

## He Diffusion Systematics in Apatite

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### ABSTRACT

Apatite (U-Th)/He (AHe) thermochronology depends on accurate knowledge of how diffusion occurs. This involves measurement of core diffusion kinetics as well as understanding the behavior of migrating He atoms. Drawing from previous studies as well as data obtained via continuous ramped heating (CRH), we assess several processes that need to be integrated into a single model for He diffusion in apatite.

CRH analyses conducted at different heating rates show a kinetic response for both the “normal” lower-temperature and the higher-temperature release peaks, with peaks shifting to lower temperatures at lower heating rates. Where we do see a rollover in Arrhenius trends it also shows a kinetic response, being deferred to higher temperatures at higher heating rates, though many samples with unimodal release peaks do not show a significant rollover; fluorapatites seem to show more prominent rollover. For samples showing multiple release peaks, we find that their Arrhenius data often transition from one lower-temperature trend to another at higher temperatures that has about the same slope and thus activation energy. This looks very much like MDD behavior in K-feldspar, and MDD domain analysis fits the observed data very well, even if mechanisms involving discrete domain sizes are implausible. This interesting and unexplained result must speak to the nature of what is happening during analysis of samples having trapped He.

To explore our data, we coded a simple diffusion model in which single He atoms are free to jump within a grid, but can also arrive at grid nodes designated as reversible sinks, escape from which depends on an exponentially temperature-dependent probability. The model includes radiogenic He production over geological thermal histories followed by laboratory CRH outgassing. When conditioned using D values observed for AHe, the model accurately predicts parameters such as closure temperature and fractional loss. When traps are introduced, the model simulates the essential nature of the dual-peak CRH results we see. Three important results emerge from this model. (1) Few sinks need be present. (2) Trapping occurs twice during diffusion, first in nature and then again during laboratory outgassing, meaning that the ratio of the gas amounts beneath each CRH peak overestimates the geological trapping. (2) Trapping in nature is very dependent on the sample’s thermal history: it is smallest for ancient rapid cooling and largest for samples that reside in the PRZ (allowing more radiogenic production to find traps before diffusion ceases). This model raises the possibility that complex CRH data record extended thermal-history information. If CRH and  $^4\text{He}/^3\text{He}$  analysis were combined the  $^3\text{He}$  lab outgassing would record the sample’s trapping dynamics, and the  $^4\text{He}$  outgassing would reflect that plus a segment of the sample’s thermal history, which could be extracted using the  $^3\text{He}$  observations.

# He Diffusion Systematics in Apatite

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Thermo2021 Santa Fe

Thanks for your interest! Here's the 2021 version of "U-Th-He dating of apatite: a potential thermochronometer".

# He diffusion systematics in apatite: topics

Motivation and background

Assessing kinetics

Conceptual model and numerical simulation

Laboratory behavior (Durango and Transantarctic Mtns (TAM))

Possible benefits from complex grains

another reason that dispersion might be beautiful

This presentation has several segments that come together at the end, so here's an outline of the pieces.

One point of this talk is to be provocative and spur debates and experiments related to the ongoing issue of unexplained age dispersion in U-Th/He apatite ages. We're making some proposals about how this system behaves based on a model-dependent interpretation of observed data obtained using the continuous ramped heating (CRH) analysis. Much of the raw data (called TAM, for Transantarctic Mountains) is discussed in Guo et al. (GCA 2021) and can be obtained via the data statement reported there.

# He diffusion systematics in apatite

All apatite grains are the same!

Radiation damage and grain size control diffusion

Maybe tweak  $rmr_0$  to reflect composition



Let's gore our community ox: currently, this is how we roll when we apply AHe analysis to geologic problems:

We assume RDAAM or similar radiation-damage models are a complete description of He diffusion behavior in apatite, with eU and grain size the sole and primary controls. Maybe we pay lip service to compositional effects by claiming we can adjust the  $rmr_0$  parameter, but really, how often is that done, and on what sound basis (like thorough chemical analyses)? At the core, we are saying that all apatites are identical other than size and eU (and maybe halogen or trace-element concentrations).

So, we all turn the [HeFTy, QTQt] crank and grind out results.



# He diffusion systematics in apatite

All apatite grains are the same!

Radiation damage and grain size control diffusion

Maybe tweak  $\text{rnr0}$  to reflect composition

All apatite grains are the same? But...

unexplained age dispersion

all crystals have different imperfections

evidence for kinetic variation even in the

even in the RDAAM calibration!

Maybe we need to do better...

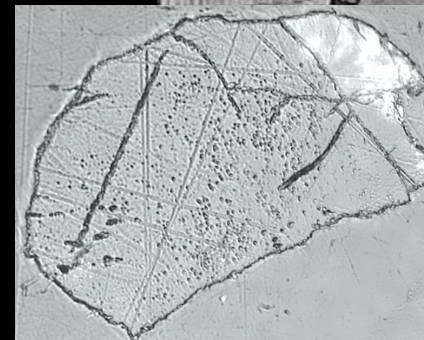


image from Annia Fayon

But really, this has to be a shared hallucination, right? It's extremely unlikely that all apatites are the same.

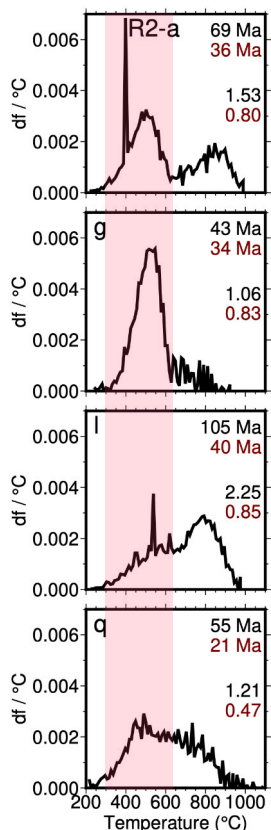
We know this phenomenologically, just because of unexplained age dispersion.

We know that all crystals are imperfect, due to: deformation, cooling rates at formation, or compositional variations leading to lattice substitutions, all in addition to radiation damage.

We have direct observed evidence for kinetic variations outside of radiation damage... even in the core data set that calibrates the RDAAM model!

We need to, at the very least, document how large such variations can be. But perhaps we can even do better and gain more thermal-history information from these variations. Otherwise, we run the risk of becoming mired in model-dependent, semi-quantitative, "rock was hot, now it's not" thermochronology.

# He diffusion systematics in apatite: observations\*



Very low solubility; Crushing can release  $^4\text{He}$

< CRH\*

all samples: "expected" lower-T release

some samples: higher-T release

both release peaks show kinetic response

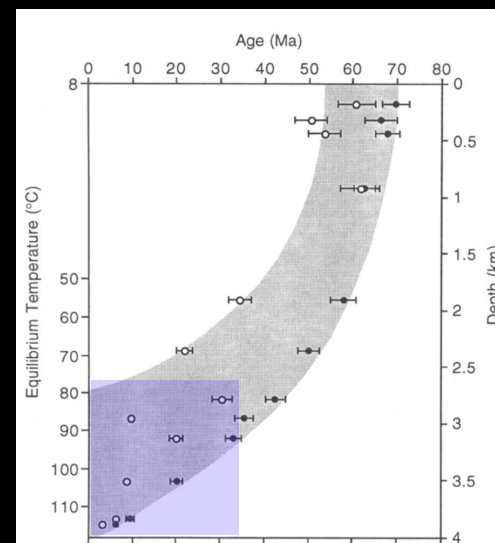
kinetic variations beyond eU and size

KTB borehole apatites >

deeper samples retain He in range 60 to 110°C

CRH spectra from these show only high-T release!

\* See poster by Guo. et al.



In this presentation we are concerned not just with specific values of kinetic parameters, but with what we're calling "diffusion systematics", the overall diffusion behavior. This includes the core kinetics but involves factors that can alter the way diffusion is manifested. What are some things we know that inform our conceptual model of He diffusion systematics in apatite?

Crushing can cause "mechanical" release of He, which perhaps is trapped in larger voids and imperfections – since we know He solubility is low, any He in a void will be stuck, even if the void is within the crystal.

Continuous Ramped Heating CRH analysis shows a range of gas-release behavior (examples at left), broadly correlated with age and with ages that are older than expected. Virtually all apatites release some He over a similar lower-temperature range, but some grains also release gas at much higher temperatures far beyond what simple volume diffusion would predict. Experiments at different heating rates confirm that these CRH release peaks show a kinetic response, with the lower-T peak matching predictions from theory. Sharp CRH gas-release spikes are consistent with the presence of near-surface voids that rupture during heating.

Apatites from the KTB borehole do drop to zero age (**bottom right**), but at much higher temperatures than would be expected from existing diffusion models. We have recently examined some of these grains using CRH analysis and almost all of their He is released only at high temperatures! (see the Thermo2021 poster presentation by Guo et al.).

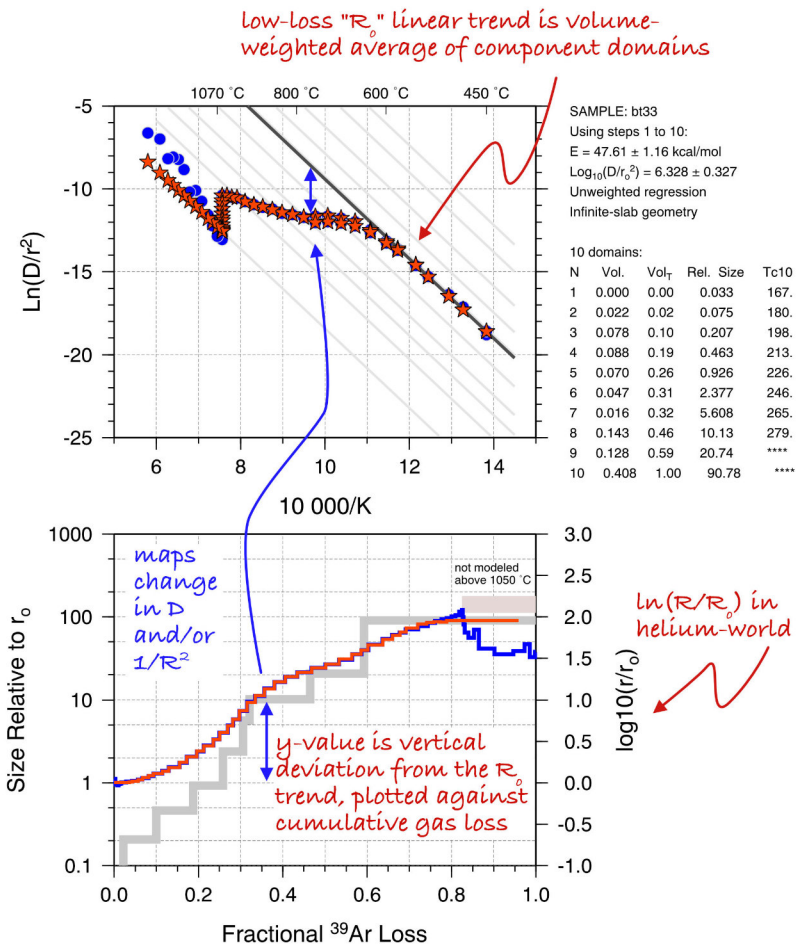
# Assessing kinetics: refresher

Arrhenius plot shows kinetics and systematics...

...but is non-linear and masks gas loss

If domains present, the linear low-T  $R_o$  trend is the weighted average of contributions from all domains

$\ln(R/R_o)$  plot shows Arrhenius behavior relative to gas release (for the reference  $R_o$  activation energy)



Let's step aside for a moment, and as part of this introduction, review how we can use laboratory noble-gas data to characterize and explore diffusion systematics.

Data from general diffusion experiments, including stepheating and CRH analysis, can be plotted on an Arrhenius plot (**top**), with the primary data being temperature, duration, and fractional gas loss. The slope of a linear trend can be interpreted as the activation energy, and the Y- intercept as  $D_o/a^2$ . If different diffusion domains (grains) are present, complex patterns can emerge as smaller domains become exhausted of gas. The apparent linear trend at low temperatures represents a weighted average of gas-loss contributions from **all** domains (because at low losses they all obey the  $\text{root}(Dt)$  relationship) (shown by the gray lines). This reference array is often dubbed " $R_o$ " but it is **NOT** the trend followed by the smallest (and/or highest D) domains.

The problem with the Arrhenius plot is that it is highly non-linear and magnifies what's going on with very small amounts of early gas loss. This can be good, but is also scary territory given how various artifacts might impact the diffusion of just 0.1% of the gas!

The way to see how diffusion varies as a function of gas release is to use a  $\ln(R/R_o)$  plot (**bottom**). This plots the difference between the Arrhenius data and the projected  $R_o$  trend, as a function of cumulative gas release. A value of 0 means you're on the line, and a horizontal trend means you're running parallel to the  $R_o$  reference. The thick gray line shows the domain distribution that gives the red fit to the blue observed data. Note that the example shown is for a K-feldspar  $^{40}\text{Ar}/^{39}\text{Ar}$  MDD analysis – the droop at the end reflects incongruent melting of the sample.

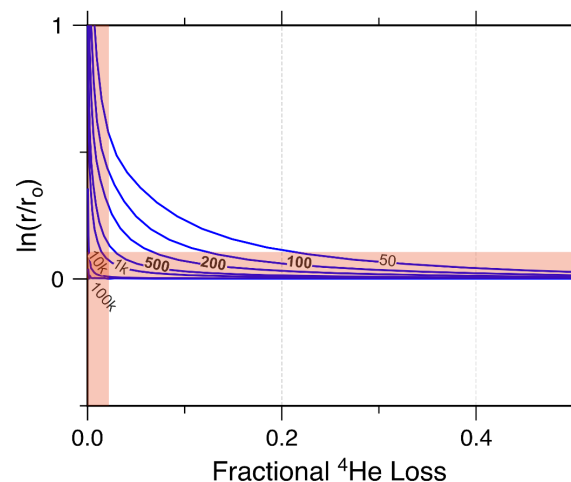
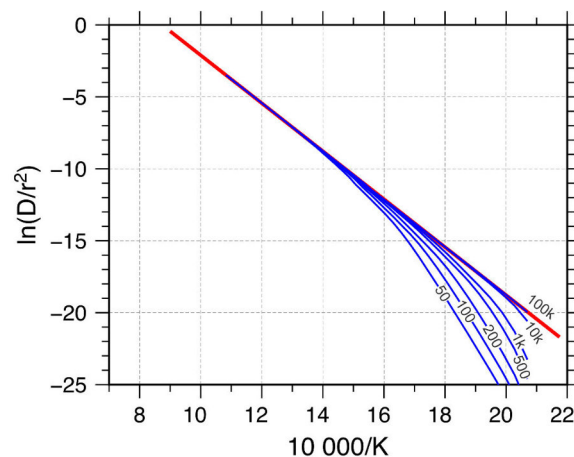
# Assessing kinetics: issues

Difficult! Temperature measurement, small signals, and artifacts:

## 1. Computational

slow-converging infinite series

need fine grid size for numerical work



Assessing kinetics can be hard, especially at low temperatures, where temperature measurement can be dicey due to low energy-transfer rates and where  $^4\text{He}$  signals are small. But there are several artifacts worth knowing about, so to be complete in discussing how we assess systematics, let's look at how we can be fooled.

First, relevant to modeling and computation, calculating small fractional losses can be a bear. The full analytical solutions are infinite series that are very slow to converge for small losses. Fortunately, the approximation formulas are very good. The problem is that these approximations only apply to simple volume diffusion, with a uniform starting concentration profile being a required condition. That rules out lots of interesting thermochronology! And it requires the use of numerical methods to handle more general cases.

But, if you use numerical methods, you have to be sure your grid size is fine enough to permit accurate calculations. The key is resolution close to the boundary. Variable grids are possible but complex and make implicit solutions difficult, so it's easier to just suck it up, use a fine uniform grid, and deal with slower run times.

Anyway, what's shown in this example is how grid size impacts accuracy at small fractional losses. The model uses a Crank-Nicolson finite-difference code to simulate a sample kept at cryogenic conditions to produce a completely flat starting profile, that is then degassed in the lab. Results in Arrhenius and RRo space are shown for 50, 100, 200, 500, 1000, 10,000, and 100,000 nodes. To keep error down to 0.1  $\ln()$  unit for  $< 2\%$  fractional loss requires use of at least about 1000 nodes, but even then the low-T Arrhenius trends are still bad. **To be clear: this is just a computational artifact.** Also bear in mind that in HeFTy, the “good”, “better”, and “best” qualities correspond to 128, 256, and 512 nodes (that's not at all an issue for normal use, just something to be aware of).

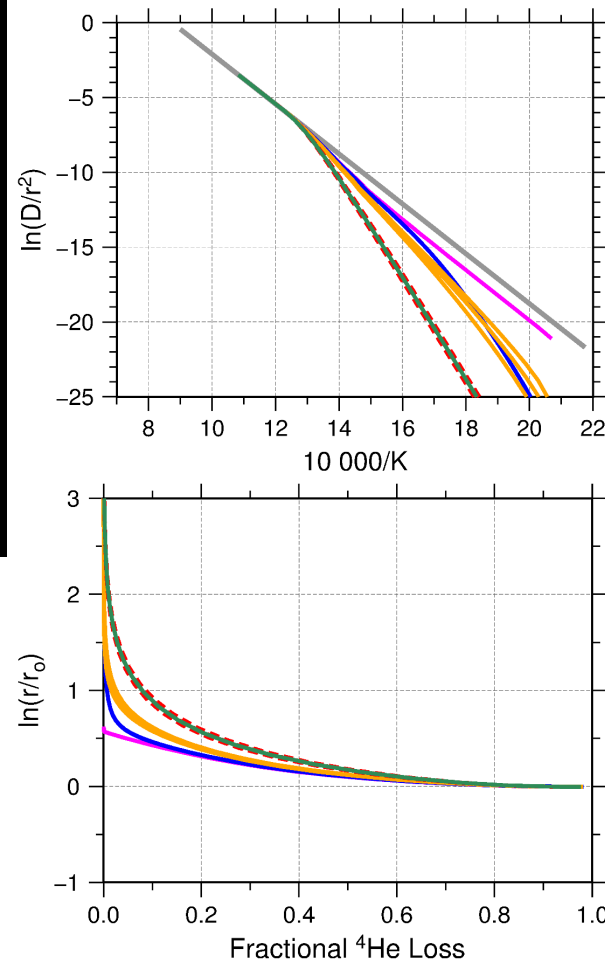
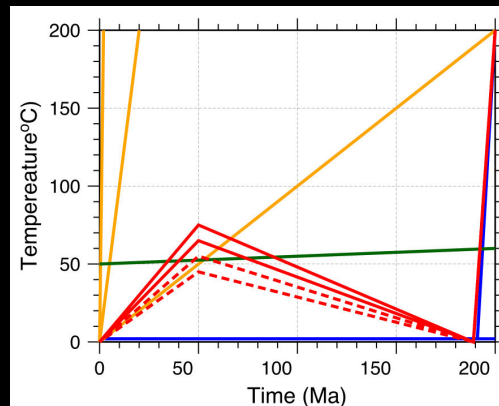
# Assessing kinetics: issues

Difficult! Temperature measurement, small signals, and artifacts:

## 2. Observational:

If using  $^4\text{He}$ , a non-uniform starting profile alters early gas release. Why?

Alpha-ejection, diffusion, zoning



OK, we just looked at a purely computational artifact, but there are also “observational” artifacts that stem from the nature of diffusion profiles and our starting assumption (for calculating diffusivities) that the initial concentration profile is uniform.

If we want to use  $^4\text{He}$  to assess diffusion systematics then we have to face up to the many reasons that  $^4\text{He}$  concentrations are unlikely to be perfectly uniform. Any diffusion will deplete the outside margins of a grain; note that even sitting at room temperature for 100 m.y. will cause a bit of diffusion in apatite. But most commonly, any normal geological history will leave some sort of concentration profile: this will be most dramatic for samples hanging out in the PRZ or being reheated into the PRZ, but not a major factor for quenched samples. All apatite grains will also experience alpha ejection, with the higher the  $Ft$ , the greater the impact (the magenta curves show the impact of just alpha ejection with no diffusion at all, for an  $Ft$  of 0.72). Finally, zoning in eU will also cause zoning in  $^4\text{He}$  (this is a mess to leave for another day).

Simulating different histories ([bottom left](#)) with a high-resolution finite-difference model (100k nodes), we can see that different styles of thermal history lead to different degrees of impact on apparent diffusion systematics. Interestingly, except in fine detail, what really matters is just the style of the history: all monotonic cooling histories have similar responses; likewise samples spending time in the prz (prz and reheating histories) respond the same. Thus, the diffusion profiles record thermal history, but not with great subtlety, reflecting the non-unique nature of diffusion profiles. But, for the purpose of documenting kinetics at low losses, you can see there's an issue no matter the thermal history.

Note that if we're using  $^3\text{He}$  then all of this goes away.

# Conceptual model

## **All crystals have imperfections**

Smaller defects impede diffusion

Larger imperfections trap (verb) He in reversible sinks (noun)

## **Trapped He is radiogenic**

produced during and above closure

## **Small volume of sinks required for trapping**

Random walks with many jumps lead to plentiful encounters

## **Trapping depends on sinks and thermal history**

Radiogenic production that is mobile is what matters

The rest of this presentation will assume a particular conceptual model for apatite He diffusion systematics, one that is derived with our and other group's observations and modeling, especially that of Cécile Gautheron and coworkers, and also Ken Farley's important early paper on diffusion in Durango apatite.

All crystals will have imperfections of varying sizes, numbers, and kind. These can occur due to deformation, strain during rapid cooling, lattice substitutions, and radiation damage. Diffusion in perfect apatite should be relatively easy ( $E_a$  of perhaps 27 kcal/mol).

Smaller defects, such as those derived from radiation damage, impede diffusion by blocking pathways. Large features, say pores derived from fluid inclusions, can act as reversible sinks that trap He: once inside a larger feature, a He atom is outside the lattice, and due to its low solubility will not have trouble returning to the lattice.

Because random walks in crystals are very long and involve many individual jumps, only a small volume of sinks is needed to lead to significant trapping because jumping He atoms explore a large fraction of the grain volume before they happen to escape. This means that trapping can occur even in crystals that appear optically pretty clean, as attested to by our solubility experiments on clean shards of the Durango standard.

The source of He in sinks could of course be partly inherited, but we will argue that the main source is simply radiogenic production from the grain that occurs above what we think of as the conventional PRZ.

Trapping into sinks can only occur when He is mobile and jumping, so the degree of trapping for any one grain will depend in its thermal history. Moreover, if retention in sinks is kinetically controlled, only a portion of a grain's radiogenic production will be retained: at higher temperatures, He escapes from sinks and then the grain.

We are using "sinks" instead of "traps" as the name of features to avoid confusion with prior literature usage.



# Numerical simulation: DIFFSIM

Diffusion as random jumps, with sinks

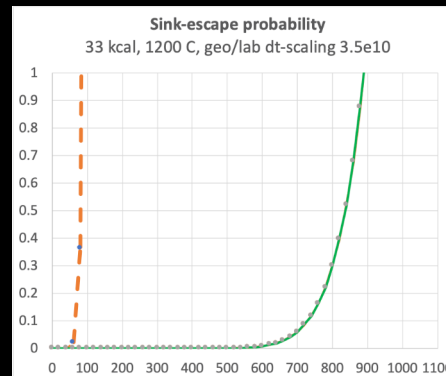
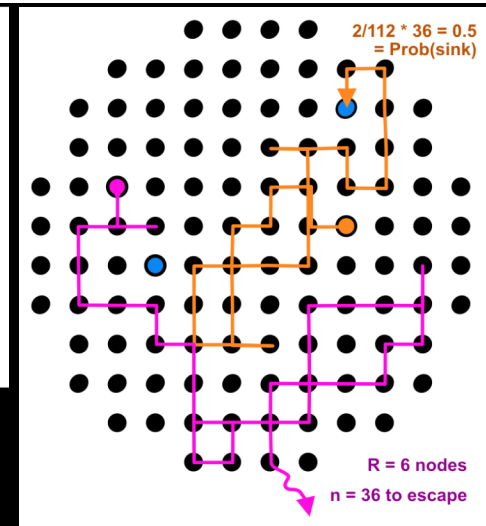
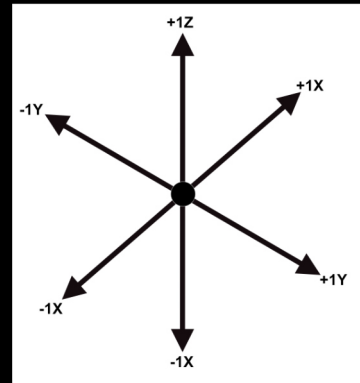
Diffusion jumps at each time step from Arrhenius and Einstein relationships:

$$6Dt = n \lambda^2 \quad n = 6D_o \frac{e^{-E/RT}}{\lambda^2}$$

Define a few nodes (< 0.001%) as sinks; multiple sink types possible

Probably of escape from sink:

$$P_e = dt \frac{e^{\left(\frac{-E_e}{RT}\right)}}{e^{\left(\frac{-E_e}{RT_o}\right)}}$$



It would be helpful to model trapping to see what the CRH observations of high-T release might mean. We have built a very simple model that simulates diffusion as a series of random 3D jumps. THIS IS NOT a sophisticated model that simulates apatite crystallography, like the kind Cecile's group has been working on!! What this model allows us to do is add a few sinks to jump nodes to see how diffusion behaves in the presence of reversible sinks.

By simulating the completely random walk of 100,000 to a million atoms in a spherical region, we can see the smooth net patterns of diffusion emerge. Setting the grid size such that each diffusion jump is of size 1, we can scale D to give results that are equivalent to diffusion in an apatite.

We can make the model geologically interesting by adding randomly distributed radiogenic production for each time step, and calculate the number of diffusion jumps for that temperature: we combine Einstein's famous formula (that relates D to the 3D random walk) with the Arrhenius relationship.

Then, we can declare a few nodes to be sinks (where "few" means maybe 500 to 5,000 sinks in a crystal having 125 million nodes – that would be 0.0004 to 0.004% !!); we allow sinks to hold multiple He atoms).

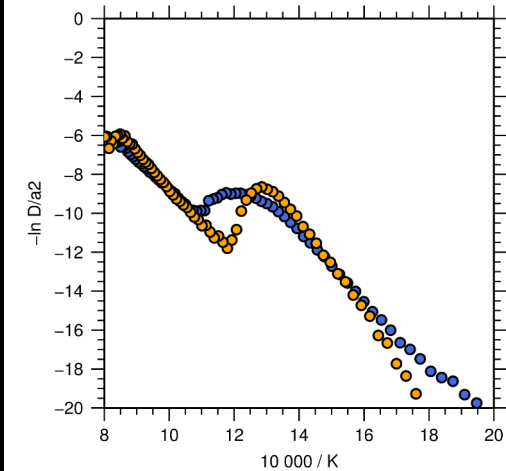
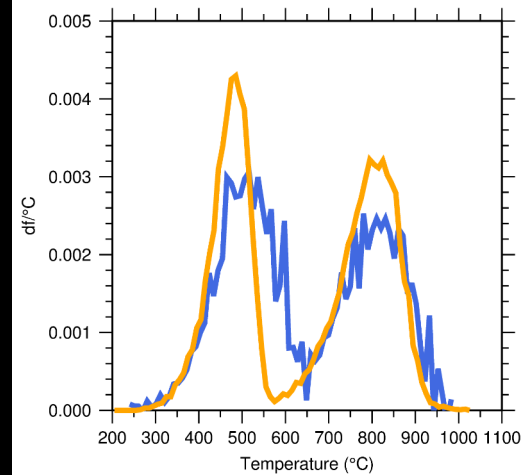
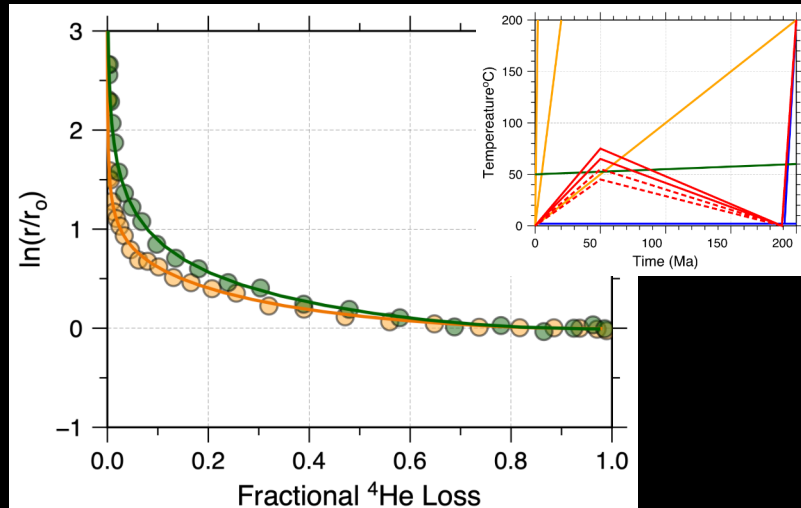
We make the assumption that the probability of escape from a sink is an exponential function of temperature (activation energy for escape of  $E$ ), and we normalize that by a exponential that includes a scaling temperature,  $T_o$ . Critically, we also include the timestep duration in the probability, allowing escape from sinks to happen proportionately in nature and during lab heating.

As coded this model simulates just volume diffusion but it would not be hard to add RDAAM-like behavior by altering the way D is calculated at each step. The code uses high-quality thread-safe random number generation and uses multiple cores; porting it to use GPU cores should be simple. Using 8 cores, run times for 100K atoms are seconds to hours depending on grid size and most important, the number of sinks.

# DIFFSIM: performance

Even just one sink type yields  
**good match** in style to  
**observed data**

Jump simulation matches finite difference code



Diffusion works! Or rather, what works is the remarkable emergent property where the ensemble behavior of many random walks amounts to smooth diffusion. Tests of DIFFSIM for fractional loss exactly match theory (and show a similar dependence of accuracy on grid resolution).

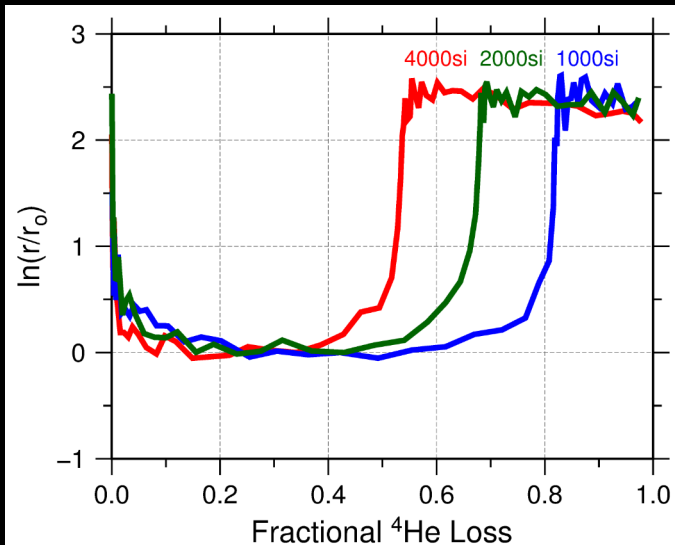
**Bottom left:** using a  $\ln R/r_0$  plot, comparison of DIFFSIM (circles) with results from a high-resolution finite-difference model, for two different thermal histories (PRZ, green) and linear slow cooling (orange).

**Right:** Arrhenius and  $df/dT$  plots for a TAM sample (blue) compared to a DIFFSIM simulation tuned for “normal” low-T release and high-T release from just a single sink type. The point is not an attempt at fitting, but just that this simple model captures much of the behavior we have observed in natural apatites (see next slides).

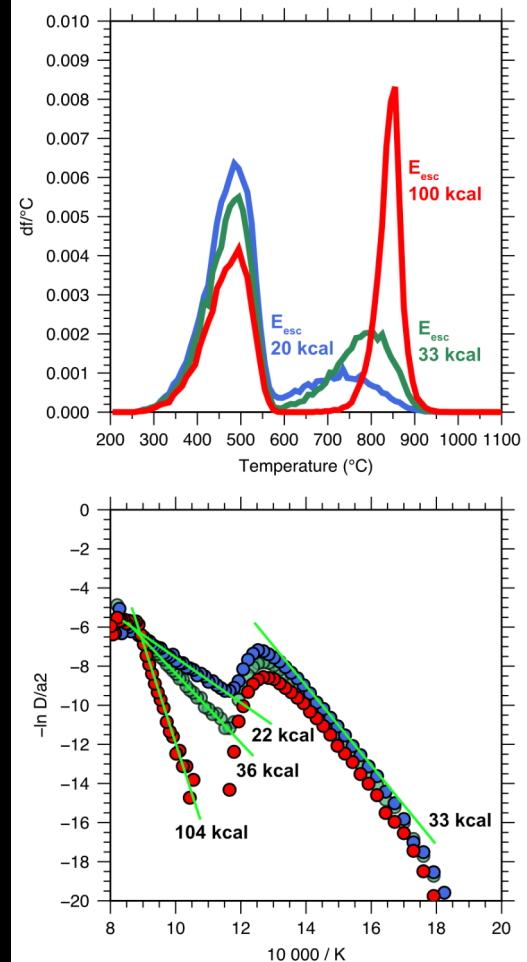


# DIFFSIM: simulating trapping

More sinks manifest as a larger fraction of He loss



High-T Arrhenius slope scales with  $E_e$



OK... if we all believe that DIFFSIM might be showing something useful about how sinks behave, let's use the code to explore a few things.

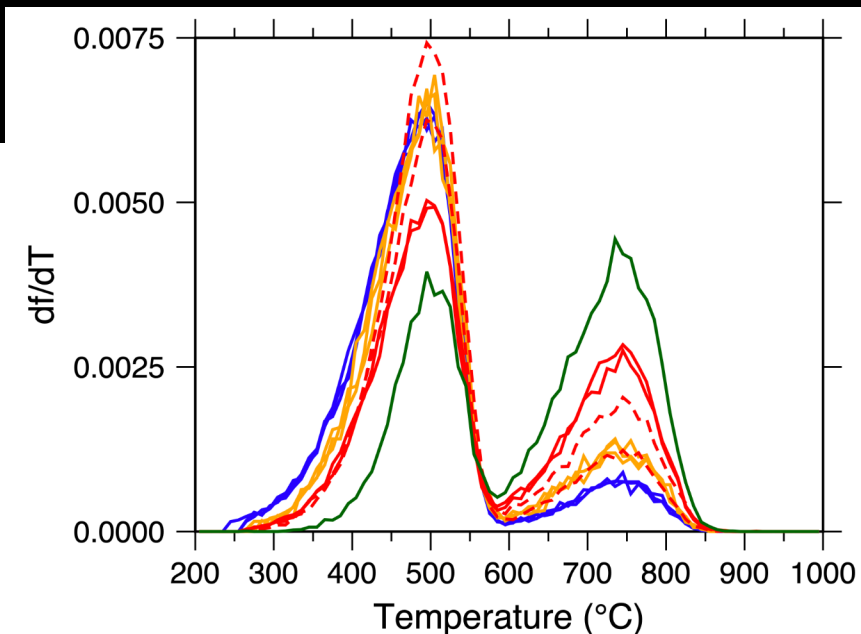
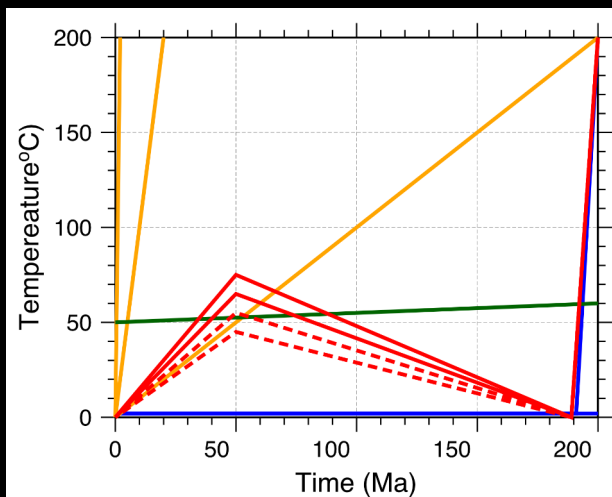
First, (**bottom left**), the amount of gas associated with sinks scales with the number of sinks present. Now, this  $\ln R/r_0$  plot was based on a simulation of a grain that had a 33 kcal activation energy for volume diffusion, and a 33 kcal activation energy for escape from sinks. Note that the late gas release has a flat trend. What happens if the escape energy is something else?

**Right:** the  $df/dT$  and Arrhenius plots show the impact of varying the escape energy. In each case the escape probability was scaled so that the simulation had a value of 50% at the same temperature. Not surprisingly, the CRH release peaks have different widths depending on the escape energy. What is interesting is that on the Arrhenius plot, the late release defines arrays having close to the value of the escape energy. This suggests that if (a big if) a natural sample contains just one sink type, then the Arrhenius slope gives us an estimate for what the escape activation energy is.

# DIFFSIM: thermal histories and trapping

Trapping happens in nature and in lab (compare blue path with others)

Amount of trapping depends on thermal history!



One more thing we can ask of DIFFSIM. For a given grain with a fixed sink distribution, what is the effect of thermal history?

Once again we are using the same suites of thermal histories (**left**; cold, linear cooling at various rates, prz and reheating). In the presence of sinks, look at how the observed CRH  $df/dT$  spectra (**right**) would vary depending on thermal history.

This is a manifestation of, in the model, trapping being more likely if He atoms are mobile (and what fraction of the atoms eventually left in the crystal felt this mobility).

Because we remove gas from samples in the lab by diffusion enhanced by heating, all of the He in the sample becomes mobile and prone to trapping. Thus, an additional feature one can glean from the above plots is that the cold or quenched histories (blue) reflect very little geologic trapping, since the atoms are formed in place with no mobility, except for the rare occasion when an alpha particle ends up by chance in a trap. Thus, at least crudely, the blue curves are recording the lab trapping, and the other curves include that plus trapping in nature.

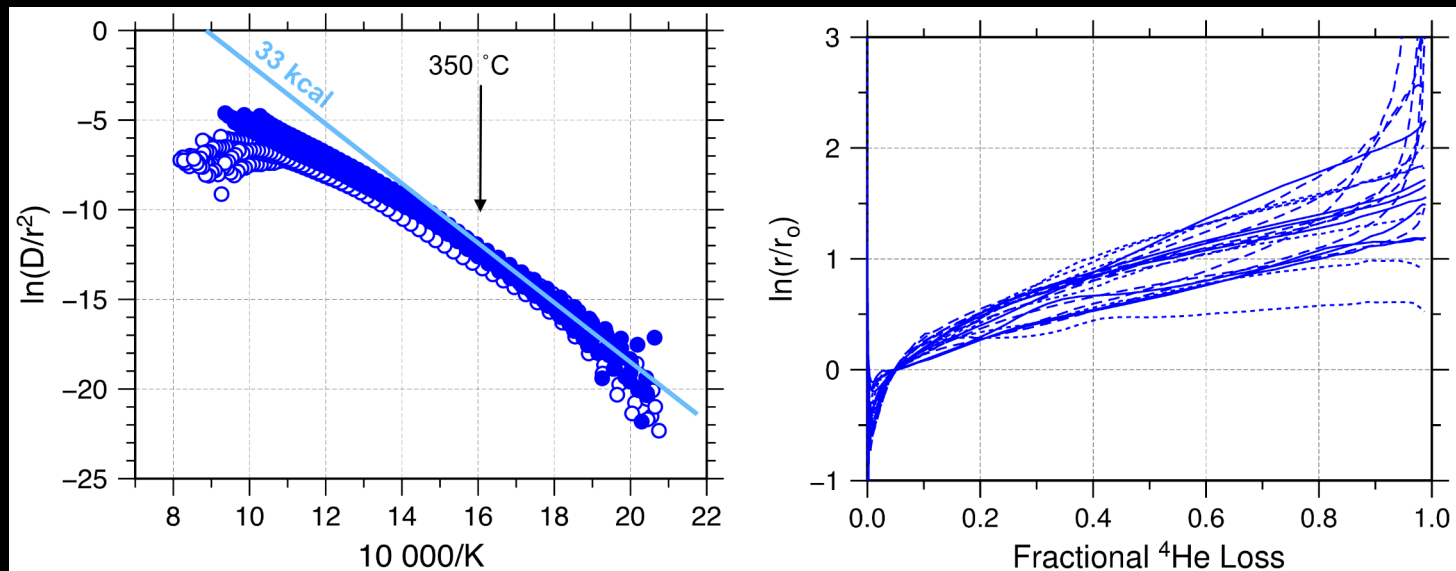
We now need to leave models behind and look at some actual observed data.

# Kinetic behavior: Durango

Common wisdom: Durango rolls over above "350°C"

CRH data suggests rollover shifts kinetically

$E_a$  is 33 kcal/mol (eU ~45 ppm)



Alright, finally, let's turn from models to observations.

**Note:** in looking at observed data, rather than struggle with line-fitting to Arrhenius arrays that could in theory be curved and also have scatter at the lowest and highest values, we began by simply fitting all data using 33 kcal (which is the nominal value for Durango apatite). To avoid significant artifacts related to the earliest gas release (concentration-profile issues) and the highest gas release (small differences between measured beams), we forced a 33 kcal line through the data point closest to 5% release.

First, let's look at Durango, which should give simple results. We examined both irregular shards from the standard we use for dating (solid circles and lines), as well as abraded "Durango balls" (open symbols and dashed lines). As expected and as is most clear in the RRo plot, Durango rolls over in Arrhenius space. No surprise: that is canon.

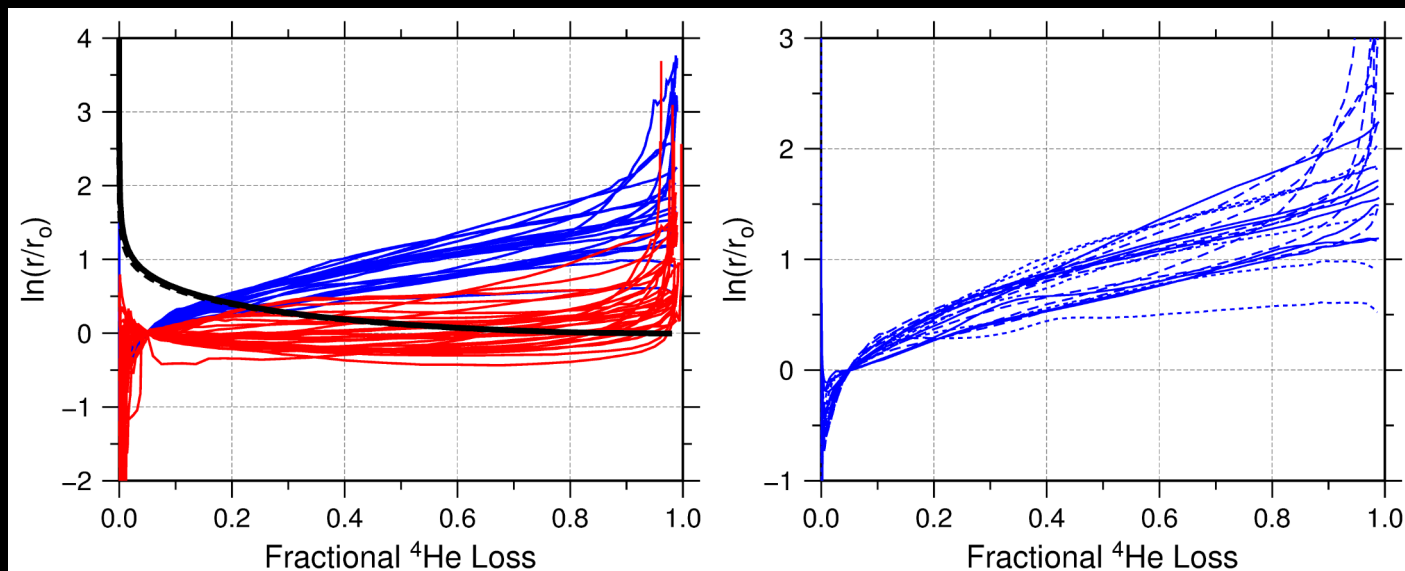
Next, we'll examine all TAM samples that gave simple unimodal CRH release spectra. We would expect a similar result, given that the presence of rollover has been reported for a number of apatites.

# Kinetic behavior: TAM unimodal

TAM: Transantarctic Mtns dispersed suite (Fitzgerald et al., 2006; Guo et al., 2021)

TAM grains show little rollover (n=28); no rounded-profile effects (??)

Near 33 kcal/mol for most of gas release; eU ~30 to 90 ppm ( $T_{c_{10}}$  @33kcal:  $82 \pm 5$  °C)



Whoa. That's interesting.

First, most of the gas release from the unimodal TAM apatites stays close to the reference line: there is no significant rollover. The late upward tick is probably an experimental artifact related to machine sensitivity over the last 1-2% of gas release.

Second, all 28 grains are pretty happy to be parallel to a 33 kcal slope. Maybe this is a coincidence related to Durango vs. TAM kinetics, but still, it's worth noting.

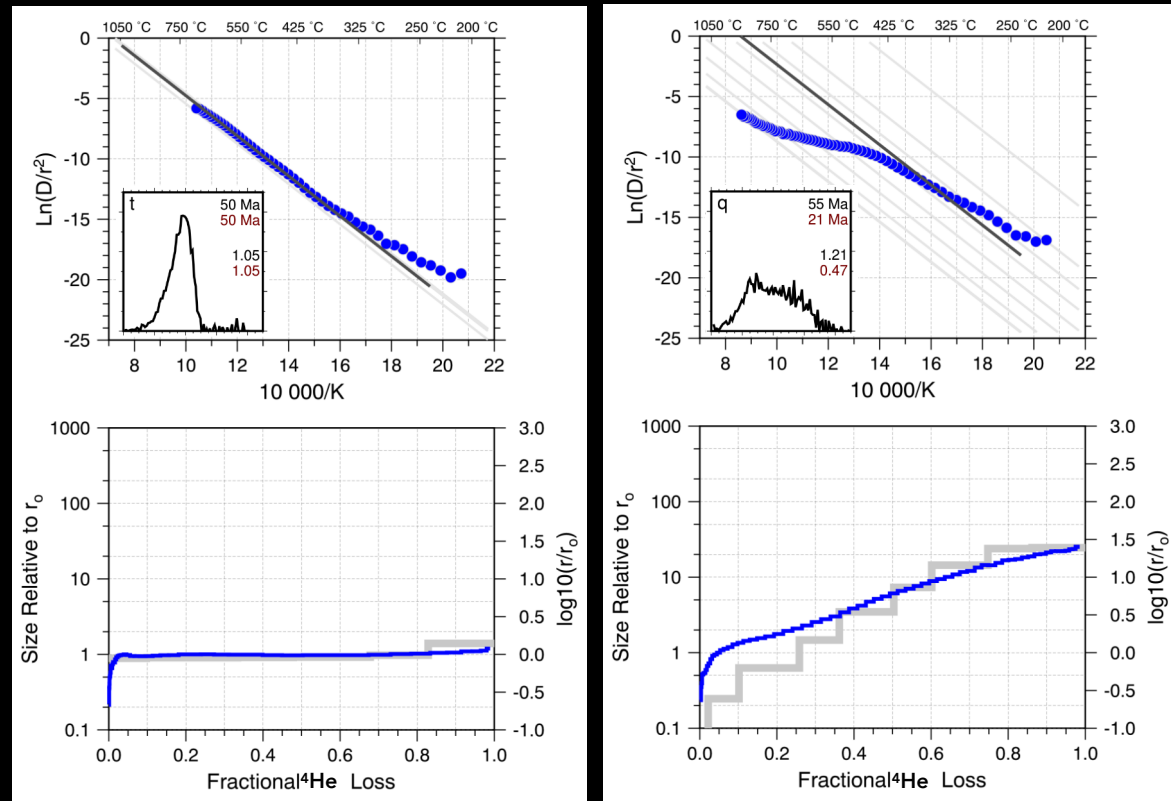
For the record, both Durango and the TAM suite are fluorapatites, so the difference in rollover can't be a function of halogen composition. Maybe Durango, the apatite we have obsessed over, is just weird.

Finally, as a technical detail, it's odd that there is little sign of the sort of diffusion artifacts we'd expect to find in the low-T release from natural samples. The dark lines show the expected trends for linear slow cooling and a cold, quenched history, scenarios that probably bracket what the TAM apatites experienced. Yes, overall the comparison is similar at loss values greater than 20%, but in the sensitive region at lower losses, observations do not match predictions very well. We have no explanation for this difference and while it is a very subtle point in one sense, it's bothersome and will require more study.

Bottom line: most of the gas released by the TAM apatites seems to be consistent with simple volume diffusion with "reasonable"-seeming kinetics. Instead of fretting about how hard and messy the lowest-T release is and how rollover is the enemy, for the moment let's accept the observational data (but remembering that we forced 33 kcal through the data!). Perhaps the lack of rollover in these data is related to the shorter cumulative heating that CRH samples experience (i.e. the point of rollover is kinetically controlled, as suggested by Idleman et al. (2018)).

# Kinetic behavior: TAM unimodal and multimodal

Almost all grains show consistent release, either:  
unimodal,  
bimodal, or multimodal  
(aside from spikes)



In Guo et al. (2021) we examined well over 300 TAM grains, so for this short talk we'll have to generalize! What do we see overall?

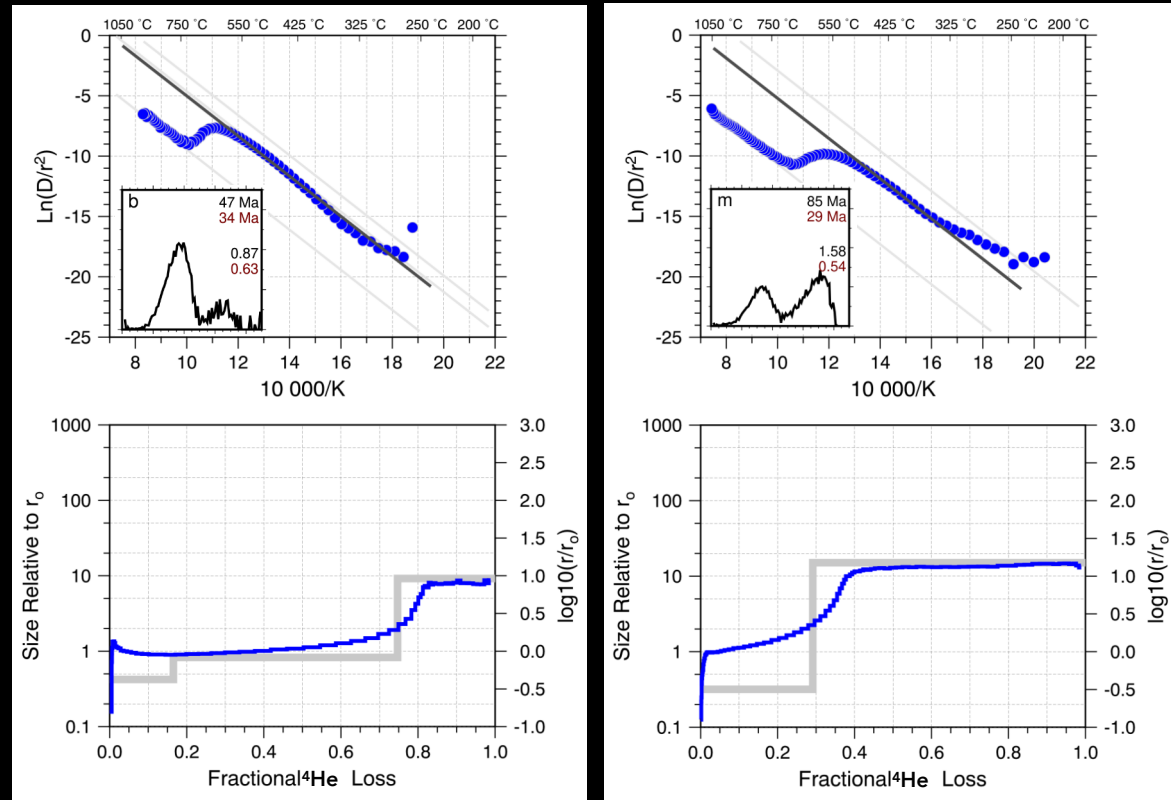
We see very few grains that gave just scattered, "messy" kinetic data. In general, samples fell into three categories of CRH release patterns (reflecting kinetic behavior): unimodal, bimodal, and multimodal.

We just saw how the 28 unimodal grains behaved; here we show one example each of unimodal and multimodal behavior. Unimodal grains yield very flat RRo plots (for 33 kcal...), whereas multimodal samples display a continuously rising ramps-and-flats pattern (reminiscent of what K-feldspar MDD data look like).

Note that in our survey, we did not consider samples that showed sharp gas-release spikes, since it's complicated to think about how to deal with the kinetics for such samples.

# Kinetic behavior: TAM bimodal

High-T release is often  
parallel to earlier release  
 at 33 kcal  
 recall DIFFSIM results?

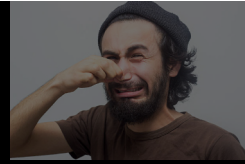


Bimodal samples were also quite common, characterized by CRH spectra with two clear peaks that manifest as two segments in Arrhenius space and two discrete RRo values.

For almost all of these samples, the second higher-temperature segment tracked parallel to the earlier one, at about 33 kcal. This was also evidence of this from multimodal samples that had sufficient gas release across the last segment.

Given the numerical experiment we discussed earlier, this suggests that the sink-escape activation energy for these samples is close to 33 kcal (if you accept our model)

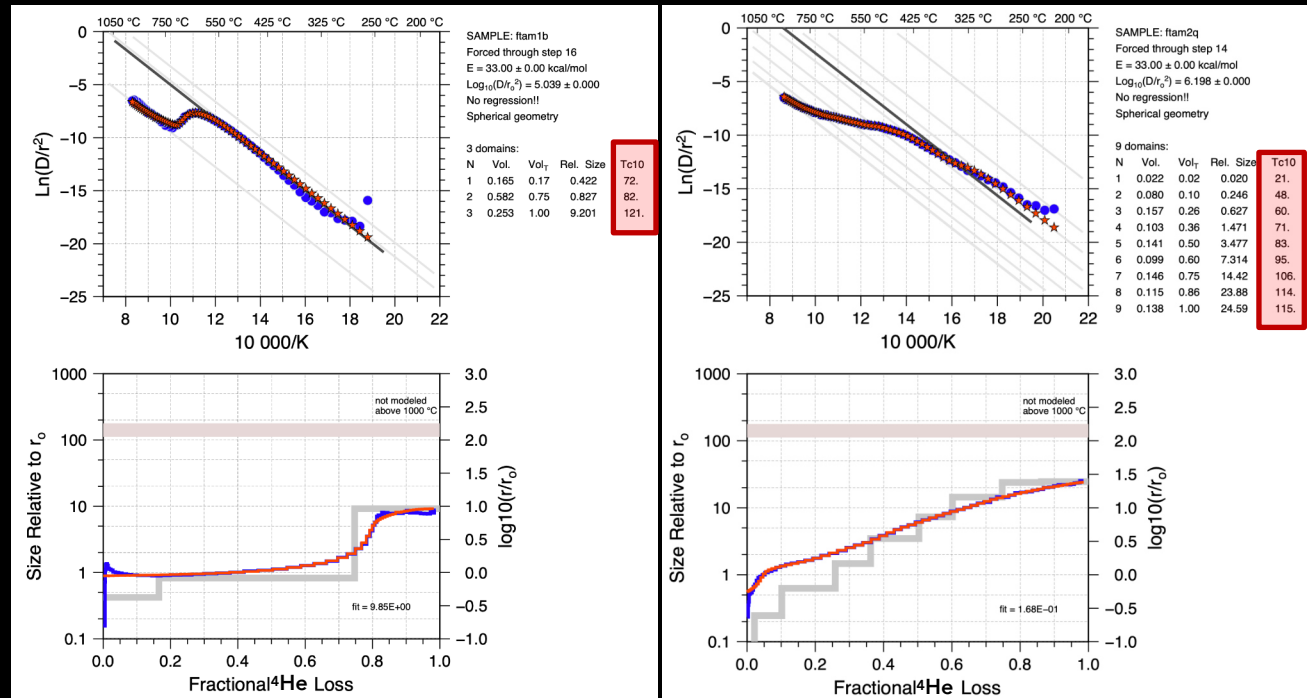
# "Virtual" diffusion domains: VDD



What if we just treat  $^4\text{He}$  release data using MDD analysis?

can't be a domain-size effect, but...

release from sinks might still emulate domain behavior



Let's now take a hold-your-nose leap of faith and ask if the lab diffusion systematics we see might be telling us something real about He retention in nature.

The previous several plots were actually made using an implementation of Oscar Lovera's domains code we use to invert for the distribution of differently sized diffusion domains in feldspar; in the previous plots we just omitted the domain kinetic info.

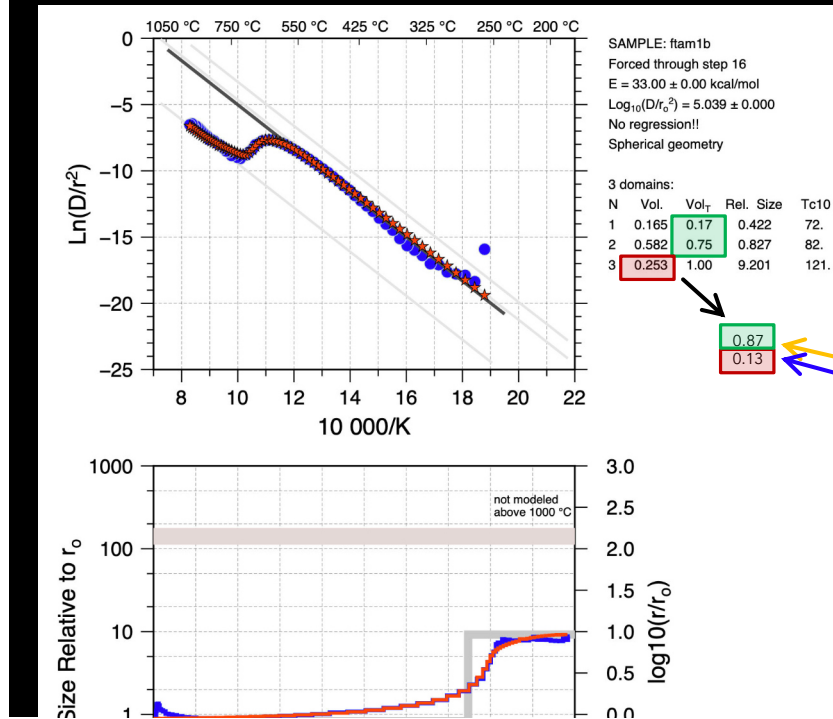
We noted earlier that the patterns from TAM apatites look a lot like MDD data from feldspars. It's implausible to us that we are seeing domain-size effects in apatites, since we know that for many samples the whole grain, the largest possible size, is the effective diffusion radius, but CRH analysis shows that all grains show similar low-T release peaks. Since breaking a grain into size domains increases  $D/a^2$ , data that shift left (down) on an Arrhenius plot can't reflect a shift to larger domains since the low-T release is already coming from the whole grain.

So what is going on? Invoking the annealing of subdomains falls afoul of the previous argument. We tentatively suggest that at higher temperatures we're seeing the escape of atoms from sinks, which, once they're out, follow the whole-grain volume-diffusion kinetics.

If all the He involved is indeed autogenic from the grain, than its retention by both closure and reversible trapping should contain temperature info. If we look at the complete report from the inversion, we can see that a very good fit to the observed data can be obtained using a small to modest number of apparent diffusion domains. Moreover, the kinetics involved lead to closure temperatures that seem reasonable (60 to 80 °C for the low-T release, and 100 to 125 °C for the higher-T release).

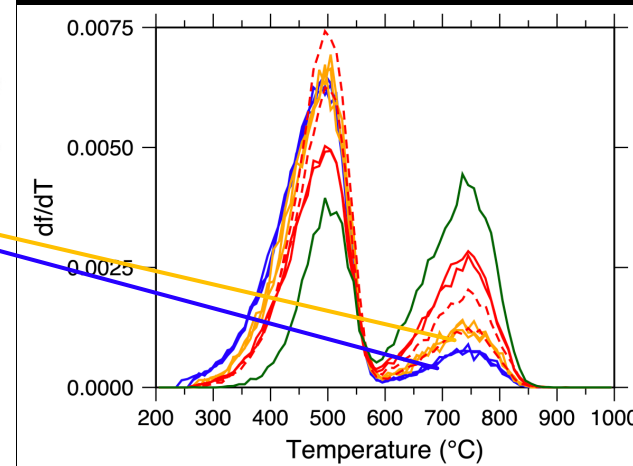
Maybe a bit tongue in cheek, we're claiming that this behavior is due to the presence of "virtual" diffusion domains: diffusion systematics that can be addressed as if there were discrete regions of differing size or D value.

# "Virtual" diffusion domains: VDD



Need to adjust observed domain volumes to account for double-trapping

Use models result for quenched vs. slow-cooling history



Plunging ahead, we're going to see how this might work, but there is one more topic to discuss.

We noted that trapping occurs both in lab and in nature, so the apparent fraction of more retentive "domains" will be over-represented. If we assume that the quench model reflects mostly lab trapping, we can see how much extra trapping should come from various thermal histories. Remember that this is not highly sensitive to details, but just the style of the thermal history. For TAM, we might assume a slow cooling history (orange in the above plot), and then compare the ratio of the area under the two curves for the two scenarios (slow and quench). This lets us adjust the observed "domain"-distribution data, downweighting the apparent volume of the more retentive domains. This is trivial for simple bimodal samples; doing this for more complex samples would require more complex calculations and assumptions.

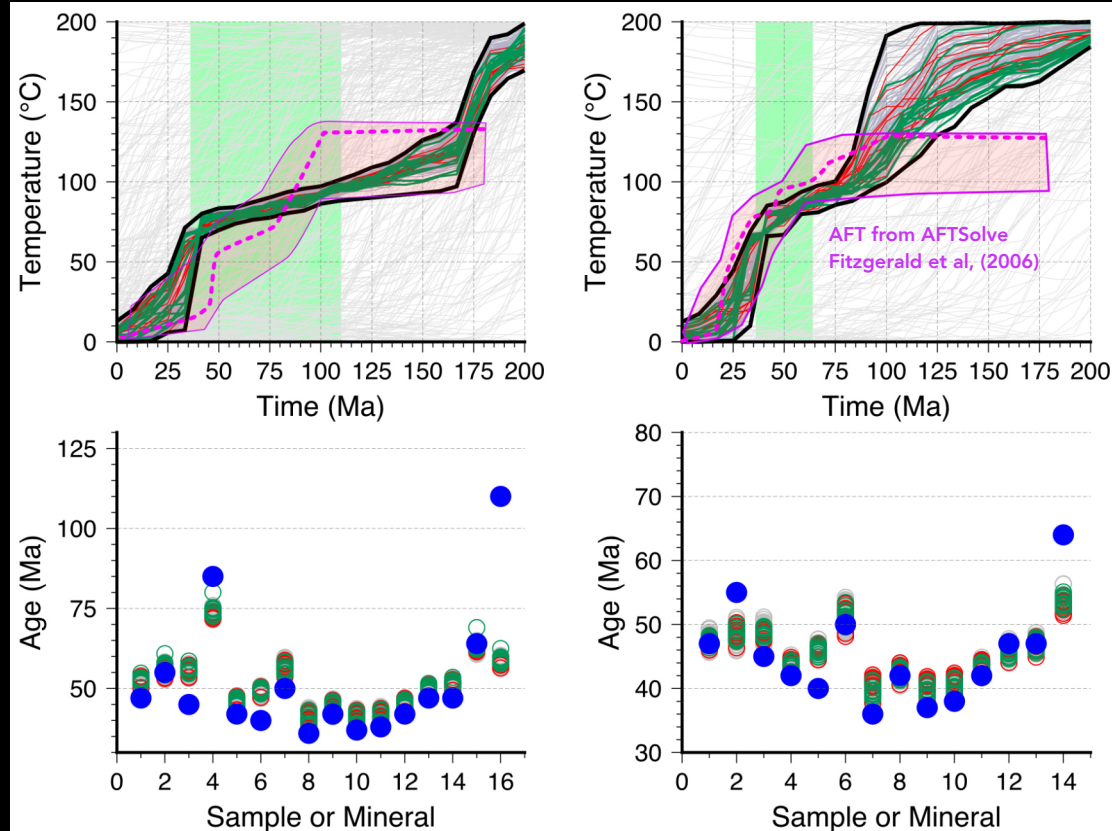


# VDD t-T inversion via CRS

Treat bulk ages as weighted average of VDD component ages

$$Age_{pred} = \frac{\sum w_i Age_i}{\sum w_i}$$

$\sum w_i$  is adjusted domain gas content



OK, what's the next and most treacherous step along this slippery slope we're on? We have a set of TAM samples each with observed ages and a VDD structure (apparent volumes and kinetics). What if we invert for thermal history by saying the the bulk age we measured reflects the "volume"-weighted average from the various component domains? To give this a try, we used our venerable Arvert code, which employs the controlled random search method (CRS) to search for best-fitting thermal histories. We simply modified the code to use the predicted bulk age instead of a  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectrum.

We tried this for our lowermost and uppermost TAM horizon, using about 15 mostly bimodal and unimodal samples that were clean without release spikes. Note that we used the observed systematics but remember, we forced a 33 kcal activation energy through the data. A proper analysis might use an Ea defined by the data, which might be 1-2 kcal/mol different.

The tT plots show the envelope around the final solution set for 150 tT histories, with the best 15 in green and the worst in red (the gray scribbles in the background are the original starting Monte Carlo pool). The green rectangle show the age interval over which the observed ages give direct constraint. The magenta envelope and dotted line given the AFTSolve results obtained by Fitzgerald et al. (2006) for just their AFT data. The bottom plots show the observed ages in filled blue circles and the color-code predictions as open circles.

Yes, many assumptions but still... this actually seems to work! The "VDD" data pick up the change in cooling rate and the temperatures that pertained between ~30 to 100 Ma. Yes, with some misses, and just for this one suite.

We could use the df spectra as an additional constraint beyond the ages, but this would involve using the diffsim code in the inversion, which would be slow until it modified to work using GPUs. But there's one more thing...

## Next steps: $^4\text{He}/^3\text{He}$ CRH?

First, see what happens with  $^3\text{He}$  and CRH

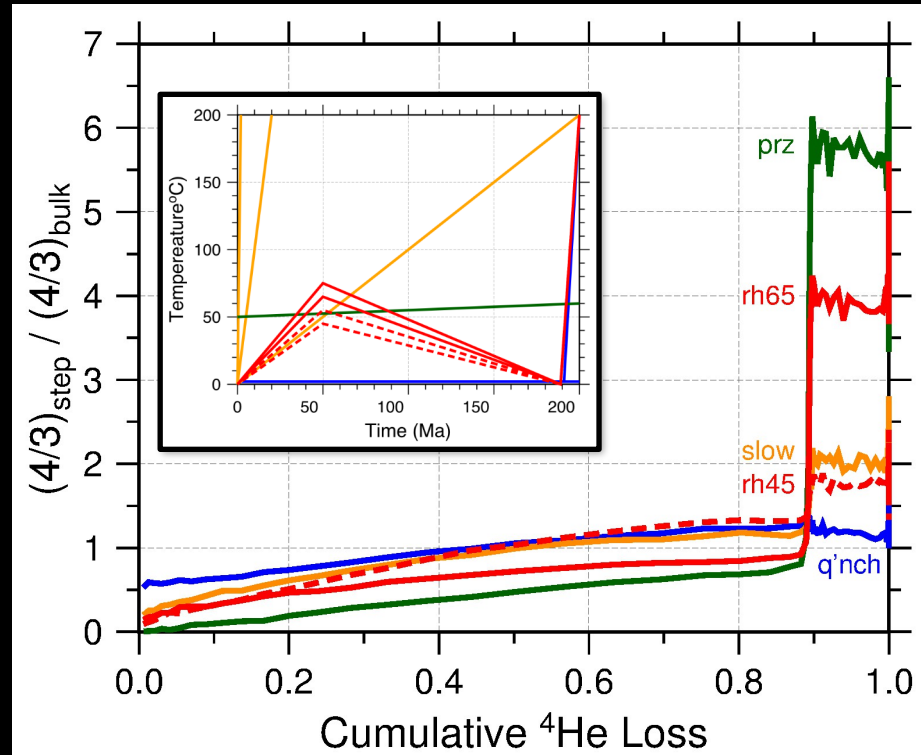
is this all an opium dream?

$^3\text{He}$  gives trapping structure (VDD distribution)

$^4\text{He}$  records that plus thermal history

By analogy to the MDD approach, invert  $4/3$  spectra for thermal history

Is conventional U-Th-He analysis of apatite like doing bulk K-Ar on feldspar grains?



DIFFSIM models of  $^4\text{He}/^3\text{He}$  ratio evolution with trapping

We think this overall conceptual model and approach has great promise. But we think the way to exploit this correctly is not to depend on just  $^4\text{He}$ .

A critical first experiment, which we plan to do but encourage others to try, is to see how  $^3\text{He}$  behaves using CRH analysis on a complex suite like the TAM apatites.

Beyond that, we suggest that the future of AHe work might involve  $^4\text{He}/^3\text{He}$  CRH analysis on a routine basis. In MDD analysis,  $^{39}\text{Ar}$  provides required info on diffusion domains, and  $^{40}\text{Ar}$  contains information about the thermal history, which can be inverted for because we can independently learn the domain structure.

By analogy, if we irradiate to create  $^3\text{He}$ , we can use its release behavior in the lab to invert for the “kinetic” (VDD) structure of the sample, and then use  $^4\text{He}$  to get the thermal history. The plot shows the predicted  $^4\text{He}/^3\text{He}$  ratio evolution for a sample containing a few sinks, for various types of thermal histories. If you look closely, you can see that for much of the gas release these just look like normal  $^4\text{He}/^3\text{He}$  spectra, but once the trapping kicks in, you can see how the different styles of thermal history are discriminated.

No one today would do bulk K-Ar analyses of K-feldspar grains. If you did, you'd see K-feldspars performing sort of OK but in detail you'd see different ages for different grains (you'd see age dispersion...). Perhaps in a few years we'll have the same view about U-Th/He dating of apatite!