Geochemistry, Geophysics, Geosystems

Supporting Information for

The Effect of Grain Size on Porewater Radiolysis

J. DeWitt[1], S. McMahon[2,3], and J. Parnell[4]

[1] Department of Physics, East Carolina University,
Howell Science Complex, 10th Street, Greenville NC 27858, US

[2] School of Physics and Astronomy, University of Edinburgh,
James Clerk Maxwell Building, Peter Guthrie Tait Road, Edinburgh EH9 3FD, UK

[3] School of Geosciences, University of Edinburgh, Grant Institute, Edinburgh EH9 3FE, UK

[4] School of Geosciences, University of Aberdeen, Meston Building, King's College, Aberdeen AB24 3UE

Contents of this file

Introduction

- This supporting information contains the algorithmic foundation of the Fortran code used in the model (Text S1) and a derivation of Equation 5 (alpha particle escape efficiency from spherical grains) used in the paper (Text S2, supported by Figures S1–S3).

Text S1.

```
PROGRAM Alpha_escape
```

```
  USE Shared
  IMPLICIT NONE
  CALL INIT_RANDOM_SEED()
  PRINT *, " "
  OPEN(Alpha_escape_txt, file='Alpha_escape.txt',
access='sequential', status='unknown', action='write',
asynchronous='yes')
  WRITE(Alpha_escape_txt, '(a9, 3a21)') "r (μm)", "n_alpha",
"E_g", "%diff" !columns
  complete = 5
  radius = MICRON !initialize radius
  ALLOCATE(percent_diff(INT(MAX_RADIUS / MICRON)))
  many_radii: DO
      IF (INT((radius / MAX_RADIUS) * 100.0_dp) == complete)
THEN !keep user apprised of progress
      WRITE(6, '(i5, a1)') complete, "%"
      complete = complete + 5 !next 5% checkpoint
      END IF
      n_alpha = 0 !initialize sum for averaging this radius
      many_alphas: DO number = 1, NUMBER_MAX
      CALL RANDOM_NUMBER(random)
      r_1 = radius * CBRT1(random) !select a random DECAY point
along this radius
      CALL RANDOM_NUMBER(random)
      theta_1 = 2.0_dp * PI * random !select a random azimuthal
DECAY angle
      CALL RANDOM_NUMBER(random)
      IF (radius < S / CM_TO_UM * 1.5_dp) THEN !select a random
polar DECAY angle
      phi_1 = ACOS(2.0_dp * random - 1.0_dp)
      ELSE
      phi_1 = 2.0_dp * PI * random
      END IF
      x_1 = r_1 * COS(theta_1) * SIN(phi_1) !x-coordinate DECAY
      y_1 = r_1 * SIN(theta_1) * SIN(phi_1) !y-coordinate DECAY
      z_1 = r_1 * COS(phi_1) !z-coordinate DECAY
      CALL RANDOM_NUMBER(random)
      theta_2 = 2.0_dp * PI * random !select a random azimuthal
EXIT angle
      CALL RANDOM_NUMBER(random)
      IF (radius < S / CM_TO_UM * 1.4_dp) THEN !select a random
polar EXIT angle
      phi_2 = ACOS(2.0_dp * random - 1.0_dp)
      ELSE
      phi_2 = 2.0_dp * PI * random
      END IF
      r_2 = 0.0_dp !my EXIT vector, also at the origin, but add
tip-to-tail later
      1 x_2 = r_2 * COS(theta_1 + theta_2) * SIN(phi_1 + phi_2)
      y_2 = r_2 * SIN(theta_1 + theta_2) * SIN(phi_1 + phi_2)
      z_2 = r_2 * COS(phi_1 + phi_2)
      x_3 = x_1 + x_2 !add x-components
```

```
      y_3 = y_1 + y_2 !add y-components
      z_3 = z_1 + z_2 !add z-components
      r_3 = SQRT(x_3**2 + y_3**2 + z_3**2) !find resultant vector,
should be the EXIT point on my sphere
      IF (r_3 > radius) THEN
      depth = r_2 !mission accomplished, actual depth of SiO2 to
be traversed before escaping from the SiO2 grain
      ELSE !extend DEPTH vector and repeat
      r_2 = r_2 + DX !looking for an r_3 that looks like the
radius of my sphere
      GO TO 1 !try again
      END IF
      x = 0.0_dp !start at the beginning
      E_i = 4.92991712862015_dp !MeV
      stopping_power_alpha: DO
      IF (dEdx_alpha(E_i) < 0.0_dp) EXIT !check for good stopping
power
      E_f = E_i - (dEdx_alpha(E_i) * DENSITY * DX) !kinetic energy
decreases in MeV while accounting for the density of the absorber
      IF (E_f < 0.0_dp) EXIT !check for good final energy
      IF (x > depth .AND. E_f > 0.0_dp) THEN !ALPHA has escaped
the SiO2 grain
            n_alpha = n_alpha + 1
            EXIT !out-of-bounds, nothing more to do
      END IF
      E_i = E_f !pass for next iteration
      x = x + DX !advance in cm
      END DO stopping_power_alpha
      END DO many_alphas
      theta = 2.0_dp * radius * CM_TO_UM !grain size is diameter
in µm
      E_g = (3.0_dp * S) / (2.0_dp * theta) - (S * S * S) /
(2.0_dp * theta * theta * theta) !McMahon
      percent_diff(NINT(radius * CM_TO_UM)) =
ABS((FLOAT(n_alpha) / FLOAT(NUMBER_MAX)) - E_g) * 100.0_dp
      WRITE(Alpha_escape_txt, '(i8, 3f21.15)') NINT(radius *
CM_TO_UM), (FLOAT(n_alpha) / FLOAT(NUMBER_MAX)) * 100.0_dp,
      &
      E_g * 100.0_dp, percent_diff(NINT(radius * CM_TO_UM))
      IF (radius > MAX_RADIUS) EXIT !cm
      radius = radius + MICRON
  END DO many_radii
  PRINT *, " "
  PRINT *, "Average percent difference:",
SUM(percent_diff(10:SIZE(percent_diff))) / SIZE(percent_diff)
  DEALLOCATE(percent_diff)
  CLOSE(Alpha_escape_txt)
  PRINT *, " "
END PROGRAM Alpha_escape
```

Text S2.

For particles with stopping distance *s* emitted in random directions and originating at random points inside a spherical grain of diameter Θ, the proportion of these particles that exit the grain rather than terminating within it can be estimated as follows.

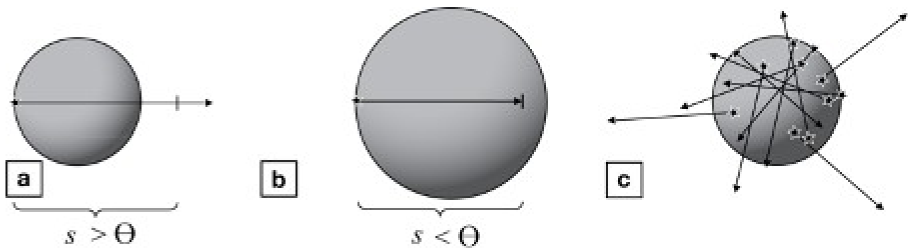

Figure S1. Alpha particle emission by sediment grains. (a) When the stopping distance exceeds the grain diameter, all alpha particles escape. (b) When the grain diameter exceeds the stopping distance, some alpha particles are trapped. (c) Alpha particles are emitted throughout each grain and travel in random directions.

If the grain diameter is less than the stopping distance, all particles emitted from anywhere in the grain will be able to escape, since the longest distance that any particle has to travel before escaping is Θ (**Figure S1a**). However, if Θ > *s*, then some of the particles (e.g., those emitted inwards from near the grain edge) will be stopped (**Figure S1b**) while others will escape (e.g., those emitted outwards from the same point).

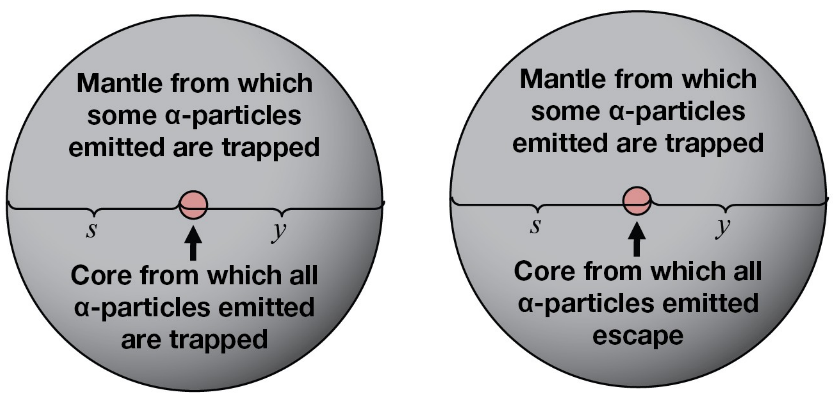

Figure S2. (Left) When the stopping distance of an alpha particle is less than the radius of the grain (i.e., $y > s$; $\Theta > 2s$), there is a "core" region such that particles emitted from this core cannot escape from the grain. Of those particles generated in the rest of the grain (the "mantle"), some escape and others are trapped, depending on their trajectories. **(Right)** When the stopping distance of the alpha particle is greater than the radius of the grain (i.e., $y < s$; $\Theta > 2s$), there is a core region from which all particles escape, and a mantle from which some are trapped.

Referring to **Figure S2**, let y be $\Theta - s$. Furthermore, let E_g be the fraction of particles emitted in the grain that escapes, which is $1 - T_g$, the fraction trapped. The case where $y > s$ (i.e., $\Theta > 2s$) is considered first. In this case, the radius of the grain is longer than the stopping distance of the particle. There is a core region of the grain from which all particles emitted are trapped (**Figure S2, left**).

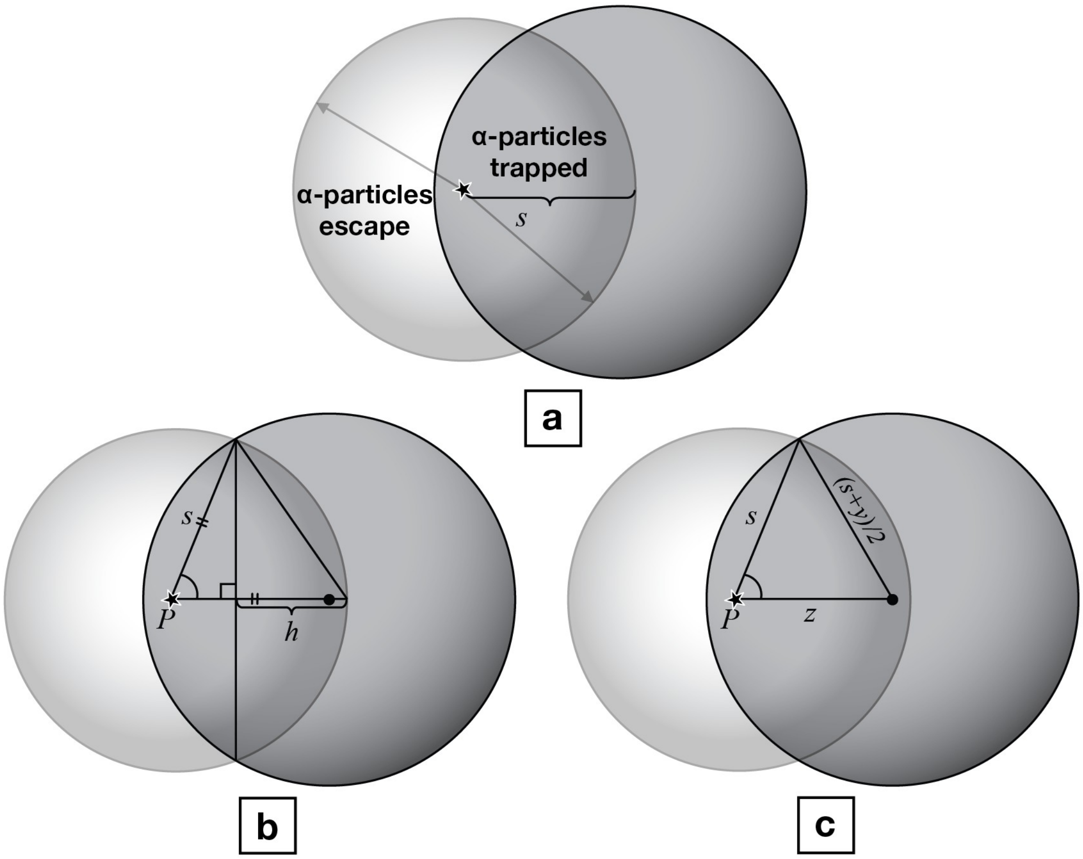

Figure S3. Alpha particles are emitted from a point (star) in a spherical grain (dark grey). **(a)** The possible trajectories of the alpha particles are indicated by the light grey sphere, whose radius is the stopping distance. Part of the surface of this sphere lies inside the grain; the area of this surface (i.e., a spherical cap) divided by the total area of the sphere gives the proportion of particles emitted from this point that would be trapped within the grain. Panels **(b)** and **(c)** show constructions used in the derivation.

This core region has diameter $y - s$ and volume V_c. The remainder of the grain is a mantle with volume V_m. Of those particles emitted inside this mantle, a certain proportion escape, and a certain proportion T_m are trapped because they have to travel a distance s into the grain (**Figure S3**). If ρ is the number of particles emitted per unit volume, then

$$T_g = \frac{\rho V_c + \rho V_m T_m}{\rho V_g}, \qquad \text{(S1)}$$

where ρ naturally cancels.

The mantle is regarded as the sum of concentric spherical shells of radius z and infinitesimal thickness dz. Each shell emits a different number of particles, a fraction of which are trapped. This fraction $T_{P,z}$ is equal to the number of particles trapped divided by the number emitted from any individual point P in the shell, i.e., at distance z from the centre of the grain. $T_{P,z}$ is equal to the proportion of the surface area of a sphere of diameter s, centred at P, that lies inside the grain. If the surface area of the sphere is $4\pi s^2$, then a partial area trapped within the grain (a spherical cap) is given by

$2\pi sh$, where h is the distance between the outer edge of the sphere and the plane where it intersects the grain (the trace of this plane appears as a vertical line in **Figure S3b**). The distance h was found using the constructions shown in **Figure S3b-c**.

The trigonometry in **Figure S3b** gives

$$\cos(P) = \frac{s-h}{s} \tag{S2}$$

Applying the law of cosines to **Figure S3c** gives

$$\cos(P) = \frac{s^2 + z^2 - \frac{(s+y)^2}{4}}{2sz} \tag{S3}$$

Equating Equations S2 and S3 gives

$$h = s - \frac{s^2 + z^2 - \frac{(s+y)^2}{4}}{2z} \tag{S4}$$

Normalizing Equation S4 appropriately gives

$$T_{P,z} = \frac{2\pi s}{4\pi s^2}\left(s - \frac{s^2 + z^2 - \frac{(s+y)^2}{4}}{2z}\right) \tag{S5}$$

Simplifying Equation S5 gives a more manageable polynomial:

$$T_{P,z} = \frac{1}{2} + \frac{(s+y)^2 - 4s^2}{16s} z^{-1} - \frac{1}{4s} z \tag{S6}$$

To find $V_m T_m$, the volumes of the infinitesimal shells of thickness dz that make up the mantle were multiplied by $T_{P,z}$ (the fraction of trapped particles from each shell) and integrated over the range of z in the mantle. The volume of each shell is naturally equal to $4\pi z^2 dz$. The limits of integration are $(y - s)/2$ at the inner edge of the mantle and $(s + y)/2$ at the surface of the grain. Therefore,

$$V_m T_m = 4\pi \int_{z=\frac{y-s}{2}}^{z=\frac{s+y}{2}} z^2 \left(\frac{1}{2} + \frac{(s+y)^2 - 4s^2}{16s} z^{-1} - \frac{1}{4s} z\right) dz \tag{S7}$$

Integrating as usual gives

$$V_m T_m = 4\pi \left[\frac{(s+y)^2 - 4s^2}{32s} z^2 + \frac{1}{6} z^3 - \frac{1}{16s} z^4\right]_{z=\frac{y-s}{2}}^{z=\frac{s+y}{2}} \tag{S8}$$

Applying the limits of integration and simplifying gives $V_m T_m = \frac{\pi}{12}$¿). Recalling Equation S1 and substituting the expressions for V_g , V_c and $V_m T_m$ gives

$$T_g = \frac{\left(\frac{(y-s)}{2}\right)^3 + \frac{1}{16}\left(2s^3 - 6s^2 y + 9sy^2\right)}{\left(\frac{(s+y)}{2}\right)^3} \tag{S9}$$

After some simplification we have

$$T_g = \frac{y^2(3s+2y)}{2(s+y)^3} \tag{S10}$$

Since $s + y$ is equal to the grain diameter Θ, we arrive at the result:

$$T_g = \frac{s^3}{2\Theta^3} - \frac{3s}{2\Theta} + 1 \tag{S11}$$

If $\Theta > s$, then $E_g = 1 - T_g$, or

$$E_g(\theta) = \frac{3s}{2\Theta} - \frac{s^3}{2\Theta^3} \tag{S12}$$

Analytically, the proportion of escaped alpha particles is given by Equation S12 as a function of grain size Θ for a given stopping distance s. In the case where $y < s$, or $\Theta > 2s$, there is a core region from which all particles escape (**Figure S2, right**); a derivation analogous to that above also produces Equation S12, which in any case provides a way to validate the geometry of the Monte Carlo method.