Chemie der Erde 71 (2011) 349–362

Contents lists available at ScienceDirect

Chemie der Erde

journal homepage: www.elsevier.de/chemer

Lanthanide tetrad effect in ferromanganese concretions and terra rossa overlying dolomite during weathering

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ARTICLE INFO

Article history:
Received 22 March 2011
Accepted 10 June 2011

Keywords:
Dolomite
Weathering
Terra rossa
Ferromanganese concretions
Rare earth elements
Lanthanide tetrad effect
Ce anomaly
Eu anomaly
Y/Ho ratio
Sm–Nd fractionation

ABSTRACT

The lanthanide tetrad effect was investigated in a 5.4 m thick terra rossa profile overlying dolomite on the Yunnan-Guizhou Plateau, China. The results demonstrate that the chondrite-normalized rare earth element pattern of dolomite bedrock displays a W-type tetrad effect. The insoluble residue from the dolomite bedrock does not exhibit any significant tetrad effect. In contrast, some ferromanganese concretions and the terra rossa show tetrad effect. It is worth noting that the conjugate M- and W-types of the tetrad effect are observed in some terra rossa samples. The tetrad effect in the ferromanganese concretions and the terra rossa possibly originates from redistribution of dissolved rare earth elements during their downwards movement in the profile and not only from water/rock interaction. Within the dolomite weathering system, the ferromanganese concretions and surrounding terra rossa present similar correlations of Eu/Eu*, Y/Ho, Sm/Nd, Ce/Ce*, with the size of the tetrad effect. The ferromanganese concretions and the terra rossa with tetrad effect are characterized by a reduced, non-chondritic Y/Ho ratio. Also the Y/Ho ratio exhibits a clear negative correlation with the size of the tetrad effect in the ferromanganese concretions and the terra rossa. In addition, the Eu/Eu* tends to increase with increasing size of the tetrad effect in the ferromanganese concretions and the terra rossa, as does the Sm/Nd ratio. The regular variation for Eu/Eu*, Y/Ho and Sm/Nd is likely a result of the fractionation of rare earth elements and yttrium with the tetrad effect. On the other hand, the correlation of the Ce/Ce* with the size of the tetrad effect in the ferromanganese concretions and the terra rossa is random. This likely indicates that the Ce behavior within weathering system is mainly controlled by redox condition, rather than tetrad effect. Comparative study indicates that the correlations of Eu/Eu*, Y/Ho, Ce/Ce*, with the size of the tetrad effect in the ferromanganese concretions and the terra rossa, are not similar to those found in a highly evolved igneous system. Nevertheless, the correlation of Sm/Nd with the size of tetrad effect in weathering system is similar to that in igneous system. In general, it appears to indicate that the tetrad effect occurrence in granitic rocks is not associated with weathering.

1. Introduction

The rare earth elements (REEs) comprise fifteen lanthanide elements (atomic number, $Z = 57–71$). It is convenient to include also yttrium ($Z = 39$; REY). They are an extremely coherent group, and their chemical behavior has long been considered as monotonic gradual variations (Ma et al., 1980; Nozaki, 2001). In the process of solvent extraction, however, Fidelis and Siekierski (1966) and Peppard et al. (1969) found that there existed a ‘tetrad effect’ in the lanthanide series, which was also considered as ‘double-double effect’ (Fidelis and Siekierski, 1971). The confirmation of lanthanide tetrad effect means that the properties of lanthanide compounds are not a smooth function of atomic number (Siekierski, 1971). The term ‘tetrad effect’ in geochemistry refers to the subdivision of the 15 lanthanide elements into four groups in a chondrite-normalized distribution pattern: (1) La–Ce–Pr–Nd, (2) Pm–Sm–Eu–Gd, (3) Gd–Tb–Dy–Ho, and (4) Er–Tm–Yb–Lu, and each group forms a smooth convex (M-type) or concave (W-type) pattern. The four groups are separated at the boundary points (cusps) between Nd and Pm, Gd, and between Ho and Er, which correspond to the 1/4, 1/2 and 3/4 filled 4*f* shell, respectively. Gd is common to the second and third tetrad groups (Jahn et al., 2001). Such an effect is explained by variations in the exchange interactions of unpaired 4*f*-electrons, spin–orbit coupling or crystal field stabilization (Fidelis and Siekierski, 1966, 1971; Jørgensen, 1970; Nugent, 1970; Siekierski, 1971; Sinha, 1978; Kawabe, 1992; Mioduski, 1997; Irber, 1999). Although the presence of tetrad effect is well confirmed by laboratory experiments in chemistry, the

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doi:10.1016/j.chemer.2011.06.001

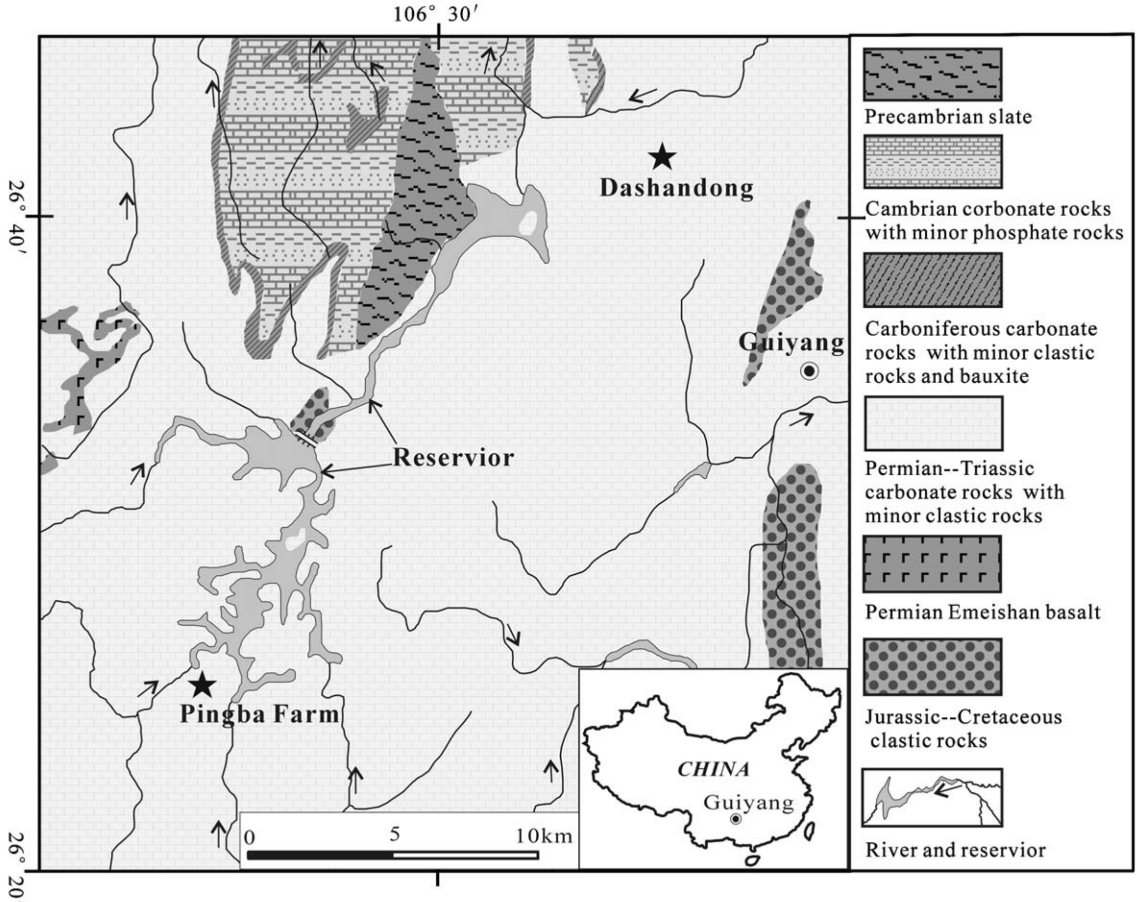

Fig. 1. Geologic sketch map of the study area (modified after Guizhou Bureau of Geology and Mineral Resources, 1987).

existence, significance and origin of the tetrad effect in geological materials are still a matter of debate (Wood, 1990; Yurimoto et al., 1990; McLennan, 1994; Byrne and Li, 1995; Pan, 1997; Bau, 1997; Masau et al., 2000).

In past decades, many investigators focus on the lanthanide tetrad effect in the highly evolved granitic system because the tetrad effect can be used as a geochemical indicator to constrain the evolution of igneous and hydrothermal systems (Masuda et al., 1987; Masuda and Akagi, 1989; Zhao et al., 1992; Lee et al., 1994, 2010; Bau, 1996; Kempe and Goldstein, 1997; Irber, 1999; Jahn et al., 2001, 2004; Monecke et al., 2002, 2007; Chen, 2004; Wu et al., 2004; Haapala and Lukkari, 2005; Liu and Zhang, 2005; Badanina et al., 2006; Boulvais et al., 2007; Schönenberger et al., 2008; Yasnygina and Rasskazov, 2008; Zhang et al., 2008; Zhao et al., 2010). All these previous results indicate that granitic whole rocks and separated minerals from highly evolved granitic systems may exhibit an M-type tetrad effect (Irber, 1999; Masau et al., 2000; Jahn et al., 2001; Monecke et al., 2002; Zhao et al., 2002; Götze et al., 2004; Wu et al., 2004, in press; Badanina et al., 2006; Haapala and Lukkari, 2005; Yasnygina and Rasskazov, 2008). Even Zhao et al. (2010) reported that a composite M- and W-type is recognized in the K-feldsparthized and silicified alkaline syenites. However, the geochemical processes that are responsible for the tetrad effect are not yet fully understood (Monecke et al., 2007; Nakamura et al., 2007). First, less is known about the origin and properties of the fluid, as well as the melt–fluid interaction processes and the timing of their separation with respect to magma evolution (Liu and Zhang, 2005; Badanina et al., 2006; Nakamura et al., 2007). Second, a complementary REE pattern with a W-type tetrad effect has not yet been found in highly evolved igneous systems (Monecke et al., 2002, 2007; Badanina et al., 2006). Third, whether or not the M-type tetrad effect in granitic rocks is associated with weathering is still debated (Masuda and Akagi, 1989; Zhao et al., 1999; Takahashi et al., 2002, 2003; Monecke et al., 2003; Lee et al., 2010; Wu et al., in press).

The lanthanide tetrad effect has been documented in the marine sediment system, such as carbonate rocks and corals (Kawabe et al., 1991, 1998; Tanaka et al., 2003; Mazumdar et al., 2003; Akagi et al., 2004; Yamamoto et al., 2004), chert (Minami et al., 1998), and hydrogenetic marine ferromanganese crust (Bau, 1996), for gaining an understanding of the incorporation of seawater REY into marine sediments (Masuda and Ikeuchi, 1979; Masuda et al., 1987; Tanaka et al., 2003; Censi et al., 2007).

Although the tetrad effect was studied in igneous systems and marine sediments, very little is known about its development during REE mobilization, transfer, precipitation, and redistribution under weathering conditions (Takahashi et al., 2002; Feng, 2010).

Furthermore, the lanthanide tetrad effect is of considerable importance to geochemistry and may have the potential for becoming a valuable indicator in geochemical studies (Akagi et al., 1993; McLennan, 1994; Bau, 1996; Takahashi et al., 2002). However, the relationship between the size of the tetrad effect and other geochemical indicators, such as the Y/Ho ratio, has not been well established. In the highly evolved igneous system, the correlations of Eu/Eu*, Y/Ho, with the size of the tetrad effect have been discussed, although their correlations are still debated (Irber, 1999; Monecke et al., 2002; Zhao et al., 2002; Wu et al., 2004, in press; Liu and Zhang, 2005; Yasnygina and Rasskazov, 2008; Zhang et al.,