

ARSENIC – THE GREAT POISONER REVISITED

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In 2006, *Elements* magazine published an issue on the subject of arsenic, an issue to which we both contributed (Vaughan 2006; Charlet and Polya 2006). Topics covered in this now widely cited publication included the mineralogy, chemistry and geomicrobiology of arsenic, along with the environmental and human health impacts of arsenic contamination of soils and waters from both anthropogenic and natural sources. A particular concern highlighted in these papers was the arsenic contamination of drinking water over large parts of southern Asia, a contamination that has led to the premature deaths of many thousands, possibly millions, of people and to a situation that the leading epidemiologist A. H. Smith has described as “the largest poisoning of a population in history”.

Since 2006, over 3000 articles concerned with this arsenic poisoning have been published in the scientific literature, and numerous others in the popular press. The present article is the first in what is hoped will be a series in *Elements* under the title ‘Mineralogy Matters’. The series will address the question as to whether research in mineralogy (broadly defined to include petrology and geochemistry) has made an impact, in this case on a pressing human health problem. Has, in fact, mineralogy ‘mattered’ in this case?

In recent decades we have learnt a lot about the geochemistry of arsenic; for example, in understanding the speciation of arsenic in sulfide- or carbonate-containing solutions (Helz et al. 1995; Neuberger and Helz 2005; Helz and Tossell 2008), or the interaction of arsenic in solution with mineral surfaces (Farquhar et al. 2002), and its incorporation into minerals such as iron oxyhydroxides and oxyhydroxy-sulfates (Cutting et al. 2012). In such studies, advanced analytical, imaging, spectroscopic and computer modelling methods have been used to considerable effect. They have been applied both to ‘model’ laboratory systems and to ‘real world’ systems such as arsenic-contaminated industrial site (Cancès et al. 2008), where the speciation of As in soils is critical for determining the bioavailability of the toxin and, hence, for a proper risk assessment.

Regarding the great contemporary problem of arsenic contamination of drinking (and irrigation) water in countries including India, Bangladesh and Vietnam, recent overviews emphasise that the original source of the arsenic is almost certainly largely rocks con-



Collecting well water in West Bengal

taining sulfide minerals in the rapidly eroding Himalayas (Polya and Charlet 2009; Fendorf et al. 2010). The breakdown products of these primary minerals include iron (oxyhydr) oxides, which can transport arsenic incorporated in their structures or sorbed to their surfaces. Following transport in this form via great rivers such as the Ganges, this material is deposited on their floodplains and contributes to the sediments hosting the aquifers that are now accessed by shallow wells from which the drinking water used by many millions of people is extracted. Release of the arsenic into the drinking water is envisaged as being particularly associated with microbial reduction of solid phase Fe(III) and of As(V) to the sometimes more labile As(III) (Islam et al. 2004). In all these processes, mineralogy plays a key role, including the possibility of controlling the distribution of As(III) versus As(V) between different biomineral species (Coker et al. 2006). As microbial reduction of Fe(III) and As(V) both require the presence of an electron donor, notably labile organic carbon, the organic geochemistry is also an important part of the story (Rowland et al. 2007; Neumann et al. 2010).

The studies mentioned above help in understanding the origins of the problem, and also inform the approaches that might be taken to remediation, both in situ and ex situ. The geology and hydrology are important here, as well as mineralogy. One approach has involved extracting water from deeper, uncontaminated aquifers, although a major concern here is the potential contamination of these aquifers by the shallower groundwaters as a consequence of extraction (Burgess et al. 2010; Winkel et al. 2011). This, and the possibility of exhausting

the deeper sources, has led to calls for the use of deeper waters only for drinking rather than for less critical uses such as irrigation (Fendorf et al. 2010). The mineralogical and geochemical aspects of remediation strategies centre on both in situ and ex situ approaches. For example, it may be possible to manipulate the carbon loading in an aquifer so as to control microbial activity, or modify both chemistry and microbial activity so as to immobilise the arsenic as a highly insoluble phase, such as a sulfide (Héry et al. 2010; Omoregie et al. 2013). Such in situ approaches are still highly speculative and require rigorous testing before any widespread use, given the dangers of creating new problems. The ex situ remediation of water at the well head or at the point-of-use, for example in households, is much more established and has a distinctly mineralogical aspect. The iron oxyhydroxides produced by the aqueous oxidation of metallic iron filings, including nano-scale zero-valent iron (NZI) particles (Kanel et al. 2005), can be used to take up arsenic from the water prior to domestic use. The decrease in the efficiency of such systems as a result of clogging with Fe-bearing precipitates and other factors, however, remains a significant practical concern (Hossain et al. 2005). Also, many chemical remediation technologies involve an oxidation step, taking advantage of the often stronger sorption of As(V) as compared to As(III), although this has now been shown not always to be the case (Dixit and Hering 2003).

When we consider more generally the poisonous nature of arsenic, it is worth noting that its toxicity and bioavailability are strongly linked to its chemical speciation. For example, it is the trioxide that has been the form commonly used by murderers and assassins since ancient times, whereas compounds such as the arsenosugars are widely thought to be essentially non-toxic. Three historical examples of accidental poisonings of communities are illustrative of three major Goldschmidt-style types of geochemical behaviour that arsenic follows. In the first case, in an incident in the 1950s, many children in western Japan were poisoned through drinking milk from a commercial supplier. Here, arsenic in the form of arsenate substituting for phosphate entered the food chain when non-pharmaceutical-grade phosphate was used to stabilise the powdered milk product (Yorifuji et al. 2011). A second example illustrates why rice is particularly susceptible to arsenic contamination when irrigated with arsenic-bearing groundwaters and grown in paddy fields under reducing conditions. Under such conditions in near neutral waters, the predominant aqueous arsenic species is H_3AsO_3 , which is of a charge (zero) and size very similar to that of H_4SiO_4 and, accordingly, follows an influx pathway for H_4SiO_4 through aquaporins (proteins forming cell

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membrane pores that control the water content of cells) into the rice plant (Ma et al. 2008). The third example has arsenic in a more familiar geochemical role – as a chalcophile element. In 1900, several thousand people in Manchester, England, were struck down by poisoned beer. The poison was arsenic introduced through the use of impure sulfuric acid in the brewing process; the sulfuric acid was contaminated by the As-bearing pyrite employed to make it. This is a story where mineralogy very clearly did matter. ■

REFERENCES

- Burgess WG and 5 coauthors (2010) Vulnerability of deep groundwater in the Bengal Aquifer System to contamination by arsenic. *Nature Geoscience* 3: 83-87
- Cancès B and 9 coauthors (2008) Change in arsenic speciation through a contaminated soil profile: A XAS based study. *Science of the Total Environment* 397: 178-189
- Charlet L, Polya DA (2006) Arsenic hazard in shallow reducing groundwaters in Southern Asia. *Elements* 2: 91-96
- Coker V and 7 coauthors (2006) XAS and XMCD evidence for species-dependent partitioning of arsenic during microbial reduction of ferrihydrite to magnetite. *Environmental Science & Technology* 40: 7745-7750
- Cutting RS and 8 coauthors (2012) Microbial reduction of arsenic-doped schwertmannite by *Geobacter sulfurreducens*. *Environmental Science & Technology* 46: 12591-12599
- Dixit S, Hering JG (2003) Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environmental Science & Technology* 37: 4182-4189
- Farquhar ML, Charnock JM, Livens FR, Vaughan DJ (2002) Mechanisms of arsenic uptake from aqueous solution by interaction with goethite, lepidocrocite, mackinawite, and pyrite: An X-ray absorption spectroscopy study. *Environmental Science & Technology* 36: 1757-1762
- Fendorf S, Michel HA, van Geen A (2010) Spatial and temporal variations of groundwater arsenic in south and southeast Asia. *Science* 328: 1123-1127
- Helz GR, Tossell JA (2008) Thermodynamic model for arsenic speciation in sulfidic waters: A novel use of *ab initio* computations. *Geochimica et Cosmochimica Acta* 72: 4457-4468
- Helz GR and 5 coauthors (1995) Oligomerization in As(III) sulfide solutions: Theoretical constraints and spectroscopic evidence. *Geochimica et Cosmochimica Acta* 59: 4591-4604
- Héry M and 7 coauthors (2010) Arsenic release and attenuation in low organic carbon aquifer sediments from West Bengal. *Geobiology* 8: 155-168
- Hossain MA and 10 coauthors (2005) Ineffectiveness and poor reliability of arsenic removal plants in West Bengal, India. *Environmental Science & Technology* 39: 4300-4306
- Islam FS and 6 coauthors (2004) Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature*: 430-431
- Kanel SR, Manning B, Charlet L, Choi H (2005) Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. *Environmental Science & Technology* 39: 1291-1298
- Ma JF and 6 coauthors (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. *Proceedings of the National Academy of Sciences* 105: 9931-9935
- Neuberger CS, Helz GR (2005) Arsenic (III) carbonate complexing. *Applied Geochemistry* 20: 1218-1225
- Neumann RB and 5 coauthors (2010) Anthropogenic influences on groundwater arsenic concentrations in Bangladesh. *Nature Geoscience* 3: 46-52
- Omeregic E and 8 coauthors (2013) Arsenic bioremediation by biogenic iron oxides and sulfides. *Applied & Environmental Microbiology* 79: 4325-4335
- Polya DA, Charlet L (2009) Rising arsenic risk? *Nature Geoscience* 2: 383-384
- Rowland HAL and 9 coauthors (2007) The control of organic matter on microbially mediated iron reduction and arsenic release in shallow alluvial aquifers, Cambodia. *Geobiology* 5: 281-292
- Vaughan DJ (2006) Arsenic. *Elements* 2: 71-76
- Winkel LHE and 7 coauthors (2011) Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century. *Proceedings of the National Academy of Sciences* 108: 1246-1251
- Yorifuji T, Tsuda T, Doi H, Grandjean P (2011) Cancer excess after arsenic exposure from contaminated milk powder. *Environmental Health & Preventative Medicine* 16: 164-170 ■

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