**Two kinds of authigenic xenotime overgrowths in response to an Early Paleozoic** [**tectonothermal event**](http://www.iciba.com/tectothermal_event) **in South China**

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**Abstract**

This study has documented two kinds of xenotime overgrowths from the Cryogenian-Ediacaran sedimentary rocks in South China. The identical tetragonal dipyramidal structures prompted one type of xenotime to overgrow detrital zircon grains, whereas the other type coexists with rutile crystals. SIMS Pb-Pb, NanoSIMS, EPMA, and TEM imaging analyses suggest these xenotime overgrowths, together with their rutile substrate could be of hydrothermal origin; formed by means of percolating fluids leaching ilmenite and REE(Y) bearing silicate minerals. Iron, Ti, and REE(Y) ions leached in this way were combined with O, S, and P anions to precipitate rutile, xenotime, iron oxides, and pyrite in other pore spaces. Such fluid induced activities were probably induced by the ca. 460-390 Ma Wuyi-Yunkai Orogeny in South China. The most important finding is that the rutile-xenotime assemblage was precipitated almost simultaneously, rendering a dissolution-reprecipitation process impossible. Absence of dissolution margins on detrital zircons suggest detrital Fe-Ti oxides are more prone to be leached by fluids than zircon grains, probably because the latter has more stable chemical properties.

**Keywords:** Hydrothermal xenotime and rutile; South China; SIMS Pb-Pb/U-Pb ages; Major element; REE and trace elements; Transmission Electron Microscopy

**1. Introduction**

In view of its typically high U content (commonly >1000 ppm), low common Pb content and closed U–Pb system, xenotime has been increasingly applied in dating geological and biological events (McNaughton et al., 1999; Kositcin et al., 2003; Rasmussen, 2005a; Lan et al., 2014a; Zhang et al., 2015). In sedimentary rocks, diagenetic xenotime commonly grows during deposition of siliciclastic sediments where the Y, rare-earth elements (REE), and phosphate supply are sufficient, and typically display pyramidal overgrowths on detrital zircon grains because of their similar crystal structures (Rasmussen, 1996; Rasmussen, 2005). This prompted McNaughton et al. (1999) to pioneer the research on directly dating the depositional age of sedimentary rocks in non-fossiliferous Precambrian successions. Subsequent research, however, found that xenotime does not necessarily grow soon after deposition, which means xenotime growth is rarely purely early diagenetic and could span a range of ages from later diagenetic through to later hydrothermal resulting in prolonged or multiple growth, provided that an adequate supply of REE+Y and P is available (Vallini et al., 2002, 2005; Lan and Chen, 2012a; Lan et al., 2013; Zhang et al., 2015). During prograde metamorphism, diagenetic and detrital xenotime in sedimentary rocks that experienced temperatures exceeding middle greenschist facies metamorphism would disappear and be replaced with metamorphic xenotime via dissolution-precipitation mechanism (Rasmussen et al. 2011).

Among different kinds of xenotime, diagenetic and hydrothermal xenotime are the most difficult to distinguish as they both appear pyramidal overgrowths onto detrital zircon grains with almost identical REE compositions (Lan et al., 2013; Tartèse et al., 2015). Preliminary studies suggest that in sedimentary rocks hydrothermal xenotime generally forms during the waning period of tectonothermal activities with complicated mineralogical and chemical composition (Hay et al., 2010; Lan et al., 2013), by means of consuming the rims of adjacent minerals such as zircon grains in a dissolution-precipitation process (Hay et al., 2010; Drost et al., 2013). Such an explanation, based on case studies, seems to be plausible in the case of detrital zircon and xenotime assemblages. In view of the complex pore fluid evolution process during diagenetic and hydrothermal activities, the detailed formation mechanism of authigenic xenotime and associated minerals in siliciclastic rocks remains uncertain.

Recently, we obtained abundant xenotime overgrowths from the Cryogenian-Ediacaran sedimentary rocks in South China with the formation were possibly induced by the Paleozoic Wuyi-Yunkai [tectonothermal event](http://www.iciba.com/tectothermal_event) (460-390 Ma). Interestingly, the xenotime not only overgrows detrital zircon grains but also rutile with a possible hydrothermal in origin. As such, they present a unique opportunity for us to further characterize the growth mechanism of authigenic xenotime with the aid of advanced SEM and TEM imaging coupled with high precision SIMS and EMPA *in situ* mineral chemical analyses. SIMS Pb-Pb/U-Pb dating analyses is also conducted to better constrain the timing of this period of hydrothermal activity as a complement to the radiometric ages obtained from igneous and metamorphic rocks and ore deposits in South China.

**2. Geological setting**

As one of the major crustal blocks in eastern Eurasia, the South China Block is composed of the Yangtze Block to the northwest and the Cathaysia Block to the southeast (Figure 1A). The two blocks comprise Archean and Paleoproterozoic basement assemblages that were merged during the ca. 1.1-0.9 Ga Sibao/Jinning orogeny along the Jiang-Shao suture zone during the closure of the Nanhua ocean (Li et al., 2007, 2009a). This was followed by the initial development of the Nanhua rift basin along the suture zone associated with crustal doming and erosion caused by a mantle plume from the mid- to late-Neoproterozoic until ca. 700 Ma (Li et al., 1999; Wang and Li, 2003). The failed rift continued to receive Ediacaran to Cambrian sedimentary successions (Yu et al., 2009). The Neoproterozoic successions in the Nanhua basin can be classified into the Yangtzian/Tonian, Nanhuan/Cryogenian and Sinian/Ediacaran systems. The Nanhuan System equals the Cryogenian system (Zhang et al., 2011), and is characterized by two Cryogenian glacial diamictite intervals as represented by the Chang’an/Dongshanfeng formations and the Nantuo/Silikou Formation, separated by interglacial Datangpo/Xiangmeng formations, ranging from 663–650 Ma (Zhou et al., 2004; Bao et al., 2018). The two Cryogenian glaciogenic units are generally >500 m thick and both composed of massive and stratified diamictites and conglomerates with sandstone and siltstone beds, with the former containing abundant dropstones, lonestones and striated clasts (Lu et al., 2010; Zhang et al., 2011; Lan et al., 2014b).

Ediacaran Lantian and Piyuancun formations are widely present in the southern Anhui Province, which overlie the Cryogenian Leigongwu Formation (equivalent of Nantuo Formation in South China) (Wan et al., 2016; Figure 1A, B). The Lantian Formation underlies the Piyuancun Formation which underlies the early Cambrian Hetang Formation, and is underlain by the Cryogenian Leigongwu/Nantuo Formation diamictite. The Lantian Formation can be divided into four lithostratigraphic units (Wan et al., 2014). A total of twenty black shale specimens were collected from the fossiliferous horizons of Member II of the Lantian Formation at Lantian Town, Xiuning County (Figure 2A, B), which is dominated by clay minerals, organic carbon, pyrite framboids, iron oxides, and an assemblage of zircon cores and xenotime overgrowths (Figure 3). To date, direct radiometric ages are lacking, which constrain the depositional age of the Lantian Formation. Nevertheless, lithostratigraphic and chemostratigraphic correlations suggest the Lantian Formation is correlative with the Doushantuo Formation in the Yangtze Gorges area, which was dated at 635-551 Ma (Condon et al., 2005), as both the Lantian and Doushantuo formations are typical of pronounced negative δ13C excursions in Member III that can be correlated with the Shuram negative δ13C excursions (Yuan et al., 2011; Lu et al., 2013; Wang et al., 2014).

Cryogenian diamictite of Chang’an Formation is exposed at the Lijiapo Section in the vicinity of Lijiapo Village, Congjiang County of SW China (Fig. 1A, C). Sedimentary successions around the study area include, in ascending order, the Neoproterozoic Longli Group, Jiangkou Group, Datangpo Formation, Nantuo Formation and Doushantuo Formation (Fig. 1C). The Xiajiang Group, Datangpo Formation, and Nantuo Formation collectively attain a total thickness of ca. 4240 m dividable into 107 beds (Lu et al., 2010). The Xiajiang Group is equivalent to the Banxi Group/Danzhou Group in Guangxi and Hunan provinces (Lan et al., 2015a). Only the Longli Formation is present around the study area. The Jiangkou Group is typical of diamictite and mudstone recorded in the Chang’an Formation and iron formations recorded in the Fulu Formation (Lan et al., 2014b, 2015b). Around the study area, the massive diamictite of the Chang’an Formation typically contains angular pebbles and authigenic pyrite (Figure 2C-E). The lower part from which sixty hand specimens were collected, is dominated by rounded quartz grains, K-feldspar, chlorite, ilmenite, rutile, apatite, and rutile cores with xenotime overgrowths surrounded by quartz cement (Figure 4). More recently, a zircon SIMS U-Pb age of 715.9 ± 2.8 Ma was acquired from the interbedded tuff horizons of the Gongdong Formation, Danzhou Group in Guangxi Province (Lan et al., 2014b), constraining the depositional age of Chang’an Formation to be <716 Ma. A zircon SIMS U-Pb age of 691.9 ± 8.0 Ma was obtained from the interbedded tuff horizon of the Xieshuihe Member, Hunan Province, which is equivalent to the Liangjiehe Member, Fulu Formation in Guizhou and Guangxi provinces (Lan et al., 2015b). This constrains the depositional age of Chang’an Formation to be >692 Ma. As such, the depositional age of the Chang’an Formation can be bracketed to 716-692 Ma.

The Early Paleozoic Wuyi-Yunkai Orogeny (Li et al., 2010a) induced low greenschist metamorphism in the Precambrian strata, the formation of NNE composite folds, regional cleavages, brittle and ductile shearing, granite emplacement, and an unconformity between Devonian and older rock units as well as the production of key hydrothermal ore deposits (Peng et al., 2003; Li et al., 2010; Hu et al., 2012; Xu et al., 2013). Available radiometric dates from metamorphic and igneous rocks and ore deposits suggest the Wuyi-Yunkai Orogeny spanned an age of 460-390 Ma but is concentrated in 445-420 Ma (Hu et al., 2012). These ages include LA-ICP-MS U-Pb zircon ages (460-425 Ma) from the Zhuguang migmatites in the Nanling Mountains, southeastern China (Xu et al., 2005), SHRIMP U-Pb zircon ages (458-425 Ma) from the metavolcanic and metasedimentary rocks in northwestern Fujian Province (Wan et al., 2007), SHRIMP U-Pb zircon ages (ca. 443 Ma) from the Ordovician tuffaceous beds at Wangjiawan Section, Hubei Province (Hu et al., 2008), LA-ICP-MS U-Pb zircon ages (441-421 Ma) from the gneissic rocks in the Yunkai terrane (Wang et al., 2007), biotite 40Ar-39Ar ages (430-390 Ma) from the mylonite at southern Wuyi Mountain (Shu et al., 2008), and scheelite Sm-Nd isochron age (ca. 402 Ma) from the Au-Sb-W ore deposits at western Hunan Province (Peng et al., 2003).

**3. Methods**

***3.1. FESEM imaging analysis of xenotime overgrowths***

Backscattered scanning electron (BSE) mode, coupled with energy dispersive spectrum (EDS), was employed to identify and image xenotime overgrowths on the Field Emission Scanning Electron Microscope instrument (Zeiss 1555 VP-FESEM, Carl Zeiss, Oberkochen, Germany) at Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing. The FESEM was specifically manipulated to get an optimal resolution at 5,000-200,000. It was tuned to an optimal working distance of 7-15 mm and a voltage of 10-20 kV.

***3.2. EPMA REE analyses of xenotime overgrowths***

Silicon, P, Ca, Fe, Y, Zr, REE, Pb, Th, and U were measured in the xenotime overgrowths from the Chang’an diamictite using a JEOL 8530F electron probe analyzer equipped with 5-wavelength dispersive spectrometers at the Centre for Microscopy, Characterization, and Analysis at the University of Western Australia. Operating conditions were 20 kV, 50 nA on a Faraday cup, 40° take-off angle, and an electron beam diameter of 2 μm. Inter-elemental interferences were removed by peak overlap corrections. The X-ray lines analyzed, and standard materials used for the analyses were Si Kα (wollastonite), P Kα (LaPO4), La Lα (LaPO4), Ce Lα (CePO4), Pr Lβ (PrPO4), Nd Lα (NdPO4), Sm Lα (SmPO4), Eu Lα (DW1 glass), Gd Lα (GdPO4), Tb Lα (DW1 glass), Dy Lα (DW4 glass), Ho Lβ (DW4 glass), Er Lα (DW4 glass), Tm Lα (DW1 glass), Yb Lα (DW2 glass), Lu Lβ (DW2 glass), Y Lα (YPO4), Zr La (CZ3 zircon), Ca Kα (wollastonite), Ti Kα (rutile), Fe Kα (Fe metal), Al Kα (corundum), Pb Mβ (crocoite), Th Mα (ThO2), and U Mβ (U metal). For both peak and background positions, counting times of 40 s were applied. Overlap factors were derived empirically from measurement of the standards. The detection limits are 40 ppm for Si, 60 ppm for P, 70 ppm for Ca, 80 ppm for Fe, 400 ppm for Y, 100–200 ppm for the REEs, 200 ppm for Pb, 100 ppm for Th, and 100 ppm for U. Chemical formulae are calculated on the basis of four oxygens.

***3.3. EPMA major and trace element analyses of rutile cores***

Major and trace element contents of rutile cores from the Chang’an diamictite were determined using a CAMECA SXFiveFE EPMA at IGGCAS. Quantitative analysis was conducted using an acceleration voltage of 20 kV, a beam current of 150 nA, a focused beam of 2 μm, with wavelength-dispersion spectrometers (WDS). A TAP, (for Si, Al, Sr), LiF, and PET crystals were used with peak counting time of 10 s on Ti, Al and Si (Ka), 30 s on Fe (Ka), 60 s on V, Cr (Ka),W (Lα) and Pb (Mα) and 180 s on Sr(La). Zirconium (La) and U(Mβ) were acquired in two spectrometers with a peak counting time of 120 s and 90 s, respectively. Natural minerals and synthetic Al2O3 and V metal were used as standards. Matrix corrections were carried with X-PHI. Detection limits for Ti, V, Fe, Cr, Al, Si, Sr, Zr, W, Pb, and U are 60 ppm, 90 ppm, 30 ppm, 10 ppm, 25 ppm, 35 ppm, 20 ppm, 40 ppm, 50 ppm, 50 ppm, and 90 ppm, respectively.

***3.4. NanoSIMS REE analyses of zircon cores and xenotime overgrowths***

REE analyses were conducted on the zircon cores and xenotime overgrowths from the Lantian Formation using a Cameca NanoSIMS 50 at the Atmosphere and Ocean Research Institute, The University of Tokyo (AORI-UOT). For xenotime REE analyses, a ca. 500 pA mass-filtered O- primary ion beam was focused on the sample surface producing a ca. 5-7 µm diameter crater. Real time imaging (RTI) technique was used by referring to the secondary ion image of the Y2O3 signal in order to precisely define the target area. ZrO2 was recorded to monitor potential primary beam overlap onto the adjacent zircon. Mass resolving power was set approximately to 10,000 to separate oxides of heavy REE and light REE. The magnet field cycled six times with a total of nineteen elements measured including 139La, 140Ce, 141Pr, 143Nd, 145Nd, 152Sm, 151Eu, 153Eu, 155Gd, 157Gd, 159Tb, 163Dy, 165Ho, 167Er, 169Tm, 173Yb, 174Yb, 175Lu, and 89Y. 89Y was used to map and locate the position of the xenotime overgrowths. It took 10 s for each measurement with a 3 s waiting time at each magnet field, or 247 s in a single cycle. As such, it would take ca. 30 minutes for one spot analysis together with pre-sputtering and tuning time. Xenotime standard BS-1 (Fletcher et al., 2004) was used to acquire the sensitivity factor and calibrate the absolute content of each element. Procedures for REE analyses of zircon cores are similar to that of xenotime. The major difference is that we used 28Si rather than 89Y as reference to map and locate the position of the zircon grains. NIST SRM 610 (Kent et al., 2017) was used to acquire the sensitivity factor and calibrate the absolute content of stoichiometric Si and other elements in the zircon.

***3.5. TEM imaging of xenotime-zircon interface***

After BSE imaging, one grain from the polished mounts was selected for a Transmission Electron Microscope (TEM) study of the interface between rutile and xenotime. For this purpose, electron-transparent foils with typical dimensions of 14.8×4.3×0.15 μm were prepared using the focused ion beam (FIB) technique at IGGCAS (Zhang et al., 2017). The TEM analytical work was carried out using a JEOL JEM-2100 operated at a 200 kV. The TEM study included bright-field imaging, high-resolution transmission electron microscopy (HRTEM) imaging, as well as electron diffraction analysis.

***3.6. Cameca IMS 1280 SIMS Pb-Pb dating of xenotime overgrowths***

The plugs, extracted from the thin sections, were mounted in epoxy resin disks and imaged with a reflected light microscope to locate analytical spots for SIMS analysis. The sample mount was carbon-coated prior to SIMS analysis. Absence of suitable xenotime standards for matrix effect correction means that U-Pb age dating was unable to be carried out. Hence, small beam technique and multicollector mode were applied only for Pb–Pb age dating. The dating work was conducted using the Cameca IMS-1280 HR ion microprobe at IGGCAS using Gaussian mode of the ion probe with a spot size of ca. 5 μm (Liu et al., 2011). The smaller primary beam allows to apply higher magnification transfer settings to ensure higher transmission (∼21 cps/ppm/nA using O2−) and higher precision (Liu et al., 2011). The secondary ion image of the Y2O signal from rastering assisted in precisely defining the target area to accommodate the finely tuned primary beam of O2−. According to Fletcher et al. (2004), there might be an interference on 204Pb because of the potential combination of two 16O with high amounts of 172Yb to form YbO2+, showing up at mass 204. However, this potential interference can be removed by carefully tuning the instrument in that Cameca IMS 1280 has an much higher mass resolution of 13,000. TiO2 was recorded to monitor potential primary beam overlap onto adjacent rutile. For Pb isotope analyses, each measurement consisted of 7 cycles, and the total analytical time was ca. 15 min. Procedures for Pb/Pb dating of xenotime using multicollector mode were described by Lan et al. (2014a).

***3.7.* *Cameca IMS 1280 SIMS U-Pb/Pb-Pb dating of rutile cores***

We also attempted SIMS U-Pb/Pb-Pb dating of rutile cores. Unfortunately, neither U-Pb nor Pb-Pb ages could be obtained because of high common Pb content >90% and thus high 207Pb/206Pb>0.8.

***3.8. Cameca IMS 1280 SIMS U-Pb/Pb-Pb dating of detrital zircon***

Measurements of U, Th and Pb isotopes were conducted using a Cameca IMS-1280 SIMS at IGGCAS. Detailed analytical procedures refer to Li et al. (2009b) and Lan et al. (2014b), and only a brief summary is described here. The primary O2– ion beam spot is about 10×15 μm in size. Positive secondary ions were extracted with a 10 kV potential. In the secondary ion beam optics, a 60 eV energy window was used, together with a mass resolution of ca. 5400 (at 10% peak height), to separate Pb+ peaks from isobaric interferences. A single electron multiplier was used in ion-counting mode to measure secondary ion beam intensities by peak jumping mode. Measured compositions were corrected for common lead using non-radiogenic 204Pb. An average present-day crustal composition (Stacey and Kramers, 1975) is used for the common Pb assuming that the common Pb is largely surface contamination introduced during sample preparation. The external uncertainties of SIMS U–Pb measurements were monitored by inter-calibration of standard zircon Plešovice. Each measurement consists of 7 cycles. Pb/U calibration was performed relative to zircon standard Plešovice (206Pb/238U age = 337 Ma, Sláma et al., 2008). During the course of this study, Qinghu zircon standard was also analyzed as an unknown to monitor the external precision.

***3.9. NanoSIMS U-Pb/Pb-Pb dating of zircon cores***

After Cameca IMS 1280 analyses, the mount was recoated with gold and was loaded into the Cameca NanoSIMS 50 airlock system at AORI-UOT followed by being baked at ~100°C overnight and being kept in the vessel at 1E-9 Torr for about one week prior to U-Pb dating analyses. Cameca NanoSIMS 50 was used to determine the U-Pb and Pb-Pb ages of the zircon cores surrounded by xenotime overgrowths. The U-Pb and Pb-Pb ages were measured separately in two sessions, with one spot being analyzed twice within the same grain. We use single Pb evolution method to obtain the common 204Pb/206Pb composition of the unknown samples. The 206Pb/238U is obtained by applying ln(Pb/UO)-ln(UO2/UO) calibration method taking 91500 as standard as detailed in Takahata et al. (2008).

**4. Results**

***4.1. FESEM imaging results for the xenotime overgrowths***

A total of 220 polished thin sections were examined and 26 were found to contain suitable xenotime. In the Lantian black shale, xenotime typically grows on zircon grains and displays a pyramidal or irregular morphology in the size range of 8-30 μm (Figure 3E-H). No apparent compositional zonation occurs in the xenotime overgrowths, despite the presence of cracks and dissolution pores and margins. The zircon cores are generally fine grained displaying an angular to sub-rounded morphology with a size range of 10-50 μm. Some relatively euhedral zircon grains show evident compositional zonation (e.g. Figure 3G). The xenotime-zircon assemblages are generally embedded into clay minerals which co-occur with quartz, iron oxides and organic material.

In the Chang’an diamictite, xenotime is associated with rutile, chlorite, ilmenite, and pyrite in the matrix of diamicite (Figure 4E-H). Xenotime exhibits an irregular morphology with a size range of 15–40 μm. Some of the rutile is euhedral with a size range of 8-40 μm (Figure 4E, F, H), whereas others show an irregular morphology with a size range of 20-50 μm (Figure 4G). The xenotime-rutile assemblage was surrounded by quartz cement and chlorite. Some localized xenotime is in corrosive contact with early quartz cement and contains quartz cement inclusions (Figure 4F). There is no apparent compositional zonation despite minor pores and inclusions in some xenotime (e.g. Figure 4E), suggesting they probably formed in a single period of [fluid circulation event](http://www.iciba.com/tectothermal_event). Approximately 5 mm diameter plugs encompassing the xenotime overgrowths >5 μm diameter were drilled out of polished thin sections and mounted in epoxy resin disks for *in situ* chemical and imaging analyses.

***4.2. EPMA REE analysis results for the Chang’an xenotime overgrowths***

Lanthanum, Ce, and Pr were below the EMP detection limit. On a chondrite-normalized distribution pattern, the Chang’an xenotime overall exhibits a left dipping trend that is typified by enrichment in MREE–HREE and depletion in LREE (Figure 5A). δEu (Eu/Eu\*=0.49–1.07) show negative anomalies or no sign of anomalies, different from igneous and metamorphic xenotime that display remarkable negative δEu anomalies (Lan et al., 2013). Of the rest of the MREE–HREE, Dy2O3 has the highest concentration up to 3.86–8.62 wt% (Table 1). Gd2O3 ranks the second most abundant oxide with values up to 1.30–5.43 wt%. Lu2O3 possesses the lowest concentration value with only 0.11–0.26 wt%. Other elements such as Er2O3, Yb2O3, Sm2O3, Tb2O3, Ho2O3, and Tm2O3 have relatively low concentration values, ranging from 0.56–3.72 wt% to 0.17–1.24 wt%. Its right dipping HREE distribution pattern makes them comparable with hydrothermal xenotime but different from diagenetic xenotime (Lan et al., 2013). Of the non-REE elements, P2O5 has the highest concentration with a value reaching 15.60–34.21 wt%, followed by SiO2 (0.25–8.79 wt%), FeO (0.06–0.64 wt%), and CaO (0–0.03 wt%). In contrast to ΣREE, the atomic proportion of Y is better correlated with that of HREE (R2=0.81) (Figure 6A). The xenotime exhibits variable U+Th+Pb and Ca in the (U+Th+Pb) versus Ca proportion plot (Figure 6B).

***4.3. EPMA major and trace element results for the Chang’an rutile cores***

Table 2 shows the major and trace element compositions of rutile cores from the the Chang’an Formatin. Rutile has moderate Fe, Si, and Zr contents in the range of 0.1415-0.8129%, 0.0302-0.4049%, and 0.0024-0.3738%, respectively. Vanadium, Cr, Al, Sr, W, Pb, and U contents varies in the range of 0-0.0242 %, 0-0.0041%, 0.0040-0.0931%, 0-0.0066%, 0-0.0238%, 0-0.0542%, and 0-0.0086%, respectively. In the Ti-100(Fe+Cr+V)-1000(W) ternary discrimination plot, sample points projected near the corner of 100(Fe+Cr+V) (Figure 7).

***4.4. NanoSIMS REE analysis result of Lantian xenotime and zircon cores***

Like Chang’an xenotime, the Lantian xenotime displays an overall left dipping trend characterized by enrichment in MREE–HREE and depletion in LREE with total REE content in the range of 123,000-182,000 ppm (Table 3; Figure 5B). δEu (Eu/Eu\*=0.62-0.86) shows only minor negative anomalies, again different from igneous and metamorphic xenotime that display remarkable negative δEu anomalies (Kositcin et al., 2003; Lan et al., 2013). On the right end of REE curve, HREE such as Yb and Lu, show slightly enrichment. Similarly, the Lantian zircon cores also show an overall left dipping trend characterized by enrichment in MREE–HREE and depletion in the LREE with total REE content in the range of 8,000-165,000 ppm (Figure 5C). δEu (Eu/Eu\*=0.96-1.23) shows only minor anomalies. One of these analyses, point 1122\_5, has a relatively higher ∑REE content and xenotime-like REE distribution pattern, which may suggest penetration of adjacent xenotime overgrowths. The relatively large errors in point 1122\_5 may indicate time variation of secondary ion signals.

***4.5. TEM imaging result of xenotime-zircon interface***

The transition zone between the rutile and xenotime exhibits a narrow range of ca. 40-50 nm without any impurities (Figure 8). The interface zone is also crystalline but are somewhat distorted like those previously documented (e.g. Drost et al., 2013). The convex and concave surfaces (Figure 8A-C) are resulted from sample preparation using FIB. High-resolution TEM images suggest lattice dislocation in the xenotime in the vicinity of the interface zone (Figure 8C). Electron diffraction of areas in the rutile exhibit fuzzy diffraction pattern, whereas both the xenotime and interface display sharp and similar diffraction patterns (Figure 8D, E). Another important feature is the presence of diffraction spot in the interface zone.The xenotime shows an interplanar spacing of 3.4086Ǻ, whereas the rutile produces an interplanar spacing of 2.3165Ǻ (Figure 9A, B).

***4.6. Cameca IMS 1280 Xenotime SIMS Pb-Pb ages***

For the Chang’an xenotime, a total of four convincing analyses were achieved, which exhibit a high correlation relationship (R2 = 0.99) between 207Pb/206Pb and 204Pb/206Pb ratios with an intercept of 0.0542 ± 0.0015 corresponding to a corrected 207Pb\*/206Pb\* age of 378.5 ± 62.3 Ma (2σ) (Table 4; Figure 10A). For the Lantian xenotime, a total of 25 analyses were obtained, which display a high correlation relationship (R2 = 0.97) between 207Pb/206Pb and 204Pb/206Pb ratios with an intercept of 0.0555 ± 0.0008 corresponding to a corrected 207Pb\*/206Pb\* age of 431.6 ± 31.7 Ma (2σ) (Table 5; Figure 10B).

***4.7. Cameca IMS 1280 U-Pb/Pb-Pb ages of detrital zircons***

Zircons from samples LT02 and LT03 of Lantian Formation are 48–140 μm long, 25–125 μm wide, euhedral to rounded in morphology (Figure 11). Dissolution margins are common, particularly on the subrounded to rounded zircon grains.. Zircon grains exhibit differential CL intensity probably because of differential U contents.During the course of analysis, a total of 22 analyses were conducted for Qinghu yielding a weighted mean 206Pb/238U age = 159.6 ± 1.0 Ma (MSWD = 0.62) (Table 6; Figure 12). This age is identical within uncertainty to the reported value of 159.5 ± 0.2 Ma (Li et al., 2013), indicating the acquired age data for the unknowns are reliable. A total of 150 analyses were obtained from samples LT02 and LT03. Of these, 68 analyses were rejected because of high U (>2000 ppm) or high common Pb contents (*f*206 > 2%). The remaining 82 analyses have ages extending from 3024 Ma to 579 Ma (Table 6). These ages fall into four major groups, peaking at ca. 827 Ma, ca. 750 Ma, ca. 701 Ma, and ca. 589 Ma, respectively (Figure 13A, B). Zircons yielding ages of ca. 589 Ma are composed of six grain analyses (Figure 13C). The zircons are small, euhedral, and have distinct magmatic oscillatory zoning. These six analyses produce a Concordia age of 590 ± 7 Ma (2σ) (MSWD=0.18) (Figure 13 D), which was interpreted as the maximum depositional age of the sampling horizon.

***4.8. NanoSIMS U-Pb/Pb-Pb ages of zircon cores***

A total of thirteen convincing U-Pb/Pb-Pb ages were obtained from the zircon cores of the Lantian Formation. The U-Pb age ranges from ca. 1266 Ma to 288 Ma with four major peaks at ca. 726 Ma, ca. 519 Ma, ca. 449 Ma and ca. 343 Ma (Table 7; Figure 14A). Of these thirteen ages, ten are concordant (Figure 14B).

**5. Discussion**

***5.1. Hydrothermal origin of xenotime and rutile***

Xenotime of detrital/igneous origin is commonly characterized by remarkable negative δEu anomaly with rounded outline (Pyle et al., 2001; Spear and Pyle, 2002; Kositcin et al., 2003; Rasmussen et al., 2011; Lan et al., 2013). The slightly negative δEu anomaly combined with their irregular and angular morphology with no erosion of the corners indicates that xenotime from the Chang’an and Lantian formations is inconsistent with a detrital/igneous origin. Metamorphic xenotime in rocks with metamorphic grade ranging from slate to amphibolite facies schists is characterized by negative δEu and δTb anomalies (Rasmussen et al. 2011). The absence of negative δTb anomaly combined with the nearly unmetamorphic nature of Chang’an and Lantian formations means their xenotime could not be metamorphic origin despite the possibility that xenotime could be transformed into metamorphic xenotime under certain metamorphic conditions (Rasmussent et al., 2011). On the basis of regional lithostratigraphic and chemostratigraphic correlation, the Lantian Formation in southern Anhui Province correlates with the Doushantuo Formation in western Hubei Province, the depositional age of which was dated at 635-551 Ma (Condon et al., 2005). The youngest detrital zircon U-Pb age of 590 ± 7 Ma (2σ, MSWD=0.18) obtained from the sampling horizon is with errors consistent with the U-Pb age of 594 ± 30 Ma (2σ) from the zircon substrate surrounded by xenotime, thus further narrowing its depositional age to be 590-551 Ma. The zircon substrate U-Pb ages fall into four major age groups peaking at ca. 343 Ma, ca. 339 Ma, ca. 519 Ma, ca. 726 Ma (Figure 14a). The U-Pb ages predating 551 Ma from the zircon substrate represents detrital/inherited zircon ages, whereas those postdating 551 Ma represents potentially hydrothermal zircon ages. In this regard, the ca. 431 Ma xenotime is not early diagenetic in origin. Similarly, the theoretical depositional age of the Chang’an Formation is in the range of 716-692 Ma. This means that the ca. 378 Ma xenotime could not be early diagenetic in origin, either. As such, neither igneous nor early diagenetic nor a metamorphic origin can account for the xenotime from Lantian and Chang’an formations. Rather, the ca. 431 Ma and ca. 378 Ma ages within errors fall in time interval (460-390 Ma) of Wuyi/Yunkai Orogeny in South China (Li et al., 2010a; Hu et al., 2012), indicating that magmatism during the Wuyi/Yunkai Orogeny was likely responsible for the hydrothermal fluids and heating responsible for the formation of the xenotime. Similar hydrothermal xenotime U-Pb/Pb-Pb ages have also been documented from the Ordovian Grès Armoricain sandstones in France (Tartèse et al., 2015), implying that the hydrothermal xenotime in these rocks grew simultaneously during the tectonothermal event associated with the waning period of the Caledonian Orogeny.

Such hydrothermal events could not only have induced the formation of xenotime, but also prompted the simultaneous formation of rutile grains despite our inability to date the rutile directly. Their common euhedral morphology and occurrence as numerous aggregated crystals within interstitial cements suggest the Chang’an Formation rutile grains probably crystallized from a fluid (c.f. Morad, 1986; Meinhold, 2010). Given that tungsten, V, Sr, Cu, Sn, and Sb (particularly the former two elements), tend to be enriched in rutile crystallized from hydrothermal fluids, Clark and Williams-Jones (2004) developed a ternary diagram Ti-100(Fe+Cr+V)-1000W to distinguish between hydrothermal rutile crystals precipitated from circulating hydrothermal fluids driven by magmatic intrusion and those precipitated in igneous and metamorphic rocks (Figure 7) (Scott and Radford, 2007; Pi et al., 2017). However, most of the Chang’an rutile crystals do not have higher W contents but appears to be hydrothermally altered (Figure 7). They do display enrichment of Fe and V (Figure 7). This may be because in typical hydrothermal ore deposits the coupled substitution 2Ti4+ → Fe2+ + W6+ commonly occurs (Rice et al., 1998; Müller and Halls, 2005). The Chang’an rutile crystals formed in an open system due to the abundant pore space within the coarse grains allowing for relatively oxidizing formation waters to initiate (Williamson et al., 2000). The coupled substitutions 2Ti4+ → Fe2+ + Cr6+ and 2Ti4+ → Fe3+ + V5+ commonly occurred during this time, resulting in the enrichment of Fe, Cr and V. Metamorphic rutile occurs abundantly along the Sulu-Dabie orogenic belt north of sampling location. This orogenic belt formed in an ultrahigh pressure environment, but its Mesozoic age and typical large size, coupled with absence of other metamorphic minerals, such as garnet and omphacite, excluded it as a possible source rock for the rutile in Chang’an Formation (Xiong et al., 2015).

***5.2. Origin of zircon cores***

Zircon cores surrounded by xenotime overgrowths from the Lantian Formation have Concordant SIMS U-Pb age groups peaking at ca. 343 Ma, ca. 339 Ma, ca. 519 Ma, ca. 726 Ma (Figure 14a). The ca. 519 Ma ages are derived from semi-rounded zircon grains indicating surficial transport or erosion, whereas the ca. 343 Ma and ca. 339 Ma zircon ages are from euhedral zircon grains suggestive of proximity to their source upon their initial formation (e.g. Lan et al., 2015a, b). From the perspective of radiometric ages, The ca. 519 Ma ages are consistent within errors with the ca. 590 Ma age determined from the extracted zircon grains, whereas the ca. 343 Ma and ca. 339 Ma zircon ages are within errors indistinguishable from the 431-378 Ma xenotime ages and seemingly represents the age of hydrothermal event. Generally speaking, hydrothermal zircons typically have porous or spongy structures exhibiting a dark CL color, and usually contain abundant inclusions such as xenotime and thorite suggestive of hydrothermal alteration of the precursor zircon grain (Hoskin, 2005). Furthermore, the hydrothermal fluids are generally enriched in LREE and their interaction with zircon grains would result in LREE enrichment (Hoskin, 2005). The zircon cores from the Lantian Formation show a bright CL surface without inclusions and a left-dipping REE distribution pattern (Figure 5C), a case that is different from the traditionally defined hydrothermal zircon. This may suggest differential hydrothermal system that contains different chemical compositions with differential temperature. Alternatively, the age derived from the zircon grains with age peaks at ca. 343 Ma and ca. 339 Ma may suggest cryptic radiogenic Pb loss given the large errors derived from NanoSIMS analyses.

***5.3. Formation mechanism of xenotime and rutile assemblage***

No hydrothermal zircon grains have been reported in the sedimentary rocks despite the wide occurrence of detrital zircon grains and other silicate minerals that could potentially provide Zr and Si ions to form zircon. In contrast, the rutile crystals could have formed from percolating pore solutions driven by hydrothermal activity that are rich in Ti ions mainly sourced from the alteration of detrital Fe-Ti oxide grains (Morad, 1986). This means that in sedimentary rocks, detrital Fe-Ti oxides are more prone to be leached and break down than detrital zircons in response to the same fluid circulation event, probably because of the highly refractory chemical properties in the detrital zircon grains (c.f. Mojzsis et al., 2001). It has been demonstrated that metamictization in zircon resulting from the decay of U and Th could potentially increases the solubility of zircon at low temperatures (Delattre et al., 2007; Hay et al., 2010). Accordingly, dissolution-reprecipitation of the zircon grain rims has been observed in detrital zircon-xenotime assemblages at <200℃ and <2 kbar. However, the dissolved margin is limited to the nanometer scale (Rasmussen, 2005b; Hay et al., 2010; Drost et al., 2013). It requires that detrital zircon grains must have already been present in siliciclastic sediments before the coming of hydrothermal fluid such that they had plenty of time to dissolve the zircon grain rims and re-precipitated zircon-xenotime cement, resulting in a dark, mottled interface between zircon and xenotime. Xenotime formed in this way typically occurs in optical and crystallographic continuity to its zircon substrate (e.g. Drost et al., 2013).

This mechanism does not apply to the rutile-xenotime assemblages in the Chang’an Formation where xenotime typically occurs in optical and crystallographic discontinuity to its rutile substrate. The lattice misfit δ = (*ɑ*b - *aa*)/*aa* is commonly used to judge coherence of the interface. The classification is judged to be coherent when δ<0.05, semi-coherent when 0.05≤δ<0.25, and non-coherent when δ>0.25 (He et al., 2006). The xenotime attains an interplanar spacing (200) of d1=3.4086Å, whereas the rutile shows an interplanar spacing (101) of d2=2.3165Å. This allow us to calculate a lattice misfit δ=(2.3165-3.4086)/3.4086=0.32, indicating a non-coherent/discontinuous interface between (200) and (101). The differential diffraction patterns between the rutile and xenotime at the interface mean that the interface could not have resulted from dissolution and re-precipitation. Both rutile and xenotime were precipitated almost simultaneously after fluid leaching of preexisting REE(Y)-bearing oxides, silicates, and ilmenite. In this case, the rutile substrate would soon be entombed by xenotime cement after it was formed. This means little time was left for the rutile to interact with surrounding fluid, thus allowing for the preservation of rutile grains without any dissolved rims. The absence of porosities and inclusions, such as thorite and/or uraninite, within the rutile-xenotime interface is also inconsistent with a dissolution-reprecipitation process (e.g. Hetherington et al., 2008). Instead, the distorted deformation on the rutile rims may have resulted from mechanical squeezing among detrital grains and/or cements during continued pile up of sediments.

Decomposition of interstitial organic matter within shallow depths of sediments provided the P to form xenotime (YPO4) in the Lantian Formation (Rasmussen, 1996). The similar crystallographic structure between the xenotime and zircon prompted the former to precipitate surrounding the latter, forming the zircon-xenotime association. The extraordinary scarcity of detrital zircon grains in the diamictite of the Chang’an Formation prompted rutile to act as host grains for xenotime because of their identical tetragonal dipyramidal structures. Diamictite from the Chang’an Formation contains no organic matter. Thus P, originating from pore waters, interacting with REE released from breakdown of clay minerals, was the most likely source for the xenotime. The observation that the Ti oxides and ilmenite are pervasively present in the diamictite from the Chang’an Formation prompted us to regard ilmenite as a major source of the Ti for rutile although it rarely shows a direct contact with ilmenite. Ti is not fluid mobile under most compositions of fluid unless fluorine appears. Apatite contains OH and F anions so the formation of apatite must require the supply of F anions in fluids. In this regard, Ti would be fluid mobile in the presence of fluorine around. During diagenesis, pyrite grains could form in the soft sediment from Fe derived from ocean water infiltrating the pore spaces in the sediment column (Lan and Chen, 2012b). However, such pyrite typically exhibits framboidal morphology. In contrast, the pyrite in this study typically appears euhedral morphology with relatively large size of centimeter grade, suggestive of hydrothermal rather than diagenetic origin (Lan et al., 2017). Ferrous iron released during ilmenite breakdown could have changed into sulfide by interacting with S anions within the pore waters. REE(Y) released from REE(Y)-bearing silicates would combine with P anions within the pore waters to form apatite. The apatite bears sharp but not rounded margins so it would not be detrital but rather authigenic origin. As such, the following chemical reaction can be inferred for the formation of rutile-xenotime-apatite-chlorite-pyrite assemblages in the Chang’an Formation diamictite:

Pore water P&S + REE(Y)-bearing silicates + Ilmenite $\rightarrow $ Rutile + Chlorite + Xenotime + Apatite + Pyrite

Xenotime overgrowths form within this unity with rapid entrapment of inclusions of quartz cement. Prior to the precipitation of xenotime, the hydrothermal fluid reworked preexisting quartz cement or infilled the pore spaces within the quartz cement, as evidenced by the presence of quartz cement inclusions in the xenotime (Figure 4F).

Xenotime not only grew during early diagenesis, but also grew during later diagenetic to hydrothermal events (McNaughton et al. 1999; Vallini et al. 2002, 2005; Rasmussen et al. 2011; Lan et al., 2014a; Zhang et al., 2015), which means xenotime commonly displays protracted or multiple states of growth. The specific chemical composition of the xenotime should mirror the composition of pore fluids from which they were precipitated. Thus the supply of REE/Y and P in the pore water/solution directly determines the time lag between different episodes of xenotime growth. Correlation between HREE and Y just suggests they have the same charge and ionic radius (Figure 6A). In the U-Th-Pb vs Ca atomic proportion binary plots, all samples show a wide distribution range (Figure 6B), where Ca seems to be controlled by Th through the mechanism of charge balance coupled substitution via 2(Y, REE)3+ substituting for (Th, U)4+ + Ca2+ (Drost et al., 2013). This suggests that the compositions of xenotime exhibits differentiated compositional trends, which do not constitute single trend line, but rather point to a variable fluid composition with possible several independent episodes of fluid activity. The frequent presence of multiple age populations resulting from prolonged xenotime precipitation means that even the early diagenetic xenotime could postdate the depositional age for several 10’s of millions of years (e.g. McNaughton et al. 1999; Rasmussen, 2005; Lan et al., 2014a; Zhang et al., 2015). In this regard, the possibility that ca. 431 Ma xenotime represent the age of later diagenetic event cannot be totally discounted.

**6. Conclusions**

This paper presents a case study of xenotime overgrowths on rutile grains in sedimentary rocks from the Cryogenian Chang’an Formation of South China. Radiometric dating constrained these xenotime overgrowths to form at ca. 378 Ma, which is much younger than the anticipated depositional age of 716-692 Ma. Similarly, xenotime overgrowths on zircon grains from the Ediacaran Lantian Formation attain a Pb-Pb age of ca. 431 Ma, which is also younger than its depositional age of 590-551 Ma. EPMA and NanoSIMS chemical analysis coupled with petrographic observations suggest that both examples of xenotime overgrowth are hydrothermal in origin. Xenotime and xenotime-rutile interface exhibit distinct and comparable diffraction patterns, whereas the rutile grains show a blurred diffraction pattern,indicating optical and crystallographic discontinuity. The typically small and euhedral rutile grains suggest they are not detrital in origin, but were formed via the breakdown of ilmenite during the introduction of hydrothermal fluids. As soon as the rutile was formed, xenotime was precipitated around it. Although the dissolution-precipitation mechanism commonly operates in the case of zircon-xenotime assemblage in sedimentary rocks, it is unlikely during the formation of rutile-xenotime as xenotime occurs in optical and crystallographic discontinuity with respect to its rutile substrate, which was possibly influenced by mechanical squeezing during the Wuyi-Yunkai Orogeny in South China. The absence of dissolution textures on the margins of detrital zircons in the sedimentary rocks means that the detrital Fe-Ti oxides were more prone to be leached by hydrothermal fluids and breakdown than the detrital zircon grains. Percolating hydrothermal fluids leached Fe, Ti, and REE(Y) from ilmenite and REE(Y) bearing silicate minerals and precipitated rutile, Fe oxides, pyrite, and xenotime in other pore spaces, which best account for the allochthonous occurrence of rutile, xenotime, iron oxides and pyrite. The possibility cannot be totally discounted that these xenotime overgrowths were formed during early diagenesis in view of the complex fluid evolution resulting in protracted and multiple growth process.

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**Figure and Table captions**

Figure 1 (A) Simplified geological map showing the Wuyi-Yunkai Orogeny influenced areas in South China (modified from Xu et al., 2016). (B) and (C) The two studied sections in southern Anhui and southeastern Guizhou provinces, the former modified from Yuan et al. (2011). The two black stars indicate the section localities.

Figure 2 Field photos showing the presence of black shales within the Lantian Formation in southern Anhui Province, South China (A, B) and massive diamictite from the Chang’an Formation in Guizhou Province, South China, which contains pebbles and authigenic pyrite (C-E). The hammer is about 35 cm long, whereas the coins are 2 cm in diameter.

Figure 3 Photomicrographs of black shale samples within the Lantian Formation showing the presence of clay minerals, organic carbon, pyrite framboids, and fine grained angular quartz (A-D). Also present are an assemblage of zircon cores and xenotime overgrowths surrounded by clay minerals (E-H).

Figure 4 Photomicrographs of massive diamictite within the Chang’an Formation showing the presence of quartz, chlorite, K-feldspar, ilmenite, rutile, and apatite (A-D). Note the chemical transition of K-feldspar and ilmenite into chlorite and rutile, respectively (B-C). Also present is an assemblage of rutile cores and xenotime overgrowths surrounded by quartz cement and chlorite (E-H).

Figure 5 Chondrite-normalized REE distribution patterns for xenotime from the Chang’an Formation (A), xenotime from the Lantian Formation (B), and zircon cores from the Lantian Formation (C). Numbers in (B) and (C) indicate analysis spot number where analysis uncertainties are also added.

Figure 6 REE (A) and non-REE (B) binary discrimination plots for xenotime from the Chang’an Formation.

Figure 7 Ti-100(Fe+Cr+V)-1000(W) ternary plot revealing the genesis of rutile.

Figure 8 Low magnification TEM bright field images of the xenotime-rutile interface (A, B). (C) High resolution TEM image of the xenotime-rutile interface. Inset represents the diffraction pattern of rutile. (D) Diffraction pattern of xenotime in the dotted frame in (C). (E) Diffraction pattern of the xenotime-rutile interface in the dotted frame of (C).

Figure 9 Inter-planar spacing of enlarged HRTEM images of xenotime (A) and rutile (B) in Figure 9C.

Figure 10 (A) 207Pb/206Pb-204Pb/206Pb inverse isochron giving an intercept 207Pb\*/206Pb\* age of ca. 378.5 Ma for the Chang’an Formation xenotime. (B) 207Pb/206Pb-204Pb/206Pb inverse isochron giving an intercept 207Pb\*/206Pb\* age of ca. 431.6 Ma for the Lantian Formation xenotime.

Figure 11 Cathodoluminescence images of detrital zircon grains extracted from the black shale of the Lantian Formation.

Figure 12 (A) Concordia age of 160 ± 1 Ma for the Qinghu zircon grains. (B) Weighted mean age of 159.6 ± 1 Ma for the Qinghu zircon grains.

Figure 13 (A) Age probability diagram showing the age distribution of zircon grains from the fossiliferous horizon within the black shales of the Lantian Formation. Note the presence of four major age peaks at ca. 827 Ma, ca. 750 Ma, ca. 701 Ma, and ca. 589 Ma. (B) Concordia plot for all the zircon grains. (C) Age probability diagram showing the peak at ca. 586 Ma. (D) Concordia age of 590 ± 7 Ma for the xenotime bearing black shale samples.

Figure 14 (A) Age probability diagram showing the age distribution of zircon cores within xenotime overgrowths from the Lantian Formation. Note the presence of four major age peaks at ca. 726 Ma, ca. 519 Ma, ca. 449 Ma, and ca. 343 Ma. (B) Tera-Wasserburg plot for U–Pb age data from zircon cores within xenotime overgrowths from the Lantian Formation.

Table 1 EPMA REE analysis results for the xenotime of Chang'an Formation.

Table 2 EPMA major element analysis results for the rutile of Chang’an Formation.

Table 3 NanoSIMS REE analysis results for the zircon and xenotime of Lantian Formation.

Table 4 SIMS 207Pb/206Pb dating results for the xenotime of Chang'an Formation.

Table 5 SIMS 207Pb/206Pb dating results for the xenotime of Lantian Formation.

Table 6 SIMS U-Pb/Pb-Pb ages for the detrital zircons of Lantian Formation.

Table 7 NanoSIMS U-Pb/Pb-Pb ages for the zircon cores of Lantian Formation.