

Mineral sources of arsenic from glacial aquifer sediments to well water in Minnesota, USA

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In Minnesota, USA, domestic wells with arsenic concentrations exceeding $10\mu\text{gL}^{-1}$ are predominantly found within the footprint of the Des Moines Lobe glacial advance (12-14 kya). The arsenic concentrations in groundwater are variable over short distances. Although the exact mineral source of arsenic remains unknown, a frequent hypothesis is that arsenic-bearing pyrites in Cretaceous shale fragments common to these glacial sediments release arsenic to groundwater. The abundance of arsenic in reduced well-water and groundwaters suggests that the solid source of some of the arsenic may be oxidized, sorbed species.

The goals of this study are to identify the mineral and chemical species of the arsenic in the solid phase, and better understand the mechanisms liberating arsenic to well-water. This information may provide guidelines to well-drillers for future well construction.

In our analysis, we use sequential extractions to identify arsenic species operationally, and whole-rock chemistry to describe total elemental abundances of the strata. Bulk and microprobe X-ray absorption spectroscopy (XAS) is used to identify and quantify arsenic and iron species. Powder and microprobe X-ray diffraction (XRD) are used to describe the bulk and arsenic-bearing mineralogy of the glacial deposits. Nested analysis of resulting datasets across the landscape and as a function of depth is accomplished in a geographic information systems (GIS) and geostatistical framework.

Glacial sediments sampled from ten rotary-sonic drill cores (20-70m depth) were examined. Arsenic speciation in strata above, at, and below transitions between fine-grained glacial tills (confining layers) and sand-gravel deposits (aquifers) was measured. Arsenic is present in three distinct oxidation states: As^{5+} , As^{3+} , and As^{1-} . The presence of three arsenic species, with varying proportions in the solids, may explain some of the observed spatial heterogeneity in well-water arsenic concentrations. These forms of arsenic will be labile under different redox conditions in waters.

Approaching a consistent set of cosmogenic ^3He , ^{21}Ne and ^{10}Be production rates

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Cross-calibrations of production rates for cosmogenic ^3He , ^{21}Ne and ^{10}Be in olivine, pyroxene and quartz have revealed an inconsistency between earlier production rate calibrations, mainly because the ^3He (ol, px)/ ^{21}Ne (qz) ratio of 8.19 ± 0.19 was found to be considerably higher than the predicted ratio of ~ 6.1 [1]. Recently however, several new ^3He and ^{10}Be production rate determinations have indicated that the discrepancy may be less severe than anticipated. In particular, three regional studies in northeastern North America, New Zealand and Norway [2, 3, 4] have yielded ^{10}Be production rates that are consistently $\sim 15\%$ smaller than the earlier 'global mean' of Balco *et al.* [5]. It seems unlikely that all calibration sites, which are at latitudes from 42° to 70°N and $\sim 44^\circ\text{S}$, are characterized by a uniform reduction in production rates due to untypical conditions of the atmosphere or the geomagnetic field. Rather, we believe that earlier work included in the 'global mean' [5] may have overestimated the ^{10}Be production rate. Similarly, a recent compilation [6] as well as an additional calibration study [7] indicate $\sim 10\%$ higher ^3He production rates in olivine and pyroxene than reported earlier [5]. Using these new production rate values, the discrepancy between direct production rate determinations and cross-calibrations is substantially reduced. In this respect, ^3He and ^{10}Be production rate values that have been scaled by the De, Du and Li methods [cf. 5 and references therein] perform distinctly better than those scaled by the St or Lm methods (11-12% vs. 19% remaining discrepancy). Indeed, the directly determined and cross-calibrated production rates overlap within error limits for the former three scaling methods. Therefore, the apparent inconsistency is largely resolved when the new set of production rates is used. ^{10}Be and ^{21}Ne exposure ages will however increase by $\sim 15\%$.

[1] Niedermann *et al.* (2009) *Geochim. Cosmochim. Acta* **73**, A940. [2] Balco *et al.* (2009) *Quat. Geochron.* **4**, 93-107. [3] Putnam *et al.* (2010) *Quat. Geochron.* **5**, 392-409. [4] Fenton *et al.* (2011) *Quat. Geochron.*, in press. [5] Balco *et al.* (2008) *Quat. Geochron.* **3**, 174-195. [6] Goehring *et al.* (2010) *Quat. Geochron.* **5**, 410-418. [7] Amidon & Farley (2011) *Quat. Geochron.* **6**, 10-21.