

## Optimization and application of engineered nanocrystalline iron oxides (nMAG) for uranium analysis in environmental samples

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Here, we demonstrate optimization and application of engineered, monodispersed, nanoscale iron oxide particles (termed nMAG) as concentration/separating agents for uranium analysis in aqueous samples. Taking advantage of favorable sorption chemistries, sorbed uranium (as uranyl species) can reach >25% by weight associated with nanoscale magnetite particles (12 nm) which are surface stabilized with an oleic acid bilayer. Because these materials exhibit strong, permanent magnetic properties, they can be selectively removed from complex samples using magnetic fields resulting in high (uranium) concentration factors. Furthermore, as these materials are surface stabilized and monodispersed, dense and extremely thin films can be formed minimizing the self-absorption of  $\alpha$ -particle emission from uranium isotopes. Taken together, engineered material features enhance uranyl detection (via  $\alpha$ -counting) by over 1000 times when compared to a commercial available, aggregated, "nanoscale" iron oxide.

## The relationship between ice volume, CO<sub>2</sub> and climate in the Middle Miocene

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The global cooling from the early Cenozoic ice-free world (~50 Ma) to today's bipolar icehouse world has long been ascribed to declining levels of CO<sub>2</sub> [1]. This overall cooling trend is recorded by a ~4 ‰ increase in deepwater benthic foraminiferal  $\delta^{18}\text{O}$  values, which reflects both a ~12 °C cooling of bottom waters, and the formation of Earth's continental ice caps. Roughly half of this signal (a ~2 ‰ increase in benthic foraminiferal  $\delta^{18}\text{O}$ ) occurs between the Miocene Climatic Optimum (~16 Ma; MCO) and today, including a ~1 ‰ step marking the Middle Miocene Climate Transition (MMCT) at ~14.5 Ma. The MMCT is thought to coincide with the expansion of the Antarctic ice sheet, changes in ocean circulation patterns, and a ~50 m lowering of global sea level. Although most pCO<sub>2</sub> reconstructions display an overall decline through the early Cenozoic, there is little agreement between them for this crucial period and estimates of pCO<sub>2</sub> during the middle Miocene are either higher (stomatal index [2]), lower (boron isotopes in foraminifera [3]), or around the same [4] as the pre-industrial. This has led to suggestions that either existing proxy records are flawed, or climate and pCO<sub>2</sub> have been decoupled for some portions of Earth's history [4] with uncertain implications for the prediction of future climate change. Here we use boron isotopes in planktonic foraminifera to show that the MCO was associated with elevated pCO<sub>2</sub> and that drawdown from this maximum was related to orbitally-paced organic carbon burial during the MMCT. Contrary to previous studies (e.g. [4]) our new boron based pCO<sub>2</sub> record therefore reaffirms the link between CO<sub>2</sub>, climate and the cyrosphere for this important part of the Cenozoic.

[1] Berner *et al.* (1983) *Am. J. Sci.*, **283**, 641-683. [2] Kürschner, *et al.* (2008) *PNAS*, **105**, 440-453. [3] Pearson & Palmer (2000) *Nature*, **406**, 695 - 699. [4] Pagani *et al.* (1999) *Science*, **285**, 876-879.