Paleosol constraints on atmospheric CO_2 levels in the Archaean and Proterozoic

N.D. SHELDON

Dept. of Geological Sciences, University of Michigan, 1100 N. University Avenue, Ann Arbor, MI 48109, USA

Precambrian atmospheric pCO_2 levels were previously estimated using simple thermodynamic models based upon the mineral assemblages in paleosols and BIFs [1–3]. However, thermodynamic approaches often require unreasonable or poorly constrained assumptions, and their results are highly dependent on the quality of the thermodynamic data available. In particular, re-evaluation of the paleosol thermodynamic model using more recent thermodynamic data [4] demonstrates that that approach [1] is unreliable and does not provide a significant contraint for atmospheric pCO_2 reconstruction.

As an alternative, a new model based upon paleosol mass-balance during weathering has been proposed [4]. The paleosol mass-balance model gives replicable results from multiple and widely distributed contemporaneous paleosols from the Paleoproterozoic (~2.2 Ga ago [4]) and Mesoproterozoic [4–5], and gives results that are consistent with independent proxies based on microfossils [6–7]. The pCO_2 curve generated by this method spans from 2.7–0.96 Ga ago [4, 5, 8] and indicates that: 1) late Archean and early Paleoproterozoic pCO_2 levels were similar, suggesting no significant change in response to the Great Oxidation Event; 2) from at least 2.7–1.8 Ga ago, pCO_2 levels were broadly consistent at 20–40 times pre-industrial levels; 3) between 1.8 and 1.1 Ga ago, there was a significant drop in pCO_2 to less than 10 times pre-industrial levels, coincident with a change in calcification and stromatolite abundance in the oceans. Climate model results using the paleosol-derived pCO_2 values indicate consistently equable conditions from 2.7–0.96 Ga ago and are also permissive of a Paleoproterozoic 'snowball' Earth event, which suggests that the paleosol mass-balance model provides a quantitatively valuable constraint on Archaean and Proterozoic pCO_2 levels.

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Effect of helium on structure of SiO_2 glass probed by Raman spectroscopy

G. SHEN[1] AND P. LAZOR[2]*

[1]High Pressure Collaborative Access Team, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439, USA (gshen@ciw.edu)

[2]Department of Earth Sciences, Uppsala University, 75236 Uppsala, Sweden

(*correspondence: peter.lazor@geo.uu.se)

SiO_2 glass represents a prototypical network-forming glass whose structure can be understood in terms of a continuous network of corner shared SiO_4 tetrahedra, with a high degree of intermediate range order. Numerous studies on structure and compressibility have been performed on SiO_2 glass under high pressure due to its importance as a model geological component, and an increased interest on polyamorphism of glasses and liquids.

In this work, SiO_2 glass was subjected to helium in diamond anvil cell at pressures up to 20 GPa. Micro-Raman measurements were performed in the back-scattering geometry utilizing argon-ion laser excitation. Single-stage, high throughput spectrometer equipped with an EM-CCD detector were used for data collection. Comparison of the evolution of Raman bands of SiO_2 glass upon compression with and without [1, 2] helium loading strongly supports incorporation of helium in the voids of SiO_2 glass structure. This is signified by a less profound narrowing of the inter-tetrahedral angle distribution, as revealed by the spectral widths of band corresponding to the symmetric bending motion of Si-O-Si linkage. Similar effect is seen in the Raman spectra of a recovered sample at ambient pressure. The shape of the corresponding Raman band is largely restored, although signs of local angular distortions remain.

The Raman results on the incorporation of helium are corroborated by a parallel x-ray diffraction study on the structure factor and compressibility [3]. Comparing these observations to the findings of other studies suggest that the effect of helium on the structure and compression of SiO_2 glass is unique. The strong effect of dissolved helium may have implications in Earth's evolution models and is also important in interpreting the high-pressure experiments in general because helium is widely used as a pressure medium.

[1] Hemley *et al*. (1986) *Phys. Rev. Lett*. **57**, 747–750. [2] Sugai & Onodera (1996) *Phys. Rev. Lett*. **77**, 4210–4213. [3] Shen *et al*. (2011) *PNAS* **108**, 6004–6007.