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Ce anomalies and trace element distribution in Sardinian lithiophorite-rich Mn concretions

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ABSTRACT

Supergene concentrations of lithiophorite found in alluvial conglomerates and residual sandy clay deposits of Messinian age in northern Sardinia, were investigated for minero-chemical composition and fractionation processes. The Mn concentration occurs as cement in conglomerate, coatings on pebbles and as concretions in clays. In the mineralisation, some transition metals including Ni, Cu, and Zn along with Ba, U, Pb, and REEs, are enriched relative to the composition of the upper continental crust. Zn and Ni co-vary with Mn, suggesting that they are hosted in lithiophorite. Also the REEs, with the exception of Ce, co-vary with Mn. Ce, due to its redox chemistry, fractionates relative to the other REEs and precipitates as cerianite during Mn^{4+} reduction. Mn mineralisation has a different Ce signature as expressed by the Ce anomaly, which varies between 0.22 and 11.75. A two-stage model was proposed for explaining the Ce anomaly fluctuations. Precipitation of the samples with positive Ce anomalies occurred in the first stage from organic matter-free fluids which favored the oxidation of cerium on the Mn phase surface; in the second stage, instead, Ce-depleted solutions, resulting from the first stage, were responsible for the precipitation of samples with negative Ce anomalies.

1. Introduction

Mn oxyhydroxides and oxides play an important role in controlling the chemistry of soils and sediments (Tan et al., 2005, and references therein). Given their great capacity to adsorb trace metals from natural waters, accumulations of these Mn minerals often represent deposits of high economic significance. In soils and laterites, as well as in other sedimentary deposits (e.g., alluvial), Mn-bearing minerals commonly form nodules, crusts, coatings on pebbles, or Mn-rich horizons (e.g., Dowding and Fey, 2007; Koschinsky and Hein, 2003; Manceau et al., 2007; Mohapatra et al., 2011; Nahon et al., 1984; Neaman et al., 2008; Sinisi et al., 2012; Tan et al., 2006).

Generally, Mn oxyhydroxides have a high rare earth element sorption capacity at pH conditions typically prevalent during pedogenesis (e.g., Laveuf and Cornu, 2009), and the Mn oxyhydroxides promote Ce oxidation by the reduction of Mn^{4+} to Mn^{3+} or Mn^{2+} (Ohta and Kawabe, 2001). Consequently, Ce anomalies are often associated with pedogenetic Mn concretions, and the Ce anomalies allow the identification of different geological processes and conditions (e.g., Beauvais, 1999; Mongelli et al., 2013, and references therein).

In this study, supergene concentrations of lithiophorite (Al,Li) $MnO_2(OH)_2$ found in alluvial conglomerates and residual sandy clay deposits of Messinian age in northern Sardinia were investigated for minerochemical composition. Our goal is to elucidate the fractionation processes that occur at the expense of REEs and trace metals, including heavy metals and high field strength elements, during Mn-oxyhydroxide accumulation and to ident\ify the conditions that promote the genesis of Mn mineralisation. By doing so, we use uneconomic Mn mineralisation, such as those in Sardinia, to provide useful insights into critical element distributions for the geochemical exploration of analogues deposits of economic interest.

2. Geology and occurrence of Mn mineralisation

The Sardinia island, located in the western Mediterranean Sea, consists of a portion of Variscan basement with a sedimentary and volcanic cover of Mesozoic and Tertiary age (Fig. 1). Its present position is due to Burdigalian counter-clockwise rotation associated with the opening of the Ligure-Provençal back-arc basin (Oudet et al., 2010).

The present study area is located in the northwestern part of Sardinia (Nurra region) where the Variscan basement is covered by Mesozoic evaporite and carbonate shelf sediments, calc-alkaline Tertiary volcanics, and Messinian to Pliocene alluvial deposits. Within this cover sequence, episodes of intense weathering occurred from the Permian to the Messinian (Combes et al., 1993; Mameli et al., 2007; Mongelli et al., 2012; Sinisi et al., 2013).

Alluvial deposits of uppermost Tortonian to Messinian age are widespread in Nurra, where they unconformably overlie metamorphic rocks, evaporite-carbonate shelf sediments and calc-alkaline volcanics. With

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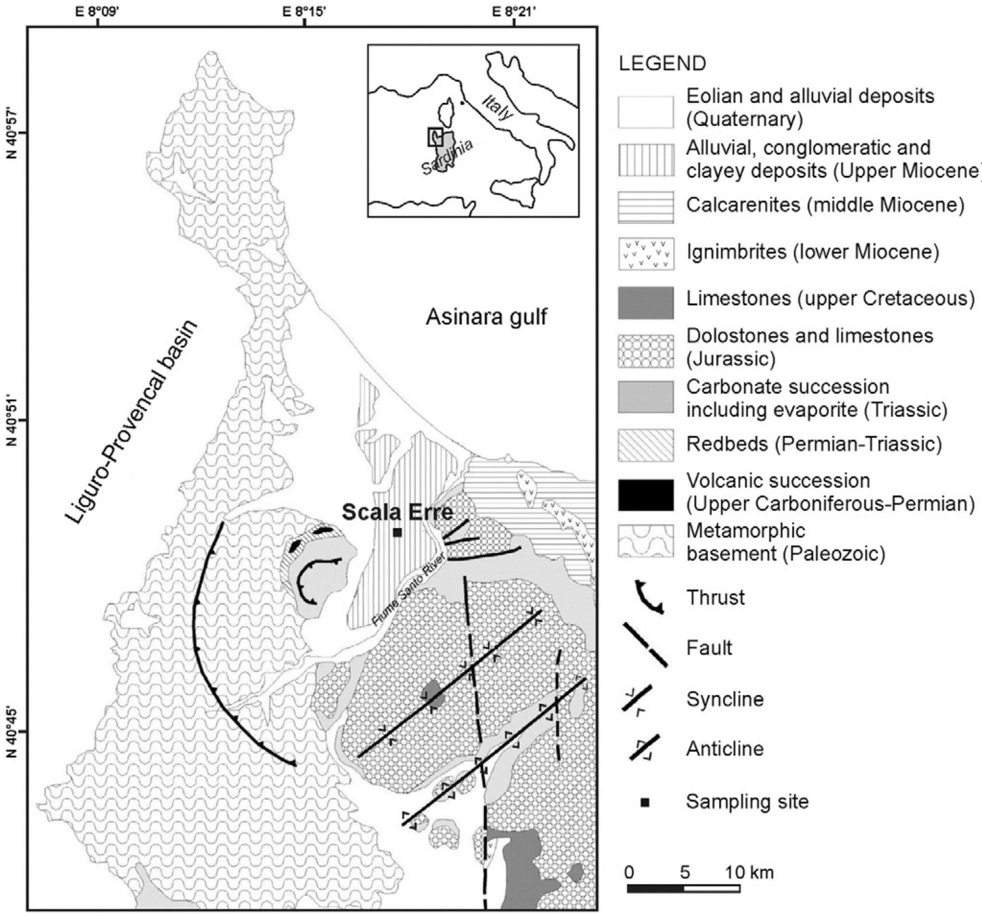

Fig. 1. Geological sketch map of the Nurra district (NW Sardinia). Modified after Mongelli et al. (2012).

an average thickness of 50 m, these alluvial deposits are particularly well developed in a morphological depression that formed in the Permian to Jurassic sedimentary cover during the lowstand associated with the Messinian Salinity Crisis.

The deposits consist of alternating bed of conglomerate and clay that have been interpreted as alluvial fans and braided river plain deposits, respectively (Funedda et al., 2000; Fig. 2). Embedded in these alluvial deposits are thick layers of residual clays affected by deep pedogenesis as testified by rizoliths and hardpan (Mongelli et al., 2012). The clays are mostly kaolinitic or illitic with minor gibbsite. The alluvial package is known as the Scala Erre succession and is composed of the following (from top to bottom): i) a debris flow layer, likely Pleistocene in age, formed by clast-supported conglomerates with subrounded quartz clasts in a sandy matrix; ii) alternating clay and channelised conglomerate consisting of mud-supported, rounded to subrounded clasts of metamorphic quartz, quartzites, and highly weathered rhyolite within

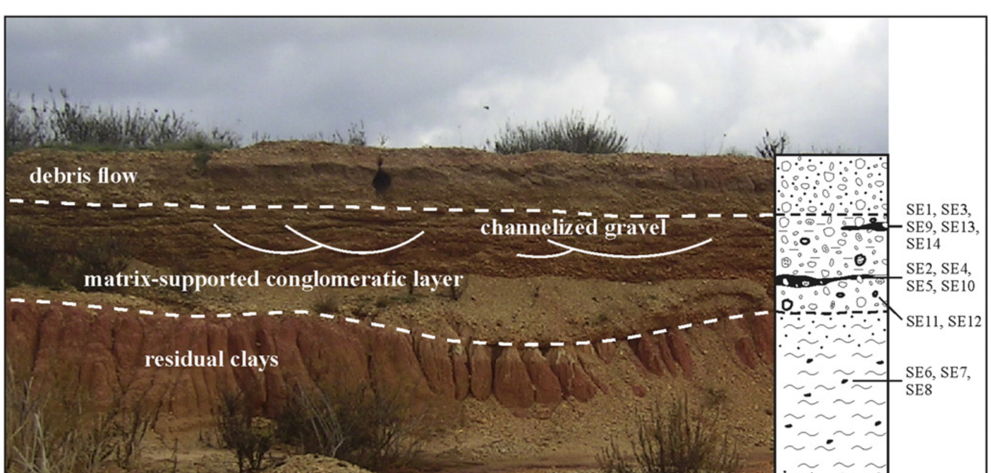

Fig. 2. Messinian succession at the Scala Erre sampling site (northern Nurra). A simplified stratigraphy with sample codes is also shown.