# Simulation and plotting code for "Optimizing the use of carbonate standards to minimize uncertainties in clumped isotope data"

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## Contents

The supplementary code to the manuscript "Optimizing the use of carbonate standards to minimize uncertainties in clumped isotope data".



See `https://github.com/japhir/stdstats` for potentially updated versions and Emacs org source files.

Please note that it takes quite some time to run all of the code, so if you want to evaluate it, make sure to do so line-by-line!

We set the seed here in an attempt to make these exact simulations reproducible, but this only works for the next random sampling call. Thus, you will not get identical results. Please load the included simulation output `.rds` files to generate identical plots (see below).

```
set.seed(1563435)
```

# 1 install required packages

Install all below packages. Some of them (e.g. `furrr`) rely on the dev version available on GitHub. Install them with

```
devtools::install_github("DavisVaughan/furrr")
```

Install the new package `stdsim` similarly, from

```
devtools::install_github("japhir/stdsim")
```

or point to the directory in which you downloaded the stdsim folder with

```
devtools::install_local("/path/to/stdsim")
```

## 2 optional packages

I use this for my theme.

```
devtools::install_github("baptiste/egg")
```

## 3 load libraries

We use the following packages for this project:

```
library(dplyr)     # for piping (%>%), mutate, and nice data manipulation
library(tidyr)     # for making tibbles tidy, (gather, spread etc.)
library(tibble)    # a better thing than a dataframe
library(ggplot2)   # plotting
library(tictoc)    # to keep track of how long the functions took
library(purrr)     # functional programming to map variables from lists of dataframes
library(magrittr)  # only used once for extract, but original package of the pipe
library(patchwork) # combine plots
library(furrr)     # furrr allows parallell purr functions w/ progress bars!

library(stdsim)    # the new R package created just for this paper!
```

## 4 multiple cores

run simulations on as many cores as possible. Note that I read somewhere that the random number generator gets less random when using multiple cores, but it is much faster and since I perform all simulations often this shouldn't effect the results.

```
plan(multiprocess)
```

## 5 set up plotting theme

We can use a different theme, but I like the one in the dev package `egg`. Install it or ignore this section of code.

```
theme_set(egg::theme_article(base_size = 11, base_family="Helvetica"))
```

# 6 set up stdinfo etc.

This uses the default functions in stdsim to generate a tibble with standard and sample information. It doesn't add $\delta_{47}$ values by default since they differ between labs and are not important for these simulations.

```
eth.info <- make_std_table()
smpinfo <- make_smp_info(c(0, 40))
stdev <- 14
# append d47 values based on actual measurement results for our MOTU
eth.info$d47 <- c(15.6, -13.2, 16.2, -13.1, NA_real_)
```

## 6.1 setup axes

# 7 calculate temperature sensitivity as a function of temperature

Now we are interested in calculating the rate of change as a function of D47, so that we can calculate the change in temperature. So we take the derivative of the original T(D47) function.

```
tempcal_simplified  <- function(Tc, slp=0.0449, int=0.167, kkelvin=273.15) {
    (slp * 1e6) / (Tc + kkelvin)^2 + int
}

tempcal_derivative  <- function(Tc, slp=0.0449, int=0.167, kkelvin=273.15) {
  -((2 * slp * 1e6) / ((kkelvin + Tc) ^ 3))
}

revcal_simplified <- function(D47, slp=0.0449, int=0.167, kkelvin=273.15) {
    sqrt((slp * 1e6) / (D47 - int)) - kkelvin
}

revcal_derivative <- function(D47, slp=0.0449, int=0.167) {
  (sqrt(-(slp * 1e6) / (int - D47))) / (2 * int - 2 * D47)
}
```

See

```
?revcal
?tempcal
```

for the actual function documentation.

### 7.1 temp_sens_pot

Calculate the sensitivity of the temperature calibration at the relevant temperature range, so that we can add an estimate of uncertainty in the temperature domain to plots.

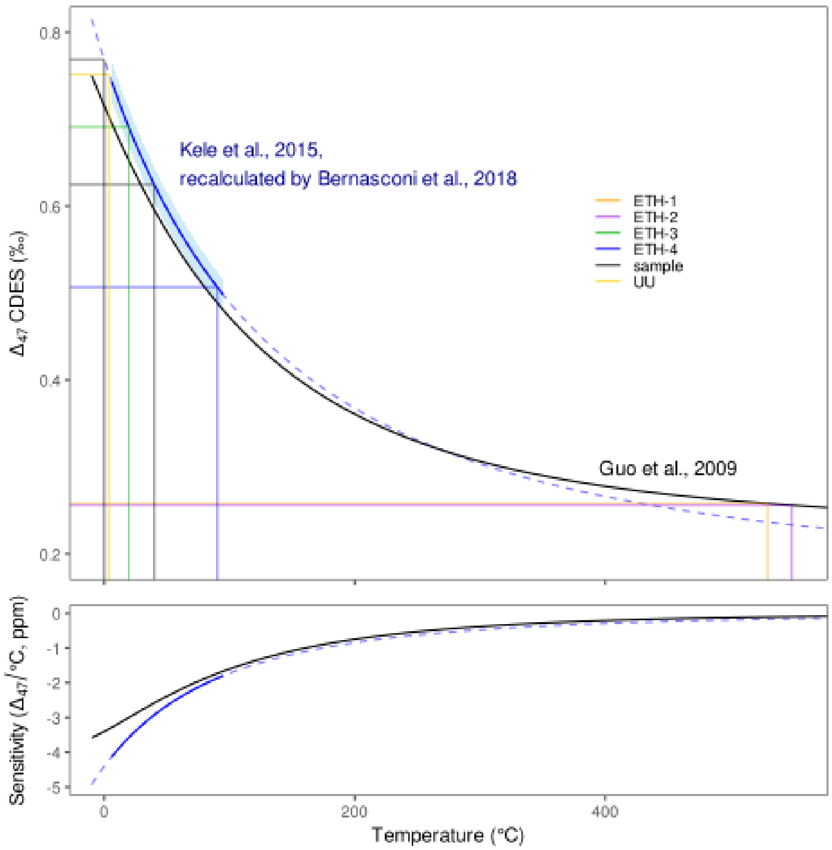
The citeA:Kele2015 temperature calibration is only valid between 6 and 95 °C, so

```
# guo 2009 eqn. 18
# takes temperature in degrees celsius, converts to D47
guo_cal <- function(temp) {
  # convert degrees celsius to kelvin
  x <- temp + kkelvin
  # apply polynomial fit
  -3.33040e9 / x^4 + 2.32415e7 / x^3 - 2.91282e3 / x^2 - 5.54042 / x + 0.23252
}

# takes D47, converts to temperature in degrees celsius
guo_deriv <- function(temp) {
  x <- temp + kkelvin
  (5.54042 * x^3 + 5825.64 * x^2 - 69724500 * x + 13321600000)/x^5 * 1000
}
```

Update standards to use Guo if ETH-1 or ETH-2. We hack it together by numerically solving it.

```
guo_temp <- tibble(Tc = rng, D47 = guo_cal(Tc))
eth1_new_temp <- guo_temp$Tc[[which(near(guo_temp$D47, eth.info$D47[[1]], tol = .000000
eth2_new_temp <- guo_temp$Tc[[which(near(guo_temp$D47, eth.info$D47[[2]], tol = .000000

guo_std_temp <- bind_rows(eth.info, smpinfo) %>%
  mutate(temp = case_when(id == "ETH-1" ~ eth1_new_temp, #802.812 - kkelvin,
  id == "ETH-2" ~ eth2_new_temp, #822.2 - kkelvin,
  TRUE ~ temp))

plot_temp <- sensdf %>%
  filter(Tc >= 6, Tc <= 95) %>%
  ggplot(aes(y = D47, x = Tc)) +
  geom_ribbon(aes(ymin = lwr, ymax = upr), fill = "skyblue", alpha = .4) +
  geom_line(colour = "blue", linetype = 2, alpha = .5, data = sensdf) +
  geom_line(colour = "blue") +
```

```
  ## geom_line(colour = "black", data = guo_temp) +
  stat_function(fun = guo_cal, colour = "black") +
  geom_segment(aes(x = -Inf, xend = temp, y = D47, yend = D47, col = id),
       alpha=.5,
       inherit.aes=FALSE,
       data = guo_std_temp) +
  geom_segment(aes(x = temp, xend = temp, y = -Inf, yend = D47, col = id),
       alpha=.5,
       inherit.aes=FALSE,
       data = guo_std_temp) +
  annotate("text", x = 60, y = .65, label = "Kele et al., 2015, \nrecalculated by Berna
  annotate("text", x = 450, y = .3, label = "Guo et al., 2009") +
  scale_colour_manual(values = c(eth.info$col[-5], smpinfo$col[[1]], eth.info$col[[5]])
  labs(x = "Temperature (°C)", y = Delta[47] ~ "CDES (\u2030)") +
  coord_cartesian(ylim = c(.2, .8), xlim = c(0, 550)) +
  theme(axis.title.x=element_blank(),
axis.text.x=element_blank(),
legend.pos=c(.75, .6), legend.title = element_blank())

plot_sens <- sensdf %>%
  filter(Tc >= 6, Tc <= 95) %>%
  ggplot(aes(y = sens * 1e3, x = Tc)) +
  geom_line(colour = "blue", linetype = 2, alpha = .5, data = sensdf) +
  geom_line(colour = "blue") +
  stat_function(fun = guo_deriv, xlim = c(-10, 1000)) +
  coord_cartesian(ylim = c(-5, 0), xlim = c(0, 550)) +
  ## geom_vline(xintercept=c(0, 40), col="#ededed") +
  labs(x = "Temperature (°C)", y = "Sensitivity" ~ "(" * Delta[47] / "°C, ppm)")

temp_sens_pl <- plot_temp + plot_sens + plot_layout(nrow=2, heights=c(3, 1))
temp_sens_pl
```




# 8 create standard intro plot

The standards as a function of composition

```
lims <- c(.15, .71)
standards_plot <- ggplot(eth.info, aes(x = d47, y = D47.noacid, col = id, label = id))
  geom_point(size = 2, show.legend = F) +
  ## geom_label(show.legend = F) +
  ggrepel::geom_label_repel(size = 2.5, show.legend = FALSE) +
  # add UU1 standard
  geom_hline(yintercept = eth.info$D47.noacid[[5]], linetype = 2, col = eth.info$col[[5
  annotate("label", x = 1.225, y = eth.info$D47.noacid[[5]], label = eth.info$id[[5]],
  scale_colour_manual(values = eth.info$col) +
  labs(colour = "", x = delta^{47}~"(SG vs WG PBL \u2030)",
    y = Delta[47] ~ "CDES" - "AFF (\u2030)") +
```

```
  scale_y_continuous(sec.axis = sec_axis(~ sqrt((0.0449 * 1e+6)/(. + kaff - 0.167)) - 2
"Sample temperature (°C)", temp_breaks,
temp_labs)) +
  coord_flip(ylim=lims) +
  theme(axis.text.x.bottom=element_blank(), axis.title.x.bottom=element_blank())
  ## coord_cartesian(clip = "off") +
  ## theme(legend.pos = c(.15, .85))
```

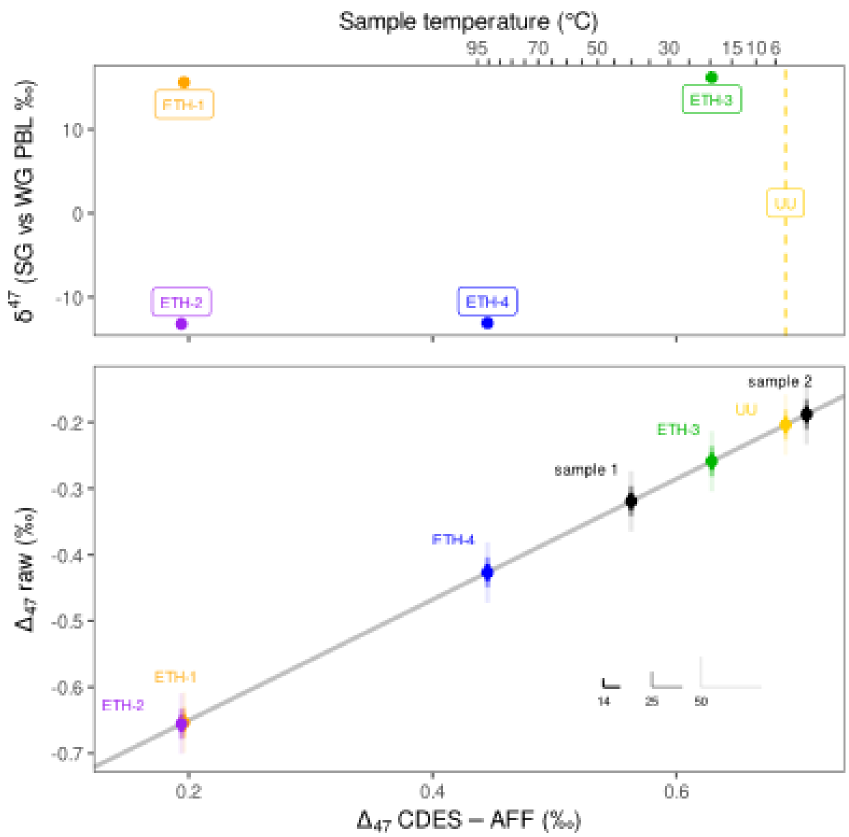
And the simulation input conditions illustrating the ETF.

```
stdevs <- c(14, 25, 50) / 1e3
xs <- .54 + c(0, .04, .08)
ys <- rep(-.6, 3)

standard_sample_data <- make_smp_info(c(0, 40)) %>%
  mutate(id=ifelse(temp == 40, "sample 1", "sample 2")) %>%
  ## mutate(id=paste(id, temp)) %>%
  bind_rows(eth.info)

base_plot <-  standard_sample_data %>%
  ggplot(aes(x = D47.noacid, y = rawcat, col = id, label = id)) +
  # add etf
  geom_abline(intercept = kintercept, slope = kslope,
    linetype = 1, size = 1, col = "gray") +
  # 50 ppm uncertainty pointrange
  geom_linerange(aes(ymin = rawcat - 50 * kslope / 1e3,
    ymax = rawcat + 50 * kslope / 1e3),
    size = 1, linetype = 1, alpha = .1) +
  # 25 ppm uncertainty pointrange
  geom_linerange(aes(ymin = rawcat - 25 * kslope / 1e3,
    ymax = rawcat + 25 * kslope / 1e3),
    size = 1, linetype = 1, alpha = .4) +
  # 14 ppm uncertainty pointrange
  geom_linerange(aes(ymin = rawcat - 14 * kslope / 1e3,
    ymax = rawcat + 14 * kslope / 1e3),
    size = 1, linetype = 1) +
  geom_point(size=2) +
  # create a manual legend with the different input uncertainties
  annotate("segment",
   x = xs, xend = xs,
   y = ys, yend = ys + stdevs * kslope,
```

```
    alpha = c(1, .4, .1)) +
  annotate("segment",
   x=xs, xend=xs + stdevs,
   y=ys, yend=ys,
   alpha=c(1, .4, .1)) +
  annotate("text",
   x = xs,
   y = ys - .02,
    label = c("14", "25", "50"), size = 2) +
  # add the input sample measurements
  ggrepel::geom_text_repel(force = 3, hjust = 1, nudge_y = .05, nudge_x = -.01, size=2
  # make it pretty, manual colour scale, samples are black
  scale_colour_manual(
      limits = standard_sample_data$id,
      values = standard_sample_data$col) +
  # nice axis labels
  labs(
    colour = "",
    x = Delta[47] ~ "CDES" - "AFF (\u2030)",
    y = Delta[47] ~ "raw (\u2030)"
  ) +
  scale_x_continuous(limits=lims) +
  theme(legend.pos = "none")
```

In the text we combine them using patchwork, to create figure 1.

```
standards_pl <- standards_plot + base_plot + plot_layout(nrow=2, heights = c(.4, .6))
standards_pl
```




# 9 micro benchmark

Calculate how long it takes for one simulation.

```
options(genplot = FALSE, verbose = FALSE)
tpersim <- microbenchmark::microbenchmark(sim_stds(out = "cis",
  stdtable = eth.info)) %>%
  summary() %>%
  pull(mean) / 100
tpersim
```

# 10 example sims

We create some example simulations for fig. 2.

```
options(genplot=F, verbose=F)

## set up small inputs dataframe
example_sims <- tibble(
  name=rep(c("Equal\nproportions", "Optimal\ndistribution", "Optimal\ndistribution + UU
  stdfreqs=rep(list(c(1, 1, 1, 1, 0), c(1, 1, 9, 0, 0), c(1, 1, 0, 0, 9)), 2),
  smpt=c(rep(0, 3), rep(40, 3))) %>%
  ## run sims with inputs dataframe
  mutate(res = purrr::pmap(select(., -name), sim_stds, stdev=25, out="all", stdn=50, sm
 # extract the default plots
 pl=purrr::map(res, plot_sim, graylines=F, point_alpha=.2, pointrange=T, labs=F, fixed=
 # add a row number for the next step
 exprow=1:n() %>% as.character())

# combine the smp and std outputs of each experiment, based on the row number
six_example_sims <- example_sims$res %>%
  map_dfr("smp", .id="exprow") %>%
  bind_rows(example_sims$res %>% map_dfr("std", .id="exprow")) %>%
  left_join(example_sims, by="exprow")
```

We create the example plot

```
exmp_plot <- ggplot(six_example_sims, aes(x=D47.noacid, y=raw, col=id, fill=id)) +
  geom_smooth(aes(group=paste0(name, smpt)), method="lm", size=.1,
      fullrange=TRUE, data=filter(six_example_sims, id != "sample")) +
  geom_violin(alpha=.3, colour=NA, scale="count", width=.5, position=position_identity(
  geom_point(shape=1, alpha=.2, size=.3) +
  facet_grid(rows=vars(name), cols=vars(paste(smpt, "°C"))) +
  ## coord_fixed(xlim=c(.1, .8)) +
  coord_cartesian(xlim=c(.14, .75)) +
  scale_colour_manual("ID",
      ## limits = c(out$cond$stdtable$id, out$cond$smpinfo$id),
      limits = c(example_sims$res[[1]]$cond$stdtable$id, example_sims$res[[1]]$cond$smp
      ## values = c(out$cond$stdtable$col, out$cond$smpinfo$col)) +
      values = c(example_sims$res[[1]]$cond$stdtable$col, example_sims$res[[1]]$cond$sm
  scale_fill_manual("ID",
    limits = c(example_sims$res[[1]]$cond$stdtable$id, example_sims$res[[1]]$cond$smpin
    values = c(example_sims$res[[1]]$cond$stdtable$col, example_sims$res[[1]]$cond$smpi
  labs(x = Delta[47] ~ "CDES" - "AFF (\u2030)",
       y = Delta[47] ~ raw ~ "(\u2030)") +
  theme(legend.pos="top", legend.key.size=unit(3, "mm"), legend.text = element_text(siz
```

```
strip.text.y = element_text(size = 8, angle = 90))
exmp_plot
```

and the table for in the text:

```
tbl_exmp <-
  forplot_0 %>%
  bind_rows(forplot_40) %>%
  filter(expname %in% c("1:1:1:1:0", "1:1:9:0:0", "1:1:1:0:9")) %>%
    select(-stdfreqs, -exprow, -meanerr, -hascoldstandard) %>%
  group_by(expname, smpt, stdev) %>%
  ## nest() %>%
  summarize(err_mean = mean(smp, na.rm = TRUE) * 1e3,
    err_ci = qt((1 - .05), length(smp) - 1) * sd(smp, na.rm = TRUE) / sqrt(length(smp)
  mutate(err_temp = err_mean / 1e3 / tempcal_derivative(smpt) %>% abs,
 err_temp_ci = err_ci / 1e3 / tempcal_derivative(smpt) %>% abs,
   ) %>%
  arrange(stdev, -err_mean) %>%
  ## bind_cols(map_dfr(.$data, ~ mean(smp))) %>%
  pivot_wider(id_cols = c(expname, stdev), names_from = smpt, values_from = c(err_mean
  # change order of things
  mutate(Name = case_when(expname == "1:1:1:1:0" ~ "Equal proportions",
  expname == "1:1:9:0:0" ~ "Optimal distribution",
  expname == "1:1:1:0:9" ~ "Optimal distribution + UU1",
  TRUE ~ "wth")) %>%
  select(Name, expname, stdev, ends_with("_0"), ends_with("_40")) %>%
  as_tibble() %>%
  mutate(
    out_0_ppm = glue::glue("{round(err_mean_0, 2)} \\pm {round(err_ci_0, 2)}"),
    ## improv_0 = round(err_mean_0 / lead(err_mean_0), 2),
    ## improv_40 = round(err_mean_0 / lead(err_mean_0), 2),
    out_0_deg = glue::glue("{round(err_temp_0, 2)} \\pm {round(err_temp_ci_0, 2)}"),
    out_40_ppm=glue::glue("{round(err_mean_40, 2)} \\pm {round(err_ci_40, 2)}"),
    out_40_deg = glue::glue("{round(err_temp_40, 2)} \\pm {round(err_temp_ci_40, 2)}")
    ) %>%
  ## rename for latex output
  select(Name,
 `Standard distribution`=expname,
 `\\sigma` = stdev,
 `0\\us\\celsius (ppm)` = out_0_ppm,
 ## `\\times` = improv_0,
```

```
‘40\\us\\celsius (ppm)‘=out_40_ppm,
## ‘\\times‘ = improv_40,
## ‘0\\u
‘0\\us\\celsius (\\celsius)‘=out_0_deg,
‘40\\us\\celsius (\\celsius)‘=out_40_deg)
```

| Name | Standard distribution | $\sigma$ | 0 °C (ppm) | 40 °C (ppm) | 0 °C (°C) |
|---|---|---|---|---|---|
| Equal proportions | 1:1:1:1:0 | 14 | 9.37 ± 0.12 | 7.21 ± 0.09 | 2.13 ± 0.03 |
| Optimal distribution | 1:1:9:0:0 | 14 | 6.8 ± 0.09 | 5.58 ± 0.07 | 1.54 ± 0.02 |
| Optimal distribution + UU1 | 1:1:1:0:9 | 14 | 6 ± 0.07 | 5.63 ± 0.07 | 1.36 ± 0.02 |
| Equal proportions | 1:1:1:1:0 | 25 | 17.03 ± 0.24 | 12.89 ± 0.16 | 3.86 ± 0.05 |
| Optimal distribution | 1:1:9:0:0 | 25 | 12.45 ± 0.18 | 10.24 ± 0.12 | 2.82 ± 0.04 |
| Optimal distribution + UU1 | 1:1:1:0:9 | 25 | 10.86 ± 0.12 | 10.11 ± 0.1 | 2.46 ± 0.03 |
| Equal proportions | 1:1:1:1:0 | 50 | 35.15 ± 0.57 | 26.35 ± 0.46 | 7.98 ± 0.13 |
| Optimal distribution | 1:1:9:0:0 | 50 | 25.08 ± 0.44 | 20.1 ± 0.27 | 5.69 ± 0.1 |
| Optimal distribution + UU1 | 1:1:1:0:9 | 50 | 22.09 ± 0.33 | 20.03 ± 0.28 | 5.01 ± 0.08 |

# 11 stddis

To simulate the distribution of the standards we create a tibble of inputs for `sim_stds()`.

## 11.1 create a list of all possible stddis combinations

```
# the proportions we want each standard to get
pr <- c(0, 1, 3, 9)

# each standard gets these proportions in all possible combinations
props <- expand.grid(
  ‘ETH-1‘ = pr,
  ‘ETH-2‘ = pr,
  ‘ETH-3‘ = pr,
  ‘ETH-4‘ = pr,
  UU1 = pr) %>%
  # we need at least 1|2 & 3|4|UU1 to be able to calculate an ETF
  # we need at least 1|2|4 & 3|4|UU1 to be able to calculate an ETF
  ## filter(‘ETH-1‘ + ‘ETH-2‘ + ‘ETH-4‘ > 0 & ‘ETH-3‘ + ‘ETH-4‘ + ‘UU1‘ > 0) %>%
  # we need at least 1 standard
  filter(‘ETH-1‘ + ‘ETH-2‘ + ‘ETH-4‘ + ‘ETH-3‘ + ‘ETH-4‘ + ‘UU1‘ > 0) %>%
```

```
  # calculate relative abundances
  mutate(sums = rowSums(.),
    f1 = `ETH-1` / sums,
    f2 = `ETH-2` / sums,
    f3 = `ETH-3` / sums,
    f4 = `ETH-4` / sums,
    fu = UU1 / sums) %>%
  # filter out the redundant ones
  distinct(f1, f2, f3, f4, fu, .keep_all = TRUE) %>%
  arrange(`ETH-1`, `ETH-2`, `ETH-3`, `ETH-4`, UU1)

# convert the proportions to a list we can put in our experimental matrix
props_list <- props %>%
  select(-c(sums, starts_with("f"))) %>%
  as.matrix() %>%
  split(seq(nrow(.)))
```

### 11.2 expand the whole grid

```
stddis <- expand.grid(
    smpt = c(0, 40),
    stdfreqs = props_list,  # this uses the list created previously
    stdev = c(50, 25, 14)) %>%
  # we add an experiment name for plot labels and easy overview
  mutate(expname = map_chr(stdfreqs, paste, collapse = ":")) %>%
  # add cold standard logical for later filtering
  mutate(hascoldstandard = grepl("[[139]]", expname))

# repeat each experiment a hundred times
megastddis <- stddis[rep(stddis %>% nrow() %>% seq_len(), 100), ] %>%
  # and add a row character for later merging of results
  mutate(exprow = as.character(seq_len(n())))
```

### 11.3 stddis runall

Note that we use the package `future` so that we can show a progress bar and use multiple cores. One could also use `purrr::pmap_dfr()` which it's based on, here.

```
## I turn off plotting and info messages
options(genplot = FALSE, verbose = FALSE)
```

```
## keep track of how long it takes
message(nrow(megastddis), " simulations started at ", Sys.time())
## very rough expected finish time (it's usually faster)
message("expected to take until ", Sys.time() + tpersim * nrow(megastddis) / 4)

## track actual duration with tictoc
tic("stddis total time")
## run sim_stds with parameters from mgstddis and global parameters after it
stddis_cnf <- furrr::future_pmap_dfr(
       select(megastddis, smpt, stdfreqs, stdev),
       sim_stds, stdtable = eth.info,
       out = "cis", stdn = 50, smpn = 50,
       .id = "exprow", # append a row name id
       .progress=TRUE   # show a progress bar
     ) %>%
  filter(id == "smp") %>%                         # filter output
  select(exprow, id, cv) %>%                      # select output
  spread(id, cv) %>%                              # make it wide format
  right_join(megastddis, by="exprow")             # join it with experimental df
toc()
message("simulations ran until ", Sys.time())
```

Save the results so that we don't have to run the simulations every time.

```
saveRDS(stddis_cnf, "stddis_cnf_2019-06-17.rds")
```

Restore the results from previous simulations.

```
stddis_cnf <- readRDS("stddis_cnf_2019-06-17.rds")
```

### 11.4 arrange results for plot

We re-organize the dataframes and make a selection of the best results for 0 and 40 degrees.

```
# the mean error of equal proportions at 0 degrees
normerr_0  <- stddis_cnf %>%
  filter(smpt == 0, expname == "1:1:1:1:0") %>%
  summarize(meanerr=mean(smp)) %>%
  pull(meanerr)
```

```
idealerr_0 <- stddis_cnf %>%
  filter(smpt == 0, expname == "1:1:9:0:0") %>%
  summarise(meanerr = mean(smp)) %>%
  pull(meanerr)

normerr_40  <- stddis_cnf %>%
  filter(smpt == 40, expname == "1:1:1:1:0") %>%
  summarize(meanerr=mean(smp)) %>%
  pull(meanerr)

idealerr_40 <- stddis_cnf %>%
  filter(smpt == 40, expname == "1:1:9:0:0") %>%
  summarise(meanerr = mean(smp)) %>%
  pull(meanerr)

forplot_0 <-
  stddis_cnf %>%
  filter(smpt == 0) %>%
  # append mean error per treatment to original dataframe
  group_by(expname) %>%
  summarise(meanerr = mean(smp, na.rm=TRUE)) %>%
  left_join(filter(stddis_cnf, smpt == 0), by = "expname") %>%
  # if there is no cold standard, it should be at least as good as normerr
  filter((!hascoldstandard & (meanerr <= normerr_0)) |
  # if there is a cold standard, it should be at least as good as idealerr
   (hascoldstandard & (meanerr <= idealerr_0))) %>%
  arrange(meanerr, expname) %>%
  ungroup() %>%
  # this is a hack to order the labels of a factor in a plot
  mutate(expname = factor(expname, unique(expname)))

forplot_40 <-
  stddis_cnf %>%
  filter(smpt == 40) %>%
  # append mean error per treatment to original dataframe
  group_by(expname) %>%  # note that we do not take into account sample temp..
  summarise(meanerr = mean(smp, na.rm=TRUE)) %>%
  left_join(filter(stddis_cnf, smpt == 40), by = "expname") %>%
  # if there is no cold standard, it should be at least as good as normerr
```

```
  filter((!hascoldstandard & (meanerr <= normerr_40)) |
  # if there is a cold standard, it should be at least as good as idealerr
   (hascoldstandard & (meanerr <= idealerr_40))) %>%
  arrange(meanerr, expname) %>%
  mutate(expname = factor(expname, unique(expname)))
```

### 11.5 create barcharts for proportion axes

```
forplot_0_x <- forplot_0 %>%
  distinct(expname, .keep_all = TRUE) %>%
  unnest(cols=stdfreqs) %>%
  mutate(std = rep(c(paste0("ETH-", 1:4), "UU"), n()/5))

x_0 <- forplot_0_x %>%
  ggplot(aes(x = expname, y = stdfreqs, fill = std)) +
  geom_col(position="fill") +
  ## geom_text(aes(label = lab), y = .5, size = 2,
  ##          data = mutate(forplot_0_x,
  ##                        lab = ifelse(expname %in% c("1:1:1:1:0", "1:1:9:0:0", "1:1
  scale_fill_manual(values=eth.info$col,
    guide = guide_legend(label.position = "top",
 direction = "horizontal",
 label.theme = element_text(size = 8, angle = 90, hjust = 0))) +
  scale_y_reverse(position = "right", expand = c(0, 0)) +
  labs(x = "Standard distribution", y = "ETH-1:2:3:4:UU1", fill = "") +
  ## labs(x = "Standard distribution", y = "ETH-<span style='color:orange'>1</span>:<sp
  coord_flip() +
  theme(axis.text = element_blank(),
axis.ticks = element_blank(),
plot.margin = margin(r = 0),
axis.title.x = element_blank(),
legend.pos = "top",
legend.justification = 12,
legend.spacing.x = unit(1, "mm"),
## legend.margin = margin(2, 0, 2, 0),
legend.key.size = unit(2, "mm"))

forplot_40_x <- forplot_40 %>%
  distinct(expname, .keep_all = TRUE) %>%
  unnest(cols=stdfreqs) %>%
```

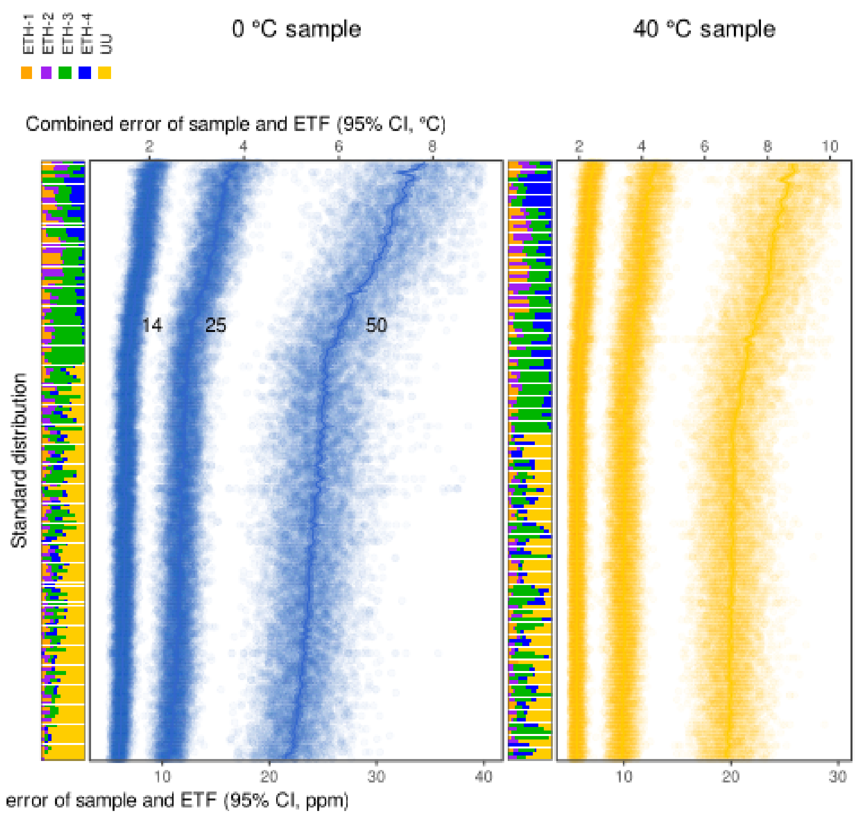
```
  mutate(std = rep(c(paste0("ETH-", 1:4), "UU"), n()/5))

x_40 <- x_0 %+% forplot_40_x +
  theme(axis.title.x = element_blank(),
axis.title.y = element_blank(),
legend.pos = "none")
```

### 11.6 stddis_pl

```
sub_vjust <- -7
sds <- tibble(expname = "1:0:9:1:0", sd = c(14, 25, 50), smp = c(.006, .012, .027) + .0

# create a plot
stddis_pl_0 <- forplot_0 %>%
  ggplot(aes(x = expname, y = smp * 1e3,  # error in ppm
    colour = factor(smpt), fill = factor(smpt))) +
  # theming
  labs(x = "Standard distribution",
    y = "Combined error of sample and ETF (95% CI, ppm)",
    fill = ktit_smpid,
    colour = ktit_smpid,
    shape = "Total standards") +
  scale_fill_manual(values = kcols[[1]], labels = "0 °C") +
  scale_colour_manual(values = kcols[[1]], labels = "0 °C") +
  scale_y_continuous(breaks = seq(0, 65, 10), lim = c(5, 40),
    sec.axis = sec_axis("Combined error of sample and ETF (95% CI, °C)",
      trans = ~. / abs(tempcal_derivative(0) * 1e3), breaks = seq(0, 20, 2))) +
  theme(
    plot.title = element_text(hjust = 0.5, vjust = -10),
    plot.margin = margin(l = 0),
    ## plot.subtitle = element_text(size = 8, hjust = -.1, vjust = -8),
    axis.title.x.top = element_text(hjust = 7),
    axis.title.x.bottom = element_text(hjust = 7),
    axis.text.y = element_blank(),
    axis.ticks.y = element_blank(),
    axis.title.y = element_blank(),
    strip.text = element_blank(),
    legend.position = "none") +
  # manual legend for input stdevs (sigma)
  # the actual data
```

```
  geom_point(alpha = .03) +
  ## annotate("text", x = -Inf, y = Inf, label = paste0("\u3c3 = ", c(14, 25, 50))) +
  geom_text(aes(label = sd), data = sds, colour = "black") +
  coord_flip(clip = "off") +
  stat_summary(aes(group=stdev), geom="ribbon", fun.data=mean_cl_normal, fun.args=list
  stat_summary(aes(group=stdev), geom="line", fun.data=mean_cl_normal) +
  labs(title="0 °C sample") #, subtitle = "ETH-1:2:3:4:UU1")
# add the average lines +- 95% CIs for all the sample temperatures

stddis_pl_40 <- forplot_40 %>%
  filter(smpt == 40) %>%
  ggplot(aes(x = expname, y = smp * 1e3,  # error in ppm
    colour = factor(smpt), fill = factor(smpt))) +
  # theming
  labs(x = "Standard distribution",
    y = "Combined error of sample and ETF (95% CI, ppm)",
    fill = ktit_smpid,
    colour = ktit_smpid,
    shape = "Total standards") +
  scale_fill_manual(values = kcols[[2]], labels = "40 °C") +
  scale_colour_manual(values = kcols[[2]], labels = "40 °C") +
  scale_y_continuous(breaks = seq(0, 65, 10), lim = c(5, 30),
    sec.axis = sec_axis("Combined error of sample and ETF (95% CI, °C)",
      trans = ~. / abs(tempcal_derivative(40) * 1e3), breaks = seq(0, 20, 2))) +
  theme(
    plot.title = element_text(hjust = 0.5, vjust = -10),
    plot.margin = margin(l = 0),
    plot.subtitle = element_blank(),
    axis.title = element_blank(),
    axis.text.y = element_blank(),
    axis.ticks.y = element_blank(),
    axis.title.y = element_blank(),
    strip.text = element_blank(),
    legend.position = "none") +
  labs(title="40 °C sample") +
  coord_flip(clip = "off") +
  # the actual data
  geom_point(alpha = .03) +
  stat_summary(aes(group=stdev), geom="ribbon", fun.data=mean_cl_normal,
       fun.args=list(conf.int=0.95), alpha=.4, colour=NA) +
```

```
  stat_summary(aes(group=stdev), geom="line", fun.data=mean_cl_normal)

## stddis_pl  <- stddis_pl_0 + stddis_pl_40 + plot_layout(widths=c(35 / 25 , 1))
stddis_pl <- x_0 + stddis_pl_0 + x_40 + stddis_pl_40 + plot_layout(widths = c(.15, 35/2

stddis_pl
```




## 11.7 prep text

This generates some dataframes so we can easily extract relevant averages for use in-text.

```
stddis_exmp_0 <- forplot_0 %>%
  filter(smpt == 0) %>%
  group_by(expname) %>%
  summarize(err=mean(smp, na.rm=TRUE), cnf = confidence(smp, n(), alpha=0.05)) %>%
```

```
  arrange(err)

stddis_exmp_40 <- forplot_40 %>%
  filter(smpt == 40, stdev == 25) %>%
  group_by(expname) %>%
  summarize(err=mean(smp,na.rm=TRUE), cnf=confidence(smp, n(), alpha= 0.05)) %>%
  arrange(err)
```

# 12 stdvssmp

Here we simulate the standards versus samples based on three input distributions,

## 12.1 setup

```
stdvssmp <- expand.grid(
  smpt = c(0, 40), stdn = as.integer(seq(12, 88, 4)),
  dist = c("equal proportions", "optimal proportions", "optimal proportions including U
  stdev = c(50, 25, 14)) %>%
  as_tibble() %>%
  mutate(smpn = as.integer(100 - stdn),
 n = as.integer(smpn + stdn),
 smpf = smpn / n,
 stdf = stdn / n,
 stdfreqs = case_when(dist == "equal proportions" ~ list(c(1, 1, 1, 1, 0)),
      dist == "optimal proportions" ~ list(c(1, 1, 9, 0, 0)),
      dist == "optimal proportions including UU1" ~ list(c(1, 1, 1, 0, 9))))

# repeat each experiment a hundred times
megastdvssmp <- stdvssmp[rep(stdvssmp %>% nrow() %>% seq_len(), 100), ] %>%
  mutate(exprow = as.character(seq_len(n())))  # row number
```

## 12.2 run sims

```
# again, I turn off plotting and info messages
options(genplot = FALSE, verbose = FALSE)

# keep track of time
message(nrow(megastdvssmp), " simulations started at ", Sys.time())
message("expected to take until ", Sys.time() + tpersim * nrow(megastdvssmp) / 4)
```

```
# run duration
tic("overview")
# run sim_stds with parameters from megastdvssmp and global parameters after it
stdvssmp_cnf <- furrr::future_pmap_dfr(
 select(megastdvssmp,
smpt, stdn, stdev, smpn, stdfreqs),
 sim_stds,
 stdtable = eth.info, out = "cis",
 .id = "exprow",          # append a row name id
 .progress=TRUE
 ) %>%
  filter(id %in% c("etf","sample", "smp")) %>%    # filter output
  select(exprow, id, cv) %>%                      # select output
  spread(id, cv) %>%                              # make it wide format
  right_join(megastdvssmp)                        # join it with experimental df
toc()
message("simulations ran until ", Sys.time())
```

### 12.3 save results

```
saveRDS(stdvssmp_cnf, "stdvssmp_cnf_2019-06-13.rds")

stdvssmp_cnf <- readRDS("stdvssmp_cnf_2019-06-13.rds")
```

### 12.4 tidy it up

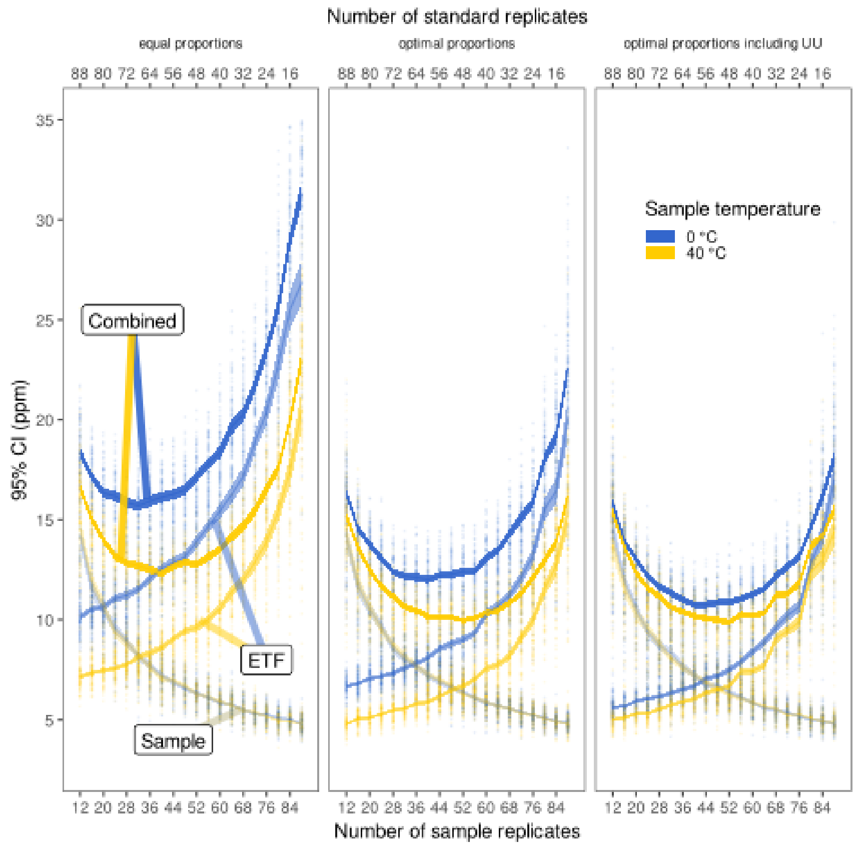
```
tidy_stdvssmp_results <- stdvssmp_cnf %>%
  gather(errortype, error, sample, etf, smp)
```

### 12.5 stdvssmp_pl

```
## create label annotation because the legend with opacity was unclear
smpn=c(76, 44, 30)
error=c(8, 4, 25)
labels = c("ETF", "Sample", "Combined")

leg <- tibble(
  ## x=c(58, 67, 28,
  ##     53, 62, 63),
  ## y=c(14.5, 5.5, 16,
```

```
  ##     10, 5.5, 12.5),
  x=rep(smpn, 2), y=rep(error, 2),
  xend=c(58, 67, 35,
 53, 67, 26),
  yend=c(15, 5.5, 16,
 10, 5.5, 13),
  smpt=c(rep(0, 3), rep(40, 3)),
  stdev = 25,
  ## lab=paste(labels, "uncertainty at", smpt, "°C"),
  lab=rep(labels, 2),
  errortype = rep(c("etf", "sample", "smp"), 2),
  dist=rep("equal proportions", 6))
      ## smpt=0)

stdvssmp_pl <- ggplot(tidy_stdvssmp_results %>% filter(stdev == 25),
  aes(x = smpn, y = error * 1e3, fill = as.factor(smpt),
    colour = as.factor(smpt), alpha = as.factor(errortype))) +
  # draw the points for all simulations, but make them very vague
  geom_point(alpha = .05, size = .3) +
  # draw an error range through the different experiments
  stat_summary(geom = "ribbon", colour = NA,  # no border
    fun.data = mean_cl_normal,
    fun.args = list(conf.int = .95, na.rm = TRUE)) +
  # draw an average through the different experiments
  stat_summary(geom = "line", fun.data = mean_cl_normal) +
  # three standard distributions on the x-facets, 3 standard deviations on y
  ## we add some ugly labels here because they are more clear than a legend in this cas
  geom_segment(aes(x=x, xend=xend, y=y, yend=yend), data=leg, size=2, show.legend=F) +
  geom_label(aes(x=x, y=y, label=lab), data=leg, colour="black", fill="white", alpha=1
  facet_grid(#rows = vars(stdev),
    ## rows = vars(stdev),
    cols = vars(dist),
    as.table = FALSE,
    ## shrink = TRUE,
    ## scales = "free_y",
    ## space = "free_y"
    ) +
  # x-axes
  scale_x_continuous("Number of sample replicates", lim = c(10, 90),
    breaks = seq(12, 88, 8),
```

```
   sec.axis = sec_axis(~ 100 - ., name = "Number of standard replicates",
     breaks = seq(88, 12, -8))) +
 scale_y_continuous("95% CI (ppm)",
    ## trans="log10",
    limits = c(3, 35),
    breaks = c(seq(0, 50, 5), seq(60, 100, 10)),
    ## sec.axis = sec_axis(~. / abs(tempcal_derivative(0) * 1e3), name = "Approximate
## breaks=c(seq(0, 20, 1), seq(25, 40, 5)))
    ) +
 ## coord_trans(y = "log10") +
 # colours
 scale_colour_manual(ktit_smpid, labels = klab_smpid, values = kcols) +
 scale_fill_manual(ktit_smpid, labels = klab_smpid, values = kcols) +
 scale_alpha_manual("Source of Error",
   labels = c("ETF", "Sample", "Combined"),
   values = c(.5, .2, .9), guide=FALSE) +
 # theming
 ## annotation_logticks(sides="l") +
 theme(legend.position = c(.85, .8), strip.text=element_text(size=8), strip.placement=
stdvssmp_pl
```




## 12.6 supplementary figure plot with all input standard deviations

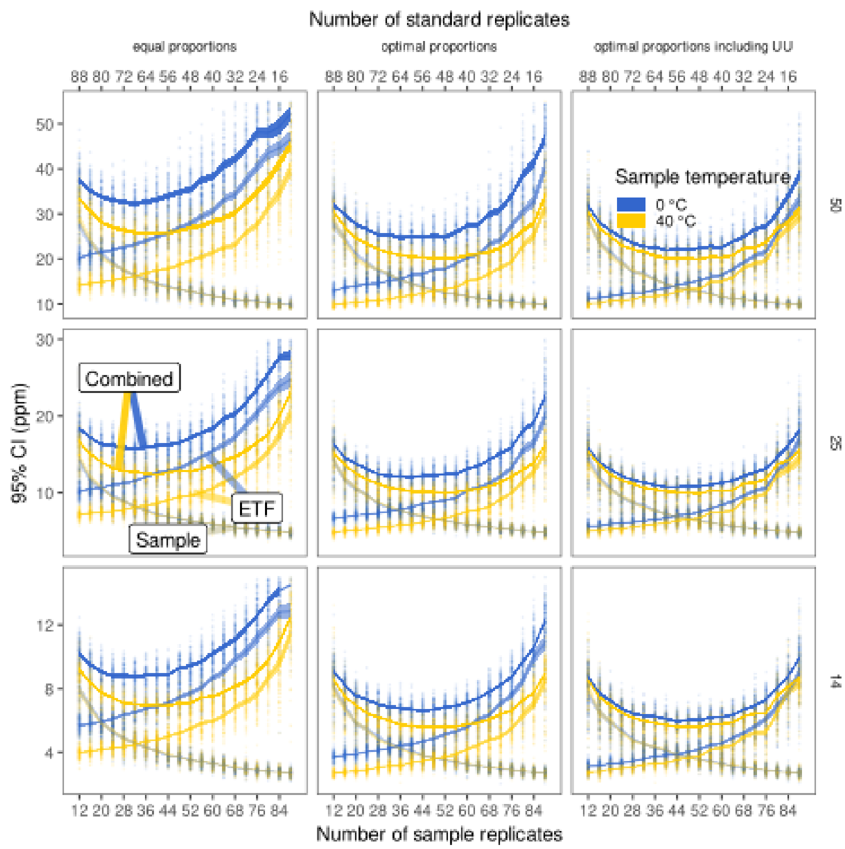
we use a new package that allows different scales on different facets

```
devtools::install_github("zeehio/facetscales")
```

```
stdvssmp_pl_all <- ggplot(tidy_stdvssmp_results,
  aes(x = smpn, y = error * 1e3, fill = as.factor(smpt),
    colour = as.factor(smpt), alpha = as.factor(errortype))) +
  # draw the points for all simulations, but make them very vague
  geom_point(alpha = .05, size = .3) +
  # draw an error range through the different experiments
  stat_summary(geom = "ribbon", colour = NA,  # no border
    fun.data = mean_cl_normal,
    fun.args = list(conf.int = .95, na.rm = TRUE)) +
```

```
# draw an average through the different experiments
stat_summary(geom = "line", fun.data = mean_cl_normal) +
# three standard distributions on the x-facets, 3 standard deviations on y
## we add some ugly labels here because they are more clear than a legend in this cas
geom_segment(aes(x=x, xend=xend, y=y, yend=yend), data=leg, size=2, show.legend=F) +
geom_label(aes(x=x, y=y, label=lab), data=leg, colour="black", fill="white", alpha=1
facetscales::facet_grid_sc(
  rows = vars(stdev),
  cols = vars(dist),
  as.table = FALSE,
  shrink = TRUE,
  scales = list(
    y = list(‘14‘ = scale_y_continuous("95% CI (ppm)", lim = c(2, 15)),
     ‘25‘ = scale_y_continuous("95% CI (ppm)", lim = c(3, 30)),
     ‘50‘ = scale_y_continuous("95% CI (ppm)", lim = c(9, 55)))
  ),
  ## space = "free_y"
  ) +
# x-axes
scale_x_continuous("Number of sample replicates", lim = c(10, 90),
  breaks = seq(12, 88, 8),
  sec.axis = sec_axis(~ 100 - ., name = "Number of standard replicates",
    breaks = seq(88, 12, -8))) +
## scale_y_continuous(,
##                    ## trans="log10",
##                    ## limits = c(NA, 50),
##                    breaks = c(seq(0, 50, 5), seq(60, 100, 10)),
##                    ## sec.axis = sec_axis(~. / abs(tempcal_derivative(0) * 1e3), n
##                                        ## breaks=c(seq(0, 20, 1), seq(25, 40, 5))
##                    ) +
## coord_trans(y = "log10") +
# colours
scale_colour_manual(ktit_smpid, labels = klab_smpid, values = kcols) +
scale_fill_manual(ktit_smpid, labels = klab_smpid, values = kcols) +
scale_alpha_manual("Source of Error",
  labels = c("ETF", "Sample", "Combined"),
  values = c(.5, .2, .9), guide=FALSE) +
# theming
## annotation_logticks(sides="l") +
theme(legend.position = c(.85, .85), strip.text=element_text(size=8), strip.placement
```

```
stdvssmp_pl_all
```




# 13 prop-eth3

In the discussion we create a new set of simulations.

## 13.1 prop-eth3 for continuous sample range

```
new_smp_info2 <- tibble(smpid = "smp", smp_D47 = seq(0.18, 0.9, 0.0025)) %>%
  mutate(smp_D47.noacid = smp_D47 - kaff,
 rawcat = smp_D47.noacid * kslope + kintercept,
 smpt = revcal(smp_D47, ignorecnf = TRUE))
prop_eth3 <- seq(.02, .98, length.out = 500)
```

## 13.2 prop-eth3 expand experimental matrices and run simulations

```
mat <- expand.grid(smp_D47 = new_smp_info2$smp_D47, prop_eth3 = prop_eth3) %>%
  left_join(new_smp_info2, by = "smp_D47") %>%
  mutate(prop_left = 1 - prop_eth3,
 exprow = as.character(seq_along(1:n()))) %>%
  mutate(stdfreqs = select(., prop_eth3, prop_left) %>% as.matrix() %>% split(seq(nrow
  select(-prop_left)
```

### 13.2.1 run many sims

```
smp_out <- furrr::future_pmap_dfr(
    select(mat, stdfreqs, smpt),
    sim_stds,
    ## here we subset the standards to ETH-3 and ETH-1, in that order
    stdtable = make_std_table()[c(3, 1), ],
    stdev = 25, out = "cis", .id = "exprow", .progress = TRUE) %>%
  filter(id %in% c("etf","sample", "smp")) %>%   # filter output
  select(exprow, id, cv) %>%                     # select output
  spread(id, cv) %>%                             # make it wide format
  right_join(mat, by = "exprow") %>% # join it with experimental df
  mutate(exp="ETH-1 and ETH-3")
```

### 13.2.2 save results

```
saveRDS(smp_out, "smp_out_new_2019-06-12.rds")

smp_out <- readRDS("smp_out_new_2019-06-12.rds")
```

## 13.3 smp_out_uu

```
smp_out_uu <-
  furrr::future_pmap_dfr(
   select(mat, stdfreqs, smpt),
   sim_stds,
   # here we subset the standards to ETH-3 and ETH-1, in that order
   stdtable = make_std_table()[c(5, 1), ],
   stdev = 25, out = "cis", .id = "exprow", .progress = TRUE) %>%
  filter(id %in% c("etf","sample", "smp")) %>%   # filter output
  select(exprow, id, cv) %>%                     # select output
```

```
  spread(id, cv) %>%                              # make it wide format
  right_join(mat, by = "exprow") %>% # join it with experimental df
  mutate(exp="ETH-1 and UU1")

saveRDS(smp_out_uu, "smp_out_uu_2019-06-12.rds")

smp_out_uu <- readRDS("smp_out_uu_2019-06-12.rds")
```

## 13.4 best_dat

```
best_range <- 1:10

best_dat <- bind_rows(smp_out, smp_out_uu) %>%
  group_by(exp, smp_D47) %>%
  arrange(smp) %>%
  slice(best_range)
```

## 13.5 smp_out_comb

combine the sims for one plot with faceting

```
smp_out_comb  <- smp_out %>%
  bind_rows(smp_out_uu) %>%
  select(exprow, smp_D47, prop_eth3, exp, smp) %>%
  spread("exp", "smp") %>%
  mutate(diff=`ETH-1 and UU1` - `ETH-1 and ETH-3`)
```

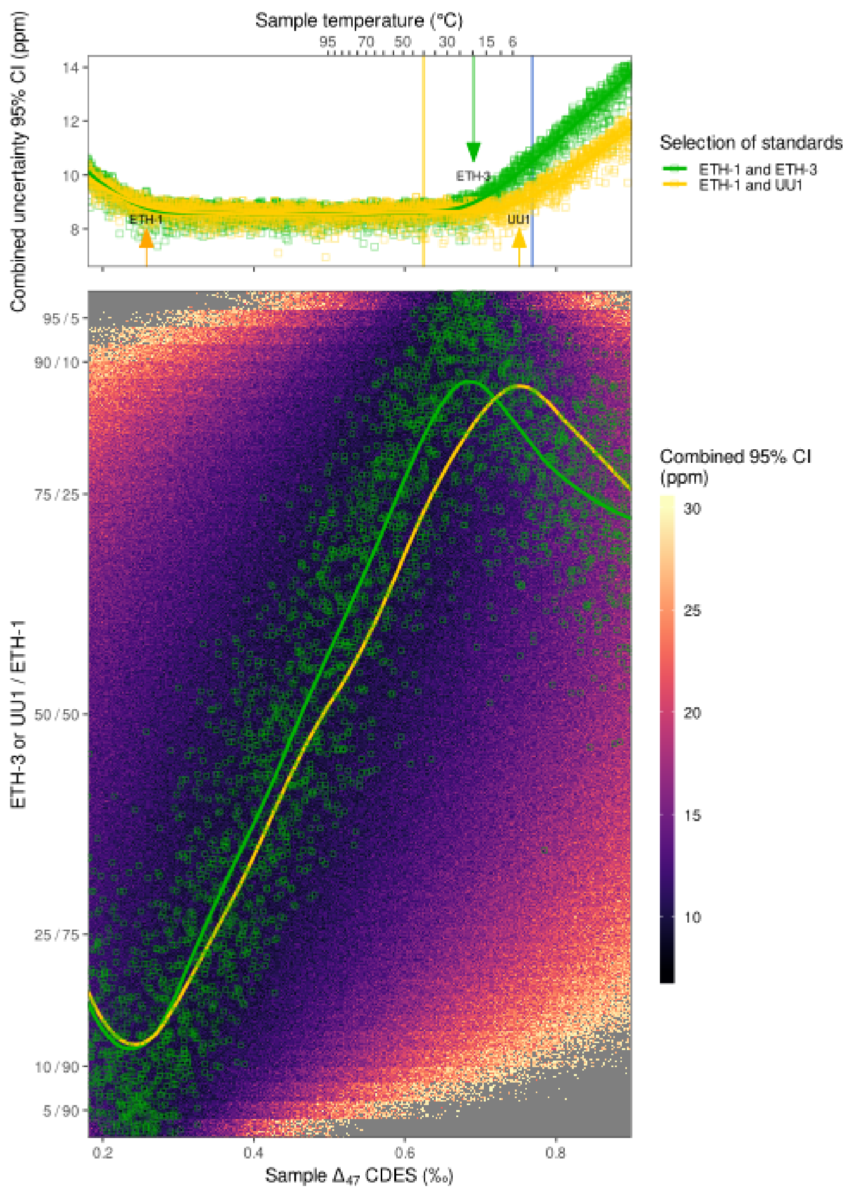
## 13.6 prop_eth3_pl

### 13.6.1 plot_best

### 13.6.2 plot_prop

### 13.6.3 combine and print

```
prop_eth3_pl <- plot_best + plot_prop + plot_layout(nrow=2, heights=c(.2, .8))
prop_eth3_pl
```



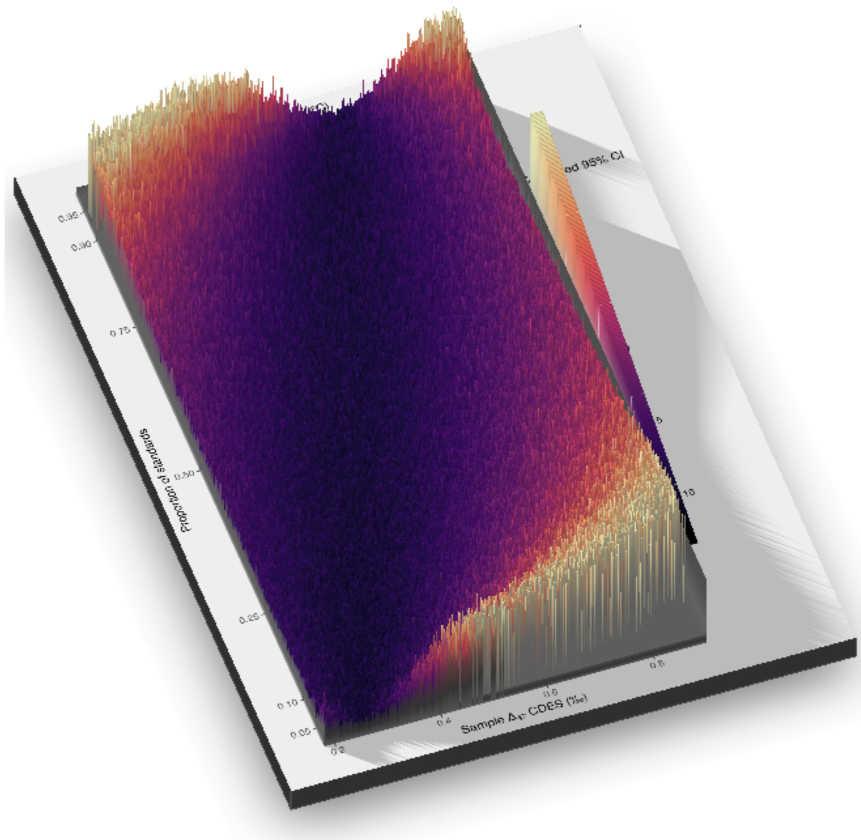

### 13.6.4 3d rayshader plot

This one is not included in the manuscript or the supplementary information pdf, but I highly recommend creating one to play around with it!

```
# new rayshader 3d option
```

```
# remotes::install_github("tylermorganwall/rayshader")
library(rayshader)

ray <- smp_out %>%
  ggplot(aes(x = smp_D47, y = prop_eth3, fill = smp * 1e3)) +
  geom_raster() +
  ## geom_smooth(aes(col = exp), se = F, method = "loess", span = .3, size = 1,
  ##            data = best_dat) +
  ## geom_point(aes(col = exp), shape = 0, size = 1, alpha = .5,
  ##             data = filter(best_dat, exp == "ETH-1 and ETH-3")) +
  labs(x = Sample~Delt[[47]]"CDES (\u2030)",
       y = "Proportion of standards",
       fill = "Combined 95% CI\n(ppm)") +
  viridis::scale_fill_viridis(
     ## the rescaler works nicely, but messes up the legend a bit
     ## rescaler = function(x, to = c(0, 1), from = NULL, newmax=30) {
     ##   ifelse(x < newmax,
     ##          scales::rescale(x, to = to, from = c(min(x, na.rm = TRUE), newmax)), 1
     ## I'll go back to simple clipping again
     limits = c(NA, 30),
     expand=c(0, 0),
     ## oob = function(x) {x},
     option = "magma",
     breaks = err_breaks, #labels = err_ticks
   ) +
  scale_y_continuous(expand = c(0, 0), breaks = c(.05, .1, .25, .5, .75, .9, .95)) +
  scale_x_continuous(expand = c(0, 0), lim=c(.18, .9),
  sec.axis = sec_axis(~ sqrt((0.0449 * 1e+6)/(. - 0.167)) - 273.15,
  "Sample temperature (°C)", temp_breaks, temp_labs)) +
  theme(legend.key.width = unit(.3, "cm"),
legend.key.height = unit(2, "cm"),
strip.placement="outside")

plot_gg(ray, multicore=TRUE, width=5, height=7, scale=350, raytrace=TRUE,
sunangle=40)

## render_movie("rayshader_movie_plot.mp4")
render_snapshot("imgs/rayshader_snapshot.png")
```

See the screenshot for a preview



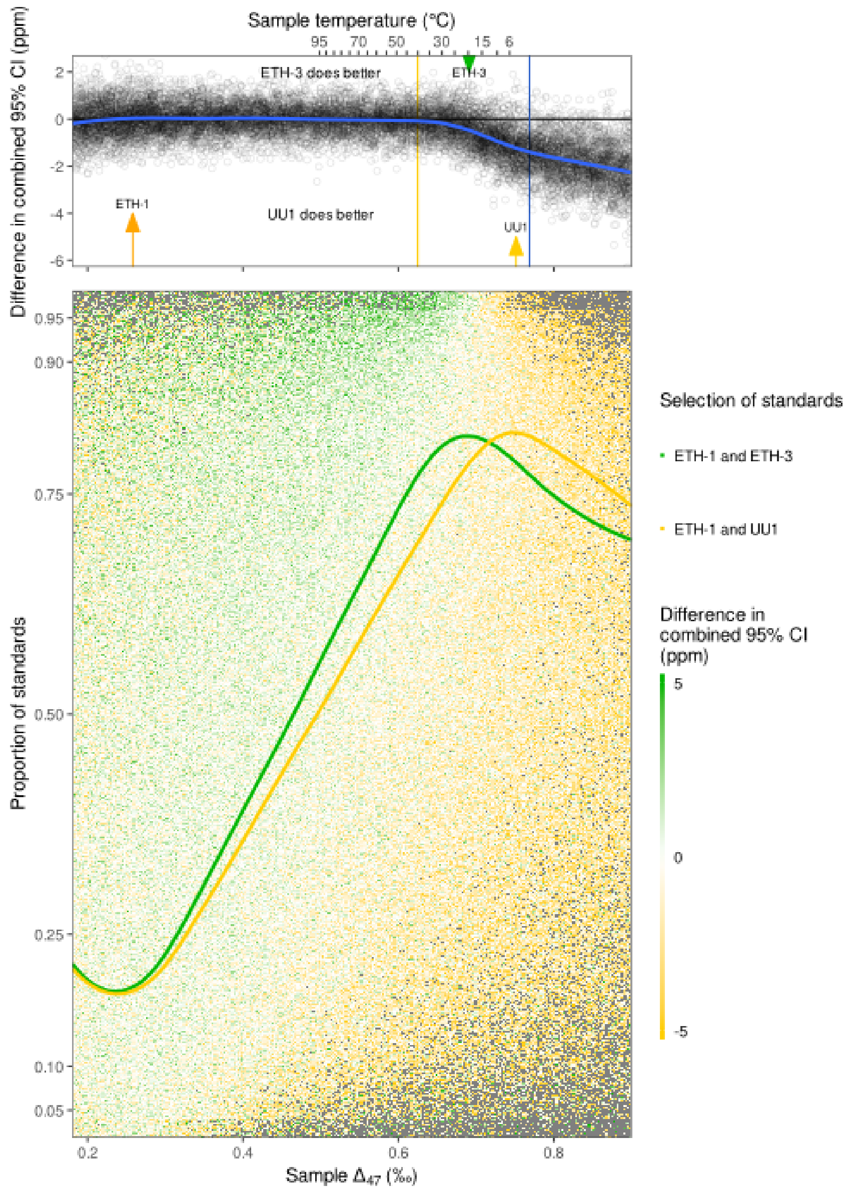
## 13.7 best_prop_diff_pl

The difference plot for the supplementary information.

```
best_dat_100 <- bind_rows(smp_out, smp_out_uu) %>%
  group_by(exp, smp_D47) %>%
  arrange(smp) %>%
  slice(1:100)

best_dat_comb <- best_dat_100 %>%
  ungroup() %>%
  select(smp_D47, prop_eth3, exp, smp) %>%
  spread("exp", "smp") %>%
```

```
  mutate(diff=`ETH-1 and UU1` - `ETH-1 and ETH-3`)

plot_best_comb <- best_dat_comb %>%
  ggplot(aes(x = smp_D47, y = diff * 1e3)) +
  geom_hline(yintercept=0) +
  annotate("text", x = c(.5, .5), y = c(2, -4), label = c("ETH-3 does better", "UU1 doe
  geom_vline(xintercept=smpinfo$D47, col=kcols[1:2]) +
  ## show ALL the points?
  ## geom_point(shape = 16, alpha = .1, data=bind_rows(smp_out,smp_out_uu)) +
  geom_point(shape = 1, alpha = .1) +
  geom_smooth(method="loess", span = .3) +
  labs(col="Selection of standards",
       x = Sample ~ Delta[47] ~ "(\u2030)",
       y = "Difference in combined 95% CI (ppm)") +
  scale_colour_manual(values=eth.info$col[c(3, 5)]) +
  scale_x_continuous(expand=c(0, 0), lim=c(.18, .9),
     sec.axis = sec_axis(~ sqrt((0.0449 * 1e+6)/(. - 0.167)) - 273.15,
 "Sample temperature (°C)", temp_breaks, temp_labs)) +
  scale_y_continuous(expand = c(0, 0)) +
  ## add arrows to ETH-1 and ETH-3 positions
  annotate("segment",
   arrow = arrow(angle = 20, length = unit(.4, "cm"), type = "closed"),
   x = eth.info$D47[c(1, 3, 5)], y = c(-Inf, Inf, -Inf),
   xend = eth.info$D47[c(1, 3, 5)], yend = c(-4, 2, -5),
   colour = eth.info$col[c(1, 3, 5)],
   alpha = 1,
   size = .4) +
  annotate("text", x = eth.info$D47[c(1, 3, 5)], # + c(0.03, -.02),
   y = c(-4, 2, -5), label = eth.info$id[c(1, 3, 5)],
   vjust= c(-.5, .5, -.5), size = 2.5) +
  theme(legend.pos=c(.2, .7),
## shared axis with bottom panel
axis.title.x.bottom=element_blank(), axis.text.x.bottom=element_blank())

plot_prop_diff <- smp_out_comb %>%
  ggplot(aes(x = smp_D47, y = prop_eth3, fill = diff * 1e3)) +
  geom_raster() +
  geom_smooth(aes(col = exp, fill=smp*1e3), se = F, method = "loess", span = .3, size =
      data = best_dat_100) +
  ## geom_point(aes(col=exp), data=best_dat_100, shape = 1) +
```

```
  scale_colour_manual(values=eth.info$col[c(3, 5)]) +
  scale_fill_gradient2(low=eth.info$col[[5]], high=eth.info$col[[3]], breaks = err_brea
       limits=c(-5, 5)) +
  labs(x = Sample ~ Delta[47] ~ "(\u2030)",
       y = "Proportion of standards",
       col = "Selection of standards",
       fill = "Difference in\ncombined 95% CI\n(ppm)") +
  scale_y_continuous(expand = c(0, 0), breaks = c(.05, .1, .25, .5, .75, .9, .95)) +
  scale_x_continuous(expand = c(0, 0), lim=c(.18, .9)) +
  theme(legend.key.width = unit(.1, "cm"),
legend.key.height = unit(1.5, "cm"),
strip.placement="outside")

best_prop_diff_pl <- plot_best_comb + plot_prop_diff + plot_layout(nrow=2, heights=c(.2
best_prop_diff_pl
```




## 13.8 calculate some summary statistics for use in-text

```
# these are some helper functions to calculate the values we put in the text
# get the confidence value at alpha value alpha from a t-distribution
confidence <- function(x, n, alpha=.05) {
```

```
  qt(1 - alpha / 2, df=n - 1) * sd(x) / sqrt(n)
}

# convert x from permil to ppm and round down to dig digits.
ppmround <- function(x, dig=2) {
  round(x * 1e3, digits=dig)
}

interp_eth3 <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and ETH-3", smp_D47 >= eth.info$D47[[1]], smp_D47 <= eth.info$D47
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

extrap_eth3 <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and ETH-3", smp_D47 >= eth.info$D47[[5]]) %>%
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

interp_uu <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and UU1", smp_D47 >= eth.info$D47[[1]], smp_D47 <= eth.info$D47[[5
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

extrap_uu <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and UU1", smp_D47 >= eth.info$D47[[5]]) %>%
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

eth3_to_uu_eth3 <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and ETH-3", smp_D47 >= eth.info$D47[[3]], smp_D47 <= eth.info$D47
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

eth3_to_uu_uu <- best_dat %>%
  ungroup() %>%
```

```
  filter(exp == "ETH-1 and UU1", smp_D47 >= eth.info$D47[[3]], smp_D47 <= eth.info$D47
  summarize(mean=mean(smp, na.rm = TRUE),
    ci=confidence(smp, n=n()))

eth3_to_uu_tempsens <- seq(eth.info$D47[[3]], eth.info$D47[[5]], .01) %>%
  tempcal_derivative() %>%
  mean()

uu_to_0_eth3 <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and ETH-3", smp_D47 >= eth.info$D47[[5]], smp_D47 <= smpinfo$D47[
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

uu_to_0_uu <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and UU1", smp_D47 >= eth.info$D47[[5]], smp_D47 <= smpinfo$D47[[1]
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

uu_to_0_tempsens <- seq(eth.info$D47[[5]], smpinfo$D47[[1]], .01) %>%
  tempcal_derivative() %>%
  mean()
```

# 14 prop-eth3 with a very very very cold and hot standard?

The reviewers requested another set of simulations.

## 14.1 prop-eth3 for continuous sample range

same as before

```
new_smp_info2 <- tibble(smpid = "smp", smp_D47 = seq(0.18, 0.9, 0.0025)) %>%
  mutate(smp_D47.noacid = smp_D47 - kaff,
 rawcat = smp_D47.noacid * kslope + kintercept,
 smpt = revcal(smp_D47, ignorecnf = TRUE))
prop_eth3 <- seq(.02, .98, length.out = 500)
```

## 14.2 prop-eth3 expand experimental matrices and run simulations

same as before

```
mat <- expand.grid(smp_D47 = new_smp_info2$smp_D47, prop_eth3 = prop_eth3) %>%
  left_join(new_smp_info2, by = "smp_D47") %>%
  mutate(prop_left = 1 - prop_eth3,
 exprow = as.character(seq_along(1:n()))) %>%
  mutate(stdfreqs = select(., prop_eth3, prop_left) %>% as.matrix() %>% split(seq(nrow
  select(-prop_left)
```

## 14.3 run many sims

```
brrr <- make_std_table(id = c("UU2", "UU3"), col = c("darkblue", "red"),
       D47_std = c(0.9252, 0.0266)) # based on Wang 2004

brrr_smp_out <- furrr::future_pmap_dfr(
    select(mat, stdfreqs, smpt),
    sim_stds,
    ## here we subset the standards to ETH-3 and ETH-1, in that order
    stdtable = brrr,
    stdev = 25, out = "cis", .id = "exprow", .progress = TRUE) %>%
  filter(id %in% c("etf","sample", "smp")) %>%   # filter output
  select(exprow, id, cv) %>%                     # select output
  spread(id, cv) %>%                             # make it wide format
  right_join(mat, by = "exprow") %>% # join it with experimental df
  mutate(exp="UU3 and UU2")
```

### 14.3.1 save results

```
saveRDS(brrr_smp_out, "brrr_smp_out_2019-08-20.rds")
```

the 0.8 U2 standard + ETH-1

```
brrr_smp_out <- readRDS("brrr_smp_out_2019-08-19.rds")
```

The heated/eq. gas equivalents

```
brrr_smp_out <- readRDS("brrr_smp_out_2019-08-20.rds")
```

## 14.4 brrr_best_dat

```
best_range <- 1:10

brrr_best_dat <- bind_rows(smp_out, smp_out_uu, brrr_smp_out) %>%
  group_by(exp, smp_D47) %>%
  arrange(smp) %>%
  slice(best_range)
```

## 14.5 smp_out_comb

combine the sims for one plot with faceting

```
brrr_smp_out_comb  <- bind_rows(smp_out, brrr_smp_out, smp_out_uu) %>%
  select(exprow, smp_D47, prop_eth3, exp, smp) %>%
  spread("exp", "smp") %>%
  mutate(diff=`UU3 and UU2` - `ETH-1 and ETH-3`)
```

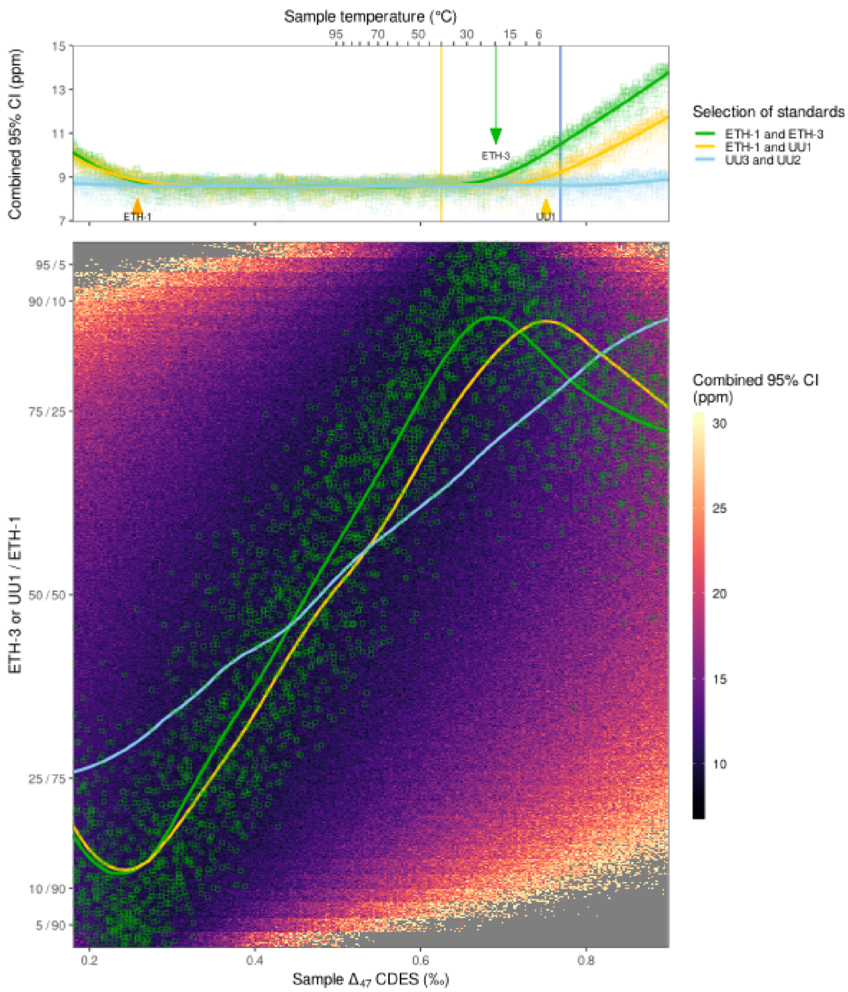
## 14.6 prop_eth3_pl

### 14.6.1 plot_best

### 14.6.2 plot_prop

### 14.6.3 combine and print

```
brrr_prop_eth3_pl <- brrr_plot_best + brrr_plot_prop + plot_layout(nrow=2, heights=c(.
brrr_prop_eth3_pl
```




## 14.7 calculate some summary statistics for use in-text

```
eth3_to_u2_eth3 <- brrr_best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and ETH-3", smp_D47 >= eth.info$D47[[3]], smp_D47 <= brrr$D47[[1]
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

eth3_to_u2_u2 <- brrr_best_dat %>%
  ungroup() %>%
  filter(exp=="UU3 and UU2", smp_D47 >= eth.info$D47[[3]], smp_D47 <= brrr$D47[[1]]) %>
```

```
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

eth3_to_u2_tempsens <- seq(eth.info$D47[[3]], brrr$D47[[1]], .001) %>%
  tempcal_derivative() %>%
  mean(na.rm=FALSE)

u2_to_0_eth3 <- best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and ETH-3", smp_D47 >= smpinfo$D47[[1]], smp_D47 <= brrr$D47[[1]])
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

u2_to_0_u2 <- brrr_best_dat %>%
  ungroup() %>%
  filter(exp=="UU3 and UU2", smp_D47 >= smpinfo$D47[[1]], smp_D47 <= brrr$D47[[1]]) %>%
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

u2_to_0_tempsens <- seq(smpinfo$D47[[1]], brrr$D47[[1]], .01) %>%
  tempcal_derivative() %>%
  mean()

eth3_to_0_eth3 <- brrr_best_dat %>%
  ungroup() %>%
  filter(exp=="ETH-1 and ETH-3", smp_D47 >= eth.info$D47[[3]], smp_D47 <= smpinfo$D47[
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

eth3_to_0_u2 <- brrr_best_dat %>%
  ungroup() %>%
  filter(exp=="UU3 and UU2", smp_D47 >= eth.info$D47[[3]], smp_D47 <= smpinfo$D47[[1]])
  summarize(mean=mean(smp),
    ci=confidence(smp, n=n()))

eth3_to_0_tempsens <- seq(eth.info$D47[[3]], smpinfo$D47[[1]], .01) %>%
  tempcal_derivative() %>%
  mean()
```

### 14.8 quick check on how much it matters if we add two hypothetical very large-range standards

```
(eth3_to_0_eth3$mean - eth3_to_0_u2$mean) * 1000
```

ppm difference, which equates to

```
 # in permil              # in permil          # in permil / degreeC
(eth3_to_0_eth3$mean - eth3_to_0_u2$mean) / eth3_to_0_tempsens
```

so… .3 °C improvement for samples between −29.8000392923437
maybe it's even more at the more extreme end?

```
(eth3_to_0_eth3$mean - eth3_to_0_u2$mean) / eth3_to_0_tempsens
```

degrees improvement for samples between ETH-3 (~20) and 0 °C.
or in terms of improvement:

```
((eth3_to_0_eth3$mean / eth3_to_0_u2$mean) - 1) * 100
```