Gas-phase protonation of oxo and hydroxo groups at the metal oxide surface

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The O-H stretching region of synthetic goethite particles evaporated in a N_2(g) atmosphere at different levels of acidity was investigated by Attenuated Total Reflectance Fourier Transform InfraRed spectroscopy (FTIR). Chemometric analyses of the spectra were used to identify subsets of bands arising from correlated surface hydroxyls. Band assignments (Figure) were supported by estimates of proton surface loadings and O-H stretching frequency calculations of all crystallographically-available surface sites from previous theoretical studies. Temperature Programmed Desorption FTIR measurements provided further constraints to this band assignment and helped formulate a possible route for surface dehydroxylation reactions.

Important cooperative effects between hydrogen-bonded surface hydroxyls are suggested to play a crucial role on the positions and intensities of discrete O-H stretching bands as a function of protonation level and temperature.

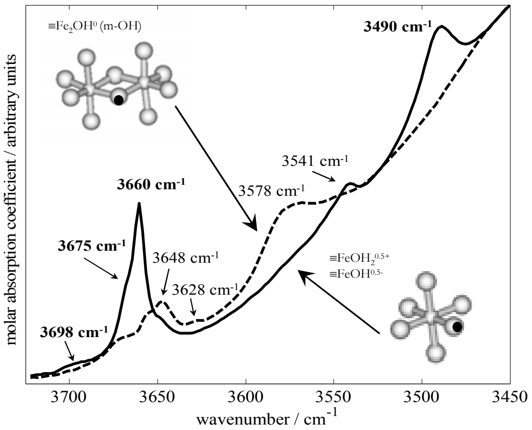

Figure 1: Molar absorption coefficients of –OH and □-OH groups of the goethite surface.

Methanogenesis-driven formation of siderite concretions in a brackish basin (the Wardie Shales, Scotland)

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Along Edinburgh's northern shore (Scotland), at Wardie, is an extensive outcrop of the Lower Carboniferous shales. This succession was apparently deposited in a large brackish basin. It hosts various ironstone concretions. The main interest of these shales has been palaeontological, for the concretions are the source of many superbly preserved fossil fish, although the great majority of the concretions contain only spiral coprolites. These may either be faecal, or the altered contents of a decayed spiral fish intestine.

Authigenic siderite and pyrite make up most of the concretion body. Precipitation of these minerals required sulfate reduction, which liberated bicarbonate to the porewaters. Stable C and O isotope analysis was performed on the carbonate fraction of the concretions. $\delta^{13}C_{PDB}$ values (from -3.5 to 12.1‰) show that, apart from sulfate reduction, methanogenesis contributed to the production of bicarbonate. Fossils are found within each of the concretions, suggesting that the decay of these organic remains provided "fuel" for the concretionary growth. The porewaters were significantly supplied with meteoric water, which is indicated by the very negative $\delta^{18}O_{PDB}$ values (from -12.8 to -4.7‰).

The concretions are mostly homogenous; only a few exhibit complex concentric zoning. One finely zoned concretion has been carefully examined with the use of microprobe. It showed that the main carbonate minerals are siderite enriched in Mg ($MgCO_3$ mole content up to 32%) and pure siderite. Some zones contain ferroan dolomite or calcite. The development of the zoning suggests that the concretionary growth proceeded generally concentrically. However, spatial relationship between the authigenic phases shows that the successive cements precipitated not only as separate outermost zones, but also pervasively within the available porespace of the last already existing zone.

Chemical composition of the zoned concretion has been compared with isotopic data. It revealed negative correlation between the $\delta^{18}O$ values and the content of Mg in the carbonates. It is concluded that the increased supply of meteoric water induced crystallization of Mg-bearing carbonates and that the outermost zones, composed of pure siderite, grew at a greater burial depth where the supply of meteoric water was reduced.