ATTACHMENT 1C
(Supplemental Documentation to the: Mogollon Rim Water Resource Management Study Report of Findings)

Report on an Isotope Study of Groundwater from the Mogollon Highlands Area and Adjacent Mogollon Rim, Gila County, Arizona

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REPORT ON AN ISOTOPE STUDY OF GROUNDWATER FROM THE MOGOLLON HIGHLANDS AREA AND ADJACENT MOGOLLON RIM, GILA COUNTY, ARIZONA

Prepared for the Town of Payson Water Department

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Introduction

As part of the MRWRMS investigation of groundwater in the area around Payson, several sets of groundwater, rainwater and surface water samples were collected for isotopic analysis. All samples were analyzed for stable oxygen and hydrogen isotopes, and many were analyzed for stable sulfur isotopes, strontium isotopes and tritium. Three samples were analyzed for carbon-14. The goals of the isotope study were to characterize local precipitation, and to constrain the origin(s) and the residence time(s) of the groundwater. Sets of isotope data are available for groundwater and precipitation along the Mogollon Rim to the west of the Payson area, and these data are compared with the new data generated for this study.

The geology and hydrogeology of the study area are described in detail elsewhere in the MRWRMS reports. Earlier descriptions of the hydrogeology of the Pine-Strawberry area were given by Highland Water Resources Consulting Inc. (2005) and Kaczmarek (2003). Bills et al. (2000) described the hydrogeology of the Flagstaff area, where the Colorado Plateau strata are similar. A brief summary only is given here to explain terms that will be used in this section.

The strata of the Colorado Plateau, including capping Tertiary basalt, contain two principal aquifer systems: (1) a perched aquifer, present locally in Tertiary volcanic rock; and (2) the Regional aquifer, occurring within Paleozoic strata and underlying Proterozoic rocks. The Regional aquifer can be divided into units that are separated by the impermeable lower Supai redbeds. Above that horizon, the water is present in the primary porosity of sandstone units, principally in the Coconino sandstone and the Schnebly Hill formation, and in fractures. This unit has been termed the C aquifer. Below the Supai group, water is present in fractures and open spaces of the Redwall and Martin formations (largely carbonate rock) and underlying Proterozoic rock, and is here termed the RMX aquifer (cf. Highland Water Resources Consulting Inc., 2005). Evidence presented in these reports suggests that the C and RMX aquifers are connected locally. Groundwater discharges from the C and RMX aquifers in a series of springs along the base of the Mogollon Rim.

South of the Mogollon Rim, another major aquifer, here termed the X aquifer, occupies fracture permeability within granitoids and other intrusive rocks of Proterozoic age. Groundwater is also discharging from downfaulted parts of the Martin formation south of the Rim. The aquifer(s) in this case may or may not be connected to the Regional aquifer of the Colorado Plateau; any connection must be through fractured Proterozoic rock. For the purposes of this study, they will be grouped as the M aquifer. Groundwater is also present in minor aquifers hosted by valley-fill sediment in the Rye basin, at Star Valley and adjacent to other streams.

Potential Usefulness of Stable Isotope Data

Stable isotope data are measured as ratios, for instance $^{2}H/^{1}H$ (or D/H), $^{18}O/^{16}O$ and $^{34}S/^{32}S$. The results are expressed using δ-notation, e.g.:

$$\delta D = \left(\frac{R(sample)}{R(s\tan dard)} - 1 \right) x1000$$

where R = D/H and the standard is Vienna Standard Mean Ocean Water.

The definition of $\delta^{18}O$ is analogous, with $R = {}^{18}O/{}^{16}O$ for oxygen, and for $*^{34}S$, $R = {}^{34}S/{}^{32}S$. For $\delta^{34}S$, the standard is CDT, Cañon Diablo troilite.

Values of δD and $\delta^{18}O$ are usually presented in a plot such as Fig. 1 in which annually-averaged precipitation from around the globe plots along a straight line (the global meteoric water line, GMWL) with slope = 8. Groundwater at a given site usually bears the time-averaged isotopic signature of precipitation in the areas where it fell as precipitation, unless evaporation or exchange with rock oxygen have taken place. In Fig. 1, point A represents a hypothetical local average precipitation. Exchange of O isotopes between water and rock leads to horizontal shifts to the right of the GMWL (e.g. line AD) and evaporation leads to trends with slope 3 to 5, also to the right of the GMWL (e.g. line AC, composition C being the water left over from intense evaporation of composition A) . The mixing of waters of different isotopic composition results in straight-line trends on the diagram, so that point B on the evaporation trend in Fig 1 could represent mixing of compositions A and C.

An advantage of using hydrogen and oxygen isotopes in groundwater is that they label the water molecules themselves (rather than solute ions or molecules) and are conservative in groundwater under typical conditions.

As groundwater passes through rock, it may dissolve sulfate minerals (usually gypsum) or oxidize sulfide minerals (commonly pyrite). If these minerals have characteristic sulfur isotope compositions, the sulfur isotope composition of the sulfate dissolved in the water may give useful information about the flow-path of water. In the study area, Permian gypsum with $\delta^{34}S$ values of 11-14‰ (Claypool et al., 1980) in the Kaibab formation and Supai group, and possibly igneous sulfide, near 0‰, are the most likely sources of high concentrations of dissolved sulfate.

Strontium isotopes, like sulfur isotopes, are labeled according to the source of solute, in this case the cations. ^{87}Sr originates from the decay of radioactive ^{87}Rb, while ^{86}Sr is unchanging. Rocks such as granite that have high Rb concentrations therefore develop high $^{87}Sr/^{86}Sr$, particularly in the case of ancient rocks such as the Proterozoic granitoids of the Payson area. Rocks such as basalt that have low initial ^{87}Rb retain low $^{87}Sr/^{86}Sr$ ratios. Marine carbonates and calcium sulfate evaporites have $^{87}Sr/^{86}Sr$ ratios reflecting those of the oceans from which they formed, the ratios varying with time (Burke et al., 1982). Rock $^{87}Sr/^{86}Sr$ ratios are imparted to groundwater in contact with the rock. In the Mogollon Rim area, the Kaibab, Naco, Supai (evaporitic facies) and Martin formations will impart marine Sr isotope ratios to groundwater, while the clastic elements of Coconino, Schnebly Hill and Supai formations may impart the Sr isotope signatures of reworked fragments of other rock types.

Tritium is continuously generated in the upper atmosphere as a result of nuclear reactions caused by cosmic rays. In Tucson, the level of cosmogenic tritium in rainwater is about 6 TU (tritium units; 1 TU = 1 atom of tritium per 10^{18} atoms of hydrogen) (Eastoe et al., 2004). Similar, but not identical, levels are expected elsewhere in the southwest USA. In addition, a pulse of tritium was added to the atmosphere between 1955 and 1975 as a result of atmospheric testing of nuclear weapons. In 1963-64, tritium levels rose briefly to about 1000 TU. The half-life of tritium is 12.4 years, so that pre-bomb tritium has now decayed to less than the level of detection, 0.6 TU in our laboratory. Bomb tritium is still present in aquifers recharged with rainwater since about 1955. We therefore use tritium to distinguish between water containing tritium below detection, which must have recharged before about 1955, and water containing tritium above detection, which must contain some water that fell as rain since 1955.

Carbon-14 can be measured in dissolved inorganic carbon species (usually bicarbonate) in groundwater. The carbon comes from two sources: carbon dioxide gas in soil or near-surface sediment through which the recharging water passes, and from carbonate minerals like calcite in rock. The soil gas has ^{14}C content near that of the atmosphere, currently about 108 pMC (percent modern carbon). Like tritium, ^{14}C is generated in the upper atmosphere and in nuclear explosions in the atmosphere. Pre-bomb levels were near 100 pMC, and during the 1960s, levels near 200 pMC were reached for a few years. Rock carbon contains no ^{14}C. The half life of ^{14}C is 5730 years, so that ^{14}C measurements enable us to estimate water ages in the range of hundreds to thousands of years. The mixing of carbon types precludes exact age determinations. If infiltrating water dissolved *only* carbon from soil gas, and then resided in an aquifer, we can calculate an age based on ^{14}C decay. But if the water also dissolved carbon from rock, the calculated age will be too old. Nonetheless, ^{14}C content in water can give useful comparative age information. In general, higher (lower) pMC indicates groundwater of shorter (longer) residence time.

Hypothetical O and H Data Arrays

The study area and potential recharge areas stretch from the Mogollon Rim to Rye, with an altitude difference of more than 1000 m. Three cases for recharge and flow of groundwater seem likely (see Fig. 2):

1. Recharge important at high elevations, where precipitation is heaviest, and unimportant at low elevations; regional groundwater flow to lower elevations. Water undergoes little evaporation prior to recharge, and does not change in isotope composition down-gradient in the aquifer. The entire aquifer will therefore contain water with a high-altitude isotope signature. Water at low

elevations is older than that at high altitude, so that tritium will be observed to decrease down-gradient.

2. Recharge and groundwater flow are mainly local, and recharge occurs rapidly from stream beds. In a given area, the source of recharge is precipitation in that area. The altitude effect in rainwater isotopes will be reflected in groundwater; high-altitude groundwater will have low δ-values, and low-altitude groundwater will have high δ-values. Young water, with detectable tritium, is found at all altitudes. Low-altitude rainwater tends to be slightly evaporated, so that the slope of a data array will be between 6 and 8.

3. Recharge occurs at all altitudes, but the source of water is at high altitude. At low altitude, some groundwater derives from regional groundwater flow from high altitude, and shows no isotopic shift due to evaporation. This may mix with water recharged at low altitude, but mainly derived from high elevations and supplied as surface water. Such water will be subject to evaporation. Mixtures of the two kinds of water will give a linear data trend with a slope between 3 and 5. Tritium will be present throughout.

A graph of $\delta^{18}O$ vs. altitude of sampling would show no altitude dependence in case 1; a clear linear relationship in case 2; and an indistinct relationship in case 3. If case 3 applies, there may be an observable isotope effect of evaporation in groundwater sampled close to major drainages.

Stable O and H Isotope Data

The new data for the study area are listed in a table in the hydrology section of the MRWRMS reports.

1. *Payson Rainwater*. Seasonal bulk samples, weighted for amount, were collected in Payson at an altitude near 5000 ft./1500 m. above sea level between Winter 2002-2003 and Summer 2007. These are not sufficient to characterize average rainfall in the area; annual variability is likely to be great, as in Tucson, where the data set extends over 24 years (Wright, 2001). The data are compared with long-term mean data for the Tucson area in Fig. 3, and demonstrate: (1) That bulk precipitation in Payson plots close to the GMWL (more closely than in Tucson, where summer precipitation at 2500 ft./750 m.a.s.l. is more evaporated than in Payson, and winter precipitation at 7400 ft/2242 m.a.s.l. shows a greater shift above the GMWL than in Payson); and (2) That the difference between summer and winter precipitation is generally similar to that in Tucson.

2. *Surface Water*. The linear array of data (Fig. 4A) generally follows the GMWL, and several points coincide with the field of groundwater. An exception is surface water from Blue Ridge reservoir, which has an isotope composition consistent with evaporation.

3. *Groundwater.* On a δD vs $\delta^{18}O$ plot, most of the data form a linear array (Fig. 4A) with a slope close to 5. Certain samples do not conform to the linear trend: (1) Samples from well HI-4 at Rye and the Doll Baby ranch, where the groundwater may be very old (see ^{14}C data, below); (2) A sample from shallow alluvium at Hunter Creek. The Hunter Creek sample is the only sample in which summer precipitation is clearly present. This is a local effect in a small pocket

of alluvium, and is not present to the same extent in the principal aquifers in fractured rock. (3) the C aquifer samples from Fossil Springs (Fig. 4B).

The linear trend can be explained in two ways.

> Hypothesis 1: The trend is as expected for Case 3, above. The single trend suggests strongly that most recharge in the study area plots in a limited field on the diagram, at the left-hand end of the trend, near $\delta^{18}O$ = -11.5‰. The source or recharge is predominantly winter precipitation, and the trend is generated by evaporation. Scatter about the trend might represent the incorporation of small amounts of summer precipitation. The identification of the linear trend as an evaporation trend is reinforced by two observations. First, the samples with highest δ-values are from the Lake Drive, Mountain View, CC-3 and CPN-13 wells, which are near the Green Valley Park Lake or various golf course ponds, and are influenced by recharge from the ponds, or from irrigation reflux (Fig. 5A). Second, Blue Ridge reservoir water plots close to the trend (Fig. 4A). The reservoir is on the Colorado Plateau at 6700 ft./2030 m. elevation, and is fed by runoff from the highest part of the Mogollon Rim in this area. The second observation suggests further that the source of recharge in the Payson area is high-elevation precipitation; a mean $\delta^{18}O$ value of -11.5‰ in winter precipitation at the Rim summit (7000 ft./2100 m. elevation) is consistent with the $\delta^{18}O$ vs altitude data of Blasch et al. (2005).
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> Hypothesis 2: Case 2 is the operative case, but is not indicated clearly on the δD vs. $\delta^{18}O$ plot because average recharge at the elevation of Payson (AREP) plots in the middle of a single linear trend of data. Local recharge clearly occurs to the X aquifer where evaporated water is available (Fig. 5A), and therefore probably occurs where non-evaporated runoff is available. The field of AREP indicated in Fig. 4B is based on the data for three wells, Round Valley (in Round Valley) and Quail Valley and Milky Way (in Star Valley). All three are drilled through valley-bottom alluvium overlying Proterozoic granitoid; in all cases the water table is shallow (25 and 40 feet below the surface, respectively). Both valleys receive only lower-elevation runoff: Gibson Creek in Round Valley rises at the south end of Payson, and the drainages entering Star Valley rise on Diamond Rim or at lower elevation. *Assuming that much of the recharge near these two wells is from the nearby streams,* the water samples should represent AREP. This is plausible: groundwater is shallow in both cases, and in both cases, total dissolved solids are low (see the MRWRMS Water Chemistry report). At Round Valley, the well screen starts 30 feet below the surface, and at Milky Way, the screen starts at 20 feet. According to this hypothesis, the trend of O and H isotope data to the right of the AREP field is an evaporation trend. To the left of the AREP field, however, the trend reflects mixing between AREP and water from the C and RMX aquifers, with a slope that is near 5 by coincidence.

In Fig. 5B, groundwater samples are grouped according to the aquifer sampled. Three of the samples from the C aquifer lie at the lower end of the evaporation trend. The lowest $\delta^{18}O$ and δD values are from the C aquifer at Fossil Springs, at the western end of the study area, and match the upper end of the field of data for the regional aquifer (equivalent to the C aquifer) beneath Flagstaff (Bills et al., 2000 –see below). The fifth sample, from Fish Hatchery Spring at the eastern end of the field area, is distinctively light. A scattering of similar samples was found in the regional aquifer beneath Flagstaff by Bills et al. (2000). Samples from the RMX aquifer conform to the mixing/evaporation trend; the least evaporated of these samples match the C aquifer samples. Samples from the M aquifer either coincide with the AREP field (Webber Spring) or fall on the mixing/evaporation trend (Tonto Natural Bridge Spring). In the X aquifer, a group of samples (Summit, Payson Pines 4, Turtle Rock, Goat Camp and Luke wells, shown as "Summit etc." in Fig. 5B) also plots on the mixing/evaporation trend to the left of the AREP field. These locations are 3 to 5 km north and west of Payson, and are separated from the base of the Mogollon Rim by the canyon of the East Verde River.

The plot of $\delta^{18}O$ vs. sampling elevation (Fig. 6) shows a linear trend including most of the groundwater samples from the Payson-Pine area. Samples from the C, RMX and M aquifers and from Rye Basin do not conform to the trend. The slope of the trend is much lower than the slopes of $\delta^{18}O$ vs. altitude trends for the region (Tucson and Santa Catalina Mts. – Wright, 2001; Verde Valley to Flagstaff – Blasch, 2005). The trend is clearly not governed mainly by the altitude isotope effect. Note that sampling altitude does not necessarily correspond with average recharge altitude, which cannot be estimated for the sample sites in this study, given the possibility of long-distance flow of groundwater. The least evaporated samples (lowest $\delta^{18}O$) on the linear trend correspond with average precipitation from about 400 m higher according to Blasch's (2005) data. The correspondence between the most evaporated samples (highest $\delta^{18}O$) and Blasch's altitude trend is coincidental. The apparent linear trend may simply reflect the fact that ponds are constructed in topographic depressions.

Fig. 7A is a map of $\delta^{18}O$ values at sample sites in the X aquifer near Payson. The association of high $\delta^{18}O$ values (indicating evaporation) with central Payson shows clearly, and can be explained by the local recharge of reclaimed water from ponds and lakes in Payson. Groundwater from north Payson has lower $\delta^{18}O$ values.

The linear δD vs. $\delta^{18}O$ trend in the Payson area (the "Payson trend", below) is compared with other data from the region in Fig. 8. Data reported by Flora (2004) and Parker et al. (2004) for springs along the base of the Mogollon Rim are largely consistent with the Payson trend. Exceptions include springs near Camp Verde and Sedona, and as far east as Blue Spring on the Verde River near Childs; these plot below the Payson trend. Data reported by Bills et al. (2000) for groundwater in the Flagstaff area differ significantly from the Payson trend. Data from perched aquifers in the volcanic rock of the San Francisco Peaks may define an evaporation trend like that at Payson, but originating at a lower $\delta^{18}O$ value, consistent with the higher altitude of the Peaks. Springs from the Sedona-Camp Verde area fall on this trend (Fig. 8). Data from the regional aquifer in the Paleozoic section underlying Flagstaff plot near the GMWL and at lower δ-values $\delta^{18}O$ between -11.9 and -12.4‰, but with scattered higher values) than in the C aquifer near Payson; presumably the lower $\delta^{18}O$ values reflect recharge from high-altitude areas of the San Francisco Peaks. Unpublished data reported to the Arizona Department of Transportation for an area along State Route 260 east of Lion Springs scatter more widely than the other data sets, and may for this reason not be accurate. Particularly suspect are the data points plotting above the GMWL. No comparable values have been observed in the other studies in the region. Water with such $\delta^{18}O$ and δD values can be generated from snow banks that have undergone sublimation prior to melting, but it seems unlikely that such an effect would be limited to the Lion Spring area.

Tritium and Carbon-14

Tritium in average precipitation from the study area appears to be close to 5 TU on the basis of 5 measurements for seasonal rain samples. The value is comparable to that for Tucson (5-7 TU) where long-term records have been kept. There has been no bomb-tritium in Tucson precipitation (or, by implication, in Mogollon Rim precipitation) since 1992 (Eastoe et al., 2004). Groundwater samples from the study area almost all contain tritium at levels between 1 and 6 TU, consistent with various degrees of mixing of recent precipitation with pre-bomb water throughout the area. Only a few wells, Turtle Rock, Rye HI-4, Doll Baby 2) yield groundwater of < 1 TU, and therefore have little to no post-bomb rainwater component. The distribution of tritium in the X aquifer is shown in Fig. 7B Values greater than 2.5 TU correlate with high $\delta^{18}O$ in Payson; presumably some tritium from rainwater is recharging with the reclaimed water. This zone contrasts with a zone of low tritium in north Payson. Tritium levels > 2.5 TU were also found at sites CPN13, Milky Way and Round Valley, where local recharge is thought to occur, as explained above.

Four ^{14}C measurements are available. Average residence times of groundwater are indicated in a semi-quantitative way by tritium and C14 data in combination, as follows.

Rye-HI4 well (2.6 pMC, 0.6 TU) yields water of long average residence time, and post-bomb recharge is insignificant. Residence times in the thousands of years are probable, and consistent with the low $\delta^{18}O$ and δD values. Late Pleistocene and early Holocene rainwater are thought to have had lower mean $\delta^{18}O$ and δD values than those of present-day rainwater (e.g. Plummer et al., 2004).

Tonto Natural Bridge spring (74.2 pMC, 2.0 TU) yields a mixture of post-bomb and pre-bomb water.

Payson Pines 4 well (82.4 pMC, 0.6 to 1.4 TU) occurs in an area of little post-bomb recharge, as noted above. The ^{14}C data, however, are consistent with pre-bomb recharge in the few decades prior to 1950.

Fossil Springs (69.2 pMC, 0.6 TU; pMC from unpublished data of A. Springer) is similar to Tonto Natural Bridge Spring, but the proportion of post-bomb water is smaller.

Sulfur Isotopes

Sulfur isotopes have been measured in a selection of samples. In Fig. 9, the data for those samples with known sulfate concentrations plot in a triangular array typical of groundwater in the region – e.g. in Tucson basin (Gu, 2005). Mixing trends on this plot are straight lines. The data therefore indicate a minimum of three sulfate sources: 1. High $\delta^{34}S$ (12-13‰) and high sulfate, corresponding to Permian marine evaporites; 2. Low $\delta^{34}S$ (near 0‰) and high sulfate, most likely corresponding to oxidized igneous sulfide; and 3. Values of $\delta^{34}S$ of 6 to 8‰ and low sulfate, corresponding to sulfate in rain and dust. The evaporite end-member might be expected mainly in C-aquifer and RMX-aquifer water, and the igneous end-member in the X aquifer, if sulfate were locally derived. No such pattern is evident. Sulfate in X-aquifer water resembles evaporitic sulfate in some cases, and there is a strong signal of rain+dust sulfate in sulfate in water from Paleozoic rocks, including the C aquifer. It is possible that other sulfate sources, of lower $\delta^{34}S$, exist in Paleozoic strata. The identification of end-member 3 as fallout is supported by the data from two runoff samples, in which this type of sulfur predominates. The lower $\delta^{34}S$ values (relative to data for groundwater in the area) may reflect industrial sulfur in the atmosphere; in Tucson basin, Gu (2005) concluded that rainwater sulfate of the last few decades has lower $\delta^{34}S$ values than earlier rainwater sulfate for this reason.

The samples approaching the end-member compositions may be informative.

End-member	**Samples**
Evaporite	Lake, Hunter Creek, Mountain View, Rye HI-4
Igneous	Round Valley, CC#3
Rain+dust	Webber, Shallow Strawberry

In fact, little can be concluded. The low $\delta^{34}S$ values at Round Valley and CC#3 may indicate concentrations of sulfide in the granites in these areas. The Lake well is influenced by recharge from Green Valley Park Lake on the basis of O and H isotopes, but the $\delta^{34}S$ value (13.3‰) is quite different from that of reclaimed water (6.1‰). A possible explanation is that partial sulfate reduction, leading to an increase in $\delta^{34}S$ of the residual sulfate, is occurring in the bottom sediment of the lake. This effect may also be responsible for the $\delta^{34}S$ value, 12.2‰, at the Mountain View well. In the case of the Rye HI-4 sample, sulfate reduction is almost certainly responsible for the high $\delta^{34}S$ value, because water from this well smells of H_2S. These three samples excluded, there is little remaining indication of evaporitic sulfate in the data set; only the Hunter Creek well at the far eastern end of the study area contains such sulfate.

Strontium Isotopes

Fig. 10 shows $^{87}Sr/^{86}Sr$ data for groundwater in the Payson area in relation to data from the literature: (1) groundwater from the regional aquifer near Flagstaff (Bills et al., 2000); (2) expected $^{87}Sr/^{86}Sr$ ratios for limestone and evaporite units in the Paleozoic section (Burke et al., 1982); (3) Neogene and Quaternary volcanic rocks of the Hickey basalt and the San Francisco Peaks (Scott, 1974); (4) Paleozoic strata of the study area (Parker et al., 2005); and (5) 1.4 to 1.7 Ga Proterozoic granites sampled as xenoliths in volcanic vents in the Four Corners area (Condie et al., 1999).

The data for groundwater near Flagstaff are classified according to flow-path rock type, and show clearly the influence of lithology on $^{87}Sr/^{86}Sr$ in groundwater solutes. The range of $^{87}Sr/^{86}Sr$ in solutes is consistent with $^{87}Sr/^{86}Sr$ ranges of limestone (Kaibab and Martin/Redwall formations) and volcanics. There is no indication of addition of strontium from radiogenic detritus in clastic sedimentary units in this area.

Samples from the Mogollon Rim near Payson differ according to the formation from which the water emerges or is drawn. Water from the Supai group has $^{87}Sr/^{86}Sr$ ratios slightly higher than those expected or measured in the Kaibab formation and the Supai group. The Tonto and Fish Hatchery samples have particularly high ratios. The Fish Hatchery spring discharges from the Fort Apache Limestone, part of the Supai Group. Two $^{87}Sr/^{86}Sr$ measurements on the he Fort

Apache Limestone gave conflicting results: one (0.7104; Parker et al., 2005) almost as high as the measurement for the Fish Hatchery sample (0.7107), but another (0.7080; this study) much lower. Water emerging from the Martin formation has distinctly higher $^{87}Sr/^{86}Sr$ ratios that water from the Supai formation. The highest $^{87}Sr/^{86}Sr$ ratios were measured in water from Proterozoic granitoid and Quaternary detritus of granitoid derivation at the Milky Way site, and from basin-fill, which must contain a large fraction of granitic detritus, at Rye ($^{87}Sr/^{86}Sr = 0.7128$, not shown in Fig. 10). Both ratios are consistent with the $^{87}Sr/^{86}Sr$ ratios for Proterozoic granitoids.

The difference in $^{87}Sr/^{86}Sr$ ratios between groundwater from the C and RMX aquifers is of interest here. All of the samples are from the Rim itself, not from downfaulted Paleozoic strata in the area immediately south of the Rim. Therefore the processes responsible for the ratios must be taking place in the Colorado Plateau. Two hypotheses can be advanced.

> (1) Groundwater from the Martin Formation is a mixture of recharge from the crest of the Mogollon Rim with upwelling water that has circulated through underlying Proterozoic granitoids and metamorphic rocks and is focused along major fractures. Crossey et al. (2006) showed that such mixtures are responsible for travertine formation at springs in the Grand Canyon. Groundwater from Proterozoic rock is more likely to affect the lower aquifer(s) in the Paleozoic section, but might locally mix with the C aquifer if suitable fractures exist. Upwelling in such a case may occur if the water is heated as it circulates through the Proterozoic rocks, or if there is a positive hydrologic head difference between the zones of recharge and discharge zones.
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> (2) Groundwater from the RMX aquifer has been exposed to radiogenic detritius (e.g. eroded from Proterozoic rocks) in clastic units below the C aquifer host strata, or by recharge through the Eocene Rim Gravels.

Rim Gravels occurs north and south of the Mogollon Rim in the study area, but not on the face or the crest of the Rim. The first occurrence of Rim Gravel to the north of the summit is at a distance of several miles from the crest. Recharge through Rim Gravel is therefore unlikely to add radiogenic Sr to groundwater discharging at the base of the Rim in this area. Derivation of radiogenic Sr from ancient granitic detritus in the clastic strata of the Colorado Plateau is also unlikely. Similar clastic strata occur in the Flagstaff area, but $^{87}Sr/^{86}Sr$ ratios are much lower in groundwater that has been in contact with them. There is no reason to suppose a facies change with concomitant variation in the fraction of Proterozoic-derived detritus in the clastic strata (C. Conway, personal communication). The first hypothesis therefore seems more tenable as an explanation of high $^{87}Sr/^{86}Sr$ ratios in the RMX aquifer. The impermeable lower Supai strata would insulate the C aquifer from this effect. The Strawberry Shallow well and the Fish Hatchery Spring (both C aquifer), however, with relatively high $^{87}Sr/^{86}Sr$ ratios, do not conform to this explanation. Groundwater in both is associated with the Fort Apache Limestone. The Sr isotope data suggest that the groundwater in these instances may be in contact with a localized body of rock containing radiogenic Sr, or that a fracture may be conveying water of deep derivation locally as far as the C aquifer. The second possibility seems unlikely for the Fish Hatchery Spring, which is near the Rim crest. If the first possibility is operative, the Fort Apache Limestone may have an unusual $^{87}Sr/^{86}Sr$ ratio. During the Permian and Pennsylvanian, two short-duration spikes in marine $^{87}Sr/^{86}Sr$ ratios are present according to the data of Burke et al. (1982), with values as high as 0.7090. This is insufficient to explain the value of 0.7107 in the Fish Hatchery sample, but suggests at least that high $^{87}Sr/^{86}Sr$ ratios are possible in certain marine limestone units.

The upwelling of water that has passed though Proterozoic granite might conceivably add water of different $\delta^{18}O$ and δD to the RMX aquifer. Such an effect is not visible in the present data set (Fig. 5B). This observation suggests that the water circulating deeply through the Proterozoic granites beneath the Colorado Plateau is of the same origin as other water in the C and RMX aquifers.

Discussion

1. Variation in $\delta^{18}O$ and δD of Mogollon Rim springs. The low $\delta^{18}O$ and δD values of springs to the west of the study area (Flora, 2004), in combination with the perched-aquifer isotope data from Bills et al. (2000), confirm the regional importance of high-altitude winter precipitation as a source of recharge for groundwater south of the Mogollon Rim. The elevation of the Rim itself is about the same from Sedona to Payson, so that snowmelt from the Rim summit should have the same average isotope content throughout. Groundwater near Flagstaff and Sedona most likely has lower $\delta^{18}O$ and δD values because recharge from the high-altitude area of the San Francisco Peaks contributes to groundwater in that area. The lower $\delta^{18}O$ and δD values are clearly present in the perched groundwater near Flagstaff, and in the C aquifer from Flagstaff to Fossil Springs. Higher $\delta^{18}O$ and δD values are found in C aquifer wells and springs directly north of Payson, and much higher values at the Fish Hatchery spring northeast of Payson.

The presence of a distinctive evaporation trend in the data of Bills et al. (2000) and Flora (2004) demonstrates that part of the recharge in these areas is evaporated water. For the Mogollon Rim springs, the regional data are therefore consistent with Hypothesis 1 (outlined above in the section on O and H isotopes), except possibly for springs from the RMX aquifer near Payson (see below).

2. Payson groundwater: Hypothesis 1 or Hypothesis 2? The two hypotheses are illustrated schematically in Fig. 11. Hypothesis 2 has the advantage of allowing for local recharge at the altitude of Payson. Local recharge can clearly be traced to artificial ponds in and near Payson. If pond water can infiltrate the X aquifer , it is reasonable to suppose that natural winter snowmelt can also infiltrate in that area. Hypothesis 1 has the disadvantage (in this area) of requiring recharge of evaporated stream water to the X aquifer in areas where the streams draining the Rim are deeply incised. If the $\delta^{18}O$ and δD values of local recharge (AREP) have been correctly characterized, the most plausible interpretation of the O and H isotope data is that given in Fig. 12. That the evaporation and mixing trends that diverge from the AREP fields have similar slopes is strictly coincidental. The AREP isotope composition is consistent with winter precipitation as the principal source of recharge. Hypothesis 2 is the preferred explanation for the O and H isotope data in the X aquifer near Payson. Local recharge around Payson would mask any evidence of recharge consistent with hypothesis 1, which may therefore also still explain some of the replenishment of the X aquifer near Payson; this cannot be proven or excluded using the present data set.

According to this interpretation, the shallow groundwater from wells near central Payson (Fig. 7), which have been pumped for many decades, is a mixture of local recharge and evaporated pond/lake/irrigation water. The North Payson wells have been pumped for a shorter time, and yield water that is a mixture of local recharge with water from the Mogollon Rim. This apparently requires upwelling of Rim-derived water into the fractured granite beneath North Payson, which is physically possible for high altitude of recharge into fractured rock at the Rim crest.

3. RMX aquifer. The $\delta^{18}O$ and δD values of RMX samples coincide with values for the C aquifer near Payson (Fig. 5B), except for Ellison well, which has higher values. The data are consistent with leakage of water from the C aquifer to the RMX aquifer, but at Ellison well some of the recharge is either evaporated runoff from the Rim crest or AREP water.

4. M aquifer. Webber Spring and Tonto Natural Bridge (TNB) Spring discharge water that has values of $\delta^{18}O$ and δD higher than those of the water in the RMX aquifer. Local recharge appears to contribute. At Webber Spring, only water of the AREP composition is required; there is no evidence for mixing with RMX water. The presence of a rain/dust $\delta^{34}S$ signature rather than a evaporite $\delta^{34}S$ signature, and chemical data presented elsewhere in the MRWRMS reports, are consistent with this interpretation. Recharge is probably limited to the area between Little Diamond Rim and the spring. At TNB spring, the sample appears to be a mixture of RMX and AREP water, the latter presumably recharging on Buckhead Mesa. The TNB spring varies greatly in discharge with time, but has been observed to vary by less than 0.5 ‰ on $\delta^{18}O$ in four samples taken between 2002 and 2004 (Flora, 2004; this study). The C-14 content is consistent with mixing of pre-bomb and post-bomb water.

4. Rye Basin samples. The Doll Baby shallow sample plots in the AREP field, and presumably represents locally derived winter precipitation. Doll Baby deep and Rye HI4 yield water that resembles C aquifer water from Flagstaff. Given the low C-14 content of the HI-4 water, however, and the remoteness of this site from the Mogollon Rim, it is more likely that the low $\delta^{18}O$ and δD values represent a colder climate regime some thousands of years ago.

5. *Residence time of water reaching the X aquifer from the Rim crest.* The North Payson wells that have low tritium and $\delta^{18}O$ and δD values matching those of the C aquifer are (up till the present, at least) replenished mainly from the Regional aquifer of the Colorado Plateau by flow through fractured rock. The Payson Pines 4 sample has a tritium content of about 1 TU, consistent with little local recharge, and a C-14 content of 82.4 pMC, suggesting a short residence time (decades to 100 years?) for the groundwater derived from the Regional aquifer, despite its remote origin.

Principal Conclusions

1. Natural replenishment of groundwater in the study area is almost entirely from winter precipitation.
2. Groundwater from the Colorado Plateau Regional aquifer is replenished from high-altitude winter precipitation. Evidence for recharge from the San Francisco Peaks is observed in the area west of (and including) Fossil Springs. Part of the recharge water evaporates before infiltration.
3. Groundwater in the X aquifer near Payson is a mixture of local recharge and groundwater from the Regional aquifer. Where pumping has continued for longest, local recharge, including evaporated water from ponds and irrigation reflux, is prominent.
4. Post-bomb precipitation has contributed to (but is not necessarily predominant in) groundwater currently being pumped throughout the study area.
5. One C-14 data point suggests short flow times (decades) for water reaching the X aquifer from the Regional aquifer.
6. On the evidence of Sr isotopes, upwelling water that has circulated through Proterozoic rock beneath the Colorado Plateau is added to the RMX aquifer, as in Muav aquifer springs in the Grand Canyon.
7. Groundwater in the C and RMX aquifers is similar isotope composition in the study area, suggesting that the RMX aquifer is fed by downward leakage from the C aquifer.
8. M aquifer groundwater is distinct from RMX groundwater in receiving a larger proportion of local, low-elevation recharge.
9. Groundwater in alluvium of the Rye Basin is isotopically lighter than groundwater in the X aquifer, and appears to be thousands of years older.

Suggestions for further work

In this study, unanswered questions remain concerning the water sources in certain springs, in particular Fossil Springs and Tonto Natural Bridge Spring where discharge is observed to increase after a wet season such as Winter 2004-2005. The implied changes in the balance of local and more remote water sources may not be reflected immediately as isotope changes. The water source for the Fish Hatchery Spring is not understood. Quarterly sampling of these locations for oxygen and hydrogen stable isotopes and tritium would most likely add greatly to the present understanding of the regional hydrology, particularly after the effects of the present (2005-2006) winter drought propagate through the aquifers. The behavior of strontium isotopes is not understood in the case of water emerging from the Fort Apache Limestone, and further study of this problem is warranted, including further measurement of $^{87}Sr/^{86}Sr$ in the limestone. Lastly, groundwater systems are dynamic, and will change with time in response to heavy pumping. Periodic (every 5 years?) sampling of Payson wells for oxygen and hydrogen stable isotopes would provide useful information on the evolution of the X aquifer.

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Figure Captions:

1. Plot of δD vs. $\delta^{18}O$, illustrating the global Meteoric Water Line (GMWL) and trends due to evaporation and exchange with oxygen from rock. See text for explanation of points A, B, C, D.

2. Plots of δD vs. $\delta^{18}O$, showing different possible arrays of data in groundwater. #1: regional groundwater flow, with recharge at high elevations only; #2: Local groundwater flow and local recharge only; #3. Recharge at high and low elevations from streams fed at high elevation. H and L indicate the predicted fields of waters sampled at high and low elevations, respectively.

3. Plot of δD vs. $\delta^{18}O$, showing data for seasonal weighted average precipitation from Payson (red symbols) in comparison with 23-year means (Wright, 2001) for precipitation from Tucson basin and the Santa Catalina Mountains (yellow symbols). W, A, S signify winter, all, summer respectively.

4. A: Plot of δD vs. $\delta^{18}O$, showing all data from this study for precipitation, groundwater, surface water and reclaimed municipal water. B. Plot of δD vs. $\delta^{18}O$ for groundwater (and the Blue Ridge reservoir), with groundwater data classified according to aquifer.

5. Plot of δD vs. $\delta^{18}O$, showing data for groundwater from the study area. A: distinguishing samples from wells near recharge ponds and irrigated land in parks in and near Payson; B: classifying samples according to the aquifer sampled. The group of blue data symbols shown as "Summit etc." includes the Summit, Payson Pines 4, Turtle Rock, Goat Camp and Luke wells.

6. Plot of $\delta^{18}O$ vs. altitude of sampling, compared with measured altitude dependences in Tucson (Wright, 2001, orange line) and Flagstaff to Prescott (Blasch et al., 2005, solid purple line). The dashed purple line is a likely altitude dependence line in the Payson area, passing through the data points for the Milky Way and Round Valley wells.

7. A. Map of the Payson area showing the distribution of $\delta^{18}O$ in groundwater. B. Map of the Payson area showing the distribution of tritium in groundwater.

8. Plot of δD vs. $\delta^{18}O$, including published data from Flora (2004), Bills et al. (2000) and Parker et al. (2004), and unpublished data reported to the Arizona Department of Transportation, for spring and well samples along the Mogollon Rim between Sedona and Payson. Green line: evaporation trend of Payson area groundwater. Red dotted line: suggested evaporation line for Flagstaff-Sedona area groundwater. "Perched" refers to the perched aquifer in volcanic rocks in the Flagstaff area; "regional" to the regional aquifer in Paleozoic strata in that area.

9. Plot of $\delta^{34}S$ vs. $1/SO_4$ (L mg $^{-1}$) groundwater samples from this study, in relation to likely end-member compositions.

10. Plot of $^{87}Sr/^{86}Sr$ ratios in groundwater from the study area), in relation to the field of data from the regional aquifer in Colorado Plateau strata near Flagstaff (Bills et al., 2000), the ratios in Neogene Hickey basalt and Quaternary San Francisco volcanics (blue bar, from Scott, 1974), the ratios in Devonian to Permian marine carbonates (black bar, from Burke at al., 1982), the ratios in Proterozoic granitoids (red bars, from Condie et al., 1999), and measured ratios in rock units from the study area (Parker et al., 2005). K, S and M indicate the likely $^{87}Sr/^{86}Sr$ ranges in the limestone and evaporite elements of the Kaibab, Supai and Martin formations respectively. Groundwater data are shown as colored diamonds (enclosed in a blue rectangle) and are classified according to aquifer host rock in the case of Payson area data, and lithology of recharge zones in the case of Flagstaff data. Circled data points are rock data set are rock data for the Fort Apache Limestone member of the Supai formation, and groundwater data for Fish Hatchery spring.

11. Schematic block diagram of the Mogollon Rim and Payson area, showing possible recharge sites and flow paths of groundwater to a well in the central highlands.

12. Summary δD vs. $\delta^{18}O$ plot, showing the principal processes affecting groundwater in the study area and the Flagstaff-Sedona area.

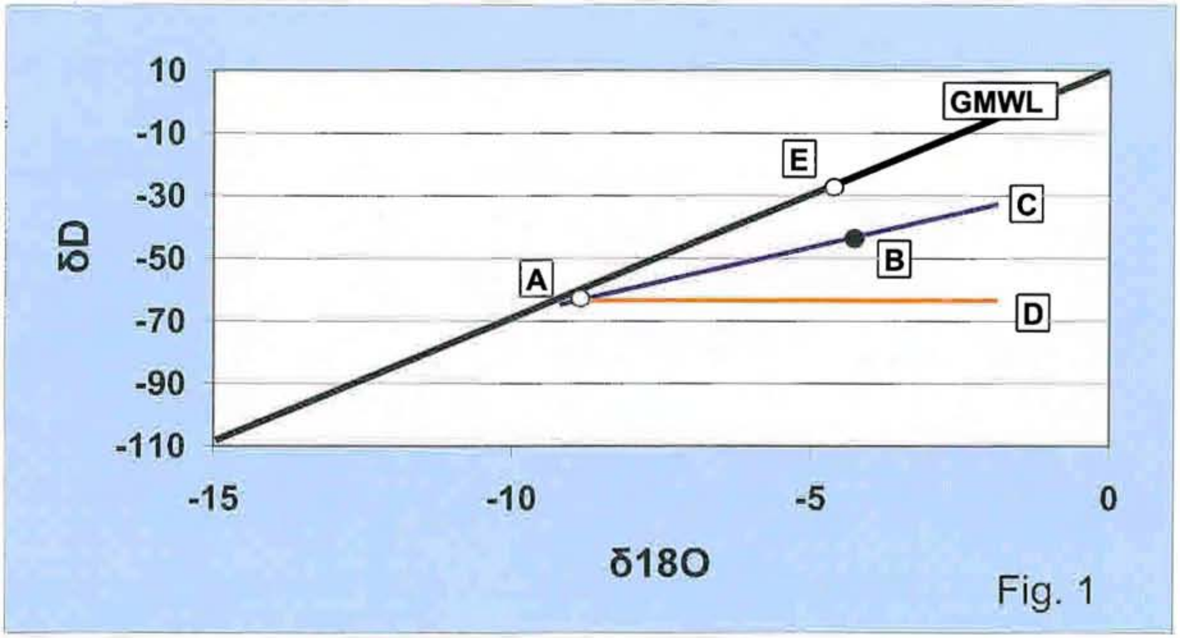
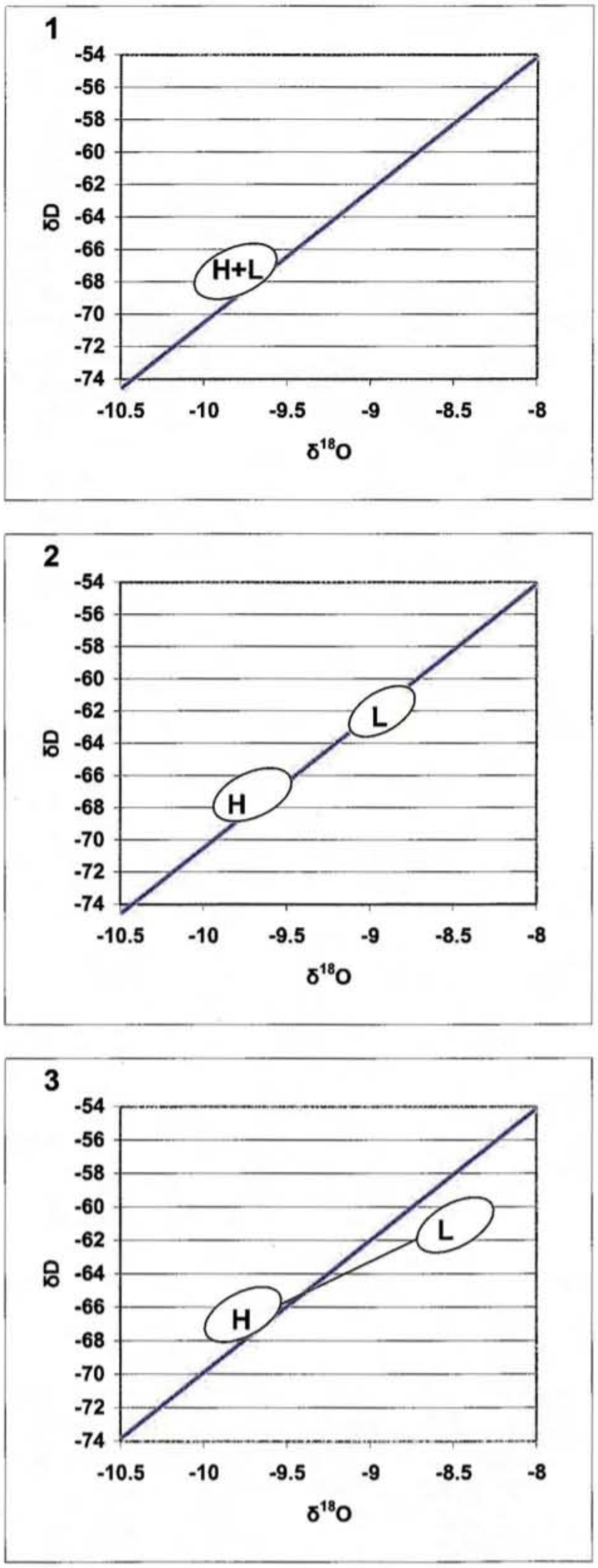


Fig. 1

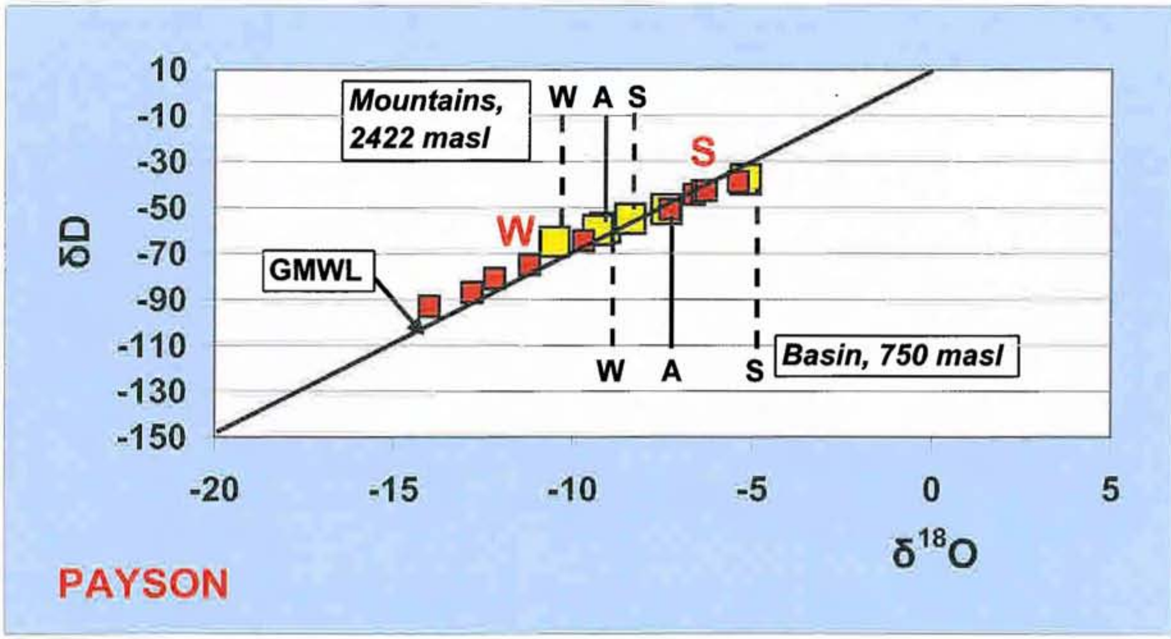


1: tritium decreases downgradient
no change in isotopes of groundwater with altitude

2: tritium present throughout.
trend slope 7-8
clear altitude dependence of isotopes

3: tritium present throughout
trend slope 3-5
altitude effect blurred

Fig. 2



10
-10
-30
-50
-70
-90
-110
-130
-150
δD
-20
-15
-10
-5
0
5
δ18O
Mountains, 2422 masl
W A S
W
S
GMWL
W A S
Basin, 750 masl
PAYSON

Fig. 3

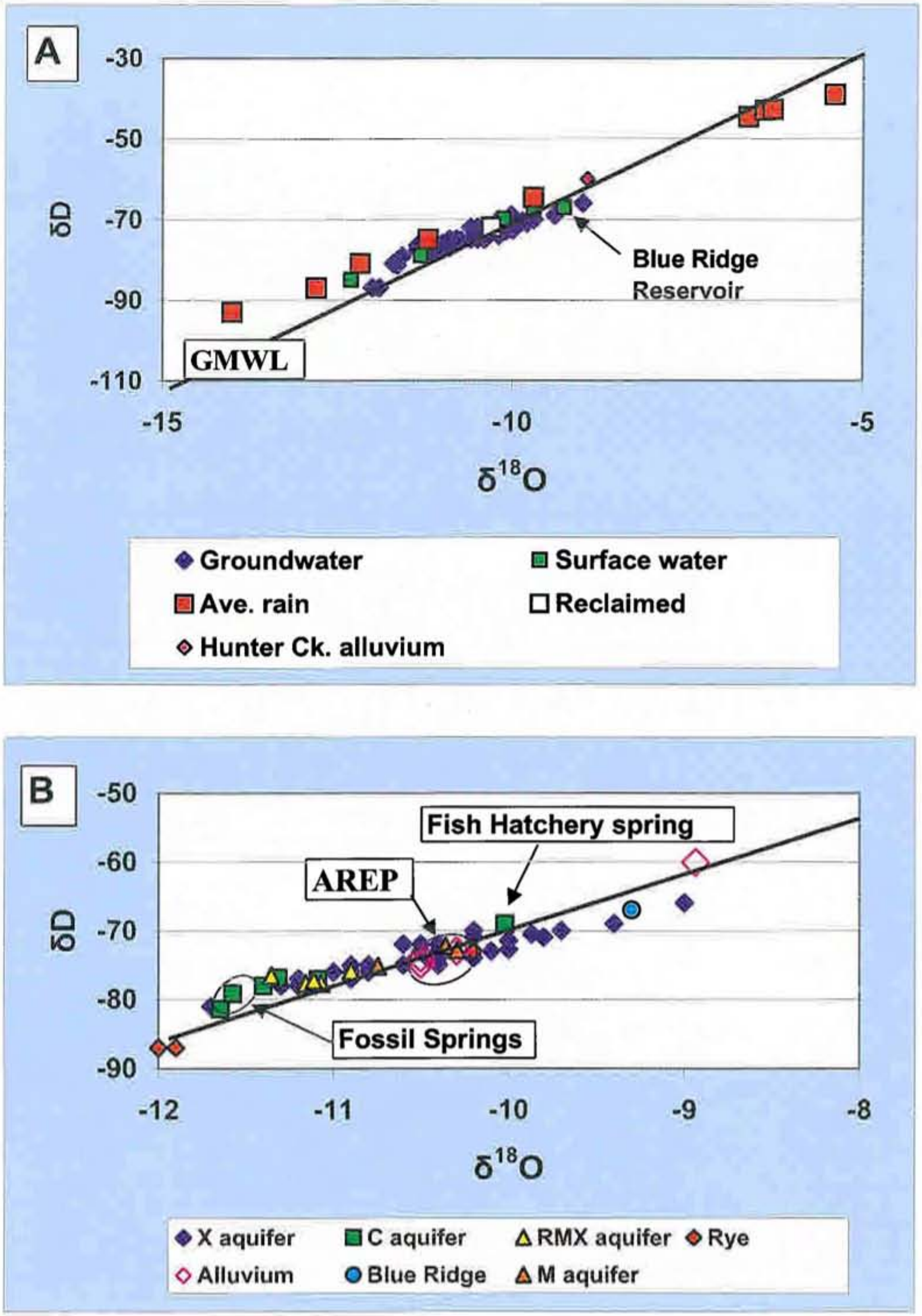
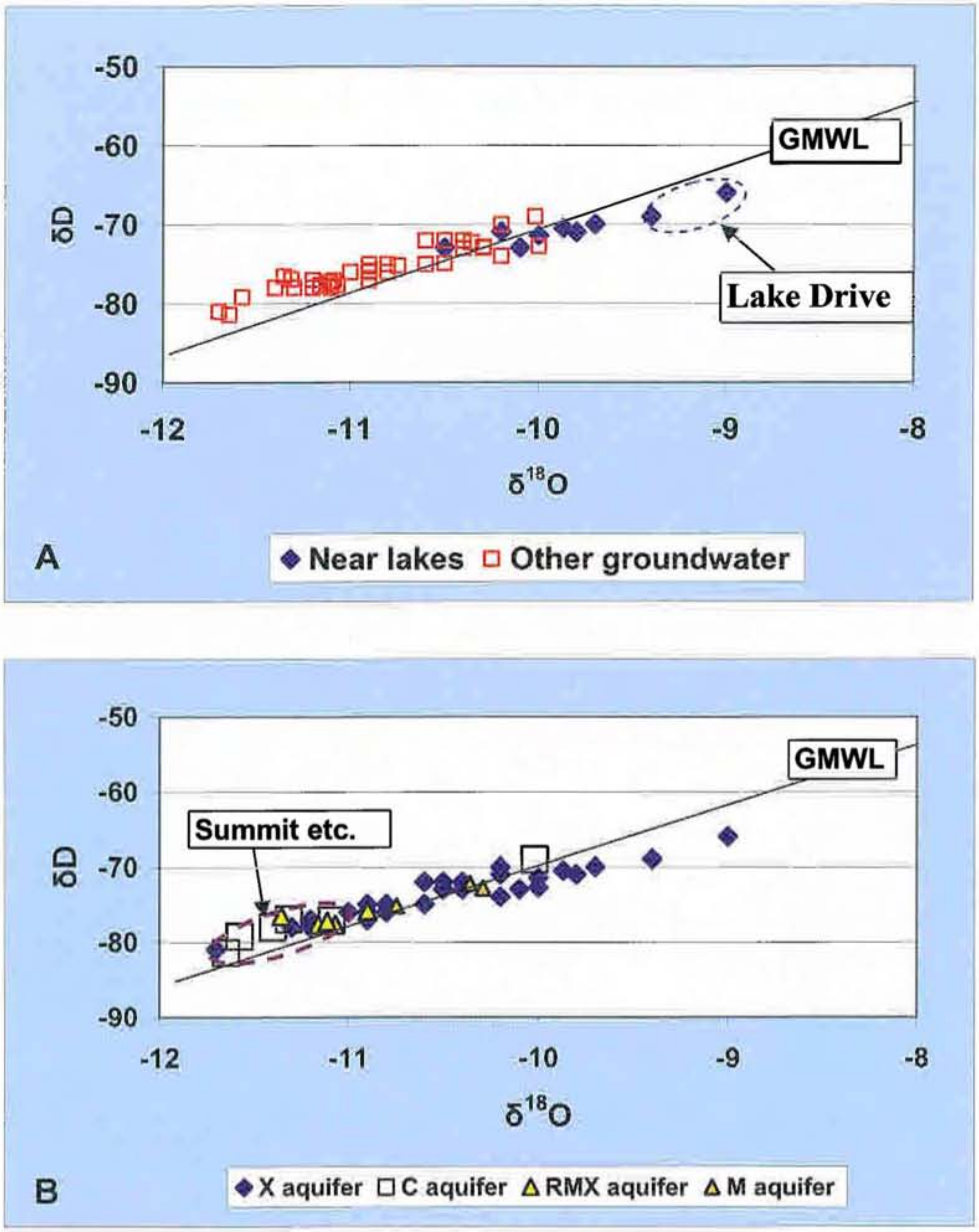
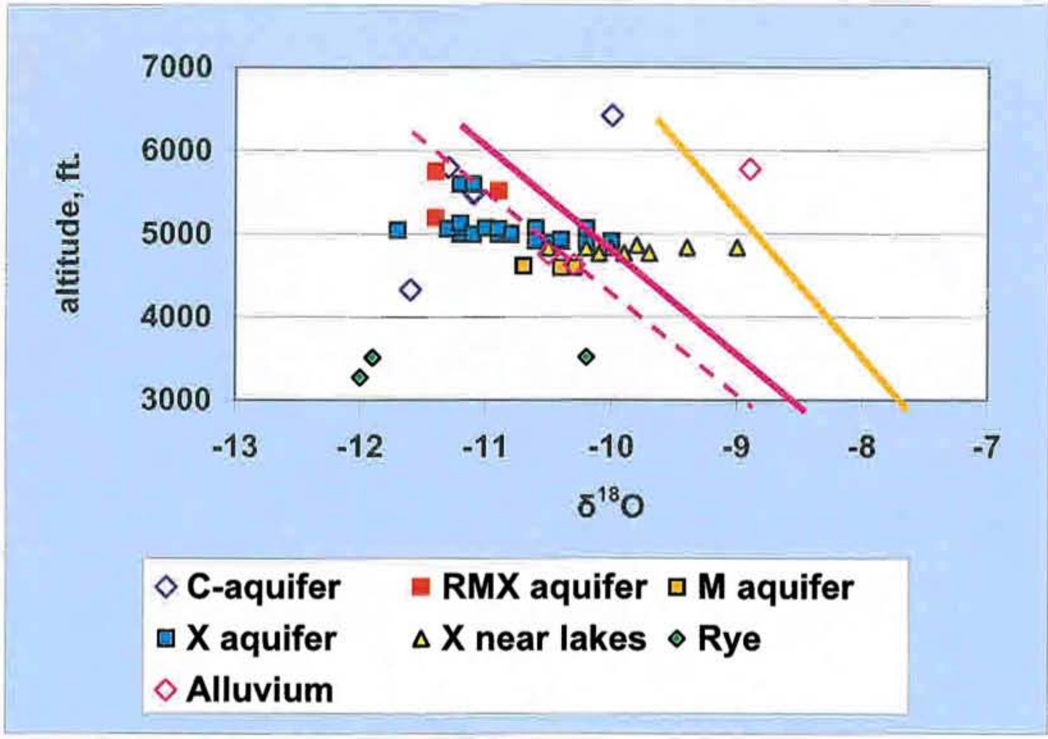

A
δD
δ18O
GMWL
Blue Ridge Reservoir
Groundwater
Surface water
Ave. rain
Reclaimed
Hunter Ck. alluvium
B
Fish Hatchery spring
AREP
Fossil Springs
X aquifer
C aquifer
RMX aquifer
Rye
Alluvium
Blue Ridge
M aquifer

Fig. 4



-50
-60
-70
-80
-90
δD
-12
-11
-10
-9
-8
δ18O
GMWL
Lake Drive
A
Near lakes
Other groundwater
-50
-60
-70
-80
-90
δD
-12
-11
-10
-9
-8
δ18O
GMWL
Summit etc.
B
X aquifer
C aquifer
RMX aquifer
M aquifer

Fig. 5



7000
6000
5000
4000
3000
altitude, ft.
-13
-12
-11
-10
-9
-8
-7
δ18O
C-aquifer
RMX aquifer
M aquifer
X aquifer
X near lakes
Rye
Alluvium

Fig. 6

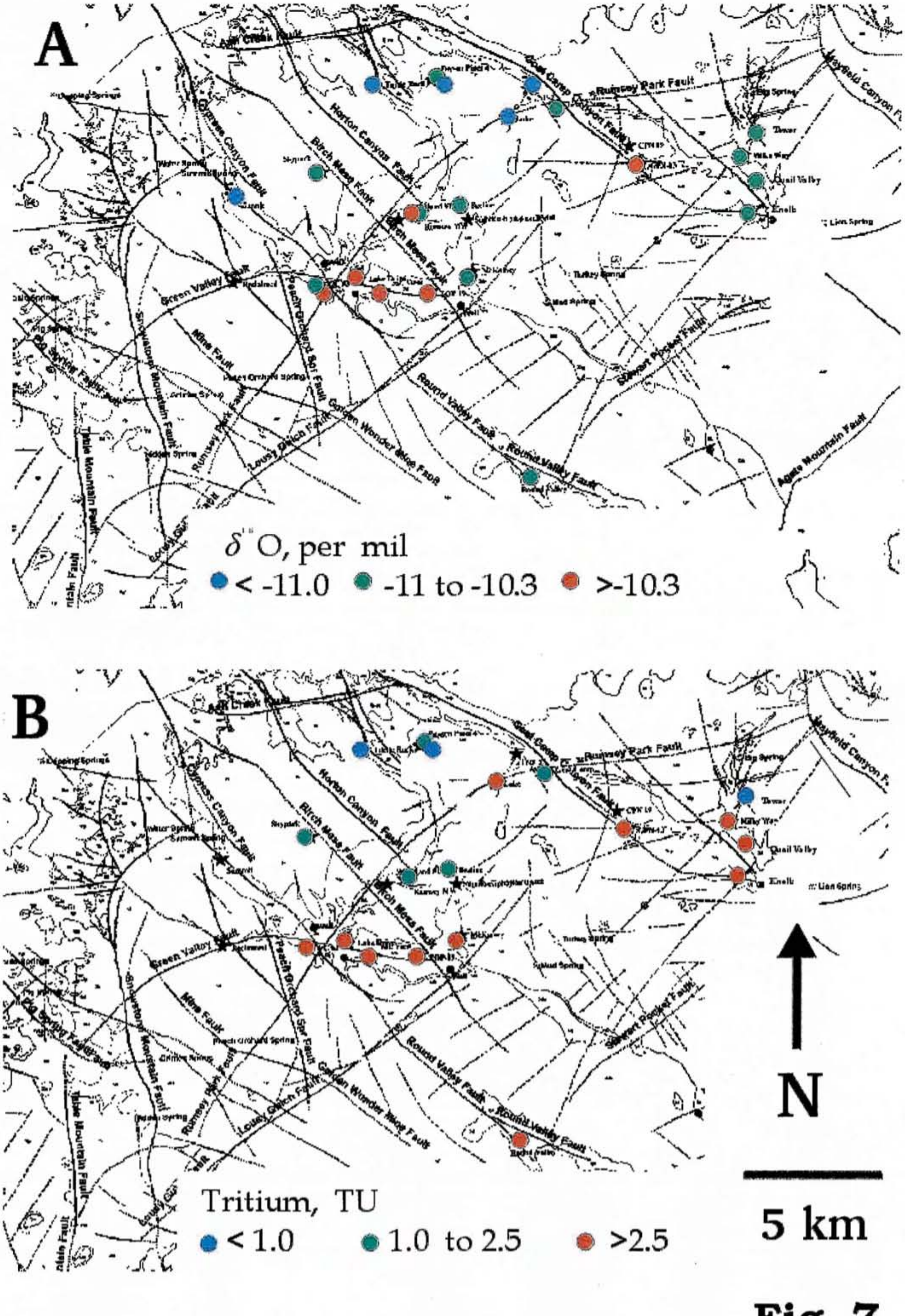

A
Ash Creek Fault
Horton Canyon Fault
Birch Mesa Fault
Rumsey Park Fault
Cypress Canyon Fault
Green Valley Fault
Mine Fault
Round Valley Fault
Stewart Pocket Fault
Agate Mountain Fault
δ18O, per mil
< -11.0
-11 to -10.3
>-10.3
B
Tritium, TU
< 1.0
1.0 to 2.5
>2.5
N
5 km

Fig. 7

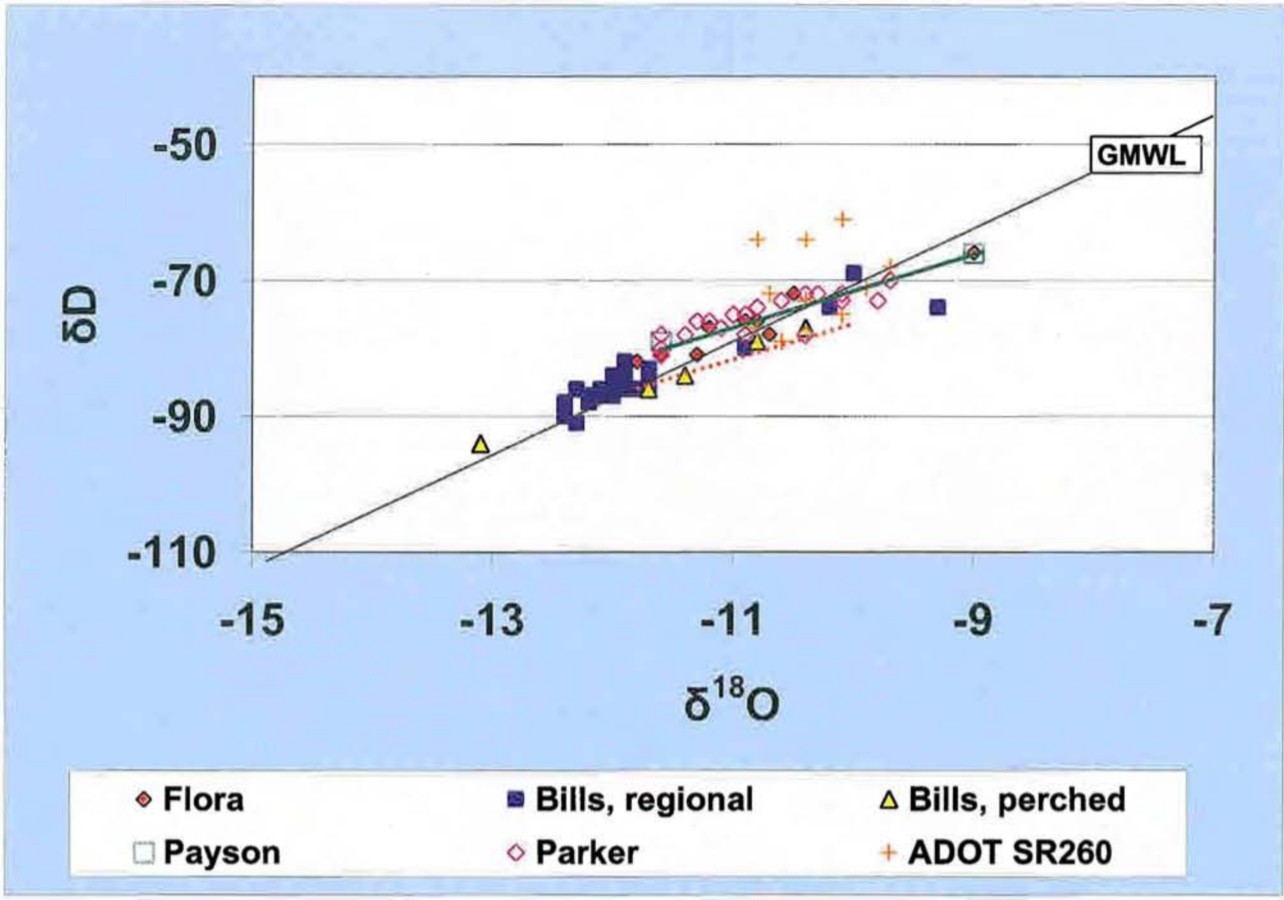
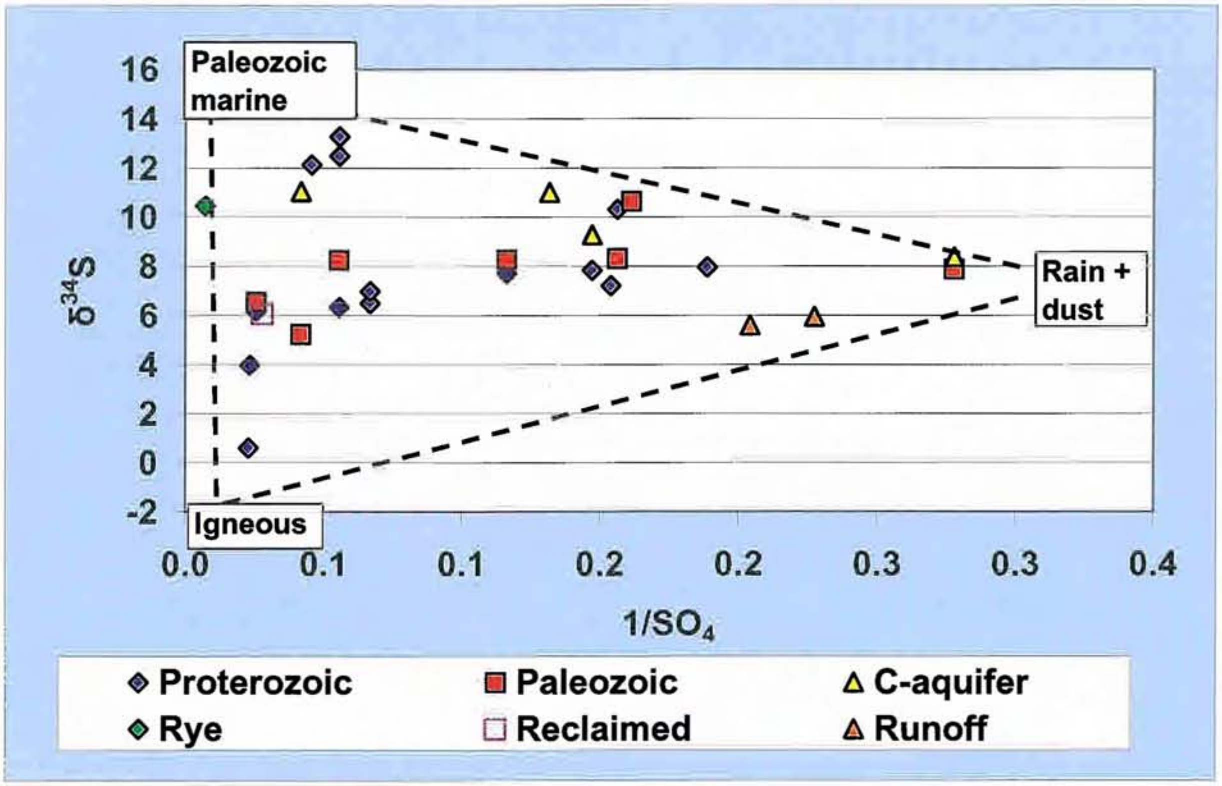
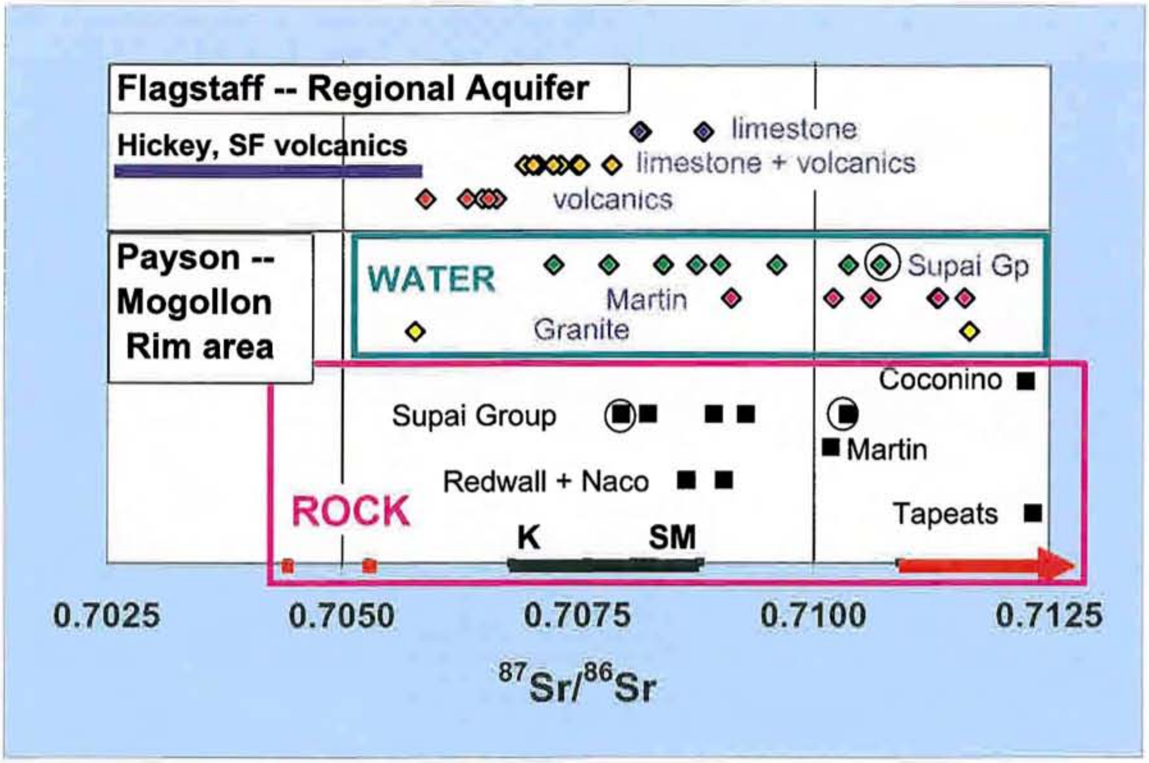

GMWL
-50
-70
-90
-110
δD
-15
-13
-11
-9
-7
δ18O
Flora
Bills, regional
Bills, perched
Payson
Parker
ADOT SR260

Fig. 8



Paleozoic marine
Rain + dust
Igneous
16
14
12
10
8
6
4
2
0
-2
δ34S
0.0
0.1
0.1
0.2
0.2
0.3
0.3
0.4
1/SO4
Proterozoic
Paleozoic
C-aquifer
Rye
Reclaimed
Runoff

Fig. 9



Flagstaff -- Regional Aquifer
Hickey, SF volcanics
limestone
limestone + volcanics
volcanics
Payson -- Mogollon Rim area
WATER
Supai Gp
Martin
Granite
Coconino
Supai Group
Martin
Redwall + Naco
ROCK
Tapeats
K
SM
0.7025
0.7050
0.7075
0.7100
0.7125
$^{87}Sr/^{86}Sr$

Fig. 10

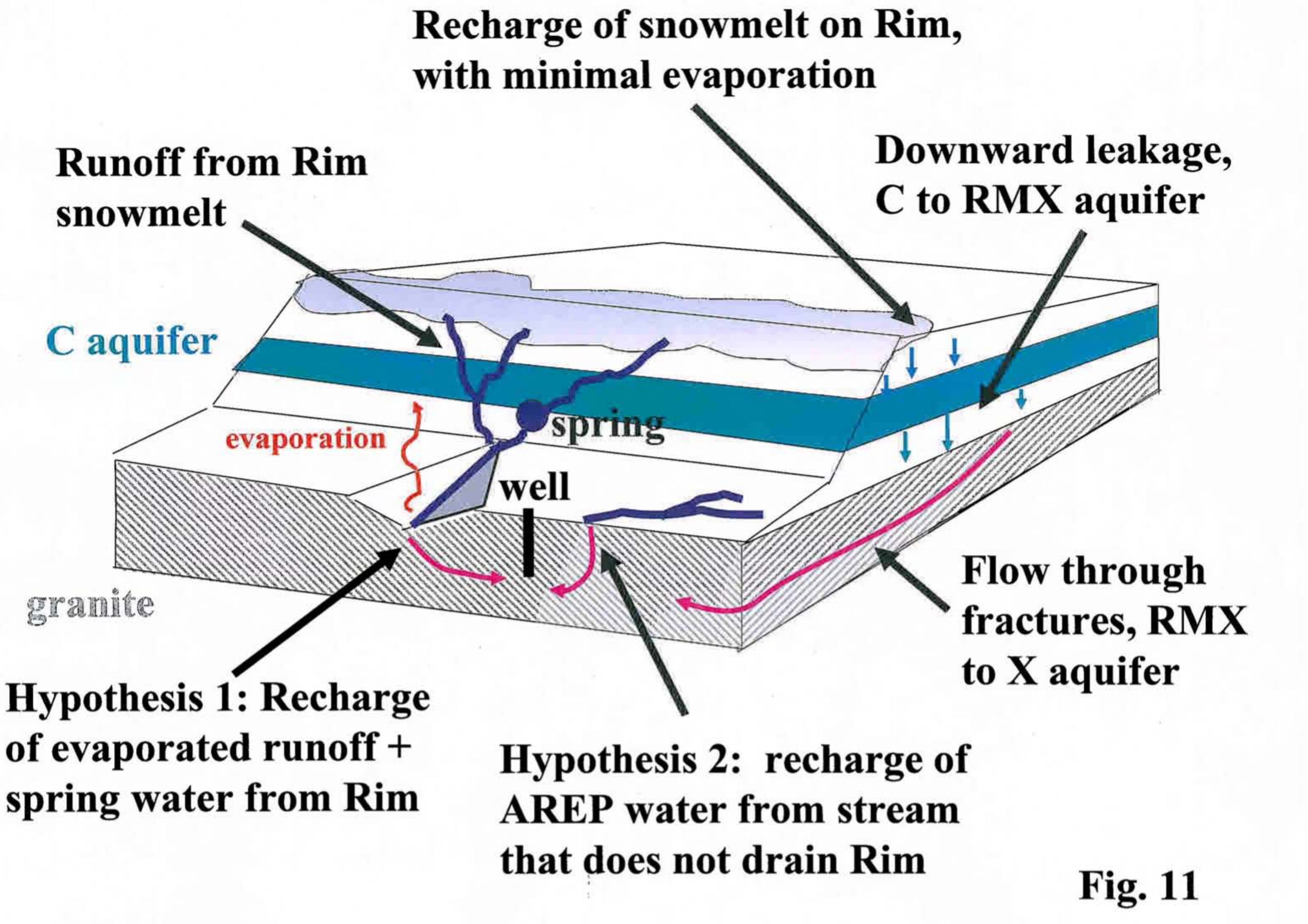

Recharge of snowmelt on Rim, with minimal evaporation
Runoff from Rim snowmelt
Downward leakage, C to RMX aquifer
C aquifer
evaporation
spring
well
granite
Flow through fractures, RMX to X aquifer
Hypothesis 1: Recharge of evaporated runoff + spring water from Rim
Hypothesis 2: recharge of AREP water from stream that does not drain Rim

Fig. 11

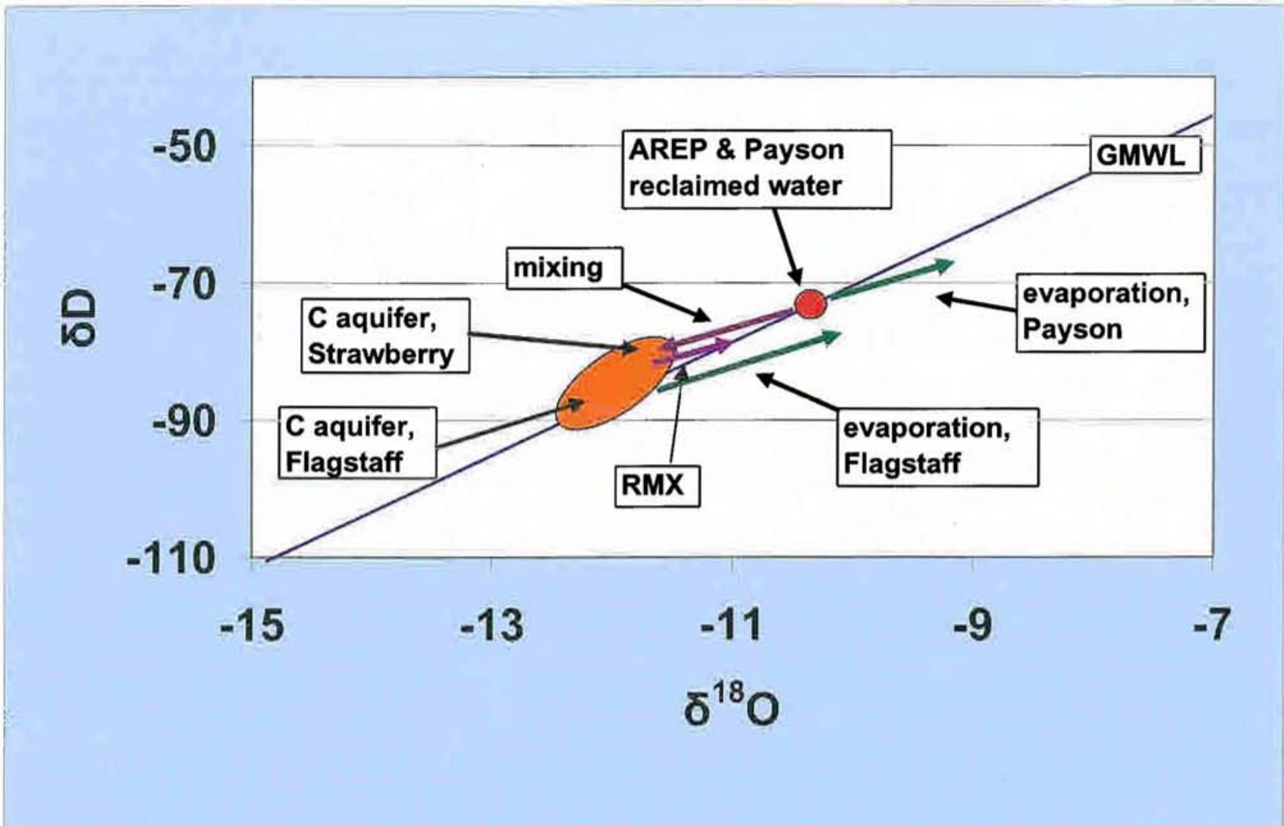

-50
-70
-90
-110
δD
-15
-13
-11
-9
-7
δ18O
AREP & Payson reclaimed water
GMWL
mixing
C aquifer, Strawberry
evaporation, Payson
C aquifer, Flagstaff
RMX
evaporation, Flagstaff

Fig. 12