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Dating rare earth element enrichment in deep-sea sediments using U-Pb geochronology of bioapatite

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ABSTRACT

Deep-sea sediments rich in rare earth elements and yttrium (REY) are promising mineral resources that are believed to be associated with the burial of fish debris. However, the nature of the REY enrichment is poorly understood, in part due to a lack of robust age constraints. We report bioapatite U-Pb ages from an Ocean Drilling Program (Leg 199, Hole 1218A) core and a REY-rich sedimentary core from the Pacific Ocean, which yielded U-Pb ages ranging from 22.8 to 18.2 Ma and 6.5 to 2.2 Ma, respectively. The U-Pb fish teeth ages from the 1218A core are consistent with biostratigraphic constraints, shed light on the application of the U-Pb bioapatite chronometer, and yield an absolute time scale for stratigraphy, especially for sequences deposited below the calcite compensation depth (CCD), where there is an absence of fossil carbonate. The successful measurement of U-Pb ages from REY-enriched fish teeth in the REY-rich sediment core suggests the mineralization occurred no later than the Miocene in the western Pacific Ocean. Uranium is positively correlated with REY, suggesting that the U and REY were incorporated into the fish teeth lattice simultaneously, making the bioapatite U-Pb chronometer suitable for constraining the timing of REY mineralization. When combined with published data, our study suggests that the Miocene REY accumulation event in the western Pacific Ocean was influenced by high P_2O_5 and MnO_2 contents correlated with oxic bottom water.

INTRODUCTION

The stratigraphic record of abyssal sediments can preserve up to 200 m.y. of Earth history. The depositional age framework of these deep-sea sequences is typically constrained by integrated magnetostratigraphic, biostratigraphic (calcareous and siliceous microfossils), and chemostratigraphic approaches (Berggren et al., 2000; Westerhold et al., 2020). However, this stratigraphic framework can be limited by low sedimentation rates, the absence of high-resolution isotope stratigraphy, and low-resolution or absent biostratigraphic control. For example, sedimentation rates strongly correlate with deposition depth, while microfossil assemblages are unstable below the calcite compensation depth (CCD) or silicate saturation depth (SSD) (Kallmeyer et al., 2012). Paleomagnetism can be used to constrain the age of sedimentary sequences, typically when coupled with other direct chronometers, e.g., when combined with ^{10}Be and ^{9}Be dating (Bourles et al., 1989). Isotopic (e.g., Os and Sr) data collected at intervals through a sedimentary sequence can also be used to constrain the depositional age by chemostratigraphic correlation, but this effort can be hampered by synsedimentary deformation or bioturbation.

In addition to the difficulties mentioned above, primary sedimentary records can be modified by postdepositional processes. Squeezing and stretching of cored intervals result in depth distortion within individual cores, and hence hiatuses and condensed intervals need to be recognized to undertake postsampling corrections (Lyle et al., 2009). Other effects, especially biological activity (e.g., bioturbation) and other postdepositional events, can also disturb the depositional records. Therefore, developing an accurate chronological framework for deep-sea sediments is essential.

The apatite uranium-lead (U-Pb) chronometer is a precise and accurate method for dating igneous and metamorphic rocks (Chew et al., 2011), as well as carbonate-fluorapatite in phosphatized marine crusts (Josso et al., 2019), with a minimum closure temperature of ∼350 °C (Chew and Spikings, 2015). Bioapatite in fish bones and teeth contains no U or rare earth elements (REEs) prior to burial, and U and REEs are believed to be rapidly incorporated into fish teeth and bones over 10^3–10^4 yr during the phosphatization process (Briggs and Kear, 1993). The U-Pb apatite chronometer has consequently been applied to shark and dinosaur teeth (Sano et al., 2006; Grün et al., 2014; Greene et al., 2018; Rochín-Bañaga et al., 2021), giving results consistent with the independent geological constraints. As a result, accurate U-Pb dating of bioapatite in sedimentary sequences could be highly beneficial for constraining the timing of phosphatization during early diagenesis.

In order to test the efficacy of this chronometer in marine sediments, we applied it first to an Ocean Drilling Program (ODP) sedimentary sequence with multiple age constraints. This core (Leg 199, Hole 1218A) was chosen because it has a high-resolution stratigraphy from the middle–late Eocene through the entire Oligocene to the early Miocene using correlated and integrated physical properties (such as paleomagnetism) and stratigraphic data (Westerhold et al., 2020). Deep-sea mud rich in REEs and yttrium (REY) is a recently discovered mineral resource in the Pacific

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Ocean (Kato et al., 2011). It occurs in areas with relatively slow sedimentation rates, mostly lower than 0.5 cm k.y.$^{-1}$. Up until now, there have been no direct chronological constraints on REY enrichment in bioapatite. Moreover, it remains unclear whether REY mineralization is continuous or linked to specific (i.e., episodic) geological events, hindering our understanding of REY enrichment. We tested the bioapatite U-Pb chronometer on fish teeth fossils from ODP Leg 199 Hole 1218A in the equatorial Pacific Ocean and then applied the chronometer to REY-bearing fish teeth from marine REY-rich deposits collected from the western Pacific Ocean. These data were then explored to build a new protocol for paleontological chronometry and constrain the timing of deep-sea REY mineralization.

SAMPLING AND METHODOLOGY

There are three major potential areas for deep-sea REY-rich sediment exploration, namely, the western, central eastern, and southeast Pacific Ocean (Fig. 1). The REY concentrations in these abyssal sediments range from 700 to 7974 ppm (average 1330 ppm), 700–1732 ppm (910 ppm), and 700–2738 ppm (1243 ppm), respectively (Bi et al., 2021).

Fish teeth were separated from deep-sea sediments collected from ODP Leg 199 Hole 1218A in the equatorial Pacific and from cruise DY-41 of the Chinese R/V *Hai Yang Liu Hao* in the western Pacific Ocean, respectively. The detailed analytical procedures are described in the Supplemental Material[1]. Bioapatite fish teeth fossils were well preserved in the ODP samples, including unbroken fish teeth (Fig. 2A) with tooth enamel exhibiting only minor cracking (Fig. 2B). The dental pulp of a fish tooth was observed to have dissolved during early diagenesis (Fig. 2C) and filled with microfossils (Fig. 2D). These microfossils included *Cyclicargolithus floridanus* (Fig. 2E) and *Discoaster calculosus* (Fig. 2F), with the latter's age constrained from 24.40–23.13 Ma to 19.00–17.95 Ma (De Kaenel et al., 2017). Fish teeth from the REY-rich sediment from cruise DY-41 core WP41 had well-preserved enamel and pulp, with the enamel being more massive than the pulp (Fig. 2G). Some of the fish tooth roots were cracked but the tips were unbroken (Fig. 2H). The fish teeth were made up of tiny fragments of mostly fluorapatite (Fig. 2I; Table S1 in the Supplemental Material).

RESULT AND DISCUSSION

U-Pb Age of Fish Teeth in the ODP Core and REY-Rich Core

Fish teeth from ODP samples 1218-7H-1, 1218-7H-4, and 1218-9H-6 yielded lower-intercept ages of 18.2 ± 2.9 Ma (2σ age uncertainties, mean square of weighted deviates [MSWD] = 1.8; $n = 76$) to 22.8 ± 2.6 Ma (MSWD = 2.3; $n = 100$) (Table S2; Fig. S1). Based on the occurrence of the microfossil *Discoaster calculosus* (Fig. 2F), the age duration is 24.40–23.13 Ma to 19.00–17.95 Ma (De Kaenel et al., 2017), thus implying that the bioapatite in these sequences has the potential to be used as a new paleontological chronometer.

We sampled 10 individual fish tooth samples at evenly spaced intervals from 60 cm of sediment core WP41 (Table S3; Fig. S1). Only sample WP41-3-9 failed to yield usable data because the sample was too small for the laser spot analysis. The remaining samples yielded ages from 6.5 ± 1.5 Ma (2σ uncertainty, $n = 181$, MSWD = 1.7) at the bottom of the sequence to 2.2 ± 1.3 Ma ($n = 120$, MSWD = 1.4) at the top (Fig. 3; Fig. S1). Without considering the uncertainties, the depositional ages ranged from 6.5 to 2.2 Ma, and the sedimentation rate (SR) was constrained at ~0.14 cm k.y.$^{-1}$. That is consistent with the previously reported SR of <0.5 cm k.y.$^{-1}$ in these areas (Kato et al., 2011).

Age Constraints on REY Mineralization in the Western Pacific Ocean

Bioapatite is known to incorporate REY and U during early diagenesis (Trueman and Tuross, 2002). Fish bones can have extended durations of REE/U intake and exchange and may not entirely close to REE/U mobility after early uptake (e.g., Kocsis et al., 2010; Herwartz

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[1] Supplemental Material. Detailed fish teeth separation and mounting procedures, scanning electron microscope (SEM) observations, and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) analytical procedures for trace-element analyses and U-Pb dating. Please visit https://doi.org/10.1130/GEOL.S.22120304 to access the supplemental material, and contact editing@geosociety.org with any questions.

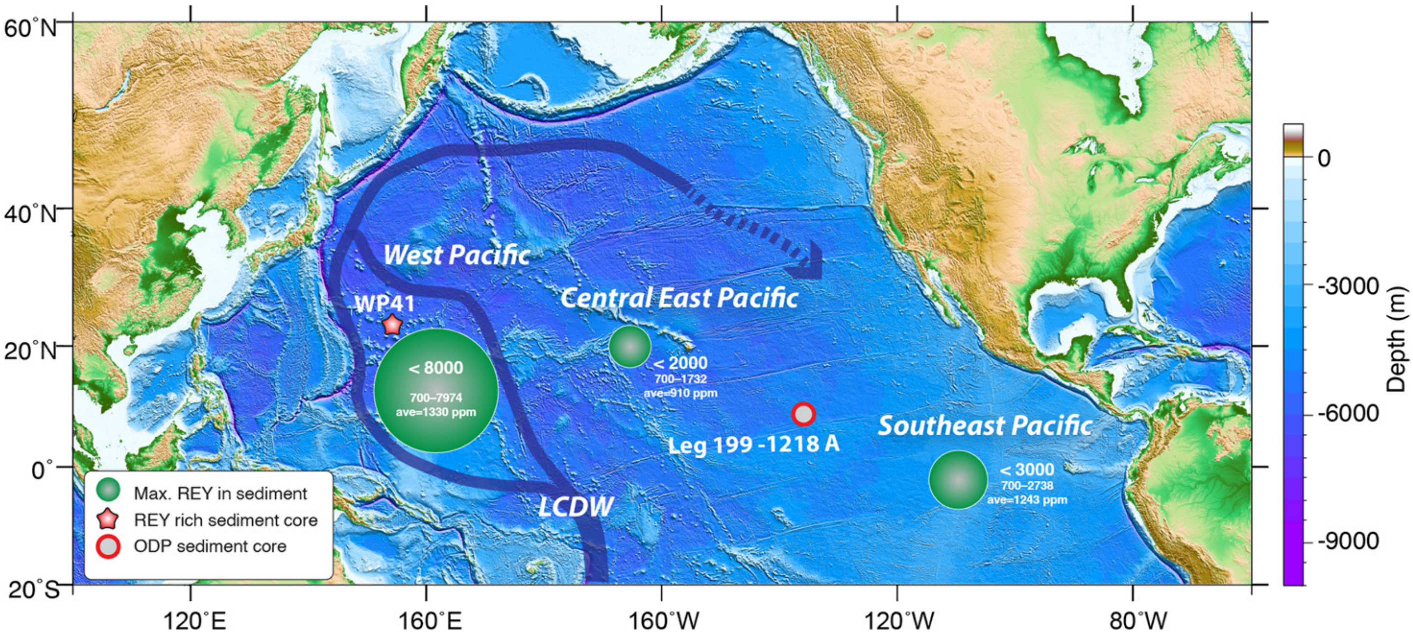

Figure 1. Locations of studied sediment samples in the western Pacific Ocean enriched in rare earth elements and yttrium (REY) and drill holes from Ocean Drilling Program (ODP) Leg 199 Hole 1218 and cruise DY-41 (of the Chinese R/V *Hai Yang Liu Hao*) core WP41. REY abundance is denoted by green circles scaled to the highest reported REY concentration, and REY resource distribution in the Pacific Ocean is sourced from Shi et al. (2021). max.—maximum; avg—average. Sampling sites of REY mineralization are from Martin and Haley (2000). Solid blue lines represent the pathway of Lower Circumpolar Deep Water (LCDW; Rella and Uchida, 2015). Bathymetric data are from ETOPO168 (https://www.ngdc.noaa.gov). This map was created by GMT V4.5 (https:// www.soest.hawaii.edu/gmt/).

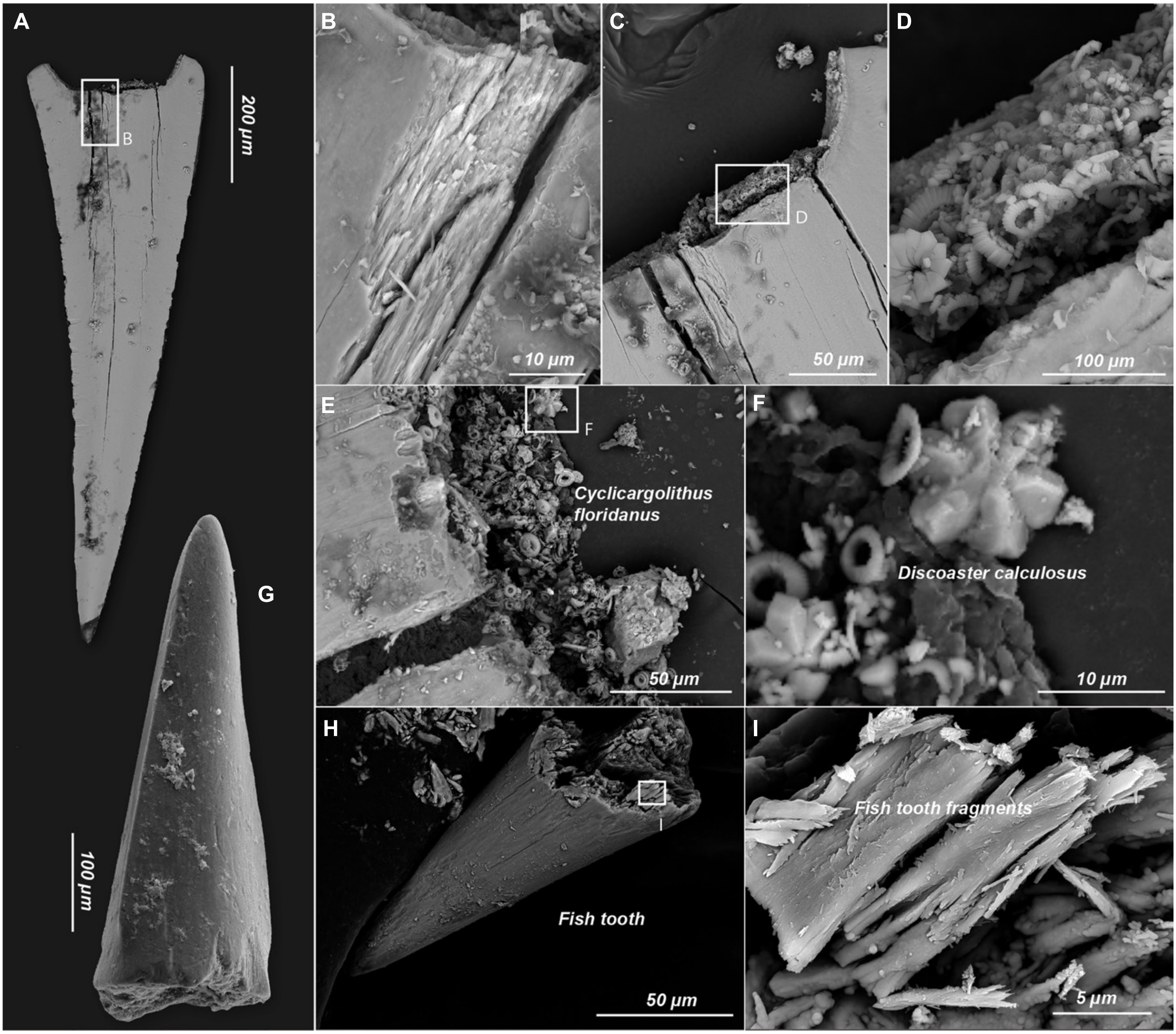

Figure 2. Backscattered-electron images of fish tooth samples from Ocean Drilling Program (ODP) and rare earth element and yttrium (REY)–enriched sediment core. (A) Whole fish tooth from ODP Leg 199 Hole 1218, sample 1218-7H-1, from a depth of 56.44 m. (B) Fibrous texture of fish tooth enamel with minor cracks in the enamel of the tooth. (C) Fish tooth with dissolved dental pulp. (D) Dental pulp filled with microfossils. (E,F) *Cyclicargolithus floridanus* and *Discoaster calculosus*. (G) Well-preserved fish tooth from REY-rich sediment. (H) REY-enriched fish tooth showing cracked roots but unbroken tips. (I) Micron-scale crystals of fluorapatite comprising fish teeth (Table S1 [see footnote 1]; Liao et al., 2019a).

et al., 2011). However, dense material, such as the enamel of fish teeth, has never been systematically tested, and it could probably retain more meaningful ages (Kohn and Law, 2006). Our bioapatite enamel U-Pb ages (1218-7H-1, 1218-7H-4, and 1218-9H-6) from the ODP fish teeth fossils are consistent with the microfossil biostratigraphic framework (Fig. S1; Westerhold et al., 2020). Recent research has excluded the possibility of multiple phases of U uptake and instead suggests that (1) it occurs as a single event during early diagenesis, and (2) the system remains closed to subsequent diffusion, with the duration of the fossilization process being short and insignificant when compared to the uncertainties in the U-Pb geochronology (Rochín-Bañaga et al., 2021). The measured U and REY contents in bioapatite of living marine vertebrates (such as fish teeth) are negligible (Liao et al., 2019a), and, consequently, it is believed that in fish teeth, U and REY are adsorbed from the pore water, and the uptake is a result of diagenetic alteration, with the complete fossilization processes (from burial to U uptake) occurring over 10^2 to 10^6 yr (Kohn and Law, 2006). The REY sorption process begins immediately upon exposure to pore waters and increases from <1 ppm to 3–4 orders of magnitude higher within the first 10^3–10^4 yr postmortem (Finlay et al., 2013). Subsequently REY concentrations do not systematically increase over geological time, consistent with REY scavenging over several thousand years and then maintenance of constant concentrations (Trueman and Tuross, 2002). Importantly, the Sr isotopes of fish tooth enamel are consistent with the global Sr chemostratigraphic curve (Fig. S2; Table S3). As a result, tooth enamel U-Pb geochronology in REY-rich sediment should approximate the age of REY mineralization following burial.

Importantly, U is positively correlated with REY in the fish teeth (Fig. 4A; Table S4), with

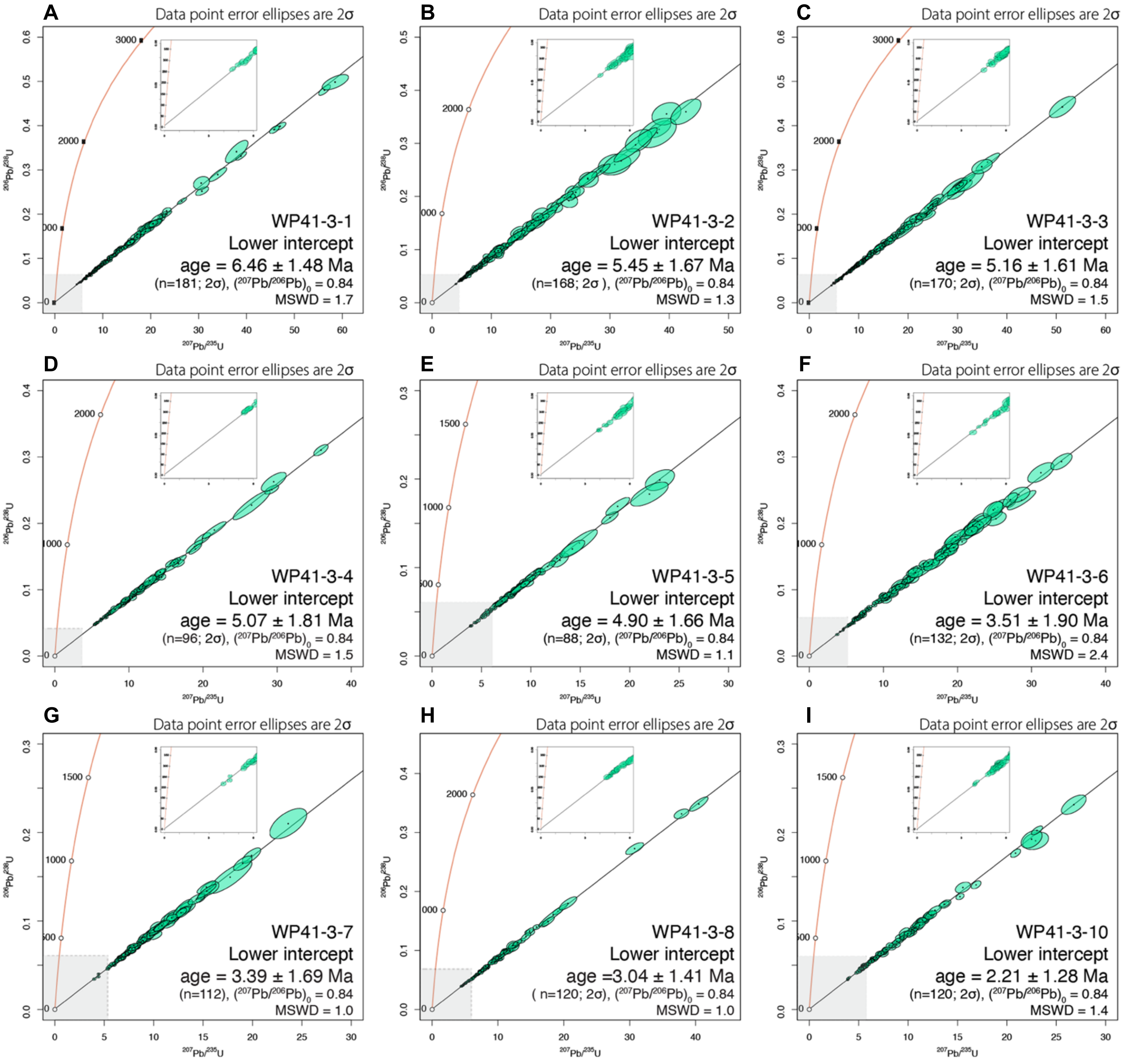

Figure 3. Wetherill concordia diagrams for nine fish teeth samples, sampled every 6 cm from sediment coreWP41 from cruise DY-41 (of the Chinese R/V *Hai Yang Liu Hao*) in the western Pacific Ocean. Data ellipses are illustrated at the 2σ level, and age uncertainties are presented at 2σ confidence levels. Total number of ablation lines (with several repeats in one large tooth) is given by *n*. MSWD—mean square of weighted deviates. All fish teeth ages are anchored to a common Pb (^{207}Pb/^{206}Pb) value derived from analysis of U-poor sediment from the same layer.

the U concentrations ranging from 1.88 to 49.7 ppm (average 19.5 ppm) and the REY ranging from 175 to 33,269 ppm (average 9120 ppm; enriched in heavy REEs with a strong Ce anomaly; Fig. S3). The REY in fish teeth is thought to be lattice-bound and exhibit coupled reactions with Si and/or Na to substitute for Ca and P in the fish tooth lattice (e.g., $REE^{3+} + Na^{+} \leftrightarrow 2Ca^{2+}$ and/or $REE^{3+} + Si^{4+} \leftrightarrow Ca^{2+} + P^{5+}$; Liao et al., 2019a). Consequently, the positive correlation between U and REY incorporation into the fish tooth lattice implies that the fish tooth bioapatite U-Pb chronometer can be used to constrain REY mineralization ages.

REY Enrichment and its Connection to Oxic Nutrient-Enriched Bottom Water

By reevaluating the distribution of REY contents in seafloor surface sediments (<2 m depth) in the Pacific Ocean (Kato et al., 2011), our findings suggest that the majority of REY-rich mud occurs at depths <0.6 m below the seafloor (mbsf; Figs. S4A and S4B). At this depth, oxidation of Fe^{2+} in ferromanganese oxides likely occurs, and the REY are released and incorporated into fish teeth (Liao et al., 2019b). Collectively, these data suggest that Mn oxides (such as micronodules) play an important role in REY scavenging, and this depth of optimum REY enrichment (~0.6 mbsf) has important significance for deep-sea REY exploration. Micronodules are Fe-Mn oxides that are important REY carriers. Their adsorbed REY will be eventually released and fixed into fish teeth (high Mn-P in quadrant 4; Fig. 4B), or, if fish teeth are rare or absent (high Mn and low P in quadrant 1),

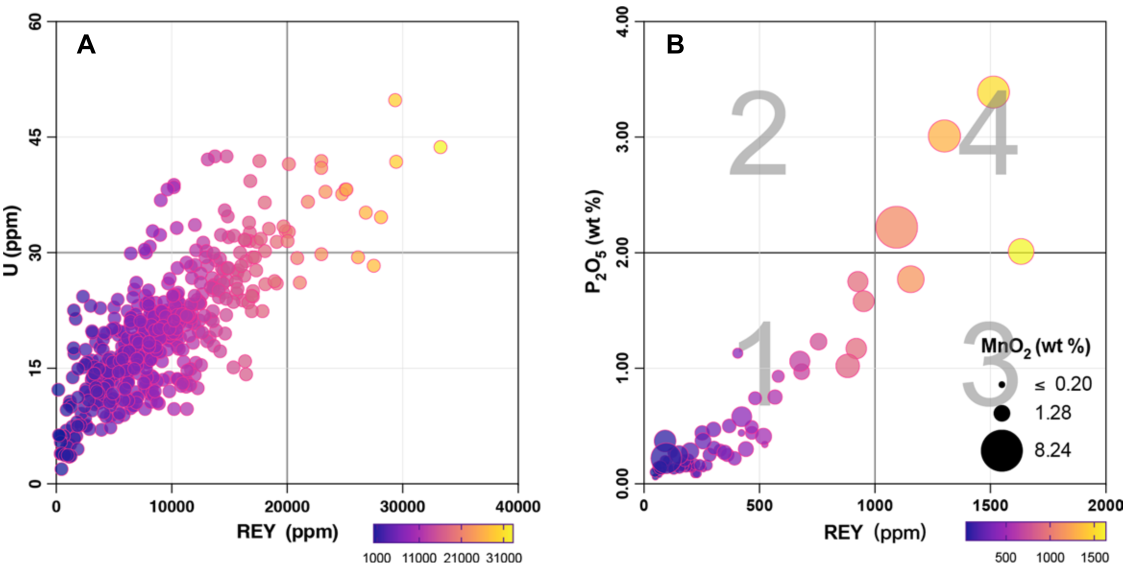

Figure 4. (A) Correlation of uranium and rare earth elements and yttrium (REY) in REY-rich fish teeth. (B) Compiled data show a correlation among REY, P_2O_5, and MnO_2 (circles are scaled with MnO2 content) in REY-rich sediment from Pacific Ocean bulk sediment samples (Kato et al., 2011). Numerals indicate quadrant number.

during early diagenesis. MnO_2, although exhibiting less correlation with the REY, is likely more amenable to geophysical exploration strategies at shallow depths for REY exploration.

The timing of enrichment and spatial distribution of REY in the Pacific Ocean are not well understood, and they may have experienced several enrichment phases during Earth history; e.g., the western North and central South Pacific Ocean areas recorded REY enrichment roughly at 34.4 Ma, concurrent with a late Eocene cooling event (Ohta et al., 2020). Our new ages for REY mineralization suggest that it began no later than the late Miocene and lasted until the early Pleistocene, and that REY enrichment is linked with the presence of micronodules (MnO_2). The growth of marine nodules on the seafloor, a precondition for REY exploration, is believed to result from the passage of oxic bottom water during early diagenesis (Klinkhammer et al., 1982). Previous studies have suggested that REY enrichment in Fe-Mn oxides is linked to the pathways of the Antarctic Bottom Water (AABW) and/or North Atlantic Deep Water (NADW) water masses (Glasby, 2006). Considering the age, seawater-like distribution pattern, and spatial distribution of REY, P_2O_5, and MnO_2 in the western Pacific Ocean, it is believed that the REY enrichment has a connection with the injection of old and oxygen- and nutrient-enriched bottom water (Kato et al., 2011). The Miocene age of the REY enrichment event was coincident with the closure of the Isthmus of Panama in the late Miocene. This resulted in the restriction of Pacific–North Atlantic Ocean throughflow and a strengthened Atlantic Ocean overturning circulation (Ling et al., 1997; Kirillova et al., 2019). During that time, the Lower Circumpolar Deep Water (LCDW) was an essential component of bottom water circulation, due to the mixing of NADW with the Antarctic Circumpolar Current in the Southern Ocean. The enhanced LCDW would have supplied nutrient- and oxygen-enriched bottom water into the Pacific Ocean, which would have promoted REY mineralization (Molina-Kescher et al., 2016). As a result, the Miocene REY mineralization event in the Pacific Ocean could have resulted from the enhanced bottom water circulation of the LCDW rather than the AABW.

CONCLUSIONS

Our results show that U and REY are positively correlated in Pacific Ocean sedimentary cores and suggest that they are incorporated into fish teeth simultaneously, implying that the fish tooth bioapatite U-Pb chronometer can be used to constrain REY mineralization ages. These new age data imply Miocene REY mineralization in Pacific Ocean sediments at shallow depths, and this REY mineralization may have resulted from the enhanced activity of LCDW bottom water rather than the AABW, where the LCDW brought nutrient- and oxygen-enriched bottom water into the Pacific and promoted REY mineralization.

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