



Diagenetic uptake of rare earth elements by conodont apatite



Lei Zhang ^a, Thomas J. Algeo ^{a,b,c,*}, Ling Cao ^a, Laishi Zhao ^{a,**}, Zhong-Qiang Chen ^{a,b}, Zhihong Li ^d

^a State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China

^b State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China

^c Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA

^d Wuhan Institute of Geology and Mineral Resources, Wuhan 430223, China

ARTICLE INFO

Article history:

Received 13 July 2015

Received in revised form 16 October 2015

Accepted 29 October 2015

Available online 6 November 2015

Keywords:

REE

Y/Ho

Bioapatite

Porewater chemistry

Diagenesis

ABSTRACT

The rare earth element (REE) composition of bioapatite has long been used as a proxy for ancient seawater chemistry and paleomarine environmental reconstruction, based on the assumption of preservation of a hydrogenous (seawater-derived) REE signal. Recent work, however, has begun to question the provenance of REEs in conodonts, emphasizing the importance of REEs released by the lithogenous fraction of the sediment and subsequently adsorbed onto conodont apatite in the burial environment. Here, we investigate patterns of REE and trace-element abundance in conodonts and their host sediments from the Early to Late Ordovician Huanghuachang and Chenjiahe sections of Hubei Province, South China. Several lines of evidence indicate that REEs in the conodont samples were acquired mainly from clay minerals in the host sediment during burial diagenesis: (1) REEs in conodonts show a strong positive correlation to Th and other lithogenic elements; (2) conodonts and whole-rock samples show general patterns of REE and trace-element enrichment that are highly similar to each other and bear no resemblance to seawater elemental concentrations; (3) similar patterns are observed in Triassic conodonts and whole-rock samples; and (4) Y/Ho ratios in conodonts are mostly <40 (mean ~33), values that are consistent with derivation of >90% of REEs from lithogenous sources. Conodonts show pronounced middle rare earth element (MREE) enrichment, a pattern that is unambiguously of diagenetic origin owing to its association with lower Y/Ho ratios. With increasing MREE enrichment of conodont samples, U concentrations and La_N/Yb_N ratios shift from high to low, and Mn concentrations from low to high. These patterns suggest that conodont diagenesis was initiated at shallow burial depths under suboxic conditions (i.e., in the zone of Mn(IV) and Fe(III) reduction) but continued at greater burial depths, with most acquisition of secondary REEs at later diagenetic stages. Our findings indicate that (1) conodont apatite frequently does not preserve a recognizable hydrogenous REE signal, and (2) the results of many earlier studies in which REEs in bioapatite were used as a paleoseawater proxy may need re-evaluation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The rare earth element (REE) composition of bioapatite has long been used for reconstruction of paleoceanographic conditions based on Ce anomalies, Nd-isotope ratios, or the shape of normalized REE distributions (e.g., Wright et al., 1984, 1987, 2002; Grandjean et al., 1987; Grandjean-Lécuyer et al., 1993; Laenen et al., 1997; Felitsyn et al., 1998; Lécuyer et al., 1998, 2004; Reynard et al., 1999; Martin and Haley, 2000; Girard and Lécuyer, 2002; Picard et al., 2002; Kemp and Trueman, 2003; Martin et al., 2005; Trotter and Eggins, 2006; Trotter et al., 2007; Chen et al., 2012; Song et al., 2012; Fadel et al., 2015). Over the years, a few studies have concluded that REEs in

bioapatite are taken up largely during diagenesis, and that they therefore have questionable utility as a paleoceanographic proxy (e.g., Toyoda and Tokonami, 1990; Bright et al., 2009). In recognition of this concern, recent studies have attempted to make use exclusively of the parts of conodont elements that exhibit lesser degrees of diagenetic alteration, as inferred from the color alteration index (CAI; Epstein et al., 1977; Rejebian et al., 1987). Thus, the albid crown of conodont elements, which is denser and lower in permeability than the basal plate or hyaline crown (Trotter et al., 2007), has become the preferred target of REE analysis (Trotter and Eggins, 2006; Song et al., 2012; Zhao et al., 2013). However, recent studies have shown that diagenetic alteration is probably a pervasive feature of conodont apatite, with all parts of conodont elements being subject to strong post-mortem adsorption of REEs as well as other trace elements from sediment porewaters (Zhao et al., 2013; Chen et al., 2015). Similar conclusions have been reached about the openness of vertebrate fossil bones to prolonged diagenetic alteration (Kocsis et al., 2010; Herwartz et al., 2011, 2013a; Tütken et al., 2011; Kowal-Linka et al., 2014).

* Corresponding author at: Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA.

** Corresponding author.

E-mail addresses: thomas.algeo@uc.edu (T.J. Algeo), zhaolaishi5@sina.com (L. Zhao).

Methods of screening conodont samples or sample sets for potential diagenetic influences on REE composition have changed over time. It has long been known that phosphatic tissues *in vivo* contain very low concentrations of REEs (a few ppb) and other trace elements, and that most uptake of non-structural elements occurs post-mortem (Wright et al., 1984; Trueman and Tuross, 2002; Trotter and Eggins, 2006). Studies that have made use of REEs and other trace elements for paleoceanographic analysis generally have argued that such uptake occurred at or close to the sediment–water interface (SWI) and, thus, that the concentrations of these elements in conodont apatite reflected their concentration in contemporaneous seawater (Elderfield and Pagett, 1986; Wright et al., 1987; Grandjean-Lécuyer et al., 1993; Lécuyer et al., 2004). The most widely used approach for putative documentation of the hydrogenous (seawater-derived) origin of REEs relies on $(La/Sm)_N$ vs. $(La/Yb)_N$ diagrams (e.g. Grandjean-Lécuyer et al., 1993; Laenen et al., 1997; Reynard et al., 1999; Girard and Lécuyer, 2002; Picard et al., 2002; Kemp and Trueman, 2003; Chen et al., 2012; Herwartz et al., 2013a; Kowal-Linka et al., 2014). However, recent studies have inferred that the composition of conodont apatite is extensively altered in the burial environment. Lu-Hf isotopes suggest open-system behavior of bioapatite with REE uptake throughout post-mortem diagenesis (Kocsis et al., 2010; Herwartz et al., 2011, 2013b). Y/Ho ratios REEs concentrations suggest that most REEs (frequently >90%) in bioapatite are lithogenously sourced, probably through release from clay minerals in the burial environment (Zhao et al., 2013; Chen et al., 2015).

In the present study, we have investigated the REE and trace-element content of conodont apatite and whole-rock samples from the Huanghuachang and Chenjiahe sections in South China in order to

(1) determine the provenance of REEs in the study sections, and (2) refine a “toolbox” of general techniques for assessing REE provenance. In the latter regard, this study builds on earlier published work by Zhao et al. (2013) and Chen et al. (2015). The Huanghuachang and Chenjiahe sections are well-suited to a study of this type because it contains abundant conodonts in beds ranging from nearly pure carbonate to marl to shale, thus allowing assessment of lithologic influences on conodont REE content. The results of this study thus have implications not only for Ordovician paleomarine conditions and diagenetic processes but also more generally for evaluation of the provenance of REEs and trace elements in bioapatite of any geologic age.

2. Geological setting

The Huanghuachang section is located in Huanghua County, about 22 km northwest of Yichang City, in the Three Gorges area of western Hubei Province, South China (Fig. 1A). It is the Global Stratotype Section and Point (GSSP) of the base of the Middle Ordovician series, with Lower to Upper Ordovician strata well exposed along the major road from Yichang City to Xinshan County. The Chenjiahe section is close to (~5 km distant from) the Huanghuachang section, as both are located on the east limb of the Huangling anticline (Fig. 1B). During the Early to Middle Ordovician, the South China Craton comprised the Yangtze Platform, the Jiangnan Slope, and several marginal uplifts including the Kangdian and Cathaysia oldlands. The Three Gorges area was located on the north-central Yangtze Platform, which accumulated shallow-marine carbonate sediments that graded into argillaceous sands in inner-shelf settings to the northwest and slope facies to the southeast (Fig. 1C) (Zhan and Jin, 2007).

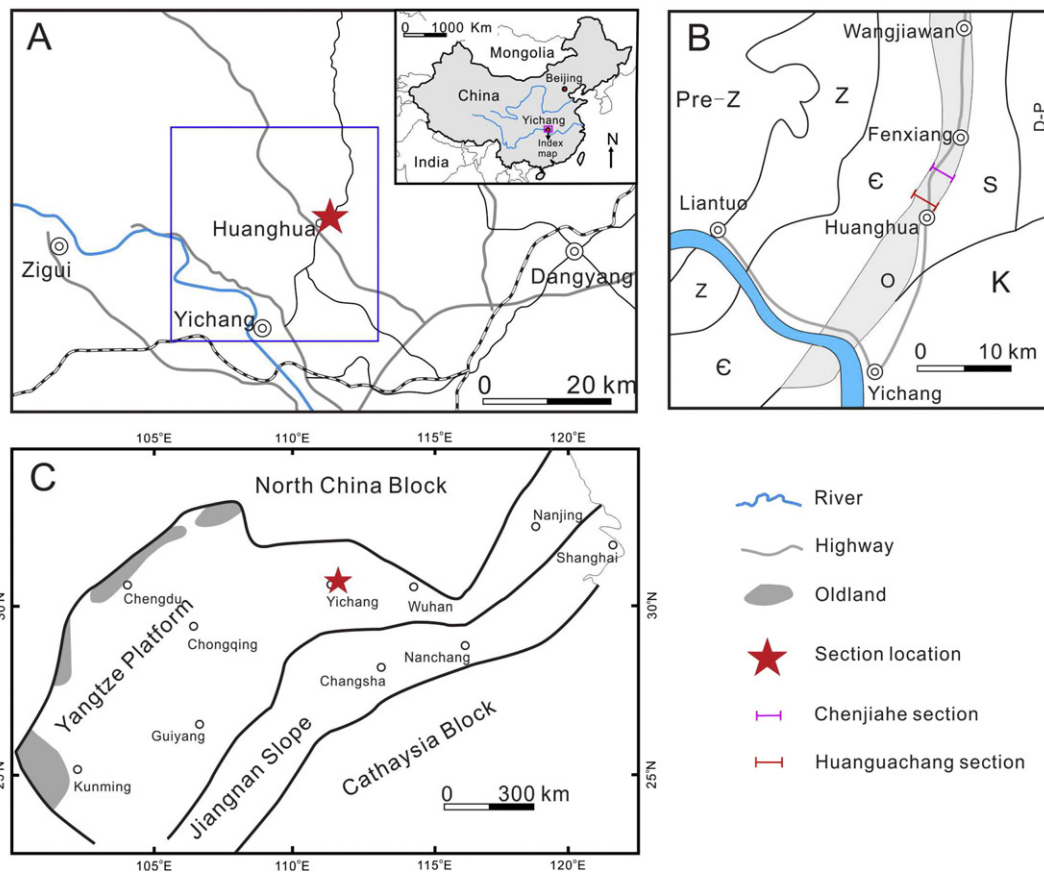


Fig. 1. (A) Geographic map of the Three Gorges area, southern Hubei Province, South China. The inset map of China in the upper right shows the location of map A, and the blue rectangle in the main map shows area of map B. (B) Geological map of Yichang area, showing the locations of the Huanghuachang and Chenjiahe sections. Z = Sinian, € = Cambrian, O = Ordovician, S = Silurian, D = Devonian, P = Permian, K = Cretaceous. (C) Early to Middle Ordovician paleogeography of the South China Craton (after Zhan and Jin, 2007).

Download English Version:

<https://daneshyari.com/en/article/4465588>

Download Persian Version:

<https://daneshyari.com/article/4465588>

[Daneshyari.com](https://daneshyari.com)