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## Rare earth elements and Nd isotope systematics in 2.9 Ga-old chemical sediments from the Kaapvaal Craton, South Africa: constraining solute sources in Archean seawater

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The Pongola Supergroup and the Pietersburg Group are contemporaneous marine sediment packages which formed on the margin of the Kaapvaal craton  $\sim$ 2.9 Ga ago. Siliclastic lithologies dominate the Pongola sequence, yet marine chemical sediments such as banded iron formations (IFs) are present, and along with the contemporaneous Witwatersrand Supergroup, these iron formations represent the oldest documented Lake-Superior type IFs. Deposition of the Pongola IFs should therefore contrast with the production of iron formation within the Pietersburg Group, which constitutes the Pietersburg Greenstone Belt (PGB), and represents Algoma type IF depositional environments. Both the Pongola IF and the Pietersburg IF were subjected to low grade greenschist facies regional metamorphism.

The Pongola IFs are pure chemical sediments, as indicated by very low concentrations of incompatible elements (e.g., Na, K, Rb, Zr, Cs, Hf, and Th). The marine origin of these samples is supported by super-chondritic Y/Ho ratios (average Y/Ho = 42), and shale-normalized rare earths and yttrium distributions ( $REY_{SN}$ ) in the Pongola IFs exhibit positive  $La_{SN}$ ,  $Gd_{SN}$ , and  $Y_{SN}$  anomalies, which are consistent with typical marine waters throughout the Archean and Proterozoic. Associated Pongola shales are generally geochemically evolved for Mesoarchean fine-grained clastic sediments, and have been interpreted as having provenances within 3.2-3.0 Ga granites which were similar in composition to Phanerozoic igneous intrusives.

The Pietersburg IFs display incompatible element concentrations that likely reflect

varying proportions of clastic detritus, with Zr between 4.3 - 60ppm and Th between 0.13 - 1.2 ppm. The purest Pietersburg samples (i.e., low amounts of Zr, Hf, Th, etc.) possess shale-normalized positive La<sub>SN</sub>, Gd<sub>SN</sub>, and Y<sub>SN</sub> anomalies indicative of marine chemical sediments, and exhibit REY distributions that are similar to older Isua and younger Kuruman IFs. The Pongola IFs are generally depleted in heavy rare earth elements (HREE) and exhibit Sm/Yb ~2.0 compared to the Pietersburg (1.0), Isua (0.9), and Kuruman (0.7) IFs. The similarities between the REY distributions of the Pietersburg and the Isua and Kuruman IFs, when compared to the Pongola IFs, suggests that Archean seawater influencing depositional environments on the Kaapvaal craton 3.0Ga was heterogeneous with respect to trace element composition. Such heterogeneity affecting coeval IF deposition on the Kaapvaal craton 2.9Ga could result from variability in solute sources and/or differences in depositional environment (e.g., Superior vs. Algoma type IFs).

Neodymium isotope systematics are used to potentially identify sediment and solute sources within the shales and IFs of the Pongola Supergroup. The  $\varepsilon_{Nd}(2.9 \text{ Ga})$  for the Pongola shales ranges from -2.7 to -4.2, whereas  $\varepsilon_{Nd}$  (2.9 Ga) values for the IFs bracket the shale values (range -1.9 to -10.9). The similarity in  $\varepsilon_{Nd}$  (t) values for the shales and IF samples suggests that mantle-derived Nd was not a significant source of REE within the Pongola depositional environment, though the presence of positive Eu anomalies in the IF samples (and some shale samples) indicates that high-*T* hydrothermal input did contribute to their REE distributions. The above observations suggest that continentally derived sources for solutes dominated the major and trace element budgets of shallow marine chemical sediments during deposition of the Pongola Supergroup.