## Nanolitic magnetic minerals in volcanic pyroclasts

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Nanometer-scale crystals of Fe-Ti oxides in volcanic glasses have been considered as the origin of remnant magnetism (Schlinger et al., 1988) as well as fine exsolution lamellae in magnetite phenocrysts (Feinberg et al., 2005) because single domains (50–76 nm for magnetite; Butler and Banerjee, 1975) are stable carriers of remnant magnetization (Néel, 1949). The finer superparamagnetic grains show even higher magnetic susceptibility than that of single domains, which increases with decreasing grain size (Maher, 1988). The presence of nanoscale crystals in volcanic rocks is thus critically important for understanding rock magnetism. However, the occurrence and origin of these crystals have poorly been clarified. From a volcanological motivation, we have been observing nanoscale crystals in the groundmass of volcanic pyroclasts erupted from the Shinmoedake, Kirishima volcano in 2011 and from the Aso volcano in 2015. Here we present a brief review of our recent nanoscale petrography studies, which we expect would be of help in interpreting the magnetic properties of volcanic rocks. The samples we observed include pumices from the sub-Plinian eruption as well as pumices and lava-like dense juvenile fragments from the Vulcanian explosions in the order of decreasing quench rate and increasing groundmass crystallinity. The interior of thick lava flows and intrusive rocks with generally low cooling rates could have different mineralogical and petrological characteristics.

Nanoscale crystals are often included in the rhyodacitic groundmass matrix of the andesitic pyroclasts from Shinmoedake, which is commonly identified as typical volcanic "glasses" using an optical microscope and a scanning electron microscope with a tungsten filament. In almost all the pumice clasts, the minimum crystal sizes are typically 100 nm. In a dense juvenile fragment, the size of titanomagnetite crystals in the interstices of microlites ranges down to 10-20 nm. Fe-rich oxide spots with a diameter of 1-2 nm, which are most likely amorphous, are also observed. Fe-Ti oxide shows size gaps; that is, crystals with diameters of 2-10 nm and widths of 20-100 nm are absent, or their number densities are too low to be measured. We defined groundmass crystals with 30 nm-1  $\mu$ m in width as "nanolites" and those smaller than 30 nm in diameter as "ultrananolites" (Mujin et al., 2017). In addition to magnetite, we found pyroxene with nanolite and ultrananolite sizes. The number densities of nanolites and ultrananolites of the Fe-Ti oxides were eight orders of magnitude greater than those of microlite. These observations show that nucleation of nanocrystals almost paused in the late stage of crystallization, whereas crystal growth was mostly continuous. The occurrence of nanoscale crystals is conspicuous in the basaltic pyroclasts. Basaltic ashes with real glass on an atomic scale comprise only 10% of the juvenile ashes corrected from the March 2015 ash plumes of the Aso volcano. The rest of the ashes are composed mostly of nanoscale crystals. Nanolites and ultrananolites are assumed to crystallize under high undercooling conditions in the shallow conduit after the crystallization of microlites.

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