

# The Crystal Size Distribution Technique

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After the last EHaz week, I realized that it might be useful for some of you (and me!) to present a short introduction of the theory of the Crystal Size Distribution (CSD) technique, and what are the concepts behind. The technique was developed and introduced in a set of papers published in Contributions, in which the theory (Marsh, 1988) and then the volcanic (Cashman and Marsh, 1988) and the the metamorphic cases (Cashman and Ferry, 1988) were described<sup>1</sup>. In this document I shall summarize Marsh (1988).

## The theory

As pointed out by Marsh (1988), the idea is the development of a equation governing the conservation of *number of crystals* as they nucleate and grow. This equation is a balance between the influx of new crystals and the loss of other given the particular process that controls the geological system<sup>2</sup>. Before introducing such balance I will need to introduce some previous concepts.

## Population density

The first idea comes from the kinetics of crystal growth, so an implicit assumption is that *the number of crystals per size and per unit of volume of rock must be known as a function of size*. We learn from my question to Dougal that this actually is the complicated<sup>3</sup> bit, involving measuring the crystals and estimating their real size from the slices in 2D in the thin sections. Let's assume  $L$  a given (bin) size and  $n(L)$  the number of crystals of such size. Recall here that  $n(L)$  is measured in a "per length" basis (i.e. per  $\Delta L$ ) so it does not depend on the bin size. If the bins are enough small, the cumulative distribution  $N(L)$  is obviously given by:

$$N(L) = \int_0^L n(L)dL \quad (1)$$

For a given value of  $L$ , the cumulative function gives the number of crystals of that size or less per unit of volume. It is clearly straightforward to *recover*  $n(L)$  from  $N(L)$ : it is simply the derivative of (1):

$$n(L) = \frac{dN(L)}{dL} \quad (2)$$

So, how many crystals are in a given range  $\Delta L$ ? Taking a population  $n_1$  of size  $L_1$  growing at (an unknown) rate  $G_1$  in a volume  $V_1$  and another<sup>4</sup> differing in size by  $\Delta L$   $n_2, L_2 = (L_1 + \Delta L), G_2, V_2$ , then *the number of crystals within such size range* is given by the difference between the bigger crystals minus the smaller crystals:

$$(V_2 n_2 - V_1 n_1) \Delta L \quad (3)$$

## The population balance

Therefore, the number balance for a range size ( $\Delta L$ ) implies that *the change with time of the volume of the system and the number density of crystals within a size range* (Equation 3) is governed by the rate at which new crystals grow into and away from such size in a time  $\Delta t$ . In the example of the two populations:  $G_1 V_1 n_1$  and  $G_2 V_2 n_2$

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<sup>1</sup>Probably you will need to go to your library and make old photocopies of them!

<sup>2</sup>I could have said magmatic here, but the technique have more broad application in metamorphic (Cashman and Ferry, 1988) or even in a sedimentary process

<sup>3</sup>and tedious

<sup>4</sup>Don't forget that both population are from the same crystalline phase

respectively and by the influx ( $Q_i n_i \Delta L \Delta t$ ) and outflow ( $Q_o n_o \Delta L \Delta t$ ). Equating these two terms gives the following conservation:

$$(V_2 n_2 - V_1 n_1) \Delta L = (G_1 V_1 n_1 - G_2 V_2 n_2) \Delta t + (Q_i n_i - Q_o n_o) \Delta t \Delta L \quad (4)$$

Equation (4) means that (net accumulation in the bin) = (growth input - growth output) + (flux in - flux out), in other words crystals enter and exit a given bin when they grow and when they are physically added or removed from the system.

Now, a little trick; if Equation (4) is divided member by member by  $\Delta t$  and  $\Delta L$  and letting them approach to zero:

$$\frac{\partial(Vn)}{\partial t} = \frac{\partial(GVn)}{\partial L} = Q_i n_i - Q_o n_o \quad (5)$$

### Influx $Q_i n_i \ll Q_o n_o$

Equation (5) is the most general population balance. A meaningful petrologic system would be for example  $Q_i n_i \ll Q_o n_o$ , i.e. the system is the volume in which the observed crystal have spent their whole growing life (i.e. nucleating and grow in a magma chamber). Adopting this condition, Equation (5) becomes:

$$\frac{\partial(Vn)}{\partial t} = \frac{\partial(GVn)}{\partial L} + Q_o n_o = 0 \quad (6)$$

### Open systems of constant volume and residence time

For systems continuously fed and emptied, the volume (magma chamber) can be taken as practically constant. Using this, it is possible to define the Residence time as  $\tau \equiv \frac{V}{Q}$ , which will change (6) to the following simpler form (remember, V is constant):

$$\frac{\partial(n)}{\partial t} = \frac{\partial(Gn)}{\partial L} + \frac{n_o}{\tau} = 0 \quad (7)$$

(we will drop the subscript in  $n_o$  from now onwards).

If the second term is expanded (i.e.  $\frac{\partial(Gn)}{\partial L} = G \frac{\partial(n)}{\partial L} + n \frac{\partial(G)}{\partial L}$ ) and everything is divided by  $nG$ , equation (7) becomes:

$$\frac{1}{G} \frac{\partial \ln n}{\partial t} + \frac{\partial \ln n}{\partial L} + \frac{\partial \ln G}{\partial L} + \frac{1}{G\tau} = 0 \quad (8)$$

because  $\frac{1}{y} \frac{\partial y}{\partial x} = \frac{\partial \ln y}{\partial x}$ .

Thus, equation (8) shows the logarithmic nature of the population densities!

### Growth rate not a function of the size

A final important assumption is that the growth rate is not a function of the size (i.e. small crystals grow at the same rate than the big ones). This is probably one of the weakest point of the methodology, since very little is known regarding growing of mineral phases in silicate systems. If this is the case, then  $\frac{\partial G}{\partial L} = 0$ , which modifies equation (7) as:

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} + \frac{n}{\tau} = 0 \quad (9)$$

solving the differential equation and evaluating the constants of integration (for the detail check Marsh, 1988):

$$n = n^0 \exp \left[ t \left( \frac{1}{\tau_0} - \frac{1}{\tau} \right) - \frac{L}{G\tau_0} \right] \quad (10)$$

in which  $n^0$  is the nucleation density (i.e. the density for  $L = 0$ ) and  $\tau_0$  is the residence time of an initial crystal distribution in the system (i.e. at  $t = 0$ ) in contrast with an "actual" residence time (i.e. at  $t = t$ ). It is straightforward that plotting  $\ln n$  vs.  $L$  should produce a linear pattern with a negative slope if the populations of crystals (all the sizes) are growing in a system with a constant volume and *constant residence time*. In effect, if  $\tau = \tau_0$  then Equation (10) becomes:

$$n = n^0 \exp \left[ -\frac{L}{G\tau_0} \right] \quad (11)$$

If the populations are taken to a different system this new system will have a new residence time controlling the influx and outflow of the crystals in a different way than the original system where the crystals were formed (i.e.  $\tau_0 \neq \tau$ ). There are two possibilities here:

### Case $\tau \ll \tau_0$

Which is the case in which the new residence time is enough shorter than the old one. This is needed, because if  $\tau$  is shorter but relatively similar to  $\tau_0$  then the solution tend to equation (11) . . . mind that subtle kinks are hidden in the noise!

Thus, because the residences are enough different we can neglect the difference and modify equation (10) as:

$$n = n^0 \exp \left[ -\frac{t}{\tau_0} - \frac{L}{G\tau_0} \right] \quad (12)$$

and the original crystal size distribution is progressively replaced by a new one whose residence time is  $\tau$ . This does not mean that the old crystals are flushed away or resorbed, in fact, the point here is that both populations are present producing an steeper slope in the diagram.

### Case $\tau \gg \tau_0$

Which produce an analogue of (12):

$$n = n^0 \exp \left[ \frac{t}{\tau} - \frac{L}{G\tau_0} \right] \quad (13)$$

which produces the that the original crystal size distribution is progressively replaced by another with a larger nucleation density and a more gentle slope.

## Conclusions

Thus, crystals that come from a “xeno-system” will have a crystal size distribution that will reflect the volume, residence time and rate of recharge in such system. Mixing such crystal size distribution (i.e crystals of all the sizes) with another crystal size distribution that depends on the characteristics of the “pheno-system” will generate the pattern with a kink. If the pheno-system has a shorter residence time, then the governing equation for the CSD will be (12), and the slope for the smaller crystals will be steeper than should it be. In the opposite case, the slope of the larger crystals will be gentler. I should stress here that possible changes in the growing rate ( $G$ ) as a function of the size  $L$  of the crystals will not produce the linear pattern but an hyperbolic-like shape. The key point here is that such pattern will be *continuous and always derivable*, no kinks with changes in the growing rate! So the converse is also useful: CSD can be also used to find whether the growing rate of the crystals is size dependent or independent. Hope this document helps!

## References

- Cashman, K. and Ferry, J. (1988). Crystal size distribution (csd) in rocks and the kinetics and dynamics of crystallization iii. metamorphic crystallization. *Contributions to Mineralogy and Petrology*, **99**(401-405).
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