

# The arsenic cycle in Late Quaternary fluvial sediments: Mineralogical considerations

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**Late Quaternary fluvial sediments have been identified as the immediate source of arsenic in groundwater in the delta region of the Ganges in India and Bangladesh as well as the Red River in Vietnam. Rock weathering in the catchment area is the obvious mechanism by which the sediments have acquired the arsenic load. A hard rock terrain in central India offers examples of such weathering reactions. Mafic and felsic igneous bed rocks of this area contain arsenopyrite and arsenian pyrite. Residual soil profiles are lateritic with goethite and kaolinite as major constituents. Desorption experiments indicated that the soil minerals had quantitatively retained arsenic. Similar adsorption sites could have contributed to the transport and deposition of arsenic in deltaic sediments. The recent mobilization into groundwater is apparently controlled by a series of competitive redox reactions.**

AFTER the alarming discovery of arsenic toxicity in groundwater of the Ganges delta in India and Bangladesh<sup>1-3</sup>, a similar situation has been recently reported from the Red River alluvial tract in Vietnam<sup>4</sup>. In each of these cases, Quaternary fluvial sediments have been identified as the immediate source of arsenic. The major site for occurrence of arsenic in these sediments is the iron oxyhydroxide coating on mineral grains. Other possibilities are clay minerals, organic matter and authigenic pyrite<sup>5,6</sup>. The geochemical cycle of arsenic obviously starts with rock weathering in the catchment area. This is followed by transport and deposition in the aquifer and final release into groundwater. The mineralogical aspects of this cycle are emphasized in the present discussion.

Most of the currently available hypotheses assume that the iron oxyhydroxide phase is a product of weathering of an arsenic-bearing rock in the upper part of the river basin. In this context, the weathering pattern of felsic and mafic igneous rocks in a hard-rock terrain of Chhattisgarh state in central India provides some examples of possible mineral transformations. Rhyolite alternating with amphibolite is the country rock around Kaurikasa (20°43'N, 80°44'E) where groundwater contains arsenic above permissible limits<sup>7,8</sup>. The amphibolite as well as rhyolite contains pyrite grains which were found to be

arsenian by SEM-EDX and EPMA line scan. Arsenic-contaminated groundwater on a relatively limited scale has also been reported further to the south of this location from the gold prospecting area near Gurwandi (20°10'N, 80°45'E)<sup>8</sup>. Here rhyolitic country rocks contain abundant arsenopyrite and arsenian pyrite. The main soil type at both locations is distinctly lateritic. The XRD pattern of the soil when compared with the bed rock (Figure 1) shows appearance of kaolinite and goethite as secondary minerals. Possible reactions for the formation of these two minerals by weathering of primary silicates and sulphides are listed in Table 1.

Iron oxyhydroxides like goethite, FeO.OH or the more hydrated Fe(OH)<sub>3</sub> are products of oxidation of ferrous iron present in the primary minerals. At the same time, oxy-alteration of arsenopyrite and arsenian pyrite involves a major increase in the oxidation state of arsenic. For example, in these minerals Fe<sup>2+</sup> is coordinated with (AsS)<sup>2-</sup> units where As<sup>1-</sup> substitutes for sulphur in the (S<sub>2</sub>)<sup>2-</sup> groups<sup>9</sup>. Experimental data<sup>10</sup>, on the other hand, show that when arsenopyrite is exposed to air and water, the oxidized layer contains As<sup>3+</sup> and As<sup>5+</sup> species.

Iron oxide-rich weathering products occurring in mining areas are known to be strong adsorbents for arsenic<sup>11</sup>. In order to verify whether such a process has operated in the Gurwandi area, a phosphate leaching technique<sup>12</sup> was adopted for a sample of the local lateritic soil for which the X-ray pattern has been shown in Figure 1. The arsenic released was measured by a colourimetric molybdate method<sup>13</sup>. Preliminary results indicated that the total arsenic in the leachate was of the order of 204 µg/g of soil. A similar experiment conducted earlier with iron-coated quartz from the Ganges delta sediments<sup>3</sup> had yielded 150 µg/g total dissolved arsenic. Such data support the idea that arsenic, adsorbed on iron oxyhydroxide-rich weathering products of catchment rocks, can be transported in the suspended load of rivers and form a part of the aquifer material in the delta region.

In the Ganges delta, the arsenic content of groundwater is generally high in the so-called 'middle-unit' aquifers. These overlie a basal unit of sand and gravel which were deposited in incised valley courses during a low stand of the sea level in late Pleistocene to early Holocene times<sup>3,14</sup>. The middle unit was deposited during the subsequent rise in sea level which had caused flooding of the partly sedimented entrenched valleys, converting them

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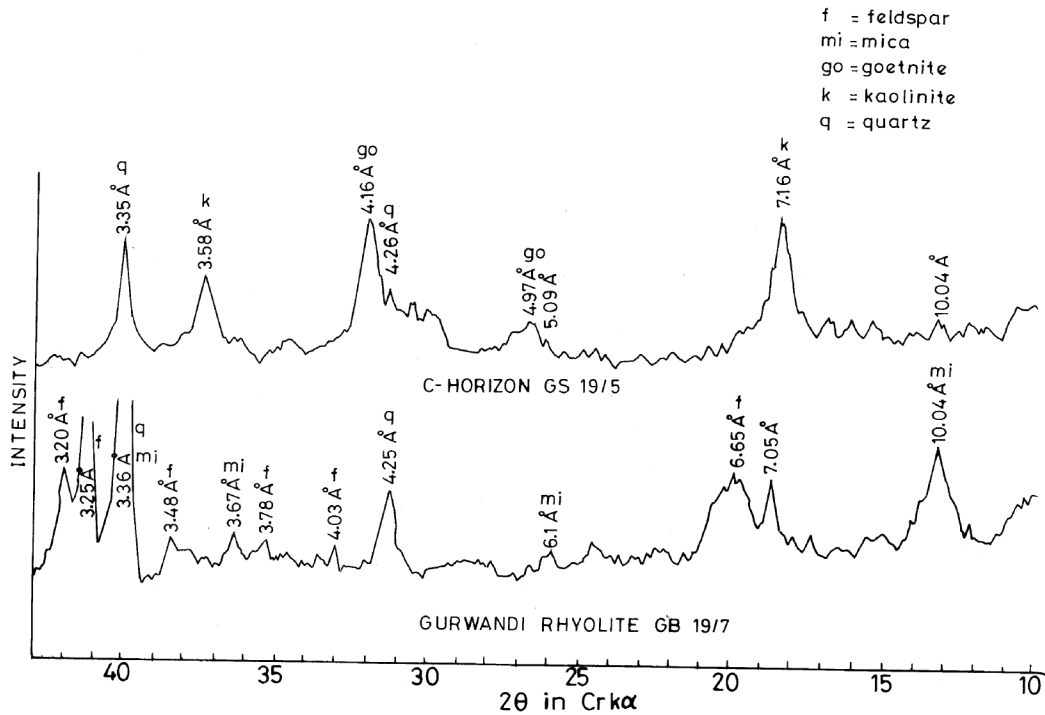


Figure 1. X-ray diffraction patterns of rhyolite bed rock and soil from C-horizon, Gurwandi.

Table 1. Formation of kaolinite and iron oxyhydroxide minerals by weathering of sulphide-bearing felsic and mafic igneous rocks

1.  $2K\text{-feldspar} + 2\text{CO}_2 + 3\text{H}_2\text{O} = \text{kaolinite} + 2\text{K}^+ + 2\text{HCO}_3^- + 4\text{SiO}_2$
2.  $2K\text{-mica} + 2\text{CO}_2 + 5\text{H}_2\text{O} = 3 \text{ kaolinite} + 2\text{K}^+ + 2\text{HCO}_3^-$
3.  $3 \text{ Augite} + 4\text{CO}_2 + 0.25 \text{ O}_2 + 4.5 \text{ H}_2\text{O} = \text{kaolinite} + \text{goethite} + \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- + \text{SiO}_2$
4.  $\text{Pyrite} + 15/4 \text{ O}_2 + 7/2 \text{ H}_2\text{O} = \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$
5.  $\text{Arsenopyrite} + 3\text{O}_2 + 4\text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{SO}_4^{2-} + \text{H}_3\text{AsO}_3 + 2\text{H}^+$

Table 2. Standard redox reactions. Eh is redox potential in volts.  $p_e = 16.9 \text{ Eh}$

1. Upper stability limit of water  
 $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$   
Eh = 1.23–0.059 pH for  $\text{PO}_2 = 1 \text{ atm}$
2. Pyrolusite reduction  
 $\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$   
Eh = 1.41–0.118 pH for  $\text{aMn}^{2+} = 10^{-6}$
3. Nitrate – nitrite equilibrium  
 $\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}$   
Eh = 0.845–0.059 pH for  $\text{aNO}_3^- = \text{aNO}_2^-$
4. Nitrate – ammonium equilibrium  
 $\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- = \text{NH}_4^+ + 3\text{H}_2\text{O}$   
Eh = 0.883–0.074 pH for  $\text{aNO}_3^- = \text{aNH}_4^+$
5. Ferrihydrite reduction  
 $\text{Fe(OH)}_3 + 3\text{H}^+ + \text{e}^- = \text{Fe}^{2+} + 3\text{H}_2\text{O}$   
Eh = 1.394–0.177 pH for  $\text{aFe}^{2+} = 10^{-6}$
6. Hematite reduction  
 $\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$   
Eh = 1.078–0.177 pH for  $\text{aFe}^{2+} = 10^{-6}$
7. As(V) – As(III) equilibrium  
 $\text{HAsO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- = \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$   
Eh = 0.846–0.118 pH for  $\text{aHAsO}_4^{2-} = \text{aH}_3\text{AsO}_3$
8. Sulphate reduction  
 $\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}$   
Eh = 0.25–0.066 pH for  $\text{aSO}_4^{2-} = \text{aHS}^-$
9. Methane formation  
 $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- = \text{CH}_4 + 2\text{H}_2\text{O}$   
Eh = 0.169–0.059 pH for  $\text{PCO}_2 = \text{PCH}_4 = 1 \text{ atm}$
10. Lower stability limit of water  
 $2\text{H}^+ + 2\text{e}^- = \text{H}_2$   
Eh = 0.0–0.059 pH for  $\text{PH}_2 = 1 \text{ atm}$

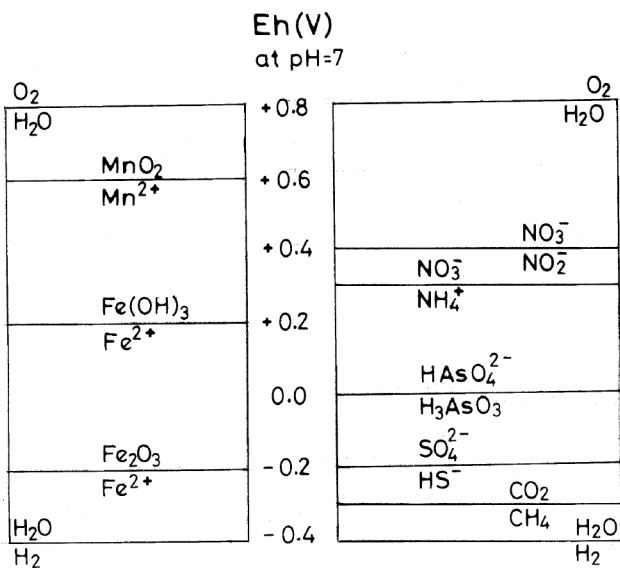


Figure 2. Schematic representation of Eh values at pH 7 for selected redox reactions. See Table 2 for details.

into fluvial marshes, lagoons and estuaries. The lithology of the middle unit consists of clay and silt rich in organic matter and interbedded with sand lenses. Another (upper) unit was deposited above this during the continuous rise in sea level with similar lithology and extensive development of marine and freshwater peat.

It is interesting to note that the stratigraphic sequence in the Red River delta near Hanoi is remarkably similar<sup>4</sup>. Here the Quaternary formation has been divided into two sequences. A lower unit of gravel, cobble and coarse sand is overlain by an upper unit of fine clay, sandy clay and fine sand. Peat layers with 2–3 m thickness are abundant.

As mentioned earlier, mineral grains occurring in the Ganges delta sediments have iron coatings which are rich in arsenic. Several mechanisms have been proposed to explain the recent mobilization of arsenic from sediment to groundwater. The most widely accepted is a process of microbially mediated reductive dissolution of the iron oxyhydroxide substrate on which arsenic occurs adsorbed. Sedimentary organic matter including peat is a strong candidate for the reducing agent<sup>15,16</sup>. Another mechanism which could operate on a local scale, is ion exchange of the adsorbed arsenic species by phosphate acquired in the aquifer from fertilizer application or decay of organic matter.

Attempts to confirm these mechanisms through groundwater chemistry are often constrained by mixing of water from different depths. On the other hand, it is clear that several competitive redox reactions taking place in the aquifer exert the primary control on arsenic mobilization. Some examples have been listed in Table 2. The redox potential (Eh) values calculated at a selected pH of 7 have been schematically represented in Figure 2. Successively decreasing Eh values would approximately represent the transition from a near-surface oxic environment to oxygen-poor zones at deeper levels in the aquifer. In the context of the role of iron oxyhydroxide minerals which has been highlighted in this discussion, it is interesting to note that poorly crystalline Fe(OH)<sub>3</sub>, e.g. ferrihydrite is reduced at a higher Eh value compared with the more stable Fe<sub>2</sub>O<sub>3</sub>, hematite. Moreover, the Eh value for hematite reduction overlaps that for sulphate reduction. Therefore, iron oxides can continue to act as

adsorption substrates for arsenic until sulphate reduction commences<sup>17</sup>. At the initial stages of sulphate reduction, some of the arsenic released by iron oxyhydroxide dissolution may be co-precipitated with authigenic sulphides. However, arsenic will be mobile once dissolved sulphide is depleted.

The ultimate application of an understanding of the arsenic cycle would be in designing an efficient method for removal of arsenic from contaminated water. Most of the available techniques are based on redox-controlled speciation and adsorption on a variety of materials. Therefore, a geochemical evaluation of natural systems should provide useful information.

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