LETTER TO THE EDITOR

Journal of Non-Crystalline Solids 358 (2012) 1624–1628

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Letter to the Editor

Heterogeneous nucleation mechanisms and formation of metastable phase assemblages induced by different crystalline seeds in a rapidly cooled andesitic melt

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ARTICLE INFO

Article history:
Received 20 November 2011
Received in revised form 10 April 2012
Available online 8 May 2012

Keywords:
Heterogeneous nucleation;
Cooling rate;
Platinum;
Olivine;
Clinopyroxene

ABSTRACT

Pt-capsules loaded with a Pt-coil and two crystalline seeds immersed into an andesitic melt were rapidly cooled from 1300 to 1100 °C with a rate of 3 °C/min at atmospheric pressure and air oxygen fugacity. Results show that the Pt-coil does not induce any heterogeneous crystallization process as well as iron diffusion process from the melt into the platinum substrate. In contrast, the presence of crystalline seeds in a solidifying andesitic melt significantly alters the phase assemblage, composition and texture of the new-forming crystals in response to a heterogeneous nucleation mechanism and the formation of metastable phases.

1. Introduction

The formation of crystals in naturally solidifying igneous melts is one of the most important processes on the Earth and other planetary bodies. This mechanism occurs homogeneously when crystal nuclei form spontaneously into the liquid and heterogeneously when new-formed nuclei preferentially develop on pre-existing crystals [1–3].

With respect to the homogeneous nucleation process, the free energy reduction imposed by a heterogeneous nucleation site roughly scales with the physical–chemical similarities at the atomic and molecular levels, i.e. short range order, among the melt, the pre-existing substrate and the nucleating phase [4,5].

Although, the heterogeneous nucleation of crystals on natural olivines [6,7] and clinopyroxenes [8] has been observed for chemically complex terrestrial and extraterrestrial igneous systems, the role of different crystalline substrates has been scarcely investigated by means of laboratory studies [1,9].

In light of this, we have performed solidification experiments using an andesitic melt already investigated by [10]. These authors demonstrated that, under cooling rate conditions, the crystallization starts homogeneously and then proceeds by heterogeneous nucleation events. It is worth stressing that the work of critical cluster formation $Wc^{(hom)}$, i.e. the minimum energy required for the homogeneous growth of a nucleus, is the major thermodynamic factor influencing nucleation [1,2,7]. However, the classical theory for homogeneous nucleation can equally be applied to the case of heterogeneous nucleation. The only difference is the lower work for critical cluster formation ($Wc^{(het)}$) that can be expressed as $Wc^{(het)} = Wc^{(hom)} \times \varphi$. The φ parameter ranges from 0 to 1 and is related to the composition of the melt from which crystals grow, the composition of the substrate and the chemical similarity between the substrate and new-forming crystals [1,2,7].

Although a wealth of studies concerned with dynamic crystallization conditions [1,3,11,12], the homogeneous nucleation process has been poorly investigated. In light of this, here we show results from textural and chemical analyses on heterogeneously nucleated microcrystals in order to highlight the role played by pre-existing igneous phenocrysts on the evolution of rapidly cooled andesitic melts.

2. Starting material and methods

The starting material (hereinafter DPP) used in this study is an andesitic glassy powder whose composition is reported in Table 1SD submitted as supplementary data. The original andesite rock is an explosive product of intermediate composition from the volcanic island of Panarea (Italy) already studied by [13,14].

Experiments were conducted in a vertical rapid-quench furnace at atmospheric pressure and air redox state. One Pt-capsule was loaded with the DPP powder alone (hereinafter S-DPP); whereas, three Pt-capsules were loaded with different foreign substrates immersed into the DPP powder, i.e. a Pt-coil with a diameter of 200 μm (hereinafter S-Pt), a crystalline seed of olivine (Fo_{67}) with a diameter of 1 mm (hereinafter S-Ol) and a crystalline seed of clinopyroxene (Di_{70}-Hd_4-En_{25}-Fs_1 augite) with a diameter of 1 mm (hereinafter S-Cpx). The experimental charges were cooled simultaneously from 1300 °C to 1100 °C under a fixed cooling rate of 3 °C/min. An additional charge loaded with the DPP glassy powder

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doi:10.1016/j.jnoncrysol.2012.04.010

alone was quenched at 1300 °C to demonstrate that (i) early-formed crystals were not present at 1300 °C and that (ii) microcrystals did not form at the time of quenching.

Analyses of run-products were performed at the HP–HT Laboratory of Experimental Volcanology and Geophysics of the Istituto Nazionale di Geofisica e Vulcanologia in Roma (Italy) using Field Emission Gun-Scanning Electron Microscopy (FE-SEM) and Electron Probe Micro Analysis (EPMA) following [10]. In particular, combined EDS-WDS (five spectrometers with twelve crystals) microprobe analyses were conducted using an accelerating voltage of 15 kV and an electric current of 10 nA. For glasses, a slightly defocused electronic beam was used with a counting time of 5 s on background and 15 s on peak. For crystals, the beam size was 1–2 μm with a counting time of 20 and 10 s on peaks and background, respectively. The following standards were used: jadeite (Si and Na), corundum (Al), forsterite (Mg), andradite (Fe), rutile (Ti), orthoclase (K), barite (Ba), celestine (S), fluorite (F), apatite (P and Cl) and spessartine (Mn). Sodium and potassium were analyzed first to accurately determine their amounts.

3. Results

S-DPP and S-Pt show identical textural and chemical features that can be summarized as follows (Tables 1SD and 2SD, and Fig. 1a–d): (i) plagioclases (9 vol.%) are characterized by different compositions

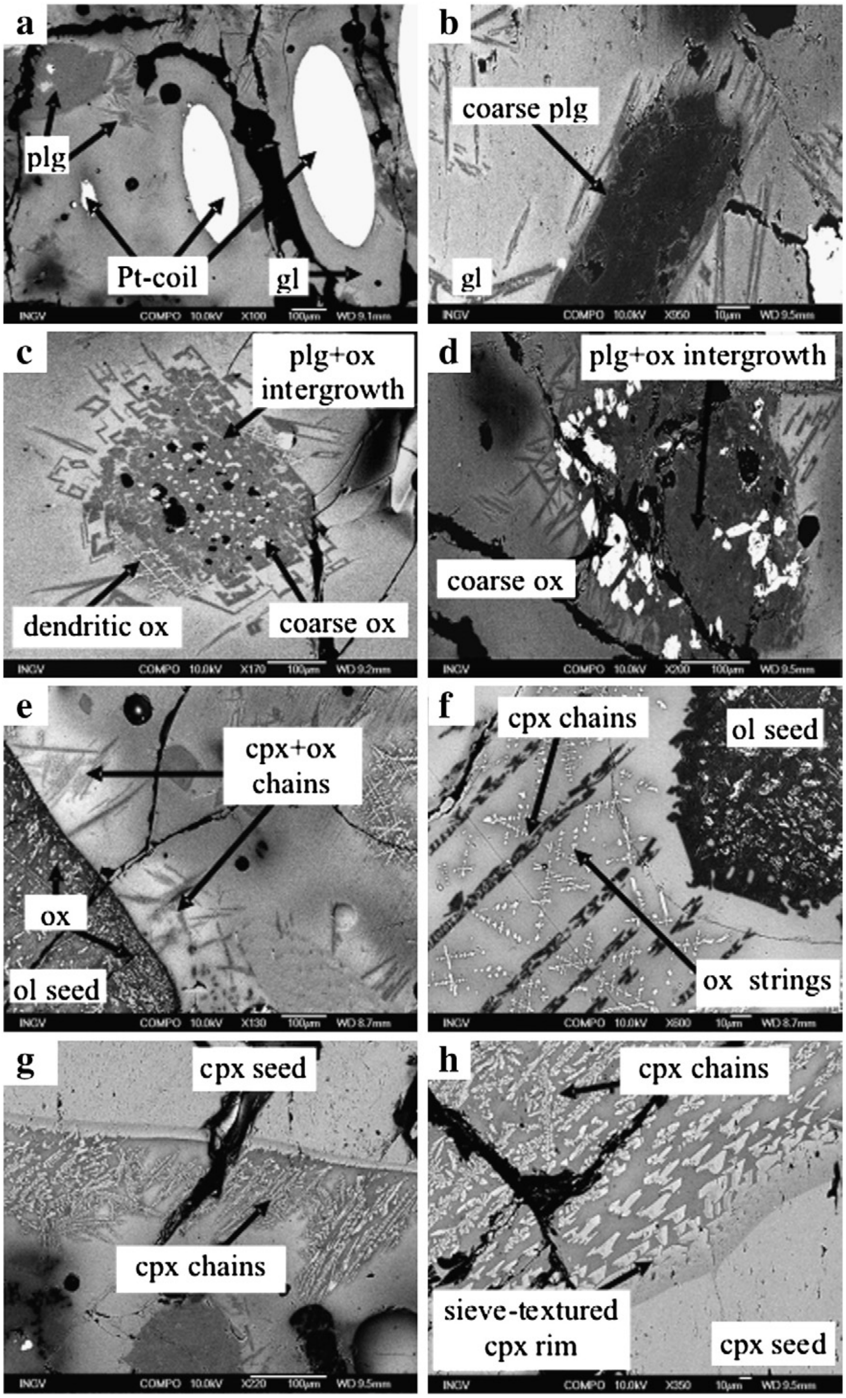

Fig. 1. Textural features of the following experimental charges: S-Pt and S-DPP (a–d), S-Ol (e–f) and S-Cpx (g–h).