

The Influence of Undercooling on Trace Element Sector Zoning in Clinopyroxene

A. MacDonald¹, T. Ubide¹, M. Masotta², S. Mollo³, A. Pontesilli⁴

¹School of Earth and Environment Sciences, University of Queensland, Australia

²Department of Geosciences, University of Pisa, Italy

³Department of Earth Sciences, Sapienza - University of Rome, Italy

⁴Department of Geology, University of Otago, New Zealand

*Current PhD Student at SEES, UQ

Introduction

Clinopyroxene is a commonly utilised mineral in petrological studies of igneous rocks, due to its favourable properties. These properties rely on the sensitive of clinopyroxene to physiochemical changes in a magmatic system. However, clinopyroxene is also sensitive to kinetic effects, which is reflected in particular zoning patterns. A commonly reported zonation is sector zoning (Figure 1), which has been reported in a range of volcanic settings globally, including Mt. Etna, Italy. Undercooling ($\Delta T = T_{liquidus} - T_{system}$) has previously been identified as being a major driver for the formation of these zonations. Previous experimental work has explored the relationship between undercooling and clinopyroxene morphology and major element sectoral partitioning, however there has yet to be an experimental investigation on the influence of undercooling on trace element sectoral partitioning. We aim to explore this relationship, to shed new insights into pre-eruptive processes.

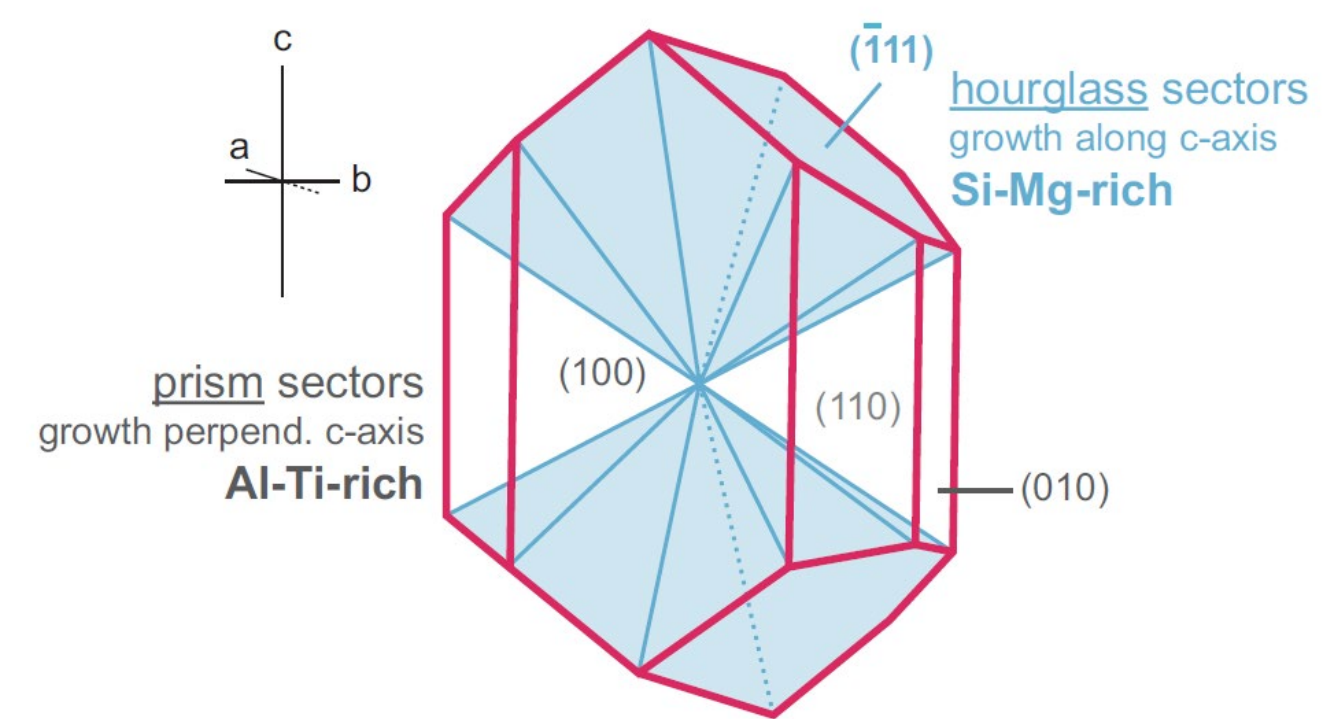


Figure 1: Model of a sector zoned clinopyroxene, modified from Ubide et al. 2019. Hourglass sectors are in blue, prism in white.

Methods

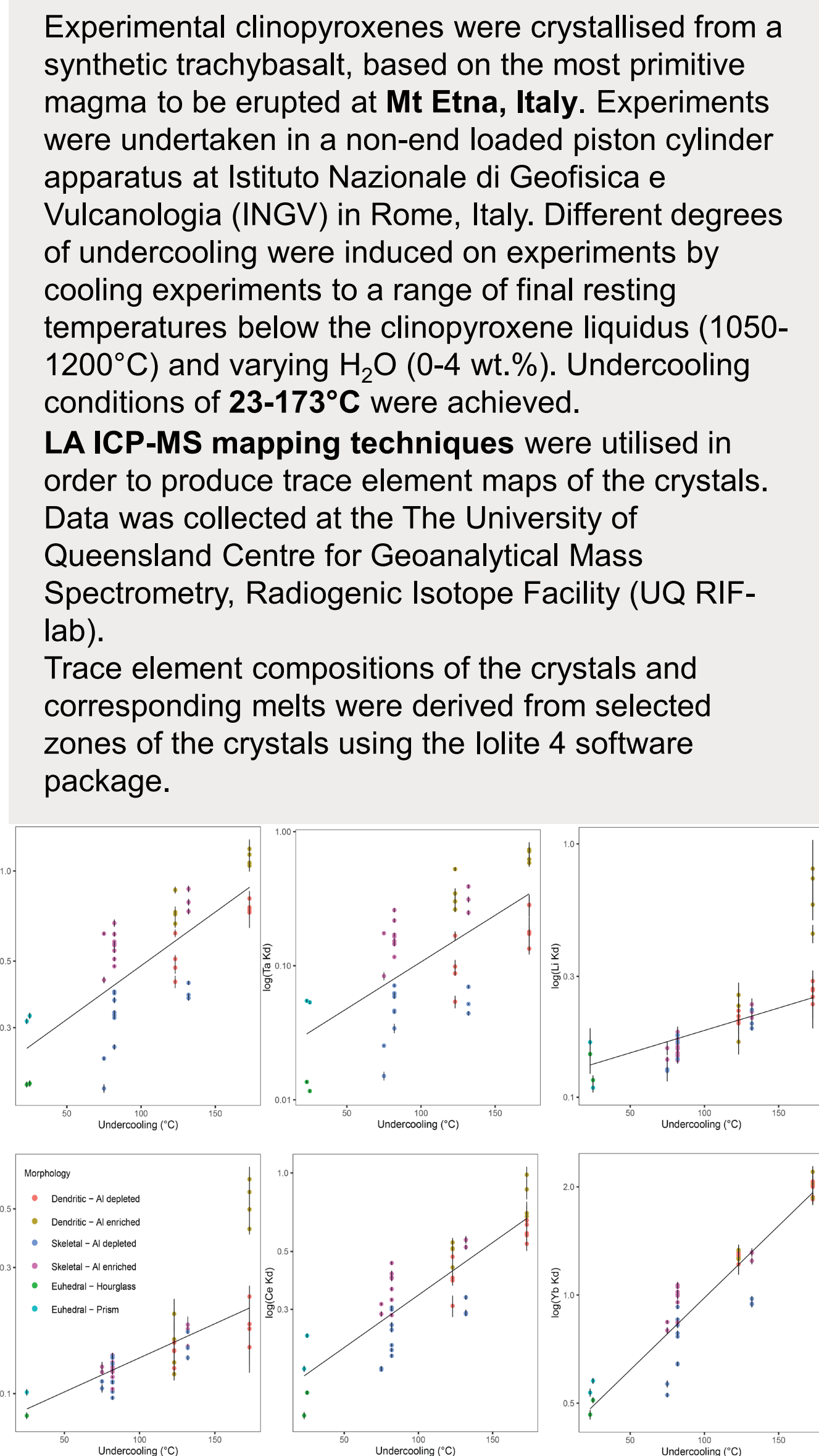


Figure 2: Partition coefficients of various trace elements with ΔT . Zr and Ta are M1 cations; Li, Sr, Ce and Yb are M2 cations.

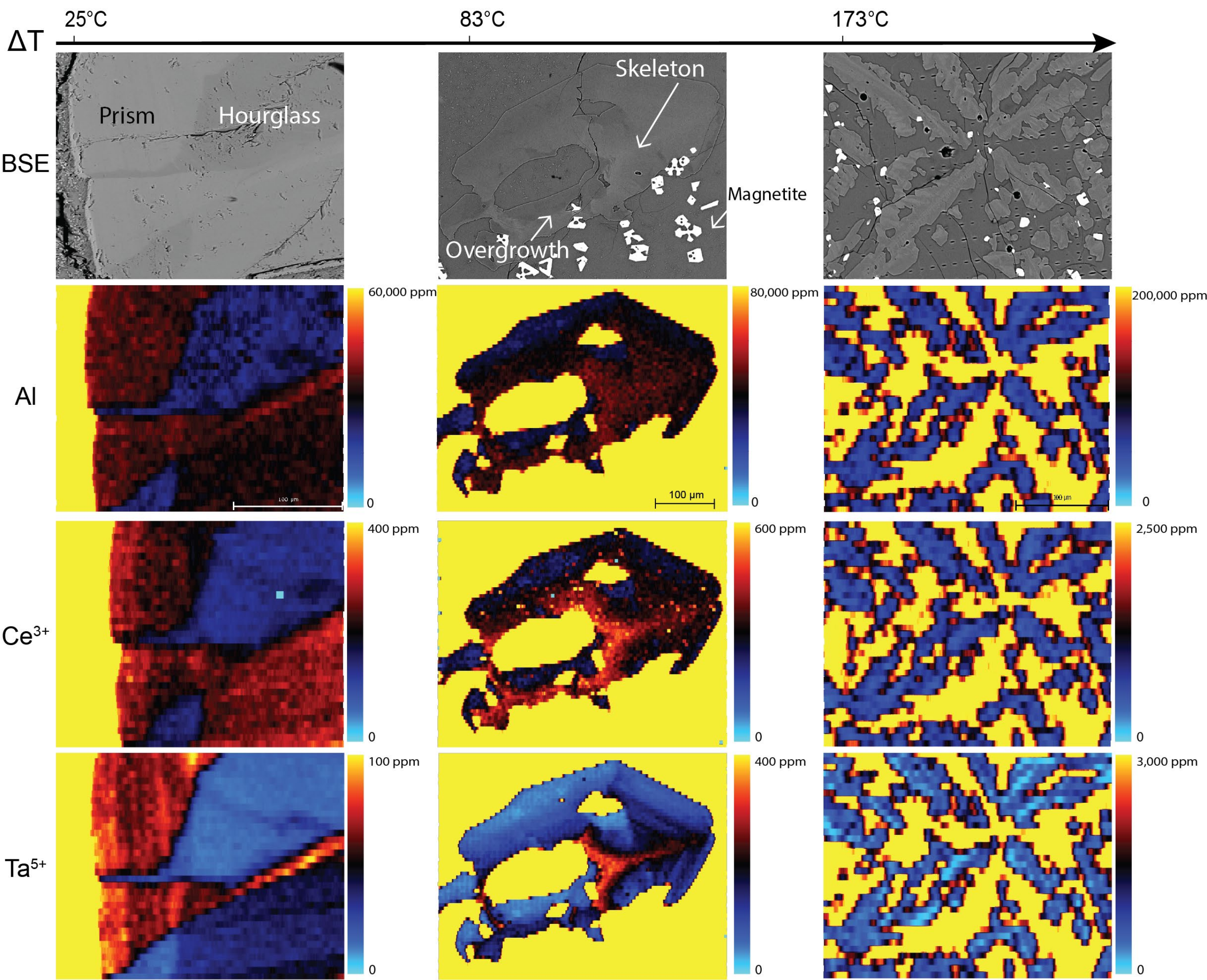


Figure 3: Back scattered electron (BSE) images and LA ICP-MS trace element (Al, Ce^{3+} and Ta^{5+}) maps of clinopyroxene crystals at varying degrees of undercooling (ΔT).

Results

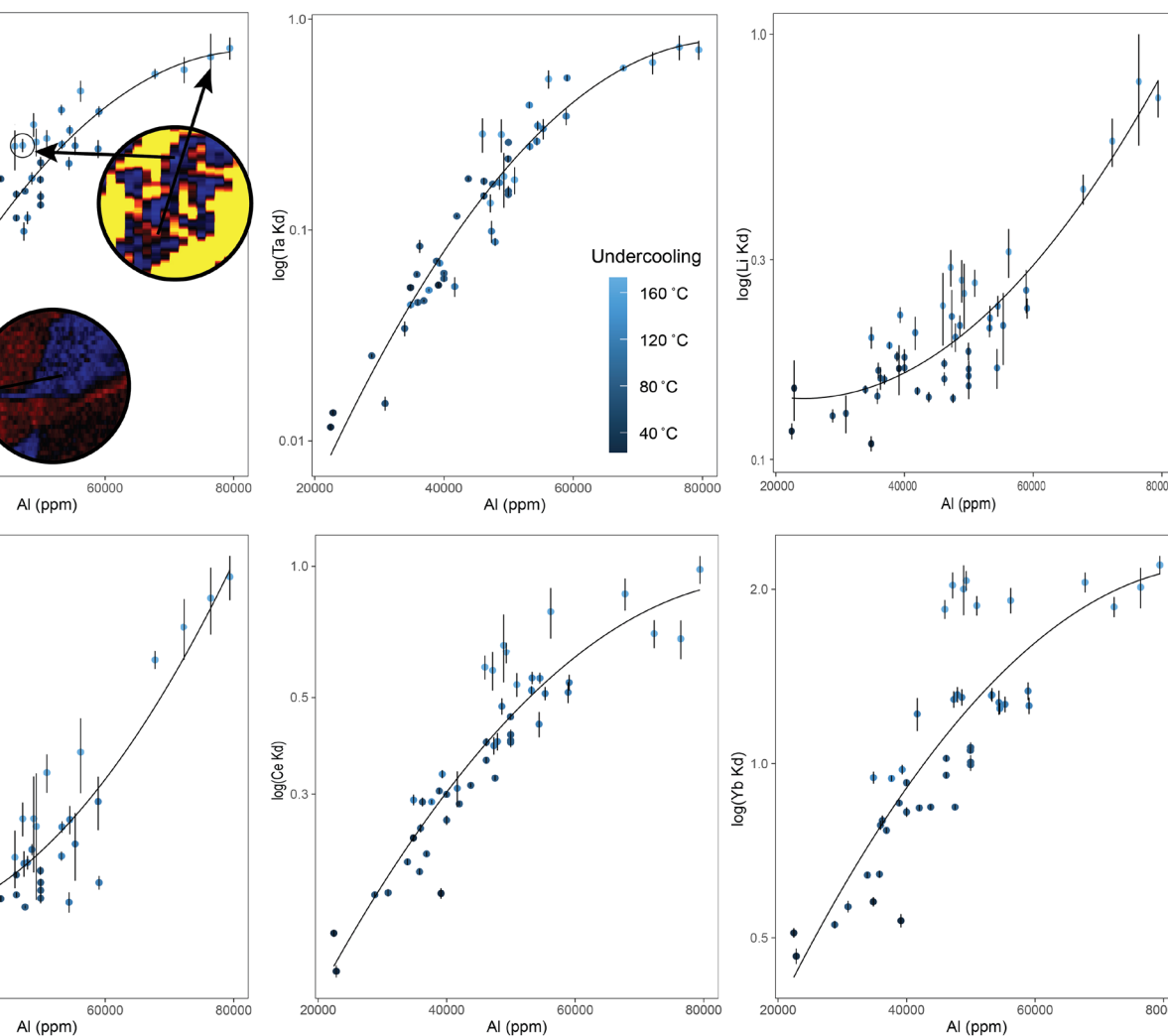


Figure 4: Relationship between partition coefficients for various trace elements with Al content. The top left plot also illustrates the difference between zones within the same crystal.

Partitioning and Undercooling

Zoning styles in clinopyroxene crystals changed with ΔT , illustrated in **Figure 3**:

- At low ΔT ($<40^{\circ}C$), clinopyroxene was **euhedral** and **sector zoned**. Highly charged cations partition between zones.
- At moderate ΔT ($73-123^{\circ}C$), clinopyroxene was **skeletal** with Al-enriched overgrowths, highly charged trace elements follow Al zoning
- At high ΔT ($>123^{\circ}C$), clinopyroxene was **dendritic** with **subtle** Al zoning

Highly charged cations in the M1 site partition strongly between Al enriched and depleted zones at all ΔT , and less strongly in the M2 site (**Figure 2**). This is in order to compensate for the **charge deficit** produced when Al substitutes for Si in the tetrahedral site. Cations with **low charge** do not partition strongly between Al enriched and depleted zones until very high ΔT , where they appear to partition strongly between Al-enriched and Al-depleted zones.

Partitioning and Al

Partition coefficients were calculated using the composition of each zone and the composition of the surrounding melt. These were plotted against Al in order to examine the role of undercooling in Al enriched and depleted zones (**Figure 4**).

- For highly charged cations, partition coefficients **increase with Al**, until very high Al (and undercooling) conditions, where the increase is not as significant
- For low charge cations, a major increase in partition coefficient is only observed at **very high Al**, in **high undercooling** experiments, similar to the trend in **Figure 3**.

Conclusions and Future Work

We find that ΔT has a significant effect on the partitioning of trace elements in sector zoned clinopyroxene, where Al-enriched zones attract higher concentrations of highly charged cations. Low charge cations are only affected in the highest ΔT experiment. We hypothesise that this may be due to rapid crystal growth in the diffusion-controlled regime at high ΔT . The low charge cations, such as Li, tend to be faster diffusers and are able to be incorporated at greater rates than at lower ΔT .

We are currently working on trace element calibrations, based on the rare earth element and high field strength element results presented here. These calibrations will be applied to **natural Etnean micro- and phenocrysts** to determine ΔT conditions, which will provide us with new insights into **polythermal and polybaric pre-eruptive processes**.