Interpreting primary versus metamorphic manganese in ancient sedimentary basins

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Manganese provides an important redox proxy because it is only oxidized by molecular oxygen, or O_2-derived species. Mn(II) is soluble in anoxic waters with its only sink as a minor constituent of carbonates (< ~1 wt.%) but when oxidized, Mn(III,IV) oxides form insoluble precipitates that enter the sedimentary record. Thus concentrated Mn in sedimentary rocks is often used as a proxy for O_2, but we do not have a good understanding of whether and how Mn might become enriched in sedimentary rocks due solely to post-depositional metamorphic and metasomatic processes that have impacted Precambrian basins. We addressed this question using the Transvaal Supergroup as a field laboratory with its well-known metamorphic gradients. We sampled the same lithologies in cores from the basin-wide ~2.5 Ga Kuruman Formation, from well-preserved strata in Griqualand West to more deeply buried and contact-metamorphosed equivalents in the Transvaal basin to the east. We analyzed a large suite of representative thin sections using synchrotron X-ray fluorescence at a 50 μm scale and chose manganese-enriched samples to measure at finer scales by X-ray spectroscopy and imaging. Results show that better-preserved samples contain Mn in low concentrations hosted by carbonates; however, in more metamorphosed samples we observed Mn in minerals that cross-cut depositional textures and laminae, including garnets, coarse-grained Mn-carbonates (manganoan siderite, calcite and ankerite), and amphiboles. Pairing these results with scanning electron microscopy, electron backscatter diffraction, electron dispersive spectrometry, and bulk ICP-MS, we conclude that Mn can become enriched in sedimentary rocks due to metamorphic processes, and our samples suggest primary Mn cycling did not occur in these strata at ~2.5 Ga. Mineralogically, metamorphic Mn mineralization is diagnostic for garnets and amphiboles but Mn-carbonates are not distinctive. However texture-specific chemical imaging techniques like those used here provide a useful approach to evaluate hypotheses for Mn mineralization (including primary oxidation) derived from other metamorphosed Archean strata.