Supplementary Material

Conservation of $^{87}Sr/^{86}Sr$ during wine-making of white wines: a geochemical fingerprint of geographical provenance and quality production

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The Vulsini Volcanic District

The Vulsini district is the northernmost volcanic cluster of the Roman Province and it is formed by the coalescence of five large volcanic apparata: the Palaeo-Bolsena, the South Vulsini, the Bolsena, Montefiascone and Latera volcanoes (Nappi et al., 1987, 1998; Palladino et al., 2010). The volcanic rocks cover an area larger than 1,500 km^2, filling up a depressed area represented by the Siena-Radicofani and Paglia-Tevere grabens. The coalescence of the five volcanic apparata formed a shield-like area with two central depressed zones occupied today by the Bolsena lake and the Latera caldera (Fig. 1). All five volcanic complexes are made up mainly of ignimbrites with subordinate lava flows, although a lava plateau has been recorded in the early history of the Latera volcano, while the South Vulsini plateau represents the southernmost extension (e.g., Conticelli et al., 1987, 1989; Vezzoli et al., 1987, Marra et al., 2020).

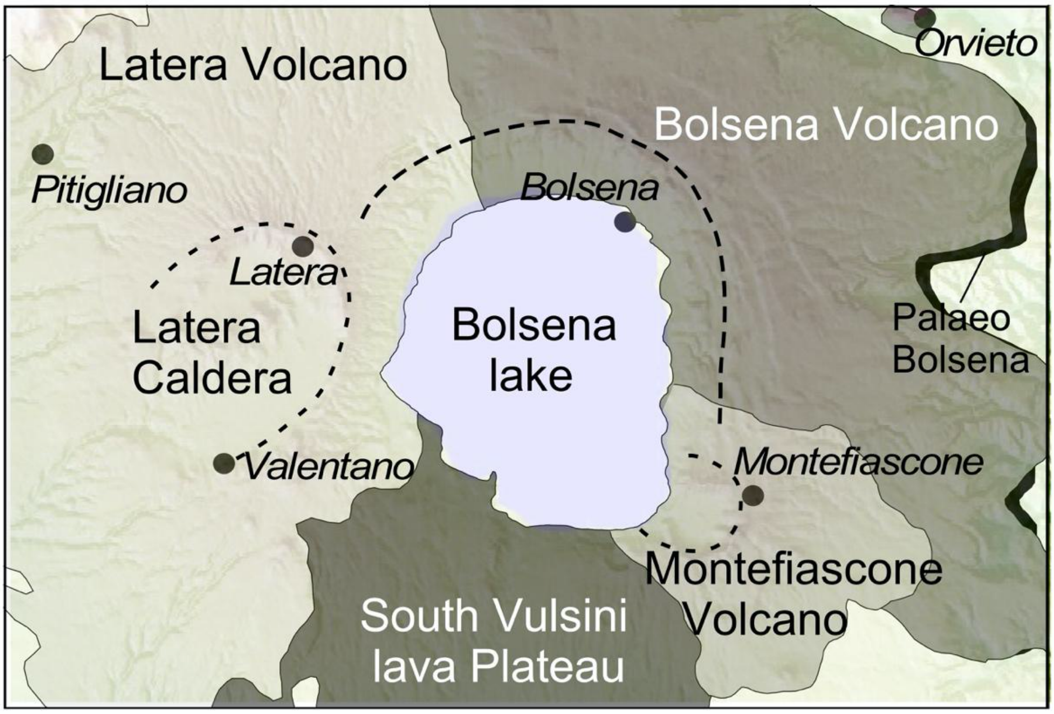

Fig. 1: The Vulsini volcanic district of the Roman Magmatic Province is made by the overlap of five volcanoes: Palaeo-Bolsena; South Vulsini plateau, Bolsena, Montefiascone and Latera (da Avanzinelli et al., 2017).

Palaeo-Bolsena volcanic apparatus is the oldest volcanic center and it is made up by the large trachytic, partly welded, ignimbrite called *Nenfro*, associated to leucititic to tephri-phonolitic lava flows and plinian pyroclastic fall horizons (Nappi et al., 1987, 1991, 1994, 1995). Volcanic activity begun with a plinian fall layer dated at 0.59 Ma (^{40}Ar-^{39}Ar, Barberi et al., 1994) and 0.58 Ma (K/Ar, Nappi et al., 1995). Several conflicting age data are published on *Nenfro* ignimbrite, which likely caused the Paleo-Bolsena calderic collapse: 0.88 to 0.4 Ma (K/Ar, Nicoletti et al., 1981a, 1981b), 0.5 Ma (^{40}Ar-^{39}Ar, Barberi et al., 1994) and 0.51 Ma (K/Ar, Nappi et al., 1995). Single crystal, laser total fusion ^{40}Ar-^{39}Ar, dating performed on a new mineral separation from the original six samples of Barberi et al. (1994) gives a well constrained age for this formation of 0.498 Ma (Laurenzi & Deino, 1996). Recently, on the basis of new ^{40}Ar-^{39}Ar ages on single crystals was confirmed the begun of volcanic activity in the Vulsini district at 0.591 Ma (Marra et al., 2020).

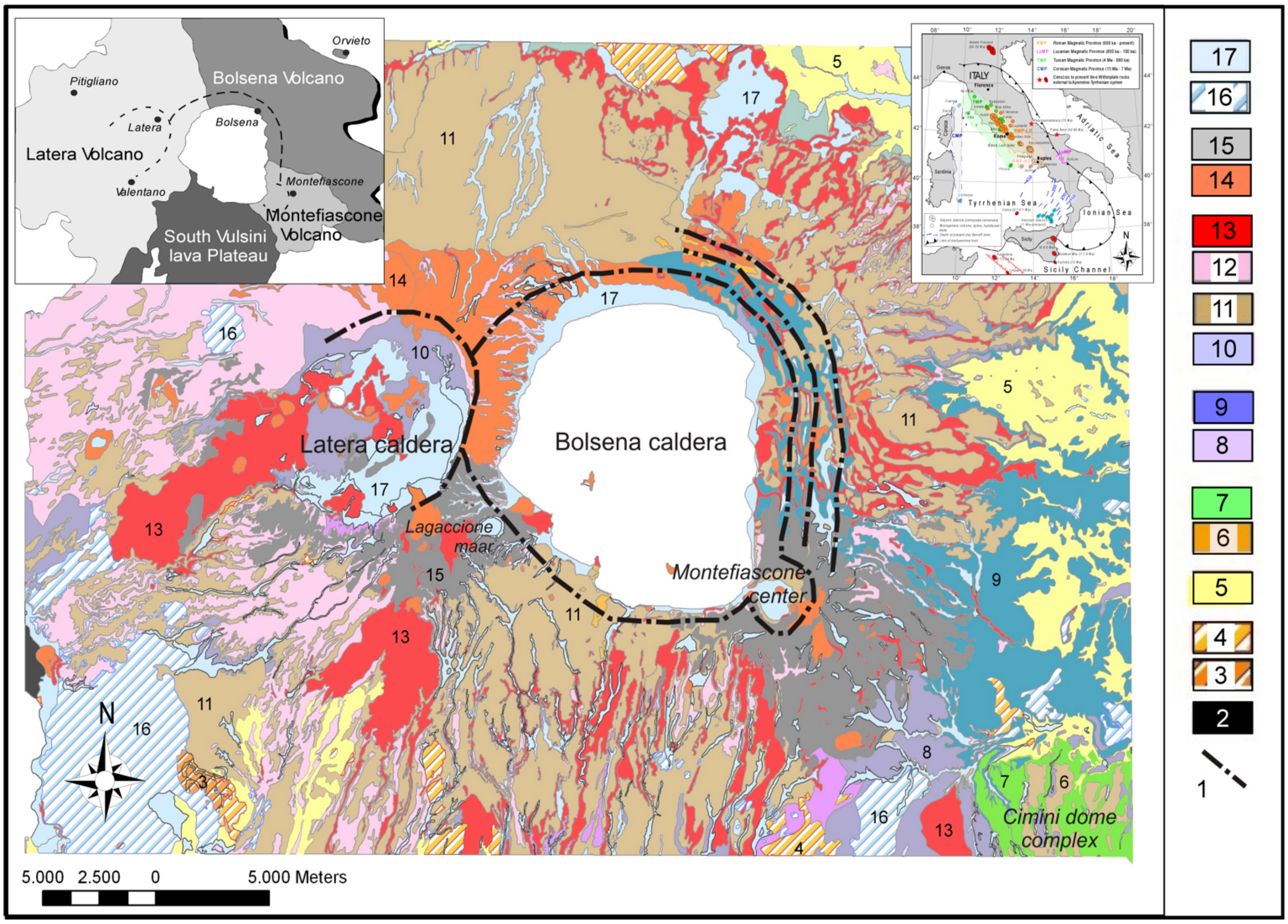

Fig. 2 - Geological sketch map of the Vulsini volcanic district. Legend: 1) caldera rims; 2) Paleozoic basement; 3) Meso-Cenozoic successions; 4) Allochtonous Flysch; 5) Pliocene-Pleistocene marine sediments; 6) Cimino: trachydacitic domes; 7) Cimino: trachyc Peperino ignimbrite; 8) Palaeo-Bolsena volcano welded to unwelded ignimbrites and tuffs; 9) Lithoidal ignimbrites; 10) spatter-rich ignimbrites; 11) fall-out and reworked pyroclastics; 12) pozolanaceous ignimbrites; 13) leucite-bearing and -free lavas; 14) phreatomagmatic deposits; 15) scoria cones; 16) travertine; 17) Holocene alluvial and lacustrine deposits (redrawn after Conticelli et al., 2010; Avanzinelli et al., 2017).

The Bolsena volcanic complex begun its activity after the formation of the Palaeo-Bolsena caldera and lasted for few hundred thousand years (Palladino *et al.*, 2010, and references included). It developed mainly in the eastern sector of the Vulsinisan district (Fig. 2) with the formation of a large caldera depression partly occupied by the Bolsena Lake, and produced two thick ignimbrite sheets, fall deposits and lava flows which built an ignimbrite shield (Freda et al., 1990; Nappi et al., 1998; Palladino et al., 2010). Fissural lava flows formed a lava plateau south of Bolsena Lake in the Marta-Tuscania area (Palladino et al., 1994).

The Montefiascone volcano (Fig. 2; ~0.29 - ~0.23 Ma: Nappi et al., 1995; Brocchini et al., 2000) evolved within the period of activity of Bolsena and partially overlapped with the Latera Volcano, developed in the western sector (~0.28 - ~0.15 Ma: Metzeltin & Vezzoli, 1983; Turbeville, 1992). Both Montefiascone and Latera volcanoes are characterized by different activities that brought to the formation of a small stratovolcano with a small summit caldera (ca. 2.5 km wide) at Montefiascone, compared to a large flat ignimbritic volcanic plateau with a large central polyphasic nested caldera (ca. 9 km wide) at Latera (Sparks, 1975; Varekamp, 1980; Conticelli et al., 1986, 1987, 1991; Vezzoli et al., 1987; Coltorti et al., 1991; Turbeville 1992, 1993; Di Battistini et al., 1998, 2001).

The final activity is represented by the Bisentina and Martana Islands, and likely other centers below the Bolsena Lake, tentatively still active around 0.13 Ma (K/Ar, Nappi et al., 1995).

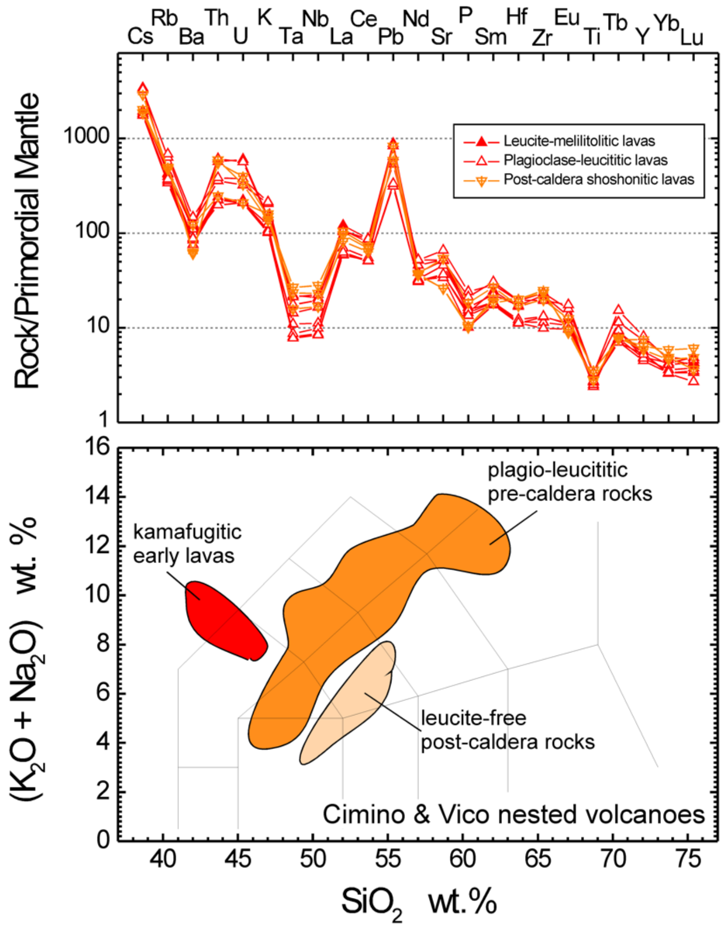

Fig. 3 - Classification and geochemical characteristics of the Vulsini leucite-bearing ultrapotassic rocks and associated shoshonitic ones (modified after Conticelli et al., 2010). Bottom: Total Alkali-Silica (TAS) classification diagram (Le Maitre, 2002). Top: Incompatible trace element patterns for mafic volcanic rocks normalised to the primordial mantle values of Sun & McDonough (1989). Data from Holm et al., 1982; Civetta et al., 1984; Rogers et al., 1985; Conticelli et al., 1987, 1991, 2002, 2007; Coltorti et al., 1991; Di Battistini et al., 2001; Gasperini et al., 2002.

The volcanic products (Fig. 3) are mainly characterised by leucite-bearing ultrapotassic rocks with few leucite-free shoshonitic rocks confined in the post-caldera activity of the Latera volcano (e.g., Conticelli et al., 1991) and some melilite-bearing leucitites (kamafugites) in the early stages of the Montefiascone volcano (Di Battistini et al., 2001).

The ultrapotassic rocks range in composition from leucite-bearing basanites, leucitites, tephrites, phonolitic-tephrites, tephritic-phonolites, and phonolites. Extremely differentiated products dominated volumetrically over mafic terms, but in some cases syn-depositional formation of analcite after leucite allowed the K_2O and alkalis loss, a characteristic capable to drive the juvenile clasts (pumice) in ignimbrite toward a trachy-phonolitic to trachytic compositions (Conticelli et al., 1987; Parker, 1989)(Fig. 3). The most mafic compositions are always found among lava flows and they are found mainly in the plateau-like structure of the southern sector of the Vulsinian district and of Montefiascone volcano, where leucite-bearing basanitic to tephritic lavas do occur (Civetta et al., 1984; Rogers et al., 1985; Conticelli et al., 2002).

Post caldera activity was particularly intense at the Latera volcano with bimodal magmatism of both leucite-bearing and leucite-free lavas. Leucite-bearing post-caldera lavas at Latera have compositions ranging from tephritic to tephry-phonolitic (Fig. 3), whereas leucite-free lavas are particularly abundant within and external with respect to the caldera in the south-eastern sector of the volcano with the *Selva del Lamone* lava flow and they have a clear shoshonitic affinity with lavas ranging in composition from K-trachybasalts to latites (Fig. 3). The shoshonitic trachy-basalts have mineralogical assemblages made up of abundant olivine, clinopyroxene and plagioclase, but they differ significantly in terms of geochemistry with respect to other post-caldera shoshonitic rocks from other volcanic districts of the Roman Province (e.g., Holm et al., 1982; Varekamp & Kalamarides, 1989; Conticelli et al., 1991, 2009; Turbeville, 1993). The most abundant mafic mineral in the Roman rocks is clinopyroxene, which differs significantly from volcanic rocks crystallized in equilibrium with leucite or not. Indeed, clinopyroxenes from lamproite-like ultrapotassic rocks are generally aluminium poor, with Si+Al not sufficient to fill completely the tetrahedral site, whereas clinopyroxenes from Roman rocks, either leucite-free or -bearing ones, are characterized by excess of Al that partitioned between tetrahedral and octahedral sites (Barton & Varekamp, 1982; Holm, 1982; Cellai et al., 1994; Bindi et al., 1999; Chelazzi et al., 2006). Clinopyroxenes in shoshonite from Latera volcano are transitional between those typical of leucite-free (i.e., Tuscan lamproites) and Roman rocks, whereas those from shoshonites in other Roman districts have also Al excess (Perini & Conticelli, 2002; Boari & Conticelli, 2007; Cellai et al., 1994). Leucite is found both as phenocryst and as groundmass phase in plagioclase leucitites and leucitites. Sanidine is present both in the most evolved phonolitic and trachy-phonolitic terms, and it is also found also in leucite-free rocks of the Palaeo-Bolsena volcano and of the post-caldera Latera volcano.

Apparently normalized incompatible trace element patterns of plagioclase leucititic rocks of the Vulsini district are similar to those of earlier magmatism (Fig. 3) characterized by leucite-free ultrapotassic rocks (i.e., lamproite) and associated shoshonites and calc-alkaline rocks (i.e., Western Alps, Western Tyrrhenian Sea, Tuscany). Vulsinian plagioclase leucititic rocks and associated shoshonites, however, display larger throughs at Nb, Ta, and Ti, the appearance of a small through at Hf, and a small peak at Sr, concomitantly to the inversion of the U/Th and Ta/Nb normalized ratios (Fig. 3), with respect to the older leucite-free ultrapotassic and associated shoshonites and calc-alkaline rocks.

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