

Titanium partitioning between pyroxenes and lunar basaltic melts: An experimental perspective

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Abstract The size of basalt fragments in Chang'E-5 (CE-5) regolith are small ($< 6 \text{ mm}^2$), resulting in large variation on the estimated bulk composition of CE-5 basalt. For example, the estimated TiO_2 content of CE-5 basalt ranges from 3.7 wt% to 12.7 wt% and the Mg# (molar percentage of $\text{Mg}/[\text{Mg} + \text{Fe}]$) also shows a wide range (26.2–42.4). Preliminary experimental studies have shown that these geochemical characteristics of CE-5 basalt are critical for investigating the crystallization sequence and formation mechanism of its parent magma. This study presents new experimental data on the distribution coefficient of titanium between pyroxene and lunar basaltic magma ($D_{\text{Ti}}^{\text{Px/melt}}$). Combining with available literature data, we confirm that $D_{\text{Ti}}^{\text{Px/melt}}$ is affected by crystallization conditions such as pressure and temperature, but it is mainly controlled by the CaO content of pyroxene. Comparing with previous experimental results under similar conditions, we parameterized the effect as $D_{\text{Ti}}^{\text{Px/Melt}} = D_{\text{Ti}}^{\text{Px/melt}} = -0.0005X_{\text{CaO}}^2 + 0.0218X_{\text{CaO}} + 0.0425 (R^2 = 0.82)$, where X_{CaO} is the CaO content in pyroxene in weight percentage.

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The new experimental results suggest that pyroxene with high TiO_2 content ($> 2.5 \text{ wt\%}$) in CE-5 basalt is not a product of equilibrium crystallization, and the CaO content in pyroxene is also affected by cooling rate of its parent magma. The TiO_2 content in the CE-5 parent magma is estimated to be about 5 wt% based on the Mg# of pyroxene and its calculated CaO content, which is consistent with those estimated from olivine grains.

Keywords Lunar basalt · Chang'E-5 · High pressure and high temperature experiments · Partitioning coefficient

1 Introduction

According to geochemical analysis on Apollo and Luna samples, lunar mare basalts can be classified as high titanium (HT, $> 6 \text{ wt\% TiO}_2$) basalt, low titanium (LT, $1 - 6 \text{ wt\% TiO}_2$) basalt, very-low titanium (VLT, less than $1 \text{ wt\% TiO}_2$) basalt (Neal and Taylor 1992). The lunar basalt samples represent partial melts from different part of lunar mantle, variably fractionated or mixed during their ascent to the surface (e.g., Grove and Krawczynski 2009). Previous studies indicate that relatively old HT basalts were in equilibrium with a cumulate mineral assemblage at shallow depths of the Moon, and the relatively young LT mare basalts and picritic glasses formed in lower lunar mantle (e.g., Longhi 1992). From a global perspective, these hypotheses are consistent with the magma-ocean differentiation model (e.g., Snyder et al. 1992) and thermal evolution of the Moon (e.g., Laneuville et al. 2013; Borg and Carlson 2023), and serve as a paradigm for studies on the petrogenesis of mare basalts. On the other hand, the special correlation between the region that elevated high K, Th, and U content in the Procellarum KREEP Terrane

(PKT, Jolliff et al. 2000) and the distribution of young basaltic eruption on the Moon (e.g., Qian et al. 2021, 2023) has been suggested to explain the heat source for the relatively young mare basalts. This hypothesis complexes the source region of young mare basalts as they show evolved geochemistry characteristics and may have experienced variable fractionation processes, hybridization of KREEP or crustal material, or are mixture of melts derived from different mantle cumulates (i.e., Day and Taylor 2007; Day et al. 2006; Elardo et al. 2011; Elardo et al. 2015; Elardo et al. 2014; Shearer et al. 2006).

Recently, geochemical analysis and isotopic studies on Chang'E-5 (CE-5) regolith and basalt fragments have shown that the young CE-5 basalt (~2.0 Ga, Che et al. 2021; Li et al. 2021) collected from the northern Oceanus Procellarum in PKT is enriched with heating-producing elements including U, Th, and K as well as other incompatible elements REEs and P, but contains little KREEP (Tian et al. 2021). Moreover, the more evolved characteristics of CE-5 basalt have been suggested to result from extensive fractionation processes after melt extraction (e.g., Tian et al. 2021; Zong et al. 2022). The young mare basalt makes it more challenging to constrain the thermochemical evolution of the lunar mantle. For example, theoretical calculation suggested that the source region of CE-5 lunar basalt is deep inside the Moon (~500–600 km) and incorporating ilmenite-bearing cumulate (IBC) (Su et al. 2022). However, small degree melting of a hybridized source with ilmenite will produce basaltic liquid enriched with TiO₂, which is not consistent with the thermochemical evolution paradigm mentioned above. These models can be tested if the crystallization process of original melt can be constrained, therefore it is crucial to confirm the parental magma composition of CE-5 basalts. However, due to the small size of basalt fragments and compositional zoning in mafic minerals, the chemical composition of CE-5 basalts determined by different methods show large variations, for examples, the Mg# ranges from ~26.5 (Che et al. 2021) to ~34 (Zong et al. 2022), TiO₂ contents ranges from 3.7 wt% (He et al. 2022) to 12.7 wt% (Jiang et al. 2022), blurs the boundary between the high- and low-Ti basalts. He et al. (2022) and Zhang et al. (2022) estimated the TiO₂ content of CE-5 basalt to be 4–6 wt% by using the TiO₂ content of olivine (Mg# = 61) and the partitioning of Ti between olivine and melt (Mg# ~ 25–35). Jiang et al. (2023) inferred the titanium content of the parental melt of CE-5 basalt to be 16.2 wt% by using TiO₂ content in clinopyroxene and the partition coefficient of titanium between pyroxene and melt estimated from its CaO concentration ($D_{\text{Ti}}^{\text{Px/melt}} = [0.0148 \times \text{CaO}_{\text{Pyroxene}} + 0.09] \pm 0.05$) (Robinson et al. 2012). To accurate evaluate the chemical

composition of CE-5 basalt, we need to constrain the partition coefficient of titanium between different mineral phases and the coexisting magma.

In this study, we carried experimental studies to determine the partitioning coefficients of titanium between pyroxene and coexisting silicate melts ($D_{\text{Ti}}^{\text{Px/melt}}$) over a range of temperatures (1020–1130 °C) and under different pressure (0.5 and 1.0 GPa) conditions. Comparing with literature experimental results, we make a study on $D_{\text{Ti}}^{\text{Px/melt}}$ and test the possible effects on $D_{\text{Ti}}^{\text{Px/melt}}$, such as pressure, temperature, and chemical composition of basaltic magma. We verify the dependence of $D_{\text{Ti}}^{\text{Px/melt}}$ on chemical composition (CaO content) of pyroxenes and make suggestion on the estimated bulk TiO₂ content of CE-5 basalt.

2 Experimental methods

2.1 Starting materials

The CE-5 regolith is mainly composed of basaltic fragments and small amount of foreign impact ejecta (<5%), therefore its average composition is taken as the bulk composition of CE-5 basalt (Li et al. 2021; Zong et al. 2022). We synthesize basaltic glasses based on chemical composition of CE-5 regolith (Table 1) following the steps: (1) certain amount of high-purity powders of SiO₂ (99.99% Aladdin), TiO₂, Al₂O₃, Cr₂O₃, Fe₂O₃, MnO, and MgO (99.95%–99.99% Alfa Aesar), CaCO₃, Na₂CO₃, and K₂CO₃ (99.95% Alfa Aesar), and NH₄PO₅ were weighed and placed in an agate mortar with ethanol (analytical pure grade) and grinded for about 3 h to fully mixed, the mixture was then placed in a vacuum oven (110 °C). (2) After drying, the mixture was packed in a platinum crucible and placed in a sintering furnace for decarbonization, after heated at 1000 °C for 7 h, the platinum crucible was taken out and cooled to room temperature. (3) The decarbonized sample was then mixed with a certain amount of iron powder, and ground with ethanol and dried in the vacuum oven. (4) After drying, the mixture was placed in the high-temperature sintering furnace with high purity nitrogen atmosphere and heated at 1640 °C for 2 h, then put in water for quenching to form homogeneous glasses. (5) A few pieces of the basaltic glass were put into mold and underwent a series of operations such as gluing, polishing, drying, and carbon coating. The carbon-coated sample was then observed with scanning electron microscopy (SEM) to check its chemical homogeneity and examined with electron microprobe (EPMA) for chemical composition analysis which should be identical to CE-5 regolith. (6) The homogeneous basaltic glasses (Table 1) were then re-grinded to powder and stored in a vacuum drying oven for future high-pressure and high-temperature experiments.

Table 1 Bulk composition of CE-5 regolith and chemical composition of glasses used as starting materials in experiments present in this study

Oxide	CE-5 regolith*	Uncertainty (k=2)	SD	This study (n=23)	Uncertainty (k=2)	SD
SiO ₂	42.20	0.34	0.80	43.47	1.08	0.55
TiO ₂	5.00	0.06	0.09	5.00	0.19	0.09
Al ₂ O ₃	10.80	0.18	0.20	10.90	0.38	0.17
Cr ₂ O ₃	0.14	0.06	0.02	0.12	0.03	0.01
FeO	22.50	0.33	0.84	22.24	1.21	0.43
MnO	0.28	0.03	0.01	0.24	0.02	0.01
MgO	6.48	0.35	0.11	6.15	0.31	0.11
CaO	11.00	0.10	0.06	10.65	0.14	0.06
Na ₂ O	0.26	0.21	0.04	0.26	0.09	0.04
K ₂ O	0.19	0.15	0.01	0.10	0.01	0.01
P ₂ O ₅	0.23	0.05	0.02	0.26	0.04	0.02
Total	98.94		0.05	99.40	1.14	0.96
Mg#	33.90			33.00		

*The data is the average bulk compositions of CE-5 regolith from Li et al. (2021). k indicates the maximum absolute difference between the levels of different oxides per test and the mean value within a 95%

confidence interval. SD means standard deviation, its formula is described as $SD = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{n-1}}$, X_i is the distinct kinds of oxides in weight percent, and $\bar{X}$ is the average compositional chemistry (or chemical composition) in wt%

2.2 Experimental techniques

The high-pressure and high-temperature experiments were all carried out by using Rockland piston cylinder and Walker type multi anvil combined press at GYIG (Institute of Geochemistry, Chinese Academy of Sciences). Experimental temperatures were controlled using a Eurotherm controller and measured with a C-type (W₅Re₉₅-W₂₆Re₇₄) thermocouple with variations less than $\pm 2^\circ\text{C}$. No pressure effect on electromotive force of the thermocouple was corrected. The experimental pressure was corrected based on phase transition between quartz and coesite and the friction coefficient

of oil chamber is less than 4%. The high-pressure press and experimental assembly are shown in Fig. 1a. About 20 mg of basaltic glass powder was placed into an iron capsule (99.995% purity) with an outer diameter of 4.5 mm and a height of 3.5 mm and dried in 110 °C vacuum oven overnight. Iron capsules were not welded prior to the experiments. However, under the applied pressure conditions (0.5 GPa), the ductility of metallic iron causes the capsule lid and body to deform and cold-seal tightly. As confirmed by scanning electron microscopy (SEM), the recovered capsules exhibited complete closure without gaps, and no sample leakage was observed, indicating that the sealing

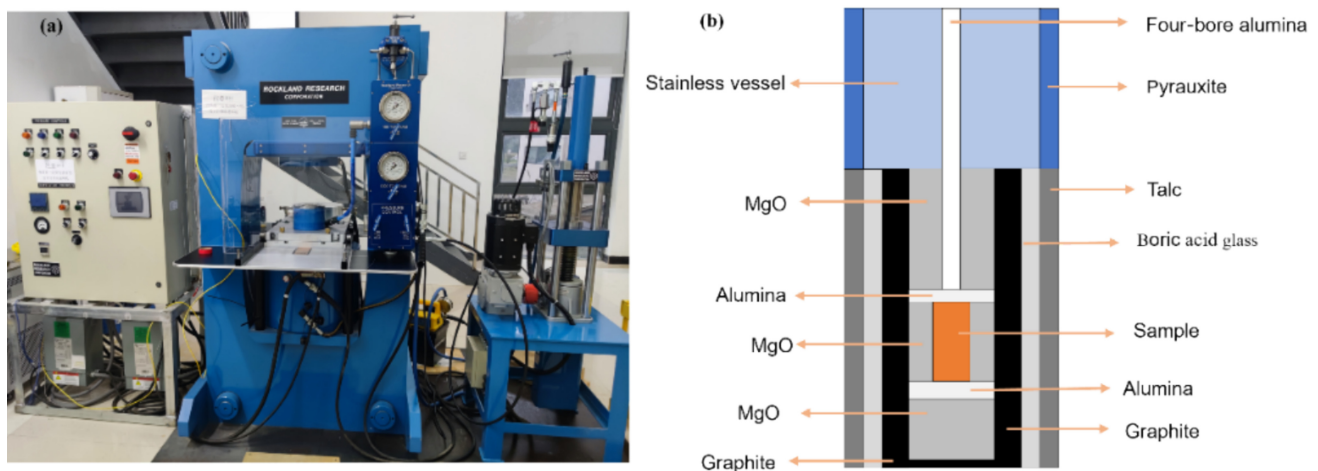


Fig. 1 Experiment setting **a** Piston-cylinder device; **b** schematic graph of cell assembly

was effective under the experimental conditions. The iron capsule was then placed into a half-inch diameter talc-boric acid glass tube assembly (Fig. 1b). The thermocouple wires were housed in a four-bore alumina sleeve, with the junction in contact with an alumina disk (0.5-mm thickness) at the top of the sample capsule. After loading the sample, the pressure was gradually increased to 0.5 GPa and then started the stepped heating process. A heating rate of 50 °C/min was chose till the temperature reached 1000 °C, and a relatively slower rate (20 °C/min) was used to get the target temperature. The total duration varied from 24 to 72 h depending on the experimental temperature and then quenched by shutting off the power. The decompressing time was extended as long as 10 h to prevent the sample chamber from cracking. The recovered capsules were sectioned, mounted in epoxy resin, and polished for optical observations and subsequent electron beam analyses.

2.3 Analytical techniques

The field emission electron probe microanalyzer (EPMA, JEOL JXA-8530F plus) at State Key Laboratory for Critical Mineral Research and Exploration (SKLCMRE), Institute of Geochemistry, Chinese Academy of Sciences, was used to quantitatively analyze the chemical composition of the starting material (synthetic glass), the mineral phases, and silicate liquid of the experimental products under different temperature and pressure conditions. The analytical acceleration voltage is 15 kV and the beam current is 10 nA. The beam size is determined by the grain size of the mineral and ranges from 1 to 10 microns in diameter. The analysis

elements were all measured using the $K\alpha$ line, and the peak analysis time for most elements (Si, Ti, Al, Cr, Fe, Co, Mn, Mg, Ca, P) was 20 s, while the peak analysis time for Na and K was 10 s. Natural and synthetic minerals were selected as the standard samples for analysis: diopside (Si, Mg, Ca), bluenite (Ti), magnesite (Al, Cr, Fe, Mn), olivine (Ni), nickelpyrite (Co), albitite (Na), potassium feldspar (K), and apatite (P). The detection limit for elemental oxides is 0.01–0.03 wt%. All data were corrected by ZAF method. For each mineral and glass phase composition, the mean and standard variance were obtained using 8–15 data.

3 Results

3.1 Experiments approach to equilibrium

To evaluate whether the experiments have reached equilibrium, we calculated the Fe–Mg exchange coefficients between minerals (olivine and pyroxene) and the coexisting melt $K_D^{Fe-Mg} = \frac{[FeO/MgO]_{mineral}}{[FeO/MgO]_{melt}}$, where $[FeO/MgO]_{mineral/melt}$ is the molar ratio of Fe and Mg in mineral and melt. The K_D^{Fe-Mg} between olivine and melt is 0.26–0.35 (Table 2), which is similar to the experimental results reported by Toplis (2005) (0.23–0.36) and close to previous experimental results on Apollo returned samples (Brown and Grove 2015; Kushiro and Walter 1998). Although the K_D^{Fe-Mg} between pyroxene and melt may be affected by experimental conditions (temperature and pressure), high field strength element content, and NBO/T (Xirouchakis et al. 2001), the K_D^{Fe-Mg}

Table 2 The assemblages and partitioning parameters (Ti, Mg and Fe) of experimental run products under different conditions

Run	P (GPa)	T (°C)	t/hr	Assemblages (modal abundance%)	$D_{Ti}^{Px-Melt}$	$K_d^{Ol-Melt}$	$K_d^{Px-Melt}$
RPW-87	0.5	1060	72	Olivine, Plagioclase, Ulvö-spinel, Pyroxene, Ilmenite, Glass (16:12: < 1:3:1:64)	0.296(53)	0.31	0.21
RPW-67	0.5	1050	24	Olivine, Plagioclase, Pyroxene, Ilmenite, Glass (21:17:26:1:35)	0.236(21)	0.27	0.14
RPW-68	0.5	1020	21	Olivine, Plagioclase, Pyroxene, Ilmenite, Glass (50:27:18:2:3)	0.272(29)	0.30	0.16
RPW-45*	0.5	1090	36	Olivine, Plagioclase, Ulvö-spinel, Pyroxene ^a , Glass (24:25: < 1: < 1:49)	0.295(84)	0.33	0.22
RPW-87*	0.5	1060	72	Olivine, Plagioclase, Ulvö-spinel, Pyroxene, Ilmenite, Glass (18:16: < 1:35:3:26)	0.287(35)	0.32	0.19
RPW-77	1	1130	24	Pyroxene, Glass (13:87)	0.162(32)		0.24
RPW-69	1	1095	20	Pyroxene, Plagioclase, Ilmenite, Ulvö-spinel, Glass (50:19:7:1:22)	0.248(56)		0.17
RPW-64	1	1090	20	Pyroxene, Olivine ^b , Plagioclase, Ilmenite, Ulvö-spinel, Glass (63:1:20: < 1:11:3)	0.263(39)	0.24	0.13

Modal abundance is calculated based on the mass balance between the compositions of the initial material and the phases and is also estimated using the ImageJ software package. $D_{Ti}^{Px-Melt} = [TiO_2]_{Px} / [TiO_2]_{melt}$, a partitioning coefficient of Ti between pyroxene and its equilibrium melt. The data in parentheses following the Ti partitioning coefficient represents its standard error, indicating the precision of the measurement. $K_d^{Ol/Px-Melt} = [FeO/MgO]_{Ol/Px} / [FeO/MgO]_{melt}$, [FeO] and [MgO] in mole, is Fe–Mg exchange parameter represented experimental equilibrium

*Was added 1000 ppm trace element into started material

^{a,b}The metastable phases, which occupy less than 1% of the modal abundance, tend to disappear over time

between the pyroxene and melt obtained in this study is between 0.14 and 0.24 (Table 2), within the range reported by previous experimental studies (0.17–0.28) (Grove and Bence 1977; Longhi et al. 1978), the noticeable difference between the previous and the present experiments are to be found in the higher Fe/Mg + Fe of the phase in this study. Moreover, the experimental products from this study also show homogeneity on element concentration for mineral phases and silicate liquid (Table 3). These results demonstrate that the high-temperature and high-pressure experiments involved in this paper have reached chemical equilibrium.

3.2 Chemical composition of pyroxene and silicate liquid

In the experiments run at 0.5 GPa, olivine is the liquidus phase, followed by plagioclase, and pyroxene crystallized in the temperature interval from 1090 °C to 1020 °C. For all the run products, the sizes of mineral grains range from less than 20 µm to larger than 100 µm and are large enough for compositional analyses. Silicate melts quenched to clear glasses in most of the run products, with several exceptions that were conducted at relatively low temperatures where the residual silicate liquid exist as small pockets (< 3 µm). Chemical composition analysis shows that the pyroxenes in all run products are augite with relatively homogeneous composition and no zoning (Fig. 2). The TiO₂ content of pyroxenes ranges from 2.15 wt% to 2.40 wt%, CaO content is between 15.64 wt% and 17.05 wt% with minor variation, and Mg# values vary from 50 to 55. The silicate liquids coexisting with pyroxenes are relatively magnesium-poor with Mg# ranging from 13.6 to 20.6, TiO₂ abundance varied from 7.58 wt% to 8.49 wt% as shown in Table 3. For experiments at 1.0 GPa, olivine is the liquidus phase and followed by pyroxene and the TiO₂ content of pyroxenes ranges from 1.17 wt% to 1.71 wt%, CaO content is 10.28–12.46 wt% with insignificant variation, and Mg# values varying from 60 to 48. The titanium content in pyroxene decreases with increasing experimental temperature and pressure from 0.5 GPa to 1.0 GPa. The partitioning coefficient of Ti between pyroxene and basaltic liquid is calculated as $D_{\text{Ti}}^{\text{Px/melt}} = \frac{[\text{TiO}_2]_{\text{mineral}}}{[\text{TiO}_2]_{\text{melt}}}$, changing from 0.16 to 0.30 for all the experimental results present in this study.

4 Discussion

4.1 Comparing with previous studies

Literature experimental studies show that the partition coefficient of titanium between pyroxene and silicate liquid

$D_{\text{Ti}}^{\text{Px/melt}}$ is generally less than 1, and gradually decreases with increasing temperature, although the overall change is small (Fig. S1a) (Green et al., 1971; Grove and Bence 1977; Longhi et al., 2010; Walker et al. 1976; Putirka et al. 1996; Grove and Vaniman 1978; Adam and Green 1994; Wagner and Grove 1997; Van Orman and Grove 2000; Hill et al. 2011; Krawczynski and Grove 2012; Dygert et al. 2013; Elardo et al. 2015; Snape et al. 2022). The pressure change also shows a certain effect on $D_{\text{Ti}}^{\text{Px/melt}}$, which may decrease as the pressure increase from 1 bar to 3 GPa (Fig. S1b) (Grove and Vaniman 1978; Adam and Green 1994; Putirka et al. 1996; Wagner and Grove 1997; Van Orman and Grove 2000; Hill et al. 2011; Krawczynski and Grove 2012; Sun and Liang 2013; Elardo et al. 2015; Snape et al. 2022). However, it is difficult to quantify the effect of pressure and temperature on $D_{\text{Ti}}^{\text{Px/melt}}$ due to the significant differences in the chemical composition of the starting materials and the assembly (oxygen fugacity) used in these experiments, and the cooling procedures. For example, Adam and Green (1994) added 10 wt% of rare earth elements (REE) and different amount of water (2–12 wt%) to the starting materials and the overall trend of their experimental results show high partition coefficient, which could be explained by the high concentration of REEs because their larger atomic radius will affect the Si and ^{IV}Al occupation in the silicate structure. Shepherd et al. (2022) carried out slow cooling rate experiments (1 °C/h) under different redox conditions and showed much larger $D_{\text{Ti}}^{\text{Px/melt}}$ (~0.6–1.0). Mollo et al. (2013) present controlled cooling rate experiments on $D_{\text{Ti}}^{\text{Px/melt}}$ and showed that $D_{\text{Ti}}^{\text{Px/melt}}$ is much larger (~1.5) at fast cooling rate (50 °C/h) than those got from equilibrium experiments. In the experimental study by Snape et al. (2022), the content of TiO₂ in the starting material changed from very-low titanium (0.46 wt%) to high titanium (15.8 wt%) and the experimental temperature was gradually dropped to the target temperature with a cooling rate of 1–2 °C/min. Therefore, the $D_{\text{Ti}}^{\text{Px/melt}}$ obtained in their experiments show large variation (0.1–0.6). For these studies, the obtained $D_{\text{Ti}}^{\text{Px/melt}}$ is not under equilibrium conditions and we thus exclude these experimental results from quantifying the effect of temperature, pressure, and chemical composition on partitioning behavior of titanium.

On the other hand, Elardo et al. (2015) carried out crystallization experiments on young lunar meteorite North-east Africa (NEA) 003A and LAP group to constrain thermal conditions of the lunar interior. Their experimental design and the cell assemblage are similar to those used in this study, and the oxygen fugacity of their experiments were lower than IW and close to that present in this study (IW–0.7). Comparing our experimental results with those reported by Elardo et al. (2015), we found that $D_{\text{Ti}}^{\text{Px/melt}}$ is in a good correlation with both pressure and temperature. The TiO₂ content in pyroxene gradually decreases

Table 3 Summary of The Chemical Compositions of Experimental Products

Run	Minerals	n	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	
P=1.0 GPa															
RPW-77 T=1130°C	Pyroxene	25	48.23	1.00	5.21	0.69	17.29	0.29	15.19	11.43	0.06	0.00	0.01	100.18	
		SD	0.63	0.17	0.80	0.20	0.98	0.02	0.67	1.10	0.01	0.00	0.01	0.322	
	Glass	12	40.47	6.83	11.42	0.10	24.49	0.25	5.05	10.43	0.34	0.13	0.30	99.92	
		SD	0.19	0.12	0.08	0.02	0.11	0.01	0.08	0.03	0.03	0.01	0.03	0.207	
RPW-69 T=1095°C	Pyroxene	25	47.66	1.71	5.09	0.32	21.00	0.33	13.05	10.28	0.05	0.00	0.01	99.49	
		SD	0.56	0.02	0.40	0.01	2.06	0.00	1.20	0.10	0.01	0.00	0.00	0.831	
	Plagioclase	5	44.90	0.30	32.99	0.01	2.42	0.03	0.36	18.22	0.83	0.14	0.05	100.27	
		SD	0.20	0.21	1.83	0.01	1.33	0.03	0.44	0.63	0.07	0.03	0.05	0.41	
	Ilmenite	4	0.29	51.21	0.53	0.17	44.94	0.30	1.61	0.46	na	na	na	99.51	
		SD	0.16	0.13	0.06	0.07	0.41	0.02	0.04	0.10				0.28	
	Ulvö-spinel	11	0.69	27.76	4.92	1.24	62.08	0.28	1.42	0.55	na	na	na	98.96	
		SD	0.82	0.71	0.05	0.17	0.76	0.02	0.06	0.29				0.40	
	Glass	26	38.51	6.41	9.83	0.02	31.25	0.31	1.38	9.30	0.45	0.59	1.36	99.42	
		SD	1.61	0.94	1.10	0.03	1.11	0.02	1.47	0.71	0.09	0.10	0.40	0.77	
	RPW-64 T=1090°C	Pyroxene	18	48.50	1.33	3.30	0.13	23.16	0.36	12.19	10.60	0.02	0.00	0.01	99.61
			SD	0.30	0.18	0.68	0.11	3.14	0.03	1.44	1.12	0.02	0.00	0.02	0.42
Plagioclase		3	45.17	0.16	33.66	0.00	2.02	0.02	0.17	18.29	0.88	0.20	0.10	100.66	
		SD	0.54	0.05	0.73	0.00	0.29	0.01	0.04	0.36	0.03	0.04	0.07	1.14	
Ilmenite		8	0.84	51.26	0.42	0.18	45.22	0.30	1.53	0.62	na	na	na	100.37	
		SD	0.41	0.84	0.14	0.07	0.55	0.01	0.19	0.20				0.60	
Ulvö-spinel		5	1.16	28.18	4.25	1.86	61.32	0.29	1.50	0.65	na	na	na	99.22	
		SD	1.14	0.61	0.18	0.07	0.94	0.02	0.20	0.30				0.37	
Olivine		9	32.68	0.73	0.49	0.02	53.71	0.47	11.63	1.22	0.01	0.00	0.07	101.05	
		SD	1.26	0.94	0.33	0.02	1.91	0.02	0.89	0.82	0.01	0.00	0.05	0.60	
Glass		16	40.96	4.82	9.06	0.01	30.09	0.33	1.56	9.63	0.40	0.67	1.69	99.21	
		SD	0.22	0.08	0.06	0.00	0.27	0.02	0.04	0.04	0.04	0.02	0.05	0.30	
P=0.5 GPa															
RPW-87 T=1060°C	Olivine	11	33.20	0.22	0.05	0.05	47.31	0.38	17.40	0.56	0.00	0.00	0.02	99.27	
		SD	0.14	0.07	0.02	0.07	0.55	0.03	0.30	0.05	0.01	0.00	0.02	0.48	
	Plagioclase	14	44.55	0.13	34.79	0.06	1.79	0.01	0.13	18.94	0.04	0.46	0.02	100.94	
		SD	0.60	0.09	0.65	0.07	0.25	0.01	0.04	0.40	0.01	0.18	0.01	0.46	
	Ulvö-spinel	13	0.25	29.34	4.38	8.60	53.41	0.00	0.30	2.62	0.31	0.00	0.01	99.31	
		SD	0.22	0.64	0.22	1.24	0.83	0.02	0.09	0.07	na	0.00	0.01	0.76	
	Pyroxene	9	47.98	2.4	2.96	0.29	18.64	0.23	10.42	17.05	0.04	0	0.02	100.12	
		SD	0.50	0.33	0.47	0.09	0.43	0.04	0.26	0.44	0.01	0.00	0.01	0.28	
	Ilmenite	15	0.10	51.94	0.57	1.12	42.57	0.30	2.81	0.21	na	na	na	99.60	
		SD	0.07	5.86	0.89	1.74	3.30	0.02	0.08	0.09				0.42	
	Glass	9	40.11	7.73	8.63	0.05	29.86	0.26	3.42	10.25	0.26	0.17	0.39	101.19	
		SD	0.29	0.99	0.58	0.06	0.38	0.05	0.26	0.31	0.02	0.01	0.14	0.61	
RPW-67 T=1050°C	Olivine	15	33.50	0.35	0.13	0.06	49.42	0.40	16.35	0.67	0.00	0.00	0.02	100.91	
		SD	0.14	0.18	0.12	0.02	0.45	0.02	0.36	0.08	0.00	0.00	0.01	0.31	
	Plagioclase	7	44.62	0.42	34.16	0.02	2.22	0.02	0.20	18.92	0.61	0.05	0.03	101.29	
		SD	0.72	0.34	1.05	0.06	0.46	0.01	0.07	0.39	0.13	0.02	0.02	0.50	
	Pyroxene	12	49.13	2.15	2.69	0.29	18.32	0.25	11.64	15.64	0.04	0	0.02	100.17	
		SD	0.19	0.16	0.20	0.12	0.96	0.02	0.50	1.00	0.01	0.00	0.02	0.36	
	Ilmenite	10	0.11	53.84	0.32	0.59	42.77	0.29	2.45	0.35	na	na	na	100.71	
		SD	0.17	0.49	0.09	0.19	0.43	0.01	0.05	0.09				0.70	
	Glass	10	41.6	8.49	8.6	0.06	27.89	0.26	2.46	10.97	0.23	0.18	0.45	101.22	
		SD	0.43	0.43	0.72	0.03	1.14	0.02	0.59	0.39	0.05	0.02	0.07	0.44	

Table 3 (continued)

Run	Minerals	n	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
RPW-68 T = 1020 °C	Olivine	12	33.89	0.29	0.07	0.07	48.04	0.38	17.78	0.62	0.01	0.00	0.02	101.17
		SD	0.28	0.03	0.09	0.02	0.59	0.03	0.55	0.08	0.01	0.00	0.02	0.50
	Plagioclase	7	44.67	0.54	33.37	0.02	2.85	0.03	0.38	18.52	0.63	0.08	0.03	101.14
		SD	0.62	0.50	1.63	0.03	1.56	0.02	0.35	0.62	0.14	0.05	0.02	0.73
	Pyroxene	8	49.19	2.36	3.31	0.43	17.16	0.24	12	16.03	0.05	0	0.01	100.79
		SD	0.34	0.15	0.27	0.11	0.41	0.03	0.36	0.60	0.02	0.00	0.01	0.51
	Ilmenite	8	0.07	53.88	0.33	0.73	42.30	0.30	2.69	0.29	na	na	na	100.58
		SD	0.01	0.27	0.01	0.06	0.34	0.02	0.06	0.08				0.41
	Glass	12	40.9	8.16	8.2	0.08	29.42	0.27	3.28	10.48	0.18	0.15	0.4	101.56
		SD	0.52	0.65	0.92	0.02	1.67	0.03	0.35	0.44	0.04	0.01	0.08	1.05
RPW-45* T = 1090 °C	Olivine	12	33.92	0.20	0.06	0.06	44.72	0.38	19.71	0.59	0.00	0.00	0.01	99.79
		SD	0.18	0.04	0.04	0.06	0.43	0.02	0.13	0.06	0.01	0.00	0.01	0.53
	Plagioclase	6	44.81	0.18	34.77	0.02	1.38	0.01	0.17	18.99	0.04	0.50	0.02	100.91
		SD	0.33	0.10	0.40	0.02	0.23	0.02	0.05	0.26	0.01	0.11	0.02	0.30
	Ulvö-spinel	9	0.10	27.14	5.23	11.97	51.63	0.00	0.30	3.15	0.07	0.00	0.01	99.73
		SD	0.02	1.03	0.46	0.82	0.40	0.03	0.08	0.03	0.00	0.00	0.01	0.29
	Pyroxene	6	48.43	2.38	3.13	0.48	17.63	0.24	11.93	16.09	0.05	0	0.02	100.54
		SD	1.22	0.72	1.31	0.12	1.76	0.05	0.99	1.73	0.02	0.00	0.02	0.47
	Glass	11	40.79	7.67	9.17	0.10	27.20	0.24	3.95	11.10	0.26	0.15	0.33	101.04
		SD	0.67	0.53	0.30	0.13	0.81	0.02	0.27	0.29	0.02	0.01	0.03	0.42
RPW-87* T = 1060 °C	Olivine	13	33.00	0.29	0.05	0.05	48.17	0.43	16.34	0.58	0.01	0.00	0.02	99.02
		SD	0.21	0.19	0.01	0.05	0.72	0.04	0.64	0.06	0.01	0.00	0.01	0.25
	Plagioclase	8	44.87	0.17	34.19	0.02	2.19	0.02	0.21	18.07	0.07	0.61	0.02	100.46
		SD	0.35	0.21	0.59	0.05	0.58	0.02	0.15	0.29	0.01	0.08	0.02	0.23
	Ulvö-spinel	10	0.12	29.64	4.23	6.02	53.65	0.00	0.28	2.49	0.22	0.00	0.00	98.42
		SD	0.03	1.05	0.46	1.10	0.79	0.02	0.10	0.05	0.00	0.00	0.00	0.54
	Pyroxene	12	47.56	2.29	3.06	0.25	17.92	0.22	10.36	16.93	0.04	0.00	0.01	98.88
		SD	0.37	0.21	0.39	0.11	0.68	0.04	0.19	0.48	0.02	0.00	0.01	0.43
	Ilmenite	11	0.07	53.07	0.33	0.36	41.66	0.32	2.60	0.29	na	na	na	98.72
		SD	0.05	0.22	0.02	0.13	0.23	0.02	0.07	0.08				0.29
	Glass	12	39.39	7.58	8.72	0.09	29.60	0.25	3.18	9.81	0.29	0.17	0.35	99.52
		SD	0.74	0.69	0.56	0.06	0.90	0.03	0.45	0.31	0.06	0.03	0.14	0.68

RPW-87* was added 1000 ppm trace element into started materials. Also, RPW-87 and RPW-87* were loaded the same assembly, where they were positioned at the upper and lower levels respectively, under 0.5 GPa and 1060 °C. “na” means the chemical content is below the detection limit of EPMA

SD means Standard Deviation

with increasing temperature and/or pressure (Fig. S2). Both pressure and temperature have a negative impact on the partitioning of titanium between pyroxene and silicate melt (Fig. 3). Specifically, the correlation between the TiO₂ content of pyroxene and the partition coefficient $D_{Ti}^{Px/melt}$ with respect to temperature is significantly stronger than that with pressure. The discrepancies in the trends of TiO₂ content in pyroxenes and $D_{Ti}^{Px/melt}$ with pressure observed in this study compared to those reported by Elardo et al. (2015) may attributed to compositional

difference between the two studies. For example, TiO₂ content in pyroxene increases from 0.14 to 2.40 wt% as the Mg# of pyroxene decreased from 77 to 49 (Table 3), and the increment of TiO₂ content in pyroxene could be caused by larger $D_{Ti}^{Px/melt}$ and can also result from the enrichment of TiO₂ content in the basaltic liquid through crystallization (1.52 – 7.70 wt%), which will potentially affect the partitioning of titanium between pyroxene and silicate liquid (Snape et al. 2022). Therefore, we should be careful to use these empirical correlations to estimate

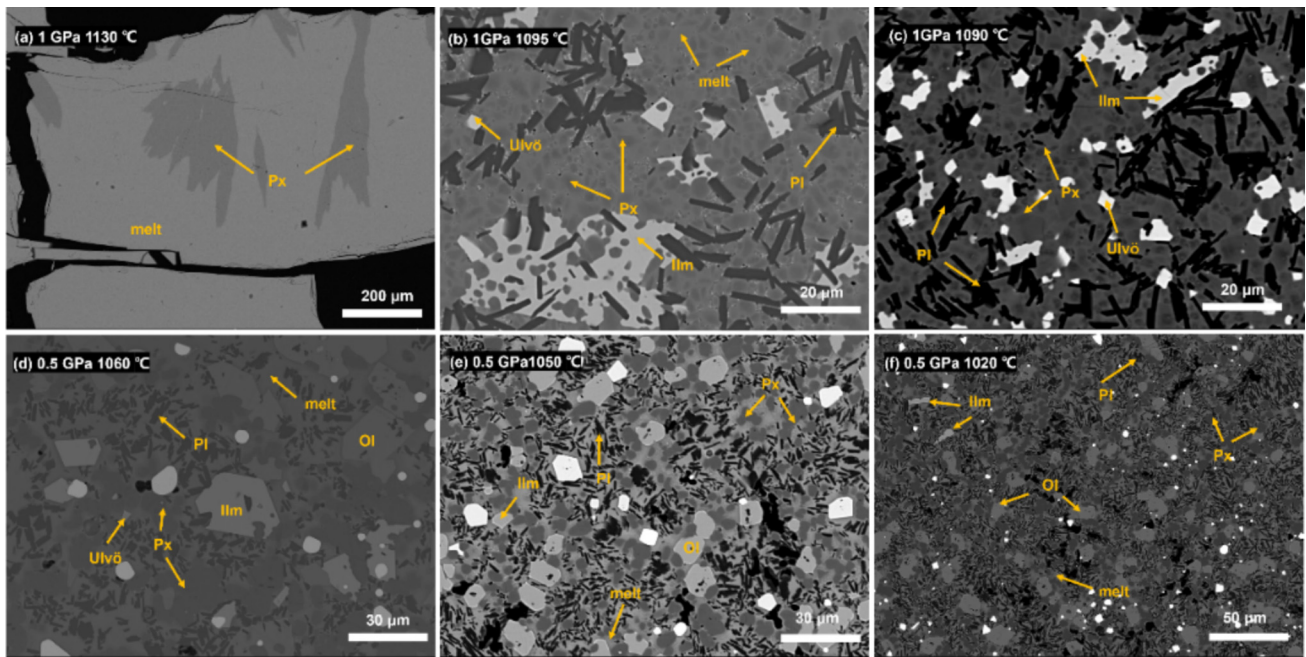


Fig. 2 Back-scattered electron (BSE) images of the run products at 1.0 GPa and 0.5 GPa. Experiment conditions are marked in the figures. Px. pyroxene, Pl. plagioclase, ilm. ilmenite, Ulvö. Ulvö-spinel, Sil. silica-rich phase, melt. silicate liquid

the crystallization conditions of natural samples by using $D_{\text{Ti}}^{\text{Px/melt}}$ or vice versa because the chemical compositions of the pyroxenes and the coexisting silicate liquids have been changing during crystallization.

4.2 Effect of chemical composition on the partitioning of Ti between pyroxene and silicate melt

The seemingly great correlation between the partition coefficient $D_{\text{Ti}}^{\text{Px/melt}}$ and temperature could also be explained by the compositional changes. As shown in Fig. 4, both TiO_2 content in pyroxene and $D_{\text{Ti}}^{\text{Px/melt}}$ show good correlation with Mg# of pyroxene (Fig. 4) and the Mg# of the silicate liquid also show great correlation with temperature (Fig. S3).

On the other hand, the equilibrium crystallization experiments show that pyroxenes formed under relatively higher pressure are orthopyroxene or low-Ca pyroxene (e.g., Putirka et al. 1996; Elardo et al. 2015) and those crystallized from starting materials as CE-5 basalt as shown by this study are mainly high-Ca pyroxenes with some compositional variation. The different CaO content in pyroxenes could be the reason for the discrepancies in the trends of TiO_2 content in pyroxenes and $D_{\text{Ti}}^{\text{Px/melt}}$ with pressure mentioned above (Fig. 3), because as argued by Robinson et al. (2012) that the partitioning of Ti between pyroxene and basaltic magma ($D_{\text{Ti}}^{\text{Px/melt}}$) is linearly correlated with the CaO contents of pyroxenes (X_{CaO}). However, it has also been shown that high-Ca pyroxene can crystallize under relatively high-pressure conditions if the parental magma was enriched with CaO (~11.28 wt%) (Putirka et al.

1996). In other word, the CaO content in pyroxene is mainly controlled by the CaO in the silicate liquid, which in turn affect the partition coefficient $D_{\text{Ti}}^{\text{Px/melt}}$. The linear relationship is reflected in a notably increase of TiO_2 (wt%) content and the partition coefficient $D_{\text{Ti}}^{\text{Px/melt}}$ with increasing CaO (wt%) content and partition coefficient $D_{\text{Ti}}^{\text{Px/melt}}$ versus CaO (wt%) content in pyroxenes present in literature studies (Fig. S4), even though the data are somehow scattered.

The experimental data obtained in this study and those got by Elardo et al. (2015) show a good correlation between CaO and TiO_2 content of pyroxenes (Fig. 5a). The high-Ca pyroxenes (augite) contain more TiO_2 (1.0–2.4 wt%) than low-Ca pyroxenes (pigeonite) (0.14–0.91 wt%). The changes of TiO_2 content of pyroxenes (X_{TiO_2}) with its CaO content (X_{CaO}) can be described as following:

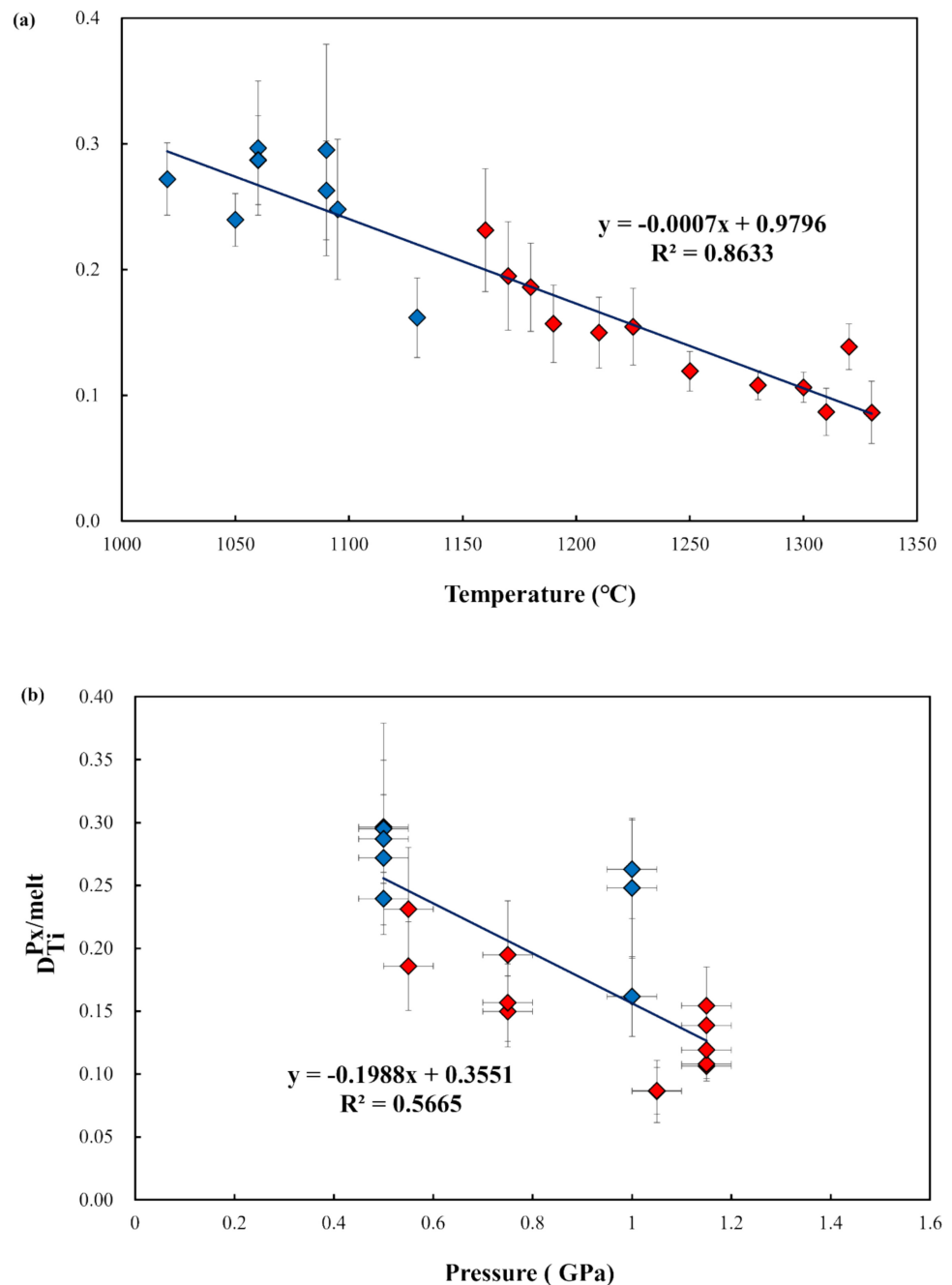
$$X_{\text{TiO}_2} = 0.004X_{\text{CaO}}^2 + 0.084X_{\text{CaO}} - 0.135 (R^2 = 0.94) \quad (1)$$

The partitioning of Ti between pyroxenes and basaltic magma ($D_{\text{Ti}}^{\text{Px/melt}}$) is not linear relationship but strongly corrected with the content dependency of the CaO contents of pyroxenes (X_{CaO}) (Fig. 5b).

$$D_{\text{Ti}}^{\text{Px/Melt}} = -0.0005X_{\text{CaO}}^2 + 0.0218X_{\text{CaO}} + 0.0425 (R^2 = 0.82) \quad (2)$$

The refined correlation between $D_{\text{Ti}}^{\text{Px/melt}}$ and CaO contents of pyroxenes partially offset the negative effect of temperature and pressure on $D_{\text{Ti}}^{\text{Px/melt}}$ as temperature and pressure show

Fig. 3 Partition coefficient of Ti between pyroxene and melt ($D_{Ti}^{Px/melt}$) changes with conditions. **a** Experimental temperatures (°C) and **b** experimental pressures (GPa). Data are from this study (blue) and previous experimental study by Elardo et al. (2015) (red)



similar effect on CaO content in pyroxene (Fig. S5). In cases that the crystallization conditions (pressure and temperature) are blurry, the TiO_2 and CaO content in pyroxenes are useful to evaluate the initial CaO and TiO_2 concentration in the parent magma, but cautions should be taken that this only works for pyroxene crystallized under approximately equilibrium condition.

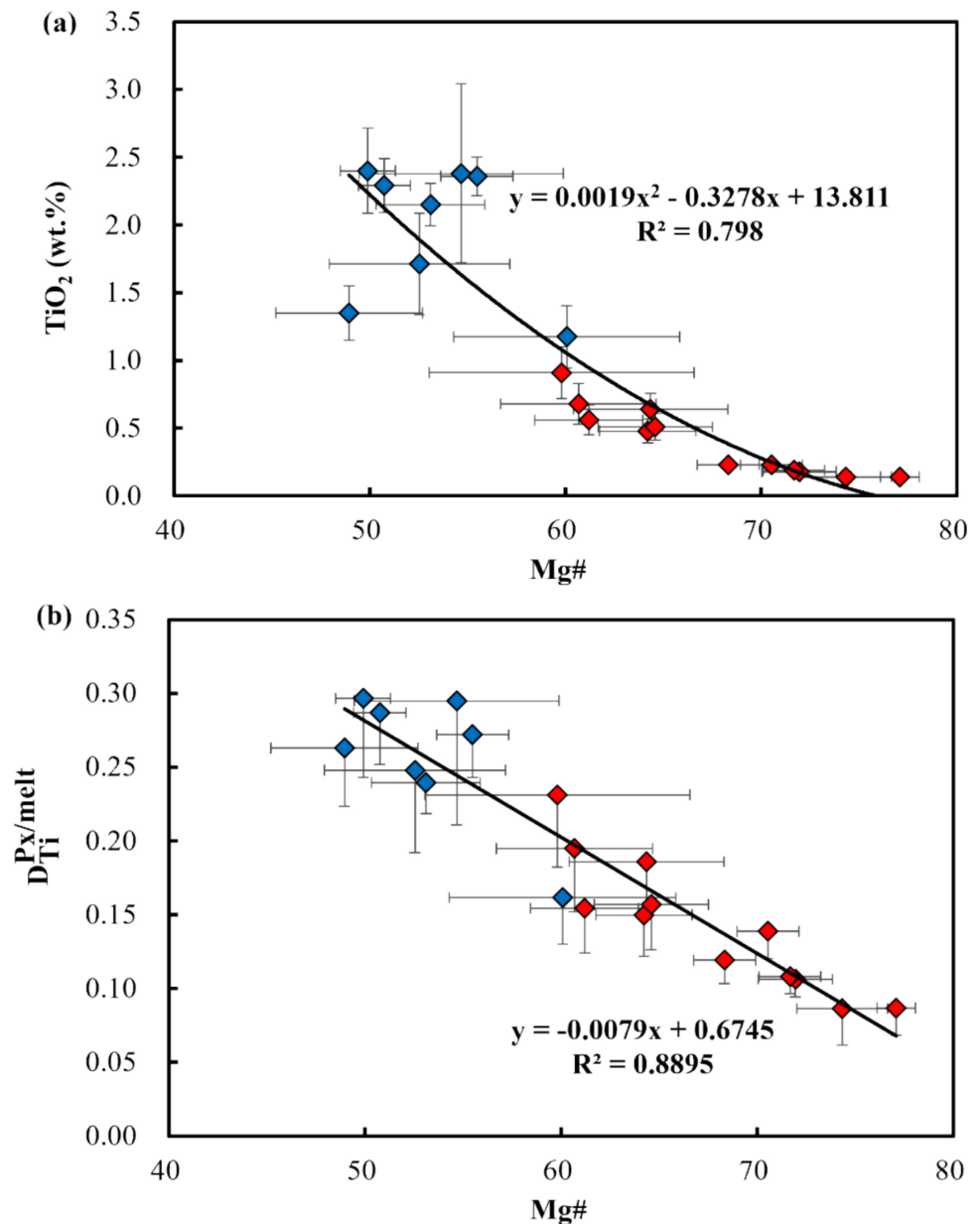
Combining data from this study with those from Elardo et al. (2015), it shows that the CaO content in pyroxene

changes linearly with its Mg# (Fig. 6) and the correlation can be described by second order quadratic polynomial equation:

$$X_{CaO} = 0.004Mg\#^2 - 1.0258Mg\# + 56.694 (R^2 = 0.788) \quad (3)$$

The data deviated from the fitted curve may be explained by the difference on experimental conditions, for example the effect of pressure.

Fig. 4 **a** The TiO_2 content in pyroxene and **b** the partition coefficient of Ti between pyroxene and melt ($D_{\text{Ti}}^{\text{Px/melt}}$) changes with Mg# of pyroxene. The data from this study is in blue and those from Elardo et al. (2015) are in red



4.3 TiO_2 content in Chang'E-5 lunar basalt

Pyroxenes in Chang'E-5 basaltic samples are predominantly augite with trace amount of orthopyroxene (e.g., Che et al. 2021; Li et al. 2021; Tian et al. 2021). The TiO_2 content in pyroxenes varies from 6.38 to 0.62 wt% as the CaO content decreases from 19.1 to 6.17 wt% and Mg# of pyroxene changes from ~60 to ~0.1 (e.g., Che et al. 2021; Tian et al. 2021; He et al. 2022; Jiang et al. 2022). Assuming pyroxene with highest Mg# crystallized very first from the basaltic silicate, Jiang et al. (2022) estimated the TiO_2 content in CE-5 basalt by using the correlation between $D_{\text{Ti}}^{\text{Px/Melt}}$ and CaO content (17.39 wt%)

and TiO_2 content (6.38 wt%) in pyroxenes and argued that CE-5 basalt is high-Ti magma ($\text{TiO}_2 \sim 18.4$ wt%). We calculated the “ideal” TiO_2 content in these pyroxenes by using Eq. (1), which gives a much lower TiO_2 content (2.54 wt%) for the most CaO enriched grain (17.39 wt%). We then use Eq. (2) to calculate the $D_{\text{Ti}}^{\text{Px/Melt}}$ and then TiO_2 content in the coexisting silicate melt, giving 9.4 wt%. This calculated result is lower than those present by Jiang et al. (2022) but is still about 4.4 wt% higher than the bulk composition of CE-5 basalt. Comparing with the pyroxenes and the bulk composition of CE-5 basalt, we suggest that either the pyroxenes crystallized late from the parent magma when the coexisting silicate liquid becoming

Fig. 5 **a** The TiO_2 content in pyroxene shows a great correlation with its CaO content. **b** the changes of $D_{\text{Ti}}^{\text{Px/melt}}$ with CaO content in pyroxene. The data in red is from Elardo et al. (2015), and those from this study are in blue

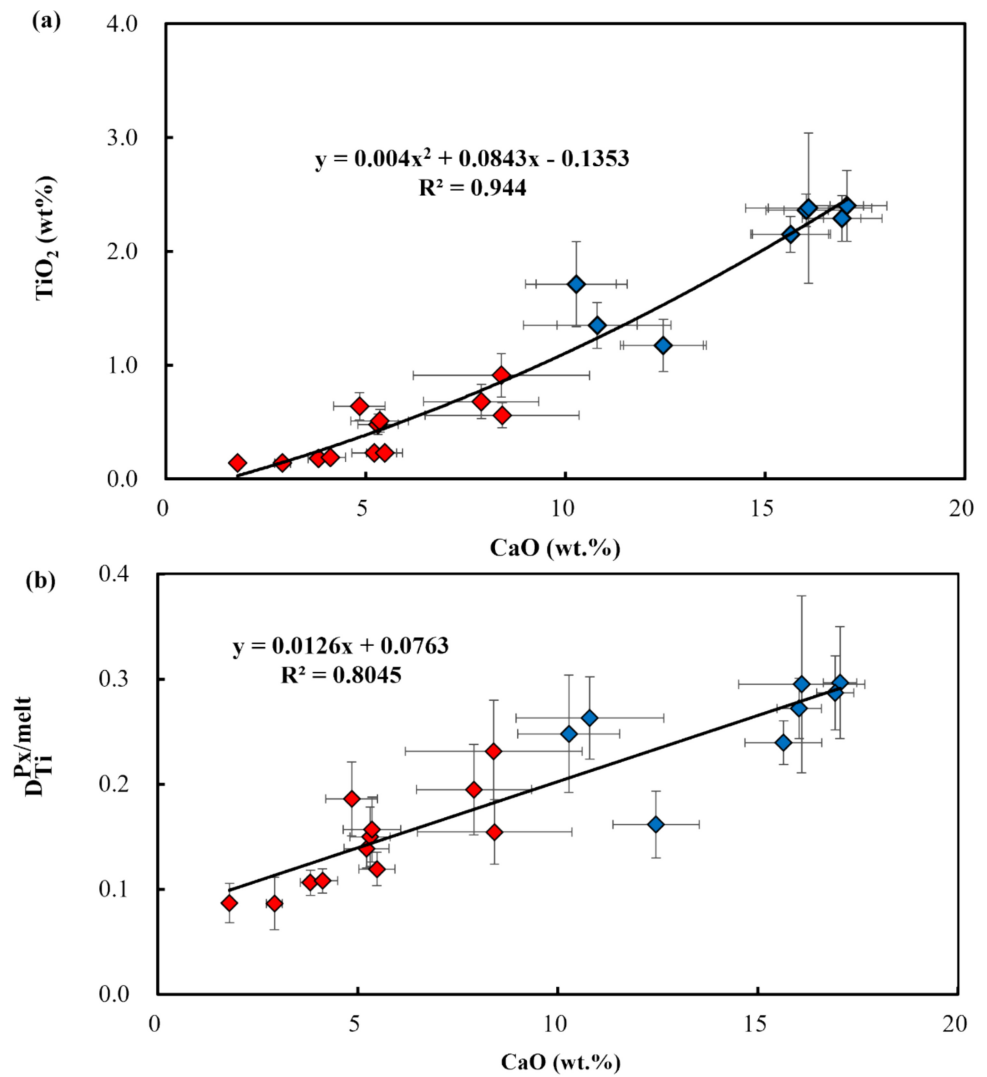
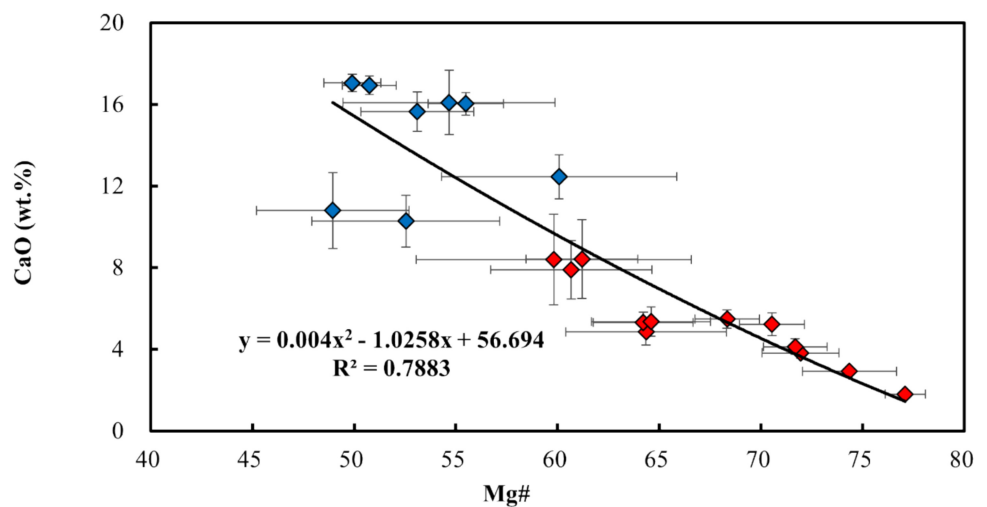


Fig. 6 The CaO content in pyroxene varies with its Mg#. The data in red is from Elardo et al. (2015), and the data in blue is from this study



enriched with TiO_2 or some other mechanism is responsible for the relatively enriched CaO and TiO_2 in pyroxenes from CE-5 basalt. Because pyroxene is not the liquidus phase for experiments at 0.5 GPa, it could explain the relatively high TiO_2 and CaO content in pyroxenes. However, these pyroxenes should also be enriched with FeO, thus smaller Mg# (< 55), which is not the case for the pyroxenes reported from CE-5 basalt.

On the other hand, if we use the correlation between Mg# of pyroxene and its TiO_2 concentration (Fig. 4), we can get the “ideal” TiO_2 content in the most magnesium-rich (Mg# ~ 60) pyroxene grains (~ 0.98 wt%). This pyroxene grain should coexist with silicate magma with TiO_2 content about 4.9 wt% by applying the $D_{\text{Ti}}^{\text{Px/Melt}}$ calculated from Mg#, which is consistent with the reported bulk composition of CE-5 lunar basalt (~ 5.0 wt%) (Li et al. 2021; Zong et al. 2022). And the calculated CaO content in the most magnesium-rich pyroxene by using Eq. (3) established from this study is about 9.55 wt%, according to 1.03 wt% of TiO_2 , which reflects a good correlation between CaO and TiO_2 content in pyroxenes. The calculated CaO and TiO_2 content in MgO-rich pyroxene is much lower than those present in CE-5 basalt, which could not be explained by the partitioning behavior of these two elements unless the CE-5 basalt formed from a basaltic magma that are super enriched with CaO. We should consider another scenario to explain the relatively super enriched with CaO and TiO_2 for pyroxenes from CE-5 basalt, such as fast cooling mechanism. Controlled cooling rate experiments on Apollo 12 samples also show that fast cooling rate can cause depression of phase-appearance temperature (Walker et al. 1976). As mentioned above, the fast-cooling experiments show larger partitioning coefficients of titanium (e.g. Mollo et al. 2013; Snape et al. 2022). Together with the possibility of delayed plagioclase formation thus the co-crystallization of pyroxene and plagioclase, we would expect a relatively higher CaO and TiO_2 content in Mg-rich pyroxenes. Nevertheless, the partition of iron and magnesium between pyroxene and liquid is independent of temperature, pressure and most likely cooling rate as olivine (Walker et al. 1976). This deduction can rationalize the consistency on Mg# of pyroxenes from equilibrium experiments and natural CE-5 samples, which can explain the similar TiO_2 content in CE-5 basalt estimated from Mg-rich olivine (He et al. 2022; Zhang et al. 2022) and Mg# of pyroxene using correlation present in this study.

5 Conclusions

- (1) Equilibrium experimental data on mare basalt shows that the TiO_2 content in pyroxene is linearly correlated with its CaO content.
- (2) The TiO_2 content in the most Mg-rich pyroxene from CE-5 basalts cannot be explained by partition of titanium between pyroxene and silicate liquid but rather implies fast cooling history of CE-5 basalts.
- (3) We suggest using the linear correlation between Mg# of pyroxene and its TiO_2 content to back calculate the TiO_2 content in the coexisting liquid.

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Author contributions Huan Gong: Investigation, experimental design and execution, experimental data collection and analysis, writing original draft and editing; Jing Yang: Methodology, experimental data analysis, writing-reviewing, and editing; Wei Du: Experimental design; methodology, data curation, manuscript structure development, writing-reviewing and editing, project administration, founding acquisition.

Declarations

Conflict of interest The authors declare that they have no conflict of interest to influence the work reported in this paper.

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