# SI1: Complementary information on the heat transfer approach and calculations

In this supplementary material, we demonstrate, in our case, that latent heat of crystallisation during lava cooling can be confidently neglected for the heat transfer calculations (necessary to estimate the cooling/quenching rates of the lava samples, cf. Fig. 2b in the main manuscript), which are detailed in the method part of the main manuscript.

Samples undergoing cooling might present crystal formation if the kinetic conditions are suitable, but the heat released during this crystallization stage would not necessarily affect the cooling of the body as a whole. Based on experiments and theoretical calculations, we show that the released heat during crystal formation can be neglected when compared to the total heat exchanged during quenching/cooling of this case study of Fani Maoré lava. (i) First, the amount of heat released during the crystallization of Fani Maoré lava flow rims is calculated, based on Differential Scanning Calorimetry (DSC) experimental data. (ii) The whole amount of heat exchanged between the Fani Maoré lava flow and the seawater during the cooling (i.e., from the eruptive temperature $T_E$ down to the glass transition $T_G$) is theoretically calculated. (iii) Finally, by comparing the two previous amounts of heat, we can exclude any significant role of the latent heat of crystallization on the cooling/quenching rates of the lava.

As described in the main manuscript, our studied case falls in the semi-infinite solid approach. A specific lava flow geometry, which respects boundary conditions of this approach (applicable to lava flows) has been specifically chosen to perform the calculations. The dimension x representing the theoretical lava thickness (1 m) must be much smaller than the other two dimensions y and z representing the theoretical lava length and width (20 m each), thus having a planar geometry. In this way, a basanite lava flow having these dimensions and a bulk density of 2700 kg $m^{-3}$ represents 1.1 $10^9$ g of material.

### (i) Heat released during the crystallization of Fani Maoré lava flows

The DSC experiment (Fig. S1), performed on a representative glassy lava flow rim sample of Fani Maoré (MAY02-DR080102), revealed that the heat released during the experimental crystallization (upon heating from room temperature up to 1000 °C) of the sample is 90.7 J $g^{-1}$. Note that this value was the highest we could get from DSC results on Fani Maoré samples, both in heating and cooling experiments. The experiments consisted of using sample chips of ca. 0.030 g, which were heated and cooled at a constant rate of 0.17 °C $s^{-1}$ in a Pt crucible under a purging, high purity Ar atmosphere (0.002 L $s^{-1}$), using a Netzsch STA 449 C/3/G Jupiter DSC instrument. A temperature calibration based on the melting points of In, Zn, $BaCO_3$ and Au, and a sensitivity calibration based on a $C_p$ measurement of a National Bureau of Standards (NBS) certified sapphire has been used. Note that the relatively low experimental heating rate (compared to the expected natural cooling rates) was chosen to let time to the sample to experimentally crystallize between 600 and 800 °C and get maximum values of heat released by crystallization (post-experimental observations also confirmed that the sample was extensively crystallized, i.e., > 50 vol.%).

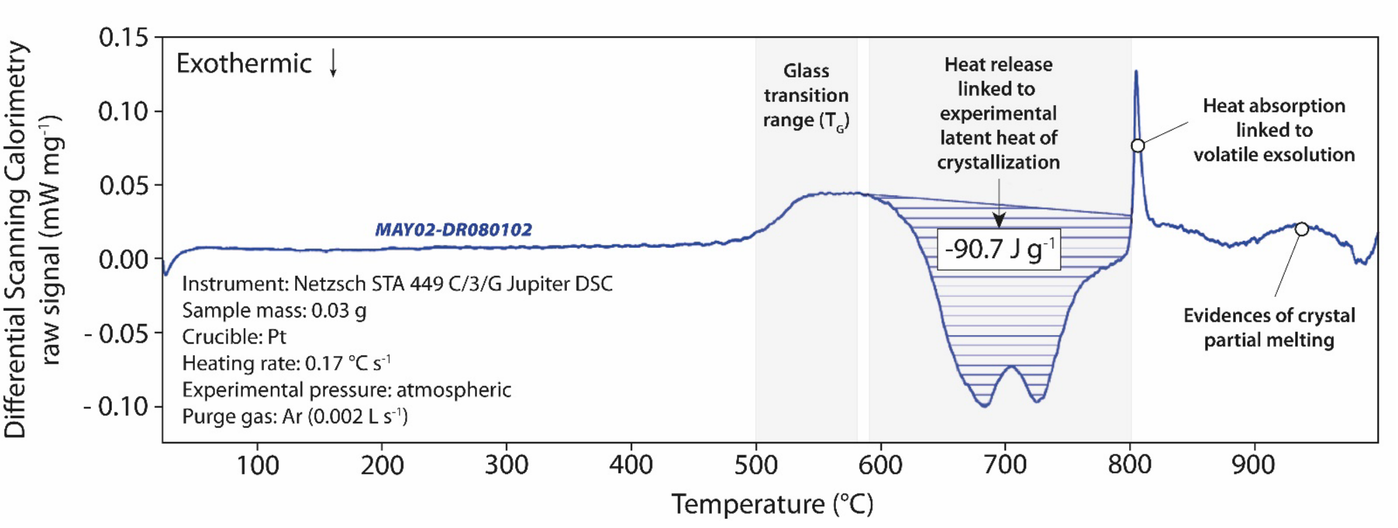


*Figure S1 – Differential Scanning Calorimetric (DSC) results on a representative glassy lava flow rim sample of Fani Maoré (MAY02-DR080102). Hatched area highlights the exothermic heat related to the crystallization of the glassy lava flow rim sample.*

In conclusion, considering the total mass of the considered lava geometry (1.1 $10^9$ g), the total heat released because of crystallization is $Q_{latent}$ = 9.8 $10^{10}$ J.

### (ii) Heat exchanged during the cooling of Fani Maoré lava flows

The whole amount of energy exchanged from $T_E$ (1095 °C) down to $T_G$ (in average 550 °C) is calculated. To do so, we first calculate the time to cool down the whole sample to the glass transition temperature. Thus, by applying Eq. (8) presented in the method part of the main manuscript, considering x equals to 1 m, and as an approximation heat extraction from one side of the lava (as most of the samples were considered originating from spreading pillows), we have that the whole sample takes 617 h to cool to $T_G$ (Fig. S2). Note that all parameters used in the following equations are also described and specified in the in the method part of the main manuscript.

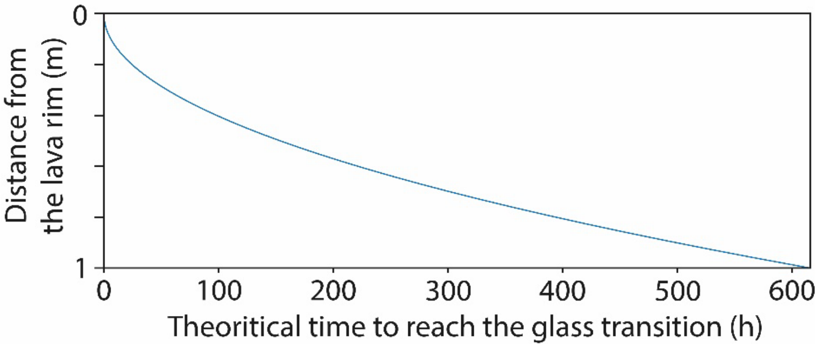


*Figure S2 – Cooling time required from the eruptive temperature ($T_E$ = 1095 °C) until the glass transition temperature ($T_G$ = 550 °C) in function of lava depth.*

Now, by deriving Eq. (8) with respect to the position x and by multiplying this new term by the negative of the thermal conductivity (-κ), we then have the heat flux defined by the Fourier's law ($q_x = -\kappa.\partial T/\partial x$). Thus, we obtain:

$$q_{x=0\ (interface)} = \frac{\kappa.(T_E - T_{SW})}{\sqrt{\pi \alpha t}}, \qquad \text{Eq. (S1)}$$

where $T_E$ is the initial eruptive temperature of lava and $T_{SW}$ is the seawater temperature. The value obtained using Eq. (S1) gives the instantaneous amount of heat exchanged at the interface. Since we are interested on the heat loss during the aforementioned calculated time ($Q_{loss}$), one should integrate the heat transfer rate over the whole cooling duration and thus multiply it by the area in which the body exchange heat:

$$Q_{Loss} = \int_0^{t=220h} Area\,.\,q_{x=0\ (interface)}.\,dt, \qquad \text{Eq. (S2)}$$

culminating therefore in the following equation:

$$Q_{Loss} = Area\,.\frac{\kappa.(T_E - T_{sw})}{\sqrt{\pi \alpha}}\,2.\,t^{1/2} \qquad \text{Eq. (S3)}$$

Hence, one can find that the whole amount of heat exchanged by this material from the eruptive temperature to the glass transition temperature is equal to $Q_{loss}$ = 1.7 $10^{12}$ J.

### (iii) Comparison of $Q_{latent}$ and $Q_{loss}$

In conclusion, these experiments and calculations confirm that the heat released during crystal formation ($Q_{latent}$ = 9.80 $10^{10}$ J) is indeed not relevant when compared to the total heat exchanged by the material when cooled down from eruptive temperature to its glass transition temperature ($Q_{loss}$ = 1.7 $10^{12}$ J).

(1) Naturally, for the crystal-free outer lava flow rims (case 1), latent heat of crystallization is not occurring.

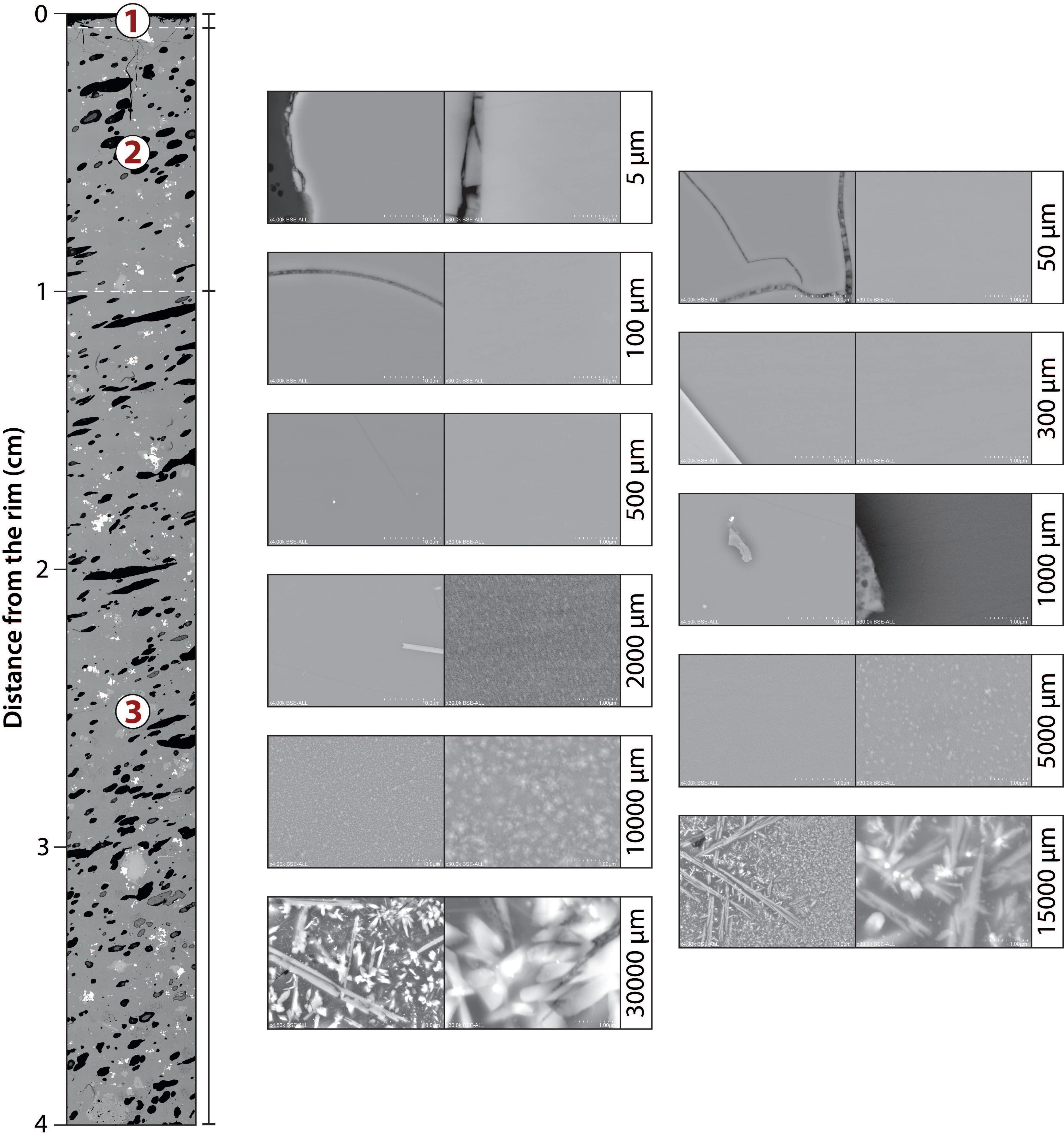
(2) The heat linked to significant crystallization (> 50 vol.%) is about 5.3 % of the total heat exchanged. Therefore, latent heat of crystallization can be confidently neglected for the partially crystallized (< 20 vol.%) inner lava flow rims (case 2).

(3) The latent heat of crystallization can be also neglected even for a high/full crystallization in the lava interiors (case 3), which would represent in any case less than 10 % of the total heat exchanged during lava cooling. Indeed, this percentage will not affect the order of magnitude of the estimated cooling rates of the lava interiors that are in any case lower than those estimated for the inner lava flow rims.

Supplementary references

- Incropera, F. P., DeWitt, D. P., Bergman & T. L., Lavine, A. S., (2007). Introduction to heat transfer. 6th Edition. John Wiley & Sons
- Lesher, C. E., & Spera, F. J. (2015). Thermodynamic and Transport Properties of Silicate Melts and Magma. The Encyclopedia of Volcanoes, 113–141. https://doi.org/10.1016/b978-0-12-385938-9.00005-5
- Whittington, A. G., Hofmeister, A. M., & Nabelek, P. I. (2009). Temperature-dependent thermal diffusivity of the Earth's crust and implications for magmatism. Nature, 458(7236), 319–321. https://doi.org/10.1038/nature07818

# SI2: Transect of the MAY15-DR150301 sample illustrated by Back-Scattered Images acquired by Scanning Electron Microscopy (BSE-SEM)



# SI3: Images of Focused-Ion Beam Scanning Electron Microscopy acquired under Continuous Dynode Electron Multiplier (FIB-SEM CDME) showing the Transmission Electron Microscopy (TEM) thin section preparation