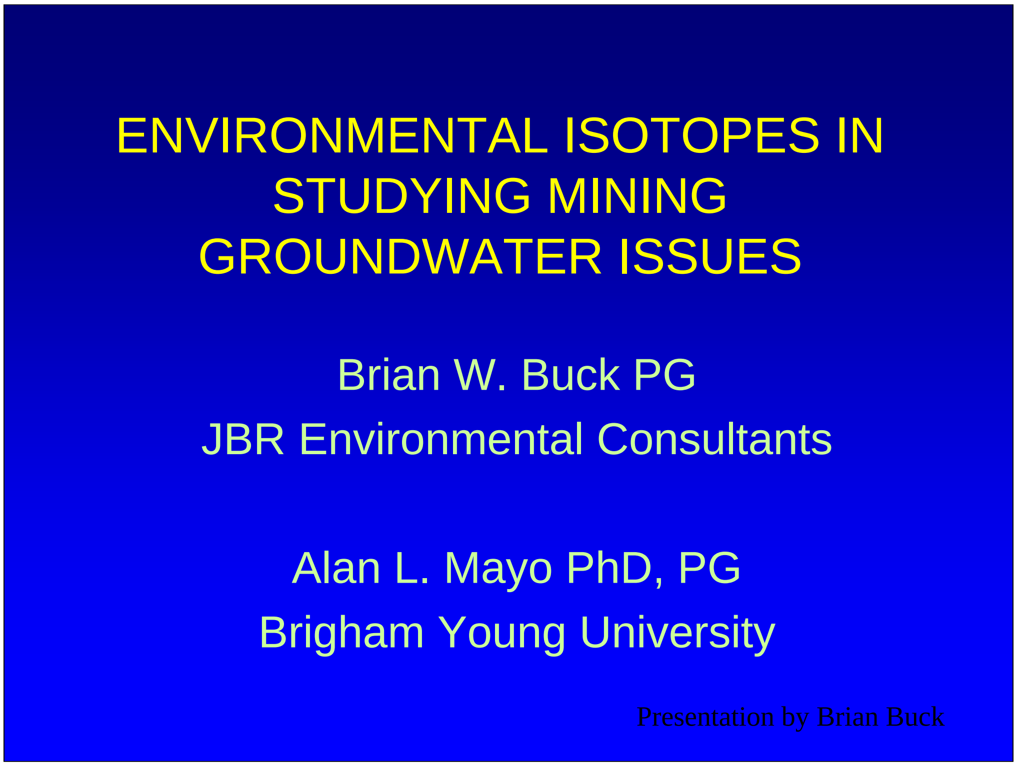


ENVIRONMENTAL ISOTOPES IN STUDYING MINING GROUNDWATER ISSUES

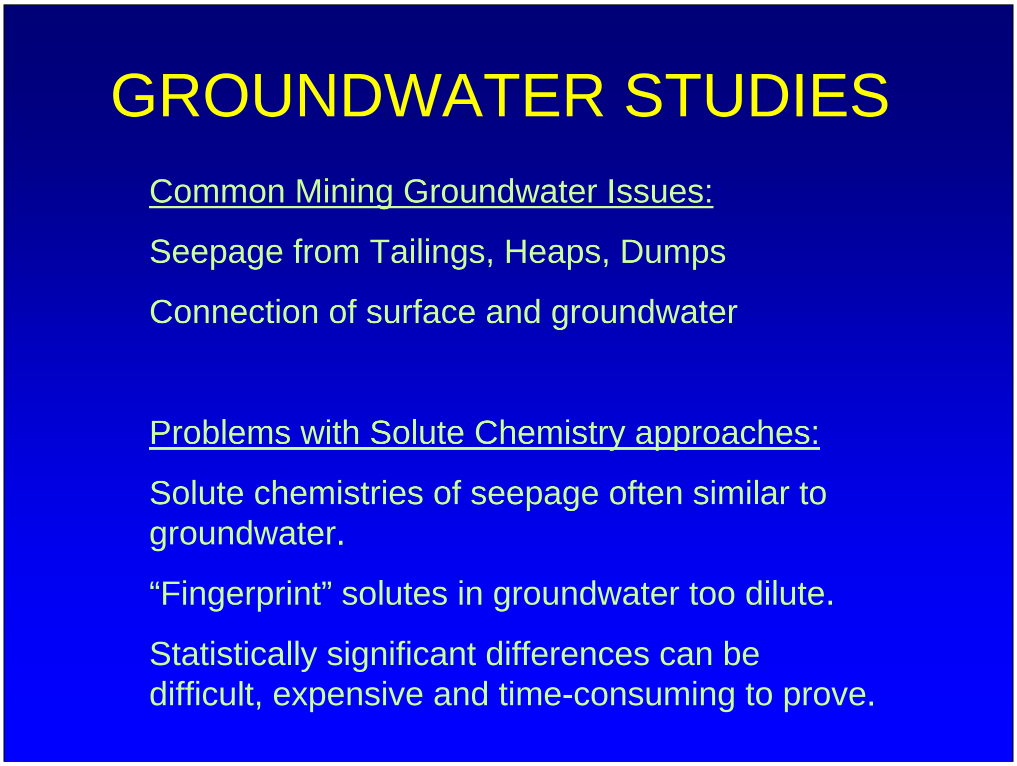
Brian W. Buck PG
JBR Environmental Consultants

Alan L. Mayo PhD, PG
Brigham Young University

Presentation by Brian Buck

Our presentation will describe the background and advantages of using environmental isotopes in mining related groundwater studies.

We will then illustrate effectiveness of this tool with a few case studies.



GROUNDWATER STUDIES

Common Mining Groundwater Issues:

Seepage from Tailings, Heaps, Dumps

Connection of surface and groundwater

Problems with Solute Chemistry approaches:

Solute chemistries of seepage often similar to groundwater.

“Fingerprint” solutes in groundwater too dilute.

Statistically significant differences can be difficult, expensive and time-consuming to prove.

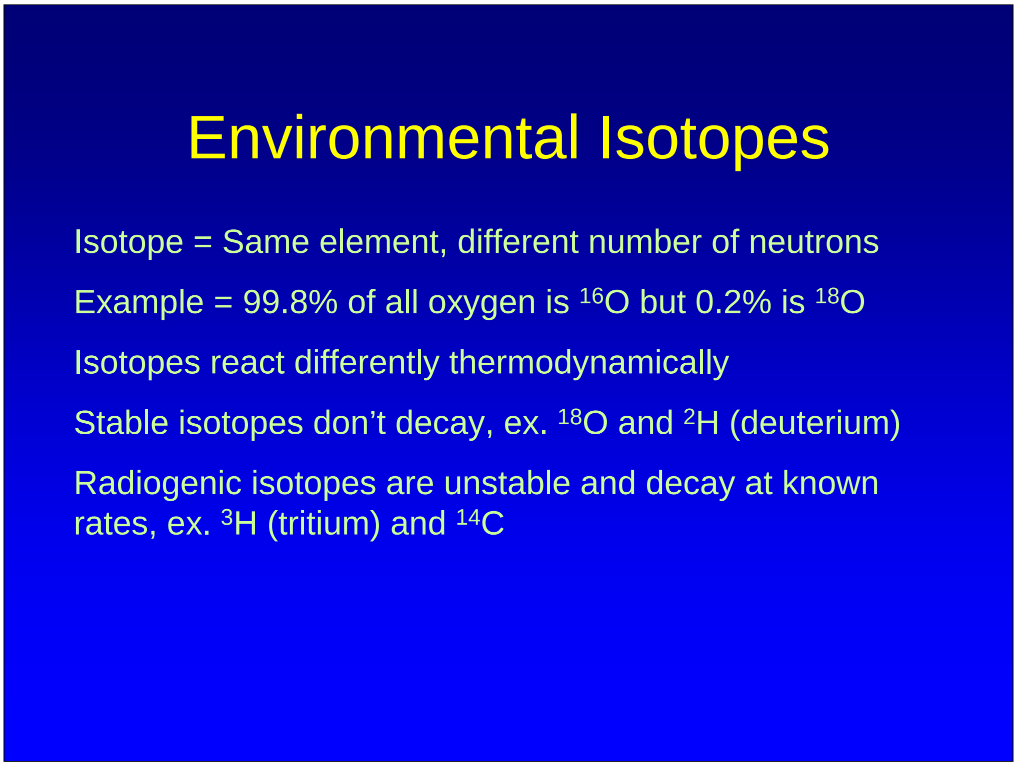
Mining-related groundwater studies commonly involve questions on contamination from seepage of tailings water, heap leach solutions or meteoric water through waste rock dumps.

There can also be questions related to the source of water discharging at springs or streams and whether or not this groundwater is connected to aquifers potentially affected by mining.

Determining groundwater quality impacts can be difficult because the major ion chemistry of natural groundwater may be very similar to that of the seepage of concern.

Fingerprint solutes like dissolved metals, sulfate, pH, or reagents in seepage may be reactive with the aquifer or too dilute to be significantly present in groundwater samples.

Regulatory agencies often require extensive monitoring to demonstrate statistical significance of positive or negative determinations of groundwater contamination and this can require multiple samples over extended periods of time increasing costs.



Environmental Isotopes

Isotope = Same element, different number of neutrons

Example = 99.8% of all oxygen is ^{16}O but 0.2% is ^{18}O

Isotopes react differently thermodynamically

Stable isotopes don't decay, ex. ^{18}O and ^{2}H (deuterium)

Radiogenic isotopes are unstable and decay at known rates, ex. ^{3}H (tritium) and ^{14}C

An element is defined by # of protons whereas the # of neutrons defines the isotope. Isotopes with more neutrons have greater atomic mass than those with fewer neutrons.

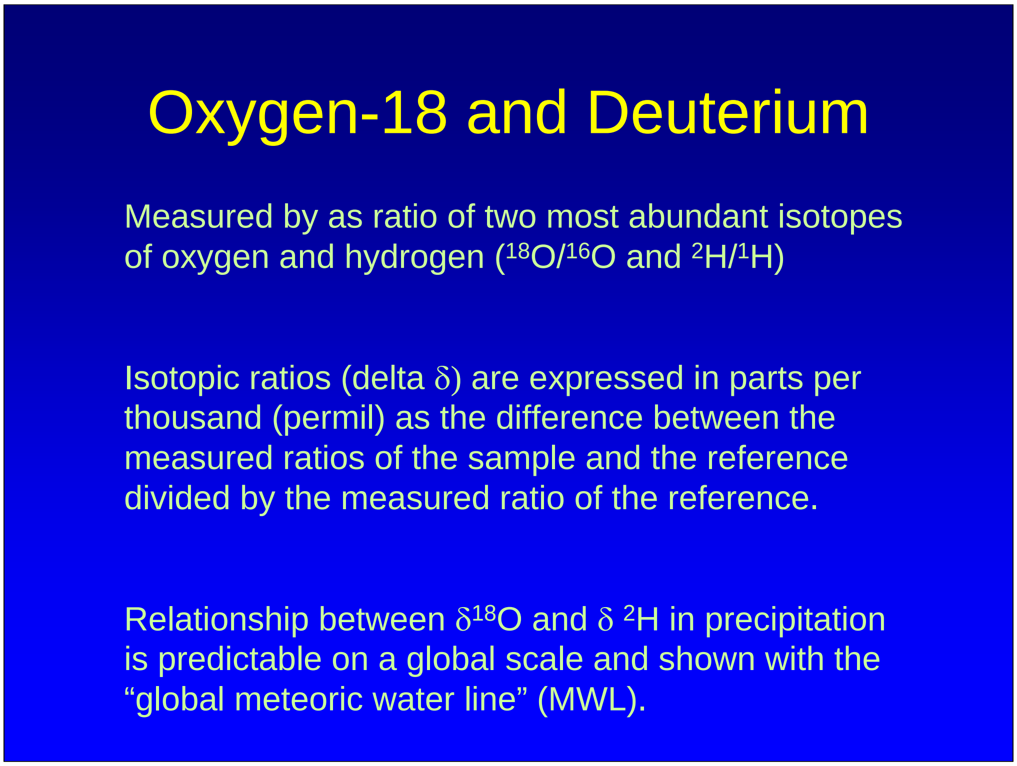
Many elements have isotopes for example, 99.8% of all oxygen on the planet has 8 protons and 8 neutrons = Oxygen-16 whereas only 0.2% has 10 neutrons = a heavier isotope known as Oxygen-18.

The different atomic masses of isotopes affects their thermodynamic properties, which can make them useful for groundwater studies as described later in this presentation.

Stable isotopes do not spontaneously disintegrate by any known mode of decay, ex. Oxygen-18 and hydrogen-2 (deuterium).

Radiogenic isotopes are those that have too many or too few neutrons to be stable so they decay with known probabilities, examples are hydrogen-3 (tritium) and carbon-14.

These four isotopes are very helpful in groundwater studies as



Oxygen-18 and Deuterium

Measured by as ratio of two most abundant isotopes of oxygen and hydrogen ($^{18}O/^{16}O$ and $^{2}H/^{1}H$)

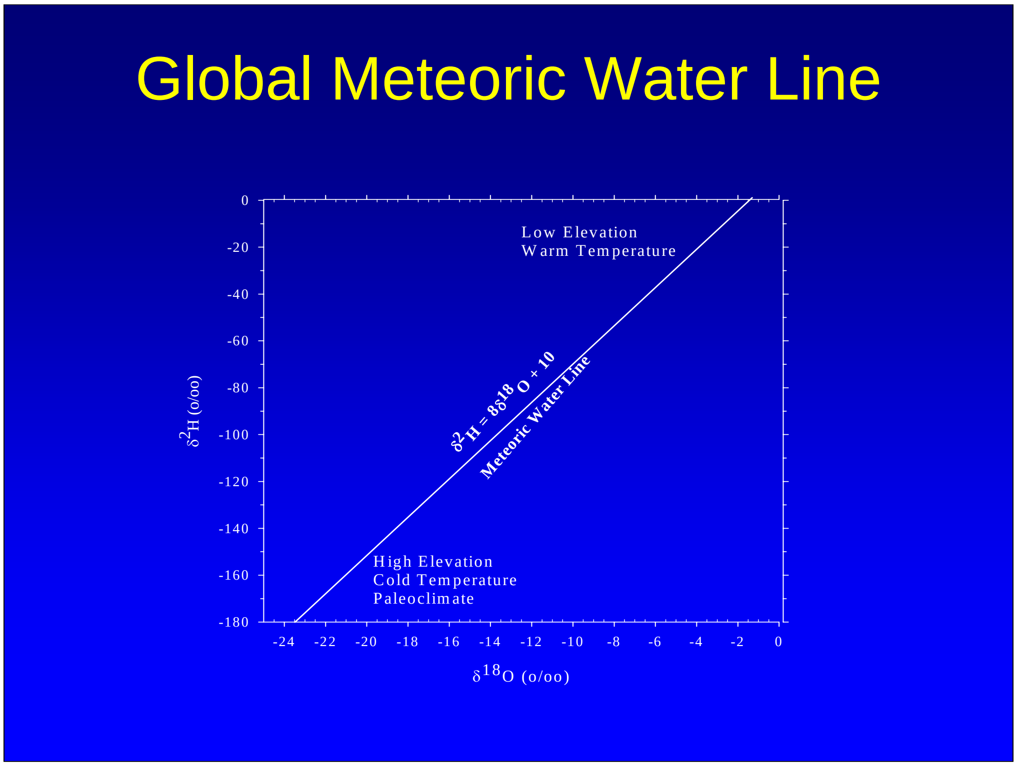
Isotopic ratios (delta δ) are expressed in parts per thousand (permil) as the difference between the measured ratios of the sample and the reference divided by the measured ratio of the reference.

Relationship between $\delta^{18}O$ and $\delta\ ^{2}H$ in precipitation is predictable on a global scale and shown with the “global meteoric water line” (MWL).

Isotopes are measured by mass spectrometers and are expressed as ratios of the heavier isotope of an element to the lighter one. So oxygen-18 is expressed as its relative abundance to oxygen-16 and deuterium is expressed in the ratio to normal hydrogen.

To eliminate the effects of machine errors, measured isotopic ratios are compared to known references that are run at the same time. The resulting ratios, in delta notation, are expressed in parts per thousand or permil.

The ratios of stable isotopes of oxygen and hydrogen are controlled by the evaporation and rainout of water in the hydrologic cycle. These ratios are predictable globally and are shown on the global meteoric water line.

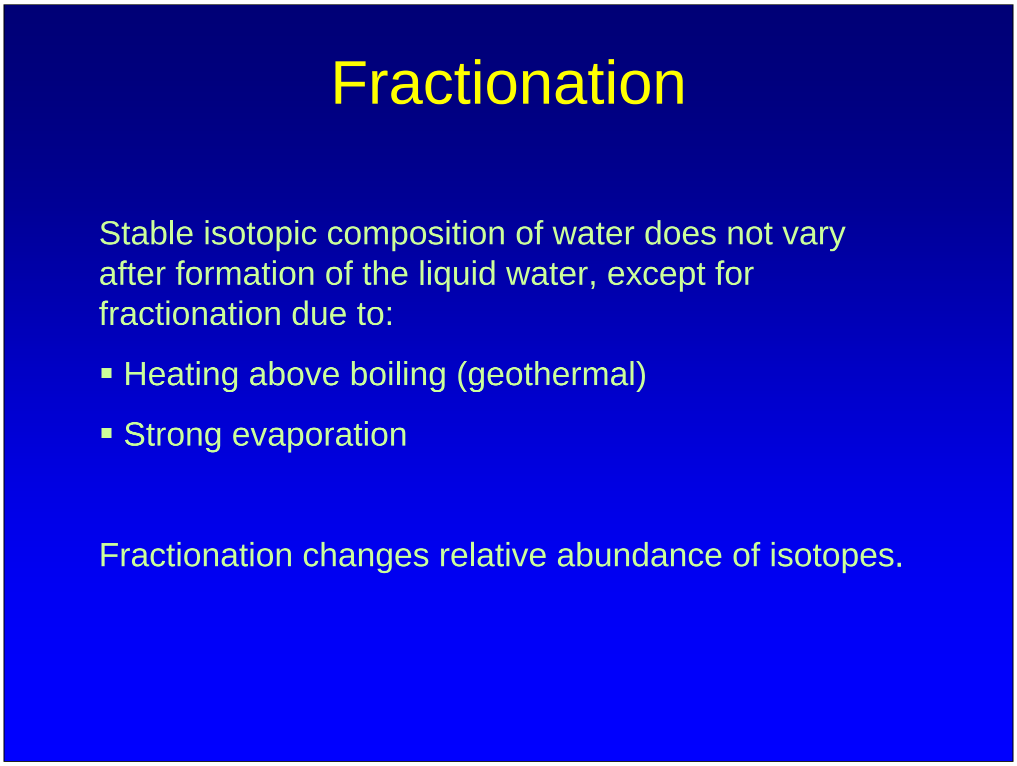


Global Meteoric Water Line

When samples are analyzed for oxygen-18 and deuterium, the reference standard that is used (Vienna Standard Mean Ocean Water) results in negative ratio values. Less negative isotope values are referred to as being relatively “enriched” in the heavier isotope whereas more negative isotope ratios are considered relatively “depleted” in the heavier isotope.

Enriched stable isotope ratios in precipitation are common in warmer regions and lower elevations.

Depleted stable isotope ratios in precipitation are common in colder regions and higher elevations. They are also typical of very old water precipitated in colder paleoclimates.



Fractionation

Stable isotopic composition of water does not vary after formation of the liquid water, except for fractionation due to:

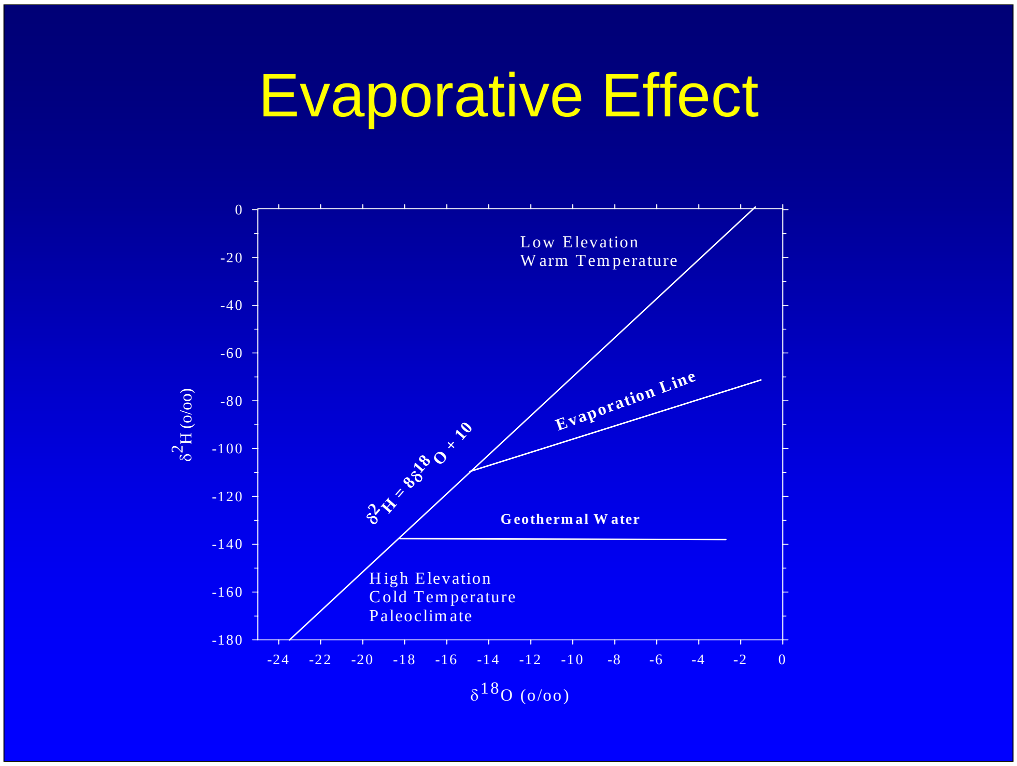
- Heating above boiling (geothermal)
- Strong evaporation

Fractionation changes relative abundance of isotopes.

The valuable characteristic of stable isotopes in water is that after the liquid water is formed from vapor, the isotopic ratios of oxygen-18 and deuterium do not change and are locked into the water molecule except for:

Strong geothermal heating or evaporation such as from ponds or lakes in dry climates.

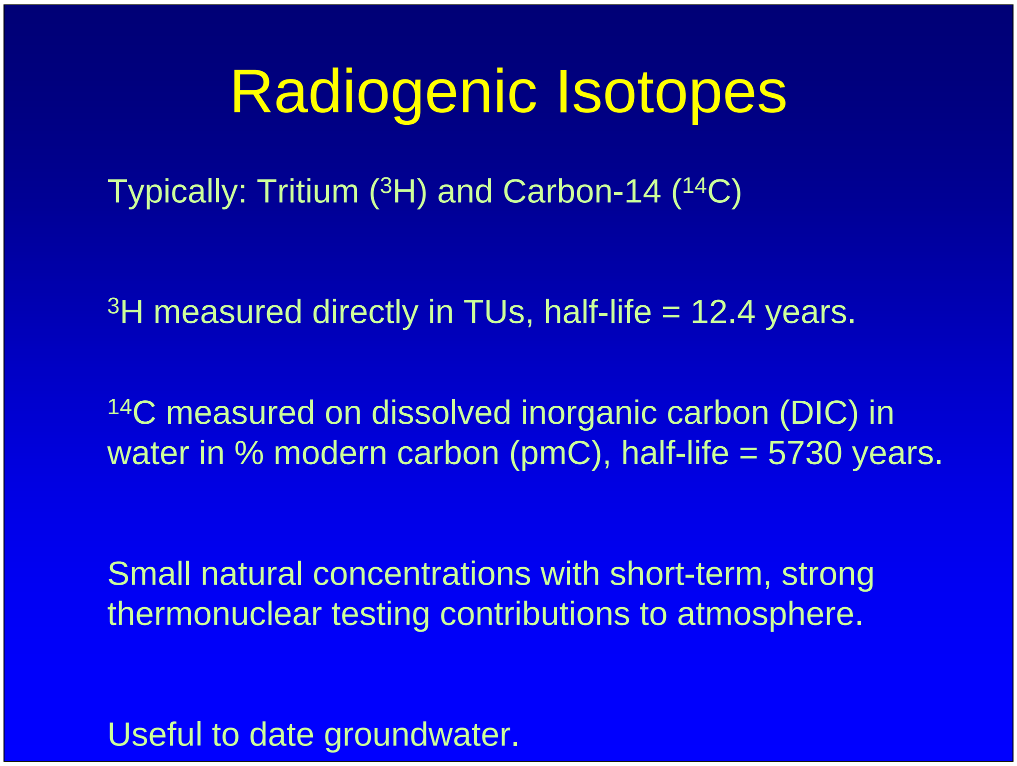
These cause fractionation or selective changes in relative concentrations of oxygen-18 or deuterium. The evaporative fractionation is very helpful in application of these stable isotopes to groundwater investigations for mining facilities.



Evaporative Effect

This figure illustrates the effect of evaporation and geothermal heating on the stable isotopic composition of water. Evaporation causes the lighter isotopes of oxygen and hydrogen to preferentially leave the water in the vapor phase causing the remaining water to be enriched in the heavier isotopes, particularly oxygen. This causes a deviation from the MWL along a line with a lower slope, known as the evaporation line.

Water that is heated geothermally becomes relatively enriched in oxygen-18 due to the water coming into equilibrium with elevated concentrations of that isotope in minerals. Hydrogen is not similarly affected.



Radiogenic Isotopes

Typically: Tritium (^{3}H) and Carbon-14 (^{14}C)

^{3}H measured directly in TUs, half-life = 12.4 years.

^{14}C measured on dissolved inorganic carbon (DIC) in water in % modern carbon (pmC), half-life = 5730 years.

Small natural concentrations with short-term, strong thermonuclear testing contributions to atmosphere.

Useful to date groundwater.

The radiogenic isotopes commonly used in environmental studies are tritium (hydrogen-3) and carbon-14.

Tritium is measured directly and expressed in tritium units. It has a half life of 12.4 years.

Carbon-14 is measured on dissolved inorganic carbon in water and is expressed as percent modern carbon (pmC) . It has a half life of 5700 years.

Although both isotopes are produced in the upper atmosphere in very small concentrations, their abundance in the atmosphere underwent a dramatic, short-term, upward spike during atmospheric nuclear weapons testing.

Hence they are useful in age dating groundwater.

Simplot Smoky Canyon Tailings, Idaho

Facility has a liner of low permeability mudstone.

Surface stream diverted around tailings facility.

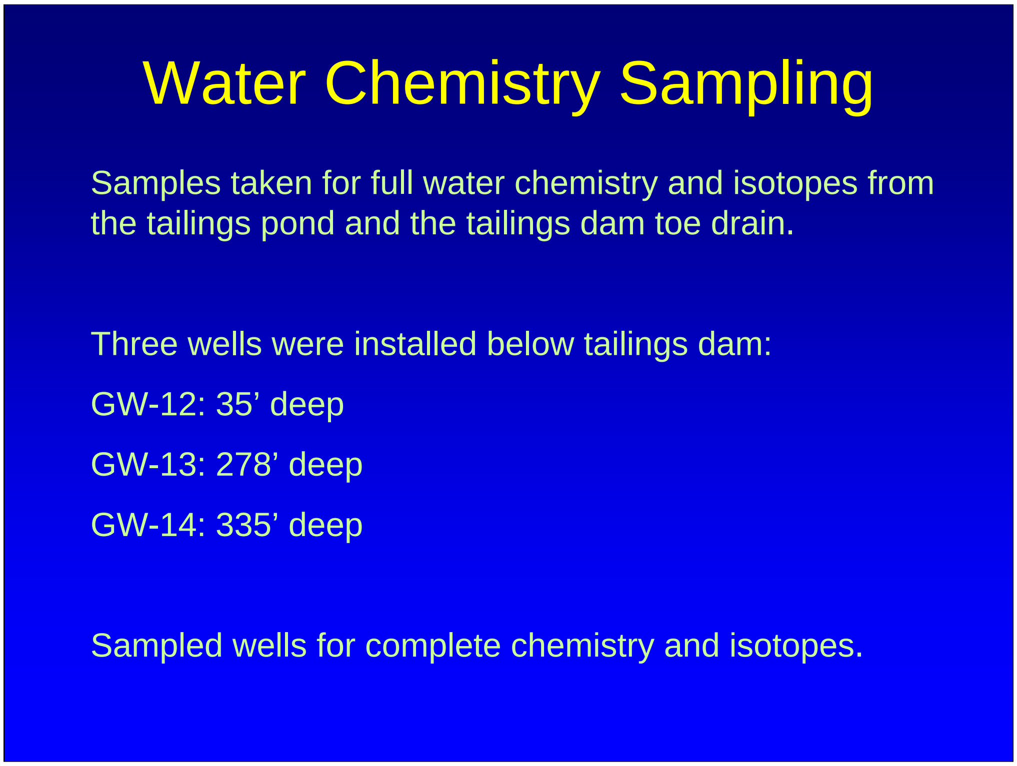
Tailings dam toe drain discharges shallow groundwater.

Concern: Is tailings seepage impacting groundwater?

With that primer on environmental isotopes in groundwater, I will illustrate their use with some case studies.

The first example is a tailings pond groundwater investigation we did in SE Idaho for J.R.Simplot Company. The tailings pond has a mudstone liner to protect groundwater. There was a surface stream that had been diverted around the tailings dam and a toe drain from the tailings dam discharged to the stream. It was thought that this drain discharged only shallow groundwater and not tailings pond seepage.

The question was, is seepage from the tailings pond impacting groundwater?



Water Chemistry Sampling

Samples taken for full water chemistry and isotopes from the tailings pond and the tailings dam toe drain.

Three wells were installed below tailings dam:

GW-12: 35’ deep

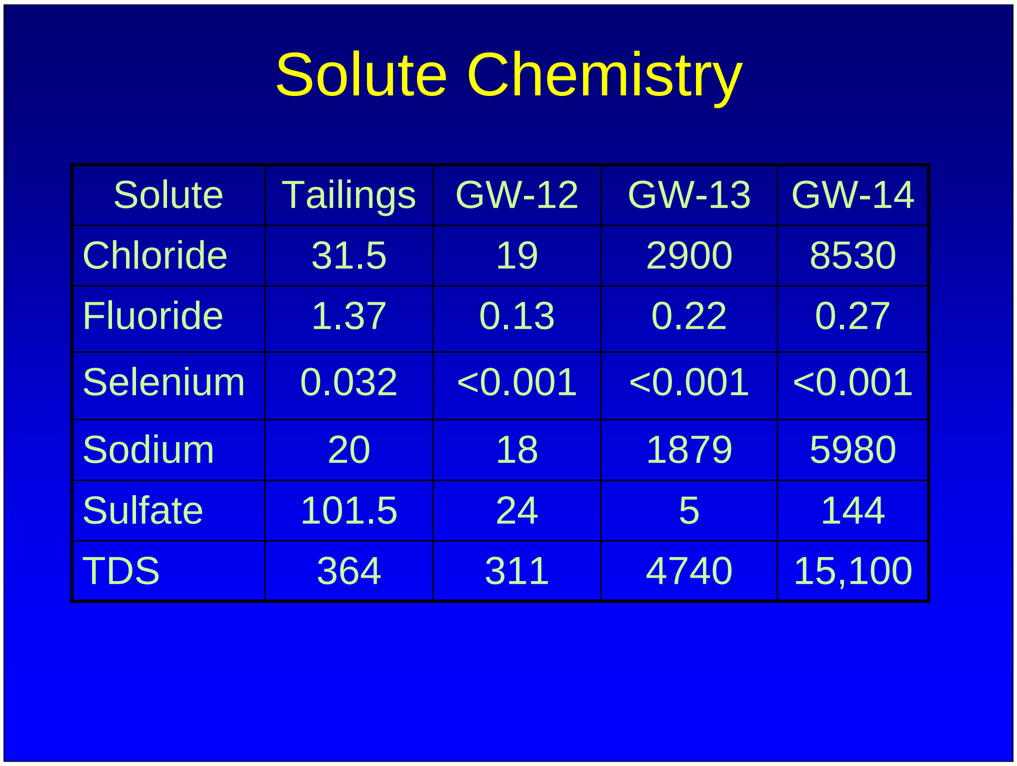
GW-13: 278’ deep

GW-14: 335’ deep

Sampled wells for complete chemistry and isotopes.

The tailings pond water itself was sampled for normal solutes and isotopes as was the toe drain.

Three monitoring wells of increasing depths were installed at the toe of the tailings dam. These were called GW-12, -13, and –14 each with increasing depth. These wells were also sampled for complete solute chemistry and isotopes.



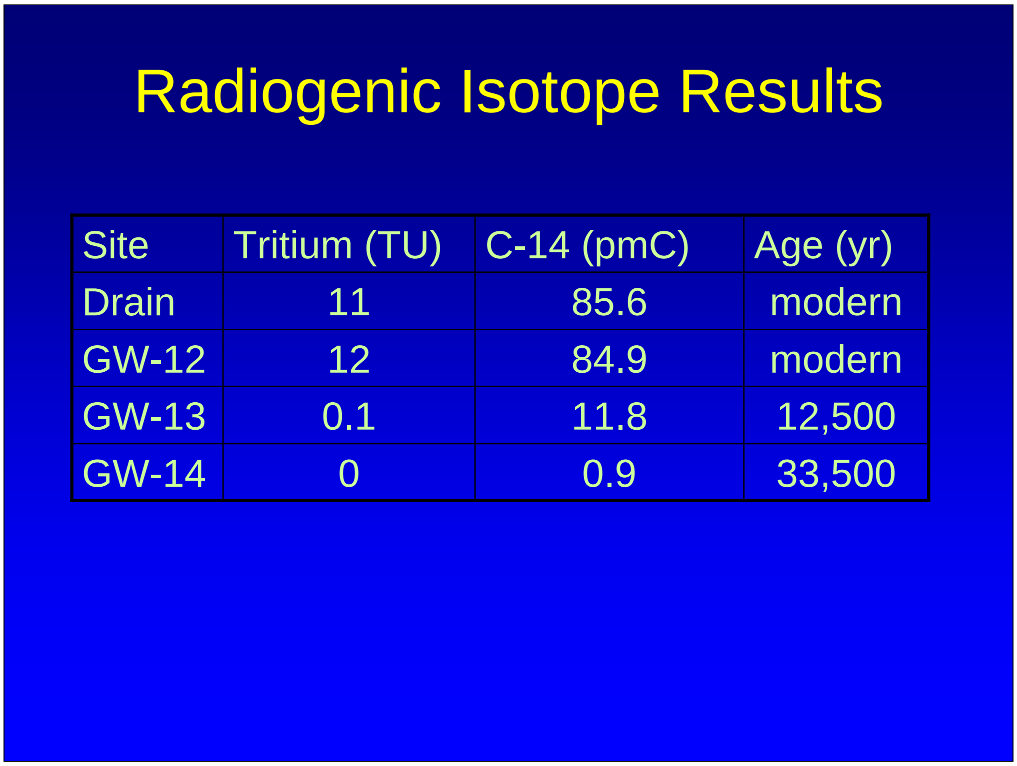
Solute Chemistry

Solute	Tailings	GW-12	GW-13	GW-14
Chloride	31.5	19	2900	8530
Fluoride	1.37	0.13	0.22	0.27
Selenium	0.032	<0.001	<0.001	<0.001
Sodium	20	18	1879	5980
Sulfate	101.5	24	5	144
TDS	364	311	4740	15,100

Compared to the tailings pond chemistry: chloride and sodium increased with depth to concentrations much higher than the tailings, indicating a natural source of soluble salt at depth.

Two “fingerprint” solutes in the tailings water are fluoride and selenium. Fluoride concentrations in shallow groundwater were much lower than tailings water and somewhat lower than deeper groundwater indicating an apparent lack of impact from tailings seepage. This was corroborated by the selenium data.

However, sulfate in the shallow groundwater did appear elevated compared to the middle depth. TDS of the shallow groundwater was less than either the tailings water or the deeper groundwater but was relatively similar to tailings water, making it less than definitive. Thus the solute chemistry was not entirely definitive whether tailings water was entering shallow groundwater or not.

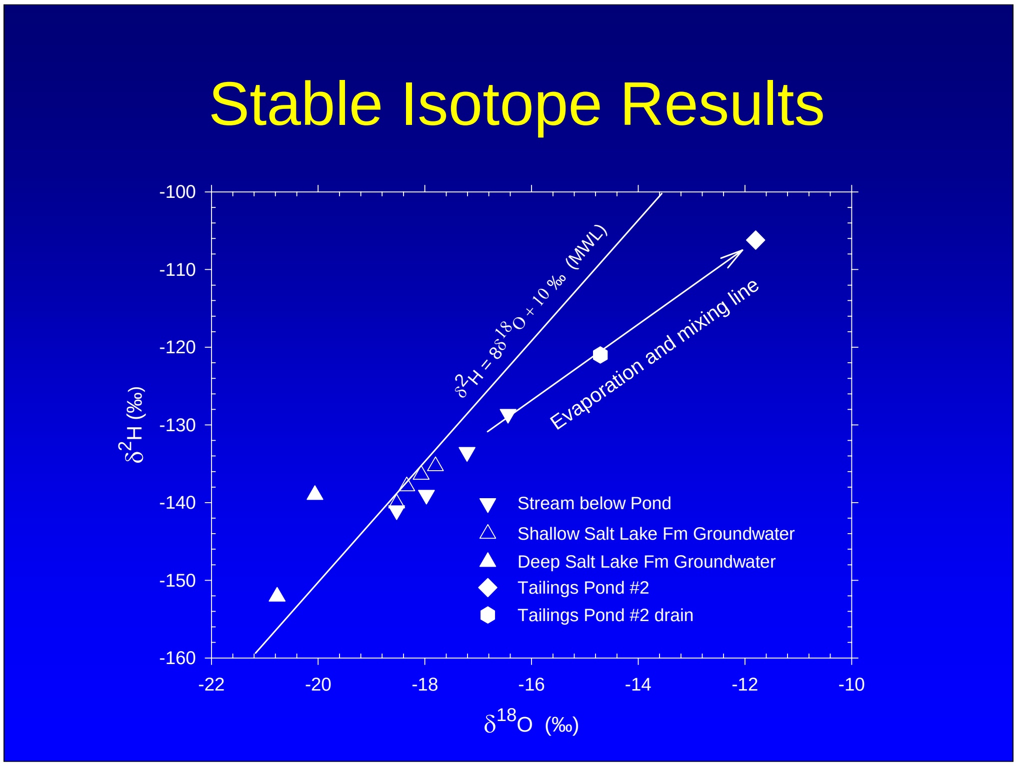


Radiogenic Isotope Results

Site	Tritium (TU)	C-14 (pmC)	Age (yr)
Drain	11	85.6	modern
GW-12	12	84.9	modern
GW-13	0.1	11.8	12,500
GW-14	0	0.9	33,500

Radiogenic isotope data showed waters in the toe drain and shallow groundwater both had significant tritium and Carbon-14 contents interpreted as modern, indicating that toe drain water was likely connected to the shallow groundwater. The tailings pond water was also modern, because it was from a surface stream source, so the potential for seepage from the tailings pond to shallow groundwater or the toe drain was not answered by the radiogenic isotope data.

However, the deeper groundwater had much lower tritium and carbon-14 contents interpreted as being very old. This indicated tailings pond water was not moving into the deeper groundwater.

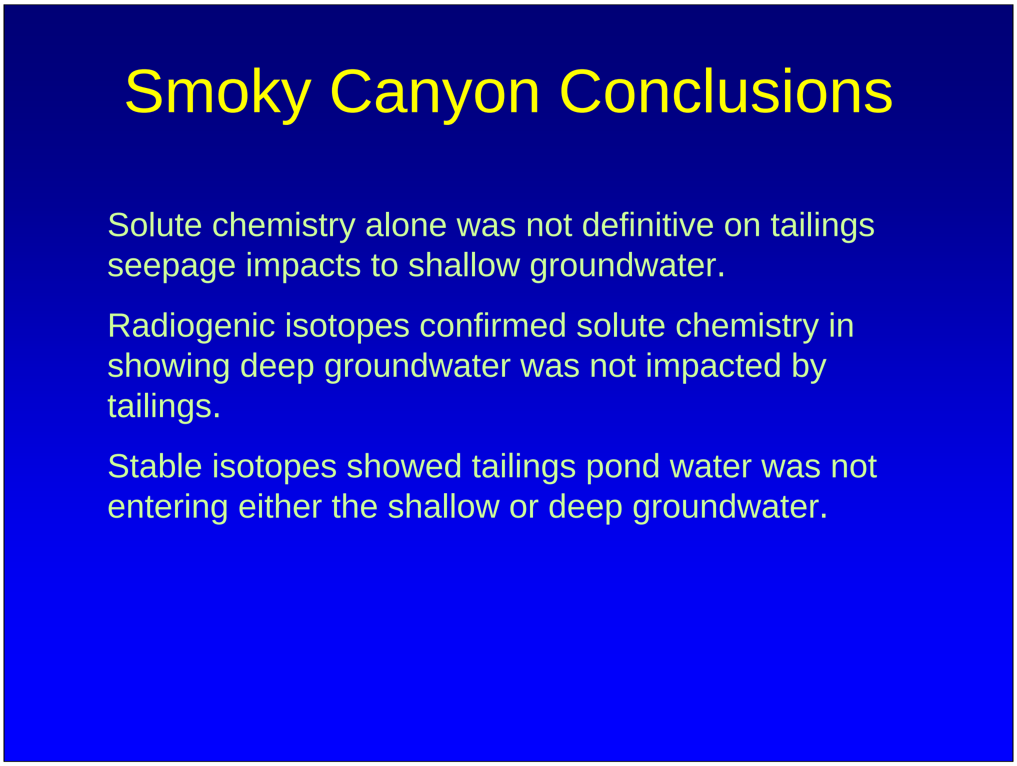


Stable Isotope Results

Stable isotopes data showed the deep groundwater was isotopically depleted relative to the MWL, which correlated with paleoclimates. The deep groundwater was quite different from the tailings pond water corroborating conclusions of no impact derived from solute chemistry and radiogenic isotopes.

Stable isotope ratios for the shallow groundwater and surface stream water below the dam fit well with the MWL indicating connection between these waters. Isotopically, shallow groundwater was quite different from tailings pond water indicating no tailings pond impact on the shallow groundwater.

The stable isotope data for the tailings pond water showed evidence of strong evaporation. The tailings dam toe drain indicated a mixture of tailings water and shallow groundwater indicating tailings pond water was exiting the facility at this point but was not affecting shallow groundwater.



Smoky Canyon Conclusions

Solute chemistry alone was not definitive on tailings seepage impacts to shallow groundwater.

Radiogenic isotopes confirmed solute chemistry in showing deep groundwater was not impacted by tailings.

Stable isotopes showed tailings pond water was not entering either the shallow or deep groundwater.

Our conclusions for the Smoky Canyon tailings pond are:

Solute chemistry alone was not definitive on describing tailings seepage impacts to shallow groundwater.

Radiogenic isotopes confirmed solute chemistry results in showing deep groundwater was not impacted by tailings pond seepage.

Stable isotope data showed tailings pond water was not entering either the shallow or deep groundwater.

Brush Resources Mill, Utah

Concern: Tailings water entering water supply wells? Solute chemistry comparisons were not definitive.

Radiogenic Isotope Results:

Water supply was extremely old and tailings pond water had modern age.

Stable Isotope Results:

Water supply had no trace of evaporative water which was very dominant in tailings pond water.

Conclusion:

Tailings pond water was not contaminating the water supply wells.

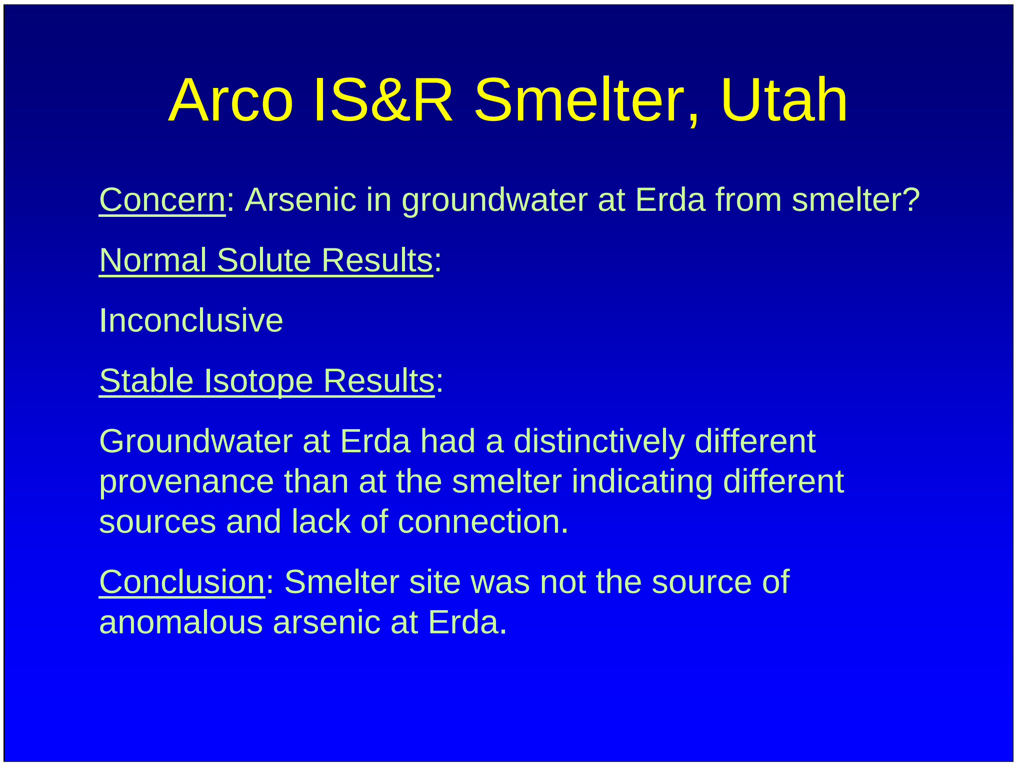
My next example is from Utah and is the Brush Resources beryllium mill north of Delta, Utah.

The concern was whether or not tailings pond seepage was entering the plant’s deep groundwater supply. Solute chemistry results between the tailings seepage and groundwater were not definitive.

Radiogenic isotope results clearly showed the groundwater was thousands of years old whereas the tailings pond water had significant tritium and carbon-14.

Stable isotopes showed the tailings pond water was strongly affected by evaporation and the groundwater was apparently unaffected by evaporation.

Our conclusion was that the groundwater was not being contaminated by tailings pond seepage.



Arco IS&R Smelter, Utah

Concern: Arsenic in groundwater at Erda from smelter?

Normal Solute Results:

Inconclusive

Stable Isotope Results:

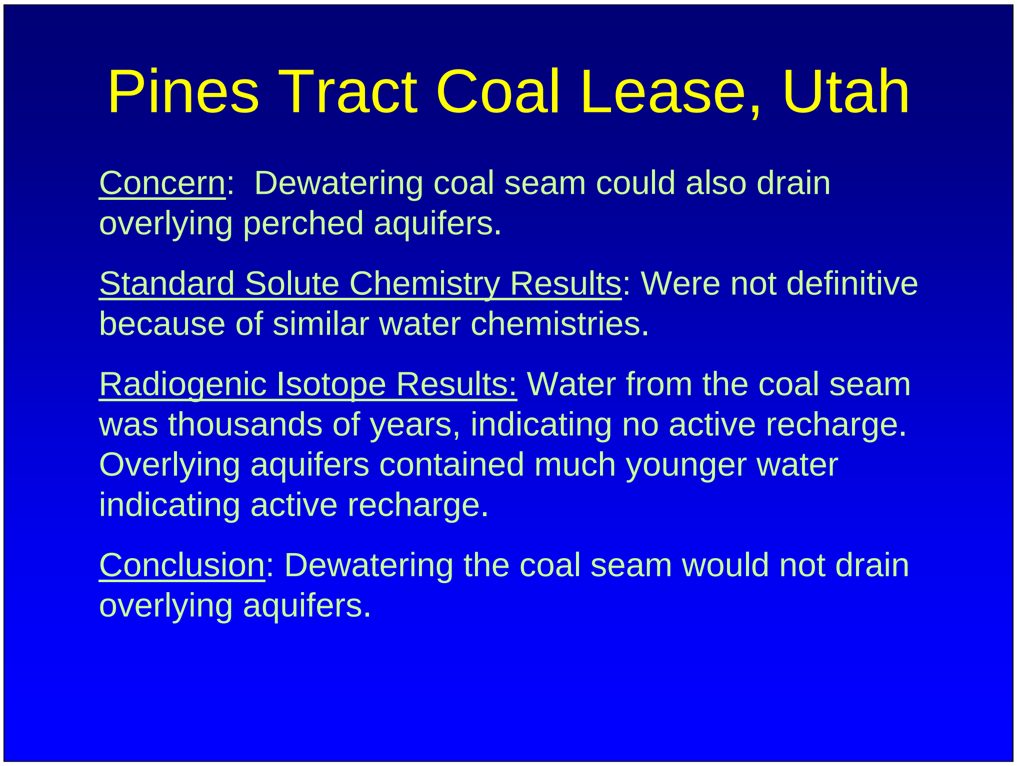
Groundwater at Erda had a distinctively different provenance than at the smelter indicating different sources and lack of connection.

Conclusion: Smelter site was not the source of anomalous arsenic at Erda.

Our second Utah example is the former IS&R smelter site outside of Tooele, Utah. The concern was whether or not anomalous arsenic concentrations in groundwater at Erda, about 5 miles north, were from the smelter site. Normal solute chemistry comparisons between the two sites were inconclusive.

Results for stable isotope samples showed that the Erda groundwater was dramatically enriched compared to groundwater under the smelter site, indicating a lack of connection between the two sites.

The stable isotope results were definitive in showing that the arsenic concentrations at Erda were not from the smelter site.



Pines Tract Coal Lease, Utah

Concern: Dewatering coal seam could also drain overlying perched aquifers.

Standard Solute Chemistry Results: Were not definitive because of similar water chemistries.

Radiogenic Isotope Results: Water from the coal seam was thousands of years, indicating no active recharge. Overlying aquifers contained much younger water indicating active recharge.

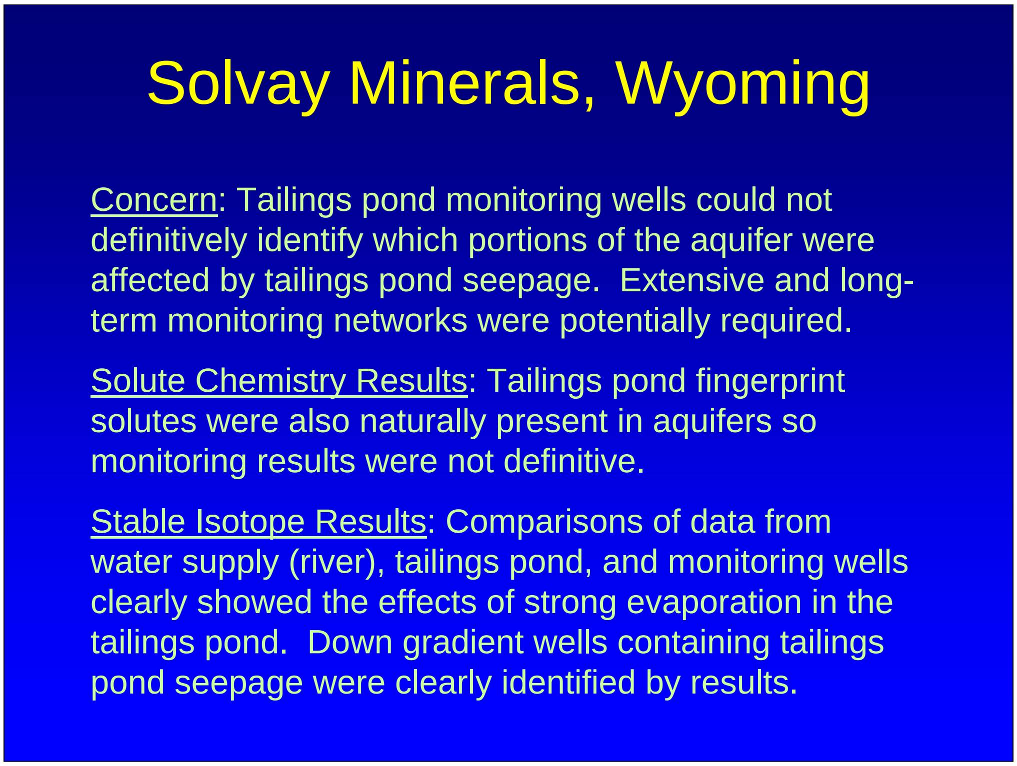
Conclusion: Dewatering the coal seam would not drain overlying aquifers.

Our last Utah example is the Pines Tract coal lease in the Wasatch Plateau coal field in central Utah. The agency concern was whether or not mining and dewatering the coal seam would drain the overlying perched aquifers.

Standard solute chemistry results from the coal and the overlying aquifers did not definitively indicate if the various aquifers were connected.

Radiogenic isotope results from the coal seam showed this water was ancient indicating to us that recharge of this aquifer was not actively occurring through the overlying rocks. However the overlying aquifers all contained much younger aged water which indicated active recharge from above.

This pattern of different groundwater ages indicated that the water in the coal seam was isolated from the overlying aquifers and dewatering the coal seam would not drain the shallower aquifers.



Solvay Minerals, Wyoming

Concern: Tailings pond monitoring wells could not definitively identify which portions of the aquifer were affected by tailings pond seepage. Extensive and long-term monitoring networks were potentially required.

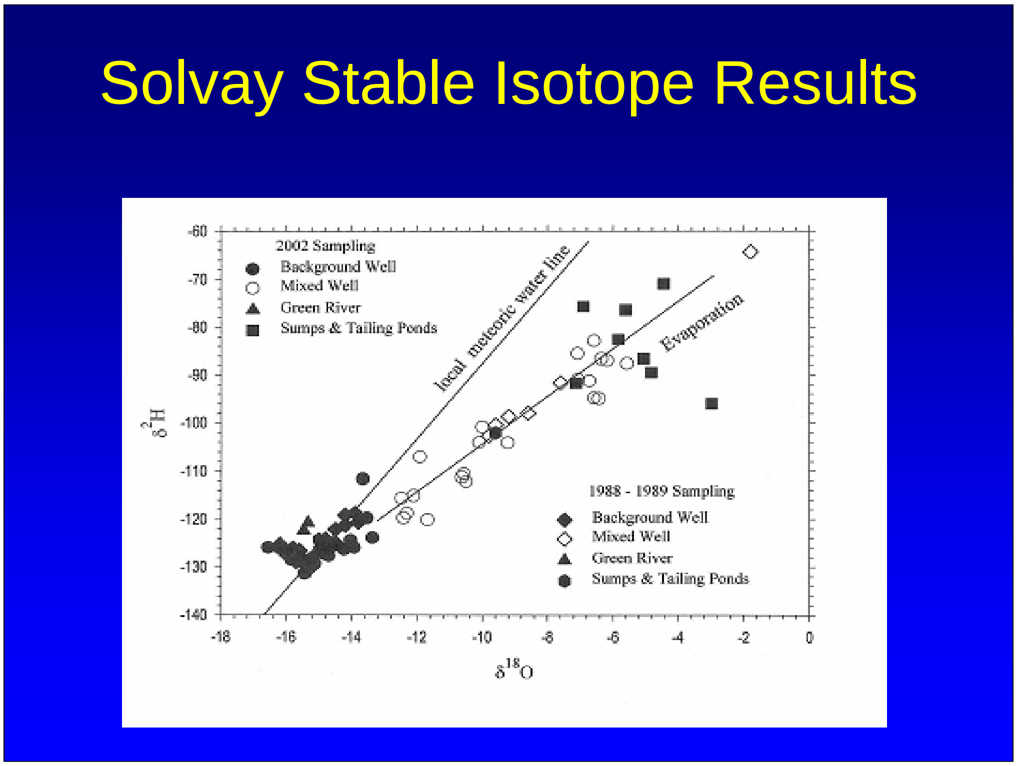
Solute Chemistry Results: Tailings pond fingerprint solutes were also naturally present in aquifers so monitoring results were not definitive.

Stable Isotope Results: Comparisons of data from water supply (river), tailings pond, and monitoring wells clearly showed the effects of strong evaporation in the tailings pond. Down gradient wells containing tailings pond seepage were clearly identified by results.

To wrap up our discussion on use of isotopes, I want to show a dramatic example of the use of stable isotopes to delineate groundwater impacts from tailings ponds in arid regions. This work was done at the Solvay Minerals trona plant near Rock Spring, Wyoming.

An extensive groundwater monitoring network of wells had been installed and the mining company desired to reduce monitoring frequency on wells that were considered outside of the influence of the seepage but could not definitively prove these wells were “background” based on groundwater solute chemistry. The alternative was to continue to monitor these wells to develop a statistical data base.

Stable isotope results for river water, tailings pond, and monitoring wells clearly showed which wells were affected by the tailings pond seepage and which were not. This provided the company with the evidence it needed to apply for reduced monitoring on certain wells.

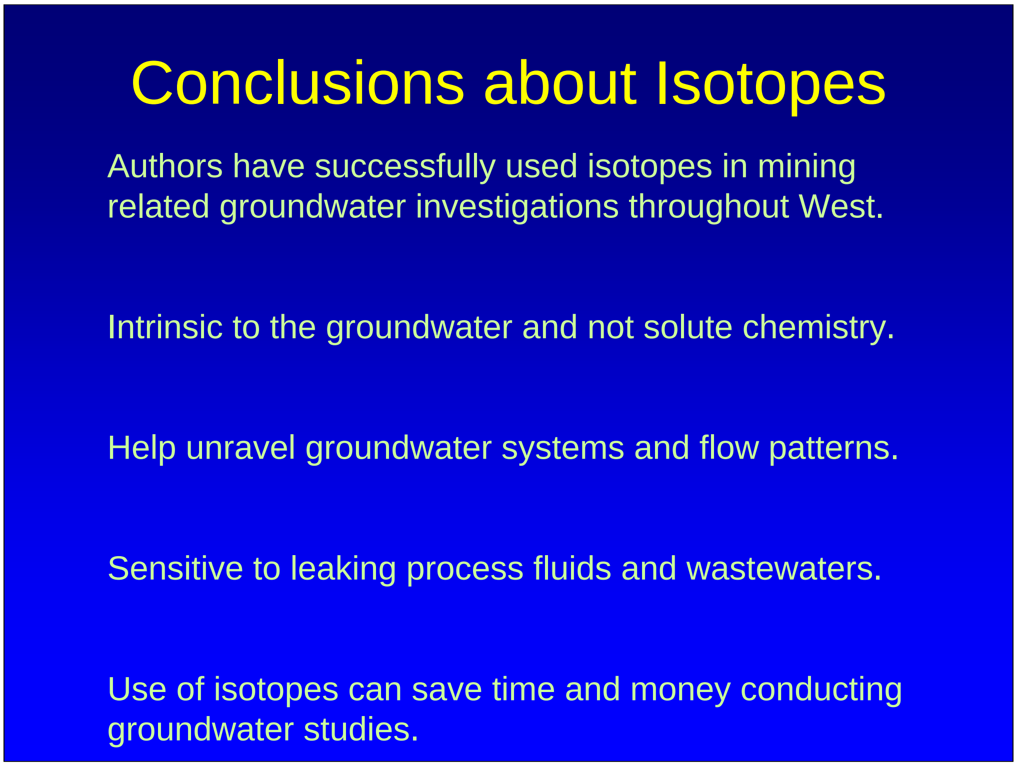


Solvay Stable Isotope Results

On this plot the black squares up to the right along the evaporation line are from the tailings ponds.

The water supply samples from the river and monitoring wells that are either upgradient or outside the influence of the tailings pond seepage are shown as black triangles and circles along the MWL.

The open circles and open diamonds are monitoring wells within the influence of the tailings pond seepage. The wells that have a greater percentage of tailings pond water are closest to the tailings pond values and the wells with the least amount of tailings pond seepage are closest to the MWL.



Conclusions about Isotopes

Authors have successfully used isotopes in mining related groundwater investigations throughout West.

Intrinsic to the groundwater and not solute chemistry.

Help unravel groundwater systems and flow patterns.

Sensitive to leaking process fluids and wastewaters.

Use of isotopes can save time and money conducting groundwater studies.

We have used environmental isotopes in concert with normal solute chemistry and hydrogeologic data to successfully answer questions related to potential mining impacts on groundwaters at mining sites in Utah, Colorado, Nevada, Idaho, and Wyoming.

The value of environmental isotopes is that they are intrinsic to the water itself and are not affected by chemical reactions in the flow paths.

Isotopes can be a valuable tool to the hydrogeologist in understanding local groundwater systems and flow patterns.

The isotopes discussed in this presentation are particularly sensitive to solving groundwater contamination problems involving mining process solutions and wastewaters.

Isotopes should be part of every such groundwater investigation to provide the highest probability of finding the answers in a timely manner and at lowest cost.