

Volcanic SiO₂-cristobalite: A natural product of chemical vapor deposition

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ABSTRACT

Cristobalite is a low-pressure, high-temperature SiO₂ polymorph that occurs as a metastable phase in many geologic settings, including as crystals deposited from vapor within the pores of volcanic rocks. Such vapor-phase cristobalite (VPC) has been inferred to result from silica redistribution by acidic volcanic gases but a precise mechanism for its formation has not been established. We address this by investigating the composition and structure of VPC deposited on plagioclase substrates within a rhyolite lava flow, at the micrometer to nanometer scale. The VPC contains impurities of the form [AlO₄/Na⁺]⁰—coupled substitution of Al³⁺ charge-balanced by interstitial Na⁺—which are typical of cristobalite. However, new electron probe microanalysis (EPMA) element maps show individual crystals to have impurity concentrations that systematically decline from crystal cores-to-rims, and atom probe tomography reveals localized segregation of impurities to dislocations. Impurity concentrations are inversely correlated with degrees of crystallinity [observed by electron backscatter diffraction (EBSD), hyperspectral cathodoluminescence, laser Raman, and transmission electron microscopy (TEM)], such that crystal cores are poorly crystalline and rims are highly ordered tetragonal α -cristobalite. The VPC-plagioclase interfaces show evidence that dissolution-precipitation reactions between acidic gases and plagioclase crystals yield precursory amorphous SiO₂ coatings that are suitable substrates for initial deposition of impure cristobalite. Successive layers of cubic β -cristobalite are deposited with impurity concentrations that decline as Al-bearing gases rapidly become unstable in the vapor cooling within pores. Final cooling to ambient temperature causes a displacive transformation from β → α cristobalite, but with locally expanded unit cells where impurities are abundant. We interpret this mechanism of VPC deposition to be a natural proxy for dopant-modulated Chemical Vapor Deposition, where halogen-rich acidic gases uptake silica, react with plagioclase surfaces to form suitable substrates and then deposit SiO₂ as impure cristobalite. Our results have implications for volcanic hazards, as it has been established that the toxicity of crystalline silica is positively correlated with its purity. Furthermore, we note that VPC commonly goes unreported, but has been observed in silicic lavas of virtually all compositions and eruptive settings. We therefore suggest that despite being metastable at Earth's surface, cristobalite may be the most widely occurring SiO₂ polymorph in extrusive volcanic rocks and a useful indicator of gas-solid reaction having occurred in cooling magma bodies.

Keywords: Cristobalite, crystalline SiO₂, atom probe, gas solid reaction, vapor phase mineralization, chemical vapor deposition, glass corrosion, rhyolite