Supplementary Text S4 - "R code of major functions used in reprocessing"

Effects of Improved ^{17}O Correction on Inter-Laboratory Agreement in Clumped Isotope Calibrations, Estimates of Mineral-Specific Offsets, and Temperature Dependence of Acid Digestion Fractionation

Petersen et al. 2019 - Geochemistry, Geophysics, Geosystems

```
#parameters
Santrock = c(0.0112372, 0.0020052,0.0003799,0.5164) #Santrock/Gonfiantini
Brand = c(0.011180, 0.0020052, 0.00038475, 0.528) #IUPAC



############## Defines a function to solve for R18 by minimizing an expression
R18_optimize <- function(d18_in, R45sam, R46sam, params) {
 R18_VSMOW = params[2]; R17_VSMOW = params[3]; lambda=params[4]
 R17sam <- R17_VSMOW*(d18_in/R18_VSMOW)^lambda  #d18_in must be wrt SMOW
    (R46sam-2*(R45sam-2*R17sam)*R17sam-R17sam^2-2*d18_in)^2        }

############## Defines a function to find d18O by solving the minimize function
solve_for_R18 <- function(R45,R46, params) {
 R18_VSMOW = params[2];
 #### Calculate the ratios of isotopes in the sample gas
     R18_in = rep(R18_VSMOW, length=length(R45)) #create input vec. of R18_SMOW as somewhere to
 start
     R18 = vector(mode="numeric", length(R45))

for (k in 1:length(R18_in)){
 R18_temp <- optimize(R18_optimize, c(0.00170,0.00230),tol=0.000000001,
 R45sam=R45[k],R46sam=R46[k], params)
 R18[k] = R18_temp[[1]];              }

 R18 = as.numeric(R18)
 return(R18)
}


############## “get_D47” is a function to calculate new D47 (raw), and d13C/d18O, given sample
 mean small delta values, working (reference) gas composition, and a chosen isotopic parameter
 set

get_D47 <- function(d4all, params, WGcomp){
 #d4all = d45, d46, d47, d48, d49 -> vector of 5 single values
 #params = vector of four parameter values (SG or Br)
 #WGcomp = composition of working (reference) gas, d13C relative to PDB, d18O relative to SMOW

#Read in param values and name them
R13_VPDB               =  params[1]    ## SG = 0.0112372, BR = 0.01118
R18_VSMOW              = params[2]     ## no change, SG = BR = 0.0020052
R17_VSMOW              = params[3]           ## SG = 0.0003799, BR = 0.00038475
lambda                 = params[4]     ## SG = 0.5164, BR = 0.528

#### calculate WORKING GAS ratios using d13C (PDB) and d18O (SMOW) of WG and params
 R13_WG = (WGcomp[1]/1000+1)*R13_VPDB
 R18_WG = (WGcomp[2]/1000+1)*R18_VSMOW
 R17_WG = R17_VSMOW*(R18_WG/R18_VSMOW)^lambda
#### call other function to calculate stochastic R45-R49 for working gas
 stR4X_WG = get_stR4X(R13_WG, R17_WG, R18_WG)
```

```
#### calculate R values
 R45 = (d4all[1]/1000+1)*stR4X_WG[1]
 R46 = (d4all[2]/1000+1)*stR4X_WG[2]
 R47 = (d4all[3]/1000+1)*stR4X_WG[3]
 R48 = (d4all[4]/1000+1)*stR4X_WG[4]
 R49 = (d4all[5]/1000+1)*stR4X_WG[5]

#### Calculate the ratios of stable isotopes in the sample gas
 R18 = solve_for_R18(R45,R46, params)
 R17 = R17_VSMOW*(R18/R18_VSMOW)^lambda
 R13 = R45 - 2*R17

#### Calculate d13C, d18O
 d13C = (R13/R13_VPDB-1)*1000
 d18O_smow = (R18/R18_VSMOW-1)*1000

#### call other function to calculate stochastic R45-R49 for SAMPLE gas
 stR4X_sample = get_stR4X(R13, R17, R18)

#### Calculate raw D47
 Cap47 = ((R47/stR4X_sample[3]-1)-(R46/stR4X_sample[2]-1)-(R45/stR4X_sample[1]-1))*1000
 Cap48 = ((R48/stR4X_sample[4]-1)-2*(R46/stR4X_sample[2]-1))*1000
 Cap49 = ((R49/stR4X_sample[5]-1)-2*(R46/stR4X_sample[2]-1)-(R45/stR4X_sample[1]-1))*1000

 return(c(d13C, d18O_smow, Cap47, Cap48, Cap49))
}


############### "get_stR4X" is a function that calculates stochastic R4X values (stR45-stR49)
 given R13, R18
get_stR4X <- function(R13, R17, R18) {

#### Calculate abundances of isotopes in sample gas
 C12 = 1/(1+R13)
 C13 = R13/(1+R13)
 O16 = 1/(1+R17+R18)
 O17 = R17/(1+R17+R18)
 O18 = R18/(1+R17+R18)

 #### Calculate abundances of isotopologues in sample gas assuming STOCHASTIC distribution
 st44 = C12*O16^2
 st45 = C13*O16^2+2*C12*O16*O17
 st46 = 2*C12*O16*O18+2*C13*O16*O17+C12*O17^2
 st47 = 2*C13*O16*O18+2*C12*O17*O18+C13*O17^2
 st48 = C12*O18^2+2*C13*O17*O18
 st49 = C13*O18^2

 #### Calculate the raw ratios of isotopologues in sample gas assuming STOCHASTIC distribution
 stR45 = st45/st44
 stR46 = st46/st44
 stR47 = st47/st44
 stR48 = st48/st44
 stR49 = st49/st44

return(c(stR45, stR46, stR47, stR48, stR49))

}
```