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Short Communication

# Crystallization kinetics of a fastest-cooling young mare basalt of Chang'E-5

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## ARTICLE INFO

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The quantitative effects of cooling kinetics on morphology and mineralogy of crystalline phases in natural basalts have been well recognized through microprobe analysis and crystallization experiments. For decades, our understanding of the crystallization and emplacement of lunar magmas has been greatly advanced through laboratory analysis of lunar mare basalts and basaltic meteorites, petrological experiments, and thermodynamic models. These investigations have revealed that the cooling rates of mare basalts can vary significantly, ranging from 0.001 °C/h (Apollo-15 basalt 15058) to ~1000 °C/h (Apollo-15 basalt 15597) (e.g., [1]). Recently, China's Chang'E-5 mission landed on a young mare basaltic unit in the northern Oceanus Procellarum and returned mare basalts with the voungest radiometric dating age reported thus far ( $\sim 2.0$  Ga. e.g., [2]). Most of the basalts have similar bulk and mineral compositions but diverse textures, including aphanitic, porphyritic, subophitic, poikilitic, and equigranular textures, implying crystallization at different depths [3]. The crystallization kinetics of lunar magmas significantly influence the dynamics of lava emplacement and migration on the lunar surface, thereby affecting the morphology of lunar lava flows [4]. However, few studies have correlated the textural features with cooling conditions for these basalts [5–7]. Consequently, this hinders the development of an accurate emplacement model for the Chang'E-5 basalts.

In this study, we present a comprehensive analysis of the petrology, mineralogy, and bulk chemistry of a basaltic clast (No. CE5C0800YJYX005GP, hereinafter referred to as 005GP), which

was allocated by the China National Space Administration. The major element composition of 005GP is comparable to those of other Chang'E-5 basalts, with a bulk Mg<sup>#</sup> of 27.8 and TiO<sub>2</sub> content of 4.79 wt% (Table S1 and Fig. S1 online). The Na<sub>2</sub>O + K<sub>2</sub>O content of 005GP (0.94 wt%) falls within the range reported for Chang'E-5 pristine basalts (0.33 wt%–1.01 wt%,  $2\sigma$ ), but beyond the range for Chang'E-5 impact glass (0–0.39 wt%,  $2\sigma$ ) [8], indicative of a volcanic origin. Moreover, the bulk MgO/Al<sub>2</sub>O<sub>3</sub> and CaO/Al<sub>2</sub>O<sub>3</sub> ratios of 005GP are similar to those of pristine basalts from Chang'E-5 (Fig. S2 online). Consequently, the studied basalt and other Chang'E-5 pristine basalts reported are likely derived from a single basaltic lava flow, as suggested by Ref. [3].

The basaltic clast 005GP consists predominantly of clinopyroxene (57%), plagioclase (25%), ilmenite (10%), and favalite (2%) crvstallites, with small grains (<5 µm) of accessory phosphates, troilite, K-feldspar, and hyalophane present as interstitial phases (Fig. 1a and Figs. S3 and S4 online). Within the clinopyroxene of 005GP, two distinct domains, namely Domain-1 and Domain-2, can be observed. Domain-2 clinopyroxene appears brighter in the backscattered electron (BSE) image and surrounds Domain-1 clinopyroxene, which is relatively darker (Fig. 1b). Domain-1 clinopyroxene exhibits a patchy shape and compositionally enriched in TiO<sub>2</sub> (5 wt%–7 wt%),  $Al_2O_3$  (8 wt%–9 wt%), and CaO (10 wt%-14 wt%) contents (Fig. 1c), resulting in elevated total Tschermak components (19%–21%, ΣTs = CaTs + CaFeTs + CaTiTs +  $CaCrTs = CaAlAlSiO_6 + CaFeAlSiO_6 + CaTiAl_2O_6 + CaCrAlSiO_6)$  compared to those in other Chang'E-5 basalts (Fig. 1d). On the other hand, Domain-2 clinopyroxene has remarkably lower Mg<sup>#</sup> (33-37), TiO<sub>2</sub> (0.7 wt%-2.5 wt%), Al<sub>2</sub>O<sub>3</sub> (1 wt%-3 wt%), CaO (10 wt%–12 wt%), and correspondingly lower  $\Sigma$ Ts





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**Fig. 1.** Backscattered electron (BSE) image of 005GP, in combination with petrology and mineralogy of clinopyroxene in 005GP. (a) Local BSE image of 005GP. The red box indicates the magnified and delineated clinopyroxene shown in (b). (b) A schematic drawing of clinopyroxene texture, illustrating the two compositional domains. (c) Mg<sup>#</sup> (Mg/(Mg + Fe)  $\times$  100% in molar percent) versus  $\sum$ Ts components of clinopyroxene analyzed in 005GP. (d) Si + Mg versus Al + Ti + Ca (in apfu) contents of clinopyroxene analyzed in 005GP. The purple regions in (c) and (d) represent compositional kernel-density plots of clinopyroxene in other reported Chang'E-5 basalts (data from Refs. [2,3,5]). The yellow bars indicate a scale of 10 µm. Cpx: clinopyroxene, PI: plagioclase, IIm: ilmenite, Fa: fayalite.

(2.5 wt%-7.5 wt%) contents compared to Domain-1 (Fig. 1d). The compositions of Domain-2 clinopyroxene are chemically similar to those of clinopyroxene in other Chang'E-5 basalts (Fig. 1c, d). The presence of these two distinct clinopyroxene domains is a unique feature observed in Chang'E-5 basalts, suggesting different crystallization kinetic conditions possibly associated with different cooling rates between the two domains (see text below). The plagioclase crystals exhibit extremely irregular shape, ranging from anhedral to subhedral, with a locally aligned structure on a submillimeter scale. Their compositions (An<sub>80-84</sub>Ab<sub>14-18</sub>Or<sub>1-4</sub>, MgO = 0.05 wt%-0.25 wt%, FeO = 1 wt%-2 wt%) show slightly higher Fe contents compared to other Chang'E-5 basalts (Fig. S5 online). The ilmenite texture varies from facets (typically <10  $\mu$ m) to laths (typically <100 µm in length) (Fig. 1a). Fayalite grains are euhedral to subhedral with a relatively small size of  $\sim 10 \ \mu\text{m}$ , and are often associated with ilmenite and/or plagioclase (Fig. 1a). Their compositions are more enriched in Fe (Fa =  $\sim$ 80–82) than olivine phenocrysts in other Chang'E-5 basalts (Fa =  $\sim$ 39–60, e.g., [5]).

The evolution of crystal morphology is controlled by magma undercooling  $(-\Delta T)$  and cooling rate (CR). As  $-\Delta T$  increases, clinopyroxene crystals become progressively enriched in tetrahedrally coordinated aluminum (<sup>T</sup>Al), leading to an increase in the

amount of  $\Sigma$ Ts components at the expense of Di and Hd components [9]. Therefore, the occurrence of early-formed Al-, Ti- and Ca-rich Domain-1 clinopyroxene (Fig. 1c, d) can be attributed to melt supersaturation resulting from high  $-\Delta T$  conditions during the early stage of crystal growth. Undercooling time-series experiments have suggested that the presence of Domain-1 clinopyroxene, as observed in this study, may imply a large  $-\Delta T$  range of 30–50 °C (e.g., [10]). Furthermore, the presence of plagioclase in the clast supports the kinetic condition of a large  $-\Delta T$  value, as high  $-\Delta T$  values facilitate the nucleation of plagio-clase. In contrast, if the  $-\Delta T$  is only several degrees Celsius, plagioclase cannot form at high CRs of up to hundreds of °C/h (e.g., [9]).

The crystal size distribution (CSD) patterns of ilmenite and plagioclase in 005GP display a linear to sublinear trend, without a decrease in population density at smaller grain sizes (Fig. 2a, b). The linear pattern suggests continuous nucleation and growth of ilmenite and plagioclase crystals without significant accumulation and fractionation. Moreover, the CSD patterns of ilmenite and plagioclase of 005GP show the steepest slopes (-262 and -106) and highest initial population densities (18.3 and 17.2) among all the ilmenite and plagioclase crystals reported for lunar basalts



**Fig. 2.** CSD patterns of ilmenite and plagioclase grains in 005GP, compared with Luna, Apollo, and other Chang'E-5 samples. (a) and (b) show the population density versus crystal length diagram of ilmenite and plagioclase in 005GP (this study) and other Chang'E-5 samples [11,14]. (c) and (d) compare the ilmenite and plagioclase CSD slopes and intercepts of 005GP with previously studied Luna, Apollo, and Chang'E-5 samples (Refs. [11,14] and references therein). The "golden spike" in (c) and (d) indicates the position of 10 °C/h, calibrated by crystallization experiments using Chang'E-5 basalt as the initial composition [12,13].

(Fig. 2c, d), indicating that 005GP may have formed under a high cooling rate compared with other lunar samples [11].

The cooling history of 005GP can be quantified by jointly estimating the temperature intervals of crystallization, growth rates and slopes of CSD patterns of ilmenite and plagioclase. Detailed information on the methods of CR quantification can be referred to Section S1.4 and Data S2 (online). Thermodynamic modeling using MELTS program indicates that ilmenite in 005GP crystallized between 1061 and 887 °C, whereas plagioclase crystallized between 1153 and 887 °C (Fig. S6 online). Assuming a  $-\Delta T$  range of 30-50 °C, the temperature intervals of crystallization are 124-144 °C for ilmenite and 216-236 °C for plagioclase. The growth rates of ilmenite  $(1.30 \times 10^{-6} - 1.79 \times 10^{-6} \text{ mm/s})$  and plagioclase  $(1.74 \times 10^{-6} - 2.10 \times 10^{-6} \text{ mm/s})$  were determined through crystallization experiments using initial compositions of Chang'E-5 basalt at lunar pressure and oxygen fugacity conditions [12,13]. By incorporating the growth rates into the slopes of CSD patterns, the CR of 005GP is estimated to fall within the range of 152-243 °C/h based on the ilmenite CSD pattern, or 143-189 °C/h based on the plagioclase CSD pattern. The estimated CR overlap in the range of 152-189 °C/h, which is comparable to the highest one reported so far (Apollo-15 sample 15597, CR =  $10^2$  to  $10^4$  °C/h [1]). Slight variations between the estimated CR ranges of ilmenite and plagioclase are likely due to the different cooling timespans of the two minerals.

Previous studies of Chang'E-5 basalts have documented the CRs of 12 samples using CSD patterns of ilmenite and plagioclase [11,14], plagioclase lath width [6], and clinopyroxene Fe-Mg diffusion [7]. Their CRs span a range from 0.00055 to 86 °C/h. Hence, our sample may represent the fastest cooling one collected at the Chang'E-5 landing site. Using the mathematical treatment for heat loss from a thermal boundary (see Section S1.6 online for details), the calculated burial depth for 005GP falls

within the range of 5.7–6.3 cm. The shallow burial depth and lack of evidence for crystal accumulation suggest that 005GP probably formed at the uppermost chilled margin of Chang'E-5 lava flow. The CRs of most Chang'E-5 samples fall within the range of 1 to 50 °C/h [11,14], corresponding to burial depths ranging from 11 to 78 cm. The scarcity of samples with faster CRs and shallower burial depths is likely due to space weathering and multiple superimposed impact events, which have significantly changed the surficial pristine volcanic lava flows into regoliths and impact glasses (e.g., [8]). Therefore, studying the morphology and mineralogy of fast-cooling samples like 005GP at lunar landing sites is crucial, as they can serve as benchmarks for identifying young lunar lava flows based on remote-sensing observations.

Moreover, the fastest-cooling basalts and other slower-cooling ones establish systematic vertical variations of CRs in Chang'E-5 lava flow (Fig. S7 online). This continuum of sampling provides an opportunity to compare the characteristics of Chang'E-5 lava flows with those observed at Apollo landing sites. For example, the significantly small volume of vesicles observed in shallowburied Chang'E-5 samples compared to Apollo samples suggests that the magma of Chang'E-5 basalts underwent a less intense degassing process with a small volume of volatile exsolution compared to Apollo basalts. The low degree of degassing implies that the heat loss rate of Chang'E-5 lava flow is likely slower than that of Apollo lava flows, which may contribute to the development of long sinuous rille systems adjacent to the Chang'E-5 landing site [15]. Further investigations of textures and CRs for more Chang'E-5 samples, combined with dynamic modeling of Chang'E-5 lava flows, are essential. This will provide more insights into the stratigraphy and petrogenesis of mare basalts and the provenance of young mare lava flows, which will lead to a better understanding of the volcanic history of the Moon.

# **Conflict of interest**

The authors declare that they have no conflict of interest.

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# **Author contributions**

Wei Tian and Wei-(RZ) Wang conceived and led the project. Zilong Wang and Wei Tian wrote the manuscript. Ben Ma provided the CSD results. Wei-(RZ) Wang, Zilong Wang, Junling Pei, Zhenyu Chen, and Jiang Wu conducted TIMA and EPMA analyses. Ping-Ping Liu revised and polished the manuscript. Chunjing Wei performed thermodynamic modeling. Zilong Wang was in charge of all data processing and figure production. Wei Tian, Wei-(RZ) Wang, Junling Pei and Chunjing Wei supervised the data processing. All authors made contributions to technical and scientific discussions.

## **Appendix A. Supplementary materials**

Supplementary materials to this short communication can be found online at https://doi.org/10.1016/j.scib.2023.06.036.

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