



P A S A D E N A  
Water & Power

**TECHNICAL MEMORANDUM ON  
STABLE ISOTOPE ANALYSIS OF  
INDUSTRIAL SOURCES OF  
PERCHLORATE, RAYMOND BASIN  
WELL SAMPLES, AND  
BIODEGRATION**

**AUGUST 2012**

## Introduction

The 2007 Technical Memorandum (TM) of the National Aeronautics and Space Administration (NASA) relies upon an analytical technique called Stable Isotope Analysis (SIA) to determine the source of perchlorate found in the Raymond Basin. Specifically, the TM argues that the degree of depletion of the ratio of  $^{18}\text{O}$  to  $^{16}\text{O}$  ( $\delta^{18}\text{O}$ ) from the expected ratio can be used to distinguish different industrial sources of perchlorate. The TM argues that there were three distinct industrial sources found, the "JPL Source", the BMI Complex in Henderson NV, and "Road Flares".

This brief memorandum will attempt to demonstrate two points: 1) the normal process of manufacturing perchlorate (electrolysis followed by anodic oxidation) normally produces a range of  $\delta^{18}\text{O}$  through mass-dependent fractionation and that any manufacturer will produce products with that same range. Thus, the degree of depletion of  $\delta^{18}\text{O}$  cannot be used to "fingerprint" the manufacturer of one perchlorate sample as opposed to another. 2) Even if it were possible, biodegradation of perchlorate in groundwater would alter those "fingerprints". Anaerobic bacteria consume  $^{16}\text{O}$  preferentially over  $^{18}\text{O}$ , changing the ratio ( $\delta^{18}\text{O}$ ) "smudging" the SIA fingerprint. This process can be clearly seen when examining the ratio of  $^{17}\text{O}$  to  $^{16}\text{O}$  ( $\delta^{17}\text{O}$ ). There is a pronounced difference in the depletion of  $\delta^{17}\text{O}$  between industrial samples and samples collected from wells in the Raymond Basin.

## Stable Isotope Analysis of Perchlorate

In the 2007 TM there are two figures (16 and 17, Figures 1 and 2 in this document) showing the SIA of perchlorate taken from a number of locations in the Raymond Basin, around Henderson Nevada, and various solid samples collected from the BMI Complex, fireworks, and a road flare. The TM argues that different sources of industrial perchlorate can be distinguished by the relative depletion of  $\delta^{18}\text{O}$  as compared to Vienna Mean Standard Ocean Water. In particular, it is argued that there are several different sources of perchlorate found in the Raymond Basin, which are readily distinguished from each other in this manner. The TM says...

*"Stable Isotope Analysis (SIA) of the oxygen and chlorine in perchlorate shows that synthetic perchlorate in the Monk Hill and JPL area is from a different source than synthetic perchlorate found in the Sunset Reservoir area. The source of perchlorate in the Sunset Reservoir area is a mixture of other, non-JPL, perchlorate sources including: perchlorate from Colorado River water (based on archive samples from the facility in Henderson Nevada taken in the late 1980s) as well as possibly perchlorate from unburned road flares, fireworks and small contributions from natural sources."*

The TM argues that there are actually three distinct sources of industrial perchlorate, which can be distinguished by their relative depletion of  $\delta^{18}\text{O}$ :

- 1) The "JPL Source" which would be the Los Angeles Facility of the Western Electro-Chemical Company (WECCO). According to NASA's TM: "Perchlorate

originating from JPL has a distinct isotopic signature, with a  $\delta^{18}\text{O}$  values ranging between approximately -19‰ and -21‰”.

- 2) The BMI Complex in Henderson Nevada, also owned by WECCO. According to NASA's TM: "The isotopic compositions of perchlorate in wells MW-19, MW-25, Sunset, Garfield, and LFWC#2 are similar to those of fireworks, road flares, perchlorate manufactured at the BMI complex in southern Nevada, and a surface water sample taken from the Las Vegas Wash as well as a groundwater sample taken near the BMI complex."
- 3) Road Flares. According to NASA's TM: "The isotopic composition of perchlorate in LFWC#2 approaches that which is characteristic of perchlorate used in road flares."

Pasadena Water and Power (PWP) has argued previously that these distinctions are unjustified for a variety of reasons. Rather, PWP has argued that the distribution of results seen in these two figures in the TM is the normal range of  $\delta^{18}\text{O}$  produced during the electrolysis and anodic oxidation processes used to manufacture perchlorate and biodegradation. While there is no need to reproduce those arguments here, there is additional information, which sheds light on this argument, which PWP feels compelled to advance.

#### **Sturchio et al. 2006**

At the bottom of both Figure 16 and 17, reference is made to a paper by Sturchio et al. 2006. This work is called "Chapter 5 Stable Isotopic Composition of Chlorine and Oxygen in Synthetic and Natural Perchlorate" in a book titled "Perchlorate: Environmental Occurrence, Interactions and Treatment Baohua Gu and John D. Coates, editors, Springer, New York (2006)". The authors, among other things, perform (SIA) on a variety of industrial perchlorate samples from American Pacific Company, which owns WECCO, and from the current WECCO facility in Utah. They also analyzed a variety of "laboratory reagents" containing perchlorate from manufacturers of laboratory chemicals such as Sigma, Aldrich (which became the same company in 1975, Sigma-Aldrich), Mallinckrodt, and Baker (which became the same company, Mallinckrodt-Baker, in 1995). One firm, Hummel-Croton, is included in this group, but it is not actually a manufacturer of laboratory reagents, but a supplier of materials for production of pyrotechnics and road flares. Tables 1 and 2 from this chapter are presented at the end of this memorandum.

If the results from laboratory reagents and the production materials from Table 2 are plotted, Figure 3 and 4 are produced. As can be seen, the range of  $\delta^{18}\text{O}$  is nearly identical to that seen in Figures 1 and 2, roughly -25 to -10 with comparatively little variability in either  $\delta^{17}\text{O}$  or  $\delta^{37}\text{Cl}$ . Indeed, the range of  $\delta^{17}\text{O}$  is extremely small for the manufactured samples, -0.04 to 0.12. This was observed in previous studies as well e.g. Böhlke et al. 2005 notes that "There is no measurable variation in the  $\delta^{17}\text{O}$  values of the synthetic perchlorates ( $\delta^{17}\text{O} = 0.00 \pm 0.06$ ,  $n = 16$ )." The range for  $\delta^{37}\text{Cl}$  was somewhat wider 0.4 to 1.3 (with one significant exception, ORNL-6 / EM lot # SX0693-2, which had a very large negative value of -3.1). Since this study was conducted in

2006, long after the BMI Complex in Henderson NV was destroyed, it is unlikely that any of these samples originated at that facility (and of course most certainly not from WECCO's Los Angeles facility). It is unlikely that all of these samples were manufactured at separate facilities, but were probably prepared from perchlorate manufactured by other firms, probably WECCO.

The perchlorate found in the samples collected from the Raymond Basin wells in 2005 originated in the 1940's and 1950's although a smaller proportion no doubt originated at a later date. The samples analyzed in the Sturchio et al. 2006 paper are undoubtedly from a later manufacture date and from different facilities. Despite these differences in time and place of manufacture, the range of  $\delta^{18}\text{O}$  is nearly identical. What this data strongly suggests is that the range of  $\delta^{18}\text{O}$  seen in the Raymond Basin well samples does not represent a series of different unique ranges from different manufacturers, but is simply the natural range of the industrial process for the production of perchlorate. All perchlorate is manufactured in the same process, electrolysis of brine and anodic oxidation of chlorate using platinum or lead oxide anodes. The process appears to favor incorporation of  $^{16}\text{O}$  and  $^{17}\text{O}$  over  $^{18}\text{O}$  and manufactured perchlorate is depleted in  $^{18}\text{O}$  as compared to  $^{16}\text{O}$  and  $^{17}\text{O}$ . This was no doubt as much the case in the 1940's as in the 2000's.

Figures 5 and 6 show the SIA for both the solid samples in Sturchio et al. 2006 and the Raymond Basin groundwater samples. As can be seen, the range of  $\delta^{18}\text{O}$  is nearly identical for the industrial samples and the Raymond Basin groundwater samples, as is the case for  $\delta^{37}\text{Cl}$  as well. Notably, the results for Bangham Well with its depleted  $\delta^{37}\text{Cl}$  value, which was supposed to be indicative of blending with Chilean Nitrate Fertilizer, is not so different from the EM solid sample. It would seem that at least one industrial source produced perchlorate with depleted  $\delta^{37}\text{Cl}$  as compared to other industrial sources.

### **Anaerobic Biodegradation**

Many of the same authors who produced Sturchio et al. 2006 also produced a second paper, Sturchio et al 2007, which examined how anaerobic biodegradation effects SIA of perchlorate. Bacteria preferentially consume the  $^{16}\text{O}$  over  $^{18}\text{O}$ , as well as  $^{35}\text{Cl}$  over  $^{37}\text{Cl}$  (this is discussed in more detail in our Technical Memorandum of June 2012). As a result, perchlorate subject to biodegradation tends to become less depleted in  $^{18}\text{O}$ , and  $^{37}\text{Cl}$  (Sturchio et al. 2006, Hatzinger et al. 2009). An examination of Figures 5 and 6 shows this same pattern. The results are arranged for the Raymond Basin wells generally lower left to upper right indicating a movement toward less depletion, which is indicative of biodegradation.  $\delta^{17}\text{O}$  probably is the most sensitive measure of biodegradation as it has the least variability in among the industrial samples by a considerable bit. The mean value was 0.022 with a standard deviation of 0.046 (the median was 0.005) while the mean for  $\delta^{18}\text{O}$  was -17.7 with a standard deviation of 3.33 and the mean for  $\delta^{37}\text{Cl}$  was 0.606 with a standard deviation of 1.03. The difference appears to be statistically significant using the Student's t-test ( $t=-2.9$ ,  $p = 0.003$ , the 95% Confidence Interval for the difference is -0.99 to -0.17).

Sturchio et al. 2011 ("Chapter 22: Isotopic Tracing of Perchlorate in the Environment" in the Handbook of Environmental Isotope Geochemistry, Volume 1 Edited by Mark Baskaran), which says "*Biodegradation of  $\text{ClO}_4^-$  produces systematic stable isotope enrichments that do not significantly affect  $\delta^{17}\text{O}$  values or  $^{36}\text{Cl}/\text{Cl}$  ratios, thus potentially allowing detection of biodegradation without masking the initial source(s) of  $\text{ClO}_4^-$*  (Sturchio et al. 2007; Hatzinger et al. 2009)." Unfortunately, Sturchio et al. 2006, Hatzinger et al. 2009 do not present any data on  $\delta^{17}\text{O}$  at all; so there is no precedent in the literature for the assessment of  $\delta^{17}\text{O}$ . However, the same principles of mass dependent fractionation should apply. If bacteria preferentially consume  $^{16}\text{O}$  over  $^{18}\text{O}$ , there is no reason not to believe that they will not also prefer  $^{16}\text{O}$  over  $^{17}\text{O}$ .

In examining Figure 5 with the  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ , not only is the data from the ground water samples arrayed along an axis of lower left to upper right as would be expected from anaerobic biodegradation, but the average value for the groundwater samples are much higher than the industrial samples, and there is a great deal more variability in the groundwater  $\delta^{17}\text{O}$  as compared to the industrial samples. The mean  $\delta^{17}\text{O}$  value for the groundwater samples was 0.604 with a standard deviation of 0.85 (the median was 0.145), which is much higher and more variable than the industrial samples. The First Order Linear Regression (1<sup>st</sup> OLR) curve for the groundwater samples had a slope of 3.0 ( $R = 0.51$ ,  $p = 0.06$ ) while for the industrial samples the slope was 0.07 ( $R=0.20$ ,  $p=0.44$ ). The difference between the groundwater samples and the industrial samples is very clear and indicates biodegradation.

The data from  $\delta^{37}\text{Cl}$  vs.  $\delta^{18}\text{O}$  (Figure 6) is more difficult to interpret. As already noted, there is a great deal more noise in the industrial samples and there is a very low  $\delta^{37}\text{Cl}$  (EM lot # SX0693-2) as there is for the groundwater samples (Bangham Well). The average values for  $\delta^{37}\text{Cl}$  is not very different between the two groups of samples (0.61 for the industrial samples vs. 0.37 for the groundwater samples) and the standard deviations are nearly identical (1.03 for the industrial samples vs. 1.29 for the groundwater samples). The 1<sup>st</sup> OLR curve for the groundwater samples had a slope of -3.1 ( $R = 0.49$ ,  $p = 0.10$ ) while for the industrial samples the slope was 0.01 ( $R=0.04$ ,  $p=0.88$ ) which provides little information. However, if both the EM lot # SX0693-2 and Bangham Well data is removed, the slope of the groundwater samples changes dramatically (2.2,  $R = 0.26$ ,  $p = 0.46$ ) while the slope for the industrial samples changes only somewhat (1.3,  $R=0.23$ ,  $p=0.39$ ). This is not nearly as conclusive as the  $\delta^{17}\text{O}$  data, but it is supportive of its conclusions.

However, even if anaerobic biodegradation were somehow excluded as a possible explanation of this very significant change in the distribution of  $\delta^{17}\text{O}$  results in the Raymond Basin well water as compared to the industrial samples, clearly some mass-dependent fractionation process is occurring. Whether the process is microbially mediated or abiotic ultimately does not change the significance of these results.

## Conclusions

The SIA data from the Raymond Basin wells, when compared with the SIA data from the industrial samples analyzed in Sturchio et al. 2006, make a compelling case that the normal industrial processes for producing perchlorate, electrolysis and anodic oxidation, produce products with very little variability in  $\delta^{17}\text{O}$ , some variability in  $\delta^{37}\text{Cl}$  and a great deal of variability in  $\delta^{18}\text{O}$  compared to the groundwater samples. Contrary to the assertions of NASA's 2007 TM, using the  $\delta^{18}\text{O}$  cannot distinguish one industrial source from another, any manufacturer can produce perchlorate anywhere along the normal range of -26 to -10. Since there is naturally very little variability in  $\delta^{17}\text{O}$ , it is the most sensitive measure of anaerobic biodegradation. Using this tool, there is clear evidence that anaerobic biodegradation is occurring.

Figure 1

Figure 16 from NASA's TM Showing the SIA Using  $\delta^{37}\text{Cl}$  and  $\delta^{18}\text{O}$  for Groundwaters and Other Solid Samples

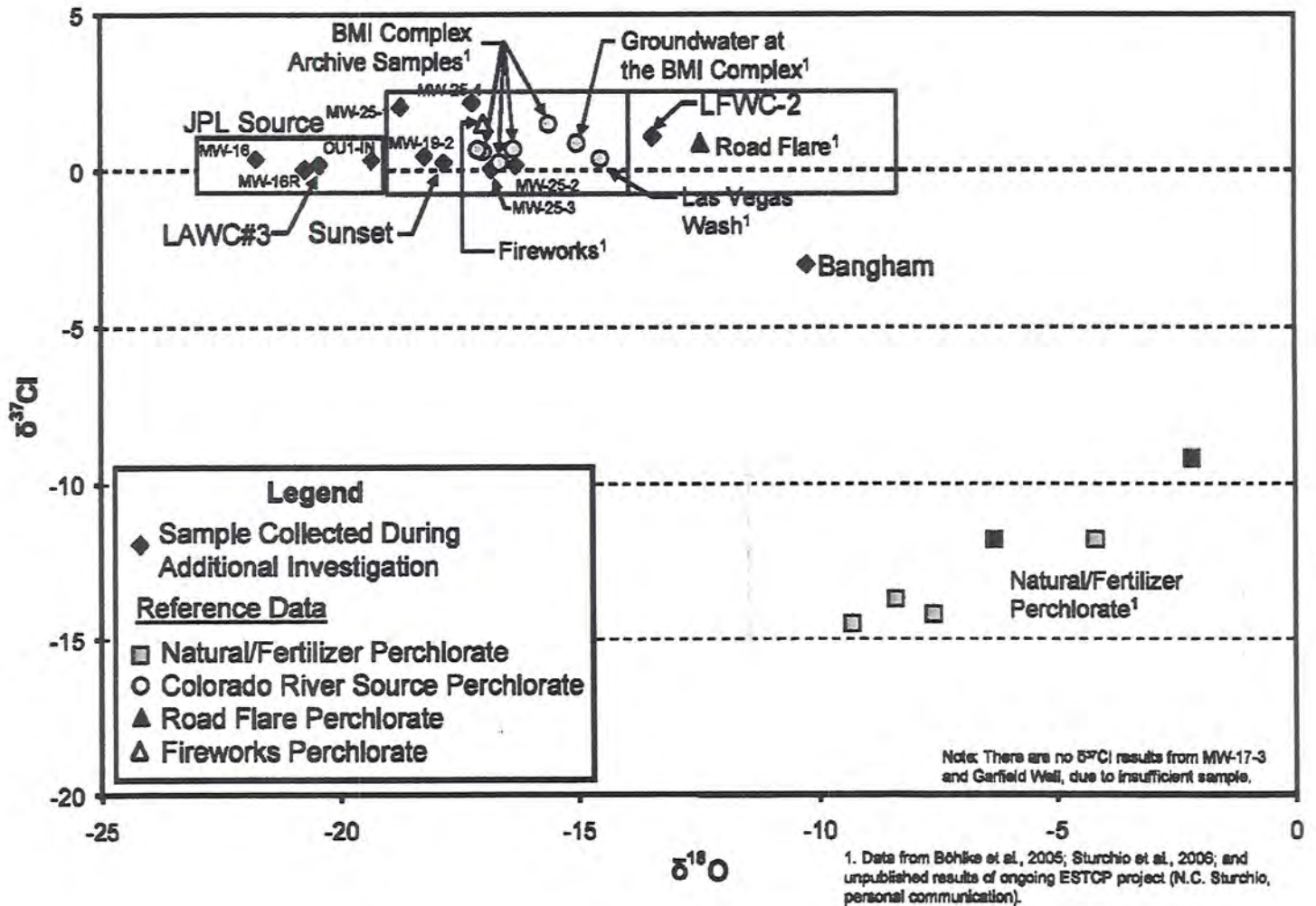


Figure 2

Figure 17 from NASA's TM Showing the SIA Using  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for Groundwaters and Other Solid Samples

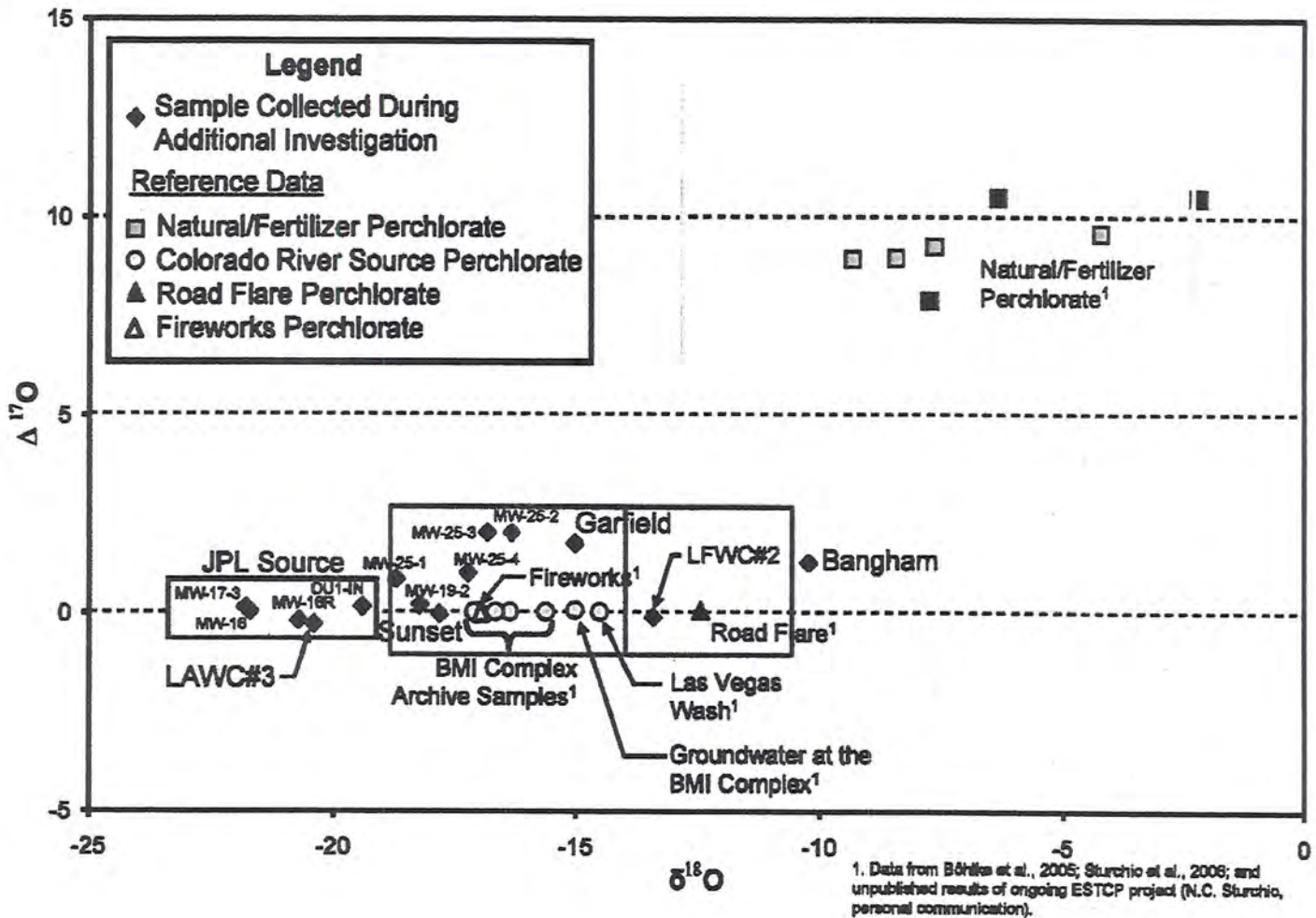




Figure 3

SIA Using  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for Solid Samples from Sturchio et al. 2006

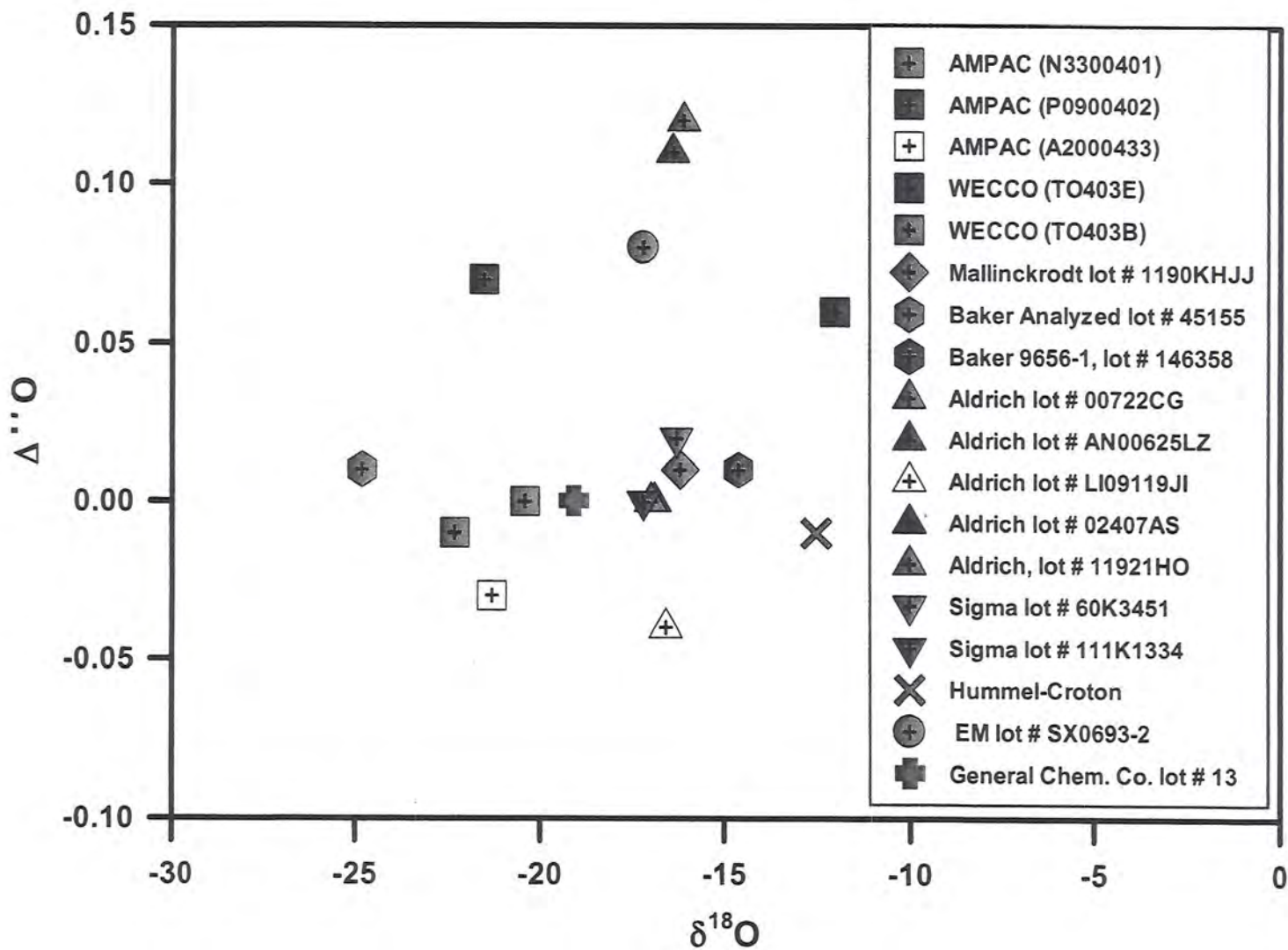


Figure 4

SIA Using  $\delta^{37}\text{Cl}$  and  $\delta^{18}\text{O}$  for Solid Samples from Sturchio et al. 2006

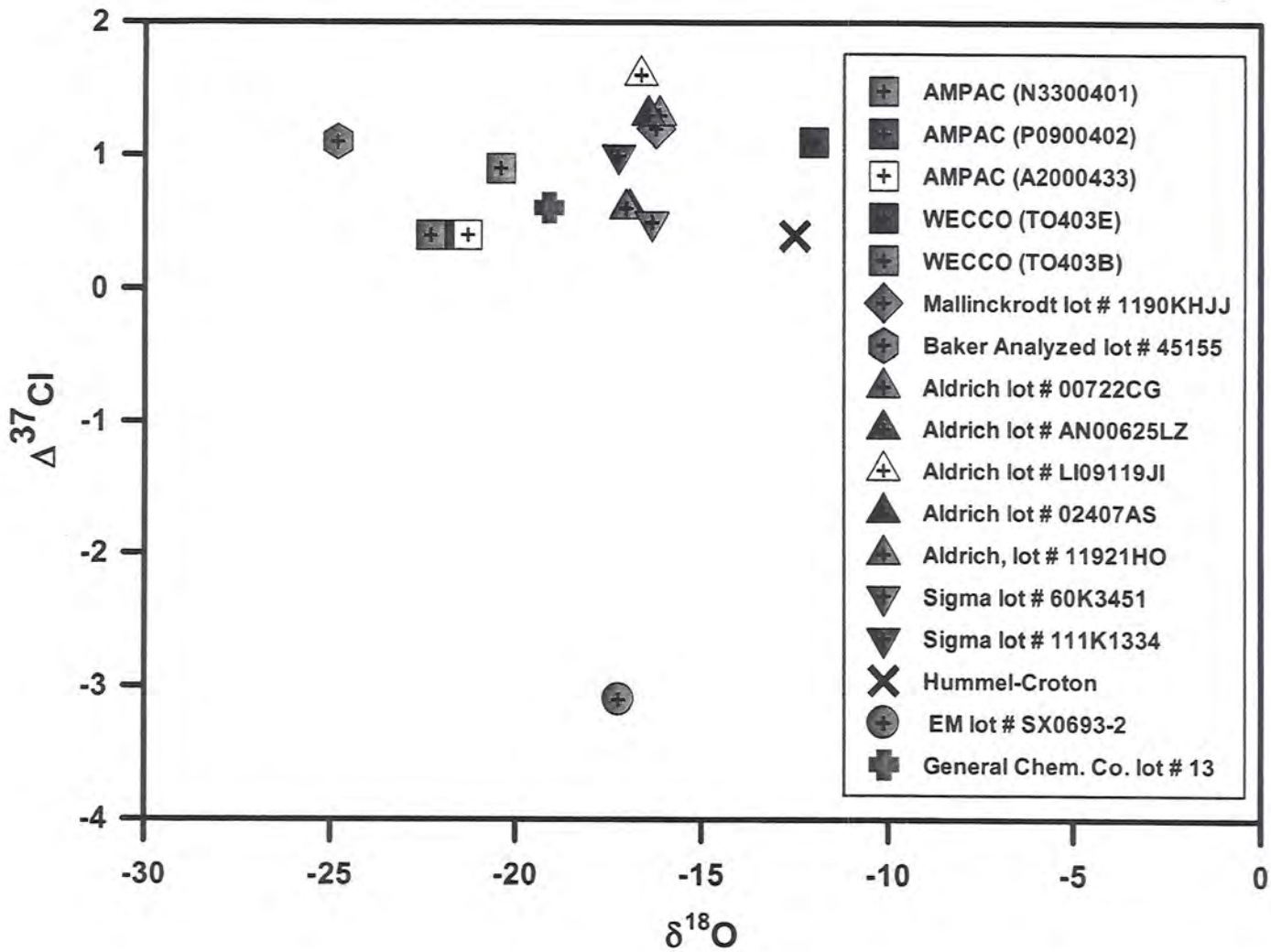


Figure 5

SIA Using  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for Solid Samples from Sturchio et al. 2006  
And Groundwater from the Raymond Basin

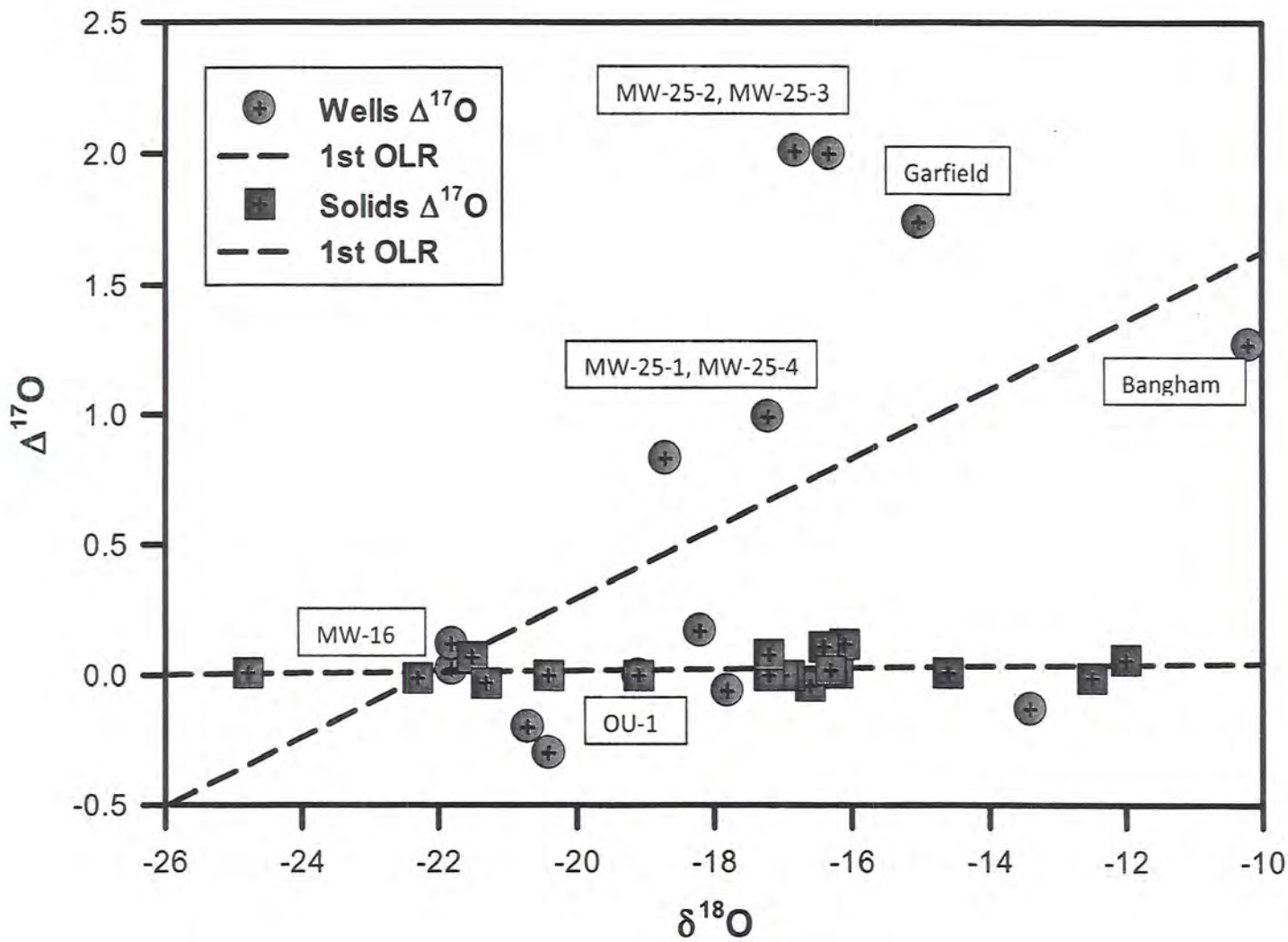


Figure 6

SIA Using  $\delta^{37}\text{Cl}$  and  $\delta^{18}\text{O}$  for Solid Samples from Sturchio et al. 2006  
And Groundwater from the Raymond Basin

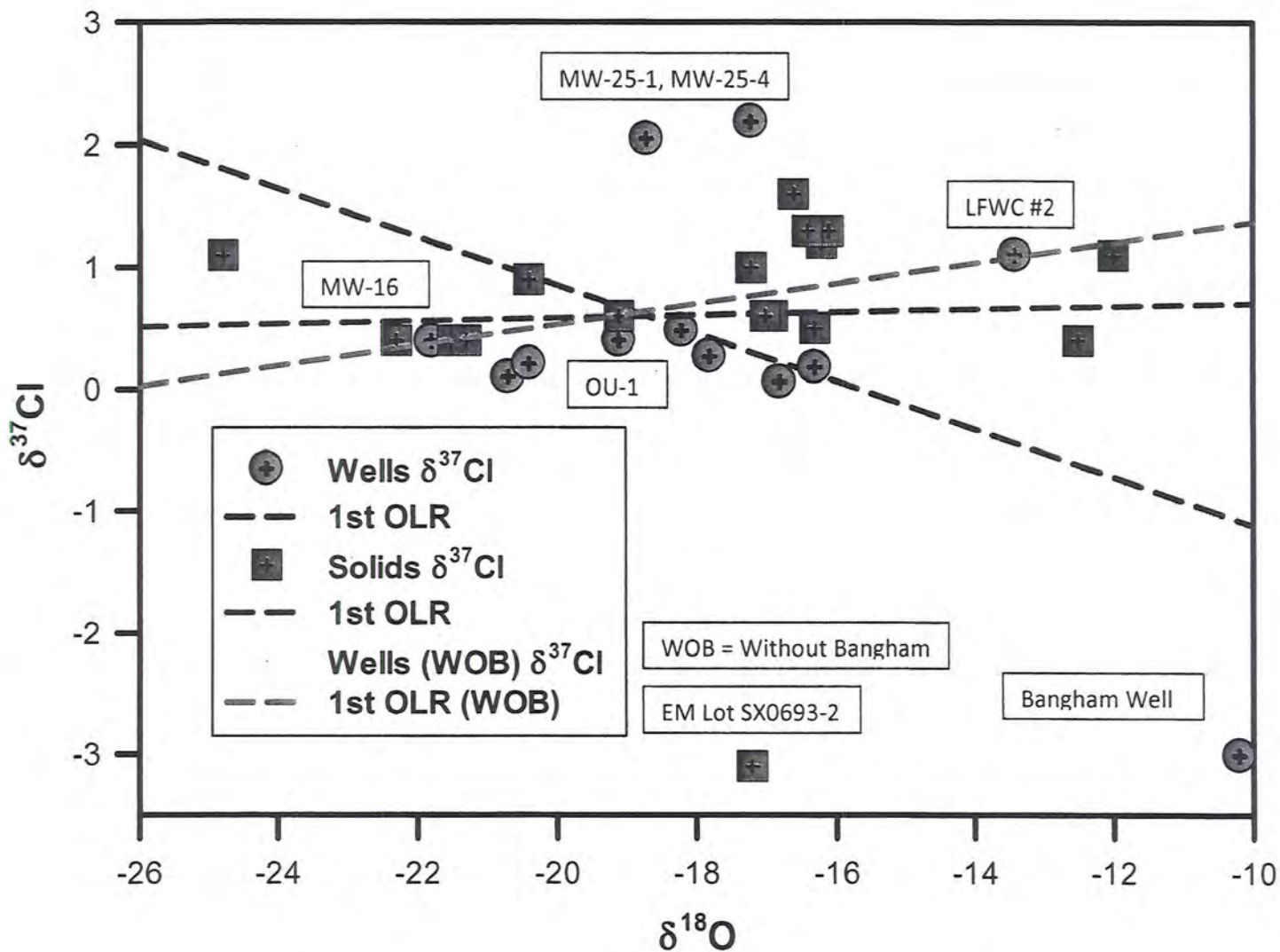


Table 1. Identification of perchlorate samples

Sample Identification	Compound	Description
<i>Laboratory Reagents</i>		
UIC-1	NaClO <sub>2</sub>	Mallinckrodt lot # 1190KHJJ
UIC-2	KClO <sub>4</sub>	Baker Analyzed lot # 45155
UIC-3	NaClO <sub>4</sub> ·H <sub>2</sub> O	Aldrich lot # 00722CG
UIC-8	KClO <sub>4</sub>	Sigma lot # 60K3451
UIC-9	NaClO <sub>4</sub>	Sigma lot # 111K1334
UIC-10	KClO <sub>4</sub>	Hummel-Croton
ORNL-6	NaClO <sub>4</sub> ·H <sub>2</sub> O	EM lot # SX0693-2
ORNL-8	KClO <sub>4</sub>	General Chem. Co. lot # 13
ORNL-9	RbClO <sub>4</sub>	Aldrich lot # AN00625LZ
ORNL-10	CsClO <sub>4</sub>	Aldrich lot # LI09119JI
ORNL-11	CsClO <sub>4</sub>	Aldrich lot # 02407AS
RSIL-2	HClO <sub>4</sub>	Baker 9656-1, lot # 146358
RSIL-4	KClO <sub>4</sub>	Aldrich, lot # 11921HO
<i>Production Materials</i>		
UIC-5	NaClO <sub>4</sub>	American Pacific Co. (N3300401)
UIC-6	KClO <sub>4</sub>	American Pacific Co. (P0900402)
UIC-7	NH <sub>4</sub> ClO <sub>4</sub>	American Pacific Co. (A2000433)
ORNL-18	NaClO <sub>3</sub>	Western Electrochemical Co. (TO403E)
ORNL-19	NaClO <sub>2</sub>	Western Electrochemical Co. (TO403B)
ORNL-20	H <sub>2</sub> O	Water used by WE (6/23/04)
NaCl (TO415D)	NaCl	NaCl feedstock used by WE
<i>Natural Perchlorate</i>		
ORNL-2	KClO <sub>4</sub>	Commercial Hoffman fertilizer
ORNL-4	CsClO <sub>4</sub>	Commercial Hoffman fertilizer
ORNL-5	CsClO <sub>4</sub>	Atacama, Chile nitrate salt (AT-74-1)
ORNL-12	CsClO <sub>4</sub>	SQM fertilizer (RSIL N7791)
<i>Groundwater and Surface Water</i>		
ORNL-14	CsClO <sub>4</sub>	Groundwater at Edwards AFB, CA
ORNL-16	CsClO <sub>4</sub>	Surface water, Las Vegas Wash
ORNL-17	CsClO <sub>4</sub>	Groundwater, Henderson NV
ORNL-21	CsClO <sub>4</sub>	West Texas groundwater (TTU-G1S)
ORNL-22	CsClO <sub>4</sub>	West Texas groundwater (TTU-M3L)
CPMW-5*	NaClO <sub>4</sub>	Indian Head, MD groundwater (2002)
TPMW-5*	NaClO <sub>4</sub>	Indian Head, MD groundwater (2002)
<i>Method Tests</i>		
ORNL-15	CsClO <sub>4</sub>	Prepared from ORNL-6
UIC-4	NaClO <sub>4</sub>	Prepared from UIC-1
RSIL-3	HClO <sub>4</sub>	Prepared from RSIL-2

\* perchlorate extracted from Indian Head samples by method of Ref. 22

Table 2. Stable Isotope Ratios of Cl and O\*

Sample Identification	$\delta^{37}\text{Cl}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}^{**}$
<i>Laboratory Reagents</i>			
UIC-1	+1.2	-16.2	+0.01
UIC-2	+1.1	-24.8	+0.01
UIC-3	+1.3	-16.1	+0.12
UIC-8	+0.5	-16.3	+0.02
UIC-9	+1.0	-17.2	0.00
UIC-10	+0.4	-12.5	-0.01
ORNL-6	-3.1	-17.2	+0.08
ORNL-8	+0.6	-19.1	+0.00
ORNL-9	+1.3	-16.4	+0.11
ORNL-10	+1.6	-16.6	-0.04
ORNL-11	+0.6	-16.9	+0.00
RSIL-2	n.a.	-14.6	+0.01
RSIL-4	+0.6	-17.0	+0.00
<i>Production Materials</i>			
UIC-5	+0.4	-22.3	-0.01
UIC-6	+0.4	-21.5	+0.07
UIC-7	+0.4	-21.3	-0.03
ORNL-18	+1.1	n.a.	+0.06
ORNL-19	+0.9	-20.4	+0.00
ORNL-20	n.a.	-13.5	n.a.
NaCl (TO415D)	+0.2	n.a.	n.a.
<i>Natural Perchlorate</i>			
ORNL-2	-13.7	-8.4	+8.95
ORNL-4	-14.5	-9.3	+8.93
ORNL-5	-11.8	-4.2	+9.57
ORNL-12	-14.2	-7.6	+9.25
<i>Groundwater/ Surface Water</i>			
ORNL-14	-0.9	-15.8	+0.04
ORNL-16	+0.4	-14.5	+0.00
ORNL-17	+0.9	-15.0	+0.02
ORNL-21	+6.2	+4.7	+0.42
ORNL-22	+5.1	+2.5	+0.49
CPMW-5	+0.2	n.a.	n.a.
TPMW-5	+1.1	n.a.	n.a.
<i>Method Tests</i>			
ORNL-15	-3.2	-17.2	n.a.
UIC-4	n.a.	-16.3	-0.13
RSIL-3	n.a.	-14.7	n.a.

\* All values reported in per mil

\*\*  $\Delta^{17}\text{O} = [[(1 - \delta^{17}\text{O} \cdot 1000) \cdot (1 + \delta^{18}\text{O} \cdot 1000)^{0.525}] - 1] \times 1000$ 

n.a. = not analyzed