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THE FATE OF ARSENIC IN NOAH'S FLOOD

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ABSTRACT

One potential consequence of Noah's Flood would be the mobilization of toxic elements such as arsenic (As), a group 15 metalloid with a significant solubility and redox chemistry in water and a high toxicity to human beings. This paper discusses the likely chemistry of arsenic during the Flood. The Flood would have released arsenic through hydrothermal activity, volcanic eruptions, and weathering of crustal rock. Arsenic in hydrothermal fluid would likely be rapidly precipitated by sulfides. Likewise, much of the arsenic in volcanoes would actually be deposited sub-surface as sulfides. In the presence of oxygen-rich waters, these sulfide minerals can undergo oxidative dissolution, releasing the arsenic back into the water to join that liberated by the weathering of the surface. Iron oxyhydroxides would form in such an environment, however, and these will sorb and remove arsenic from the water once again. In waters rich in organic-carbon, reducing conditions can return periodically. This would lead to reductive dissolution to liberate the arsenic from the iron oxyhydroxides. However, these conditions can also reduce sulfates to sulfides and thus reprecipitate the arsenic sulfide minerals. Furthermore, the extremely rapid formation of sedimentary rock during the Flood would likely bury both the original sulfide minerals and the arsenic-sorbed iron oxyhydroxides before they could be significantly dissolved. The modern distribution of arsenic gives evidence of this; the element is often concentrated in large sedimentary basins adjacent to orogenic belts. It appears that arsenic sulfides (formed during the Flood) were in some cases subject to uplift during orogenesis associated with the Flood and underwent oxidation, resulting in the arsenic being sorbed to iron minerals and clays. These eroded into the foreland basins and were buried before the arsenic could leach into local waters to a major degree. In modern times, however, reductive dissolutions of these deposits has resulted in arsenic poisoning. While arsenic does not threaten the Flood model (rather the Flood explains the modern distribution of arsenic), modern arsenic contamination is an ongoing result of the judgement of the Flood.

KEY WORDS

Arsenic, Genesis Flood, toxic elements

INTRODUCTION

Noah's Flood was the greatest catastrophe in world history, causing massive geochemical upheaval across the planet. Much of the sedimentary rock in existence today was laid down by the Flood. The sediments these rocks were formed from were primarily igneous crust rocks that were crushed and redeposited by the Flood waters (Snelling 2009). This would potentially result in dissolving and mobilizing many elements found within those rocks, including a number of toxic elements. In fact, the potential of the Flood to release mercury into the environment has been raised as an objection to the Flood model (Morton 1998). While this objection does not hold up under examination (Hutchison 2009), mercury is not the only toxic element that might be mobilized by the Flood. An element of particular concern would be arsenic. While to the best of the authors' knowledge, no anticreationists have cited arsenic release as an objection to the Flood, it would be a reasonable issue to raise and one no Young Earth creationists appears to have addressed yet.

Arsenic is a highly toxic metalloid. In water, it is mostly found in the +3 or +5 oxidation state, generally as the oxoanions arsenite (As^{3+} , AsO_3^{3-} with 0, 1, or 2 H^+ ions attached) and arsenate (As^{5+} , AsO_4^{3-} with 0, 1, or 2 H^+ ions attached) (Henke and Hutchison 2009). Acute arsenic poisoning (involving doses in the mg per kg body weight range) results in extreme gastrointestinal illness that can lead to fatal dehydration and shock, damage to the heart,

and a burning sensation or loss of feeling in the hands and feet. Chronic poisoning is more common and also very serious. It has been associated with cardiovascular disease, including Blackfoot Disease in Taiwan, which is characterized by numbness in the extremities, followed by formation of black, scaly lesions on the skin and gangrene. Chronic arsenic exposure is also clearly linked with the development of lesions on the liver and, perhaps most seriously, skin and bladder cancer (Hughes et al. 2009). While the mechanism behind arsenic poisoning is not well understood, it is believed to primarily involve two chemical processes. As^{5+} can replace P^{5+} in phosphates, which hinders the production and function of ATP. As^{3+} can strongly bind to $-\text{SH}$ groups in enzymes, hindering the enzymes' activity. It is also possible that arsenic redox reactions in the body could lead to oxidative stress and free radical production (O'Day 2006, Hughes et al. 2009). In general, As^{3+} is considered to be more toxic than As^{5+} , but both valence states are quite dangerous.

Dissolved arsenic in groundwater is a serious issue in today's world. The World Health Organization recommends drinking water contain no more than 10 ppb As (Bowell et al. 2014). Studies have found arsenic levels elevated above this in ground and surface waters on every continent but Antarctica and there have been major episodes of poisoning in Southeast Asia and the Americas. The problem is especially acute in the Bengal Basin of

India and Bangladesh, where as many as 50 million people may be exposed to groundwater arsenic concentrations greater than 50 ppb (Mukherjee et al. 2009). If arsenic contamination is such a major problem in today's world, why wouldn't the Flood have elevated arsenic levels high enough to poison Noah and other life in the post-Flood world? This is an issue to address in developing a viable Flood model. Specifically, how would arsenic get into the Flood waters, what chemistry would it undergo in them, and what would be its ultimate fate? In this paper we will survey the conventional literature and integrate the data found there with a Young Earth Flood model to answer these questions.

THE SOURCE OF ARSENIC IN THE FLOOD

A clear starting point for assessing this issue is to determine the source of arsenic in the Floodwaters. One way of approaching this would be to assume that all the sedimentary rock that currently exists represents igneous rock crushed by the Flood. This assumption could then be used along with the concentration of arsenic in the Earth's crust to estimate how much arsenic could be mobilized by that process (Hutchison 2009). Arsenic concentrations in the modern crust are quite inconsistent, but we can take 5.1 ppm as an estimate for the uppermost portion of the continental crust, with 2.5 ppm as an upper estimate for the crust as a whole (Bowell et al. 2014; Henke 2009a). Assuming the current ocean volume of 1.4×10^{21} L as an estimated Flood waters volume; that 4.77×10^{17} m³ of igneous rock was eroded in the Flood to produce the current sedimentary rock layers; and that rock had a density of 3300 kg/m³ (Morton 1998), we estimate that the Flood waters could contain between 2.81 ppm and 5.73 ppm arsenic. These are obviously maximum values, since they are assuming complete solubility of the arsenic. Arsenic solubility is complex and closely related to the chemistry of the waters they are interacting with; we will discuss arsenic solubility at length later in this study. These values are significantly higher than we would expect the actual arsenic concentration to reach, but they are also three orders of magnitude higher than the maximum permissible concentration of arsenic in drinking water.

However, a more nuanced picture emerges if we do not treat the entire crust as a single uniform body. Arsenic is generally found today either as sulfide minerals (of hydrothermal or volcanic origin) or as oxides which are usually oxidation/weathering products of those sulfides (O'Day 2006; Howell et al. 2014). The most common As-rich minerals are arsenopyrite (FeAsS), Realgar (As₄S₄), and Orpiment (As₂S₃), which oxidize to form H₃AsO₃ and H₃AsO₄ (O'Day 2006; Henke 2009a). These and other arsenic rich sulfides generally form from As-rich hydrothermal waters (Henke 2009a) or volcanic gasses (Henley, Mavrogenes, and Tanner 2012). The arsenic we find in the upper crust today can generally be traced back to deep-earth (lower crust) origins, brought to the surface by hydrothermal, volcanic, and tectonic activity (Mukherjee et al. 2014). The creation model holds that there was intense hydrothermal and volcanic activity throughout Noah's Flood (Snelling 1984; Snelling 1994; Silvestru 2007; Silvestru 2008; Snelling 2009a). Some of the hydrothermal fluid likely originated with subterranean water stored within the pre-Flood crust; this is consistent with the phrase "fountains of the deep" in Genesis 7:11 (Snelling 2009b). There is evidence for hydrothermal

activity in the pre-Flood world (Snelling 2009a). However, there are other logical sources for hydrothermal fluids and the arsenic within them during the Flood. One of the currently most favored models for the geology of the Flood, catastrophic plate tectonics, involves essentially the entire oceanic crust undergoing subduction (Snelling 2009a). This subduction of tectonic plates would be a source of hydrothermal waters (Henke 2009a). Today there is more arsenic in the continental crust than in the oceanic crust (Henke 2009a) but that may not always have been the case. In general, sedimentary rock has a higher concentration of arsenic than igneous rock (Smedley and Kinniburgh 2002; Escobar, Hue, and Cutler 2008; Basu et al. 2014) and while there undoubtedly were some sedimentary rock in the pre-Flood crust (Snelling 2009), a great deal of the sedimentary rock we see today was formed by the Flood. If we focus on igneous rock, it seems evident that both pre- and post Flood ocean crust is more basaltic whereas continental crust is granitic (Snelling 2009). Arsenic concentrations in modern igneous rock vary greatly and it is hard to determine an average for various types of rock (Henke 2009a), but commonly cited values for the arsenic content of basalts is 2.3 mg/kg and for granites is 1.3 mg/kg (Smedley and Kinniburgh 2002; Basu et al. 2014; Howell et al. 2014). So it is possible that the basaltic pre-Flood oceanic crust had a somewhat higher concentration of arsenic than the granitic continental crust, with the element being redistributed between the oceanic and continental crusts during the Flood. This would provide a source for the arsenic to form the sulfide deposits found today. It would also have the effect of making it less likely that dangerous concentrations of arsenic would leach into groundwater used by humans and so is consistent with the original "very good" creation. The arsenic in the oceanic crust would have been mobilized into hydrothermal fluids and magma (from which some high arsenic hydrothermal fluids also originate today (Henke 2009a)) during the subduction associated with catastrophic plate tectonics.

The mention of magma raises a second major source of arsenic. The Flood involved abundant volcanic activity. Volcanoes release arsenic into the atmosphere; it is estimated that today 1.715×10^7 Kg of arsenic a year is mobilized this way (Henke 2009a). The volcanic activity of the Flood would dwarf current levels, so we would expect the amount of arsenic released would be correspondingly greater. Much of the arsenic actually released from volcanoes would be absorbed onto particulate matter (Henke and Hutchison 2009) and would return to the surface either thorough solid deposition or in rain. Of course, there was a great deal of rain during the Flood – hence, we can expect that this arsenic would ultimately find its way into the Flood waters as AsO₃³⁻ or AsO₄³⁻ with varying degrees of protonation. However, studies have suggested that there is approximately twice as much arsenic in volcanic gasses as in the ash and particulate matter emerging from a volcano (Henley and Berger 2013). This gaseous arsenic is mostly in the form of As(OH)₃ (Pokrovski et al. 2002) and mainly reacts with H₂S to deposit the arsenic as sulfides (generally associated with Fe and Cu) in the rock adjacent to the volcano (Henley and Berger 2013; Henley and Berger 2012). One study has suggested that more than 90% of the arsenic content in the volcanic gasses is actually deposited below the surface (Henley, Mavrogenes, and Tanner 2012). Hence the amount of arsenic deposited in the rock around the volcano is likely to be higher than the amount being

released by the volcano.

As mentioned earlier, the pre-Flood oceanic crust may have been higher in arsenic than the continental crust. However, there was presumably some arsenic in the continental crust. A good deal of this would have been released by the massive weathering associated with the Flood. Ultimately, the arsenic would probably have been dissolved in water as AsO_3^{3-} or AsO_4^{3-} , once again with varying degrees of protonation. Taken together, these sources (hydrothermal, volcanic, and mechanical weathering) would have mobilized a great deal of arsenic, much of it being deposited as sulfide minerals but some being truly dissolved as well. How that arsenic would have interacted with the environment and where it would ultimately have resided is dependent on the chemistry of arsenic itself and of the Flood waters, which we will consider next.

THE CHEMISTRY OF ARSENIC IN THE FLOOD WATERS

The geochemistry of arsenic is highly complex, dominated by changes in oxidation state and solubility. In almost any water conditions there are some forces moving the arsenic towards dissolving in the water and some promoting precipitation out of the water. We cannot simply say “arsenic minerals in the Flood waters would have dissolved” or “arsenic minerals in the Flood waters would have remained insoluble”. Rather, we have to consider the possible conditions of the waters and the factors that would promote precipitation or dissolution under those conditions.

Throughout the Flood, there was a great deal of hydrothermal activity, with the fluids both mixing with pre-Flood seawater and infiltrating into rock. These hydrothermal fluids were almost certainly rich in arsenic. Most hydrothermal fluids are chemically reducing and of low to neutral pH, so arsenic within them would have been the more reduced As^{3+} form, H_3AsO_3 . Modern studies have found a wide variety of arsenic concentrations in hydrothermal waters and hot springs, ranging from 0.0003 to 47 ppm (Henke 2009a). Yellowstone geothermal water has been reported to have arsenic concentrations from 0.16 to 10 ppm, Waiotapu geothermal waters in New Zealand range from 0.710–6.5 ppm, and El Tatio geothermal in Chile averages a stunning 45–50 ppm As (Bowell et al. 2014). It is reasonable to assume that the hydrothermal waters of the flood would have contained ppm level concentrations of arsenic as well. Hydrothermal fluids also can have extremely high sulfide concentration, with a recent source reporting an average of approximately 1 wt% H_2S (10,000 ppm) for magmatic-hydrothermal fluids and 1.0×10^{-4} to 1% (1–10,000 ppm, with concentration decreasing with temperature) for metamorphic fluid (Fontbote et al. 20173). Another work suggested an average of 5.0 mM H_2S (170 ppm) for deep sea hydrothermal vents (Jannasch 1989).

When these fluids cooled either upon mixing with the relatively colder ocean waters or infiltration into existing rock layers, the arsenic would precipitate as sulfides. The exact mineral that would form would have depended on the composition and temperature of the fluid. In the presence of significant amounts of iron and at temperatures between 450°C and 150°C, arsenopyrite or arsenian pyrite (FeS_2 containing from 0.02–6% As) would precipitate first. At lower temperatures (below 150–200°C) and in the absence of iron, realgar and orpiment would precipitate; if the temperature

drops quickly enough and iron is abundant, all three minerals could form (Henke 2009a). In that situation, one would expect to find both As-sulfides and pyrite with As incorporated into its structure as it formed; the As-containing pyrite would probably predominate (Saunders et al. 2008). $\text{As}(\text{OH})_3$ in volcanic vapor reacts with H_2S , FeS_2 , and CuCl to form enargite ($\text{Cu}_3\text{As}_4\text{S}_{13}$) and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) (Henley, Mavrogenes, and Tanner 2012; Henley and Berger 2012).

As long as they are exposed to only reducing conditions, which in natural waters generally corresponds to a relatively low oxygen content, the arsenic would remain in these minerals. So as long as these minerals were buried and/or exposed only to water depleted of oxygen by the massive amount of decay attendant to the Flood, the arsenic would remain trapped in them, where they either remained stable until undergoing weathering more recently (Mukherjee et al. 2014) or remain trapped today. This is consistent with the current distribution of arsenic in the crust, where most of the toxin is associated with sulfides, especially pyrite (Bowell et al. 2014). Such arsenic would pose no threat to life immediately post-Flood.

However, arsenic does not always remain precipitated in sulfides; these minerals can release arsenic under oxidizing conditions. Pyrite and arsenopyrite dissolve in the presence of oxygenated-water to release Fe^{3+} , SO_4^{2-} , and any arsenic associated with the minerals. This is how acid mine drainage is created today, which is a modern route of arsenic release. This process is encouraged by certain bacteria and oxidizing chemicals such as nitrates (Henke 2009a; Lazareva et al. 2015). Both realgar and orpiment can also oxidize under these conditions with realgar initially converting to orpiment and then both converting to H_3AsO_3 . Even in a low oxygen environment, high concentrations of carbonate (CO_3^{2-}) can also dissolve orpiment (Henke 2009a). Orpiment would be less stable than realgar and arsenopyrite under those conditions, but all three minerals would be likely to release at least some of their arsenic.

So there are mechanisms by which some of the arsenic sulfides could dissolve. We would expect this dissolved arsenic to be in the +3 oxidation state and assuming a pH of 9 or below, it would take the form of H_3AsO_3 , which is rather unreactive (Henke and Hutchison 2009). In the presence of oxygenated water, the arsenic would slowly oxidize to As^{5+} . This process is very slow in and of itself, but the rate can be increased by the presence of Fe^{3+} , manganese oxides, nitrates, organic matter, and some microorganisms (Henke and Hutchison 2009). We would expect most of these to be present in the Floodwaters. Iron would be especially common due to its high abundance in the crust and because one primary method of arsenic release is oxidation of iron sulfides, generating Fe^{3+} right alongside the arsenic. Therefore we would expect the dissolved As to be oxidizing to As^{5+} , in the form of H_3AsO_4 (at extremely low pH), H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} . Added to this arsenic released from sulfides would be the arsenic mobilized by other sources in the Flood. While roughly 2/3 of the arsenic in a volcanic system is believed to be in the gas phase rather than the ash (Henley and Berger 2013), there would still be a great deal in the ash. Much of this would be leached into the Floodwaters, presumably as AsO_4^{3-} with varying degrees of protonation based on the pH of

the surrounding water. Likewise, much to all of the arsenic in the continental crust would be leached by the massive weathering of the Flood. These sources would combine to yield a significant concentration of arsenic. Under oxidizing conditions this would exist primarily as As^{5+} oxides.

However, these arsenic compounds would obviously not be the only compounds present in the Floodwaters. The continental crust is estimated to be 15.9% Al_2O_3 and 6.71% iron oxides (Rudnick and Gao 2003). While there may be some variations between the modern and pre-Flood crust, these elements were still presumably a large part of the continents before the Flood. This is important because As^{3+} oxoanions will readily sorb to iron oxyhydroxides. Iron oxyhydroxide is a general name for compounds of iron (mostly +3 but possible including some +2 ions) with a variable number O^{2-} and OH^- attached. Aluminum oxide, manganese oxide, clays, and carbonates such as calcite will bind to arsenic also, but generally not as well as the iron oxyhydroxides (Henke 2009a; Meng et al. 2016; Mukherjee et al. 2014; O'Day 2006). Arsenate forms a very strong attachment to these; chemically the arsenate replaces water or hydroxide on the iron resulting in some oxygen atoms directly linking Fe and As and tightly bonding the arsenate to the iron compounds (Waychunas et al. 1996). Both As^{3+} and As^{5+} oxoanions will bind, but the +5 compounds bind more strongly (Moncur et al. 2015). As^{+3} oxoanions bind in a way that is chemically similar to the As^{+5} compounds with higher pH favoring the lower oxidation state (Manning et al. 1998). At a pH of less than 6, iron oxyhydroxides tend to have a net positive charge on their surface, which encourages the arsenic oxoanion to bind to them (O'Day 2006; Henke 2009a), but such binding has been computer modeled under basic conditions as well (Waychunas et al. 1996). Pure iron oxyhydroxides are not required; when the iron is released by the oxidation of pyrite, iron sulfate oxyhydroxides can result and also sorb As^{5+} oxoanions (Henke 2009a). These compounds are generally insoluble and so as they precipitate they remove the sorbed arsenic from water. This principle is important for modern arsenic remediation; arsenic contaminated waters are often filtered through zero-valent iron, such as nails (which oxidizes in part as it rusts), or more successfully iron oxyhydroxides to remove the arsenic (Henke 2009b). During the Flood, massive amounts of iron would be mobilized and iron oxyhydroxides would be common in oxidizing environments. These would sorb much of the arsenic and at least some of what was not sorbed by the iron would be sorbed to carbonates or aluminum oxides (clays) greatly lowering the amount of dissolved arsenic in the water. This would be a major route for the precipitation of arsenic dissolved in the Flood waters.

The sorption behavior of arsenic is effected dramatically by the presence of dissolved and suspended organic matter. On the one hand, naturally occurring organic matter can itself sorb arsenic and can dramatically increase the sorption capacity of iron; lignin is especially important in this respect (Molinari et al. 2013; Molinari et al. 2015). If the resulting arsenic-organic or arsenic-iron-organic compound is insoluble, that compound's precipitation is a route for the removal of arsenic from water. However, organic material can also hinder the removal of arsenic from water in several ways. It often forms soluble complexes with arsenic, binding in place

of the Fe and keeping the arsenic in solution. It also competes with the arsenic for binding sites on the Fe resulting in a lower sorption capacity for the iron oxyhydroxides (Redman et al. 2002). The Flood waters would, of course, contain massive amounts of organic material, essentially all the vegetation of the planet. While the chemistry involved is complex, it seems the general trend would be for this to reduce the amount of arsenic sorbed to iron oxyhydroxides by 5-10% (Redman et al. 2002).

Organic material is not the only substance that competes with arsenic for sorption onto iron oxyhydroxides. Similarly, carbonate, bicarbonate, phosphate, and silica can compete with and displace arsenic from iron oxyhydroxides (Holm 2002). This effect seems especially serious due to the often high concentrations of carbonate/bicarbonate in many natural waters, and has the potential to dramatically decrease the adsorption capacity of the iron compounds and dramatically increase the concentration of arsenic in alkaline waters (Appelo et al. 2002). For example, 120 ppm inorganic carbon at pH 7 can result in an approximately 30% (or greater) decrease in the amount of arsenic sorbed (Holm. 2002). However, the sorption of arsenate over these other species is much higher at low pH; under acidic conditions this is not a significant problem (Holm 2002). This is important when we consider the Flood waters. The volcanic activity related to the Flood would presumably release a great deal of sulfur dioxide, essentially generating acid rain and lowering the pH of the Flood waters. Hydrothermal fluids were venting into the Flood waters and these fluids today are generally acidic (Ding et al. 2005; Tivey. 2007). Furthermore, the planet wide erosion of the Flood had the potential to generate something similar to acid mine drainage on a vast scale. Of course, somewhat counteracting these effects, basic salts would be dissolved by the Flood as well, but if taken as a whole it seems reasonable that the Flood waters were at least slightly acidic. If that is the case, the effect of these competing anions on arsenic sorbtion would be minimized.

Redox reactions present a bigger problem. Under normal conditions there will be an equilibrium between arsenic and other competing substances for the sorption sites on iron oxyhydroxides with a great deal of the arsenic being bound at any given time. As we have seen, As^{5+} sorbs more strongly than As^{3+} . However, dissolved organic material can provide food for microorganisms that reduce arsenic from the +5 state to the +3 (Majumder et al. 2016). This creates a situation in which some arsenic is displaced from the iron oxyhydroxides then reduced to the +3 state. Hence it is less able to compete for its former binding site due to the decreased affinity of As^{3+} oxoanions for iron compounds at low pH. This results in an overall increase in the concentration of arsenic in the water (Meng et al. 2016).

Reducing water also opens the door to a process that potentially remobilizes virtually all the sorbed arsenic: the reductive dissolution of the iron oxyhydroxides. Under reducing conditions, the Fe^{3+} in the iron oxyhydroxides can be reduced to Fe^{2+} , resulting in the iron oxyhydroxide mineral itself dissolving and any arsenic that is bound to it being remobilized. This process is fueled by dissolved organic carbon that is relatively recently derived from surface sources (Lawson et al. 2016; Majumder et al. 2016). The carbon provides energy to bacteria and its metabolism consumes oxygen

which makes the environment far more reducing in nature (Henke 2009a). It also produces bicarbonate that drives As off of the iron oxyhydroxides (Majumder et al. 2016). The result is the reduction of the iron oxyhydroxides and the release of arsenic, initially as As^{5+} but under these conditions a substantial amount will convert to As^{3+} (Meng et al. 2016; Molinari et al. 2015). Studies have shown the key role of microbes in this process; adding glucose as a feedstock for them can effectively double the arsenic released (Meng et al. 2016). This is the mechanism by which much of the modern arsenic-contamination of drinking water in South East Asia occurs; an influx of organic carbon leads to reducing conditions for waters in contact with As-rich iron oxyhydroxides. These minerals then undergo reductive dissolution to release the arsenic (Biswas et al. 2014; Nickson et al. 2000; Xie et al. 2014). During the Flood this could have happened as well. The decay of the abundant organic material could have led to oxygen depleted reducing areas where the majority of the sorbed arsenic would then be liberated.

So, while oxidizing conditions would lead to the release of arsenic from sulfide minerals to join dissolved arsenic from other sources in the Flood waters, they would also generate iron oxyhydroxides and similar minerals that would sorb the arsenic and remove it from solution. However, if the water subsequently became reducing, this could remobilize the sorbed arsenic. Reductive conditions would be encouraged by organic material and organic material would certainly be available during the Flood. However, there are several factors that mitigate the seriousness of this problem. As waters become more reducing, they soon reach a point in which not only iron and arsenic are being reduced but also sulfates by sulfate reducing bacteria. This generates sulfides, which in turn remove arsenic from solution (Harvey et al. 2002; Meng et al. 2016; Saunders et al. 2008). The primary mechanism for arsenic removal seems to be the formation of pyrite when the sulfide combines with the Fe^{2+} generated by the reduction of the iron. Arsenic sorbs to the surface of developing pyrite and is then incorporated into its structure as it continues to form (Saunders et al. 2008). This is essentially the reaction whose occurrence in hydrothermal waters we discussed at the beginning of this section. It does not occur to a great extent in most of the areas of South East Asia experiencing arsenic poisoning today because the arsenic-contaminated waters are low in sulfate; in fact, the addition of sulfate to those waters has been suggested as a remediation method (Saunders et al. 2008). However, one would expect some sulfate to be present in much of the Flood waters. As already mentioned, the SO_2 released from the volcanoes would have generated acid rain that would contribute a relatively small amount of sulfate to the Flood waters. More significantly, the oxidative weathering of any sulfides on the surface during the Flood would generate sulfate. Oxidative dissolution of arsenic sulfides and arsenic rich pyrite, which has been discussed as a source of arsenic in the water, would also generate sulfate. So in at least some of these environments we would expect a significant amount of sulfate which could be converted to sulfide and precipitate the arsenic.

Even if sulfate is not available, research has shown that reductive dissolution of iron oxyhydroxides does not result in as high a concentration of arsenic in groundwater as might be predicted. This is because, rather than all becoming truly dissolved, some of

the Fe^{2+} will form new, undissolved, minerals such as magnetite, siderite, and vivanite. Some arsenic can sorb on to these, resulting in less than half of the arsenic released by reductive dissolution being truly dissolved in the water (Neidhardt et al. 2014). Even that amount of mobilization has proved catastrophic in Southeast Asia, but it obviously greatly lowers the potential for arsenic to remain soluble in the Floodwaters.

Of course, the most significant factor in mitigating issues related to the reductive dissolution of iron oxyhydroxides is simply the extremely rapid rate of sedimentation during the Flood. The iron oxyhydroxides and their associated arsenic were being buried very swiftly. This does not permanently protect them from encountering groundwater and being remobilized, this is in fact what we will argue is the source of the arsenic contamination problems today, but it would remove them from the immediate proximity of the surface and surface waters.

To summarize, during the Flood arsenic would have been brought near the surface in hydrothermal fluids and volcanos, and released by the rapid weathering of arsenic-containing rock and volcanic ash. Much of this arsenic would have been precipitated with sulfur and under reducing conditions would remain stable, not leaching into the surrounding waters. Much of it would have been precipitated subsurface or been rapidly buried in this form and so have posed no danger to the post-Flood world. Some, however, would have come in contact with oxidizing waters, which would dissolve these minerals and liberate the arsenic. Nevertheless, oxidizing conditions promote the formation of iron oxyhydroxides and arsenic will sorb to these (as well as to carbonates and clays), effectively removing it from water. Other dissolved substances will also sorb, creating some competition for binding sites, but under acidic-conditions sorption would still be expected to remove most of the arsenic from the water. Once again, rapid sedimentation would bury many of these minerals before the arsenic could be remobilized off of them. However, organic carbon can promote reducing conditions, which leads to reductive dissolution of the iron minerals in water if they are not buried quickly enough or deeply enough, freeing the arsenic again. This occurs today and is a primary factor in the current arsenic crisis. While the sheer speed at which sedimentary layers were being laid down during the Flood would have worked against this process, presumably some arsenic would have been remobilized this way. However, although they change form, some iron minerals will persist and continue to sorb arsenic, so no more than 50% of the sorbed toxin is likely to be freed. Furthermore, reductive dissolution requires reducing waters. If sulfate is also present in those waters, it can be reduced to sulfide and the arsenic will once again be sequestered in pyrite or arsenic sulfides. Meanwhile, the rapid deposition of sedimentary layers during the Flood was constantly burying the sorbed or mineralized arsenic, largely removing the opportunity for that arsenic to redissolve.

These are the chemical processes which would govern the behavior of arsenic during Noah's Flood (Figure 1). They are highly complex, but two trends stand out. Under virtually all conditions a significant amount of arsenic will not actually be dissolved in water, but will rather be sorbed or associated with some solid substance. Furthermore, the very processes that could free the

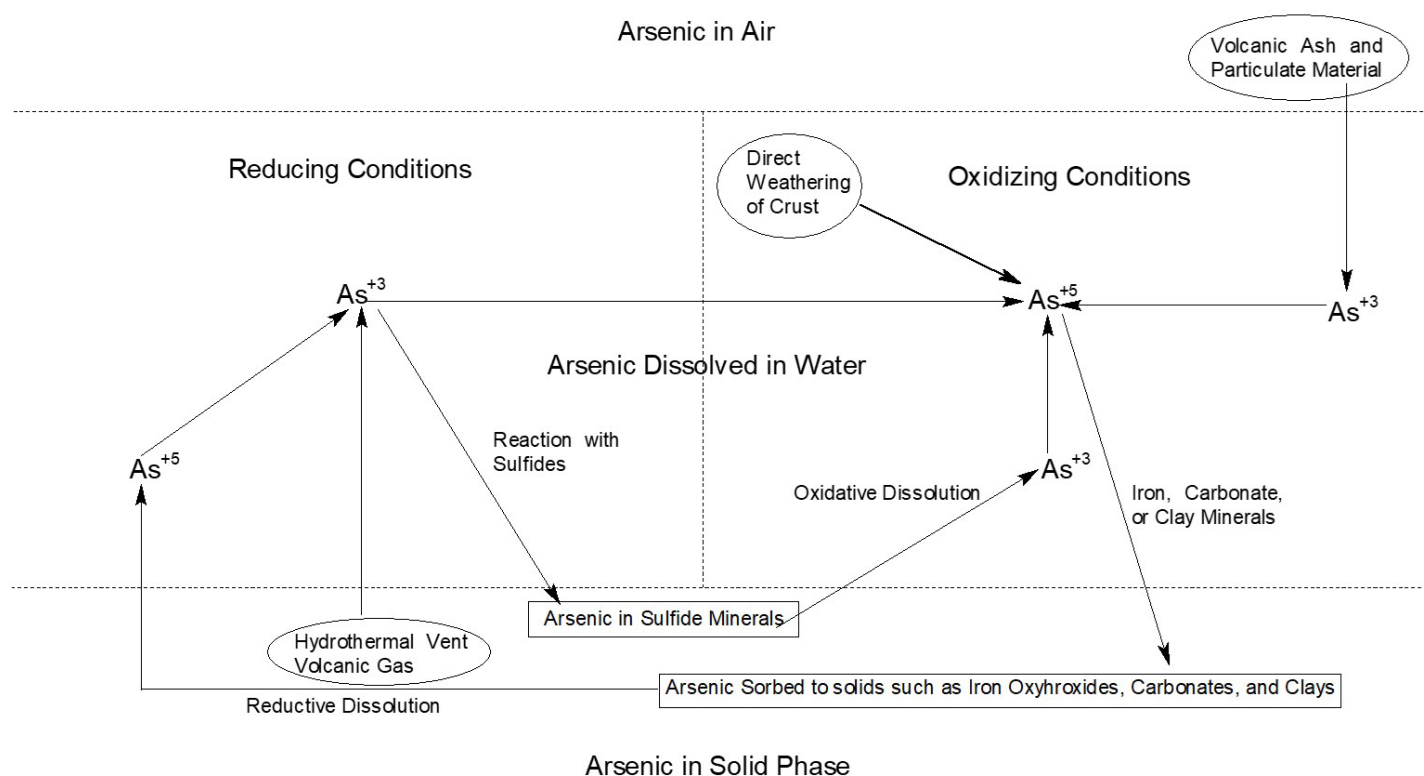
arsenic invariably hold the potential to also remove it from the water. In light of this, we can consider how the Flood model is consistent with the current geology of arsenic.

THE FATE OF ARSENIC IN THE FLOOD

Most modern areas of arsenic-contaminated groundwater are geologically close to sedimentary basins adjacent to orogenic belts (Mukherjee et al. 2014). Orogenesis occurs at convergent plate boundaries, generating mountain ranges. Foreland sedimentary basins are depressions adjacent to these ranges, which contain the sedimentary layers believed to have formed from the erosion of these mountains. The mountains themselves contain sulfur-rich reduced arsenic minerals. These can be oxidized upon exposure to air and surface water both before and during erosion, resulting in a mixture of arsenic associated with pyrite, arsenic sulfide minerals, and both iron oxyhydroxides and clays with a large amount of sorbed arsenic all ending up in the sedimentary basins. Generally reductive dissolution and substitution of other ions on the sorption sites of these minerals results in arsenic leaching into groundwater flowing through the basins (Biswas et al. 2014; Xie et al. 2014). It is probable this is the source of much of the world's arsenic contamination issues: the source of the arsenic contamination in Southeast Asia is primarily water running through basins adjacent

to the Himalayas, the source of South American contamination is the sedimentary basin adjacent to the Andes, and in the Western United States it is the Rocky Mountain foreland basin (Mukherjee et al. 2014).

This argument, while originally made in the uniformitarian literature, fits well with the Flood model. We have argued that significant amounts of arsenic were deposited as sulfide minerals due to hydrothermal activity and subsurface deposition from volcanic gasses during the volcanism associated with the Flood. If these minerals were never exposed to oxidizing conditions, they posed little threat of mobilizing the arsenic. However, many times this volcanism was associated with regions that would become mountain ranges. During the rapid uplift of the modern mountain ranges immediately post-Flood (Snelling 2009), some of these minerals were exposed to oxygenated water and underwent weathering. Concurrent formation of clays and iron oxyhydroxides as the sulfides were oxidized would lead to sorption of the arsenic. The end results would be arsenic-rich iron oxyhydroxides and clays, along with some unchanged arsenic sulfides, being deposited in foreland basins adjacent to mountains by erosion. The close proximity of these basins to volcanic ash would also contribute some arsenic. This would also be primarily



Key:

Boxes represent precipitated forms of arsenic, showing processes removing the element from the Floodwaters.

Ovals represent the main sources of arsenic for the Flood waters.

Figure 1. Summary of arsenic geochemistry during the Flood.

sorbed to iron oxyhydroxides and clays. Hence the foreland basins became enriched in arsenic. Over time, however, as groundwater flowed through the basins, those minerals were exposed to both competition for sorption sites and reductive dissolution, slowly releasing the arsenic into the groundwater and leading to the modern problems of arsenic contamination. (Figure 2)

All the arsenic, of course, was not concentrated in foreland basins adjacent to orogenic belts, even though many of these are enriched in the element. Some remained subsurface as sulfides in other areas. Some was deposited as sulfides in areas where they were exposed to oxidative dissolution and became dissolved in the Flood waters. Some was released by the Floodwaters' erosion of the continental crust. Some of the arsenic dissolving out of volcanic ash presumably didn't end up in the foreland basins. Most of this arsenic was oxidized in the Floodwaters to As^{5+} species and bound to iron and aluminum oxyhydroxides, causing it to precipitate out at various locations. In the presence of organic carbon, these minerals could undergo reductive dissolution to remobilize the arsenic. But the controlling factor would be the incredibly rapid sedimentation associated with the Flood. The sedimentary layers were simply forming too quickly, burying the sorbed arsenic. It was trapped in shales, clays, and iron oxyhydroxide minerals throughout the world,

with especially significant amounts concentrated in the foreland basins. Hence, the concentration in the post-Flood surface waters never became devastatingly high. The normal chemistry of arsenic combined with a biblical understanding of Earth history logically explains the current distribution of this toxic element.

There is a significant implication of this model. Arsenic contaminated groundwater was not a problem pre-Flood because the Flood led to the formation of the minerals in the foreland basins which are the primary source of this contamination today. The current presence of arsenic in groundwater in no way reflects on God's original, good creation. Rather, the tragedy of arsenic poisoning we see around the world today is a direct result of the judgment of the Flood, another reminder of how man's sin can have consequences that echo down through the centuries.

CONCLUSIONS

When all the data is considered, we can safely conclude that the mobilization of arsenic would not have posed a threat to the reestablishment of life on Earth post-Flood. That does not mean the Flood did not mobilize a great deal of arsenic. However, much of it would have been immobilized as arsenic-sulfides or incorporated into solid pyrite. As long as the waters surrounding them remain reducing in character, these minerals would remain

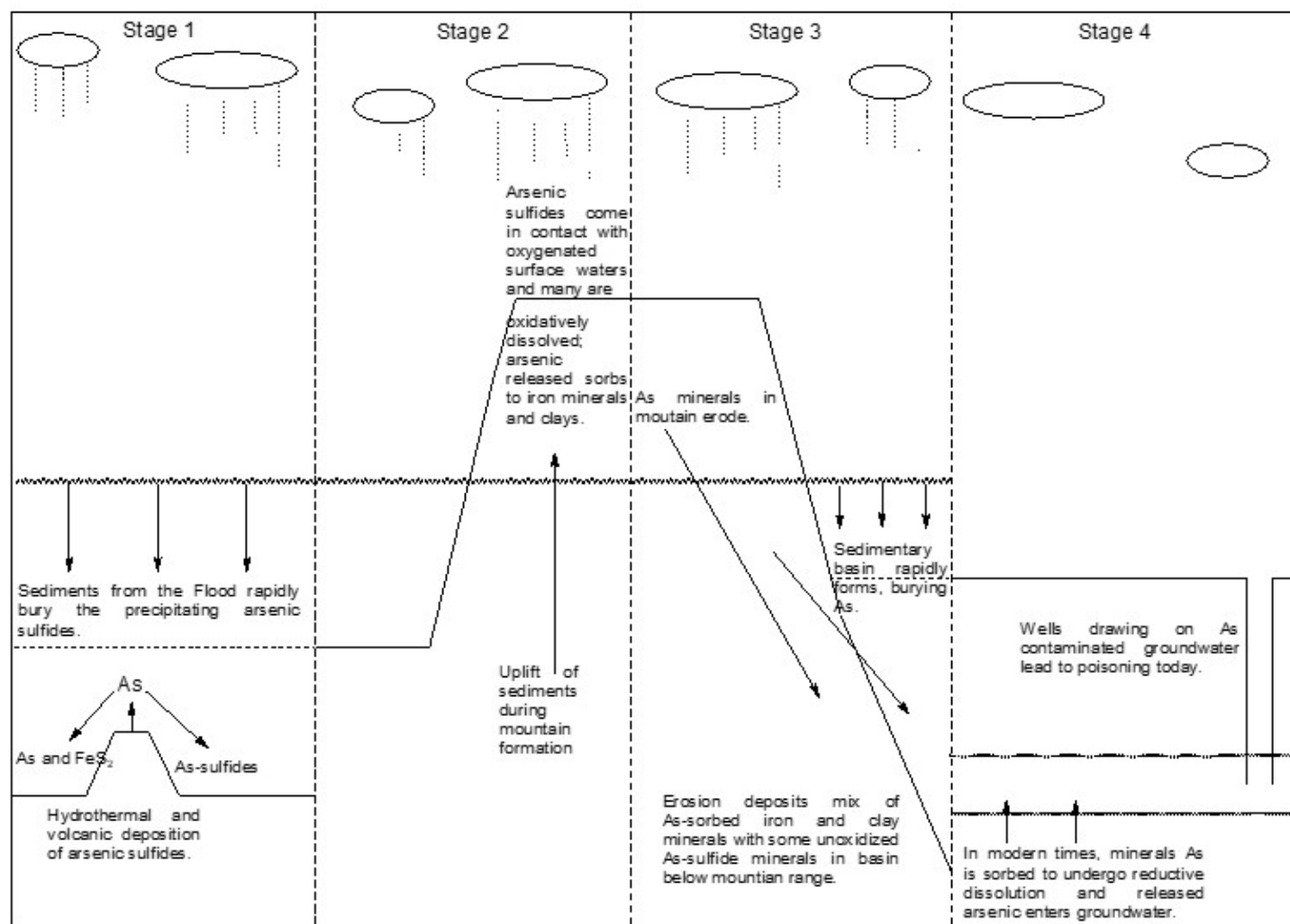


Figure 2. Arsenic enrichment in sedimentary basins adjacent to orogenic belts leading to modern groundwater contamination.

insoluble. Meanwhile, the rapid sedimentation of the Flood would have been burying the minerals. However, if the waters around them became oxidizing, they could dissolve the minerals and liberate the arsenic. A likely scenario for this occurrence would be if the minerals were incorporated in rock layers that underwent uplift to form modern mountain ranges. This arsenic would not just be released as a dissolved element in the water. The same processes that liberated it, primarily from pyrite, would have formed iron oxyhydroxides which sorb arsenic. In the case of mountain uplift, many of these minerals would have eroded into foreland sedimentary basins, where they are found today. Likewise, arsenic released from other sources would likely be oxidized to the As^{5+} form and sorbed to iron oxyhydroxides. These iron minerals would have been rapidly incorporated into sedimentary rock. The incredible rate of sedimentary rock formation during the Flood effectively isolated the arsenic from the surface waters. So while an immense amount of arsenic was released, the amount of it actually dissolved in water would have been relatively negligible by the end of the Flood. However, reductive dissolution post-Flood has resulted in significant amounts of that arsenic leaching into groundwater, so that the contamination became a significant problem when that groundwater was accessed in modern times. Hence, the natural geochemistry of arsenic indicates we would not expect it to pose a problem for the reestablishment of life after the Flood, but does explain how that great judgement resulted in the current contamination issues.

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