

# An Experimental Determination of the Solubility of Oxygen in Marine Brines

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## ABSTRACT

*The results are briefly presented of an experimental determination of the solubility of oxygen in marine brines at 22° and 50°C and at the atmospheric partial pressure of oxygen. The data show that even where well mixed and fully oxygenated evaporite brines, which are precipitating halite, are very close to being anaerobic in a biological sense. It is suggested that the very low solubility of dissolved molecular oxygen is the major cause of the high organic content of many evaporite deposits, aerobic oxidative destruction being largely inhibited.*

## INTRODUCTION

Evaporites and associated sediments display a variety of features which are evidently related to the oxygen budget prevailing at or very soon after their deposition. We have initiated a study aimed at defining these features rather more specifically and at defining the sources and sinks of oxygen in evaporite environments. On searching the literature we found that there were almost no data on the equilibrium solubility of molecular oxygen in marine brines. The initial experimental study was carried by Boardman as a senior undergraduate research project but the analytical data indicated that problems existed with the techniques being used. More precise determinations from both undersaturation and oversaturation were performed by Borcsik. Data synthesis and interpretation have been the responsibility of Kinsman.

### Sources of oxygen

Oxygen in natural aquatic environments exists in several different forms or reservoirs, for example as dissolved molecular oxygen, as dissolved species such as nitrate or sulphate ions, as dissolved molecular carbon dioxide and related dissociation products, and together with hydrogen

as water itself. These several forms and associations of oxygen exhibit quite different biogeochemical cycling. The consumptive use of oxygen in earth surface environments is overwhelmingly for respiration and biochemical decomposition of organic matter. A rather small amount of oxygen is consumed in inorganic oxidative reactions.

However, only three of the possible oxygen reservoirs need be seriously considered (a) dissolved molecular oxygen, (b) nitrate and nitrite ion oxygen, and (c) sulphate ion oxygen.

Molecular oxygen is derived from atmospheric or photosynthetic sources. The solubility of molecular oxygen in water is a function of total pressure, oxygen partial pressure, temperature and salinity. Pure water at 25°C saturated with air of average sea level composition contains close to 8.5ppm of dissolved molecular oxygen. Sodium chloride solution data (Fig. 1) suggest that under comparable conditions a halite-saturated brine will contain only 1–3 ppm dissolved molecular oxygen. Aerobic oxidative metabolic activities of metazoans and some micro-organisms consume dissolved molecular oxygen until concentrations reach between 1 and 2 ppm. Below this concentration anaerobic oxidative metabolism by micro-organisms commences and dissolved molecular oxygen values are reduced still further, to values lower than 0.1 ppm. At concentrations of about 0.5–1.0 ppm dissolved molecular oxygen, nitrate and nitrite ions are used by some micro-organisms (denitrifiers) as sources of nitrogen for protein synthesis. When dissolved molecular oxygen concentrations reach about 0.1 ppm then sulphate ion oxygen is exploited.

The oxygen budget can be seen to be complex and as a first contribution to this problem we describe below the equilibrium solubility of molecular oxygen in marine brines.

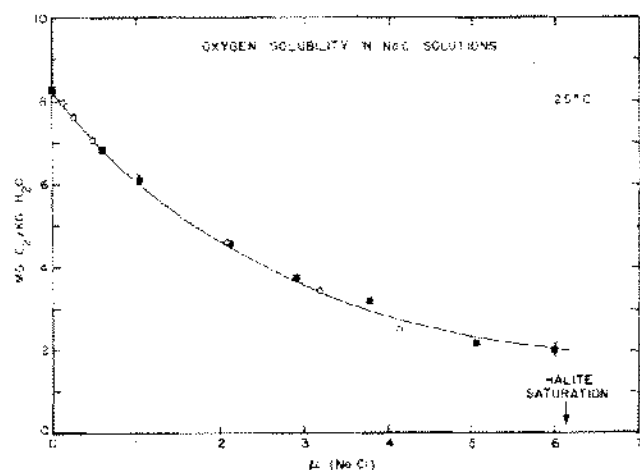


Figure 1. The solubility of molecular oxygen in sodium chloride solutions at 25°C. The oxygen partial pressure is 0.2 atmospheres (the average value found in air at sea level). The solubility is described as milligrams of oxygen dissolved per kilogram of water; for this measure we have used parts per million (ppm) throughout the paper. The sodium chloride solutions are described in terms of their ionic strength ( $\mu$ ), at 25°C a saturated solution having an ionic strength of just over six. The open circles are the recalculated data of MacArthur (1916). The solid squares are determinations by Boardman (this paper), the vertical bars on two data points indicating the uncertainty of the determinations.

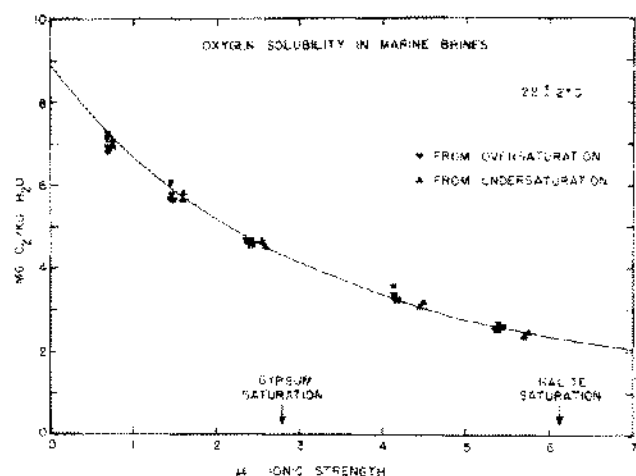


Figure 2. The solubility of molecular oxygen in artificial marine brines at  $22 \pm 2^\circ\text{C}$ . Oxygen partial pressure 0.2 atmospheres; oxygen solubility expressed as ppm, as previously defined; brine salinity described as ionic strength but calculated assuming no complex ion formation (a poor assumption at higher salinities).

## EXPERIMENTAL STUDIES

Samples of artificial sea water brines were prepared, maintained at a selected temperature, gently stirred in open contact with the atmosphere and sub-samples removed periodically for oxygen and chloride analyses. Oxygen was determined by standard Winkler techniques and chloride by standard silver nitrate titration. In a run

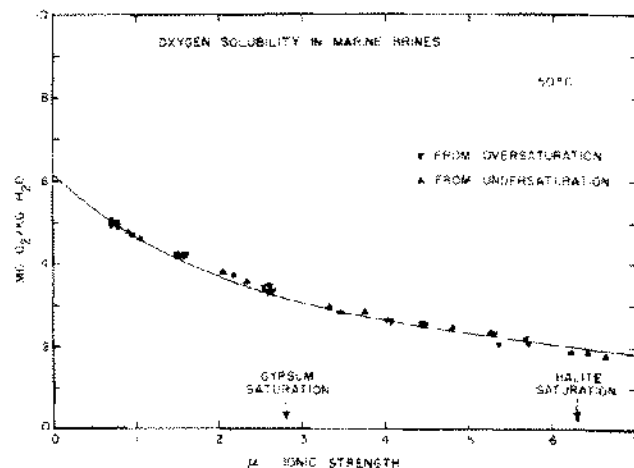


Figure 3. The solubility of molecular oxygen in artificial marine brines at 50°C. Other details as in Figure 2.

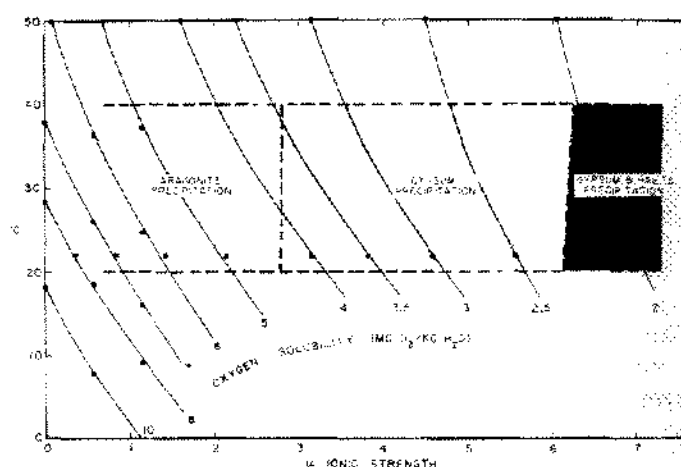


Figure 4. Cross plot of molecular oxygen solubility in ppm against temperature and ionic strength of brine. The dashed line encloses the temperature envelope 20–40°C, the temperature range of formation for the majority of evaporites. Once gypsum starts to precipitate, solubilities have fallen to less than four ppm and when halite starts to precipitate, values are less than 2.2 ppm and the environment is almost anaerobic.

from undersaturation the sample was first equilibrated for several hours at 20–30°C above the final temperature of the run. As the solubility of oxygen is inversely related to temperature, on cooling, oxygen entered the sample; equilibration was completed in a few hours. In runs from oversaturation, initial samples were cooled, equilibrated, and then raised to final temperature. The data of Figures 2 and 3 summarize the results. In Figure 4 the data are plotted in a more useful way, showing the equilibrium oxygen solubility of the different evaporite mineral facies at the temperature conditions under which most evaporites are formed (20–40°C). The conclusion of the study is that halite precipitating brines will be essentially anaero-

bic under all but the most turbulent condition. These data now permit us to compare other oxygen sources such as nitrate and sulphate ions and eventually to construct realistic oxygen budgets for evaporite basins.

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