

Dissolved gas and isotopic tracers of denitrification

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We present results from field studies in California (USA) where tritium-helium age dating is used in conjunction with major gases (N₂, O₂, CH₄, CO₂), noble gases (He, Ne, Ar, Kr, Xe), and stable isotopes (¹⁵N/¹⁴N, ¹⁸O/¹⁶O) in order to document nitrate loading and denitrification associated with confined animal agricultural operations and septic systems. Preliminary results show that in-field extraction of the full suite of dissolved gases will be possible using a new Gas Extraction System under development to augment the current Noble Gas Mass Spectrometry and Membrane Inlet Mass Spectrometry techniques.

Ascribing observed groundwater nitrate levels to specific current and past land use practices is often complicated by uncertainty in groundwater age and the degree and locus of denitrification. Groundwater age dating at dairy field sites using the ³H-³He method indicates that the highest nitrate concentrations (150-260 mg/L-NO₃) occur in waters with apparent ages of <5 yrs, whereas older waters contain excess N₂ from saturated zone denitrification [1]. At a residential septic system site in Livermore, CA, waters with young apparent ages (<1 yr) proximal to leach line drainage have lower nitrate concentrations and elevated nitrate δ¹⁵N and δ¹⁸O values consistent with denitrification, but little evidence for excess N₂, indicating that denitrification is occurring in the unsaturated zone.

Degassing of groundwater can complicate efforts to calculate travel times [2] and to quantify denitrification. Degassed groundwater underlying dairy operations is formed by two distinct mechanisms: (1) recharge of manure lagoon water affected by biogenic gas ebullition [3] and (2) saturated zone denitrification producing N₂ gas above solubility in groundwater. Gas loss due to both mechanisms is evident in the concentrations of noble gases and major gases in dairy groundwater samples.

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[1] McNab, W. W., Singleton, M. J., Moran, J. E. & Esser, B. K. (2007) *ES&T* **41**, 753-758. [2] Singleton, M. J., Esser, B. K., Moran, J. E., Hudson, G. B., McNab, W. W. & Harter, T. (2007) *ES&T* **41**, 759-765. [3] Visser, A., Broers, H. P. & Bierkens, M. F. P. (2007) *WRR* **42**, W10434 (1-14).

The nature of magmatism associated with breakup of super-continents: Constraints from geochemical and Pb, Sr, Nd and Hf isotopic studies from the Appalachian Orogen

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The assembly of supercontinents and their subsequent dispersals is one of the most challenging research frontiers in earth science. The duration of supercontinent cycles, including the creation of supercontinents as well as the causes associated with their fragmentation have been linked to distinct mantle processes such as slab avalanche, mantle upwelling, superplumes and plate boundary driving forces. The central Appalachian region provides a geologic record of the assembly and dispersal of two supercontinents, Rodinia and Pangaea. The Catoctin Volcanic Province (CVP) is associated with breakup of Rodinia and the Central Atlantic Magmatic Province (CAMP) is associated with breakup of Pangaea. CVP and CAMP are nearly co-incident in location, and require either melting of a common source region at depth that evolved over time, or sources with different geochemical histories. A comparison of incompatible element ratios between CVP basalts (e.g., Zr/Y = 4.91, La/Yb = 5.73, Th/Ta = 1.37 and Hf/Th = 2.82) and CAMP (e.g., Zr/Y = 2.30, La/Yb = 2.16, Th/Ta = 6.97 and Hf/Th = 0.96) suggests source heterogeneity. Age corrected lead isotopic ratios for CAMP have elevated ²⁰⁷Pb/²⁰⁴Pb for a given ²⁰⁶Pb/²⁰⁴Pb relative to CVP and Pb/Pb ratios positively correlate with ⁸⁷Sr/⁸⁶Sr (CVP ~ 0.7035; CAMP ~0.706). Measured Nd and Hf isotopes for CVP and CAMP plot on or below the oceanic basalt mantle array, suggestive of residual garnet in the source. We suggest that CVP maybe derived from a sub-cratonal lithospheric mantle (SCLM) that had undergone geochemical modifications associated with subduction processes during Grenville orogeny, and modified through interaction with a plume (OIB) component. In contrast, CAMP magmas maybe modeled as melts derived from the same SCLM that had been previously depleted during CVP magmatism, and with minimal plume component. However, we also consider the possibility of deriving CAMP from an arc substrate wedged at depth during Paleozoic orogenesis.