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The impact of unusual mineralogy on the iron speciation redox proxy: A case study from the Cambrian Harkless Formation

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The iron speciation proxy is a powerful tool in assessing the redox state of local bottom waters at the time of deposition. The proxy quantifies the proportion of iron in sedimentary systems that can participate in redox reactions on early diagenetic timescales, termed highly reactive, as this has been empirically demonstrated to be higher in anoxic settings. This is accomplished using a series of extractions which are operationally designed to remove iron sequestered in different minerals or mineral groups. To get an accurate assessment of paleoredox state, it is critical that only phases containing highly reactive iron are dissolved and that they are dissolved completely.

Here we use the iron speciation proxy, in combination with mineralogical analyses and other redox proxies (Mn abundances and total iron to aluminum ratios), to assess redox conditions during the deposition of shales from the Cambrian Harkless Formation. Results from iron speciation analyses suggest that water column conditions were oxic or equivocal (potentially oxic or anoxic), but the presence of total iron enrichments indicates intervals of at least intermittent anoxia. This is further supported by consistently depleted Mn relative to the crustal average, suggesting Mn reducing conditions. Mineralogical analysis of Harkless Formation samples shows high abundances of the Fe-rich clay minerals glauconite and chamosite, averaging 6 and 10 weight percent respectively. Based on petrographic analysis, it is likely that these minerals formed authigenically at or just below the sediment-water interface and that they likely incorporated highly reactive iron from the local environment. Mineralogical analyses before and after each step of the sequential iron reactions show that glauconite and chamosite are partially removed by the extractions. This causes an underestimate of the proportion of highly reactive iron in the system and affects redox interpretations. Based on these findings, we advocate for the use of caution when applying the iron speciation proxy to rocks with particular Fe mineralogies and for mineralogical analyses to be used to help refine interpretations based on the iron speciation proxy.