$MV^{2+}$ . Likewise, Tris–HCl buffer (25 mM, pH 7.5 with 100 mM KCl) solutions of GroEL– CdS complex and  $\therefore$  cpn–CdS complex (2 ml, 700 nm based on Cd<sup>2+</sup>) were titrated. Emission ( $\lambda_{\text{ext}} = 370 \text{ nm}$ ) spectra were recorded on a FP-777W spectrophotometer (JASCO).

## Thermal stability

Fluorescence spectra ( $\lambda_{\rm ext} = 370\,{\rm nm}$ , wavelength of observed fluorescence  $\lambda_{\text{obsd}} = 530 \text{ nm}$ ) of GroEL–CdS complexes and  $\Box$  cpn–CdS complexes were recorded at designated temperatures on a FP-777W spectrophotometer (JASCO), where the fluorescence intensities at 4 °C were used as the bases for relative fluorescence intensities. The temperature was directly controlled by a ECT271 Peltier thermometric apparatus (JASCO;  $40^{\circ}$ C min<sup>-1</sup> on heating and 25 °C min<sup>-1</sup> on cooling).

## ATP response

To a 2-ml Tris–HCl buffer (25 mM, pH 7.5 with 100 mM KCl) solution of  $\therefore$  cpn–CdS complexes (0.5  $\mu$ M based on cpn) were added aqueous solutions of ATP (100 mM) and MgCl<sub>2</sub> (1 M) ([ATP] =  $20 \mu$ M, [Mg<sup>2+</sup>] =  $25 \text{ mM}$  after mixing), and the mixture was incubated at 70  $\mathrm{^{\circ}C}$  for 10 min. The supernatant solution was subjected to fluorescence spectroscopy and analytical SEC with an UV/fluorescence dual detector.

Received 11 November 2002; accepted 14 April 2003; doi:10.1038/nature01663.

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 $(Fe_{HR} = Fe_{D} + Fe_{P})$  and  $Fe_{T}$ , and the ratio  $Fe_{P}/(Fe_{P} + Fe_{H})$ , known as the degree of pyritization (DOP), have been used successfully to evaluate the redox state of ancient oceans<sup>10–13</sup>.  $DOP < 0.45$  and Fe $_{\rm{HR}}$ /Fe $_{\rm{T}}$   $< 0.38$  are generally found for sediments depositing from oxic bottom water, whereas DOP  $>0.45$  and  $\rm{Fe_{HR}/Fe_{T}}>0.38$  may be diagnostic for euxinic sediments<sup>10,12</sup>. The enrichment of Fe<sub>HR</sub> and high DOP in euxinic sediments arises fundamentally from sea sediments are comparable in magnitude, but oxic environments record a much greater range of values<sup>13,20</sup>.

The same is true for Phanerozoic examples. Gauthier<sup>21</sup> measured  $\delta^{34}$ S values for pyrites deposited beneath oxic and anoxic bottom waters of the Cretaceous seas that flooded North America. Like our Roper samples,

The documentation of euxinic and low sulphate conditions in mid-Proterozoic marine basins paves the way to an improved understanding of early life and environments. In such oceans, methanogenic archaeans could have played an enhanced role in the carbon cycle, contributing to long-lived greenhouse conditions<sup>27</sup>. Low sulphate may also help to explain the prominence of penecontemporaneous dolomite in mid-Proterozoic and older carbonate platforms<sup>28</sup>. Through its effects on biologically important trace elements, seawater chemistry may help to explain the ecological and evolutionary distributions of early eukaryotic photoautotrophs<sup>8</sup>. And, if sulphate levels remained low until the latest Proterozoic, oxygen probably also remained well below present levels, influencing the early diversification of animals<sup>29</sup>. Further biogeochemical research carried out in the framework of sequence stratigraphy