

Geochemical controls on cation substitution and hydrogen generation during serpentinization of Archean komatiites

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Komatiites, magnesium-rich ultramafic lavas, played a pivotal role in the Archean Earth system, shaping both the geochemical composition of the early oceans and the redox evolution of the atmosphere. One of the most significant processes affecting komatiites was serpentinization, an aqueous alteration reaction that leads to the production of molecular hydrogen (H_2) through Fe oxidation. Despite the well-documented role of serpentinization in modern peridotite systems, its occurrence in Archean komatiites remains unexplored. Given their distinctive chemical composition, particularly their elevated Al_2O_3 content compared to modern ultramafic rocks, serpentinized komatiites likely followed unique reaction pathways that influenced H_2 production during serpentinization. In this study, we investigate serpentinized komatiites from the Weltevreden Formation in the Barberton Greenstone Belt, integrating literature data with our own XRD, Raman, and XANES analyses to better understand the nature and implications of komatiitic serpentinization. The significantly elevated Al content in these komatiite samples led to cation substitution in serpentine along the $(2Al^{3+}) \leftrightarrow (R^{2+}Si)$ exchange vector, promoting the formation of serpentines characterized by a lizardite-amesite solid solution. This substitution pathway dominates over the formation of Mg-cronstedtite via $(2Fe^{3+}) \leftrightarrow (R^{2+}Si)$ substitution, a common process in serpentinized peridotites today. Although serpentinized komatiites are predominantly Mg-rich (Mg#: 0.95), a limited amount of total Fe is also incorporated into the octahedral layer of serpentine. XANES analysis indicates that a portion of this Fe is present in the ferric state. To simulate komatiitic serpentinization under plausible environmental conditions, we developed reaction path models that incorporate the specific characteristics of the serpentine solid solution system outlined above. The thermodynamic properties of the relevant serpentine minerals were calculated using the PyGeochemCalc (PyGCC) software package. Model results suggest that the overall higher Mg content and the limited Fe^{3+} substitution in serpentine minerals might have resulted in significantly lower H_2 production in komatiites compared to modern serpentinizing systems. Ultimately, these results underscore the need to re-evaluate the geochemical signatures of Earth's early oceanic environments, particularly in relation to new models of komatiitic serpentinization and their implications for the biogeochemical evolution of Earth in deep time.