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The aftermath of Snowball Earth: Ca- and Mo- isotope constraints on post-glacial ocean conditions

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Worldwide occurrence of cap-carbonates over terminal Proterozoic glacial sediments suggests that changes from icehouse to greenhouse conditions were due to enhanced atmospheric $p\mathrm{CO}_2$ levels. Because the global Ca budget and ocean Ca-isotope composition are mainly controlled by continental Ca-input and carbonate precipitation, invigorated continental runoff and increased ocean alkalinity caused by high $p\mathrm{CO}_2$ at the end of glaciations are expected to cause important perturbations in both Ca parameters. As for ocean oxygenation, pronounced perturbations in the global S- and C-cycles in the aftermath of the Marinoan glaciation (c.a 0.64 Ga) have been attributed to anoxia/euxinia. Although important enrichments in redox-sensitive elements in the cap-carbonates overlying the Marinoan glacial deposits also support such low oxygen levels, the extent of ocean oxygenation in the post-glacial Neoproterozoic oceans needs yet to be assessed.

We report Mo- and Ca- isotope data from cap-carbonate successions in NW Canada (Twitya Fm. and Ravensthroat-Hayhook Fms) overlying 0.74 Ga (Rapitian) and 0.64 (Marinoan) glaciogenic deposits.

While Ca-isotope composition of cap-carbonates from the Twitya Fm shows a range of 1‰; that of the Ravensthroat-Hayhook Fms. is twice as high (2‰). This suggests different extents of perturbations in the Ca-cycle of oceans after deglaciation. Contrasting fashions of global deglaciation, differences in rate of continental input and variable carbonate sedimentation rates could explain such range differences. The stratigraphic increase in $\delta^{44/40}Ca_{(sw)}$values in the lowermost Twitya Fm., from -2‰ to –1‰, may suggest initial perturbation of the Ca-cycle, with high continental input after deglaciation and immediate return to steady state conditions. They may also suggest pronounced changes in ocean temperature. The non-monotonic trend in $\delta^{44/40}Ca_{(sw)}$values of the Ravensthroat-Hayhook Fms cap-carbonate succession suggests a more complex evolution. They are -1‰ at the base; they evolve to –1.9‰ in the middle and shift back to 0‰ at the very top. We speculate initial meltdown of ocean and continental shelf ice covers, and weathering of pre-glacial carbonates to explain the $\delta^{44/40}Ca_{(sw)}$values slightly below continental input at the base of the succession. Posterior continental ice melting strongly enhanced continental input and brought the $\delta^{44/40}Ca_{(sw)}$values down to –1.9‰. When pCO_2levels return to normal levels due to continental weathering, a drastic increase in $CaCO_3$precipitation resulted in higher $\delta^{44/40}Ca_{(sw)}$values. Very importantly, Ca-isotope data from cap-carbonates overlying Marinoan glacial deposits in Namibia (Kasemann et al., 2005) and from cap-carbonate overlying Rapitian glacial deposits in NW Brazil (Jacoca Fm.) show identical Ca-isotope stratigraphic patterns than the Canadian cap-carbonates.

$\delta^{98/95}Mo_{(MOMO)}$values (MOMO=Mean Ocean Water Molybdenum) in the Twitya Fm. cap-limestone average –1.4‰. Cap-dolostones from the Ravensthroat Fm display an upsection increase in $\delta^{98/95}Mo_{(MOMO9}$values, from –3.2‰ to –2.3‰. Those values continue to increase to 0‰ at the top of the overlying Hayhook Fm cap-limestone. While most of the $\delta^{98/95}Mo_{(MOMO)}$values displayed by the studied cap-carbonate successions are indistinguishable from those published for Ediacaran black shales (between -1.2‰ and -2.4‰), suggesting anoxic conditions during their sedimentation; those very negative values (-3.2‰) at the base of the Ravensthroat Fm. are paradoxical and need further investigation.

Main messages:

1. Ca-isotope composition of cap-carbonates appears to reflect a global signal (Canada, Brazil, Namibia). Ca-isotopes can thus, be used to correlate cap-carbonate successions

2. Ca-isotope composition of post-glacial seawater seems to have been controlled by miscellaneous factors.

3. The Rapitian and Manrinoan glaciations may have had different deglaciation patterns.

The Ca- and Mo- isotope compositions and stratigraphic trends of the post-Rapitian and post-Marinoan cap-carbonates are very different, suggesting different perturbations of the post-glacial ocean conditions.