Trace and rare earth elements contents of a Sardinian sedimentary Mn-rich deposit: Preliminary results.

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Abstract. Mn oxides are important scavengers of trace elements from waters. They often form deposits with high metals concentrations that sometimes have economic significance. Within a thick sedimentary deposits of northern Sardinia, Mn oxide mineralization was found as both matrix and coatings on clasts of a conglomeratic deposit, and subrounded nodules in residual clays. Lithiophorite and birnessite are the sole Mn phases that are also accompanied by variable amounts of Fe oxides and hydroxides, clay minerals, and phyllosilicates. Chemical analysis of the studied samples revealed high concentrations of most of trace metals (Co, Ni, Zn, Cu, Ba, Y, U and Pb) and all rare earth elements (REE). The latter were used to provide the first hypothesis regarding environmental conditions and chemical processes determining the precipitation of Mn oxides.

Keywords. Lithiophorite, Birnessite, Rare earth elements, Sardinia

1 Introduction

Manganese is the tenth most abundant element in the Earth's crust. In natural environments, the geochemical behaviour of Mn is mainly controlled by pH and oxidation potential (Eh). It exists as Mn^{2+}, which is soluble under reducing and acidic conditions, as well as Mn^{3+} and Mn^{4+}, which are less soluble and stabilize as Mn oxides under relatively oxidizing and alkaline conditions (Robb 2005). Hydrous Mn oxides are ubiquitous forming in a wide variety of geological environments where participate in several types of chemical reactions (Tan et al. 2006; Dixon and Skinner 1992; McKenzie 1989). The Mn oxides phases in fact are surface-active minerals with large amounts of pH-dependent surface charges, very low point of zero charge (pzc), large surface areas, and high oxidizing capacity (Post 1999).

Among natural particles, Mn oxides have long been recognized as playing an important role in controlling the chemistry of soils and sediments (Tan et al. 2005, and references therein). Owing to their high adsorption capability of trace metal from natural waters, Mn oxides accumulations often represent deposits with high economic significance. In soils and laterites, as well as in other sedimentary deposits (e.g. alluvial), Mn-bearing minerals commonly occur forming nodules, crusts, coatings on clasts, or Mn-rich horizons (Nahon et al. 1989; Neaman et al. 2008; Koschinsky and Hein 2003; Sinisi et al. 2012; Tan et al. 2006).

In northern Sardinia Mn oxides mineralizations were found into alluvial conglomeratic and residual clayey deposits of the Messinian age. In this paper the preliminary data on mineralogical and chemical composition of these Mn mineralizations are provided with the aim to decipher the environmental conditions and chemical processes occurring during Mn oxides accumulation.

2 Geology and Mn occurrences

Sardinia (western Italy) belongs to the Sardinia-Corsica microplate located in the Mediterranean Sea, and shows evidences of numerous large-scale tectonic events which lasted throughout the Phanerozoic time. Its geological evolution has been first strongly affected by the Paleozoic tectonic activity that led to the closure of Rheic Ocean and subsequent collision of the Gondwana and Laurasian continents. During Mesozoic, the whole island was tectonically stable until the lower Burdigalian when the Sardinia-Corsica plate detached from south-european edge causing the opening of the Liguro-Provencal backarc basin.

NW Sardinia, commonly named the Nurra district, consists of a structural high that represents the uplifted part of a wide, tilted block (Fig. 1).
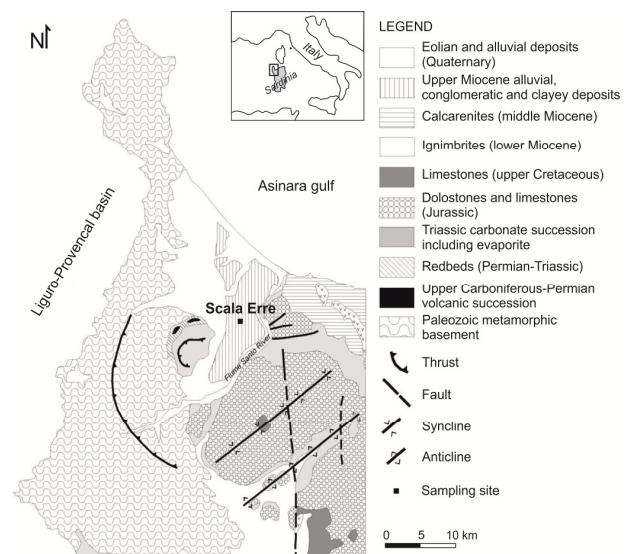

Figure 1. Geological sketch map of the Nurra district (NW Sardinia). Modified after Mongelli et al. (2012).

To the west, this structural high borders the eastern passive margin of the Liguro-Provencal backarc basin; to the east, it abuts the edge of a N–S-trending Miocene halfgraben (the Porto Torres Basin, Thomas and

Gennessaux 1986). Upper Burdigalian to Tortonian carbonate marine deposits of the Porto Torres Basin onlap the structural high, where Mesozoic and Palaeozoic sequences are exposed. The Permian and Mesozoic sequences unconformably overlie Variscan low-grade metamorphic basement and in turn are overlain by an alluvial deposit of the Messinian age (Mongelli et al. 2012 and references therein).

At the northern Nurra, where Tortonian transgression did not occurs, the Messinian continental deposits are widespread and represent the infillings of a wide depression formed between Jurassic uplands and Variscan basement after the Messinian salinity crisis. The deposits consist of an alternation of clays and conglomerates which has been interpreted as alluvial fan and braided-river plain sediment, respectively (Fig. 2, Funedda et al. 2000). However, associated to these alluvial deposits, wide outcrops of residual clays, currently under excavation, are found at the "Scala Erre" site where the sampling was carried out.
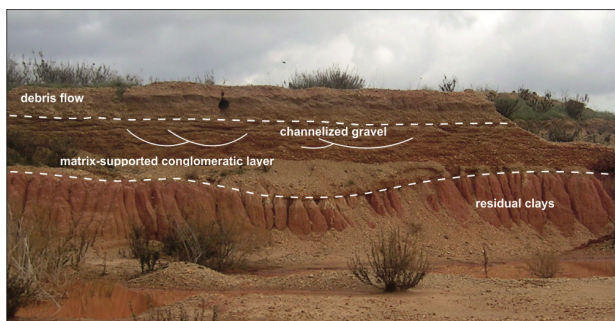
Figure 2. Messinian succession at the Scala Erre sampling site (northern Nurra).

In detail, from top to bottom, the Scala Erre succession is composed of the following: i) a debris flow layer, likely Holocenic or Pleistocenic in age, formed by clast-supported conglomerates with prevailing subrounded quartz clasts and sandy matrix; ii) a 1–3 m thick, channelized gravel horizon consisting of rounded–subrounded clasts of metamorphic quartz, quartzites, and highly weathered rhyolite within a silty–sandy matrix; iii) a 10 m-thick unit of clays and sandy clays, which show evidence of intense pedogenesis, including rhizoliths and strongly Fe-depleted zones. Locally, 1 m thick gravel layers are interbedded with the clays. The contact between the conglomeratic horizon and the clayey deposit is sharp and marked by the presence of a calcrete level, while the base of the residual clays is not exposed.

Within both conglomerate and clay deposits, hydrogenous Mn-oxyhydroxides locally occur forming the matrix of conglomerates (Fig. 3a), thin patinas covering the conglomerate clasts (Fig. 3b) and centimeter-size nodules widespread in the clays.

2 Analyses and results

Seven Mn-oxides patinas and matrix samples and three Mn-rich nodules from Scala Erre Messinian deposit have been analyzed to obtain the mineralogical and chemical composition data. X-ray diffraction (XRD), inductively coupled plasma-mass spectrometry (ICP-MS), and instrumental neutron activation analysis (INAA) were performed on all powdered, whole rock samples at Activation Laboratories (Ancaster, Canada). At present, no microscopic data are available for these mineralizations which will be subject of our future research.

2.1 Mineralogy

The main Mn phase of analysed samples is lithiophorite. Birnessite also occurs in most samples as associated Mn mineral, except for a sample where birnessite is the sole Mn mineral phase. Quartz, Fe-oxides and hydroxides (hematite and goethite), clay minerals (mainly kaolinite and scarce illite) and phyllosilicates (muscovite) complete the mineralogical association. In two samples only, feldspars are also presents with low contents.
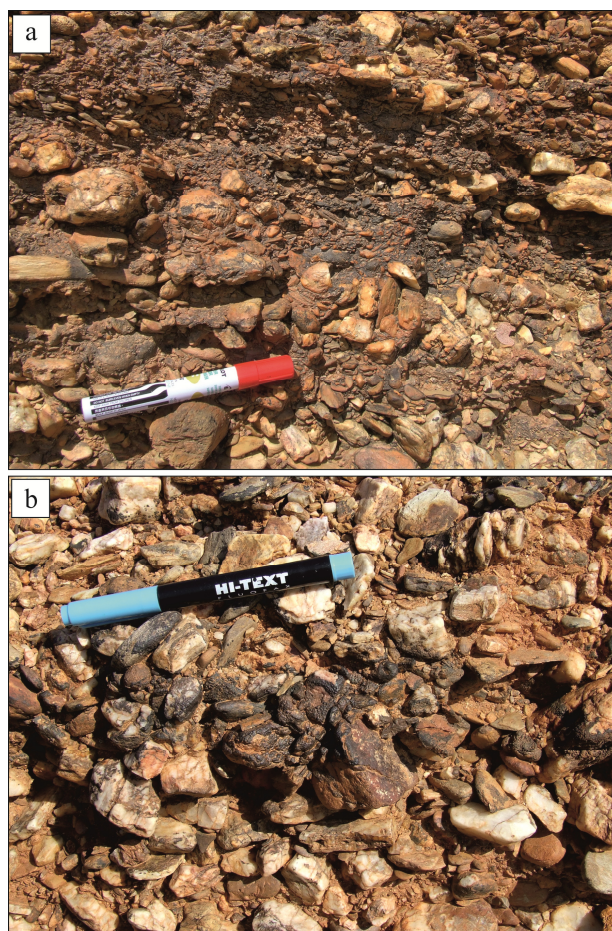

Figure 3. Mn oxides forming the matrix in a micro-conglomerate (a) and coatings on metamorphic quartz and quartzite clasts (b).

2.1 Chemistry

Normalization diagrams of major, trace and rare earth elements are shown in Fig. 4. Major elements show the same distribution patterns in all our samples. MnO contents are very high exceeding 10 to 120 times those of the GLOSS (Global Subducting Sediments; Plank and Langmuir 1998), used as reference standard. Other major

elements have concentrations constantly lower than those of the GLOSS, with the exception of Fe_2O_3, Al_2O_3, and P_2O_5 which in few sample have higher contents. Finally, large depletions are observed for alkaline and earth alkaline elements (MgO, CaO, Na_2O).

Regarding trace elements, the GLOSS-normalization patterns of both conglomerate matrix and nodules share the same elemental features. Compared to the reference standard, the analysed samples are strongly enriched in most transition metals, such as Co, Ni, Zn and Cu (the latter more enriched in the nodules), moderately enriched in Ba, Y, U and Pb (the latter strongly enriched in nodules only), and moderately depleted in the other trace elements. Among these Zr, Ta, and Cr show the lowest contents.
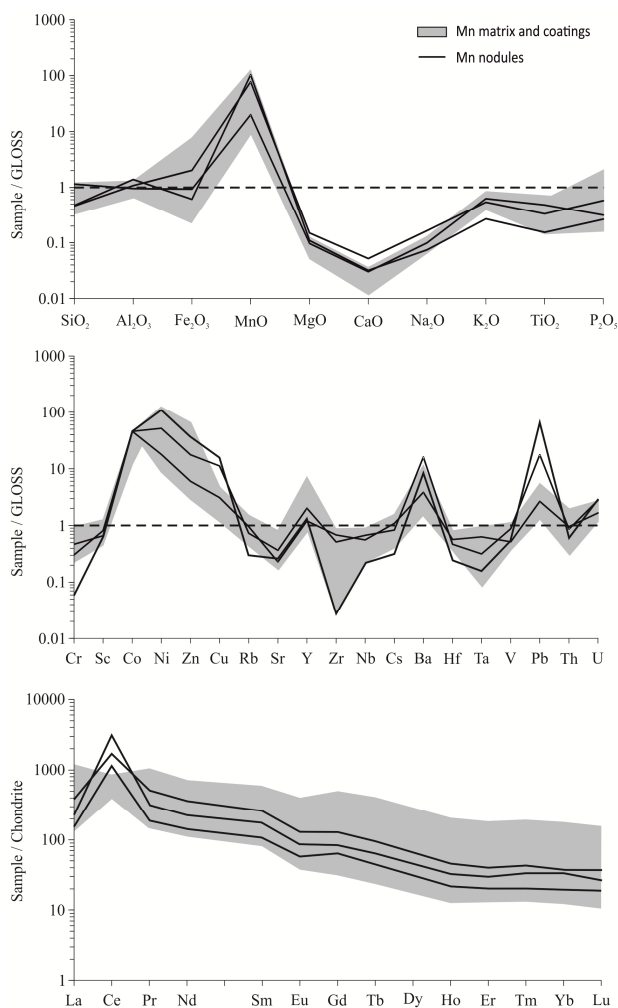
Figure 4. Major, trace and REE normalization diagrams.

The chondrite-normalized REE patterns (chondrite data are from Evensen et al. 1978) of the two types of the studied samples are comparable referring to element concentrations and distributions. However, some differences between nodules and the other Mn-rich samples are observed. Nodules are characterized by very high ΣREE values that are between 3398.5 and 1368.8 ppm; high values of LREE/HREE fractionation index ($6.82 < (La/Yb)_{ch} < 9.96$); and strongly positive Ce anomalies resulting in very high values of the Ce/Ce* ratio (3.90-11.75). The Mn-oxides matrix and coating are characterized by a wide range of REE contents, varying

from 640.01 to 2121.60 ppm; a significant LREE/HREE fractionation with $(La/Yb)_{ch}$ values of 6.88-13.73; both positive and negative Ce anomalies expressed by values of Ce/Ce* ratio between 0.49 and 3.39.

3 Discussion and conclusions

Mn oxides are ubiquitous in rocks, soils, and sediments, and the geochemistry of Mn implies that these oxides can precipitate in a wide variety of geological settings. Lithiophorite and birnessite, the Mn-bearing minerals in the studied samples, are commonly found in soils (Koppi et al. 1996; Post 1999). These minerals are hydrous oxides of Mn and are characteristic of oxidizing environments. In lateritic sediments, their precipitation typically occur at the weathering front where the high concentration of dissolved Mn^{2+}, the alkaline pH, and high Eh values enable the formation of Mn^{4+}-bearing phases (Nahon et al. 1989). Both lithiophorite and birnessite have a layer structure consisting of edge-sharing MnO_6 octahedra sheets and interlayer spaces that commonly host water molecules and a wide range of cations (mainly trace metals, Post 1999). Due to their structure, these Mn phases readily participate in oxidation-reduction and cation-exchange reactions playing a significant role in sediment chemistry. This is consistent with trace metal enrichments of the studied samples.

On the contrary, the association between high REE contents and lithiophorite and/or birnessite is more unusual. Nevertheless, the high correlation (r=0.83) between ΣREE and MnO contents in the studied samples suggest a significant relationship between REE and Mn-bearing minerals. Therefore, as yet supposed for other Mn oxides (mainly pyrolusite, hollandite, and cryptomelane; Sinisi et al. 2012), even lithiophorite and birnessite likely exert a significant adsorption effect on REE.

The Mn oxides also play a significant role in trapping Ce and therefore generating positive Ce anomalies, commonly used to identify redox processes during weathering (Mongelli and Acquafredda, 1999; Feng 2010; Laveuf and Cornu 2009; Laveuf et al. 2012). Positive Ce anomalies occur as a result of a scavenging process including the oxidation of Ce^{3+} to Ce^{4+} (leading to the precipitation of cerianite) and the reduction of Mn^{4+} on the Mn oxides surface (Bau 1999). However, the presence of organic matter in sediments inhibits the development of negative Ce anomalies in oxidizing waters for two main reasons: (1) because Ce cannot be oxidized at the surface of Mn oxides; (2) because all of the REEs form complexes with organic molecules, meaning that Ce is not selectively removed from the solution (Davranche et al. 2005, 2008).

In the Mn-rich matrix and coatings at Scala Erre, the variation (from negative to positive) of Ce anomalies, is likely due to the presence of organic-rich and organic-poor fluids incoming during the formation of Mn phases. Therefore, the studied samples with negative to positive Ce anomalies likely formed in an environment where REE organic speciation and the formation of organic-REE complexes had an important reducing effect on

cerianite precipitation. In contrast, the Scala Erre Mn nodules, having strongly positive Ce anomalies despite their residence in lateritic clays, likely formed in an environment with little or no organic matter, where REE speciation in circulating fluids was dominated by inorganic species.

Furthermore, it is known that neutral or alkaline pH conditions may easily account for the fractionation of LREE-HREE (Henderson 1996). In non-acidic pH environment, in fact, the HREE form more soluble complexes than the LREE and thus are preferentially retained in solution. The high values of $(La/Yb)_n$ index of studied samples, therefore, might suggest that the fractionation between light and heavy REE was due to a different geochemical behaviour of REE rather than a different REE uptake capability of Mn oxides.

Acknowledgements

References

Bau M (1999) Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: experimental evidence for Ce oxidation, Y Ho fractionation and lanthanide tetrad effect. Geochim Cosmochim Acta 63:67–77

Davranche M, Pourret O, Gruau G, Dia A, Le Coz-Bouhnik M (2005) Adsorption of REE(III)-humate complexes onto MnO2: experimental evidence for cerium anomaly and lanthanide tetrad effect suppression. Geochim Cosmochim Acta 69:4825–4835

Davranche M, Pourret O, Gruau G, Dia A, Jin D, Gaertner D (2008) Competitive binding of REE to humic acid and manganese oxide: impact of reaction kinetics on development of Cerium anomaly and REE adsorption. Chem Geol 247:154–170

Dixon JB, Skinner HCW (1992) Manganese minerals in surface environments. In: Skinner HCW, Fitspatrick RW (Eds) Biomineralisation Processes of Iron and Manganes-Modern and Ancient Environments. Catena 21:31–50

Evensen NM, Hamilton PJ, O'Nions RK (1978) Rare earth abundances in chondritic meteorites. Geochim Cosmochim Acta 42:1199–1212

Feng J (2010) Behaviour of rare earth elements and yttrium in ferromanganese concretions, gibbsite spots, and the surrounding terra rossa over dolomite during chemical weathering. Chem Geol 271:112–132

Funedda A, Oggiano G, Pasci S (2000) The Logudoro basin: a key area for the Tertiary tectono-sedimentary evolution of North Sardinia. Boll Soc Geol Ital 119:31–38

Henderson P (1996) The rare earth elements: introduction and review. In: Rare earth elements. Chemistry, origin and ore deposits. Jones AP, Wall F, Williams T (eds) The Mineralogical Society Series (7), 1st edn .Chapman and Hall, London, pp 1-19

Koppi AJ, Edis R, Field DJ, Geering HR, Klessa DA, Cockayne DJ (1996) Rare earth elements trend and cerium–uranium–manganese association in weathered rock from Koongarra, Northern Territory, Australia. Geochim Cosmochim Acta 60:1695–1707

Koschinsky A, Hein JR (2003) Uptake of elements from seawater by ferromanganese crusts: solid-phase associations and seawater speciation. Marine Geol 198:331–351

Laveuf C, Cornu S (2009) A review on the potentiality of rare earth elements to trace pedogenetic processes. Geoderma 154:1–12

Laveuf C, Cornu S, Guilherme LRG, Guerin A, Juillot F (2012) The impact of redox conditions on the rare earth element signature of redoximorphic features in a soil sequence developed from limestone. Geoderma 170:25–38

McKenzie RM (1989) Manganese oxides and hydroxides. In: Dixon JB, Weed SB (eds) Minerals in Soil Environments. SSSA Book Ser. 1. SSSA, Madson WI, USA. pp 439-465

Mongelli G, Acquafredda P (1999) Ferruginous concretions in a Late Cretaceous karst bauxite: Composition and conditions of formation. Chem Geol 158:315–320

Mongelli G, Mameli P, Oggiano G, Sinisi R (2012) Messinian palaeoclimate and palaeo-environment in the western Mediterranean realm: Insights from the geochemistry of continental deposits of NW Sardinia (Italy). Int Geol Rev 54:971–990

Nahon DB, Herbillon AJ, Béauvais A (1989) The epigenetic replacement of kaolinite by lithiophorite in a manganese-lateritic profile, Brazil. Geoderma 44:247–259

Neaman A, Martínez CE, Trolard F, Bourrie G (2008) Trace element associations with Fe- and Mn-oxides in soil nodules: Comparison of selective dissolution with electron probe microanalysis. Appl Geochem 23:778–782

Plank T, Langmuir CH (1998) The chemical composition of subducting sediment and its composition for the crust and mantle. Chemical Geology 145:325–394

Post JE (1999) Manganese oxide minerals: Crystal structures and economic and environmental significance. Proc Natl Acad Sci USA 96:3447–3454

Robb L (2005) Introduction of ore-forming processes. Blackwell Science Ltd, Oxford

Sinisi R, Mameli P, Mongelli G, Oggiano G (2012) Different Mn-ores in a continental arc setting: geochemical and mineralogical evidence from Tertiary deposits of Sardinia (Italy). Ore Geol Rev 47:110–125

Tan W, Liu F, Feng X, Huang Q, Li X (2005) Adsorption and redox reactions of heavy metals on Fe-Mn nodules from Chinese soils. J Coll Inter Scie 284:600–605

Tan WF, Liu F, Li YH, Hu HQ, Huang QY (2006) Elemental composition and geochemical characteristics of iron-manganese nodules in main soils of China. Pedosphere 16:72–81

Thomas B, Gennessaux M (1986) A two stage rifting in the basin of the Corsica-Sardinia strait. Marine Geol 72:225–239