°C).

$\Delta G^{0'}$ = standard free energy change of reaction, where the H⁺ standard state is the specified pH.

R = gas constant = 8.3143 J °K⁻¹ mol⁻¹

K = equilibrium constant or 1000 ohms

[] = concentration

P = partial pressure

% (w/v) = g/100 ml

% (v/v) = percentage by volume

% (w/w) = percentage by weight

EDTA = ethylene diamine tetraacetate

TCA = trichloroacetate

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