Magma-carbonate interaction under dynamic conditions: experimental insights on crystallization kinetics and multiphase rheology

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INTRODUCTION

Volcanic systems that develop within carbonate basement rocks represent distinctive geological environments where magma interacts with carbonate-rich lithologies, such as limestone and dolostone. These interactions give rise to a range of complex processes that significantly affect the physicochemical evolution, rheology, and eruptive behavior of the magma (Fig. 1).

Magma-carbonate interaction is a well-documented phenomenon in numerous volcanic systems worldwide (Freda et al., 2008; Gaeta et al., 2009; Mollo et al., 2010; Troll et al., 2012; Jolis et al., 2015). The outcomes of these interactions are observed through various indicators, including the presence of crustal xenoliths in volcanic deposits, variations in mineral assemblages, crystallization patterns, and influences on degassing processes and eruption styles. Evidence of these interactions occurs on multiple timescales, ranging from seconds to days for short-term processes, and from years to thousands of years for long-term processes (Knuever et al., 2023).

When exposed to the heat of magma, carbonate minerals undergo decarbonation, breaking down into their constituent oxides (CaO and MgO) and releasing carbon dioxide (CO_2) gas. The decarbonation process not only dissolves carbonate clasts but also introduces a significant amount of CaO and MgO into the surrounding magma. The diffusion of these oxides is facilitated by thermal gradients between the high-temperature magma and the cooler carbonate rocks, as well as by mechanical processes, such as convective currents within the magma chamber driven by contrasts in magma viscosity and density. The increase of CaO and MgO profoundly affects the physicochemical properties of the magma, as these oxides act as network-modifying agents in silicate melts. The impact of CaO and MgO on magma viscosity extends beyond their effects on the liquid phase; experimental studies highlight that crystallization of minerals rich in these oxides is promoted. Following, the crystallization process involves two simultaneous effects on the system's rheology (lquid+crystal): *i)* chemically, the addition of CaO and MgO to the liquid phase leads to decreased polymerization, as the concentration of network modifiers increases and *ii)* physically, the introduction of crystallizing particles impact magma mobility hindering its flow and increasing its viscosity (Vona et al., 2011; Kolzenburg et al., 2022). As crystal content rises, viscosity increases exponentially, causing the magma to transition from fluid-like to more rigid, solid-like behavior.

At the margins of a magma chamber where assimilation and crystallization are most pronounced and intense, stratified shells rich in mineral assemblages containing CaO and MgO may form. Skarns develop from the reaction of magma-derived fluids with surrounding carbonate rocks, leading to progressive metamorphism and mineralogical transformation. This process is crucial because skarns act as physical barriers at the magma chamber margins, limiting further decarbonation and assimilation of the carbonate host rock. However, skarn recycling introduces fragments of CaO- and MgO-rich crystallized rocks back into the system, which further alters the chemical composition of the evolved magma, promoting further crystallization, thereby enhancing heterogeneity. Simultaneously, convective stirring within the magma chamber and the injection of new magma from deeper parts of the system promote magma mixing. This mixing can be further enhanced by chemical gradients introduced by the decarbonation/assimilation process and differences in crystallization across various parts of the magma chamber. The result is the formation of hybrid magmas, some of which achieve complete homogenization, while others retain evidence of incomplete mixing. Hybrid magmas often exhibit distinct rheological properties due to introduced chemical heterogeneity and variations in crystal content (Morgavi et al., 2022).

Although numerous studies have underscored the key role of magma-carbonate interactions in volcanic dynamics and eruptions, as well as the influence of deformation regimes on crystallization processes and resulting rheology, there remains a notable gap in experi-

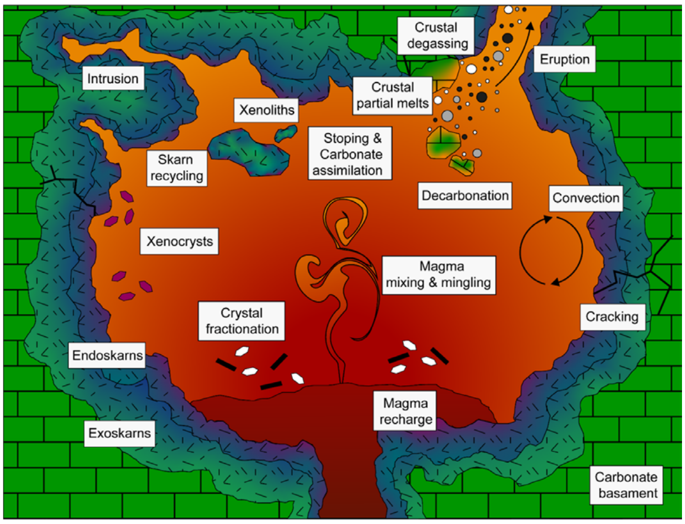

Figure 1 Schematic sketch showing various magma chamber processes (not to scale). Some of these processes, e.g., endoskarn/exoskarn crystallization, stoping and carbonate assimilation, decarbonation, magma mixing & mingling, cracking and skarn recycling, are examined in detail in the thesis. Sketch modified after Deegan (2010).

mental investigations that examine the combined effects of stirring and carbonate assimilation. This gap is particularly evident in the context of CaO-MgO-contaminated hybrid magmas, whose rheological properties remain largely unexplored.

Aims of the thesis

The main objective was to address the following questions:

What is the effect of carbonate assimilation on the rheology of single-phase (liquid) melts?

How do dynamic conditions influence crystallization and rheological behavior in multiphase (liquid+crystals) melts affected by carbonate assimilation?

Based on current understanding of magma-carbonate interactions and magma rheology, this project systematically investigated for the first time how carbonate assimilation and deformation regimes affected crystallization kinetics and the rheological evolution of magmas.

Specifically:

For single-phase (liquid) melt, the investigation determined how the addition of CaO and CaO+MgO influenced the crystal-free viscosity across both high- and low-temperature regimes.

For multiphase (liquid+crystals) magmas, the study assessed how these compositional changes, together with deformation regimes, affected rheological behavior under dynamic conditions.

MATERIALS AND METHODS

The research integrated a diverse set of complementary experimental and analytical techniques to provide a comprehensive investigation of magma-carbonate interactions. Experimental petrology and geochemistry were employed to simulate and assess the mechanisms and rates of these interactions in controlled laboratory settings, using natural materials from Somma-Vesuvius (Italy) as representative starting samples. To mimic carbonate assimilation, phonotephrite rock powder from the 472 CE Pollena eruption was doped with varying amounts of CaO and CaO+MgO, obtained from the thermal decomposition of $CaCO_3$ (Fig. 2).

The following techniques were employed:

Major Element Analysis: Electron microprobe analyses of starting and residual glasses were performed at the Bayerisches Geoinstitut (Germany) and the Natural History Museum in London, United Kingdom.

High-Temperature Crystal-Free Viscosity Measurements: Conducted at the EVPLab of the University of Roma Tre using a concentric cylinder apparatus (CC).

Low-Temperature Crystal-Free Viscosity Measurements: Conducted at both the EVPLab of the University of Roma Tre and the GLASS Laboratory of the CNR (Italy), using differential scanning calorimetry (DSC) and micropenetration viscometry (MP).

High-Temperature Crystallization Experiments: Carried out at the EVPLab of the University of Roma Tre, using a CC.

Spectroscopic Techniques: Raman spectroscopy was performed at the EVPLab of the University of Roma Tre, and at the GLASS Laboratory of the CNR (Italy), while Brillouin spectroscopy was carried out at the Bayerisches Geoinstitut (Germany).

Microphotography and Textural Analysis: Microphotographs were taken at the *HP-HT* Laboratory of the National Institute of Geophysics and Volcanology in Rome.

THE EFFECT OF CARBONATE ASSIMILATION AND NANOHETEROGENEITIES ON THE VISCOSITY OF PHONOTEPHRITIC MELT FROM VESUVIUS

This study addressed this gap by presenting novel viscosity data for a leucite-bearing phonotephritic melt from the 472 CE Pollena eruption (Vesuvius, Italy), doped with varying amounts of CaO and CaO+MgO. The chosen compositions closely matched those of melt inclusions and interstitial glasses from skarns at Vesuvius, interpreted as the result of magma mixing with carbonate-derived components (Fig. 2).

Viscosity measurements were conducted across a wide temperature range using concentric cylinder viscometry, differential scanning calorimetry, and micropenetration methods. Specifically, experiments were performed at high temperatures (1150–1400°C) and low temperatures (640–760°C). The integrated approach, which combined Brillouin and Raman spectroscopy with these techniques,

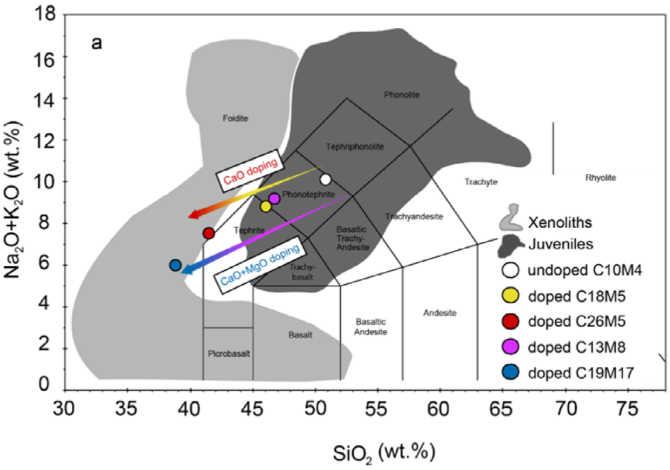

Figure 2 Total alkali vs. silica (TAS) diagram showing the undoped and doped glass compositions used in this study. The undoped material (C10M4) is represented as the white symbol. CaO-doped samples are represented by the yellow (C18M5) and red (C26M5) symbols, whilst purple (C13M8) and blue (C19M17) symbols correspond to samples doped with CaO and MgO. Areas represent the compositional variations of the products erupted from Vesuvius, specifically, the dark grey area represents juvenile materials (Rosi & Santacroce, 1983; Santacroce et al., 2008; Jolis et al., 2015; Macdonald et al., 2016), while the light gray area represents xenoliths (Fulignati et al., 2000, 2004; Del Moro et al., 2001; Jolis et al., 2015).

accurately predicted the viscosity changes induced by carbonate assimilation and identified the formation of nanoheterogeneities during low-temperature viscosity experiments (Fig. 3).

Experimental data revealed a significant viscosity/temperature crossover when CaO and CaO+MgO were added. Above 750°C, the undoped melt exhibited the highest viscosity, whereas doped melts showed substantially lower viscosities. Below this threshold, the trend reversed. Among the doping agents, CaO addition induced a much larger viscosity decrease compared to CaO+MgO addition, underscoring the predominant role of CaO in modifying the viscosity of the silicate liquid (Fig. 3).

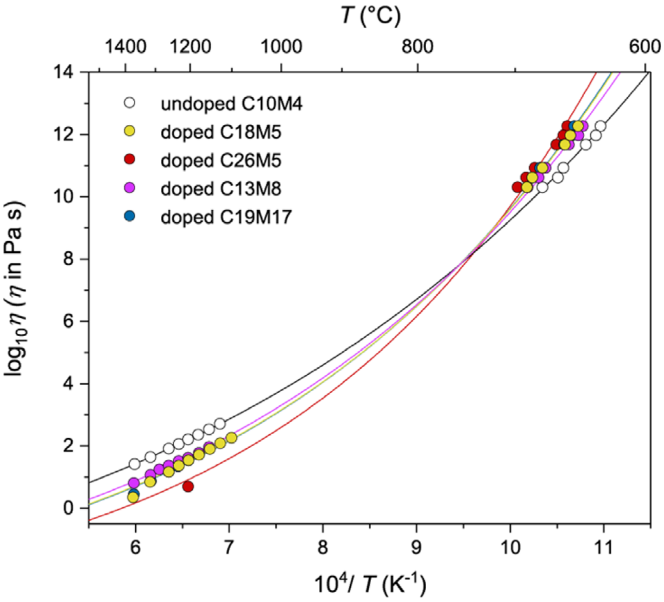

Figure 3 Viscosity data from differential scanning calorimetry and concentric cylinder measurements, and MYEGA fits (Mauro et al., 2009).

Importantly, empirical viscosity models from existing literature (Giordano et al., 2008; Langhammer et al., 2021) failed to reproduce these experimental observations, particularly for highly doped melts and across both temperature regimes, highlighting the limitations of purely chemistry-based models and emphasized the necessity of integrated spectroscopic and experimental approaches for predicting the rheology of carbonate-contaminated magmas.

These results provide new constraints on magma transport properties in volcanic plumbing systems where magma-carbonate interaction occurs. The insights gained into viscosity reduction and the effects of nanoheterogeneities shed light on how carbonate assimilation can promote the mobility, mixing, and hybridization of magmas, ultimately influencing eruption dynamics. Such processes are especially relevant at Vesuvius and similar volcanoes, where carbonate assimilation is well documented and can enhance explosivity through CO$_2$ release.

THE RHEOLOGICAL EVOLUTION OF A PHONOTEPHRITIC MELT UPON VARIABLE DEGREES OF CARBONATE ASSIMILATION AND DEFORMATION REGIMES

This study presented new insights from isothermal static experiments (ISEs) and isothermal deformation experiments (IDEs), performed at CC, which investigated the rheological evolution of a phonotephritic melt from Somma-Vesuvius (Italy) under varying shear rates (0, 1 and 5 s^{-1}) and doping levels of CaO and CaO+MgO. By examining the interaction between mechanical deformation and melt contamination, the study explored the

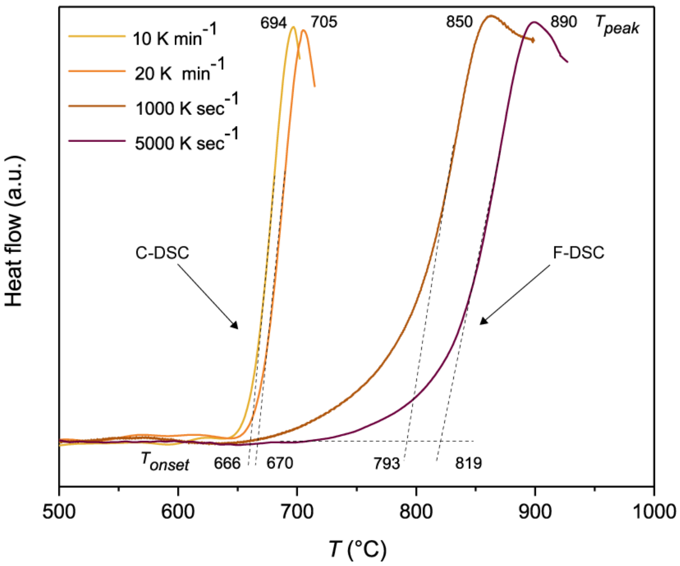

Figure 4 Heat flow of CaO+MgO-doped residual glass measured as a function of temperature using conventional (C-DSC) and Flash (F-DSC) differential scanning calorimetry. Dashed lines correspond to the second upscan during measurements performed at 10 and 20 K min^{-1} and at 1000 and 5000 K s^{-1} using the rate-matching method (Di Genova et al., 2020).

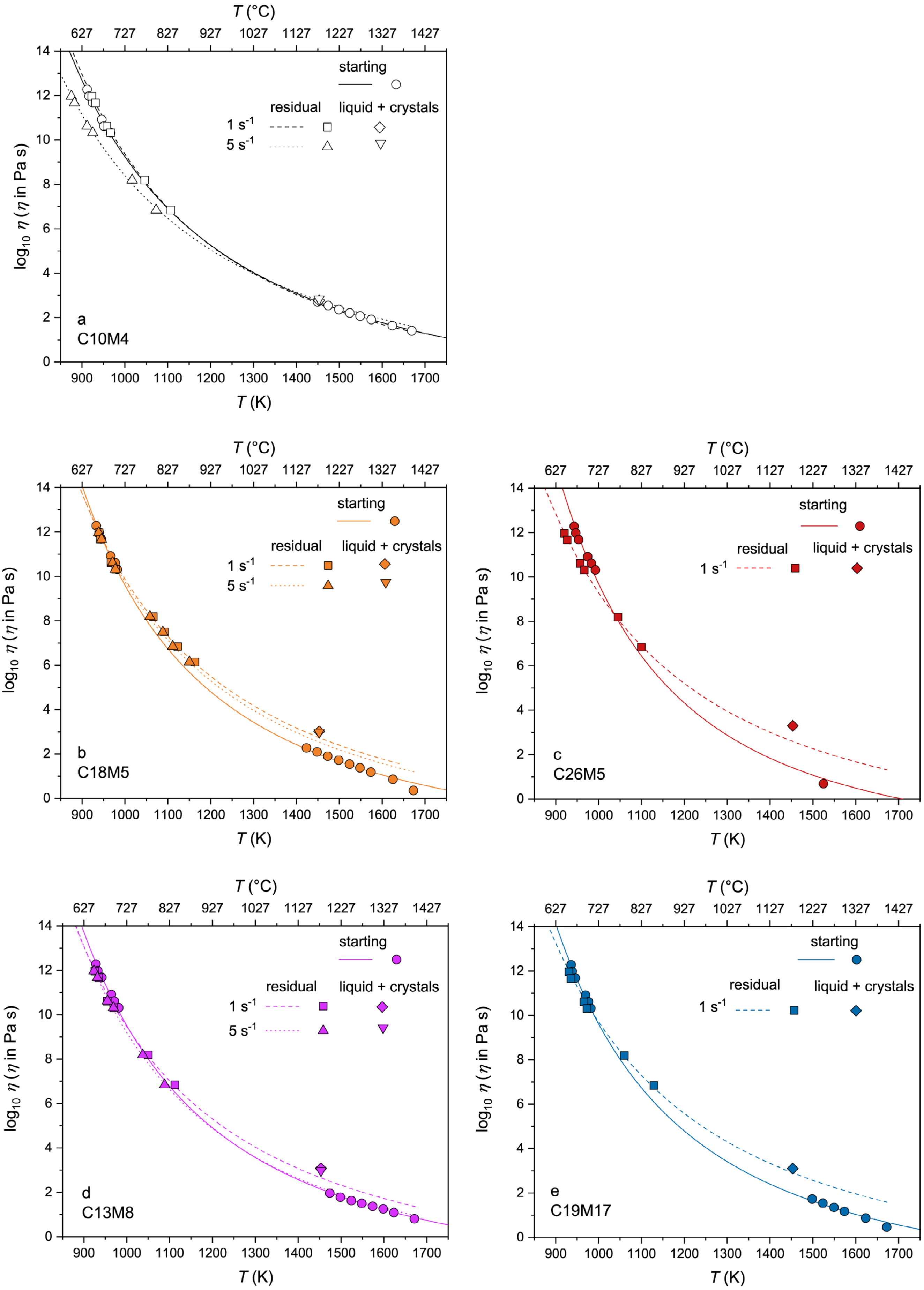

Figure 5 *Temperature-dependence of the viscosity measured for starting and residual glasses. The MYEGA fits from the equation of Mauro et al. (2009) refer to viscosity data obtained by C-DSC and F-DSC measurements at low and high temperature regimes. The viscosities of starting melts are displayed as solid lines and circles. The viscosities of residual melts and their modeling are displayed as squares and dashed lines for a shear rate of 1 s^{-1}, and triangles and dotted lines for a shear rate of 5 s^{-1}. The melt+crystal viscosities from IDEs performed at 1180°C are also displayed as diamonds and inverted triangles for shear rates of 1 and 5 s^{-1}, respectively. The panels show the temperature-dependence of the viscosity measured for the undoped sample C10M4* ***(a)****, the low CaO-doped sample C18M5* ***(b)****, the high CaO-doped sample C26M5* ***(c)****, the low CaO + MgO-doped sample C13M8* ***(d)****, and the high CaO + MgO-doped sample C19M17* ***(e)****.*

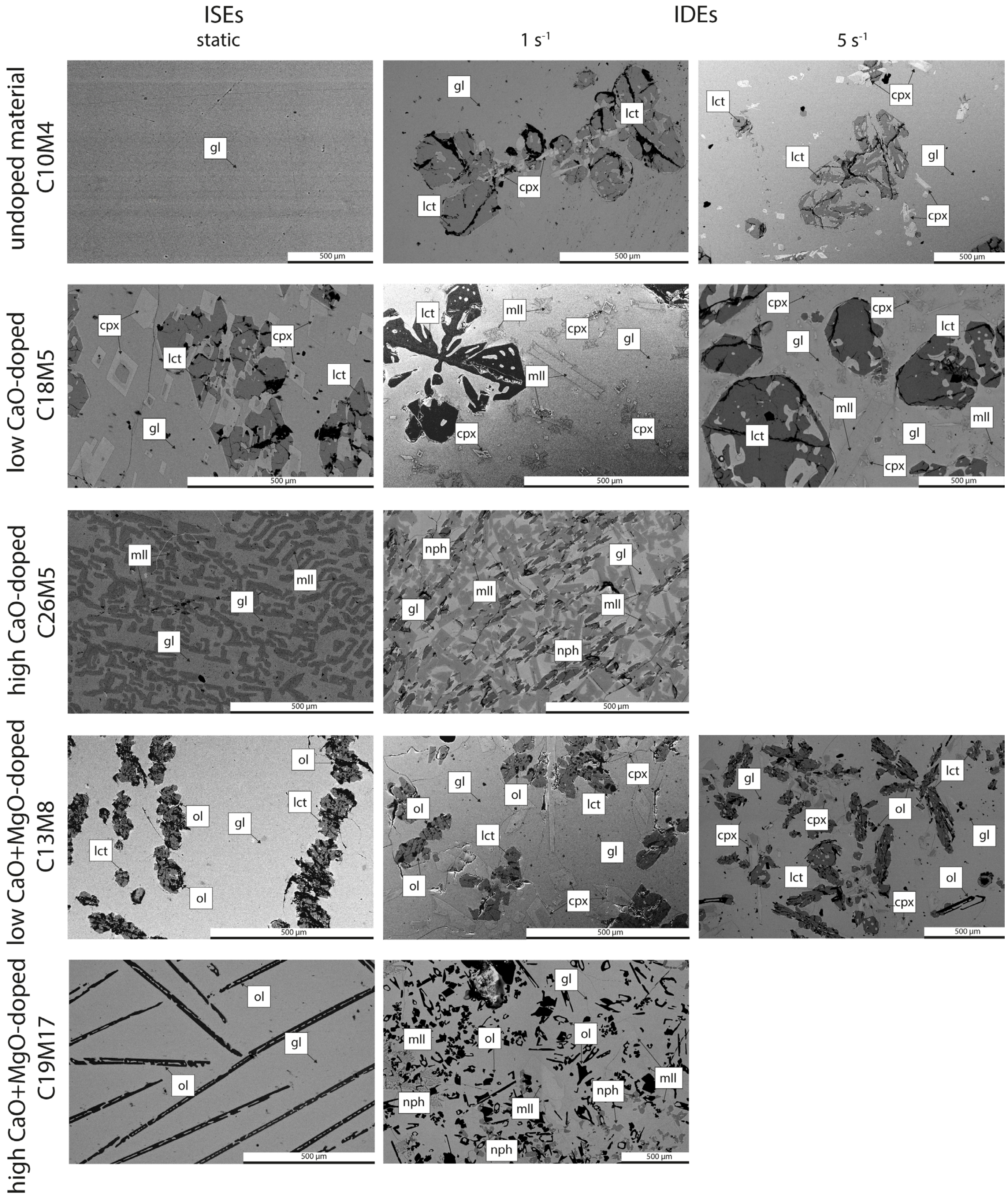

Figure 6 BSE photomicrographs illustrating the phase assemblage and textural features resulting from ISEs and IDEs. Gl: glass, Ol: olivine, Cpx: clinopyroxene, Lct: leucite, Nph: nepheline, Mll: melilite.

processes that governed the nucleation and growth of crystals, as well as the resulting changes in viscosity.

To elucidate the impact of dynamic deformation on the rheological evolution of magmas during crystallization, two interrelated effects were considered: i) changes in crystallinity due to enhanced crystal nucleation and growth process, and ii) compositional evolution of the residual melt as crystallization progressed.

Flash differential scanning calorimetry was employed to directly determine the viscosity of the interstitial melt, enabling the first direct assessment of how crystallization affected melt rheology without relying on empirical models (Fig. 4 and Fig. 5).

IDEs revealed two distinct rheological regimes: (1) viscous deformation characterized by uniform flow, and (2) non-homogeneous deformation marked by shear localization and viscous or brittle rupture of the magma. With increasing shear rate and carbonate doping, melts displayed non-Newtonian behavior resulting from stress localization and fracturing processes, which were promoted by the formation of a crystal network (Fig. 6). The presence of crystals introduces mechanical heterogeneities that disrupt the uniform flow of the melt, leading to localized stress and premature crack formation.

The measured viscosity range from IDEs was narrower than that predicted by the model (Frontoni et al. 2022) of purely viscous behavior, indicating that shear localization and fracturing processes reduced the resistance to flow in the doped, crystal-rich samples. These observations suggested that the complex rheology of CaO- and CaO+MgO-doped melts, which represent varying degrees of carbonate assimilation, likely reflected the disaggregation of skarn shells at the periphery of magma chambers. This disaggregation favored skarn recycling and enhanced the potential for magma contamination.

Furthermore, the extensive crystallization occurring in skarn-rich environments increased the susceptibility of the system to viscous rupture and brittle failure, thereby influencing the mechanical response of the magmatic system under stress conditions.

Residual melts exhibited nearly isoviscous behavior, facilitating the efficient mixing of magmas during the extraction of interstitial melts from the crystalline framework. This enhanced mixing capability was especially significant at the margins of mature magma chambers in contact with carbonate wall rocks, where CaO- and CaO+MgO-enriched melts maintained high mixing efficiency within solidification fronts.

These findings underscore the critical role of dynamic deformation and carbonate assimilation in controlling the evolution of magmatic rheology and highlight the need for integrated experimental studies to better understand the complex behaviors of contaminated, multiphase magmatic systems.

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