

## Chromium Enrichment in sedimentary rocks deposited in shallow water in the 3.2 Ga Moodies Group, South Africa

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Although the temporal change in trace element concentrations in Banded Iron Formations (BIFs) can be useful in reconstructing Earth's Precambrian surface environments and associated biological activity, BIFs from various sedimentary settings, particularly of Archean age, will be investigated to increase our understanding of these environments. In this study, we investigated geological, petrographic and geochemical characteristics of ferruginous rocks deposited in a shallow water environment in the Moodies Group, in the Barberton Greenstone Belt, South Africa. Samples were obtained from an outcrop in the Moodies Hills Block and at a cross cut in the Sheba mine.

The petrographic relationships between hematite and magnetite in the samples resemble those observed in typical oxide-type BIFs. Geochemical data show that Fe and Cr are enriched relative to Ti in the ferrous rocks. Although various detrital minerals are observed, including detrital quartz, the proportion of refractory elements and rare earth element (REE) patterns show that the sediment was predominantly derived from felsic rocks. Therefore, the results of geochemical analyses of these rocks indicate that both Fe and Cr are chemical precipitates or of an early diagenetic origin. Oxygen isotope analyses of individual chromite grains by Secondary Ion Mass Spectrometry (SIMS) reveal they are depleted in <sup>18</sup>O compared to previously reported values for magmatic chromite, indicating that the chromite was formed under sub-magmatic temperatures (e.g., hydrothermal). Therefore, our detailed petrographic and geochemical investigations of the chemical and clastic sedimentary rocks show that some geochemically important elements (i.e., Fe, Cr, and U) were already mobile and fixed in a shallow water environment at 3.2 Ga.

## Dissolution of Amorphous Silica in the Presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> at pH 6 and 9

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Silica dissolves into natural waters as monosilicic acid (Si(OH)<sub>4</sub>) through a break of siloxane bonds by attack of water molecule. Factors controlling the silica dissolution reaction are important subject in geochemistry to elucidate circulation of silicon in hydrosphere. Especially, because an alkaline and alkaline earth metal ions exist abundantly in natural water, the effect of these metal ions on the dissolution of silica has been investigated and the acceleration of the dissolution of silica has been reported<sup>1-4</sup>). However, the acceleration mechanism of dissolution of silica by cations has been uncertain even at present. In the previous studies, only the variation of silicic acid concentration was mainly examined. No researcher has been investigated quantitatively the behavior of cations during the dissolution reaction. The purpose of this study is to elucidate the effect of Ca<sup>2+</sup> and Mg<sup>2+</sup> on the dissolution of silica from both the variation of silicic acid concentration with time and behavior of Ca<sup>2+</sup> and Mg<sup>2+</sup>.

From the behavior of Ca<sup>2+</sup> and Mg<sup>2+</sup> during the dissolution of silica, it was revealed that the acceleration mechanism of each metal ion was clearly different by reaction pH. At pH 9, the dissolution of silica is controlled by the interaction between Ca<sup>2+</sup> and Mg<sup>2+</sup> and silicic acid: the formation of Ca<sup>2+</sup>-silicic acid complex and of an insoluble magnesium silicate-like structure. Although no adsorption of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions occurred at pH 6, the dissolution of silica was accelerated. This may be caused by attack of water molecules to siloxane bonds hydrated to Ca<sup>2+</sup> and Mg<sup>2+</sup> ions due to fast exchange reaction with the bulk water near the surface of silica.

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