DIFFSIM 3.0 Background Documentation (current version is 3.14) August 15, 2023

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DIFFSIM 3 simulates the diffusion of radiogenic helium in mineral grains having discrete sinks into which helium can become reversibly trapped. Volume diffusion simulated using a 3D orthogonal isotropic random walk in a crystal. It allows for randomly distributed continuous production of new atoms during a "geologic" phase and then a "laboratory" outgassing phase that simulates continuous ramped heating (CRH); alpha ejection is included. Atoms can become trapped in sinks and can escape from these sinks. The geological thermal history can be arbitrary as long as sufficient time nodes are provided for the model.

While the model applies to volume diffusion generally, it was constructed with helium diffusion in apatite in mind, partly to investigate how diffusion and trapping might interact.

Run without trapping, the model is a nice tool for demonstrating how the bulk diffusion behavior used in noble-gas thermochronology emerges from the random and therefore directionless motions of individual atoms. The model accurately simulates such processes as closure temperature and episodic loss (see below).

At the very end of this document there are a few plots demonstrating **DIFFSIM** results for various scenarios.

Simulation of Volume Diffusion

DIFFSIM combines the Einstein expression for the diffusion coefficient in terms of a 3D random walk (where *n* is the number of jumps and λ is the jump distance):

$$D = \frac{1}{6} * \frac{n}{\Delta t} * \lambda^2$$

with the Arrhenius relationship:

$$D = Do * exp^{\frac{-E}{RT}}$$

to get an expression for the number of jumps per time increment at a particular temperature:

$$n = 6 * Do * \Delta t * \frac{1}{\lambda^2} * exp^{\frac{-E}{RT}}$$

In the simple jump model used by **DIFFSIM** a jump can occur in any of six orthogonal directions. This jump has a distance of one node. If we arbitrarily set the jump distance λ to be 1 cm, it is

easy to scale *Do* and the stopping distance as needed to be realistic and simulate diffusion kinetics as seen in real minerals. The stopping distance is calculated using the Ft value entered by the user.

Assumptions and iffy things we tolerate:

- Atoms jump along either of three orthogonal axes, with equal probability.
- At each time increment, each atom being tracked jumps *n* times in a completely independent manner; there is no interaction between atoms
- Multiple atoms can end up at the same node
- At the start of each time increment, a constant number of new atoms is produced, located randomly within a spherical volume defined across a Cartesian grid. Before walking begins, these atoms are randomly relocated by one stopping distance (random distribution across a spherical surface area)
- Atoms that jump to locations that are more than one radius from the center are considered permanently lost, as are those who end up outside the crystal due to alpha ejection

Simulation of Reversible Trapping into Sinks

A specified number of nodes in the crystal grid can be randomly assigned to be reversible sinks. Atoms that enter and escape from sinks are tracked; multiple atoms can be located in one sink, and sinks are simply the "size" of a grid node. It is possible to specify sets of multiple sink types having different properties.

The probability of escaping from a sink is offered once to each trapped atom at the start of each time increment. If an atom escapes, it then obeys the normal volume diffusion rules about jumps for that time increment. If a walking atom encounters a sink, its walk ends.

The probability of escaping from a sink follows a Boltzmann-style distribution normalized by an empirical partition-like function to produce a maximum probability of 1 at an empirically set scale temperature; the probability is also scaled by the duration of each time increment (geologic vs. laboratory):

$$p = dt\ exp^{\frac{-Etrap}{RT}} / exp^{\frac{-Etrap}{RTscale}}$$

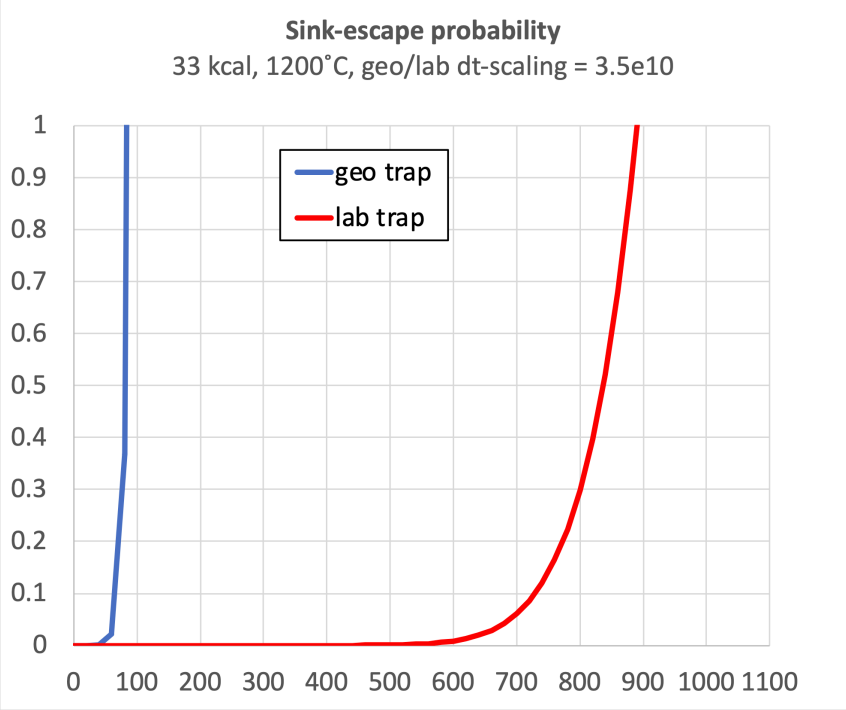
This probability distribution can be empirically calibrated, for example, such that during laboratory heating, an apatite-like high-temperature release peak occurs at say 800 ˚C (e.g., using Etrap of 30,000 and Tscale of 900 ˚C).

For either phase (geologic or lab), to actually implement the probability of a single atom escaping from a sink, a random number is selected between 0 and 1, and compared to the

value of (*1-p*). If the probability *p* of having sufficient energy to escape from a sink is high, (*1-p*) will be small, and so compared to a uniform random number selected from the range 0 to 1, a decision to jump will be likely.

Note that it might feel more accurate to offer escapes from sink at every step of the random walk, but this would just rescale the probability functions and would VERY much slow down the code. Given the rough nature of this code with respect to an actual simulation of diffusion in a crystal and fine-scale interactions with different sorts of defects, it's not worth worrying about the way the code offers escapes from traps. Certainly, different expressions could be substituted for what we empirically know is a temperature-dependent escape probability.

Relatively speaking, a high Etrap narrows the range over which escape happens or not, with its location pinned by Tscale. The following figure shows the nature of these probability distributions and how the lab and geologic cases might compare.



Performance

DIFFSIM compares well with standard numerical models of diffusion, correctly showing the dependence of closure temperature with cooling rate, and correctly calculating the fractional loss from a sphere as a result of a square-pulse heating event.

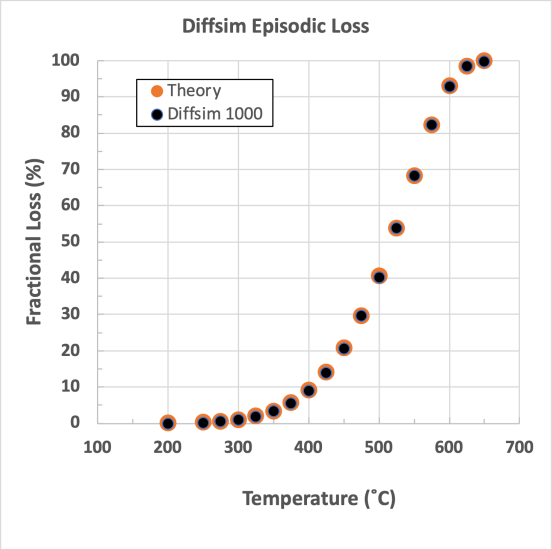
Closure temperature

cooling rate	Dodson	numerical	DIFFSIM
100	80	82	52

10	64	66	66
1	50	51	83

Fractional loss from sphere (1000-node model)

T isothermal	theory	DIFFSIM
250	0.273	0.123
300	1.09	0.98
350	3.46	3.40
400	9.17	8.98
450	20.8	20.6
500	40.7	40.1
550	68.3	68.3
600	93.0	92.9
625	98.5	98.5
650	99.9	99.9



More notes about accuracy. It's not surprising that this model, based on granular randomness, agrees perfectly with predictions of diffusion as an emergent phenomenon – this gets to the very heart of what the diffusion process represents. Note that this applies to the diffusive component of **DIFFSIM**, not the trapping model, which is *ad hoc* and just designed to explore how a trapping process might interact with random walkers.

If you have worked with numerical simulations of diffusion such as finite-difference models, you'll know that to get highly accurate results for low fractional losses or the equivalent, a very large density of grid nodes is needed near the simulated grain boundary. Coarse grids of 100 or even 500 nodes work well enough for geological simulations, but for small fractional losses below perhaps 1%, a near-surface density equivalent to 10,000 nodes or more becomes necessary. Interestingly, the same constraint applies to **DIFFSIM**. When you have fewer nodes, you less accurately portray the surface boundary and one diffusion jump becomes a much larger fraction of the total radius. While increasing the node density will allows slow down code, it's more of an issue for **DIFFSIM** since is a 3D model, so the number of diffusion jumps will escalate rapidly and the code execution speed will plummet.

Execution speed and tradeoffs regarding accuracy. So, as you'd expect, the number of nodes in the grid is a key control on execution speed. Models with 100 nodes runs fast but the accuracy of diffusion profiles is not so great, which also shows up in the rounding of Arrhenius plots. 500 nodes is better, and 1000 is great but is quite slow. As a compromise I suggest 200 nodes, knowing that fine-scale accuracy will be imperfect.

Another control on speed is the number of walkers. This derives from the combination of geological time steps and production rate per step. Secondarily, the number of walkers in play also depends on how many are lost in the geological stage; you can see the model speed up in

the lab stage as outgassing eliminates walkers. FYI, this means that the model slows down as the geological stage proceeds because more walkers come into play through radiogenic production, and then the model speeds up in the lab stage as walkers are outgassed. You should get decent results if the total walker production is something like 50,000 to 100,000 – more would be better for accuracy but the goals of your modeling need to be kept in mind.

Finally, model run time is strongly impacted by the number of traps, since more code comes into play to handle these, and also more trapped atoms means more walkers being released later in the lab heating.

So, expect vastly different runtimes for having 50,000 walkers, 50 geologic time steps, no traps, and only 100 grid nodes (maybe a minute), compared to 200,000 walkers, 200 times steps, 1000 or more traps, and 500 grid nodes (hours or more!). One suggestion would be the classic one: experiment with scenarios using fast models, then use slow models for final documentation of results.

This version of diffsim tries to take advantage of multiple CPU cores using OpenMP (I believe the use of random numbers in the code is thread-safe). On an eight-core M2 Macbook Pro, use of OpenMP increases execution speed by a factor of nearly five compared to a standard compilation.

By compiling using OpenACC on a machine having lots of GPU cores, it should be possible to greatly speed up this code since the individual random walks are independent and so **DIFFSIM's** jump routine falls into the category of embarrassingly parallel.

Preliminary Observations and Thoughts

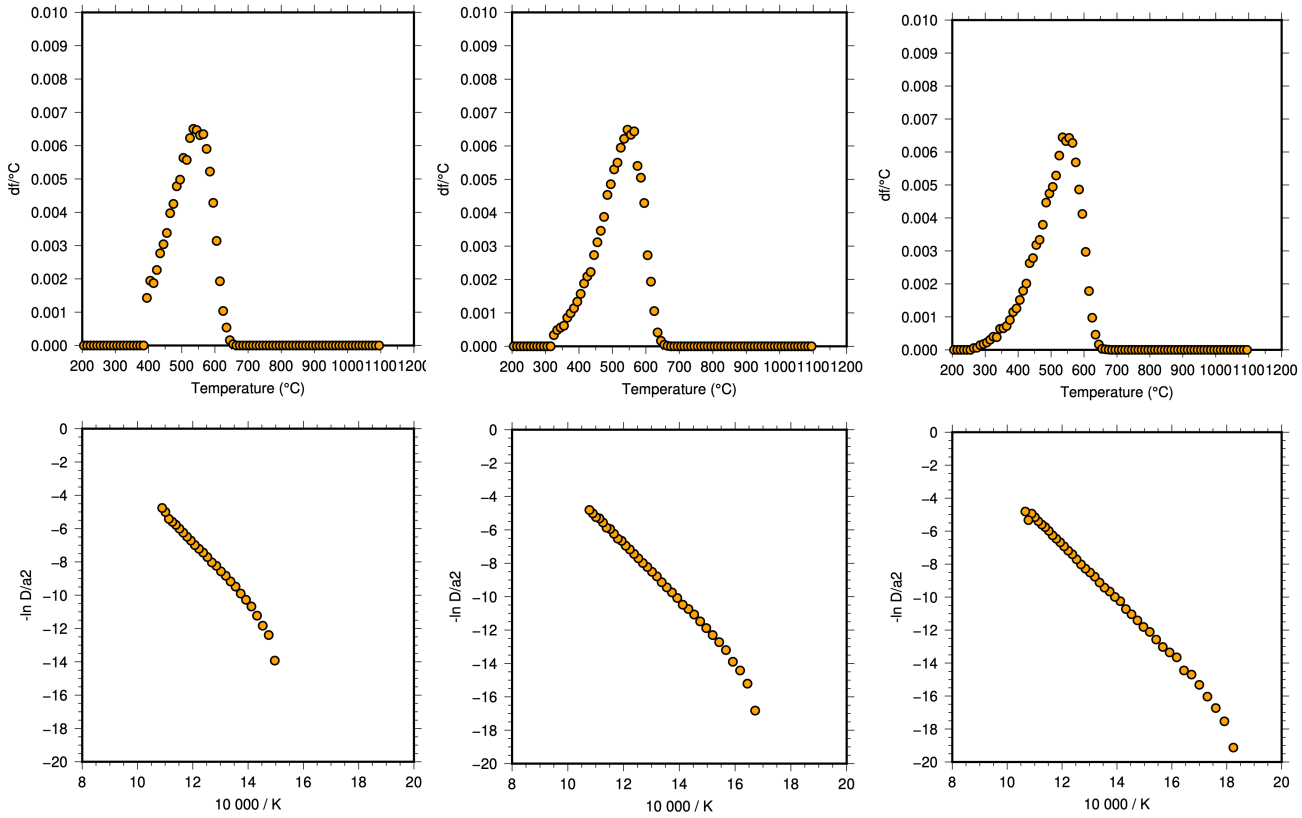
- With kinetic and trapping parameters tuned to give a "normal" low-temperature CRH peak at 550 to 600 ˚C, and a typical high-T anomalous peak at 800 ˚C, **DIFFSIM** results look eerily like actual CRH observations in both *df* and Arrhenius space. True, to some degree this reflects the tuning involved and the underlying construction of the model.
- A key control on trapping seems to be the nature of the thermal history near the partial retention zone (PRZ). Interesting, very different rates of linear cooling gave quite similar trapping results. It is prolonged PRZ residence that really shows up as a larger amount of trapping. **DIFFSIM** makes it clear that the amount of trapping depends on the thermal history.
- If (if) the adjusted trapping probability model is ok (scaling trapping probability by the ratio of the lab and geologic time steps), then there is less need to worry about extended trapping at high temperatures, because even over very long geologic durations, trapped atoms will escape. Thus, extraneous radiogenic accumulation should be finely tuned to the trapping probability near the closure temperature. In other words, it's probably not a worry that ancient basement apatites could trap gigayear amounts of helium following their formation but before closure. Experimental data from the KTB hole seem to bear this out.

- Although there certainly could be cases where extraneous He becomes incorporated into grains, the secondary CRH release peak often seen in the lab can be well explained by trapping of “normal” radiogenic helium.
- The significance of ages from samples that show trapping will vary. Seeing high-temperature CRH release is a warning sign that sinks are present, but the significance of the age based on conventional expectations will depend on the thermal history. Specifically, a sink-laden grain that is quenched should still give decent age that records the timing of that quench, whereas the same sample in the PRZ would show strong trapping and a highly anomalous age compared to expectations.
- Following Pete Reiner’s early comment on CRH analysis, if “self-pollution” by radiogenic production is the main source of perceived excess gas, and if the sink distribution is singular or at least simple, then it would seem that trapping actually amounts to additional kinetic information, and that would mean that the bulk age is useful, representing a grain that is more retentive than conventional eU-radius assumptions would predict.
- Following from this, it might be possible to take a MDD-like approach, and use the Arrhenius data plus $^{4}He/^{3}He$ age data as a target for an inverse model. The degree of trapping would be a function of thermal history and number and nature of sinks. If you analyzed multiple grains with the same thermal history, then the main variable would be the number of traps. Better, one could use the lab trapping seen for ^{3}He to determine the nature of the sinks and then knowing that, invert the $^{4}He/^{3}He$ ratio evolution diagram for thermal history.

Examples of DIFFSIM RESULTS

The following plots show a predicted CRH release pattern and the associated Arrhenius plot. All the simulations are for a Durango-like apatite having an activation energy of 33 kcal/mol and Do of 50 cm^2/s. The CRH lab heating rate is 30˚C/min.

(1) The following plots show simulations of the simplest case: a very cold -50 ˚C for 100 m.y. – essentially no diffusion. The successive plots show the use of different numbers of nodes in the model (form left to right, 50, 200, and 1000).



(2) The plots on the next page show simulations involving trapping for three different thermal histories. From left to right, these are **(a)** the isothermal cold case shown above, **(b)** linear slow cooling from 100 ˚C to 0 ˚C over 100 m.y., and **(c)** cooling that includes protracted residence near the partial retention zone (100 ˚C at 100 m.y., 70˚C at 90 m.y., 50 ˚C at 10 m.y, and 0 ˚C at 0 m.y. Each of these models was run with 200 nodes and 1000 sinks (traps); the escape activation energy was 33 kcal and the scale temperature was 1200 ˚C (this produces a secondary peak at ~ 800 ˚C much like those commonly seen in real apatites).

Note two things. First, even the simulation that has no geologic mobility of helium (left) shows trapping that occurs during the lab heating, Second, the size of the secondary high-temperature peak increases for thermal histories that involve progressively more time at temperatures near and probably slightly above the PRZ.