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Uranium migration and retention during weathering of a granitic waste rock pile

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ABSTRACT

This study investigates the post-mining evolution of S-type granitic waste rocks around a former uranium mine, Vieilles Sagnes (Haute Vienne, NW Massif Central, France). This mine was operated between 1957 and 1965 in the La Crouzille former world-class uranium mining district and is representative of intra-granitic vein-type deposits. 50 years after mine closure and the construction and subsequent re-vegetation of the granitic waste rock pile, we evaluate the environmental evolution of the rock pile, including rock alteration, neo-formation of U-bearing phases during weathering, and U migration. Vertical trenches have been excavated through the rock pile down to an underlying paleo-soil, allowing the investigation of the vertical differentiation of the rock pile and its influence on water pathways, weathering processes and U migration and retention. Arenization dominantly drives liberation of U, by dissolution of uraninite inclusions in the most alterable granitic minerals (i.e. K-feldspar and biotite). Retention of U in the matrix at the base of the waste rock pile, and in the underlying paleo-soil most likely occurs by precipitation of (nano-) uranyl phosphates or a combination of co-precipitation and adsorption reactions of U onto Fe (oxy)hydroxides and/or clay minerals. Even though U-migration was observed, U is retained in stable secondary mineral phases, provided the current conditions will not be modified.

1. Introduction

In the near future, the combination of an intensifying demand for uranium resources, declining ore grades, and the exploitation of lower commodity grade ores will lead to an exponential increase of the annual volume of waste rock (Kahouli, 2011). The largest volume of waste products are produced in the nuclear fuel-cycle during mining and milling (Abdelouas, 2006), triggering a growing interest in waste rock management (e.g., Kipp et al., 2009; Miao et al., 2013; Schindler et al., 2013; Neiva et al., 2014). The term 'waste rock' is defined as untreated rocks that do not contain enough U to be economically processed. Waste rock piles are highly heterogeneous in their nature, comprising barren rock remobilized from the mine surroundings (access roads, mining works), overburden from overlying soils and rock covering the ore deposit and un-reclaimed, sub-economic ore extracted from the mine. A major characteristic of waste rock piles is their increased erosional surface compared to natural granitic outcrops, inducing an accelerated weathering rate. Apart from being potentially harmful for the environment this enhanced weathering provides an end-member example of accelerated continental alteration processes. Rock pile weathering overprints the late hydrothermal alteration of the rock and the natural supergene pre-mining alteration of the site.

For a long period, U vein-type deposits yielded the bulk of global U production, whereas less than 10 percent of the U was produced from deposits of this type at the end of the 1980s. This mining activity left behind a significant amount of granitic waste rock that form the oldest U-bearing rock piles in many inhabited areas, hence their importance for the evaluation of the weathering evolution of mine wastes for remediation strategies. One of the most representative regions with granitic vein-type deposits is the 'La Crouzille' district in the French Massif Central. S-type granites of the Massif Central region have an elevated U concentration, often larger than 20 ppm (Barbier, 1970; Cuney, 2014). Such a high background concentration dominantly arises from resistate U-bearing phases, located in accessory phases (zircon, sphene, allanite, monazite, apatite, or magmatic uraninite, ect.) (Bajo et al., 1983; Berzina et al., 1975; Cuney, 2009), as opposed to secondary U phases within primary minerals (Speer et al., 1981; Tieh et al.,

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1980), concentrated at textural heterogeneities (grain boundaries, mineral cleavages and fractures) in late-stage deuteric and early weathering materials (Dill et al., 2010; Guthrie and Kleeman, 1986; Kikuchi et al., 2007; Leroy and Turpin, 1988; Waber et al., 1992).

A question of major environmental relevance with respect to U waste rocks concerns the extent of U mobilization since the pile's construction. A mine-impacted wetland in the La Crouzille mining area has U values of up to 14,000 ppm. Wetlands often act as sinks for U and other trace metals, with U accumulating up to several thousand ppm (Owen and Otton, 1995; Regenspurt et al., 2010; Wang et al., 2013). Wang et al. (2013) recently showed that for the La Crouzille wetland the presence of U(IV) in soil, as a non-crystalline species is bound to amorphous Al–P–Fe–Si aggregates, and in pore water, occurs as a distinct species associated with Fe and organic matter colloids. Also, natural soils in this same region demonstrate that uranium exerts a high pressure on soil bacterial communities and suggest the existence of a uranium redox cycle mediated by bacteria in the soil (Mondani et al., 2011). Furthermore, naturally occurring high U concentrations of up to 3000–4000 ppm are common in alpine soils even though the surrounding granitic bedrock only contains trace amounts of U (Owen and Otton, 1995; Regenspurt et al., 2010). Experimental work revealed that U, liberated by granitic weathering in this region, was concentrated in soil organic matter (rather than to mineral phases) and was present primarily in the hexavalent state (Regenspurt et al., 2010).

This study refers to the influence of weathering on U migration in a re-vegetated granitic waste rock pile constructed 50 years ago on the site of the Vieilles Sagnes uranium mine, with the greater aim of improving mine waste management in this context. The Vieilles Sagnes site is located in the La Crouzille former mining district, Massif Central, France (Fig. 1a) and bears one of the oldest and most geologically representative waste rock piles in the region, constructed between 1957 and 1965. The weathering-driven differentiation of the waste rock pile was directly investigated by excavating trenches down to the underlying paleo-soil (Fig. 1b and c). Geochemical and mineralogical data on the different horizons within the waste rock pile and the paleo-soil enable an evaluation of the impact of weathering processes over 50 years. The appearance of neo-formation of uranyl-phosphate minerals results from weathering and more generally from the complex interplay between rock weathering, U migration and its fate. A major role is played by the paleo-soil underlying the pile and its highly U sorbing phases, resulting from weathering, that limit the extent of U mobility to the immediate surroundings.

2. Geological background

Uranium deposits related to granites are best exemplified by the mid-European Variscan uranium province, which extends over more than 2000 km from Spain to the Bohemian Massif (Cuney, 2014). They are located in late Carboniferous peraluminous leucogranites (French Massif Central) and in their metamorphic host rocks. Uranium deposition occurred 30–50 Ma after the emplacement of the granites, at 270 ± 15 Ma (Holliger et al., 1986; Kříbek et al., 2009) during a regional extensional event. The ore forming fluids are low-salinity and low-temperature fluids (Dubessy et al., 1987). Uranium deposition results from the mixing of oxidized meteoric fluids leaching magmatic uraninite from granites with fluids derived from an overlying basin (Turpin et al., 1990). This implies that waste rocks derived from French Massif Central have experienced a multiphase geological history, responsible for an important mineralogical heterogeneity. At least three periods of U-mineral formation, alteration or neo-formation can

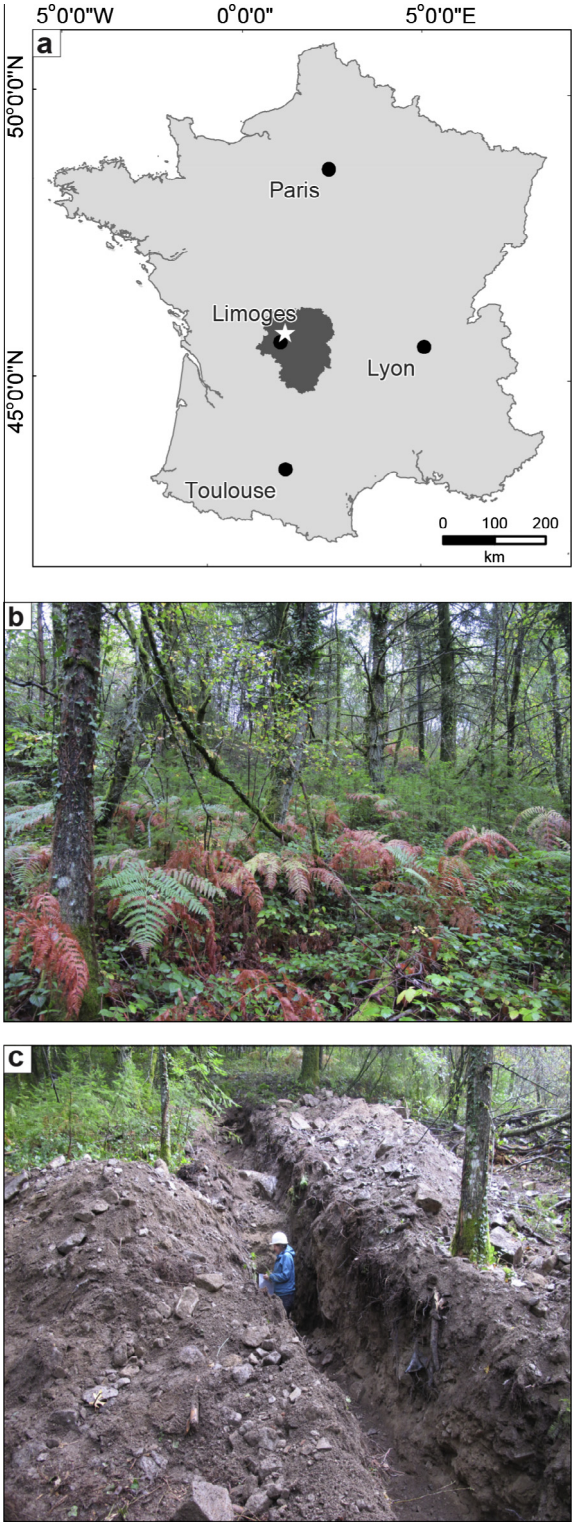

Fig. 1. Vieilles Sagnes site. (a) Map of France indicating the location of the Vieilles Sagnes site with a star. The shaded area represents the Limousin region. (b) The re-vegetated Vieilles Sagnes waste rock pile in La Crouzille mining district, French Massif Central, before trench excavation. (c) VSA trench through (upper part of) the Vieilles Sagnes waste rock pile exposing vertical cross sections down to the underlying paleo-soil.

be distinguished in this region (Fig. 2). The first period is the emplacement of S-type granites (Fig. 2a) (324 ± 4 Ma), in which most U is located in accessory phases such as zircon, monazite, apatite and magmatic uraninite (hereafter referred to as uraninite