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In situ U-Pb isotopic dating method on titanite, and application to determine REE-Fe-Cu mineralization age of the Sin Quyen deposit, Lao Cai province

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ABSTRACT

Titanite ($CaTiSiO_5$) is an important common accessory mineral in hydrothermal deposits, with appreciable amounts of U and Th incorporated into their structures for age dating. Titanite crystals are usually larger than zircon and monazite and may have zoning in texture and geochemistry which represent different parageneses likely related to multiple hydrothermal or mineralization events. In line with the development of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) that has high sensitivity and spatial resolution, in-situ U-Pb isotopic dating method on titanite has become a powerful tool to investigate the ages of different zones from a mineral. Titanite typically accommodates a significant amount of Rare Earth Elements (REEs) and High Field Strength Elements (HFSEs) and the titanite generated from different origins exhibits distinct trace element geochemistry. Therefore, the trace element geochemistry of titanite can serve as an indicator of its formation environment. Titanite occurred in different mineralization stages of the Sin Quyen deposit, making it a suitable mineral for investigating the timing of mineralization. In this paper, we present the U-Pb age of titanite from different stages of the Sin Quyen deposit used to constrain the timing and origin of such events. The hydrothermal titanites are dated by in situ LA-ICP-MS technique and have U-Pb ages of 873±12 Ma and 844±12 Ma which indicate two mineralization/hydrothermal events at the same time, respectively. These ages from the Sin Quyen deposit are well correlated with regional tectono-thermal events during the long-lived Neoproterozoic subduction in the western Yangtze Block.

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1. Introduction

The Iron Oxide Copper Gold (IOCG) deposits have a protracted mineralization history because multiple tectono-thermal events occurred in most Precambrian IOCG provinces (Barton, 2014). Some IOCG deposits have endured several temporally discrete mineralization events leading to geochronological analyses that may not be able to adequately distinguish such multiple hydrothermal events. Therefore, in order to obtain well-constrained mineralization ages, particularly for deposits formed in complex geological environments, it is necessary to date minerals that record different hydrothermal or metamorphic episodes. Dating minerals formed from different stages is important for the understanding of the historical metallogeny in correlation with regional tectono-thermal events. Like zircon, titanite can contain considerable amounts of U and has high closure temperatures of up to 700^{0}C, but it is more susceptible to high-temperature hydrothermal alteration than zircon (Li et al., 2010). Titanite is widely distributed in the Sin Quyen deposit, which is why it is very suitable for dating in this case. Nevertheless, the issue that titanite commonly incorporates non-negligible common Pb makes it difficult to yield a concordant age (Frost et al., 2001). Besides, owing to a lack of universal high-quality titanite standard for in-situ laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) dating, many laboratories use zircon as an external standard and some use raster scan mode instead of spot mode to reduce the matrix effect during laser ablation may have little effect to the age obtained (Storey et al., 2006). However, recent cross-calibration with other titanite standards demonstrates that MKED1 can be used as a primary standard for determining U-Pb ages of titanite ranging in age from Precambrian to Neogene. Simultaneously, MKED1 may also be used as a standard for in situ trace element microanalysis on the provision that locations for analytical sampling are selected with consideration to grain-scale elemental zoning (Spandler et al., 2016). Therefore, in this study, to enhance the accuracy and precision of U-Pb titanite ages we used MKED1 standards for cross-calibration to date the age of titanite.

In this paper, we describe two types of titanite in the Sin Quyen deposit and report the precise LA-ICP-MS U-Pb ages. The age dataset reveals that titanite has formed in two different hydrothermal stages. We propose that the REE ore was formed prior to Fe oxide and Cu sulfide ore formation in the Sin Quyen deposit. These ages possibly clarify the ore-forming time and are helpful in solving the remaining problems related to the whole metallogenic province. We also favor a temporal link between the multiple stages of mineralization in the Sin Quyen deposit and the formation of the Ailao shan-Phan Si Pan copper belt in the western Yangtze Block of China.

2. Sin Quyen deposit geology and mineralization

The Sin Quyen Cu-Fe-Au-REE deposit is situated adjacent to the Red River Fault zone and belongs to the Phan Si Pan (PSP) belt in northern Vietnam (Figure 1). The PSP belt separates the South China and Indochina tectonic plates and has complex tectonic and magmatic histories. The Sin Quyen deposit contains 52.8 Mt ore with 0.91 wt.% Cu, 0.7 wt.% LREE (La, Ce, Pr, and Nd), and 0.44 g/t Au (Ta, 1975; McLean, 2001). Recent drillings down to -550 m in depth have proven reserves of over 90 Mt ore with an average grade of 0.9 wt.% Cu (Pham, 2015). The mining district is divided into two areas by the Ngoi Phat River, which are the Eastern and Western mining areas. Seventeen lenticular and sheet-like orebodies occur along the horizon of host rocks (Figure 2). These orebodies are commonly deformed and fragmented due to the strain in the Song Hong zone. Orebodies are hosted in the gneiss, mica-schist, and marble of the upper Sin Quyen Formation. The ore occurs mainly as massive or banded bodies, 50÷600 m in length, 5÷100 m in width, and vertically extends from 50÷400 m. Locally, the chalcopyrite-quartz veins vary in width from tens of centimeters to a few meters and dip at various angles to the northeast. Ore minerals include chalcopyrite, magnetite, pyrrhotite, allanite, gold, and pyrite. The alteration is dominated by skarn-like rocks, consisting of 30% pyroxene, 30% hessonite-grossularite garnet, 10% allanite, 6% calcite, 5% epidote, 5% quartz, and 5% amphibole with minor apatite and titanite.

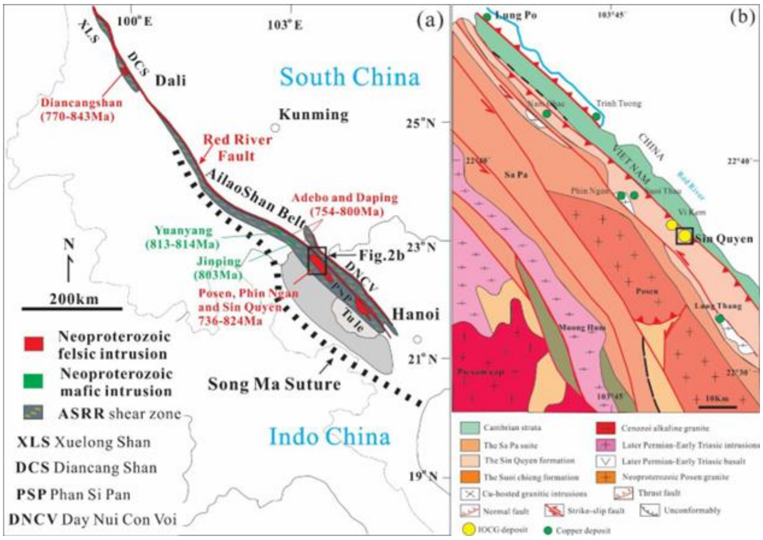

Figure 1. (a) Simplified tectonic map shows the study area relative to northwestern Vietnam and southwestern China; (b) geological map of the Sin Quyen-Lung Po belt shows the spatial distribution of Fe-Cu-Au deposits (after Tran et al., 2016).

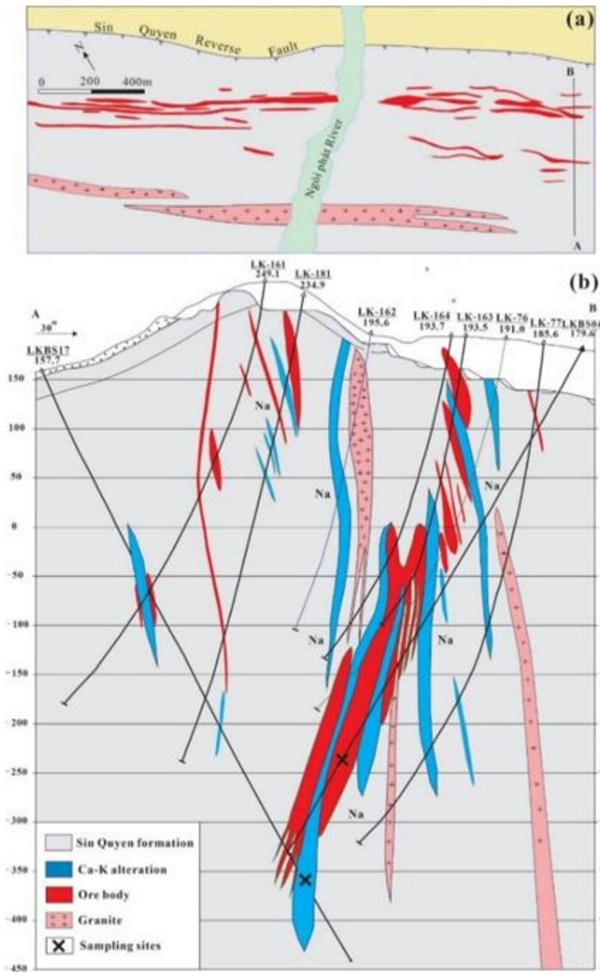

Figure 2. (a) Simplified geological map of the Sin Quyen deposit (modified from Ta, 1975; Pham, 2015); (b) the cross-section shows the shape and distribution of orebodies.

The intergrown between allanite and garnet suggests that the skarn-like alteration was synchronous with the REE mineralization (Ngo et al., 2020).

3. Titanite dating

3.1. Sample description

Two samples from the drill hole LK30, at 492 and 505m respectively, were collected for this study (Figures 3 a, c). The first sample taken from the Ca alteration (Figure 3a) consists of hornblende (30%), allanite (25%), titanite (20%), epidote (7%), fluorapatite (5%), biotite (5%), plagioclase (3%) and minor chalcopyrite (Figure 3b). Therefore, this episode is considered the stage of REE-only mineralization formation in the Sin Quyen deposit. This episode is interpreted as the REE-only mineralization of episode 1. The second sample taken from the K alteration (Figure 3c) consists of magnetite (40%), chalcopyrite (15%), biotite (15%), epidote (5%), plagioclase (5%), titanite (3%), allanite (3%), hornblende (3%), and minor quartz and pyrrhotite (Figure 3d). Thus, this episode is considered the stage of Fe-Cu mineralization formation in the Sin Quyen deposit.

Thin section petrographic analysis has identified two types of titanite in the Sin Quyen deposit. Type 1 titanite (Ttn_1) occurs as euhedral to subhedral crystals that are 0.5÷2 mm in diameter and are closely associated with amphibole and allanite (Figure 3b). Observation of petrographic images reveals that some type 1 grains also have core-rim textures, with the primary titanite being replaced by the secondary varieties, whereas type 2 titanite (Ttn_2) occurs as homogeneous, small grains closely associated with magnetite (Figure 3d).

3.2. Analytical techniques

Type 1 titanite from the thin section of the first sample was used for in situ ICP-MS U-Pb isotopic analysis while type 2 titanite in the second sample was handpicked after heavy-liquid and magnetic separation before being mounted in a 2.5 cm puck for the in situ ICP-MS U-Pb isotopic analysis. Before analysis, back-scattered electron (BSE) images of titanite were used to further characterize the shape and internal texture of titanite. BSE images were acquired using an FEI Quanta200 environmental scanning electron microscope (SEM) fitted with an energy dispersive spectrometry (EDS) system operated

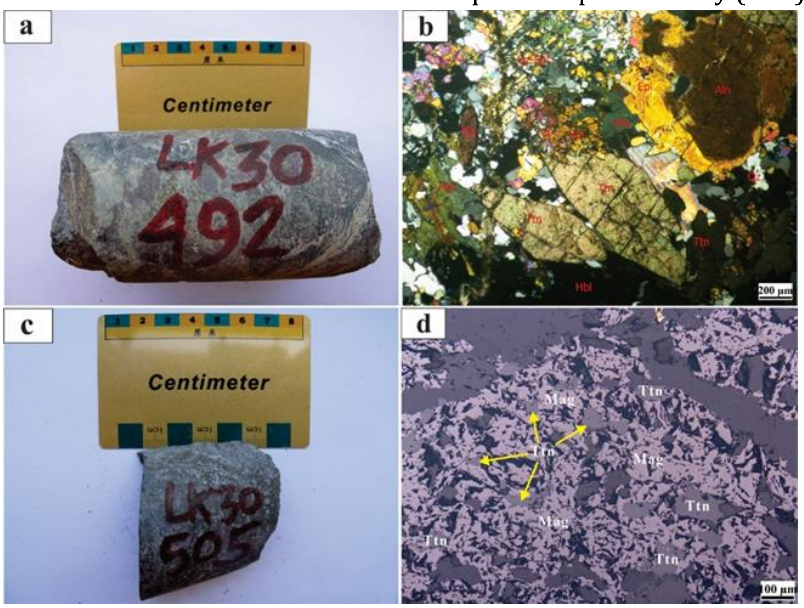

Figure 3. (a) Photography of the first sample taken from a depth of 492 m; (b) thin section petrographic study of the first sample, showing titanite (type 1) and allanite grains associated with hornblende and less amount of late epidote; (c) photography of the second sample taken from the depth of 505 m; (d): thin section petrographic study of the second sample show titanite (type 2) of small size forms with magnetite and biotite in the second mineralization event. Abbreviations: Aln-allanite; Ttn-titanite; Hbl: hornblende; Epi-epidote; Bt-biotite; Qz-quartz; Mag-magnetite.

at 20 kV, 20 nA, and a working distance of 11.5 mm. Cathodoluminescence (CL) was used to guide analytical spot selection for U-Pb dating and CL images were undertaken from a carbon-coated polished disk using a JEOL JXA-8100 environmental scanning electron microscope instrument and a MonoCL detector to characterize grain size and internal structure. U-Pb dating was analyzed using an Agilent 7700x ICP-MS apparatus equipped with a GeoLas 2005 laser-ablation system with a DUV 193 nm ArF-excimer laser at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences, Wuhan. The detailed analytical procedures and data reduction method have been fully described by Spandler et al. (2016). A spot size of 32 μm was used for all analyses. The internal standard isotope used for data reduction was ^{43}Ca which was previously measured by EPMA analysis. NIST SRM610 was used as a bracketing external standard (Spandler et al., 2016). The laser fluence on the sample was set to 5 J/cm^2, repetition rate of 10 Hz. These conditions were selected after extensive testing to maximize analytical sensitivity while maintaining titanite ablation with minimal down-hole elemental fractionation. Each set of 3 analyses was followed by one measurement of MKED1 and NIST SRM 610 to calibrate the geochemical and isotopic analyses. The MKED1 standard derives from the Elaine Dorothy Cu-Au-REE deposit in Mount Isa Inlier, Queensland, Australia. Concordia diagrams and $^{206}Pb/^{238}U$ weighted mean calculations of titanite were made using Isoplot/Ex_ver3 (Ludwig, 2003).

4. Results and Discussion

The U-Pb ages for the two types of titanite are summarized in Tables 1 and 2 and the Concordia diagrams are shown in (Figure 4). Thirteen spot analyses on the 5 titanites grain of type 1 yield concordant U-Pb ages with a weighted mean $^{206}Pb/^{238}U$ age of 873 ± 12 Ma (n=13, MSWD = 0.026). Twelve spot analyses on the 12 titanite grains of type 2 yield concordant U-Pb ages with a weighted mean $^{206}Pb/^{238}U$ age of 844 ±12 Ma (n=12, MSWD = 0.03).

Table 1. In situ LA-ICP-MS U-Pb ages of the type 1 titanite in the Sin Quyen deposit.

Spot	U	Pb	$^{206}Pb/^{238}U$		$^{206}Pb/^{238}U$		Conc
	ppm	ppm	Ratio	1σ	Age (Ma)	1σ	(%)
X474-1	163	1.30	0.144	0.003	872	22	99
X474-2	148	0.00	0.144	0.003	869	22	99
X474-3	113	0.29	0.145	0.004	877	23	98
X474-4	173	2.36	0.143	0.003	867	22	99
X474-5	139	1.31	0.145	0.004	877	22	99
X474-6	136	2.43	0.145	0.004	877	22	99
X474-7	108	1.13	0.145	0.004	873	22	99
X474-8	115	1.90	0.144	0.004	872	22	88
X474-9	206	0.00	0.143	0.003	867	21	98
X474-10	248	0.02	0.145	0.003	876	21	99
X474-11	438	2.66	0.145	0.003	873	21	99
X474-12	146	1.37	0.145	0.004	874	22	99
X474-13	129	1.02	0.145	0.004	876	22	99

Table 2. In situ LA-ICP-MS U-Pb ages of the type 2 titanite in the Sin Quyen deposit.

Spot	U	Pb	$^{206}Pb/^{238}U$		$^{206}Pb/^{238}U$		Conc
	ppm	ppm	Ratio	1σ	Age (Ma)	1σ	(%)
X505-1	355	2.3	0.140	0.004	845	22	99
X505-2	573	3.3	0.140	0.004	844	21	99
X505-3	446	1.4	0.140	0.004	843	21	99
X505-4	239	0.8	0.140	0.004	845	21	99

X505-5	308	1.7	0.140	0.004	845	20	99
X505-6	399	1.8	0.140	0.004	842	21	99
X505-7	308	0.1	0.140	0.004	846	21	99
X505-8	277	1.2	0.140	0.004	844	21	99
X505-9	336	1.2	0.140	0.004	845	21	99
X505-10	335	1.2	0.140	0.004	843	21	99
X505-11	418	1.5	0.140	0.004	843	21	99
X505-12	442	2.2	0.140	0.004	844	21	99

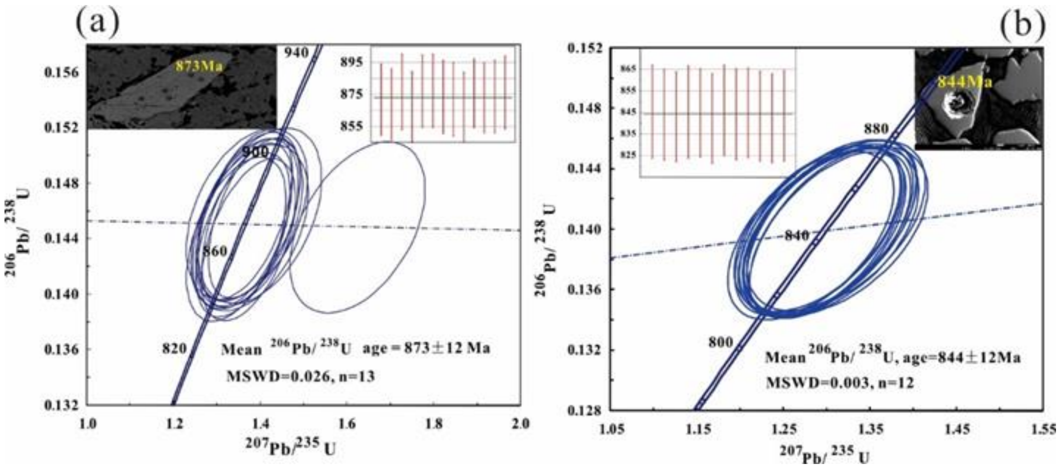

Figure 4. (a) Concordia diagram of U-Pb dating results for titanite 1 and (b) Concordia diagram of U-Pb dating results for titanite 2.

Our U-Pb titanite dates, together with previously reported data, provide robust evidence for the multiple nature of hydrothermal mineralization at the Sin Quyen deposit. Our new titanite U-Pb ages reveal two hydrothermal events in the Sin Quyen deposit at ~880 Ma and ~840 Ma, respectively. The Ttn_1 have indistinguishable U-Pb ages of 873±12 Ma, and the titanite 1 is generated with allanite, the dominant REE mineral, which is interpreted as the age of the early, REE-only mineralization of episode 1 (Figure 3b). The Ttn_2 have consistent U-Pb ages of 844±12 Ma, these ages are reproducible within analytical uncertainties and consistent with U-Pb ages of hydrothermal zircon and monazite (841±12 Ma and 836±18 Ma) reported by Li et al. (2018). The titanite 2 is associated with Fe-Cu mineralization and thus the U-Pb age of 844±12 Ma represents the timing of Fe-Cu mineralization (Figure 3d). Collectively, the titanite U-Pb ages presented here, together with previous zircon and monazite U-Pb data (Li et al., 2018), substantiate two episodes of hydrothermal mineralization events at the Sin Quyen deposit. This suggests that bulk-mineral geochronology is unlikely to provide the true ages of hydrothermal mineralization for the deposit that has undergone several stages of hydrothermal fluid flux. In situ, titanite dating is helpful for a better understanding of the chemical evolution of mineralization in geological time. It is noted that these ages correlate well with the regional tectono-thermal event, the Neoproterozoic long-lived subduction in the western Yangtze Block (Zhao et al., 2008; Cai et al., 2014; 2015). Furthermore, these age data also imply that the Neoproterozoic hydrothermal events along the Ailaoshan-Phan Si Pan belt have important potential for REE mineralization.

5. Conclusion

Our study highlights the importance of accurate and precise in situ age dating of mineral deposits for understanding ore genesis or genetic relations with regional tectono-thermal events. Two types of titanite formed in two different stages can be selected to determine the ages of the two ore-forming episodes. Episode 1 is dominated by intense Ca alteration and associated REE-only mineralization. Episode 2 includes pre-ore Na alteration, syn-ore Ca-Fe, and K-Fe alteration with associated IOCG mineralization. New titanite U-Pb dating results provide precise constraints on the timing and evolution of REE and Fe-Cu-Au mineralization at ~880 Ma and ~840 Ma, respectively.

It is recommended that the formation of the Sin Quyen deposit involve multiple mineralization or hydrothermal events. These results place important constraints on the onset timing of Fe-Cu-Au mineralization along the Ailao Shan-Phan Si Pan belt which is known as a series of Fe-Cu-Au polymetallic deposits in Southwest China. In addition, the Ailao Shan-Phan Si Pan belt probably has some places where rare earth mineralization has not yet been discovered. If so, Neoproterozoic intrusions in this belt are important targets for REE exploration.

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Contribution of authors

Dac Xuan Ngo, Son Hai Trinh, Tin Duc Quach, Hung The Khuong - conception, design of the study, and drafting of the manuscript; Thu Thi Le, Thoa Thi Hoang, Giang Hoang Phan - acquisition of data; Dac Xuan Ngo, Hung The Khuong - analysis and interpretation of data.

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