The ultra-high pressure phase diagrams of SiO_2 and $MgSiO_3$

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As a result of condensation sequences in protostellar nebulae and subsequent metal/silicate differentiation, planetary mantles are to first order close to an average $MgSiO_3$ composition. Indeed, large uncertainties exist about the Mg/Si ratios but in all cases, the question of the dissociation of $MgSiO_3$ or Mg_2SiO_4 into MgO and SiO_2 is crucial for understanding the mantles of terrestrial planets, the putative rocky cores of giant planets and possibly the early Earth. In this study, we have investigated the ultra high pressure phase diagram of SiO_2 using ab initio quantum calculations. We have observed an increase with pressure of the average effective Si-O coordinence from 4 to 9 in both solid and liquid phases. We have calculated the melting line and extracted elementary thermodynamic parameters for the solid and liquid phases which were then used to infer dissociation pressures and temperatures of $MgSiO_3$. The ab initio calculated electrical conductivity of the SiO_2 liquid phase allowed us to determine the position of liquid metallic SiO_2 in the phase diagram. The thermodynamic connections between SiO_2 metallization and $MgSiO_3$ dissociation and the implications for rocky cores of giant planets and early terrestrial mantle will be discussed. Finally, all these results from theory will be compared with experimental results acquired at ultra high pressures in dynamical compressions, including very recent ones.

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Prebiotic Simulations of Shallow Sea Hydrothermal Vents: Photochemical Reduction of CO_2 on Sphalerite

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A key requirement to understand the origin of life is to explain how early metabolism could have emerged. In the model of central universal metabolism [1], all carbon fixation pathways used by living organisms share at least one common intermediate [2], implying that all carbon fixation mechanisms are linked, and that a prebiotic mechanism should have used key organic compounds from present anabolic cycles. Photoelectrochemical reactions on semiconductor mineral surfaces have been proposed to play a central role in this scenario.

In this study sphalerite (ZnS) semiconductor mineral is used as a model catalyst to explore prebiotic reactions occurring in a shallow sea hydrothermal vent [3]. Sunlight free energy drives otherwise unviable reactions in the prescence of ZnS mineral produced *in situ*. The material and photoelectrochemical characterization of the ZnS colloidal suspensions and comparison to commercial samples includes powder X-ray diffraction, transmission electron microscopy, energy dispersive spectroscopy, and dynamic light scattering.

Experimental sesults show the photoreduction of dissolved carbon dioxide (C+IV) and the coevolution of species produced from sulphide hole scavenger. The photoreduction reaction proceeds to generate formate as the main initial photoproduct. The quantum efficiency of formate production (Φ) in the ultraviolet spectrum at pH relevant to the early ocean waters ($7 < pH < 9$) follows a dependence on wavelengths described by the equation: Φ (%) = 10.730 - 0.031 × λ (nm), with a coefficient of correlation $r^2 = 0.991$. The quantum efficiency does not depend on temperature between 283 and 328 K. The mechanism provides a way to capture energy from the environment while producing carbon feedstock useful in anabolism. The results of this study suggest that central metabolites could have participated in a viable enzyme-free cycle for carbon fixation in a shallow sea hydrothermal vent, where light, sulfide minerals, carbon dioxide, and other organic compounds interacted on the prebiotic Earth to generate an autonomous chemical cycle [1].

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