

1 Temporal variability in the isotopic composition of meteoric  
2 water in Christchurch, New Zealand; Can we create reliable  
3 isoscapes?

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6 **Abstract**

7 Stable isotopes are being used world wide in order to understand hydrologic,  
8 biologic, and climatic changes due to natural and human processes. Using stable  
9 isotopes as a tool can give detailed accounts of the past and origin of certain processes.  
10 While the earth is undergoing abrupt changes in atmospheric temperatures, demand for  
11 information on hydrologic processes is increasing. Unfortunately, there is limited data  
12 available to predict isotopic processes in the hydrological system. A current study in  
13 New Zealand is constructing a computational model that is attempting to predict  
14 isoscapes through a computational model. In this study, this model will be compared  
15 against past-observed data in order to prove or disprove the reliance of the GNS  
16 isoscape model.

17 **Introduction**

18 Stable isotope analysis can be used globally in order to understand the historical  
19 lifespan of any natural system containing nitrogen, carbon, oxygen, and hydrogen. For  
20 this study the process of focus is the hydrologic system, but stable isotopes can be used  
21 in biologic and anthropologic investigations as well. The value of isoscapes has  
22 increased because it allows opportunities to use isotopic variability as a source of  
23 information on the connectivity, variability, and sensitivity to change of climatological,  
24 hydrological, and biogeochemical processes (Isoscapes 2011). On a global scale, the  
25 understanding of the hydrologic system is relatively low because of the dynamic shifts  
26 in hydrology. Analysis of these elements allows for investigations into the atmospheric  
27 conditions occurring during the origination of a particular molecule. The focus of  
28 discussion here is the hydrologic system. This system is a very complicated and is hard  
29 to map as an isoscape because of the continuous fluctuations in the water cycle. Bowen,  
30 attempted to construct an isoscape for oxygen-18 in precipitation, but found much  
31 difficulty when mapping the oxygen isotopes due to high variability of precipitation

32 (2003). An example of this isoscape is shown in figure 1.

33 GNS, New Zealand's leading science/isotope research agency has developed a  
34 computational model that attempts to map New Zealand's hydrologic isoscape based on  
35 oxygen and hydrogen compositions. Stable isotopes such as oxygen and hydrogen are  
36 well known for the abundance of information that can provide about the past and also  
37 modern climatic processes. This information provides opportunities to exploit  
38 spatiotemporal variability in isotopes as a source of information on the sensitivity of  
39 climatic, biologic, and hydrologic changes (Isoscapes 2011). Creation of computational  
40 models creates controversy due to the inconclusiveness of the maps, the extreme level  
41 of difficulty producing these maps and also, the models have not been rigorously tested  
42 against observational data sets and used outside of the climate modeling community  
43 (Bowen 2010).

#### 44 **Background**

45 In order to do a complete and accurate analysis of water isotopes, the basics of  
46 water isotopes must be understood. In Gat's (1996) synthesis to the hydrologic system,  
47 he notes that the isotopic composition of precipitation will become increasingly  
48 important in the interpretation of past climates but further studies of stable isotopes  
49 and application to the hydrologic system need to be investigated. Throughout the past  
50 few decades, more accounts on water isotopes have been produced to conclude a few  
51 factors are necessary for complete understanding of the variability of water isotopes. In  
52 general, the paleoclimate of a given area can be understood by tracing the hydrological  
53 cycle through the isotopic signatures provided by the water molecules (SAHRA 2005).  
54 Hydrogen and oxygen ratios are analyzed based on their isotopic fractionation formed  
55 through different phase changes during an event (Schmidt, 2006), therefore different  
56 ratios will mean different areas of origination. That being said, humid environments  
57 have high deuterium (more d-excess) values, while arid environments are low in  
58 deuterium (less d-excess). Figures 2 and 3 provide a visual explanation of this  
59 information along with examples of regions and where they lie in the plot. Additionally  
60 figures 2 and 3 display the global meteoric water line and exemplify seasonal changes  
61 along this line. *Because  $d_{18O}$  and  $d_2H$  values have a strong positive correlation with*  
62 *temperature, their measurements in ice cores are valuable indicators of climate variability.*  
63 *Values can be used to date snow and determine average snow accumulation rates.*

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## 65 **Geologic Setting**

66 On a local scale, Christchurch sits in the Canterbury plains with the Southern  
67 Alps to the West and the Pacific Ocean to the East. Christchurch, therefore, experiences  
68 rain shadow effects on a frequent basis due to the high altitude Southern Alps (See  
69 figure 4a, and 4b). Since Christchurch only receives about 600-800 mm of rainfall per  
70 year, so they rely on surface and ground water to replenish human and agricultural uses  
71 but are rather limited when it comes to water sources being replenished.

72 In an area that is already lacking in water recharge from precipitation, global  
73 climate change will begin to increase evaporation rates higher than what they are now.  
74 The Canterbury plains are located geographically in an area where evaporation rates  
75 exceed precipitation rates (Blackstock 2010); therefore further research into climate  
76 and water sources is needed to understand the changing weather patterns in  
77 Christchurch.

78 The importance of studying meteoric water has become very popular over the  
79 years, and studies have become refined, but also more complex. Sourcing and  
80 understanding the processes that occurred during origin can give us good clues into  
81 past climate structures (SAHRA 2005).

## 82 **Methods**

83 Several methods were used in order to calculate the data sets. First and foremost,  
84 observed data sets were used from two different sources of research. Both forms of  
85 information used isotopic analyses when obtained the isotopic compositions of the daily  
86 and monthly data, therefore the data is 100 percent reliable. The daily and hourly isotopic  
87 compositions were used from Blackstock 2010 in order to compare the calculated isotopic  
88 compositions from the GNS computational model. The data used for the monthly averages  
89 was used from Taylor 1990. These data sets were then compared against calculated data  
90 from the GNS isotopic composition model for precipitation events. The Virtual Climate  
91 Station Network (VCSN) provided the rain data used to calculate isotopic compositions  
92 using the GNS computational model. Wind data was also obtained for these models for the  
93 years of 1984-1986 from The National Climate Database (CliFlo). All data was used from  
94 the same latitude and longitude coordinates of -43.525 and 172.575 respectively. During

95 original data collection approximately 70% of the precipitation was collected (Blackstock,  
96 2010), although a few discrepancies were found during this data check. These  
97 inconsistencies are displayed in Chart 1.

98 Several aspects of precipitation were looked at during this experiment. In no  
99 particular order, the isotopic compositions of oxygen-18, hydrogen-2 and d-excess were  
100 calculated using the GNS model. These calculations include 18 daily calculations, during  
101 24 hour periods of time (from Blackstock, 2010), as well as monthly calculated data for the  
102 years of 1984-1986. The daily and monthly calculations were then used to plot the GNS  
103 model against the observed data as well as along the Global Mean Water Line.

#### 104 **Results**

105 Attempts to model isoscapes based on computation have been proven unreliable  
106 during this experiment. On a larger scale, monthly data was used in order to compare the  
107 modeled data against observed and analyzed data. In figures 5 through 7, the GNS  
108 modeled data is plotted against observed monthly data (Taylor, 1990). Figure 5 presents  
109 the  $\delta^{18}\text{O}$  oxygen data, which shows no significance based on the r-squared value of 0.32, 0.31,  
110 0.12 for 1984, 1985, and 1986 respectively. Figure 6 also displays no significance through  
111 all three years ( $R^2 = 0.23, 0.21, 0.03$ , respectively). Figure 7, also with no significance,  
112 represents d-excess values over the three years. Figure 8 is the two sets of data, observed  
113 and modeled, plotted against the GMWL over a three-year period. The trends shown are  
114 plotting along the same line trending with each other.

115 The GNS isotope model was used in order to calculate monthly data. In figures 9-  
116 12, values produced by the GNS model were plotted against values from observed and  
117 analyzed daily/hourly models (Blackstock, 2010). Figure 9 displays the computed GNS  
118 model plotted against observed data in regards to Oxygen-18 isotopes. The data  
119 produced shows no significance with an R-squared value of 0.07. In figure 10 the same  
120 plot was used in order to display Hydrogen-2 isotopes. This data was also insignificant  
121 with an r-squared value of 0.17. Values shown in the plot in regards to d-excess in  
122 figure 11 also show no significance with an r-squared value of 0.02. In figure 12 the  
123 projected hydrogen-2/oxygen-18 values were used to plot along the GMWL along with  
124 the observed data. The plots show little correlation along this line.

#### 125 **Discussion**

126 Mapping and understanding the water cycle is a lengthy and complex task that

127 requires a number of analyses for higher reliability. Because of the variability of  
128 precipitation patterns, hydrogen-2 and oxygen-18 values are relatively difficult to map  
129 into isoscapes and have only been mapped by atmospheric circulation models (Bowen,  
130 2010). Unfortunately, GNS's attempt to create a computational model that can calculate  
131 isotopic compositions is showing low reliability rates based on the values found in the  
132 results.

133         The monthly data was used to observe the model over a larger amount of time  
134 versus daily isotopic models. The calculated isotopic composition was plotted against  
135 observed data in order to display whether there was a correlation between the two  
136 values. These calculations were used for hydrogen-2, oxygen-18 and d-excess and there  
137 was no significance found in any of the isotopic compositions at any point over the three  
138 years evaluated (figures 4, 5, and 6). In figure 7, it can be assumed that there is a  
139 correlation based on r-squared values and general observations but due to the large  
140 amount of values used to produce the figure, it has a percentage of presumed error.

141         The daily data followed the format from above; plotting the GNS modeled data  
142 against the observed data. There was, again, no significance found in any of the plots in  
143 figures 8, 9, and 10. In figure 11 the ratio of hydrogen-2 and oxygen-18 were plotted  
144 along the GMWL. A noticeable difference is seen in the variation of the two different  
145 data sets. The observed data is displaying isotopes of warmer, low-latitude/altitude  
146 and coastal regions while the GNS modeled isotope data is showing a cooler, high-  
147 latitude/altitude, and inland region.

148 Due to the insignificance of the data, it is conclusive to say that the computational model  
149 produced needs to be refined and tested against real isotopic compositions.

## 150 **Conclusion**

151         Although a computational model would advance research in the field of isotopes  
152 and precipitation, the data produced through calculations show insignificant trends for  
153 this model to be considered reliable in creating isoscapes for New Zealand. It has been  
154 dually that prediction models for isotopic compositions may never be developed  
155 because of the low accuracy level (Bowen, 2010), Bowen also notes that isotopic  
156 predictions are highly generalized because they reflect climatological systems versus  
157 meteorological systems (2010). Regardless of the outcome of this model, the science

158 and understanding of meteoric water is becoming increasingly popular especially with  
159 global climate change, which allows for more interest and support from a larger  
160 community. Future research is definitely required in order to create a model that can  
161 be reliable on large and small-scale events.

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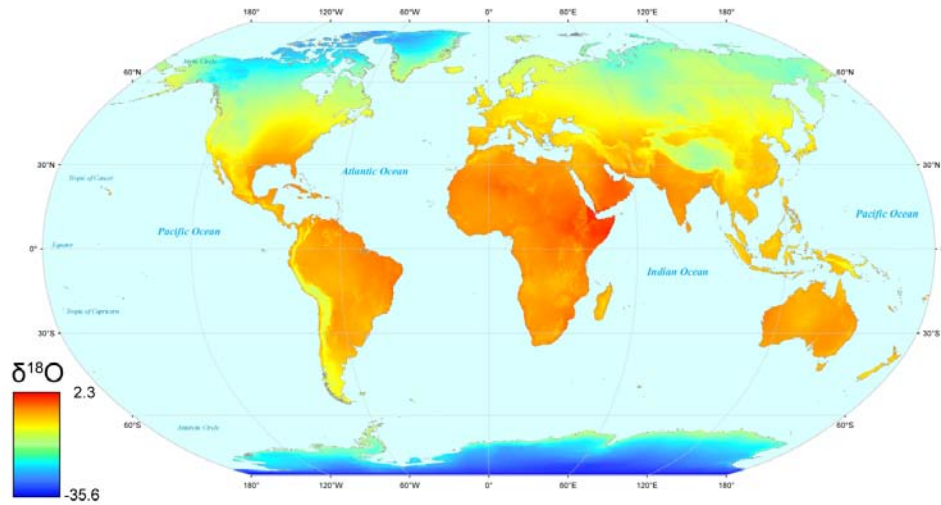
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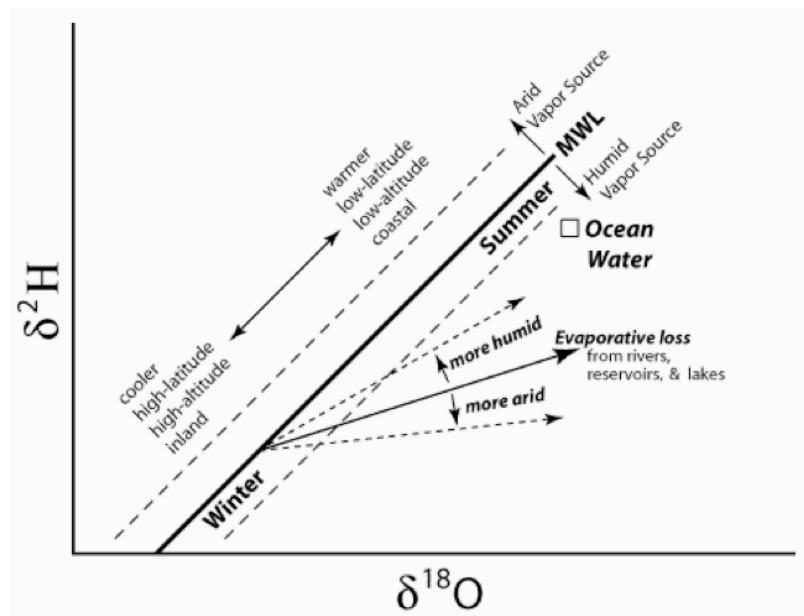
189 **Appendix**



190

191 **Fig 1.**

192 Projected isoscapes on a global scale (Bowen et al, 2003).

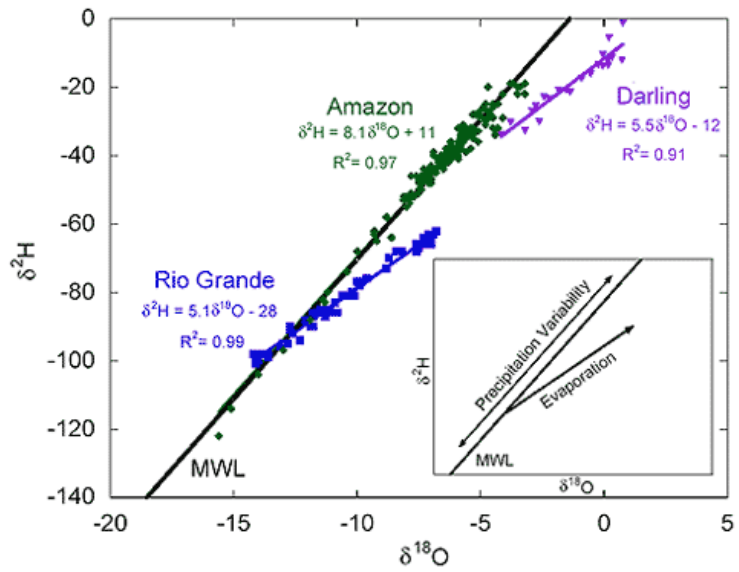


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195 **Fig. 2**

196 Oxygen-18 against deuterium plot in order to show Global Meteoric Water Line including three regions of  
197 climatic variability (SAHRA, 2005).



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199 **Fig. 3**

200 The Global Meteoric Water Line plot along with hydrologic processes demonstrating changes based on  
 201 climatic settings and seasonal changes (SAHRA, 2005).

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216 (a)



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218 (b)

219 Fig. 4

220 a) zoomed out view of study area in the South Island, New Zealand. b) zoomed in focus of research area  
221 with a latitude/longitude of -43.525, 172.575.

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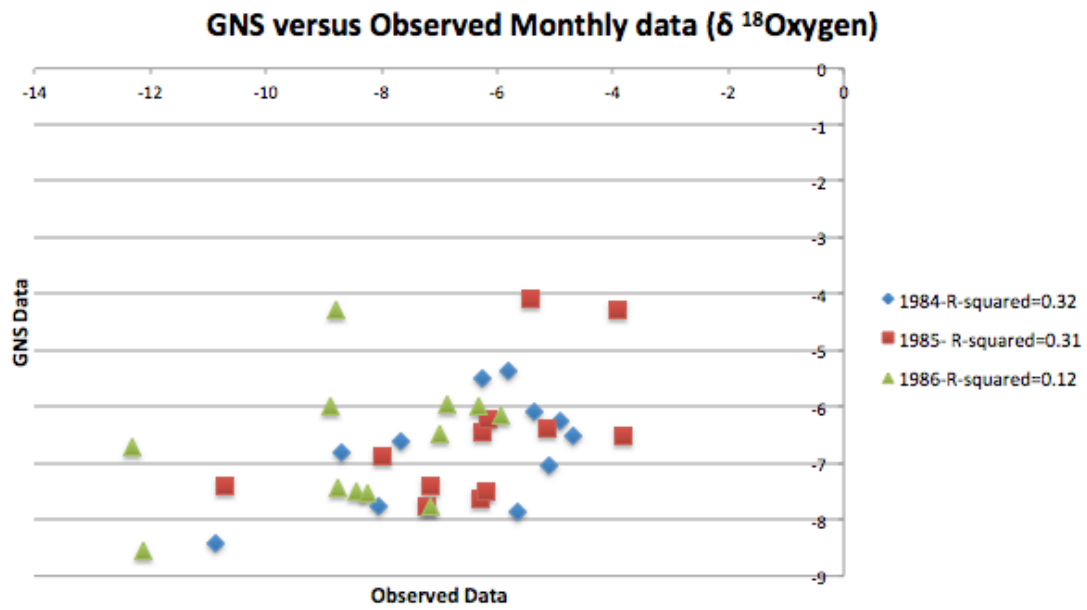


Figure 5. GNS derived data plotted against the observed monthly data during 1984-1986. All data is in regards to oxygen-18 values. R-squared values are displayed next to the years they pertain to.

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Fig 5

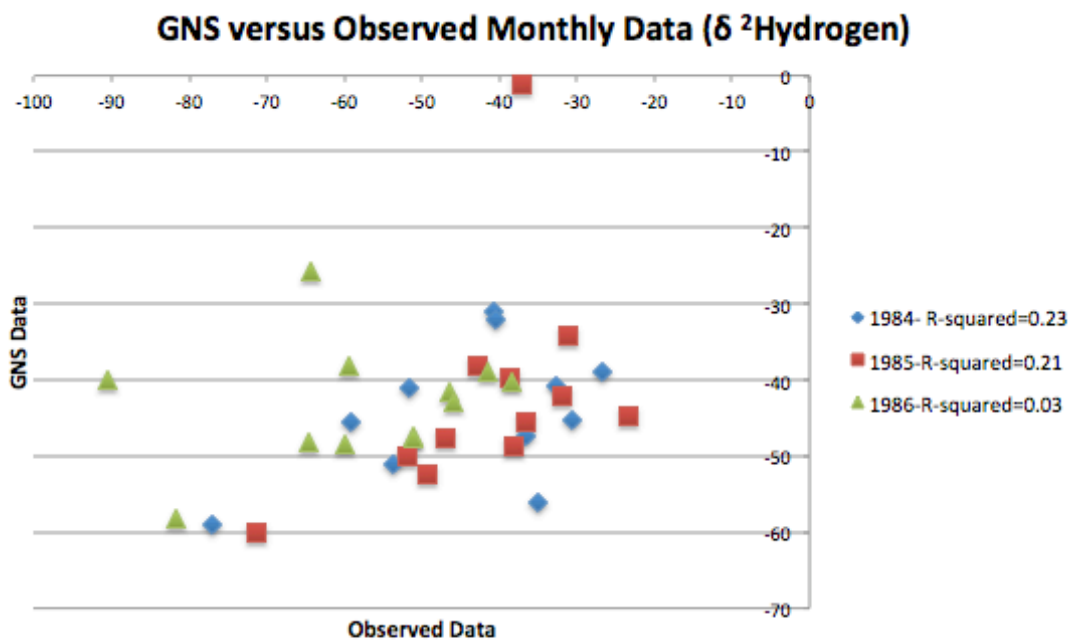


Figure 6. Data computed from the GNS model plotted against the monthly data from Taylor 1990. All data is based on hydrogen-2 values and from the years of 1984-1986. R-squared values are shown next to the years.

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Fig 6

### GNS versus Observed Monthly Data (d-excess)

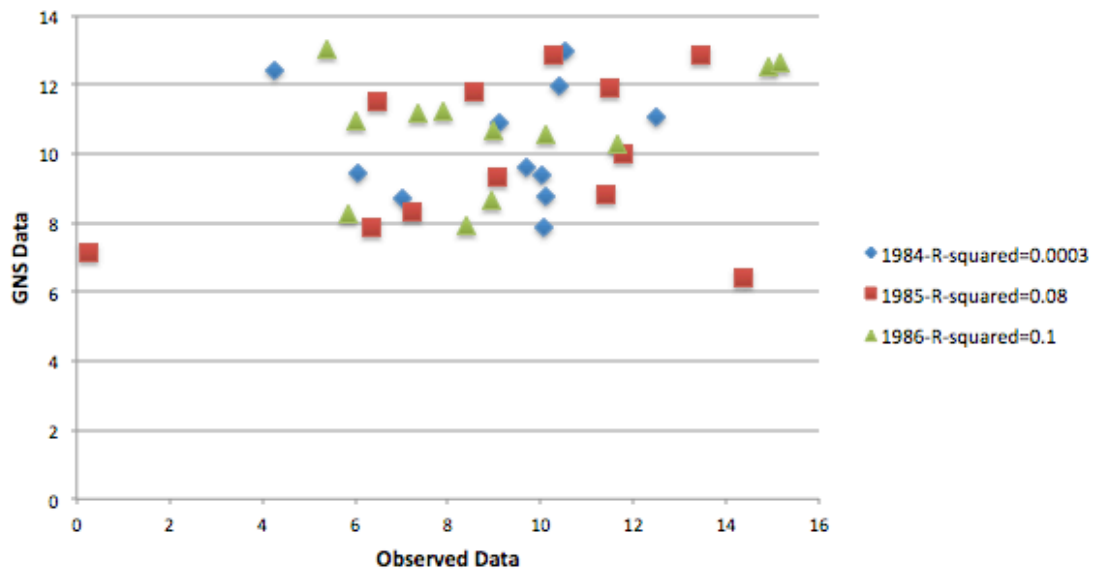


Figure 7. GNS versus monthly data from Taylor 1990. All data shown is values of d-excess. Years are shown with r-squared values beside them.

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Fig 7

### $\delta^2\text{H}/\delta^{18}\text{O}$ Monthly Data

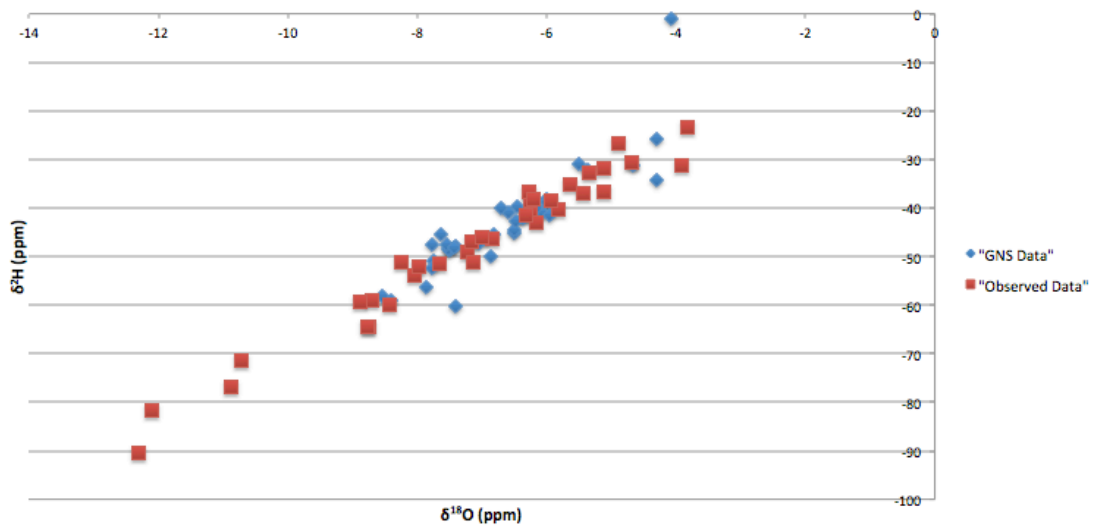


Figure 8. Ratios of hydrogen and oxygen shown along the global mean water line. Two sets of data are set here, the GNS isotopic compositions and the data derived from Taylor.

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Fig 8

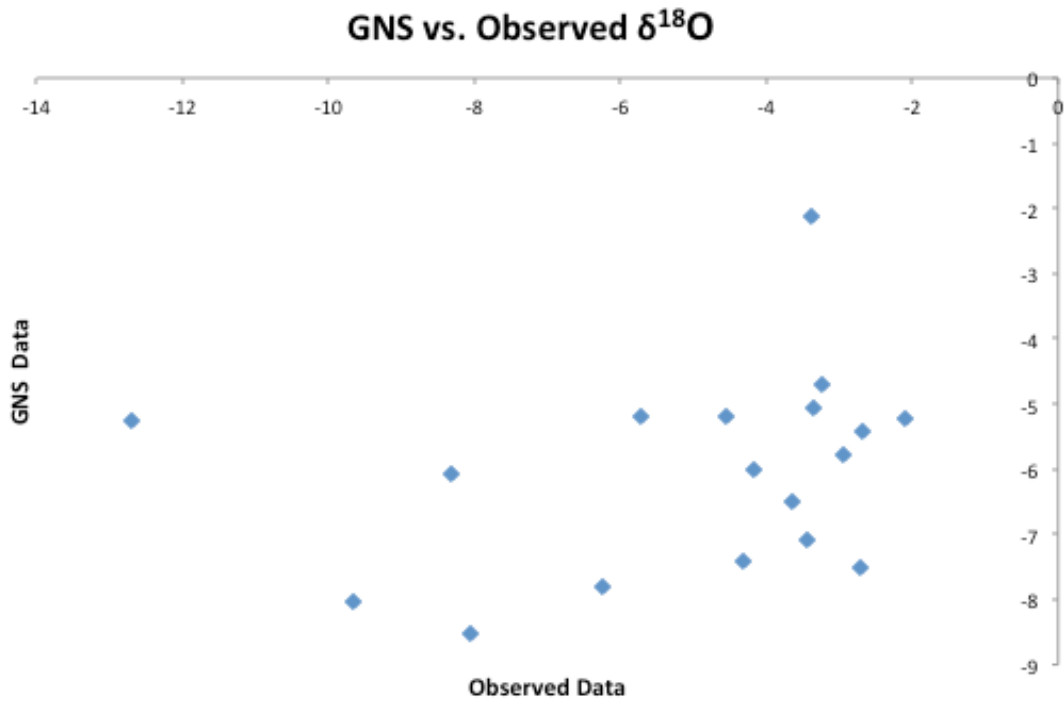


Figure 9. GNS derived data versus observed data from Blackstock 2010 for oxygen-18 isotopes over daily time periods. Measurements were taken for 24 hours on 18 different dates. R-squared values are 0.07.

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Fig 9

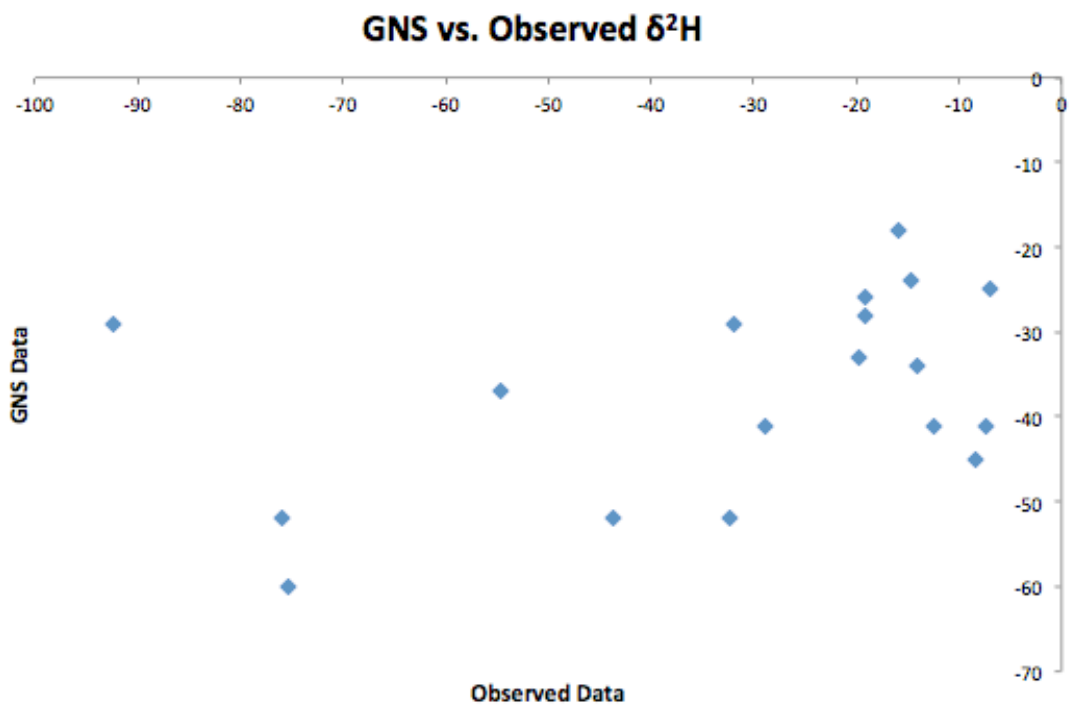


Figure 10. GNS data versus observed data for the hydrogen-2 isotopes over a daily time period. All measurements were taken for 24 hours on 18 different dates. R-squared values are 0.17.

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Fig 10

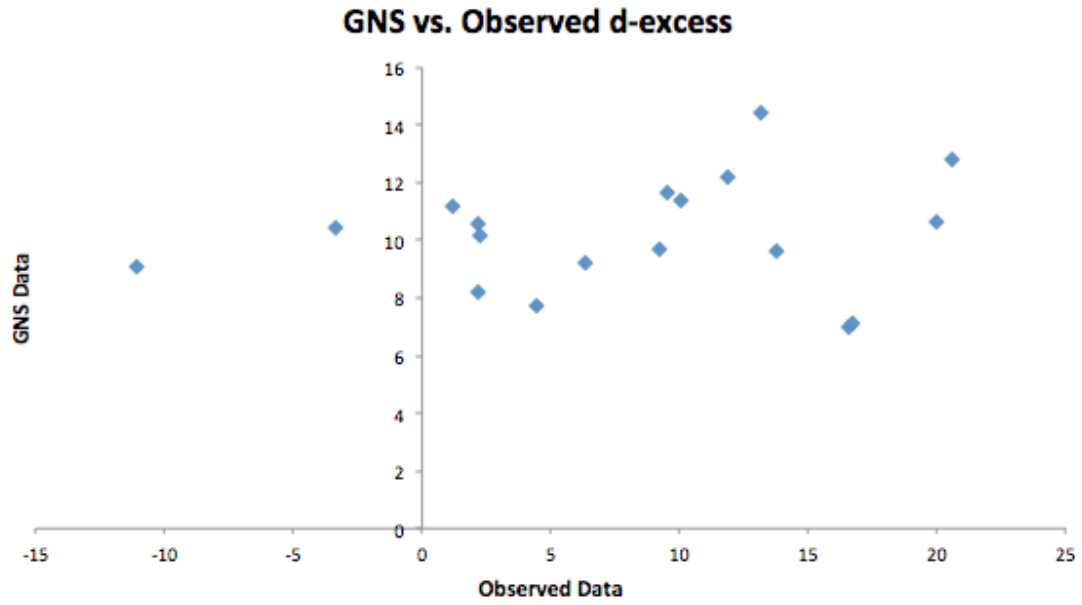


Figure 11. GNS data versus observed data for d-excess over a daily time period. All measurements were taken over a 24 hour period for 18 different days. R-squared value is 0.02.

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Fig 11

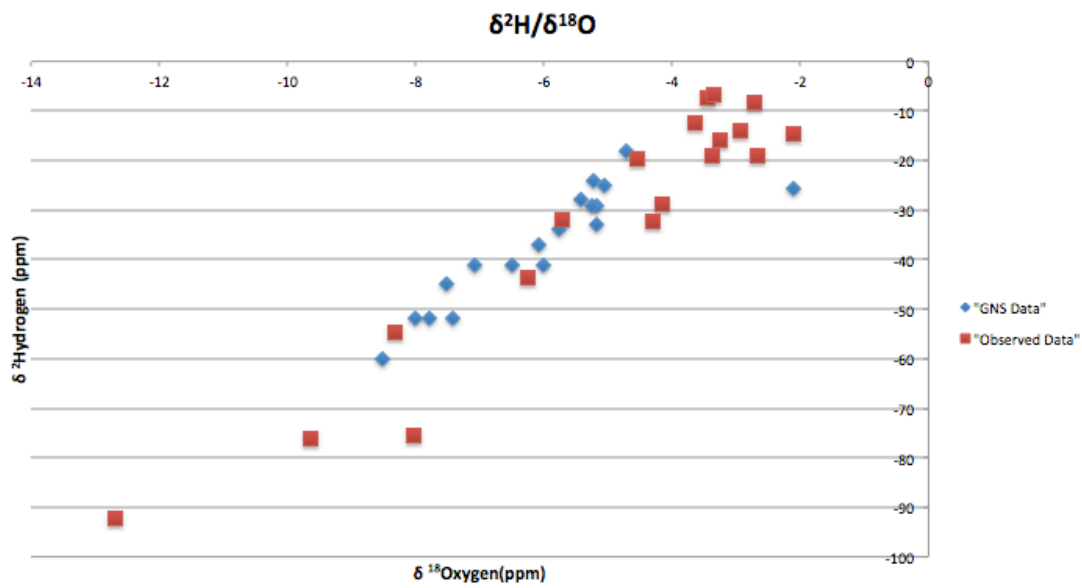


Figure 12. Hydrogen-2 versus oxygen-18 ratios plotted for GNS derived data as well as the observed data from Blackstock 2010. All values are produced from daily collection over 18 different days.

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Fig 12

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Sample	Date	Daily total	VCSN Total	Percent collected
6	24-Sep	2.1	0	n/a
8	4-Oct	1.4	0	n/a
12	16-Oct	3	1.7	176.4705882
15	28-Nov	6.9	2.1	328.5714286
18	2-Dec	6.6	3.9	169.2307692
20	6-Dec	2.6	2.6	100
21	10-Dec	1.2	0	n/a
22	14-Dec	12.4	16.6	74.69879518
23	20-Dec	5.1	7.2	70.83333333
29	11-Jan	0.8	11.8	6.779661017
33	14-Jan	1.7	2.3	73.91304348
34	16-Jan	3.4	4.9	69.3877551
37	22-Jan	14	23.8	58.82352941
39	17-Feb	3.1	9.1	34.06593407
40	18-Feb	7.2	4.5	160
41	26-Feb	1.1	0	n/a
42	17-Mar	2.1	0	n/a
43	24-Mar	1	1.2	83.33333333

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Chart 1. Percentage of daily precipitation collected based on Blackstock 2010, and the VCSN data. In 7 of the sample dates percentage collected was above 70%. In some cases data was unavailable due to “zero” rain collection.

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