

Article

The Influence of Oxygen Fugacity and Water on Silicate Crystallization in the Emeishan Large Igneous Province: Constraints from Thermodynamic Modeling Using MELTS

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Abstract

The Emeishan Large Igneous Province (ELIP) contains high-Mg volcanic rocks, evolved basalts, and Fe-Ti-V-oxide-bearing layered intrusions, providing a natural system for investigating the coupled effects of H₂O and the redox state on silicate crystallization. We modeled three representative starting melts, namely Melt-6 (basaltic), Melt-8 (meimechitic), and Melt-10 (komatiitic), at 5 kbar under prescribed f_{O_2} conditions spanning $\Delta FMQ = -3$ to $+3$ using rhyolite-MELTS. The simulations show that the starting melt composition sets the liquidus temperature and controls whether olivine saturates first. H₂O depresses silicate saturation temperatures, with the strongest effect on plagioclase, whereas f_{O_2} modifies phase relations mainly through Fe^{2+}/Fe^{3+} , effective FeO activity, and competition with Fe-Ti oxide saturation. The orthopyroxene saturation temperature and enstatite-ferrosilite (En-Fs) composition show the strongest redox response, whereas clinopyroxene is buffered by Ca occupancy in the M2 site and plagioclase records mainly the H₂O content and residual melt evolution. These results support a coupled model in which the starting melt, H₂O, and f_{O_2} jointly control crystallization paths and Fe-Ti-V oxide enrichment in ELIP layered intrusions.

Keywords: Emeishan Large Igneous Province; silicate crystallization; Fe-Ti-V oxide mineralization; oxygen fugacity; H₂O; rhyolite-MELTS



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1. Introduction

The evolution of LIP magmatic systems is governed by the source composition, degree of partial melting, magma replenishment, fractional crystallization, volatile activity, and redox state [1–5]. In mafic–ultramafic magmas, olivine, clinopyroxene, orthopyroxene, and plagioclase are the principal silicate phases, and their compositions and textures record the crystallization history of the magma [6–9]. Their saturation temperatures, crystallization sequence, and mineral compositions can be used to infer parental magma Mg, Ca–Al–Ti activities, H₂O activity, Fe^{2+}/Fe^{3+} ratios, and the timing of Fe–Ti oxide saturation [10–14]. The ELIP spans compositions from high-Mg picritic to evolved basaltic magmas and hosts giant Fe–Ti–V oxide deposits, including Panzhihua, Taihe, Hongge, and Baima [15–19]. The

ELIP offers a natural laboratory for investigating the coupled effects of $f\text{O}_2$ and H_2O on silicate crystallization [20].

Previous petrological studies have commonly treated $f\text{O}_2$ and H_2O as separate variables [21]. The $f\text{O}_2$ value has been invoked to explain oxide saturation, Fe-Ti-V enrichment, and Fe-Mg partitioning in silicates, whereas H_2O has been used to account for liquidus depression, delayed plagioclase saturation, and residual melt evolution [22]. In natural magmatic systems, however, these two factors do not operate independently. H_2O modifies the melt structure, viscosity, and phase relations, while $f\text{O}_2$ changes the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and effective FeO activity. Silicate minerals record an integrated response to the starting melt composition, H_2O -mediated melt properties, and $f\text{O}_2$ -driven redox conditions.

Previous studies have constrained ELIP primitive magma compositions and Fe-Ti-V ore genesis using isotopes, whole-rock geochemistry, melt inclusions, and layered-intrusion petrology [6,12,20,23]. Olivine-hosted melt inclusions have been used to constrain primitive magma compositions [6], and trace-element data from olivine and melt inclusions in low-Ti, intermediate-Ti, and high-Ti picrites reveal variable proportions of pyroxenite in the mantle source [21]. For layered intrusions, body-scale modeling, PGE-isotope data, wall-rock contamination studies, and chilled-margin constraints have clarified parental magma compositions and ore-forming processes in the Panzhihua and Hongge intrusions [20,24]. Microtextures and olivine compositional variations have further constrained crystal-melt processes during Fe-Ti oxide mineralization in the Baima intrusion [11,19]. However, an unified thermodynamic framework for evaluating how $f\text{O}_2$ and H_2O jointly regulate crystallization through crystal-site occupancy, coupled cation substitutions, and mineral-melt partitioning is still lacking.

Here, we combine MELTS phase-equilibrium modeling with crystal-chemical analysis to evaluate silicate crystallization in three representative ELIP starting melt compositions at $f\text{O}_2$ from FMQ − 3 to FMQ + 3 (FMQ = fayalite-magnetite-quartz redox buffer, in lg $f\text{O}_2$). The specific aims are threefold: (1) to evaluate the relative contributions of starting melt compositions, H_2O , and $f\text{O}_2$ to liquidus and mineral saturation temperatures; (2) to clarify how M1 and M2 sites in olivine, M1, M2, and T sites in pyroxene, and the T site (Al-Si ordering) in plagioclase respond to these physicochemical variables; and (3) to establish multi-mineral criteria based on Fo, Wo-En-Fs, Ti-Al, and An-Ab-Or systematics for identifying ELIP starting melt compositions with variable H_2O contents, distinguishing crystallization paths, and constraining Fe-Ti-V oxide enrichment mechanisms in layered intrusions.

2. Geological Setting and Starting Melt Compositions

The ELIP is located on the western margin of the Yangtze Block and was emplaced at ~260 Ma during the Late Permian, covering more than $5 \times 10^5 \text{ km}^2$ [1,2]. The rock assemblage includes extensive flood basalts, picrites, meimechites, mafic-ultramafic layered intrusions, and minor felsic volcanic rocks [25]. Based on the volcanic thickness, rock types, and mantle-plume thermal anomalies, the ELIP is subdivided from west to east into inner, middle, and outer zones [6] (Figure 1). The inner zone has the thickest volcanic pile and the most diverse rock types and hosts world-class Fe-Ti-V oxide deposits including Panzhihua, Hongge, Baima, and Taihe [16,26,27].

ELIP basalts are commonly divided into low-Ti ($\text{Ti}/\text{Y} < 500$) and high-Ti ($\text{Ti}/\text{Y} > 500$) series based on their Ti/Y ratios [11]. Kamenetsky et al. (2012) further recognized an intermediate-Ti series transitional between these two compositional groups and suggested that the low-Ti and high-Ti picritic end-members reflect distinct mantle source compositions and degrees of partial melting [28]. Because parental melt compositions inferred for ELIP intrusions vary among studies, we evaluated 14 literature-derived compositions during the initial stage of this study. Three representative starting melts were subsequently selected

for systematic comparative simulations (Table 1). The complete MELTS simulation results are provided in the Supplementary Materials (Supplementary Data Table S1). These compositions span the basaltic-to-komatiitic range and are used to evaluate how the starting melt composition, H_2O , and fO_2 influence silicate crystallization, rather than to reproduce the parental melt of any specific intrusion. All three compositions were taken from published petrological and geochemical studies of the ELIP [6,21,23].

For clarity, the three compositions used as inputs to the simulations are hereafter referred to as Melt-6, Melt-8, and Melt-10. Following the IUGS classification of high-Mg and picritic volcanic rocks, they are classified as basaltic, meimechitic, and komatiitic, respectively (Table 1). These compositions are used as comparative starting melts for MELTS simulations and are not interpreted as products of a single continuous differentiation sequence. Because the three starting melts are natural literature-derived compositions, they are not compositionally orthogonal. We therefore use the fO_2 series within each fixed starting melt to assess redox effects, whereas comparisons among Melt-6, Melt-8, and Melt-10 are used to evaluate the first-order combined effects of the starting composition and initial H_2O content.

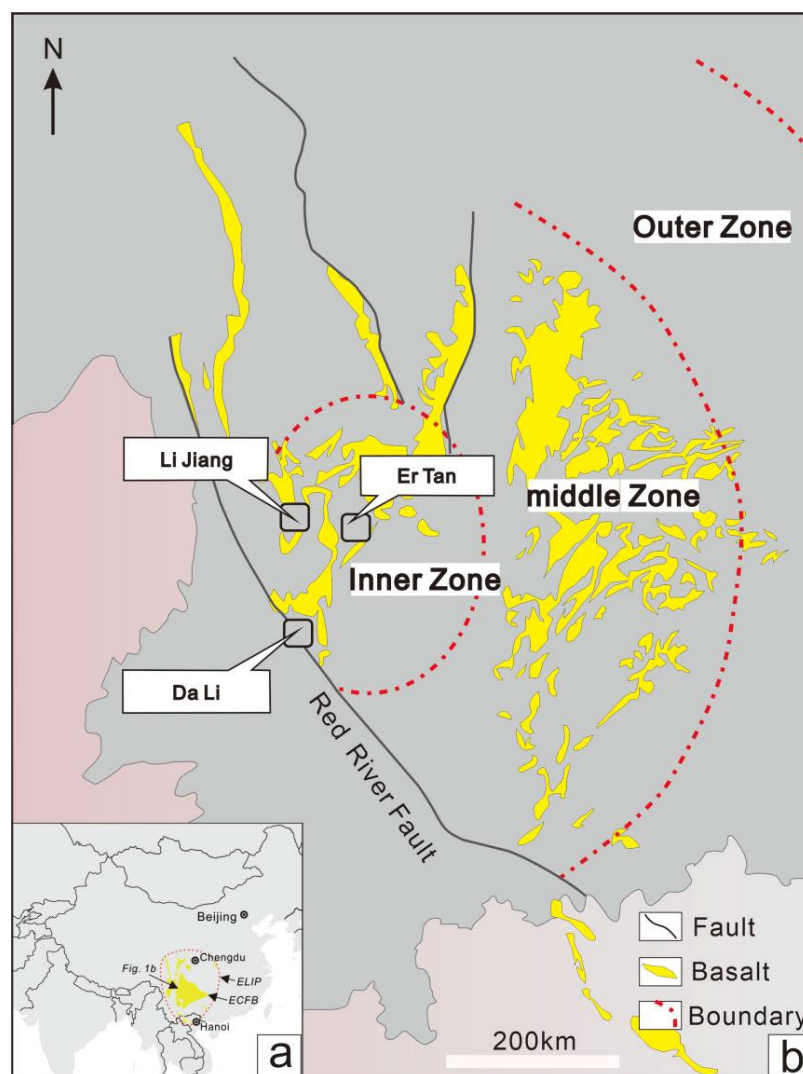


Figure 1. (a) Location of the Emeishan Large Igneous Province (ELIP), SW China and northern Vietnam. (b) Zonation of the ELIP showing the inner, middle, and outer zones and sample localities [6,21].

Table 1. Starting melt compositions and simulation results from MELTS modeling.

IUGS Classification	Composition wt%	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O
Basaltic	Melt-6	45.45	2.73	12.61	13.47	-	0.22	8.46	12.01	2.77	0.29	0.29	0.1
Meimechitic	Melt-8	46.38	2.25	7.91	1.23	11.06	0.07	19.68	9.25	1.41	0.4	0.18	0.5
Komatiitic	Melt-10	46.36	0.96	9.42	1.80	8.68	0.09	20.98	9.91	1.30	0.34	0.16	0
		FMQ	Liquidus Temperature	Olivine	Clinopyroxene			Mineral Saturation Temperature	Apatite	Biotite	Orthopyroxene	Hornblende	
		−3	1257.03	1157.03	1257.03			1177.03	1117.03	897.03	857.03	857.03	
		−2	1258.59	1158.59	1258.59			1178.59	1118.59	898.59	938.59	878.59	
		−1	1260.94	1140.94	1260.94			1180.94	1120.94	900.94	1000.94	880.94	
	Melt-6	0	1265.04	1125.04	1265.04			1185.04	1125.04	925.04	1085.04	845.04	
		1	1271.68	1011.68	1251.68			1191.68	1111.68	911.68	1131.68		
		2	1282.81		1262.81			1202.81	1122.81	882.81	1162.81		
		3	1363.48		1263.48			1203.48	1123.48	843.48	1143.48		
		−3	1468.16	1468.16	1248.16			988.16	1088.16	948.16	1168.16	948.16	
		−2	1466.6	1466.6	1246.6			986.6	1086.6	946.6	1166.6	946.6	
		−1	1464.06	1464.06	1244.06			964.06	1084.06	944.06	1164.06	944.06	
	Melt-8	0	1460.55	1440.55	1240.55			940.55	1080.55	940.55	1280.55	940.55	
		1	1455.27	1435.27	1255.27			935.27	1095.27	955.27	1295.27	935.27	
		2	1527.15	1427.15	1247.15			947.15	1087.15	967.15	1327.15	907.15	
		3	1619.92	1419.92	1259.92			979.92	1079.92	939.92	1359.92	819.92	
		−3	1505.86	1505.86	1285.86			1225.86			1145.86		
		−2	1504.49	1504.49	1284.49			1224.49			1164.49		
		−1	1502.15	1502.15	1302.15			1222.15			1162.15		
	Melt-10	0	1498.83	1478.83	1298.83			1218.83			1158.83		
		1	1494.14	1484.14	1304.14			1184.14			1324.14		
		2	1487.89	1477.89	1307.89			1157.89			1347.89		

3. MELTS Modeling and Crystal-Chemical Framework

Isobaric equilibrium crystallization simulations were performed using rhyolite-MELTS version 1.2.0 [29], which calculates equilibrium phase assemblages by minimizing the Gibbs free energy of the system under the specified *P-T* conditions, starting melt composition, volatile content, and *f*O₂. Rhyolite-MELTS is a recalibrated version of MELTS that retains the general thermodynamic framework of MELTS, while improving phase-equilibrium calculations for silica-rich, fluid-bearing magmatic systems. Although the model was optimized for silicic systems, it inherits the broader MELTS formulation for multicomponent magmatic liquids and has been applied to both hydrous and anhydrous crystallization calculations. All runs were conducted at 5 kbar, equivalent to a crustal depth of approximately 15 km. This pressure was selected to represent a mid-crustal storage and crystallization level for the inner ELIP. Published petrological and geological constraints suggest that the Panzhihua and related inner-zone layered intrusions were emplaced and began crystallizing at pressures close to 5 kbar [15,26]. Thus, 5 kbar is used as a representative reference condition rather than as a universal pressure for all ELIP magmas. The temperature was varied from 2000 °C to 800 °C at a constant step size of 20 °C. Because phase appearance was evaluated at 20 °C intervals, the reported saturation temperatures should be regarded as step-resolution estimates, and differences smaller than one temperature step are not over-interpreted. Because the calculations are equilibrium crystallization runs, they do not simulate crystal accumulation, compositional stratification, or the fractional removal of solids.

The *f*O₂ value was expressed as an offset from the FMQ buffer. Seven prescribed redox conditions were considered: FMQ − 3, FMQ − 2, FMQ − 1, FMQ, FMQ + 1, FMQ + 2, and FMQ + 3. In rhyolite-MELTS, *f*O₂ was imposed using the *f*O₂ Constraint command. The Compute Redox State command was then used to calculate the Fe³⁺/Fe²⁺ ratio of the input melt under each prescribed *f*O₂ condition, followed by the Normalize command to renormalize the input composition while preserving the specified redox state. These *f*O₂ values represent controlled redox scenarios for the isobaric equilibrium-crystallization simulations, rather than a continuous *f*O₂ evolution path during the crystallization of a natural intrusion.

The model outputs provide three key types of information [30]: (1) the liquidus temperature, defined as the temperature at which the first solid phase appears; (2) the saturation temperatures of olivine, clinopyroxene, orthopyroxene, and plagioclase, defined as their respective first appearance temperatures; and (3) oxide contents in the residual melt and crystallizing minerals.

We interpret the outputs within the framework of mineral-melt partitioning and crystal-chemical site occupancy [31,32]. Olivine Fo records Mg^{2+} - Fe^{2+} exchange between the M1/M2 octahedral sites and the melt [33]. Clinopyroxene Wo is buffered by preferential Ca^{2+} occupancy in the M2 site [34,35]. Orthopyroxene lacks an equivalent Ca-rich site, making its En-Fs exchange more sensitive to effective FeO activity [36]. Plagioclase An-Ab exchange mainly reflects Ca/Na activity and crystallization temperature [37]. Mineral compositions thus record the coupled effects of the site capacity, melt-component activity, and competition among co-crystallizing phases.

Additional sensitivity tests were performed using the Melt-8 composition to evaluate the effect of H_2O independently of the main comparison among the three starting melts. The Melt-8 was modeled at 5 kbar and FMQ – 1 under nominally anhydrous and hydrous conditions. These tests were designed to assess whether feldspar delay can be reproduced when the starting melt composition, pressure, and $f\text{O}_2$ are held effectively constant, rather than to represent a full factorial simulation of all ELIP melt compositions.

Because the present simulations were designed to investigate silicate crystallization and Fe-Ti oxide saturation, sulfur contents, sulfur speciation, and sulfide compositions were not independently prescribed in the model. Sulfide saturation and SCSS were therefore not evaluated in this study.

4. Results

4.1. Liquidus Temperature

Liquidus temperatures are primarily controlled by the starting melt MgO content (Figure 2). The MgO-rich Melt-8 and Melt-10 have higher liquidus temperatures than the evolved, basaltic Melt-6, in which olivine saturation is delayed.

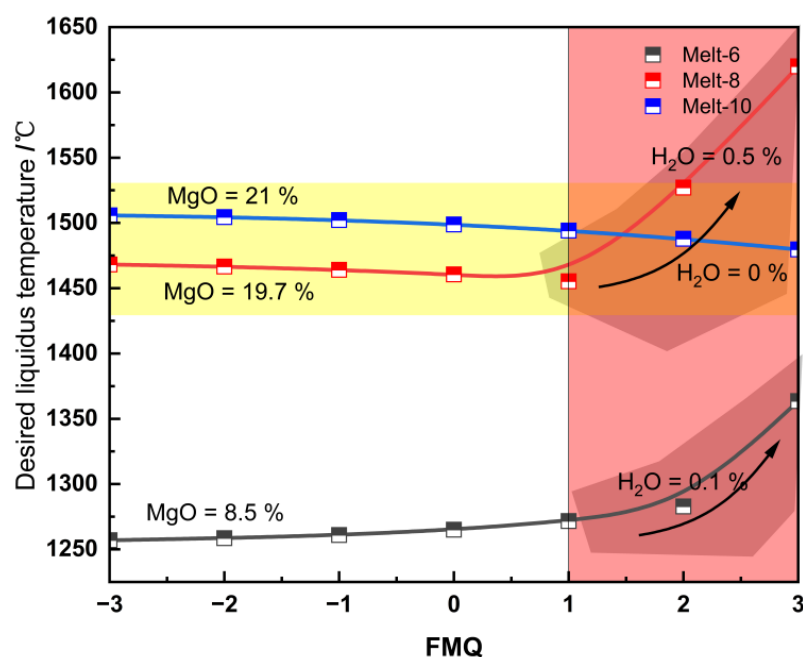


Figure 2. Liquidus temperatures of the three starting melt compositions as a function of $f\text{O}_2$.

The liquidus response to fO_2 varies with the H_2O content. In anhydrous Melt-10, the liquidus decreases by $\sim 22^\circ\text{C}$ as fO_2 increases from FMQ – 3 to FMQ + 2. Hydrated Melt-8 and Melt-6 have systematically lower liquidus temperatures than Melt-10, consistent with a liquidus-depressing effect of H_2O ; this effect is isolated more directly by the fixed-composition S8 sensitivity test. At the oxidized end, however, the hydrated compositions show a sharp liquidus increase, suggesting that H_2O can amplify the fO_2 response through changes in Fe^{2+}/Fe^{3+} , melt polymerization, and early phase saturation. Thus, ELIP mafic-ultramafic magma liquidus temperatures reflect coupled control by MgO , H_2O , and fO_2 rather than fO_2 alone.

4.2. Mineral Saturation Temperatures and Crystallization Sequence

The MELTS simulations reveal distinct saturation temperatures and crystallization sequences for olivine, clinopyroxene, orthopyroxene, and plagioclase among the three systems (Figure 3). Olivine saturates first in high-MgO melts, whereas clinopyroxene and plagioclase appear earlier in the low-MgO melt. Increasing fO_2 systematically raises the orthopyroxene saturation temperature and shifts orthopyroxene to earlier positions in the crystallization sequence (Figure 4).

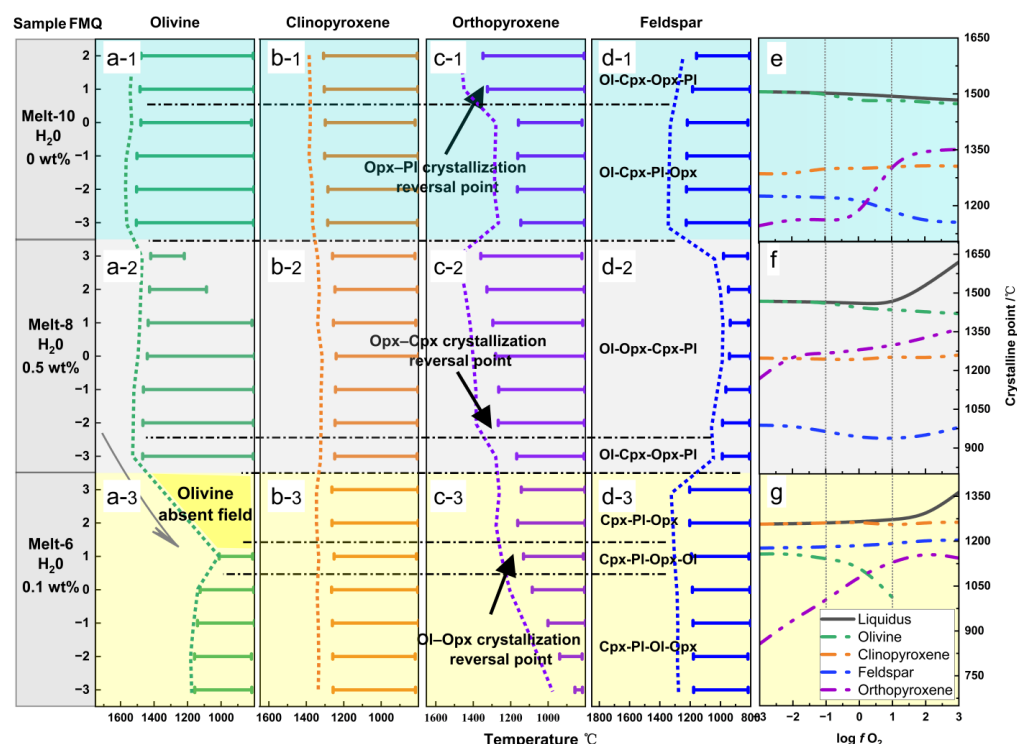


Figure 3. Saturation temperatures of silicate minerals and their crystallization sequences as a function of fO_2 . Panels (a-1–d-1) show the saturation temperatures of olivine, clinopyroxene, orthopyroxene, and feldspar, respectively, for Melt-10. Panels (a-2–d-2) show the corresponding results for Melt-8, whereas panels (a-3–d-3) show the corresponding results for Melt-6. Panels (e–g) present the combined crystallization-temperature curves, including the liquidus, olivine, clinopyroxene, orthopyroxene, and feldspar, for Melt-10, Melt-8, and Melt-6, respectively. These combined plots illustrate the relative crystallization sequence of the minerals under different oxygen-fugacity conditions.

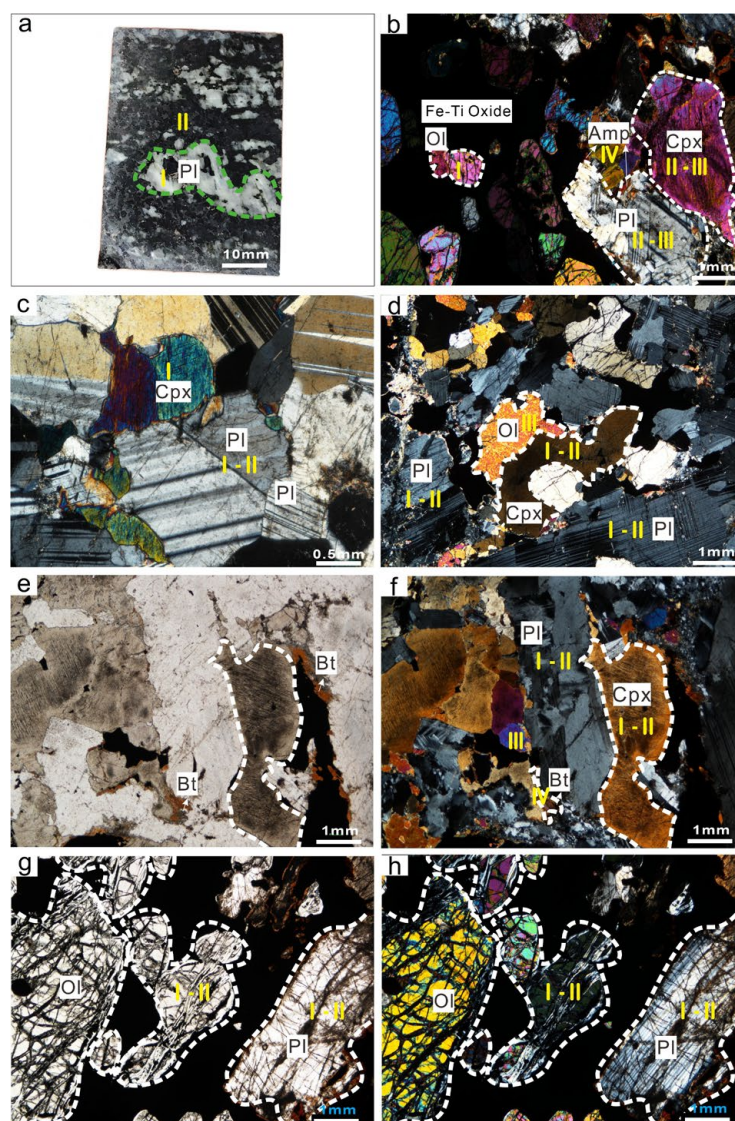


Figure 4. Petrographic features of silicate minerals and Fe-Ti oxides in layered intrusions of the Emeishan Large Igneous Province. (a) Hand-specimen photograph showing early coarse-grained plagioclase intergrown with late fine-grained clinopyroxene in gabbro from the Baima intrusion; (b) photomicrograph of a polished thin section under cross-polarized transmitted light showing plagioclase, olivine, clinopyroxene, and amphibole that texturally predate Fe-Ti oxides in olivine gabbro; (c) photomicrograph of a polished thin section under cross-polarized transmitted light, showing granular clinopyroxene enclosed by plagioclase grains in gabbro; (d) photomicrograph of a polished thin section under cross-polarized transmitted light, showing late-formed, cleavage-free olivine filling interstices between plagioclase and clinopyroxene in olivine gabbro; (e) photomicrograph of a polished thin section under plane-polarized transmitted light, showing late-formed biotite enclosing clinopyroxene in gabbro; (f) photomicrograph of a polished thin section under cross-polarized transmitted light, showing plagioclase and clinopyroxene grains of a similar size in gabbro; (g) photomicrograph of a polished thin section under plane-polarized transmitted light, showing coarse-grained plagioclase intergrown with fine-grained olivine and enclosed in Fe-Ti oxides in troctolite; (h) the same area as in (g), under cross-polarized transmitted light. Roman numerals I–IV indicate the relative crystallization order of the minerals shown, with I–III marking the main silicate phases and IV marking Fe-Ti oxides. Abbreviations: Pl, plagioclase; Ol, olivine; Cpx, clinopyroxene; Amp, amphibole; Bt, biotite. The images document natural petrographic relationships among silicate minerals and Fe-Ti oxides and are not direct outputs of the MELTS simulations.

4.2.1. Anhydrous High-MgO System

Olivine is the liquidus phase in the anhydrous high-MgO system, with the highest saturation temperatures (1488–1506 °C) (Figures 3e and 4g,h). Its saturation temperature decreases only slightly with increasing fO_2 , indicating that olivine stability in anhydrous high-Mg melts is primarily controlled by MgO activity, whereas fO_2 exerts only a limited influence on Fe-Mg exchange through changes in the Fe^{2+}/Fe^{3+} ratio (Figure 3(a-1)) [33]. The plagioclase saturation temperature decreases from 1226 °C to 1158 °C with an increasing fO_2 (Figure 3(d-1)). The clinopyroxene saturation temperature remains relatively stable (1284–1308 °C) and shows little dependence on fO_2 , suggesting that its saturation is governed mainly by Ca-Mg-Si component activities (Figure 3(b-1)). Orthopyroxene is the most fO_2 -sensitive phase: its saturation temperature increases from 1146 °C under reduced conditions to 1348 °C under oxidized conditions, shifting the crystallization sequence from Ol-Cpx-Pl-Opx at FMQ – 3 to Ol-Cpx-Opx-Pl between FMQ and FMQ + 2 (Figure 3(c-1)).

4.2.2. Hydrous High-MgO System

Olivine remains the liquidus phase in hydrous high-MgO Melt-8 (Figure 3f), but its saturation temperature (1420–1470 °C) is lower than in Melt-10 (Figure 3(a-2)). Clinopyroxene saturates at 1240–1260 °C and varies slightly with fO_2 (Figure 3(b-2)). Orthopyroxene crystallizes earlier as fO_2 increases, with the saturation temperature rising from 1168 °C to 1320–1360 °C (Figure 3(c-2)). Except at FMQ – 3, the dominant sequence is Ol-Opx-Cpx-Pl (Figure 4b). The effect of H₂O on the liquidus is comparatively modest and composition-dependent, whereas its influence on plagioclase saturation can be substantially larger. Plagioclase has the lowest saturation temperature (935–988 °C) (Figure 3(d-2)), reflecting strong suppression of the plagioclase stability field by H₂O.

4.2.3. Hydrous Low-MgO System

The crystallization sequence of Melt-6 (0.1 wt% H₂O) differs markedly from those of Melt-8 and Melt-10, with olivine saturation strongly delayed in the low-MgO melt (Figure 3(a-3)). Clinopyroxene is the first phase to saturate under all fO_2 conditions (1251–1265 °C), indicating that Ca-Mg-Si component activities favor early clinopyroxene crystallization (Figure 3(b-3)). Plagioclase saturates shortly thereafter at approximately 1178–1203 °C (Figure 3(d-3)). Olivine is present only between FMQ – 3 and FMQ + 1, with its saturation temperature decreasing from 1158 °C to 1011 °C with an increasing fO_2 and is absent at FMQ + 2 and FMQ + 3 (Figure 3g). Orthopyroxene crystallizes significantly earlier with an increasing fO_2 , and its saturation temperature increases from 857 °C to 1162 °C (Figure 3(c-3)). The crystallization sequence thus changes from Cpx-Pl-Ol-Opx under reduced conditions, through Cpx-Pl-Opx-Ol (Figure 4a,d–f) at intermediate fO_2 , to Cpx-Pl-Opx (Figure 4c) under strongly oxidized conditions, where olivine is absent.

In summary, olivine saturation is controlled mainly by the melt MgO content (Melt-10 > Melt-8 >> Melt-6), clinopyroxene saturation is buffered by Ca-Mg-Si component activities, orthopyroxene shows the strongest positive response to fO_2 , and plagioclase saturation is most strongly depressed by H₂O. Crystallization sequences such as Ol-Cpx-Pl-Opx, Ol-Opx-Cpx-Pl, and Cpx-Pl-Opx can thus serve as mineralogical indicators of the starting melt MgO content, H₂O content, and redox state in ELIP magmas.

4.3. Sensitivity Tests for H₂O and Pressure

The sensitivity tests further illustrate that H₂O and pressure affect different parts of the crystallization sequence. In the Melt-8 at 5 kbar and FMQ – 1, the addition of 0.5 wt% H₂O lowers the liquidus temperature only slightly, from 1482 °C to 1464 °C. In contrast, feldspar saturation is strongly delayed, from 1162 °C in the nominally anhydrous run to 964 °C

in the hydrous run, and the initial An component decreases from 0.46 to 0.38 (Figure 5a). Orthopyroxene and clinopyroxene saturation temperatures decrease by approximately 78 °C and 38 °C, respectively. These results show that the delayed feldspar saturation in the hydrous Melt-8 is reproduced when the starting melt composition, pressure, and fO_2 are held effectively constant.

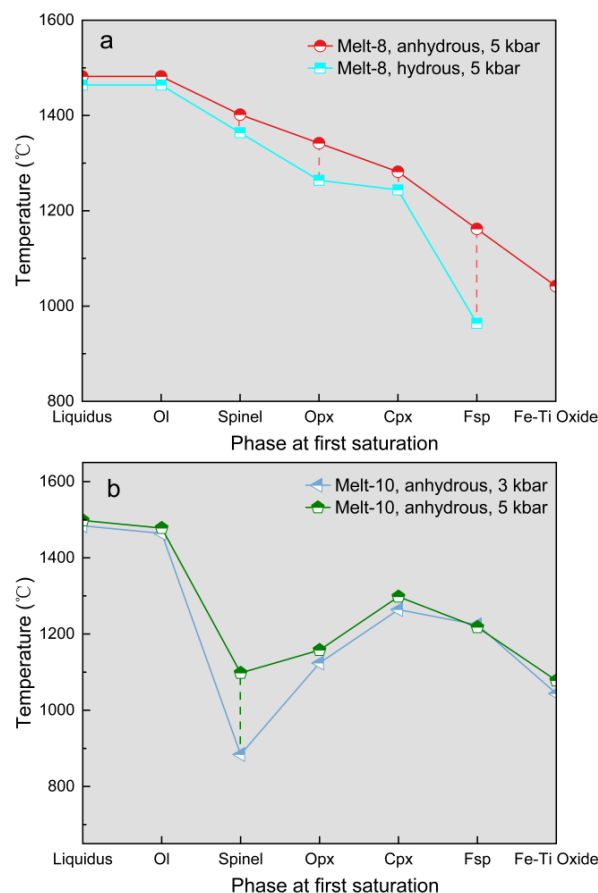


Figure 5. Sensitivity tests showing first-saturation temperatures of major mineral phases. (a) comparison between nominally anhydrous and hydrous Melt-8 at 5 kbar and FMQ – 1. (b) Pressure sensitivity test comparing anhydrous Melt-10 at 3 and 5 kbar under FMQ-1 conditions. Ol = olivine; Opx = orthopyroxene; Cpx = clinopyroxene; Fsp = feldspar.

The pressure test shows that changing the pressure from 5 to 3 kbar modifies the absolute saturation temperatures of spinel, pyroxenes, feldspar, and Fe-Ti oxides, although the high-Mg melt remains olivine-saturated at the liquidus (Figure 5b). This result supports the use of 5 kbar as a representative reference pressure for mid-crustal layered-intrusion crystallization, while also confirming that pressure-dependent shifts in phase stability should be considered when comparing the model results with natural ELIP rocks.

4.4. Mineral Compositions

4.4.1. Olivine Fo and Fe-Mg Partitioning

The olivine end-member composition is expressed as Fo (Equation (1)). Fo values follow the order Melt-10 > Melt-8 > Melt-6, confirming that the starting melt MgO content is the first-order control (Figure 6). For a given initial composition, higher- fO_2 runs generally produce higher-Fo olivine because oxidation converts Fe^{2+} to Fe^{3+} in the melt [38,39]. Since olivine M1 and M2 sites mainly accommodate divalent cations, increasing fO_2 lowers the effective FeO activity available for Fe-Mg exchange and makes olivine relatively Mg-rich. With a falling temperature, Fo decreases in all systems as Mg is preferentially consumed

and Fe^{2+} becomes enriched in the residual melt. High $f\text{O}_2$ suppresses this Fa increase by reducing the Fe^{2+} available for incorporation into olivine [33].

$$Fo = 100 \times \text{Mg} / (\text{Mg} + \text{Fe}^{2+}) \quad (1)$$

where Mg and Fe^{2+} are the mole fraction of Mg and Fe^{2+} elements in olivine.

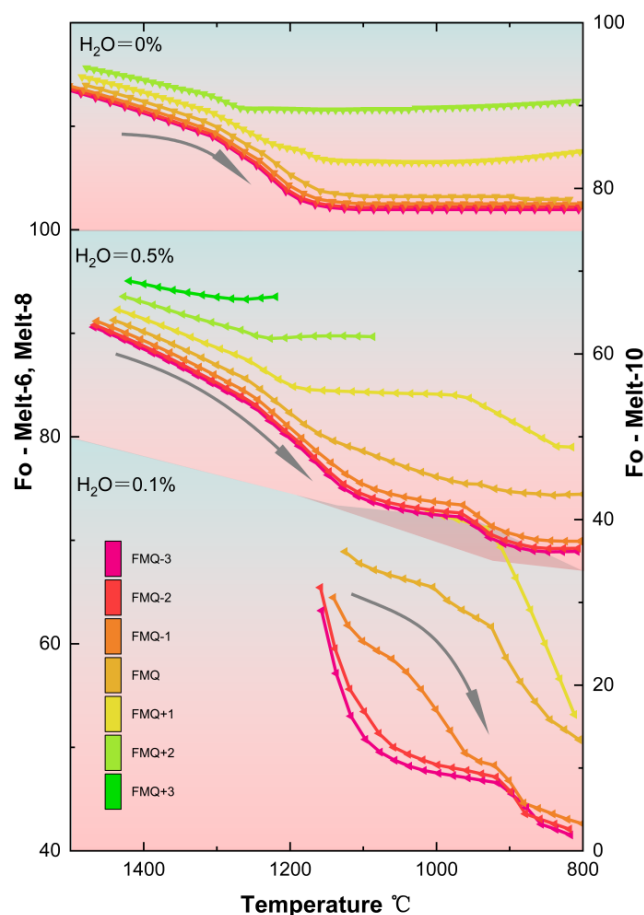


Figure 6. Variation in olivine Fo with temperature and $f\text{O}_2$ for the three end-member systems.

The olivine-melt Fe-Mg exchange coefficient K_D (Equation (2)) was calculated following Roeder (1970) [38]. The modeled K_D decreases from 0.36 to 0.25 as $f\text{O}_2$ increases from FMQ − 3 to FMQ + 3 (Figure 7), which is consistent with experiments showing lower K_D at a higher melt $\text{Fe}^{3+}/\Sigma\text{Fe}$ [40]. This trend indicates that $f\text{O}_2$ regulates Fe-Mg partitioning by changing the melt $\text{Fe}^{3+}/\text{Fe}^{2+}$ and, where Fe-Ti oxides saturate, by partitioning Fe into coexisting oxide phases. H_2O further lowers the viscosity and enhances interfacial exchange, allowing Fo to track the melt differentiation more closely.

$$K_D^{\text{Fe-Mg}} = (X_{\text{FeO}}/X_{\text{MgO}})_{\text{ol}} / (X_{\text{FeO}}/X_{\text{MgO}})_{\text{liq}} \quad (2)$$

where X_{FeO} and X_{MgO} denote the mole fractions of the FeO and MgO components, respectively, and the subscripts “ol” and “liq” refer to olivine and liquid (melt), respectively. Only ferrous iron (Fe^{2+} , expressed as FeO) is included in the calculation. $K_D^{\text{Fe-Mg}}$ is dimensionless.

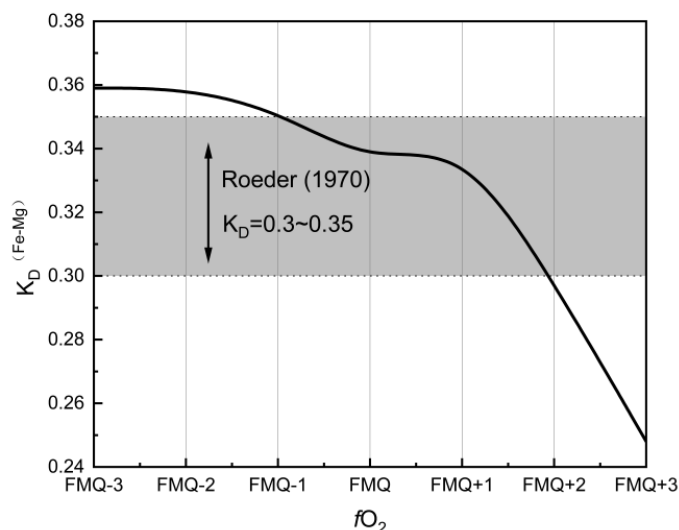


Figure 7. Covariation of olivine-melt Fe-Mg exchange coefficient (K_D) with fO_2 .

The stronger Fo decrease in Melt-8 than in Melt-10 is consistent with enhanced Fe-Mg exchange under hydrous conditions. Overall, olivine Fo mainly records the starting melt MgO content, with fO_2 modifying effective Fe-Mg partitioning and H_2O amplifying exchange kinetics.

4.4.2. Ca Buffering and Ti-Al Substitution in Clinopyroxene

Clinopyroxene compositions are expressed as Wo (wollastonite), En (enstatite), and Fs (ferrosilite) [7]. Clinopyroxenes from all three systems plot in the diopside-augite field (Figure 8), are enriched in Wo and En, and have low Fs contents. This indicates crystallization from relatively primitive mafic melts rather than Fe-rich evolved liquids.

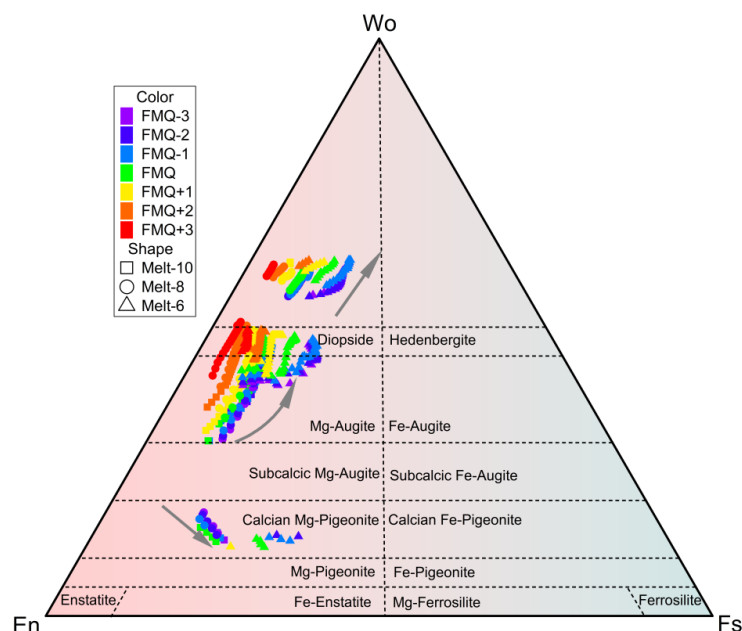


Figure 8. Clinopyroxene end-member compositions as a function of temperature and fO_2 .

The clinopyroxene in Melt-10 has the widest compositional range (Wo15.3–49.52, En44.16–68.55, and Fs3.9–20.19). Fs decreases from 11 to 4 mol% with an increasing fO_2 , consistent with lower effective Fe^{2+} activity under oxidized conditions. Melt-8 is similar to Melt-10 but contains more high-Wo clinopyroxene, probably because H_2O enhances Ca

diffusion and delayed plagioclase saturation keeps Ca activity high in the residual melt. Melt-6 contains the most Fs-rich clinopyroxene, reflecting the higher Fe^{2+}/Mg ratio of the evolved low-MgO melt.

The effect of $f\text{O}_2$ on the clinopyroxene end-member composition is mainly expressed as a systematic decrease in Fs. Under reduced conditions (FMQ – 3 to FMQ – 1), some data points shift toward the low-Wo (<25 mol%) and high-Fs (>15 mol%) calcic magnesian pigeonite field, suggesting that higher Fe^{2+} activity at low $f\text{O}_2$ promotes Fe^{2+} incorporation into the M1 site. As $f\text{O}_2$ increases to FMQ + 2 and FMQ + 3, Fs generally decreases to <8 mol%, and clinopyroxene compositions shift toward Ca-Mg-rich, Fe-depleted values.

The T site in clinopyroxene is occupied mainly by Si^{4+} , with Al^{3+} substituting for Si^{4+} . The M1 site primarily accommodates Mg^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , and Ti^{4+} (Figure 9), whereas the M2 site preferentially accommodates Ca^{2+} , Na^{+} , and minor Fe^{2+} and Mg^{2+} [8,30]. Clinopyroxene can therefore adjust its composition through the buffering reactions shown in Equation (3).

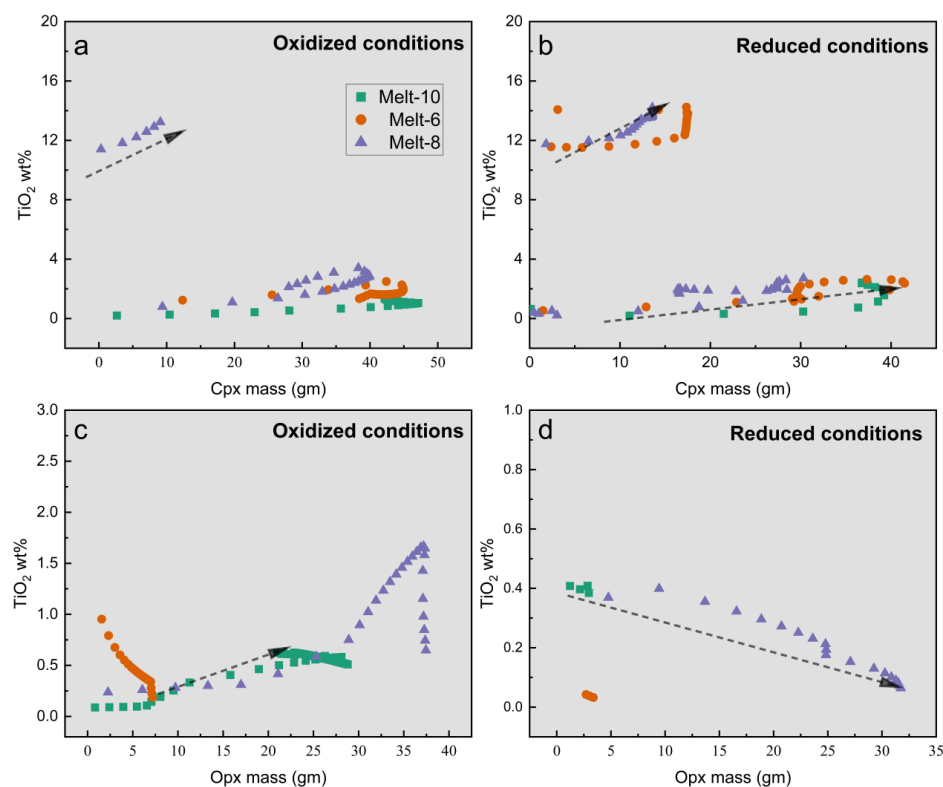
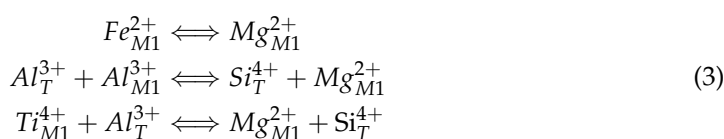


Figure 9. Variation in TiO_2 content with the relative mass proportions of clinopyroxene and orthopyroxene under different redox conditions. (a) TiO_2 content versus clinopyroxene mass under oxidized conditions. (b) TiO_2 content versus clinopyroxene mass under reduced conditions. (c) TiO_2 content versus orthopyroxene mass under oxidized conditions. (d) TiO_2 content versus orthopyroxene mass under reduced conditions. Green squares, orange circles, and purple triangles represent Melt-10, Melt-6, and Melt-8, respectively. Dashed lines and arrows indicate the principal compositional trends.

Preferential Ca occupancy in the M2 site limits Fe^{2+} incorporation there and confines most Fe^{2+} to M1. Increasing $f\text{O}_2$ lowers the melt Fe^{2+}/Mg and reduces Fs, but stable Ca occupancy keeps Wo relatively constant. Clinopyroxene therefore shows weaker $f\text{O}_2$ -driven end-member shifts than olivine or orthopyroxene.

4.4.3. Orthopyroxene: A Highly Sensitive Response Mechanism

The simulation results show that orthopyroxenes from all three systems plot along the enstatite-ferrosilite solid-solution series, with Wo generally lower than 5 mol% (Figure 10). This indicates that the orthopyroxene lattice has limited capacity for Ca incorporation and that its end-member variation is controlled mainly by Mg-Fe exchange.

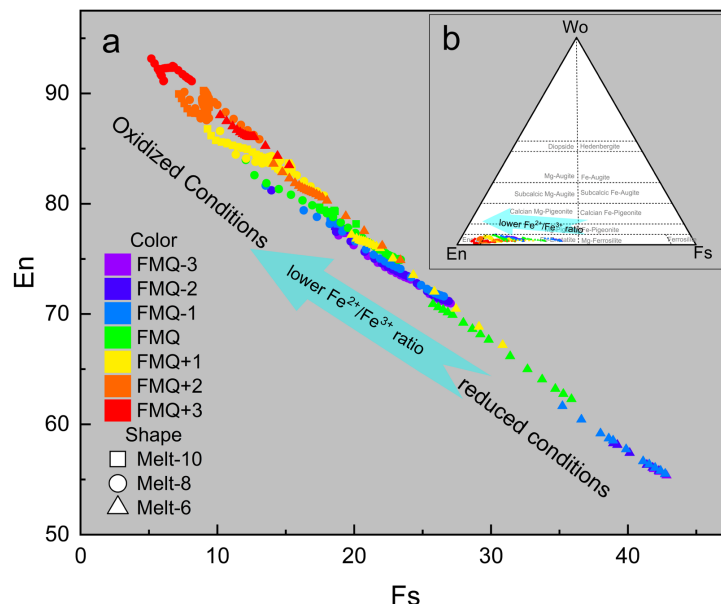


Figure 10. (a) Wo-En-Fs ternary diagram of orthopyroxene compositions from the three end-member systems. (b) En versus Fs diagram.

The orthopyroxene in Melt-10 is the most En-rich (Wo0.75–4.37, En77.32–90.27, and Fs7.18–20.13), reflecting the high-MgO primitive melt. Melt-8 has the widest range (Wo0.75–4.83, En70.98–93.16, and Fs5.17–27.05), consistent with a stronger response to fO_2 and differentiation under hydrous conditions. Melt-6 is the most Fs-rich (Wo1.25–3.34, En55.36–88.02, and Fs10.21–42.83), reflecting the higher Fe^{2+}/Mg ratio of the evolved low-MgO melt.

Oxygen fugacity exerts a strong influence on the orthopyroxene end-member composition. As fO_2 increases from reduced to oxidized conditions, all three systems show a systematic increase in En and decrease in Fs, with this trend being most pronounced in Melt-6. From FMQ – 3 to FMQ + 3, Fs decreases from 42 mol% (En ~55–56) to 10–15 mol% (En ~83–88). This variation indicates that increasing fO_2 promotes the conversion of Fe^{2+} to Fe^{3+} in the melt and reduces the effective Fe^{2+} activity available for incorporation into the orthopyroxene lattice. Consequently, the Fs component is suppressed and the En component increases.

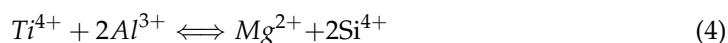
Orthopyroxene is a low-Ca chain silicate in which the M1 and M2 sites are occupied mainly by Mg^{2+} and Fe^{2+} . Ca occupancy at the M2 site is much lower than in clinopyroxene. The smaller M1 site preferentially accommodates Mg^{2+} , whereas the larger M2 site can accommodate Fe^{2+} and minor Ca^{2+} [31]. Owing to structural constraints, however, the capacity of the M2 site for Ca^{2+} is extremely limited, so Ca enters the lattice only as a minor Wo component. En-Fs exchange is therefore more directly sensitive to effective FeO activity and the evolving composition of the residual melt.

H_2O mainly expands the range of Opx end-member variation. In Melt-8, the large En-Fs range indicates that lower viscosity and faster Fe-Mg diffusion allow Opx to record fO_2 -driven changes in the melt Fe^{2+}/Mg more effectively. Melt-10 remains En-rich and

displays a narrower compositional range, whereas Melt-6 produces Fs-rich Opx under reduced conditions because of its low-MgO, high-Fe/Mg melt composition.

Overall, orthopyroxene is the most sensitive silicate recorder of fO_2 in these simulations. Its low Wo content and wide En-Fs variability allow a direct response to the melt Fe^{2+}/Mg , whereas fO_2 controls Fs through Fe^{2+}/Fe^{3+} [31]. The high-Fs, low-En Opx in Melt-6 indicates an evolved, Fe^{2+} -rich melt, whereas the high-En Opx in Melt-8 and Melt-10 reflects high-MgO melts and reduced effective Fe^{2+} activity under oxidized conditions.

The incorporation of Ti into pyroxene requires charge balance. A typical Ti-Tschermak-type coupled substitution can be expressed as Equation (4):



4.4.4. Plagioclase Response to H_2O

Plagioclase compositions are expressed as An, Ab, and Or [7,22]. All three systems are dominated by An-Ab solid solutions, with Or generally <5 mol% (Figure 11b). With a decreasing temperature, plagioclase evolves from An-rich to Ab-rich compositions: An decreases from ~65–80 to ~35–50 mol% in Melt-10, from ~55–75 to ~25–40 mol% in Melt-8, and from ~50–70 to ~20–35 mol% in Melt-6. This trend reflects the decreasing melt Ca/Na during crystallization differentiation.

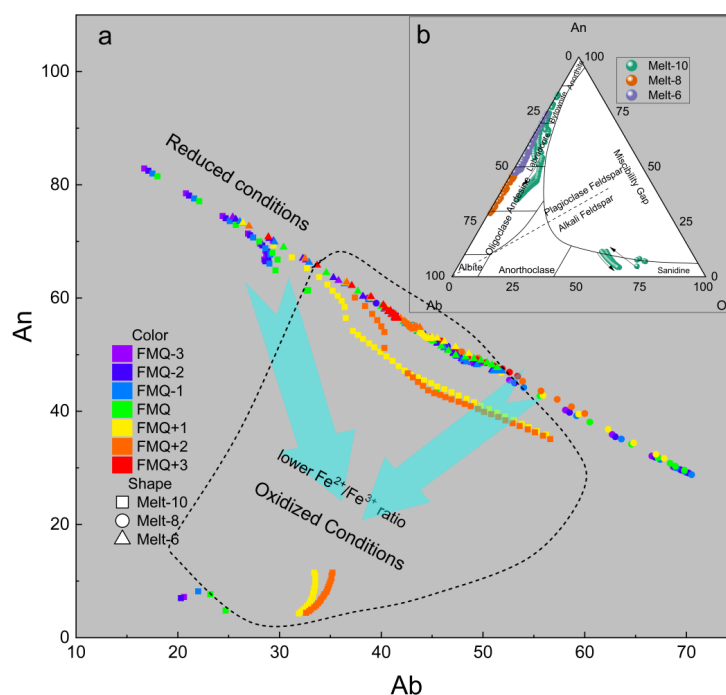
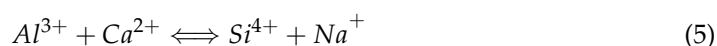


Figure 11. (a) An-Ab-Or ternary diagram of plagioclase compositions from the three end-member systems. (b) An-versus-Ab diagram.

fO_2 has only a limited direct effect on the plagioclase composition, with An shifts generally <10 mol%, because Ca, Na, K, Al, and Si are not redox-sensitive. Plagioclase An-Ab exchange is governed mainly by coupled CaAl-NaSi substitution (Equation (5)) [31]. Limited Fe^{3+} substitution for Al^{3+} may slightly increase An under oxidized conditions by requiring additional Ca^{2+} for the charge balance, an effect most evident in Melt-6.



H_2O affects plagioclase more strongly than fO_2 (Figure 11a). In hydrous melts, plagioclase saturation is delayed to lower-temperature, Na-rich residual liquids after Ca has been

preferentially partitioned into pyroxene and other early-crystallizing phases [20]. Thus, fO_2 influences plagioclase through changes in residual melt Ca-Na-Al activities, not through direct Fe^{3+} -Ca lattice coupling.

4.4.5. Residual Melt Evolution

Under high- fO_2 conditions (FMQ + 2 to FMQ + 3), residual melts in all three systems show differentiation and incompatible-element enrichment, with paths depending on the starting melt composition and early-saturating phases (Figures 12–14). In Melt-6, early clinopyroxene and Fe-Ti oxides partition Mg, Fe, Ca, and Ti, driving SiO_2 from ~46 to ~70 wt%, while MgO, FeO, CaO, and TiO_2 decrease. Na_2O , K_2O , and H_2O accumulate, and P_2O_5 peaks before apatite saturation and then declines. In Melt-8 and Melt-10, olivine and spinel dominate initially; MgO drops during olivine–orthopyroxene–clinopyroxene crystallization, and then, SiO_2 , Al_2O_3 , and alkalis increase during pyroxene–plagioclase co-crystallization. H_2O delays plagioclase saturation in Melt-8, shifting Si-alkali enrichment to lower temperatures.

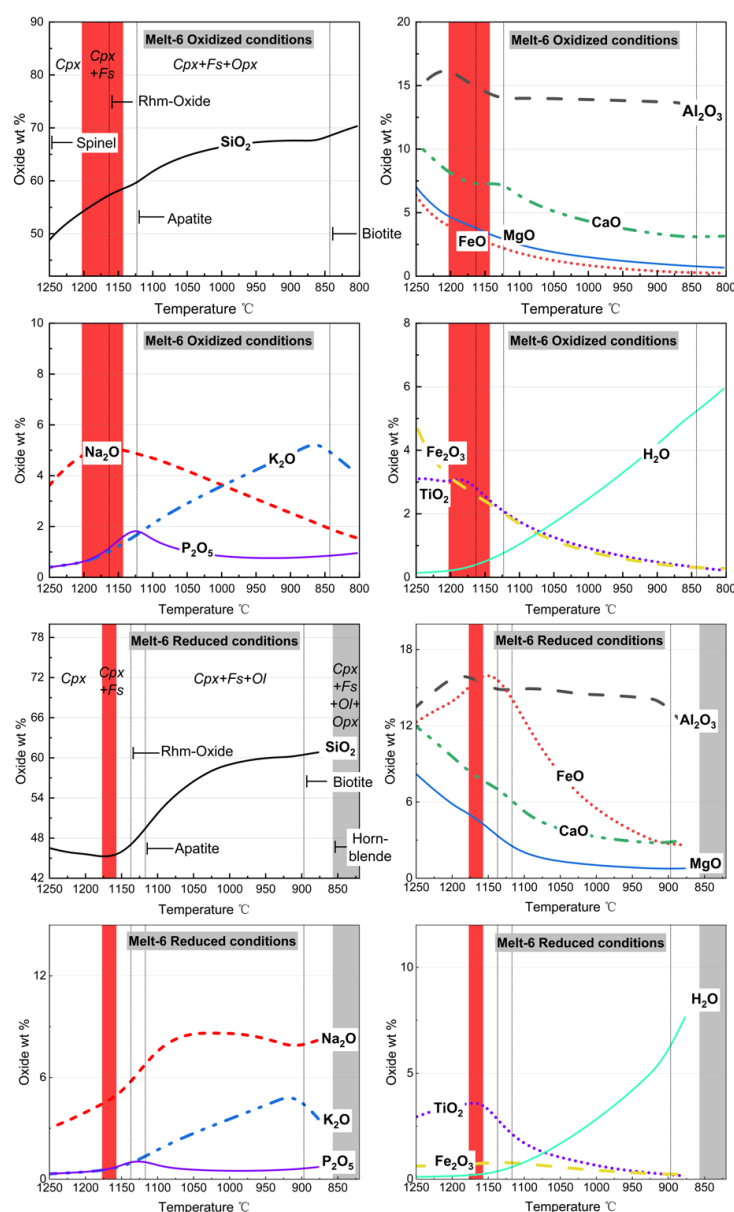


Figure 12. Variations in major oxides in the residual melt during isobaric equilibrium crystallization for the run Melt-6 ($H_2O = 0.1$ wt%).

At FMQ – 3, residual melts still evolve toward Si- and alkali-rich compositions, but Fe remains mainly as Fe^{2+} . In Melt-6, SiO_2 decreases slightly during early clinopyroxene crystallization and then rises after the continued progressive equilibrium crystallization of pyroxene and olivine; FeO rises then falls as pyroxene consumes Fe (Figure 14). Fe-Ti depletion is delayed relative to high- $f\text{O}_2$ runs. In Melt-8 and Melt-10 (Figures 12 and 13), early olivine causes rapid MgO depletion, but FeO remains high over a broad temperature interval because Fe^{3+} enrichment and early Fe-Ti oxide fractionation are suppressed. Na_2O , K_2O , and H_2O accumulate in both systems.

Thus, low- $f\text{O}_2$ runs are characterized by a longer FeO residence and delayed TiO_2 depletion, whereas high- $f\text{O}_2$ runs remove Fe-Ti earlier and drive residual melts toward SiO_2 and alkali-rich, Fe-Mg-Ti-poor compositions. Oxygen fugacity thus modifies the residual melt evolution by regulating Fe valence and the timing of Fe-Ti oxide saturation.

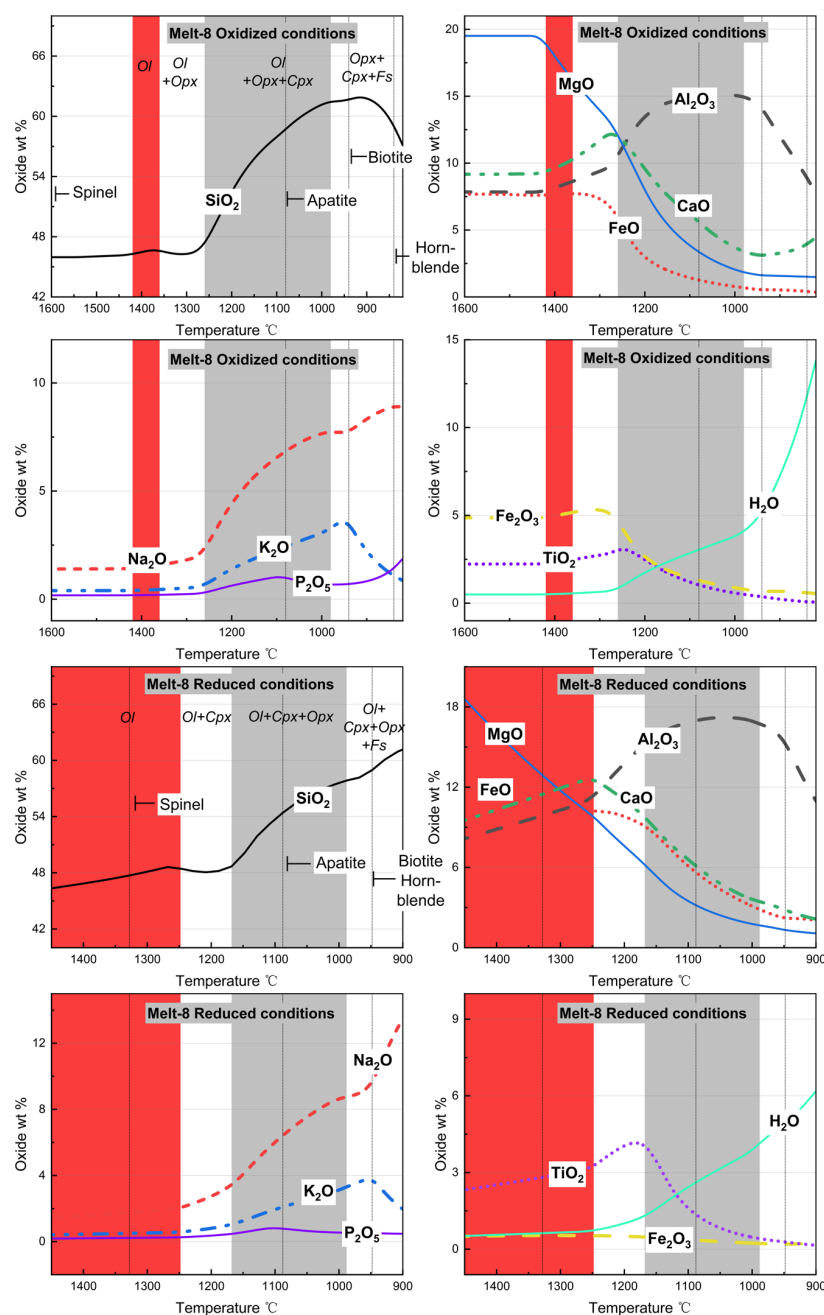


Figure 13. Variations in major oxides in the residual melt during isobaric equilibrium crystallization for the run Melt-8 ($\text{H}_2\text{O} = 0.5 \text{ wt}\%$).

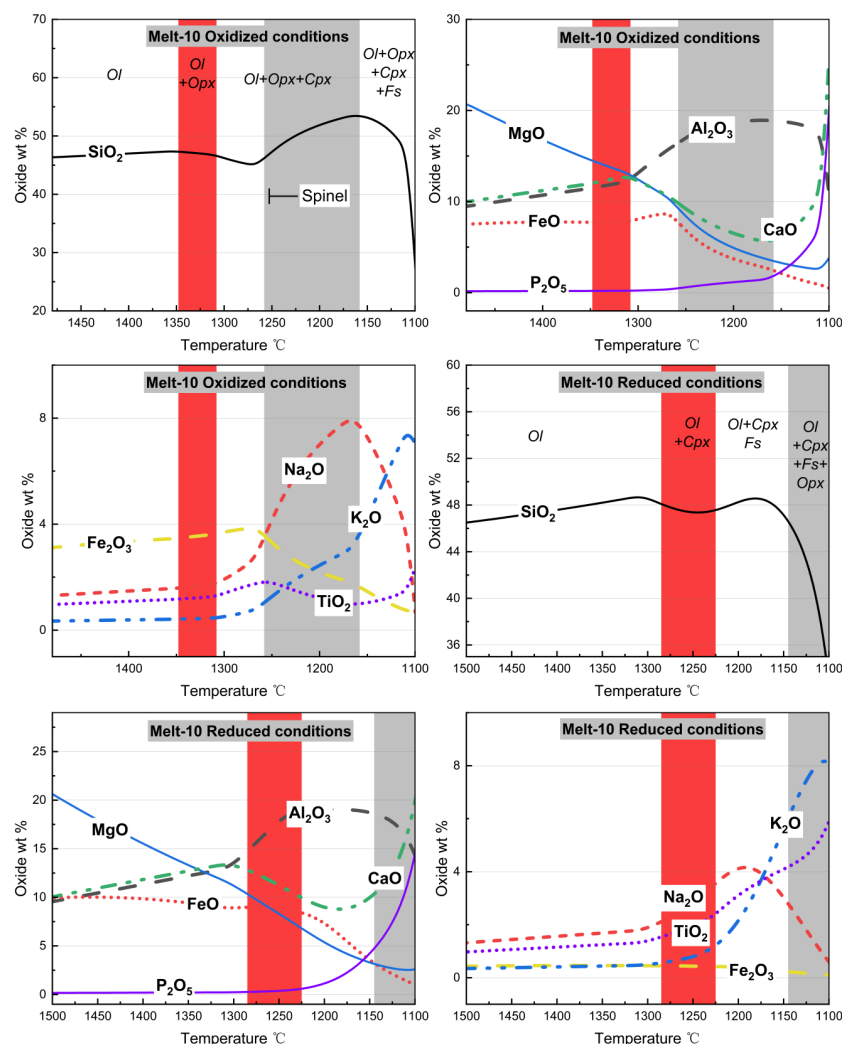


Figure 14. Variations in major oxides in the residual melt during isobaric equilibrium crystallization for the run Melt-10 ($\text{H}_2\text{O} = 0 \text{ wt}\%$).

5. Discussion

5.1. A Coupled Control Model for Silicate Crystallization

The simulations indicate that silicate crystallization in ELIP mafic–ultramafic magmas is controlled by three linked factors: the starting melt composition sets the baseline, H_2O modifies the melt structure, and $f\text{O}_2$ regulates the iron valence and competition with oxide crystallization. This framework improves on models that treat H_2O and $f\text{O}_2$ as independent controls. This interpretation is hierarchical rather than strictly orthogonal: MgO effects are inferred mainly from contrasts among starting melts, H_2O effects from the hydrous and anhydrous high-MgO systems, and $f\text{O}_2$ effects from the redox series calculated for each fixed starting composition.

- (1) The starting melt composition defines the baseline [38,39]. The main control on the liquidus temperature and mineral saturation sequence is the melt MgO content. High-MgO Melt-10 and Melt-8 have liquidus temperatures far above low-MgO Melt-6, and olivine is the liquidus phase only in high-MgO melts. Effects of H_2O and $f\text{O}_2$ must therefore be evaluated relative to this compositional baseline.
- (2) H_2O modifies the melt structure. Water depolymerizes the silicate network, lowers viscosity, and depresses liquidus temperatures. Its strongest effect is delayed plagioclase saturation [7,20], as shown by the much lower plagioclase saturation temperature in

Melt-8 than in Melt-10. H₂O does not simply delay all silicate phases; it also changes the relative positions of pyroxenes in the crystallization sequence [33].

- (3) fO_2 controls the iron valence and oxide competition [20,24]. By changing Fe^{2+}/Fe^{3+} , fO_2 modifies the effective FeO activity and the timing of Fe-Ti oxide saturation. High fO_2 lowers the Fe^{2+} available for Fe-Mg exchange and promotes earlier Fe-Ti oxide removal [16]. This can suppress olivine in evolved low-MgO melts, but it raises the Opx saturation temperature and shifts Opx earlier in the crystallization sequence [34]. Low fO_2 allows Fe^{2+} to remain in the melt for longer, producing more Fe-rich residual liquids.

Across the modeled systems, the MgO content produces the largest liquidus differences (~200–300 °C), H₂O adds a further ~50–150 °C depression, and fO_2 causes smaller but systematic shifts (~30–80 °C). The fO_2 effect is therefore mechanistically important but subordinate in magnitude to the starting melt composition and H₂O content.

5.2. Crystal-Chemical Mechanisms for the Differential Response of Minerals to Oxygen Fugacity

The sensitivity of the four silicate minerals to fO_2 follows the following order: orthopyroxene > olivine > plagioclase > clinopyroxene. This order can be explained by differences in the crystal-chemical site occupancy and structural buffering capacity [31,32].

Clinopyroxene is relatively insensitive because of Ca buffering at the M2 site [34]. Although Wo varies among runs, preferential Ca occupancy at the M2 site maintains a Ca-dominated clinopyroxene component and buffers fO_2 -driven compositional shifts relative to orthopyroxene. This reflects the preferential occupancy of the M2 site by Ca^{2+} , which limits Fe^{2+} to the M1 site and allows the clinopyroxene lattice to buffer fluctuations in the melt composition [41]. Clinopyroxene is therefore more suitable as a recorder of magma Mg and Ca activity than as a sensitive indicator of fO_2 .

Orthopyroxene is highly sensitive because it lacks Ca-site buffering. Its Wo contents are <5 mol%, and both M1 and M2 sites participate in Mg-Fe exchange. En-Fs compositions therefore respond directly to the Fe^{2+}/Mg ratio of the melt. As fO_2 increases from FMQ – 3 to FMQ + 3, Fs in Melt-6 decreases from ~42 to ~10–15 mol%. This compositional trend does not contradict the earlier saturation of orthopyroxene under high- fO_2 conditions. In these simulations, the saturation temperature reflects the redox-dependent stability of orthopyroxene relative to coexisting phases, whereas Fs records the effective Fe^{2+}/Mg ratio of the melt during crystallization. Thus, higher fO_2 can promote earlier orthopyroxene saturation while simultaneously producing more En-rich and Fe-poor orthopyroxene through the oxidation of Fe^{2+} to Fe^{3+} and the consequent decrease in effective Fe^{2+} activity.

Olivine shows intermediate sensitivity because it involves a simple Fe-Mg exchange. Fo-Fa exchange in olivine directly records Mg-Fe partitioning between the M1/M2 sites and the melt [33,38], without the T-site Al-Si-coupled substitution that buffers pyroxene compositions. Its sensitivity is therefore intermediate between orthopyroxene and clinopyroxene. Olivine is directly affected by the melt Fe^{2+}/Mg ratio, but under high- fO_2 conditions, it disappears from the assemblage rather than continuing to adjust its composition.

Plagioclase responds only indirectly to fO_2 . Its direct redox sensitivity is weak because Ca, Na, Al, and Si are not redox-sensitive [22,38]. Minor Fe^{3+} substitution for Al^{3+} at the T site may shift An by <10 mol%, but plagioclase records mainly a decreasing temperature, H₂O content, and Ca/Na differentiation.

5.3. Implications for ELIP Magmatic Evolution and Fe-Ti-V Mineralization

These results constrain differences between high-Ti picritic magmas in the inner ELIP and evolved basaltic magmas in the middle ELIP, and they bear on the genesis of Fe-Ti-V oxide deposits.

Different end-members follow distinct crystallization paths. Melt-10 follows Ol-Cpx-Opx-Pl, with olivine stable over a broad temperature interval. Melt-8 follows Ol-Opx-Cpx-Pl, with earlier Opx crystallization and delayed plagioclase saturation. Melt-6 follows Cpx-Pl-Opx ($\pm$ Ol) or lacks olivine at high fO_2 , indicating insufficient MgO activity to stabilize olivine as the liquidus phase. These paths correspond to different ELIP magmatic states rather than a single differentiation trend.

High fO_2 promotes early Fe-Ti oxide crystallization and removes Fe-Ti components from silicate competition, favoring oxide enrichment in conduit systems [15,20]. In Melt-6, Fe-Ti oxides saturate nearly contemporaneously with clinopyroxene, whereas in S8 and Melt-10, they appear after olivine. This suggests that oxidized shifts during ascent or staging could help high-Ti magmas generate oxide-rich assemblages. The Cpx + Fe-Ti oxide + Pl assemblage predicted at a high fO_2 is consistent with oxide-pyroxene-plagioclase associations in the Panzhihua intrusion [16,26,27].

Water appears to play an indirect role in mineralization. H_2O delays plagioclase saturation but does not markedly advance Fe-Ti oxide saturation in Melt-8 [20,42]. Water alone is therefore insufficient to generate Fe-Ti oxide enrichment; high fO_2 and the oxide saturation timing are more decisive. This is consistent with hydrous high-Ti ELIP magmas not being universally mineralized [40,43].

5.4. Comparison with Natural Rocks

The textures shown in Figure 4 are used as natural examples illustrating the diversity of local crystallization relationships in ELIP layered intrusions. They are not intended to define a unique crystallization sequence for the entire province, because crystal accumulation, trapped melt migration, magma replenishment, and rhythm-scale textural variation may modify modal and textural relationships within individual intrusions.

The modeled crystallization sequences are broadly consistent with natural ELIP assemblages. The Cpx + Pl + Fe-Ti oxide assemblage in the Panzhihua intrusion is qualitatively consistent with the phase assemblage predicted by oxidized Melt-6 simulations [20], whereas the Ol + Cpx + spinel phenocryst assemblage in the Yongsheng picrite resembles early Melt-8 crystallization at FMQ to FMQ + 1. This agreement supports the first-order validity of the simulations, although natural systems also involve magma recharge, accumulation, and open-system processes.

The modeled sequences also provide a thermodynamic context for the troctolitic textures shown in Figure 4g. In the MgO-rich Melt-8 and Melt-10, plagioclase saturates after olivine, and H_2O further delays plagioclase saturation in the Melt-8. These conditions may favor an early olivine-dominated cumulate followed by plagioclase crystallization, although the formation of troctolite additionally requires crystal accumulation and other physical processes that are not explicitly simulated here.

Notably, olivine Fo values in natural ELIP rocks (Fo ~91.7 in the Yongsheng picrite and Fo ~93.5 in the Dali picrite) are consistent with the Fo ranges modeled for Melt-8 and Melt-10 under low- to moderate- fO_2 conditions [6,21]. This suggests that crystallization of ELIP primitive magmas likely occurred under moderately oxidized conditions, approximately FMQ to FMQ + 1, rather than under highly reduced or strongly oxidized conditions. This inference is consistent with previous fO_2 estimates for ELIP basalts based on V/Sc ratios, which yielded Δ FMQ values of approximately 0 to +1.

5.5. Limitations of Melts Modeling and Future Perspectives

Several limitations should be noted. MELTS may overestimate spinel and Fe-Ti oxide stability, as reported for Jeju Island simulations [29]. In addition, biotite and amphibole results under hydrous conditions are less reliable because hydrous mineral thermodynamic

parameters are less well calibrated [44]. Late hydrous mineral sequences in Melt-8 and Melt-6 should therefore be treated as qualitative.

The additional sensitivity tests are not intended to replace a full factorial exploration of composition–H₂O–pressure–*f*O₂ space. Rather, they provide controlled comparisons showing that H₂O can substantially delay feldspar saturation at a fixed Melt-8 composition and that pressure changes can shift the absolute saturation temperatures of spinel, pyroxenes, feldspar, and Fe-Ti oxides. Accordingly, the model results are interpreted mainly in terms of relative crystallization trends and phase-stability relationships, rather than as precise estimates of absolute saturation temperatures for all ELIP magmas.

It should be emphasized that the present simulations provide only qualitative constraints on V behavior. The rhyolite-MELTS version used in this study does not explicitly track V valence or its partitioning among silicate melt, spinel, and Fe-Ti oxides. Nevertheless, because V enrichment in ELIP oxide deposits is closely associated with Fe-Ti oxide saturation and crystallization, the modeled oxide saturation sequence can be used to evaluate the relative timing of potential V enrichment. Quantitative modeling of V will require a thermodynamic framework that explicitly incorporates the V valence and mineral-melt partitioning.

Future studies should combine experimental petrology with the phase-equilibrium calibration of hydrous minerals. Systematic simulations over broader pressure conditions (1–10 kbar) and a wider range of H₂O contents (0–3 wt%) are also needed to establish a more comprehensive thermodynamic framework for ELIP magmatic evolution.

The ore-forming implications discussed here are restricted to Fe-Ti-V oxide enrichment. Although sulfide saturation is also relevant to the metallogenic evolution of ELIP magmas, it cannot be constrained by the present simulations because no sulfur-bearing phase-equilibrium calculation was performed. A quantitative comparison between sulfide and Fe-Ti oxide saturation will require dedicated sulfur-bearing modeling that considers sulfur speciation and sulfide–silicate partitioning.

6. Conclusions

1. This study used MELTS simulations to constrain how *f*O₂ and H₂O jointly affect silicate crystallization in ELIP mafic magmas. The main conclusions are as follows.
2. Silicate crystallization is governed by three coupled controls. The starting melt MgO content sets the liquidus baseline; H₂O lowers saturation temperatures, especially for plagioclase; and *f*O₂ shifts phase boundaries through Fe²⁺/Fe³⁺ and Fe-Ti oxide competition.
3. *f*O₂ regulates silicate stability mainly through Fe²⁺/Fe³⁺, effective FeO activity, and Fe-Ti oxide saturation. Mineral sensitivity follows Opx > Ol > Pl > Cpx. The Opx saturation temperature and En-Fs composition are the most sensitive silicate redox indicators, whereas plagioclase An is more strongly influenced by H₂O-dependent phase relations, the temperature, and the residual-melt Ca/Na evolution.
4. High *f*O₂ promotes early Fe-Ti oxide crystallization, removes Fe-Ti components from the melt, and drives residual liquids toward SiO₂- and alkali-rich compositions. Low *f*O₂ retains Fe mainly as Fe²⁺ and maintains Fe-rich residual melts. This mechanism provides a thermodynamic explanation for Fe-Ti-V oxide enrichment in the inner ELIP.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16090946/s1>, Table S1: Supplementary Data.

Author Contributions: Conceptualization, M.H. and F.C.; methodology, M.H. and F.C.; software, M.H.; validation, Z.W.; formal analysis, M.H.; investigation, M.H.; resources, S.G.; data curation, M.H. and S.G.; writing—original draft preparation, M.H.; writing—review and editing, M.H., Z.W.,

Y.H., F.C., and W.H.; visualization, M.H.; supervision, W.H.; project administration, W.H.; funding acquisition, F.C. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: S.G. is an employee of Panzhihua New Baima Mining Co., Ltd., Pangang Group. M.H., Z.W., Y.H., and F.C. are affiliated with Panzhihua Iron & Steel Research Institute and/or the State Key Laboratory of Vanadium and Titanium Resources Comprehensive Utilization. The paper reflects the scientific views of the authors and not those of their employers. The remaining author declares no conflict of interest. The funder had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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