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Research paper

Origin and paleoenvironmental significance of Fe—Mn nodules in the Holocene perialpine sediments of Geneva Basin, western Switzerland

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ABSTRACT

Perialpine areas of central Europe have undergone significant changes following the last Alpine glaciation and especially through the Holocene time. This study relies on geochronological, mineralogical and geochemical clues to explain the formation and paleoenvironmental significance of Fe—Mn nodules reported from the young soils (~4.5 ka BCE) of Geneva Basin in western Switzerland. Having on average 2 mm in diameter, the nodules usually possess an onion-like and quasi-layered internal architecture defined by selective enrichments in Fe and Mn. Fe-rich mica is largely present in soil matrix and has served as a main source of Fe and Mn. Susceptible to favourable Eh-pH conditions several steps in mica weathering were recognised leading to the formation of nodules – vermiculitization, microcracking, Fe—Mn segregation and re-precipitation. Mineral alterations were boosted by long periods of summer warm climate during Boreal and Atlantic times as suggested by the increasing illite-smectite content and a disappearance of hydroxyl-interlayered clays from analysed colluvium. Moreover, archaeological ages and radiocarbon dating of charcoal yielded coherent Fe—Mn encrustation ages (4.8–4.3 ka BCE and 4.5–4.4 ka BCE, respectively) that coincide with the Holocene temperature maximum (~4 ka BCE) in Central Europe. Terrain morphology that led to better water retention formed earlier than ~8 ka BCE ago, during undefined Late Glacial time, promoting seasonal changes in redox conditions, thus facilitating the mobilization, distribution and re-precipitation of Fe and Mn. Established conditions lasted until Late Neolithic (3.4–2.2 ka BCE) when different agricultural practices changed favourable hydromorphic environment effectively putting an end to further nodule formation.

1. Introduction

Following the Last Glacial Maximum (LGM) in the European Alps around 20 to 22 ka BP, substantial areas of western Switzerland (Fig. 1) had become free of ice due to global warming and subsequent glacier retreat (e.g. Fiore et al., 2011). In Geneva area, the newly exposed land surface consisted mainly of glacial and glaciolacustrine sediments that overlain a thick molasse bedrocks of Tertiary age (e.g. Amberger, 1978; Moscariello et al., 1998; Girardclos et al., 2005). From that time the level of the proglacial/periglacial Lake Geneva was continuously dropping and attained a level close to the present-day at about 12 ka BP (Fiore, 2007). Ancient flooded lake basin was transformed into a terrestrial landscape that has been exposed to alteration, colluvial and alluvial sedimentation giving rise to the formation of loose, unconsolidated, and relatively thin Holocene perialpine soils (Houbolt and Jonker, 1968). Along the hillside of Grand-Saconnex (425 masl), a locality situated within the Geneva city limits (Fig. 1), recent archaeological excavations have revealed a ~1.5 m thick exposure of soils and sediments that included a basal glacial till and reworked glacial till proceeded by several distinct clayey to sandy horizons (Fig. 2; Besse and Steimer-Herbert, 2015, 2017). At the interface of two colluvial units, the upper very fine grained and the lower marked by a brown-orange alteration, a cm-thick dark zone rich in Fe—Mn nodules has been reported (Fig. 3; Šegvić et al., 2017). The nodules have up to 5 mm in

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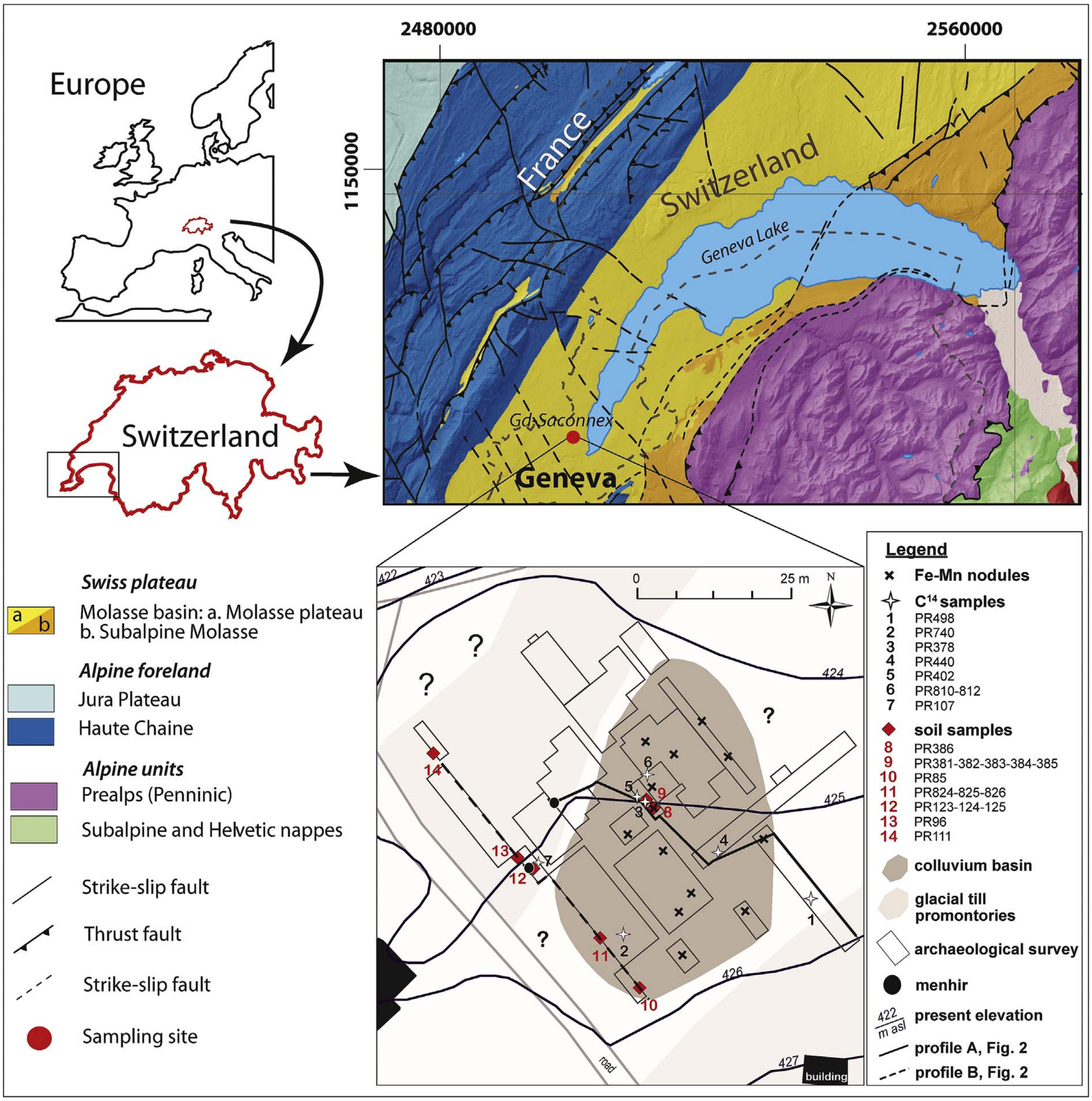

Fig. 1. Location of archaeological site of Grand-Saconnex with an overview on regional geology of western Switzerland (up). Geological map adapted after Lombard and Paréjas (1965). Detailed plan of archaeological site with the positions of sampling locations indicated (down).
Modified after Besse and Steimer-Herbert (2015, 2017).

diameter size with an onion-like quasi-layered internal architecture marked by selective enrichments of Fe and Mn. The ages obtained from ^{14}C dating of organic macro-remains present in the nodule layer confine its deposition to the Middle Neolithic time (Besse and Steimer-Herbert, 2015, 2017; ~4.5 ka BCE).

The Fe—Mn accumulations are nowadays known from a range of geological environments such as ocean floors, lacustrine and riverine sediments, and especially soils (e.g. Palumbo et al., 2001; Cornu et al., 2005). The soil Fe—Mn bodies may emerge in various forms – as nodules, concretions, spheroids, crust, and coatings (e.g. Palumbo et al., 2001; Gasparatos et al., 2005) however the first two are likely the most commonly encountered (Gasparatos, 2012). Their shape, size, and colour vary depending on the characteristics of host soils and prevailing environmental conditions. Hence, the Fe—Mn nodules and concretions were mainly documented as spherical, oval, tabular, or irregularly shaped with maximal sizes up to 4 cm (Gaiffe and Kübler, 1992; White and Dixon, 1996; Latrille et al., 2001). With regard to elemental concentrations it has been shown that Fe—Mn nodules, especially from marine sediments, may contain valuable metals such as Ni, Cu, and Co in economical quantities (e.g. Ram et al., 2001). Further to this, Mn is usually enriched up to 60 times compared to the normal abundances it attains in soils and sediments (e.g. Tan et al., 2006). High adsorption capacity of soil Fe—Mn nodules was shown as a factor that effectively controls the dynamics of many toxic metal pollutants found in soils thus placing a great deal of research attention to the nodules utilized in the remediation of contaminated surface sediments (e.g. Timofeeva and Golov, 2007).

Although the exact mechanism of the formation of Fe—Mn soil nodules and concretions is not fully understood, it has been reported that the alternating seasonal redox conditions may facilitate the mobilization of Fe and Mn and their dispersion throughout the soil matrix (e.g. Rhoton et al., 1991; Zhang and Karathanasis, 1997; Vepraskas, 2001;). Redox conditions in soils are largely controlled by microbial activity and presence of carbon used by these organisms as electron donors