

## Anthropogenically induced changes in groundwater flow regimes in shallow high arsenic aquifers: Evidence from $^3\text{H}$ & $^{14}\text{C}$ data

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An estimated 100 million people in Asia are exposed to hazardously high concentrations of naturally occurring arsenic (As) in groundwater [1]. Although regional groundwater flow in high As aquifers is driven by topographically controlled hydraulic gradients, groundwater abstraction is thought to have altered the natural flow regime by developing transient flow paths, changing the location and mode of recharge, and the timescales over which these various processes operate [2]. The Nadia district of West Bengal is an example of such an area where there has been massive groundwater abstraction for 10s years. In contrast, the Kean Svay district of Cambodia has been relatively undeveloped, and as such provides a useful analogue for the assessment of conditions prior to massive groundwater abstraction [3]. We present here isotopic data collected from these two contrasting areas.

In Cambodia,  $^3\text{H}$  data indicates that, even in the absence of extensive groundwater abstraction, there is considerable interaction between surface waters and the underlying shallow (< 20 m) groundwater operating over < 50 year timescales. Dissolved inorganic carbon (DIC)  $^{14}\text{C}$  ages, however, indicate longer mean groundwater residence times of 100s to 1000s years at depths > 55 m. In West Bengal, groundwater contains a clear contribution of tritium active recharge to depths of as deep as 63 m in 90% of the samples. This is consistent with younger mean residence times of groundwater at depths of up to 100 m obtained from DIC  $^{14}\text{C}$  ages.  $^{14}\text{C}$  ages of dissolved organic carbon (DOC) are younger at greater depths in West Bengal compared to that present in Cambodian groundwaters. These data suggest that groundwater pumping practices may play a key role in the groundwater DOC composition which may ultimately influence the temporal evolution of groundwater arsenic.

[1] Ravenscroft *et al.* (2009) *Arsenic Pollution, A Global Synthesis*. Wiley-Blackwell. [2] Harvey *et al.* (2002) *Science* **298**, 1602–1606. [3] Polya *et al.* (2005) *MinMag* **69**, 807–823.

## Halogen concentrations and $\delta^{37}\text{Cl}$ in apatite as a fluid probe to decipher fluid-rock interaction

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Fundamental questions associated with fluid-rock interaction concern fluid flow in low-permeability crystalline rocks – How are fluids channelled? What is the geochemical signature of fluid flow on a regional scale? To better understand flow pattern formation and reaction front propagation, we need chemical tracers for the fluids involved (e.g. halogen ratios and  $\delta^{37}\text{Cl}$ ) and fluid-composition indicative minerals that provide fluid probes. Apatite is a typical accessory vein-mineral in hydrothermal systems over a wide range of conditions. Apatite also reacts rather sensitively to changes in fluid composition by dissolution-reprecipitation, making it a reasonable candidate as a fluid probe. A primary advantage of apatite is that it routinely incorporates measurable concentrations of halogens.

We have performed ion microprobe (Cameca IMS1280, Nordsims facility) halogen isotope and elemental ratio measurements *in situ* on examples of 1) a hydrous shear zone cross cutting a dry gabbro (Kråkeneset, Norway) and, 2) the regional-scale scapolitization of gabbroic rocks (Bamble Sector, Norway). Within the shear zone sequence of study (1) we found a linear decrease in apatite F/Cl from  $14,000 \times 10^{-3}$  in gabbro to  $\sim 2,000 \times 10^{-3}$  in sheared rock, while I/Cl decreased from  $\sim 30 \times 10^{-6}$  to  $\sim 4 \times 10^{-6}$ . Conversely, apatite Br/Cl increased from  $\sim 0.2 \times 10^{-3}$  to  $1.1 \times 10^{-3}$  from the most pristine gabbro to the centre of the shear zone.  $\delta^{37}\text{Cl}$  in the gabbro apatites ranges from  $-1.0$  to  $-0.5$  ‰, and those of the shear zone cluster around  $+0.3$  ‰. This implies a single fluid infiltration event that changed its composition during progressive fluid rock interaction.

In study (2), the least metasomatized gabbro has apatite F/Cl  $\sim 2,000 \times 10^{-3}$ , I/Cl of  $\sim 5 \times 10^{-6}$  and Br/Cl of  $\sim 0.9 \times 10^{-3}$ . Overprinting apatite (Cl-Ap) has F/Cl  $\sim 1.5 \times 10^{-3}$ , I/Cl of  $\sim 0.27 \times 10^{-6}$  and Br/Cl of  $\sim 0.013 \times 10^{-3}$ , subsequently replaced by OH-Ap with F/Cl  $\sim 250 \times 10^{-3}$ , I/Cl of  $\sim 2-3 \times 10^{-6}$  and Br/Cl of  $\sim 0.08 \times 10^{-3}$ . Apatite of the least metasomatized gabbro has  $\delta^{37}\text{Cl}$  values of  $\sim -1$  ‰, Cl-Ap of  $-0.2$  ‰ and OH-Ap of  $+1.1$  ‰. While the  $\delta^{37}\text{Cl}$  values describe a continuous trend, the halogen ratios clearly require two distinct fluid events.