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Rare earth elements of a 1000-year paddy soil chronosequence: Implications for sediment provenances, parent material uniformity and pedological changes

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ABSTRACT

A series of paddy soil profiles with approximately 50, 300, 700 and 1000 years of paddy cultivation history and an uncultivated mud beach profile under nearly identical landscape and climate conditions were studied. The signatures of rare earth elements (REEs) were used to identify sediment provenances and parent material uniformity of the studied profiles and to assess long-term paddy management effects on REE mobilization and fractionation. The distribution patterns of samples on a δEu_N–ΣREEs plot indicate that the parent materials of paddy soils and the uncultivated soil mainly originate from Yangtze River sediments. The REE chondrite-normalized curve could be used to adequately evaluate parent material uniformity, thus allowing further studies of soil REE changes along a time sequence of paddy cultivation. To understand anthro-pedogenic effects on REE mobilization and fractionation, the REE concentrations of paddy soils were normalized to those of the uncultivated soil. Paddy management resulted in accumulation of all REEs within the upper 100 cm, possibly due to anthropogenic inputs such as irrigation water and phosphate fertilizers. In particular, a distinct positive Ce anomaly was observed. This was likely due to periodic reduction and oxidation processes caused by artificial submergence and drainage. These REE signatures are especially marked in the anthrostagnic epipedon (Ap), as compared with the hydragric horizon (Bg). The positive Ce anomaly increased gradually with increasing paddy cultivation age. This demonstrates the utility of Ce anomaly as a trace of the frequency and intensity of redox conditions. The relative enrichment of all REEs and gradual accumulation with paddy cultivation time in the Ap horizons imply low mobility of REEs in the investigated paddy soils. In conclusion, our study demonstrates the effectiveness of various REE proxies as tracers of sediment provenances and parent material uniformity in present paddy soils. It also reveals the effects of long-term paddy management on REE enrichment and positive Ce anomalies.

1. Introduction

Rare earth elements (REEs), or the lanthanides, comprise 15 elements with periodic numbers 57 through 71, that is, from La to Lu. REEs have a close but distinct geochemical behavior in natural systems, according to the individual REEs or the group of REEs under consideration (Henderson, 1984). The coherent chemical behavior of the lanthanides (Thompson et al., 2013) and their high resistance to chemical mobilization (Taylor and McLennan, 1985) underlie the use of REEs in sediments as provenance indicators (Jiang et al., 2009; Xu et al., 2011, 2012; Yang et al., 2002). The patterns of chondrite-normalized curves and similarly Ce/Eu against Eu/Sm plots have been used to evaluate parent material uniformity and lithologic discontinuities (Egashira et al., 1997; Xing et al., 2004). However, Egashira et al. (2004) concluded that the above-mentioned REE indicators did not differentiate among various parent materials. The effectiveness of REE curves and Ce/Eu against Eu/Sm plots in evaluating the parent material uniformity needs further examination.

Although the REEs have a similar chemistry, the phenomenon known as "lanthanide contraction" permits some differences in chemical reactivity and possible preferential migration of individual REEs (Aide and Smith-Aide, 2003). The behavior of REEs within aquatic systems and estuarine sediments has been extensively investigated (e.g. Cidu et al., 2013; Morgan et al., 2012; Polyakov et al., 2009 and references therein) and REEs have been used to trace geochemical processes in hydrology (Zhou et al., 2012) and geology (Yuan et al., 2003; Zhou et al., 2010). However, pedological behavior of REEs remains poorly understood, which limits their application as tracers of pedogenetic processes (Aide and Smith-Aide, 2003; Laveuf et al., 2008). Recently, Laveuf and Cornu (2009) and Laveuf et al. (2012) emphasized the potential of REEs to trace pedogenetic processes, especially past redox conditions. They both recommended further study of the REE behavior (migration, enrichment, fractionation, and anomaly) in different

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pedological environments in order to visualize and quantify different pedogenic processes.

Paddy soils are an important soil resource for food production especially in monsoonal Asia. Knowledge of soil dynamics and directions of pedogenic evolution under long-term wet cultivation are useful for the improvement and sustainable use of these important soil resources (Chen et al., 2011; Zhang and Gong, 2003). One way to obtain the knowledge of soil changes with time is to study chronosequences—soils formed on the same parent material in the same climate but for varying weathering durations (Brantley, 2008). Despite the importance of paddy soil chronosequence studies, information from these is limited. The difficulty in identifying the original cultivation age of paddy soils and the general lack of well-dated sites are the main limitations in paddy soil chronosequence studies (Chen et al., 2011). Paddy soils located on a coastal plain in Cixi (Hangzhou Bay), Zhejiang Province, facing the East China Sea (Fig. 1) provide an excellent opportunity to establish a millennium-scale paddy soil chronosequence due to long-term rice cultivation history (more than 1000 years) and the well-dated sites in this region (Chen et al., 2011; Cheng et al., 2009; Wang, 2004). However, several issues need to be resolved, namely identifying sediment provenances and evaluating the uniformity of the parent materials of the paddy soils with different cultivated age at different sites. By geographic proximity, the soils in the coastal plain originate from marine sediments from the East China Sea, with some river alluvium from the Qiantang River (Fig. 1). However, the East China Sea receives a tremendous amount of terrigenous materials from the Yangtze River, the Yellow River, and local small rivers (Jiang et al., 2009; Xu et al., 2011). Despite several studies of the Cixi coastal plain, the sediment provenance in this region is still unclear. Verification of parent material homogeneity and sediment provenances is a prerequisite to establish model soil chronosequence and contributes to validating and advancing our understanding of pedogenic and biogeochemical studies of the same chronosequence reported in previous studies (Cheng et al., 2009; Ho et al., 2011; Roth et al., 2011; Wissing et al., 2011, 2013; Zou et al., 2011).

As anthropogenic soils, paddy soils are significantly affected by human activities such as plowing and puddling, artificial and seasonal submergence and drainage, and manuring and fertilization. Recently, studies on a millennium-scale paddy soil chronosequence showed that these paddy management practices had obvious impacts on soil physical, chemical and microbiological properties, which exhibited clear temporal trends over this time scale (Chen et al., 2011; Cheng et al., 2009; Ho et al., 2011; Roth et al., 2011; Wissing et al., 2011, 2013; Zou et al., 2011). However, information on the dynamic changes of REEs under long-term wet cultivation is limited. Knowledge of the behavior of REEs during long-term evolution of paddy soils can improve our understanding of the impact of paddy management on REE mobilization and fractionation and is critical for using the signature of REEs to quantitatively trace pedogenitic processes. The objectives of the present study were (i) to identify sediment provenances of a 1000-year paddy soil chronosequence using REEs, (ii) to examine the effectiveness of the chondrite-normalized curve of REEs and the plot of Ce/Eu against Eu/Sm in evaluating parent material uniformity, and (iii) to investigate the chronosequential changes of REEs in paddy soil profiles at a millennial timescale.

2. Materials and methods

2.1. Sites and sampling

The study area is located on a coastal plain in Cixi (Hangzhou Bay), Zhejiang Province, facing the East China Sea (Fig. 1), with a longitude range of 121°12′–121°42′, and a latitude range of 30°21′–30°24. The region belongs to the southern margin of the north subtropical monsoon climate zone and has a mean annual air temperature of 16.3 °C with an average range from 9.3 °C to 38.5 °C and a mean annual precipitation of 1325 mm with summer monsoon from April to October. By geographic proximity, the soils in the study area originate from marine sediments from the East China Sea, with some river alluvium from the Qiantang River (Fig. 1).

As the coastline is continuously receiving alluvial deposits and prograding toward the sea, over time the land surface has gradually become elevated and free from tidal effects. Subsequently, seawalls to prevent tidal flooding are built by local farmers when the surface of the land becomes stable, thus converting the land inside the seawall for agricultural production. Along the coastline extension, such seawalls were built successively at different stages of land formation from south to north (Fig. 1). Wang (2004) collected and compiled a series of Cixi County annals that chronologically recorded the seawall construction in detail. Based on the time of dyke construction (Wang, 2004) sites with approximately 50 (cultivated since 1952), 300 (cultivated since 1735), 700 (cultivated since 1403) and 1000 (cultivated since 1047) years of paddy cultivation history were identified. Sampling was conducted in June 2008 after the harvest from four paddy sites (P50, P300, P700, P1000) (Fig. 1). In addition, we selected an uncultivated mud beach profile to represent the original soil (time zero, P0). Within each area of identical paddy cultivation history, one representative profile was chosen for soil sampling based on the soil landscape and morphological characteristics of that area. Soil profiles were described and sampled according to genetic horizons following standard field description guidelines (FAO, 2006). Soil classifications and site descriptions are given in Table 1.

2.2. Laboratory analyses

Soil samples were dried at room temperature and gently crushed using a wooden pestle and mortar, and then passed through a 2 mm nylon sieve. Soils were pulverized with an agate mortar and pestle to a fine powder prior to being oven dried at 110 °C for 1 h and then were digested in a capped Teflon beaker using HNO_3, HF, and $HClO_4$ (Jiang et al., 2004). Dilute sample solutions were analyzed for REEs by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS; Finnigan Element II), at the State Key Laboratory for Mineral Deposits Research of Nanjing University. We estimate the

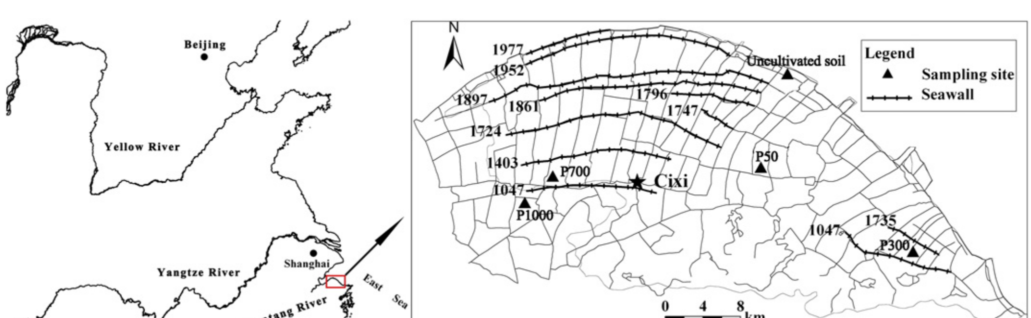

Fig. 1. Location of study area and sampling sites. Numbers beside the seawall positions represent the year of the seawall construction after Chen et al. (2011).