


Article

Apatite U-Pb Dating and Composition Constraints for Magmatic–Hydrothermal Evolution in the Giant Renli Nb-Ta Deposit, South China

Yongsheng Cheng^{1,2}, Zhuobin Xu^{1,2,*}, Hongfei Di^{1,2,*} , Zewen Zhang^{1,2}, Chunwang Mao^{1,2}, Huajie Tan^{1,2}, Jianzhong Huang³, Fangchun Zhou⁴, Liping Zhang⁴, Jianfeng Chen³ and Chunhua Wen³

¹ Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment Monitoring (Central South University), Ministry of Education, Central South University, Changsha 410083, China; cys968@163.com (Y.C.); zzw205001002@163.com (Z.Z.); mchunwang@126.com (C.M.); huajietan23@163.com (H.T.)

² School of Geosciences and Info-Physics, Central South University, Changsha 410083, China

³ Hunan Institute of Geological Survey, Changsha 410116, China; ddyhjz@126.com (J.H.); chenjianfeng021041@163.com (J.C.); herowch2004@163.com (C.W.)

⁴ Hunan Institute of Geological Disaster Investigation and Monitoring, Changsha 410100, China; zhoufangchun311@163.com (F.Z.); zhang907690548@163.com (L.Z.)

* Correspondence: 8205180302@csu.edu.cn (Z.X.); 8211180903@csu.edu.cn (H.D.)

Abstract: Apatite is a nearly ubiquitous accessory phase in igneous rocks that crystallizes during the entire magma evolution process and has great implications for geochronology and petrogenesis. Previous studies suggested that Nb-Ta mineralization in the giant Renli deposit was genetically related to Late Jurassic two-mica monzogranite or Early Cretaceous muscovite monzogranite. Moreover, the magmatic–hydrothermal evolution of these two stages is poorly understood. In our study, we confirm that the muscovite monzogranite, biotite monzogranite, and two-mica monzogranite are all spatially associated with Nb-Ta pegmatites. We present new apatite U-Pb ages to constrain the timing of Nb-Ta mineralization and related magmatism. The results show that apatite from the two-mica pegmatite yield a lower intercept age of 130 ± 2 Ma (2σ), and apatite grains from two two-mica pegmatite samples yield a lower intercept age of 135 ± 8 Ma (2σ) and 134 ± 3 Ma (2σ), respectively. Apatite and whole-rock geochemistry suggest the oxidation degree of the Nb-Ta mineralization increases from north (RL-6) to south (RL-16) in the giant Renli deposit. This study demonstrates that a combination of apatite composition and U-Pb ages can be used to constrain the magmatic–hydrothermal evolution of granite and pegmatite-type Nb-Ta deposits.

Keywords: apatite U-Pb age; trace elements; magmatic–hydrothermal evolution; Renli pegmatite Nb-Ta deposit; South China



Citation: Cheng, Y.; Xu, Z.; Di, H.; Zhang, Z.; Mao, C.; Tan, H.; Huang, J.; Zhou, F.; Zhang, L.; Chen, J.; et al. Apatite U-Pb Dating and Composition Constraints for Magmatic–Hydrothermal Evolution in the Giant Renli Nb-Ta Deposit, South China. *Minerals* **2022**, *12*, 344. <https://doi.org/10.3390/min12030344>

Academic Editor: Kunfeng Qiu

Received: 28 December 2021

Accepted: 10 March 2022

Published: 11 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The Nb-Ta deposits represent an important source of critical metals and minerals, and therefore they play an important role in the national defense industry, the aerospace industry, the nuclear industry, super-hard materials industry, and other industries [1,2]. Apatite is a ubiquitous accessory mineral in granite and pegmatite-type Nb-Ta deposits and can carry many trace elements during the entire magmatic–hydrothermal evolution process [3,4]. The occurrence of trace elements (e.g., U, Th, Sr, and REE) in apatite is controlled by melt/phosphate mineral equilibria, the composition of the host rock, and physico-chemical conditions [4–7]. Therefore, apatite can be used to decipher petrogenesis and constrain magmatic processes. The crystal structure of apatite and the radioactive decay of U and Th make it an ideal mineral for thermochronology and yields crystallization ages of rapidly cooled plutonic rocks using the U–Pb system [8–11]. LA-ICP-MS (Laser ablation-inductively coupled plasma-mass) apatite U-Pb dating can exhibit weighted mean

age uncertainties as low as 1–2% [12]. Therefore, apatite U-Pb geochronology can provide valuable information on the timing of thermal events.

The Renli ore field is an important resource area of rare elements in the Mufushan region, South China [13]. The relationship between Nb-Ta mineralization and granite (two-mica monzogranite or muscovite monzogranite) in the giant Renli Nb-Ta deposit has been reported [14,15]. However, it continues to be a controversial topic. Moreover, the magmatic–hydrothermal evolution of the mineralization in this giant Renli Nb-Ta deposit is poorly understood. Three interspersed pegmatite veinlets with various compositions in the granite of the Renli Nb-Ta deposit were identified. In this study, we investigate the textures and composition of apatites of granites from the giant Renli Nb-Ta deposit to constrain the Renli granite ages and the magmatic–hydrothermal evolution.

2. Geological Setting

2.1. Regional Geological Setting

The giant Renli Nb-Ta deposit is located at the southwestern margin of the Mufushan composite granite, which belongs to the central Jiangnan Orogen in South China (Figure 1a). It is considered a continent–continent collisional belt between the Yangtze Block and Cathaysia Block [16–19]. The exposed strata in the area are the Qingbaikou, the Sinian, the Cambrian, the Cretaceous, and the Quaternary system [20]. The Lengji-axi group of the Qingbaikou system is a set of shallow metamorphic clastic rock series, which are exposed in the southwest of the Mufushan complex and belong to the metamorphic basement of the Yangtze block (Figure 1b). The Jiangnan Orogen belt is characterized by a series of NE-, EW-, and WNW-trending faults, including the NE-trending Taolin fault, the Jiujiutou–Sugujian deep fault, the Zhangguchong–Fenglin compressive torsional fault, the Tianbaoshan–Shijiang compressive torsional fault, the NW-trending Changtang–Yuetian–Nanjiang deep fault, and the Baowan–Yaojiadong compressive torsional fault [21,22]. Regional-scale NE-trending faults control the distribution of Late Mesozoic granites along them, which are the most common type of pluton.

Four major magmatic events have been documented in South China; in particular, magmatic rocks formed during the Early Cretaceous (130–129 Ma) exhibit similar geological characteristics [14,19,23–26]. The Mufushan composite granite in the middle of the Jiangnan orogenic belt was formed during the Yanshanian stage and is closely related to rare-metals mineralization (Figure 1). It consists of complex intrusions, such as monzogranite, biotite granodiorite, biotite monzogranite, and two-mica monzogranite, which are Neoproterozoic–Late Mesozoic rocks [27]. Abundant rare-metal deposits have been discovered to be associated with the Mufushan composite granite, including the Renli Nb-Ta, Chuanziyuan Li-Nb-Ta, and Baishawo Be-Nb-Ta deposits [20,28–30].

2.2. Geological Setting of the Renli Nb-Ta Deposit

The Renli Nb-Ta deposit is hosted within the pegmatite that is one part of the Mufushan composite granite [31] (Figure 2). It is a high-grade Nb-Ta rare-metal deposit (14,057 t of Nb₂O₅, average grade at 0.047 wt.%; 10,791 t of Ta₂O₅, average grade at 0.036 wt.%; [15,32]). The strata exposed in the mining area, from young to old, are the Quaternary sequences and the Neoproterozoic Pingyuan formation of the Lengji-axi group, respectively. The Lengji-axi group includes mainly banded slate, sericite schist, and garnet-bearing mica schist [32]. The main structures in the mining area are the NE-trending Tianbaoshan–Shijiang fault, the NNE-trending Jiangjiafang–Nanjiang fault, the Tuozhuangqiao–Jiangbei fault, and the SN-trending Huangboshan fault (Figure 2). The NE-trending Tianbaoshan–Shijiang fault and the Huangboshan fault control the Renli–Chuanziyuan deposit (Figure 2 [14]).

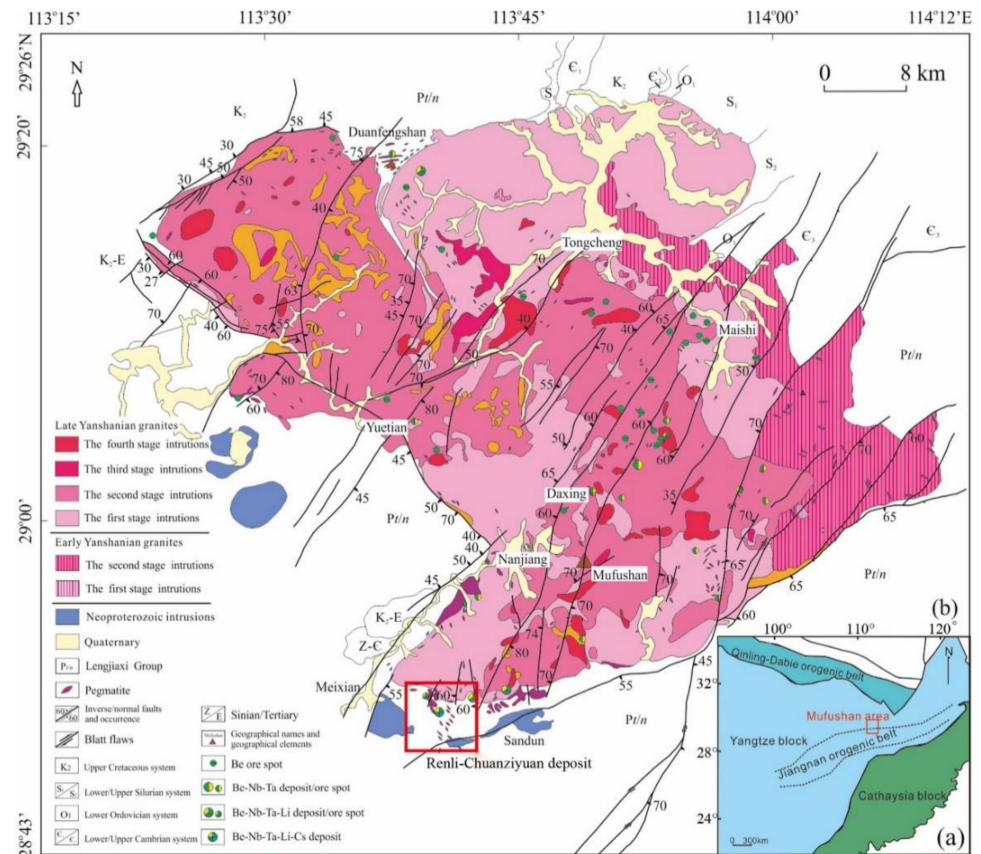


Figure 1. The location of the study area (a) and geological map (b) of the Mufushan area (modified after [19,27]).

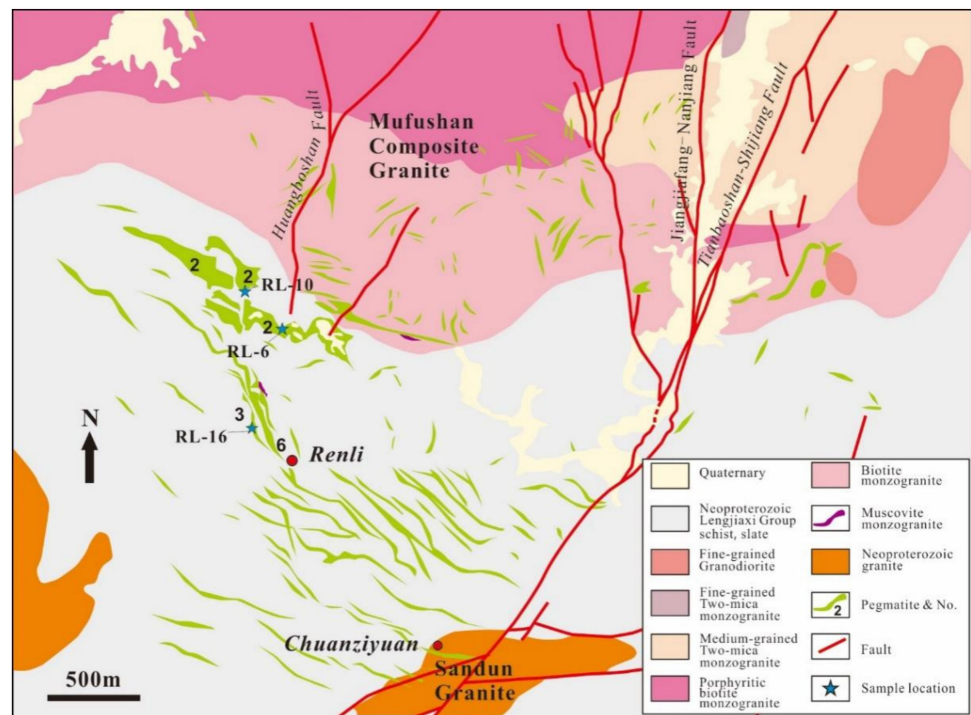


Figure 2. Geological map of the Renli Nb-Ta deposit (modified after [14]). RL is the abbreviation for Renli.

The magmatic activity in the area was intense, and the outcropping magmatic rocks contain the Neoproterozoic and Yanshanian granitic rocks. The magmatic rocks can be divided into three types: (1) The large-size Yanshanian Mufushan granitoid found in the north, and composed of the Late Jurassic coarse- to medium-grained biotite monzogranite and Early Cretaceous fine-to-medium-grained muscovite monzogranite. Biotite monzogranites appear in a large area of the batholith and are divided into marginal and transitional phases. The muscovite monzogranite is in a rocky area and has a clear boundary with the first stage intrusion, generally sericitization and albitization [30]. They are closely related to rare-metal mineralization [19]. (2) The Neoproterozoic coarse-to-medium-grained biotite monzonitic granite is outcropped in the west (including the Meixian and Sandun plutons). (3) The Neoproterozoic medium-to-fine-grained two-mica plagioclase granite is developed in the southeast (Figure 2). The biotite monzogranite and two-mica monzogranite are closely spatially related to pegmatites (Figure 3a,b). The biotite monzogranites show a porphyritic structure in hand specimens and consist of quartz (35–45 vol.%); K-feldspar (15–20 vol.%); plagioclase (15–20 vol.%); biotite (8–10 vol.%); and minor amounts of zircon, chlorite, apatite, and pyrite (Figure 3a). The two-mica monzogranites consist of quartz (30–35 vol.%), K-feldspar (25–30 vol.%), plagioclase (20–25 vol.%), muscovite (5–10 vol.%), and biotite (5–10 vol.%) (Figures 3b and 4c).

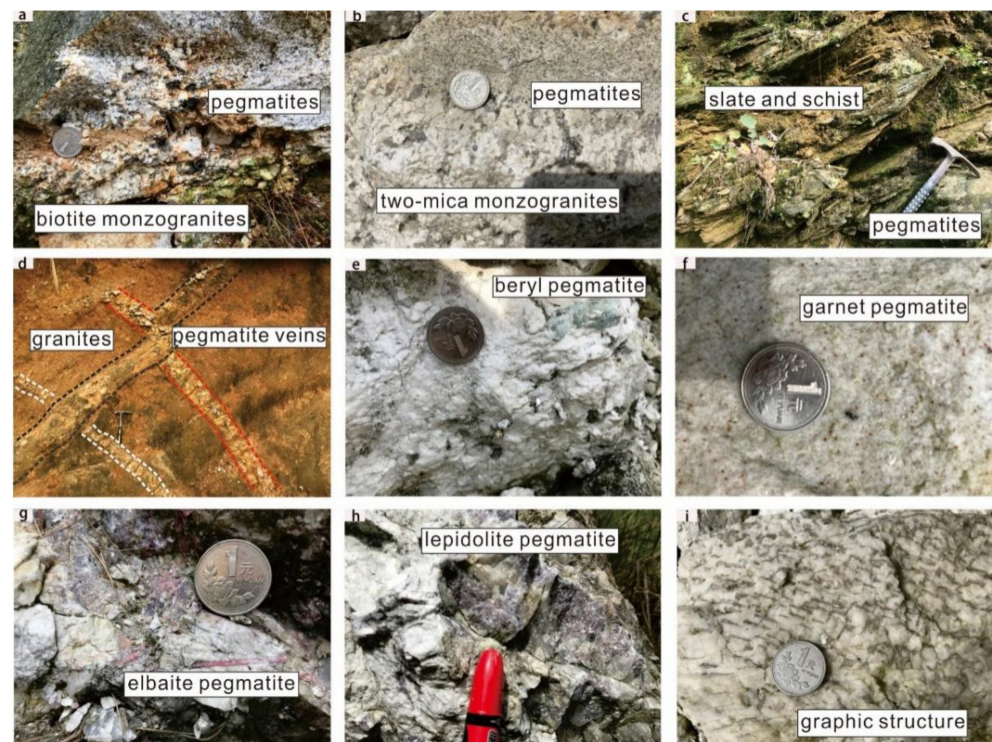


Figure 3. Field photographs showing features of granites and pegmatites in the Renli Nb-Ta deposit: (a) biotite monzogranites with porphyritic structure; (b) weakly gneissic two-mica monzogranites; (c) pegmatite contact with schist of the Lengjiaxi group; (d) three pegmatite veinlets with various compositions interspersed in the granite; (e–h) beryl pegmatite, garnet pegmatite, elbaite pegmatite, and lepidolite pegmatite in the Renli deposit; (i) pegmatite with graphic structure.

A total of 926 pegmatite veinlets have been discovered in the Renli Nb-Ta deposit, and 712 and 214 veinlets crosscut into the granite intrusions and the Lengjiaxi group schist, respectively [15,19]. Nb-Ta pegmatite veinlets occur mostly in the Lengjiaxi group adjacent to the contact zone and cut the slate and schist of the Lengjiaxi group and the Mufushan composite granite (Figures 3c,d and 4f). The occurrences of Nb-Ta-rich pegmatite dikes are controlled by the bedded structure of sedimentary rocks and Mesozoic granite [14]. From the northeast to the southwest of the Renli Nb-Ta deposit, the volume of the veins

decreases, and the mineralization type become complex ($\text{Be} \rightarrow \text{Be} + \text{Nb} + \text{Ta} \rightarrow \text{Be} + \text{Nb} + \text{Ta} + \text{Li}$) [13,27].

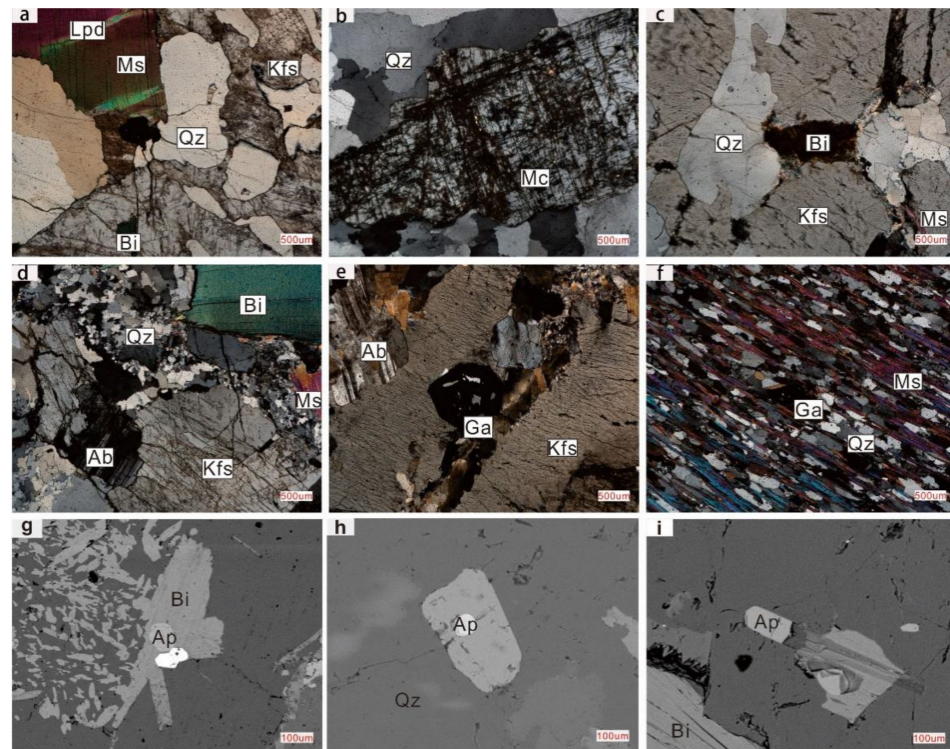


Figure 4. Photomicrographs showing the features of granite and pegmatite from the Renli Nb-Ta deposit: (a) lithium mica pegmatite; (b) microcline pegmatite; (c) two-mica monzogranites; (d) beryl pegmatite; (e) garnet pegmatite; (f) garnet-bearing schist; (g–i) BSE images of apatite in pegmatite. Ab = albite; Bi = biotite; Grt = garnet; Kfs = K-feldspar; Lpd = lepidolite; Mc = microcline; Ms = muscovite; Qz = quartz.

3. Samples and Methods

Samples RL-6 and RL-10 were collected from the No. 2 pegmatite, and RL-16 was collected from the No. 3 pegmatite in the Renli deposit (Figure 2). Other samples were all collected near the central part of deposit. All samples were analyzed for whole-rock geochemistry, LA-ICP MS apatite U-Pb dating, and apatite geochemistry. After crushing the rock samples, apatite grains were separated by standard heavy liquid and magnetic separation techniques, and then handpicked under a binocular microscope, mounted in an epoxy resin, and polished. Before apatite U-Pb dating and analysis of major and trace elements, samples were polished into thin sections (50 μm thickness) for microscopic observation; backscattered electron (BSE) and cathodoluminescence (CL) imaging of the apatite grains was undertaken at the Guangzhou Tuoyan Analytical Technology Co., Ltd., Guangzhou, China.

3.1. Whole-Rock Geochemistry Analyses

The whole-rock geochemistry was analyzed at the Guangzhou Tuoyan Analytical Technology Co., Ltd., Guangzhou, China. All the samples from pegmatites were ground to a c. 200 mesh size in an agate mortar. Major element content was determined using an X-ray fluorescence (XRF) spectrometer (XRF-1500) and fused glass discs. Ferric and ferrous iron measurements were performed via wet chemical analyses: acid decomposition and titration with potassium dichromate [15]. The analytical precisions were ≤ 0.01 wt.% for major elements analyses. An Agilent 7500a system was used to determined trace element concentrations by inductively coupled plasma-mass spectrometry (ICP-MS). The detailed

experimental procedure can be found in Xiong et al. [14]. The analytical precisions were $\leq 5\%$ for the trace element and rare-earth element (REE) analyses.

3.2. Major and Trace Element Analyses of Apatite

The chemical compositions of apatite were analyzed at the Guangzhou Tuoyan Analytical Technology Co., Ltd., Guangzhou, China, with a JEOL JXA-8100 Electron Micro Probe Analyzer (EMPA) equipped with four wavelength-dispersive spectrometers (WDS). Before the analysis, the samples were first coated with a thin conductive carbon film. We used an accelerating voltage of 15 kV, a beam current of 20 nA, and a 5 μm spot size. The peak counting time was 10 s for Ca and P, and 20 s for Na, Mg, Si, Fe, Mn, Sr, F, and Cl. The following standards were used: olivine (Fe), rhodonite (Mn), diopside (Mg), celestite (Sr), phlogopite (F), tugtupite (Cl), apatite (Ca, P), and jadeite (Na, Si). Precision was generally better than 5% for element content > 0.5 wt.% and better than 1% for element content > 10 wt.% [4]. LA-ICP-MS analysis of trace elements in apatite was also carried out at the Guangzhou Tuoyan Analytical Technology Co., Ltd., Guangzhou, China, using an Agilent 7500a ICP-MS and Geolas 193 nm laser. The SRM 610 glass standards and the two MAD glasses were repeatedly analyzed after every eight apatite samples. A 33 μm spot size, a 10 Hz repetition rate, and a corresponding energy density of ~ 3 J/cm² were used. The Ca measured by EMPA was used as the internal standard to correct the low and high content of trace elements in apatite.

3.3. LA-ICP-MS Apatite U-Pb Dating

Apatite U-Pb dating was conducted at the Guangzhou Tuoyan Analytical Technology Co., Ltd., Guangzhou, China, by a laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) instrument using a Resolution 193 nm laser-ablation system coupled to a Thermo iCAP RQ ICP-MS instrument. The Madagascar apatite (MAD) U-Pb ages of 485.0 ± 1.7 Ma were used as the external isotopic calibration reference material [33]. The $^{206}\text{Pb}/^{238}\text{U}$ ratio is 0.0762 and $^{207}\text{Pb}/^{235}\text{U}$ ratio is 0.6013 for the MAD measurements. Each set of eight or nine sample analyses was followed by one measurement of SRM 610 and three measurements of MAD. Before analysis, single apatite grains were mounted in epoxy and polished. Then, they were ablated in a continuous He stream. Before entering a Thermo iCAP RQ ICP-MS, the He stream was mixed with N₂ and Ar downstream. Samples and standards were ablated with a 33 μm laser spot, a repetition rate of 8 Hz, and a 4 J/cm² energy density. Furthermore, the $^{206}\text{Pb}/^{238}\text{U}$ ages are reported at an uncertainty level of 2σ [19]. The detailed data reduction process can be found in Chew et al. and Petrus et al. [34,35].

4. Results

4.1. Apatite Texture

The micrograph and backscattered electron (BSE) images of apatite from the Renli Nb-Ta deposit are shown in Figures 4 and 5. The pegmatite consists of quartz, K-feldspar, albite, muscovite, beryl, garnet, tourmaline, and lepidolite and has a figurative structure (Figures 3e–i and 4a,b,d,e). Apatites from pegmatite of the Renli Nb-Ta deposit is subhedral to anhedral and up to 50–100 μm in length (Figure 4g–i). The apatites also show homogeneous texture without obvious fractures and inclusions in BSE images (Figures 4g–i and 5). They usually occur as a single mineral or as an inclusion in other minerals.

4.2. Whole-Rock Geochemistry

Major and trace elements composition of pegmatite from the Renli Nb-Ta deposit are listed in Tables 1 and 2. The levels of loss on ignition (LOI) of most samples are less than 1 wt.%, indicating that post-magmatic alteration or weathering is not obvious. The pegmatite has a relatively wide range of chemical compositions in the Renli Nb-Ta deposit. Al₂O₃ and K₂O content broadly decrease with increasing SiO₂; the content of

Na_2O increases with increasing SiO_2 , whereas CaO , MgO , and Fe_2O_3 content do not show an obvious correlation with SiO_2 (Figure 6).

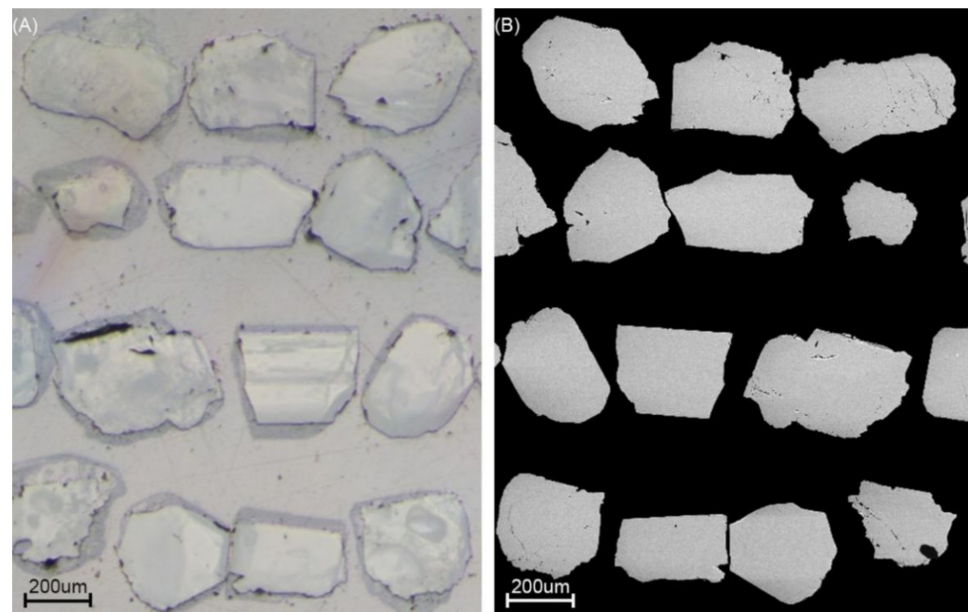


Figure 5. The (A) micrograph and (B) backscattered electron (BSE) images of apatite from RL-6, RL-10, and RL-16.

Table 1. Major elements composition of the pegmatite from Renli Nb-Ta deposit (wt.%).

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	BaO	LOI
RL-1	72.26	0.01	14.74	0.38	0.01	0.02	0.08	2.25	9.60	0.04	0.01	0.19
RL-2	76.28	0.04	14.26	0.93	0.03	0.10	0.71	5.29	1.67	0.08	<0.01	0.84
RL-5	73.80	0.01	14.20	0.56	0.04	0.03	0.19	2.89	6.95	0.04	0.01	0.55
RL-6	76.30	0.05	14.48	0.82	0.02	0.12	1.11	4.92	1.49	0.02	0.01	0.76
RL-7	74.68	0.04	14.72	0.64	0.02	0.09	0.78	3.64	4.41	0.02	0.01	0.81
RL-8	71.86	<0.01	14.94	0.32	0.01	0.01	0.06	1.62	10.35	0.02	0.02	0.38
RL-10	73.93	0.03	15.01	0.71	0.03	0.07	0.19	3.78	4.73	0.01	0.01	0.83
RL-11	74.61	0.02	14.53	0.96	0.03	0.09	0.11	2.51	5.99	0.02	0.01	1.00
RL-16	66.04	<0.01	18.66	0.11	0.01	<0.01	0.03	2.29	12.25	0.05	<0.01	0.50
RL-19	64.69	<0.01	18.88	0.07	0.01	0.01	0.02	1.94	13.35	0.04	0.01	0.27
RL-20	72.36	0.01	17.03	0.45	0.03	0.04	0.76	7.98	0.84	0.03	<0.01	0.65
RL-21	68.04	0.69	15.62	5.75	0.13	1.62	0.51	1.16	3.39	0.13	0.06	2.74
RL-22	70.47	0.71	14.27	5.81	0.11	1.40	0.38	0.86	3.65	0.10	0.07	2.16
RL-23	74.50	0.03	14.38	0.90	0.04	0.06	0.26	3.04	5.67	0.02	<0.01	0.86
RL-24	65.13	<0.01	18.92	0.20	0.01	<0.01	0.04	2.46	12.90	0.05	<0.01	0.33

RL: abbreviation of "Renli deposit"; <0.01 indicate that the value is under MDL.

Table 2. Trace elements composition for the pegmatite from Renli Nb-Ta deposit (ppm).

Sample	RL-1	RL-2	RL-5	RL-6	RL-7	RL-8	RL-10	RL-11	RL-16	RL-19	RL-20	RL-21	RL-22	RL-23	RL-24
Li	21.1	78.7	41.8	111	59.3	24.1	141	163	115	222	188	194	258	176	48.2
Be	1.92	10.4	10.7	6.74	8.41	1.07	7.27	6.92	3.76	2.45	12.3	3.20	2.26	5.56	2.40
Sc	0.10	0.80	0.40	2.00	1.70	0.20	1.40	0.50	0.10	<0.1	0.20	14.6	13.2	0.80	<0.1
Cr	5.00	7.00	14.0	7.00	4.00	5.00	8.00	15.0	3.00	3.00	7.00	58.0	56.0	5.00	2.00
Co	0.10	0.20	0.60	0.30	0.30	0.20	0.20	0.20	<0.1	<0.1	0.10	12.9	13.6	0.20	0.10
Ni	0.30	0.30	1.30	0.30	0.40	0.40	0.30	0.70	<0.2	<0.2	0.50	27.5	25.2	0.30	<0.2
Cu	1.00	2.30	2.70	0.80	1.20	3.20	4.40	1.30	0.80	0.30	6.80	1.10	45.6	11.5	2.10
Zn	9.00	30.0	12.0	14.0	12.0	3.00	26.0	56.0	4.00	<2	24.0	113	103	37.0	2.00
Ga	15.1	25.7	22.6	29.4	25.9	15.1	24.7	34.0	20.8	22.6	30.4	22.2	20.6	29.0	21.1
Rb	716	174	724	139	294	566	370	820	1650	3390	152	197	337	675	1290

Table 2. Cont.

Sample	RL-1	RL-2	RL-5	RL-6	RL-7	RL-8	RL-10	RL-11	RL-16	RL-19	RL-20	RL-21	RL-22	RL-23	RL-24
Sr	40.6	24.4	17.1	73.3	65.0	121	17.5	7.80	12.6	6.60	4.80	104	70.3	6.30	12.3
Y	6.50	29.4	4.80	2.00	18.7	2.20	29.8	0.90	0.60	0.30	1.80	36.2	34.0	5.80	2.10
Zr	4.00	59.0	18.0	3.00	32.0	2.00	39.0	3.00	<2	<2	5.00	213	233	11.0	<2
Nb	2.00	12.7	10.4	11.8	11.2	1.00	8.40	34.8	1.30	0.30	11.2	13.5	13.2	20.0	0.50
Mo	0.50	0.84	1.14	0.73	0.40	0.50	0.83	1.28	0.34	0.34	0.63	0.66	0.41	1.02	0.34
Cs	27.1	6.94	25.6	5.57	12.8	17.2	13.4	30.8	132	835	8.40	25.9	74.6	29.4	41.3
Ba	40.0	15.2	34.4	9.30	41.8	181	37.7	40.4	16.2	3.50	2.70	497	497	11.6	14.3
Ta	0.80	3.70	2.10	1.60	1.80	0.30	1.10	3.60	0.90	0.60	1.20	1.00	1.00	4.50	0.10
Bi	0.28	0.19	0.20	0.15	0.14	0.09	0.60	0.15	18.5	3.78	8.20	0.32	0.37	12.1	0.74
Pb	65.0	19.9	32.4	19.7	37.6	84.3	46.1	20.8	57.1	62.0	17.6	28.9	21.4	38.8	57.1
Th	2.75	13.3	3.04	1.13	16.5	2.34	9.39	0.50	0.16	<0.05	0.88	14.0	13.9	2.37	0.16
U	1.18	4.23	0.91	0.63	2.52	0.50	4.08	0.31	0.55	0.14	1.04	2.97	2.78	2.23	0.18
P	200	360	200	110	100	110	50.0	110	230	190	150	570	430	110	230
Mn	55.0	156	270	110	97.0	44.0	178	181	50.0	21.0	164	899	789	286	63.0
Tl	4.19	0.74	4.09	0.51	1.38	3.13	1.92	4.25	10.9	25.7	0.66	0.83	1.61	3.75	7.58
Ag	0.07	0.06	0.01	0.06	0.02	0.09	0.12	0.09	0.07	0.14	0.14	0.03	0.04	0.29	0.23
As	9.40	9.70	9.90	10.9	8.90	9.90	11.2	10.9	10.2	18.3	9.50	9.70	8.90	11.1	8.80
Ge	0.14	0.16	0.14	0.13	0.13	0.15	0.17	0.16	0.11	0.12	0.12	0.23	0.24	0.17	0.13
La	1.50	13.4	3.10	3.40	14.0	4.10	8.60	0.80	1.10	0.60	1.90	36.5	38.1	2.50	2.10
Ce	2.80	26.6	5.50	5.60	27.2	6.60	16.1	2.30	1.60	0.50	3.20	75.5	79.9	5.20	3.20
Pr	0.24	2.81	0.56	0.46	2.76	0.66	1.70	0.13	0.19	0.05	0.35	8.96	9.33	0.56	0.30
Nd	0.80	9.00	1.80	1.40	8.80	2.10	5.30	0.50	0.60	0.20	1.00	33.60	34.40	1.80	1.10
Sm	0.34	2.82	0.43	0.31	2.20	0.48	1.74	0.12	0.17	0.04	0.30	7.13	7.17	0.58	0.23
Eu	0.16	0.11	0.07	0.19	0.24	0.36	0.15	0.04	0.03	<0.02	0.02	1.46	1.32	0.03	0.05
Gd	0.53	3.22	0.44	0.32	2.19	0.38	2.31	0.12	0.11	0.05	0.23	6.64	6.54	0.51	0.30
Tb	0.12	0.65	0.10	0.06	0.39	0.06	0.52	0.02	0.02	0.01	0.04	1.09	1.02	0.11	0.05
Dy	0.82	4.35	0.61	0.33	2.76	0.30	3.93	0.13	0.10	<0.05	0.24	6.43	6.05	0.65	0.26
Ho	0.19	0.88	0.13	0.06	0.59	0.07	0.86	0.03	0.02	0.01	0.05	1.35	1.23	0.12	0.05
Er	0.62	2.80	0.39	0.17	1.83	0.21	2.92	0.07	0.05	<0.03	0.15	3.91	3.46	0.37	0.12
Tm	0.10	0.49	0.08	0.02	0.28	0.03	0.54	0.01	<0.01	<0.01	0.03	0.59	0.52	0.07	0.02
Yb	0.74	3.41	0.63	0.14	1.89	0.15	3.61	0.07	0.03	<0.03	0.29	3.64	3.23	0.56	0.15
Lu	0.10	0.52	0.10	0.02	0.27	0.02	0.57	0.01	<0.01	<0.01	0.04	0.56	0.53	0.10	0.03
Hf	0.20	2.50	1.00	0.20	1.10	0.10	1.20	0.10	<0.1	<0.1	0.20	5.70	6.30	0.50	<0.1
LREE	5.34	51.8	11.0	10.9	52.8	13.5	31.7	3.73	3.49	1.35	6.45	155	162	10.1	6.70
MREE	2.16	12.0	1.78	1.27	8.37	1.65	9.51	0.46	0.45	0.11	0.88	24.1	23.3	2.00	0.94
HREE	1.76	9.72	2.20	0.55	5.37	0.51	8.84	0.26	0.08	0.00	0.71	14.4	14.0	1.60	0.32
LREE/HREE	3.03	5.33	4.98	19.7	9.82	26.4	3.59	14.3	43.6	-	9.08	10.7	11.5	6.29	20.9
REE+Y	15.8	103	19.7	14.7	85.2	17.8	79.9	5.35	4.62	1.76	9.84	229	233	19.5	10.1
REE	9.26	73.56	14.94	12.68	66.50	15.62	50.05	4.45	4.02	1.46	8.04	193	199	13.7	7.96
(La/Sm) _N	2.78	2.99	4.53	6.90	4.00	5.37	3.11	4.19	4.07	9.44	3.98	3.22	3.34	2.71	5.74
(Gd/Yb) _N	0.58	0.76	0.56	1.84	0.94	2.04	0.52	1.38	2.96	-	0.64	1.47	1.63	0.73	1.61
(La/Yb) _N	1.37	2.65	3.32	16.4	4.99	18.4	1.61	7.71	24.7	-	4.42	6.76	7.95	3.01	9.44
Ce/Ce*	1.02	0.99	0.93	0.94	0.99	0.88	0.96	1.56	0.78	0.53	0.88	0.98	0.99	1.02	0.86
Eu/Eu*	1.15	0.11	0.49	1.83	0.33	2.49	0.23	1.01	0.63	-	0.22	0.64	0.58	0.17	0.58

Notes: <: under detection limit; -: beyond number.

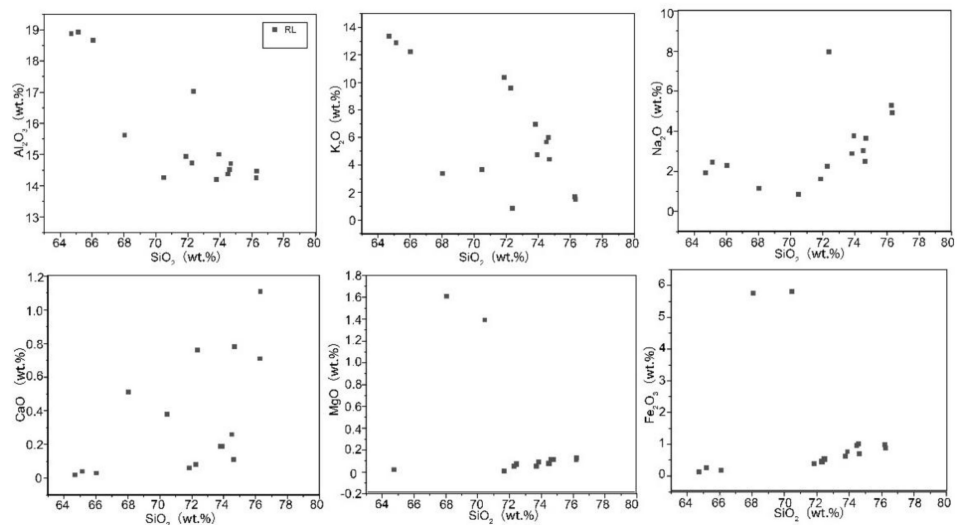


Figure 6. Variation diagram of Al₂O₃, K₂O, Na₂O, CaO, MgO, and Fe₂O₃ content versus the SiO₂ content.

The chondrite- and primitive-mantle-normalized REE [36] and trace element patterns for the studied pegmatite are shown in Figure 7. The average total rare earth element (Σ REE) contents of pegmatite in Renli is 56.63 ppm. The (La/Yb)_N ratios range from 1.37 to 24.72, and the Eu/Eu* ratios range from 0.11 to 2.49 in the Renli deposit. The pegmatite

from Renli has high LREE/HREE (3.03–43.63). The pegmatites from Renli are enriched in light rare earth elements (LREEs) and depleted in medium (MREEs) and heavy rare earth elements (HREEs) slightly.

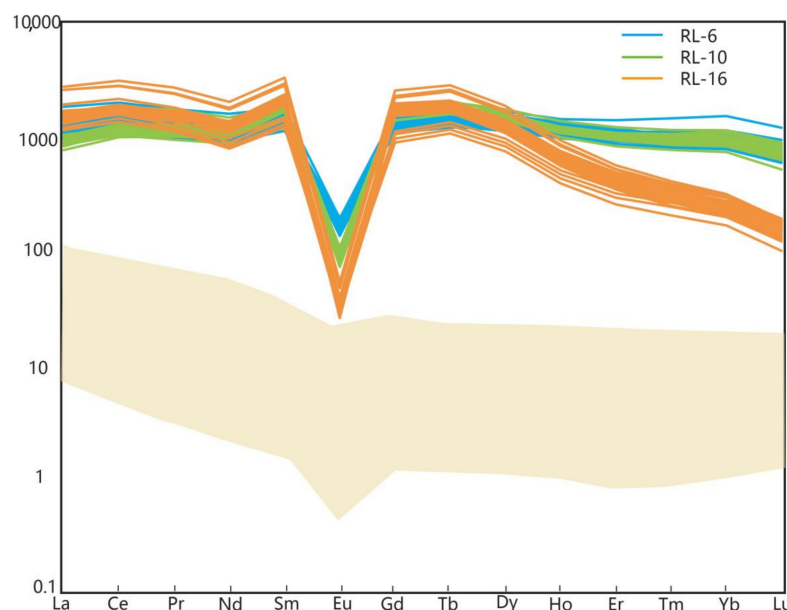


Figure 7. Chondrite-normalized REE patterns of apatite from the RL-6, RL-10, and RL-16 samples [36]. Pale yellow area is the REE pattern of host pegmatite.

4.3. Compositions of Apatite

4.3.1. Major Elements

The major element composition of apatite from the RL-6, RL-10, and RL-16 samples are summarized in Table 3. The apatite from the RL-6 and RL-16 samples has a narrow variation range of 47.39–48.83 wt.% and 47.58–49.99 wt.% P₂O₅ content, respectively, and a range of 50.31–51.76 wt.% and 49.18–51.86 wt.% CaO content, respectively. However, the RL-10 sample has a wide variation range of 44.22–49.18 wt.% P₂O₅ content and a range of 49.91–54.77 wt.% CaO content. The Na₂O content of apatite from all the samples has the same average content (0.12 wt.% in RL-6, 0.13 wt.% in RL-10, and 0.11 wt.% in RL-16), but RL-16 has a wide variation range of 0.03–0.16 wt.%.

Table 3. Major element composition for the apatite from pegmatite of Renli Nb-Ta deposit (wt.%).

Spot	Na ₂ O	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Total	Na(apfu)	P(apfu)	K(apfu)	Ca(apfu)	Ti(apfu)	Total
RL-6@1	0.12	48.24	0.00	50.95	0.00	99.30	0.02	3.38	0.00	4.53	0.00	7.93
RL-6@2	0.11	48.27	0.00	50.93	0.00	99.32	0.02	3.38	0.00	4.53	0.00	7.93
RL-6@3	0.11	48.01	0.00	51.19	0.00	99.31	0.02	3.37	0.00	4.56	0.00	7.95
RL-6@4	0.12	48.28	0.00	50.91	0.00	99.31	0.02	3.39	0.00	4.53	0.00	7.93
RL-6@5	0.11	48.27	0.00	50.92	0.00	99.31	0.02	3.39	0.00	4.53	0.00	7.93
RL-6@6	0.11	48.11	0.00	51.11	0.00	99.33	0.02	3.38	0.00	4.55	0.00	7.94
RL-6@7	0.13	48.16	0.00	50.88	0.00	99.18	0.02	3.38	0.00	4.53	0.00	7.94
RL-6@8	0.13	48.25	0.00	50.81	0.00	99.19	0.02	3.39	0.00	4.52	0.00	7.93
RL-6@9	0.14	48.16	0.00	50.88	0.00	99.17	0.02	3.38	0.00	4.53	0.00	7.94
RL-6@10	0.12	48.14	0.00	51.04	0.00	99.30	0.02	3.38	0.00	4.54	0.00	7.94
RL-6@11	0.12	47.77	0.00	51.31	0.00	99.20	0.02	3.36	0.00	4.58	0.00	7.96
RL-6@12	0.12	47.94	0.00	51.19	0.00	99.25	0.02	3.37	0.00	4.56	0.00	7.95
RL-6@13	0.11	48.22	0.00	50.95	0.00	99.28	0.02	3.38	0.00	4.53	0.00	7.93
RL-6@14	0.11	48.26	0.00	50.89	0.00	99.26	0.02	3.39	0.00	4.53	0.00	7.93
RL-6@15	0.12	47.85	0.00	51.36	0.00	99.33	0.02	3.36	0.00	4.58	0.00	7.96
RL-6@16	0.12	47.75	0.00	51.37	0.00	99.24	0.02	3.36	0.00	4.59	0.00	7.97
RL-6@17	0.12	47.73	0.00	51.42	0.00	99.27	0.02	3.36	0.00	4.59	0.00	7.97
RL-6@18	0.13	48.01	0.00	51.08	0.00	99.22	0.02	3.37	0.00	4.55	0.00	7.95
RL-6@19	0.14	47.62	0.00	51.38	0.00	99.13	0.02	3.36	0.00	4.59	0.00	7.97
RL-6@20	0.11	47.91	0.00	51.28	0.00	99.30	0.02	3.37	0.00	4.57	0.00	7.96

Table 3. Cont.

Spot	Na ₂ O	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Total	Na(apfu)	P(apfu)	K(apfu)	Ca(apfu)	Ti(apfu)	Total
RL-6@21	0.12	48.17	0.00	51.04	0.00	99.32	0.02	3.38	0.00	4.54	0.00	7.94
RL-6@22	0.11	48.16	0.00	51.00	0.00	99.27	0.02	3.38	0.00	4.54	0.00	7.94
RL-6@23	0.12	48.23	0.00	50.96	0.00	99.31	0.02	3.38	0.00	4.53	0.00	7.93
RL-6@24	0.15	48.00	0.00	50.90	0.00	99.04	0.02	3.38	0.00	4.54	0.00	7.94
RL-6@25	0.12	48.83	0.00	50.31	0.00	99.26	0.02	3.41	0.00	4.46	0.00	7.89
RL-6@26	0.13	48.17	0.00	50.90	0.00	99.19	0.02	3.38	0.00	4.53	0.00	7.94
RL-6@27	0.12	48.26	0.00	50.82	0.00	99.21	0.02	3.39	0.00	4.52	0.00	7.93
RL-6@28	0.12	47.99	0.00	51.09	0.00	99.21	0.02	3.37	0.00	4.55	0.00	7.95
RL-6@29	0.12	48.32	0.00	50.84	0.00	99.27	0.02	3.39	0.00	4.52	0.00	7.93
RL-6@30	0.12	47.93	0.00	51.22	0.00	99.27	0.02	3.37	0.00	4.57	0.00	7.95
RL-6@31	0.12	48.20	0.00	51.00	0.00	99.33	0.02	3.38	0.00	4.54	0.00	7.94
RL-6@32	0.12	48.17	0.00	50.99	0.00	99.28	0.02	3.38	0.00	4.54	0.00	7.94
RL-6@33	0.13	48.16	0.00	50.92	0.00	99.21	0.02	3.38	0.00	4.53	0.00	7.94
RL-6@34	0.12	47.68	0.00	51.46	0.00	99.26	0.02	3.36	0.00	4.59	0.00	7.97
RL-6@35	0.12	47.71	0.00	51.46	0.00	99.29	0.02	3.36	0.00	4.59	0.00	7.97
RL-6@36	0.14	47.71	0.00	51.18	0.00	99.03	0.02	3.36	0.00	4.58	0.00	7.96
RL-6@37	0.12	47.39	0.00	51.73	0.00	99.24	0.02	3.34	0.00	4.63	0.00	7.99
RL-6@38	0.12	47.51	0.00	51.64	0.00	99.27	0.02	3.35	0.00	4.62	0.00	7.99
RL-6@39	0.12	47.55	0.00	51.60	0.00	99.27	0.02	3.35	0.00	4.61	0.00	7.98
RL-6@40	0.12	47.39	0.00	51.76	0.00	99.27	0.02	3.34	0.00	4.63	0.00	7.99
RL-6@41	0.12	48.04	0.00	51.09	0.00	99.25	0.02	3.38	0.00	4.55	0.00	7.95
RL-6@42	0.12	48.32	0.00	50.85	0.00	99.30	0.02	3.39	0.00	4.52	0.00	7.93
RL-6@43	0.12	47.95	0.00	51.22	0.00	99.29	0.02	3.37	0.00	4.56	0.00	7.95
RL-6@44	0.12	48.39	0.00	50.79	0.00	99.29	0.02	3.39	0.00	4.51	0.00	7.92
RL-6@45	0.12	47.78	0.00	51.35	0.00	99.24	0.02	3.36	0.00	4.58	0.00	7.96
RL-10@1	0.13	47.22	0.00	51.86	0.00	99.21	0.02	3.34	0.00	4.65	0.00	8.01
RL-10@2	0.14	47.05	0.00	52.00	0.00	99.19	0.02	3.33	0.00	4.67	0.00	8.02
RL-10@3	0.14	47.31	0.00	51.73	0.00	99.18	0.02	3.34	0.00	4.63	0.00	8.00
RL-10@4	0.13	46.94	0.00	52.14	0.00	99.21	0.02	3.32	0.00	4.68	0.00	8.03
RL-10@5	0.13	47.48	0.00	51.60	0.00	99.21	0.02	3.35	0.00	4.62	0.00	7.99
RL-10@6	0.14	47.40	0.00	51.68	0.00	99.22	0.02	3.35	0.00	4.62	0.00	7.99
RL-10@7	0.13	47.81	0.00	51.25	0.00	99.19	0.02	3.37	0.00	4.57	0.00	7.96
RL-10@8	0.14	47.42	0.00	51.56	0.00	99.12	0.02	3.35	0.00	4.62	0.00	7.99
RL-10@9	0.13	47.76	0.00	51.32	0.00	99.22	0.02	3.36	0.00	4.58	0.00	7.97
RL-10@10	0.12	47.82	0.00	51.30	0.00	99.25	0.02	3.37	0.00	4.58	0.00	7.96
RL-10@11	0.13	47.14	0.00	51.91	0.00	99.19	0.02	3.33	0.00	4.65	0.00	8.01
RL-10@12	0.12	47.57	0.00	51.54	0.00	99.23	0.02	3.35	0.00	4.61	0.00	7.98
RL-10@13	0.14	47.23	0.00	51.83	0.00	99.21	0.02	3.34	0.00	4.64	0.00	8.00
RL-10@14	0.14	47.93	0.00	51.15	0.00	99.23	0.02	3.37	0.00	4.56	0.00	7.95
RL-10@15	0.14	47.74	0.00	51.30	0.00	99.18	0.02	3.36	0.00	4.58	0.00	7.97
RL-10@16	0.14	47.81	0.00	51.23	0.00	99.18	0.02	3.37	0.00	4.57	0.00	7.96
RL-10@17	0.12	47.30	0.00	51.87	0.00	99.28	0.02	3.34	0.00	4.64	0.00	8.00
RL-10@18	0.13	48.03	0.00	51.05	0.00	99.21	0.02	3.38	0.00	4.55	0.00	7.95
RL-10@19	0.12	48.61	0.00	50.57	0.00	99.30	0.02	3.40	0.00	4.49	0.00	7.91
RL-10@20	0.14	44.22	0.00	54.77	0.00	99.14	0.02	3.19	0.00	5.01	0.00	8.23
RL-10@21	0.12	48.46	0.00	50.68	0.00	99.27	0.02	3.40	0.00	4.50	0.00	7.92
RL-10@22	0.12	48.45	0.00	50.67	0.00	99.24	0.02	3.40	0.00	4.50	0.00	7.92
RL-10@23	0.12	48.51	0.00	50.59	0.00	99.22	0.02	3.40	0.00	4.49	0.00	7.91
RL-10@24	0.13	48.51	0.00	50.58	0.00	99.22	0.02	3.40	0.00	4.49	0.00	7.91
RL-10@25	0.13	49.18	0.00	49.91	0.00	99.23	0.02	3.43	0.00	4.41	0.00	7.86
RL-16@1	0.13	49.69	0.00	49.43	0.00	99.24	0.02	3.45	0.00	4.36	0.00	7.83
RL-16@2	0.13	49.58	0.00	49.53	0.00	99.24	0.02	3.45	0.00	4.37	0.00	7.84
RL-16@3	0.11	49.99	0.00	49.18	0.00	99.29	0.02	3.47	0.00	4.32	0.00	7.81
RL-16@4	0.11	49.12	0.00	50.05	0.00	99.29	0.02	3.43	0.00	4.43	0.00	7.87
RL-16@5	0.13	49.67	0.00	49.48	0.00	99.28	0.02	3.45	0.00	4.36	0.00	7.83
RL-16@6	0.13	49.51	0.00	49.57	0.00	99.21	0.02	3.45	0.00	4.37	0.00	7.84
RL-16@7	0.11	49.08	0.00	50.13	0.00	99.31	0.02	3.42	0.00	4.43	0.00	7.87
RL-16@8	0.13	49.69	0.00	49.42	0.00	99.24	0.02	3.45	0.00	4.36	0.00	7.83
RL-16@9	0.12	49.53	0.00	49.63	0.00	99.28	0.02	3.45	0.00	4.38	0.00	7.84
RL-16@10	0.10	49.22	0.00	50.01	0.00	99.33	0.02	3.43	0.00	4.42	0.00	7.86
RL-16@11	0.04	49.21	0.00	50.45	0.00	99.71	0.01	3.42	0.00	4.45	0.00	7.87
RL-16@12	0.12	48.87	0.00	50.32	0.00	99.32	0.02	3.41	0.00	4.46	0.00	7.89
RL-16@13	0.13	48.73	0.00	50.33	0.00	99.19	0.02	3.41	0.00	4.46	0.00	7.90
RL-16@14	0.13	48.60	0.00	50.49	0.00	99.23	0.02	3.40	0.00	4.48	0.00	7.91
RL-16@15	0.12	48.83	0.00	50.35	0.00	99.30	0.02	3.41	0.00	4.46	0.00	7.89
RL-16@16	0.12	48.28	0.00	50.86	0.00	99.27	0.02	3.39	0.00	4.52	0.00	7.93
RL-16@17	0.11	48.80	0.00	50.44	0.00	99.36	0.02	3.41	0.00	4.47	0.00	7.89
RL-16@18	0.16	49.03	0.00	49.66	0.00	98.84	0.03	3.43	0.00	4.41	0.00	7.86
RL-16@19	0.12	48.17	0.00	51.01	0.00	99.30	0.02	3.38	0.00	4.54	0.00	7.94
RL-16@20	0.07	47.58	0.00	51.86	0.00	99.51	0.01	3.35	0.00	4.63	0.00	7.98
RL-16@21	0.08	48.41	0.00	50.97	0.00	99.46	0.01	3.39	0.00	4.52	0.00	7.92
RL-16@22	0.11	47.99	0.00	51.16	0.00	99.26	0.02	3.37	0.00	4.56	0.00	7.95
RL-16@23	0.04	49.16	0.00	50.50	0.00	99.70	0.01	3.42	0.00	4.45	0.00	7.88
RL-16@24	0.05	48.30	0.00	51.26	0.00	99.62	0.01	3.38	0.00	4.55	0.00	7.94
RL-16@25	0.12	48.38	0.00	50.70	0.00	99.20	0.02	3.39	0.00	4.51	0.00	7.92
RL-16@26	0.14	49.38	0.00	49.68	0.00	99.20	0.02	3.44	0.00	4.39	0.00	7.85
RL-16@27	0.14	49.19	0.00	49.85	0.00	99.18	0.02	3.43	0.00	4.41	0.00	7.86
RL-16@28	0.12	49.20	0.00	49.99	0.00	99.30	0.02	3.43	0.00	4.42	0.00	7.87
RL-16@29	0.11	49.45	0.00	49.77	0.00	99.33	0.02	3.44	0.00	4.39	0.00	7.85

Table 3. Cont.

Spot	Na ₂ O	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Total	Na(apfu)	P(apfu)	K(apfu)	Ca(apfu)	Ti(apfu)	Total
RL-16@30	0.14	49.33	0.00	49.71	0.00	99.17	0.02	3.44	0.00	4.39	0.00	7.85
RL-16@31	0.13	49.34	0.00	49.77	0.00	99.23	0.02	3.44	0.00	4.40	0.00	7.85
RL-16@32	0.11	49.73	0.00	49.44	0.00	99.28	0.02	3.45	0.00	4.35	0.00	7.83
RL-16@33	0.16	49.21	0.00	49.59	0.00	98.96	0.03	3.44	0.00	4.39	0.00	7.86
RL-16@34	0.16	49.54	0.00	49.25	0.00	98.94	0.03	3.45	0.00	4.35	0.00	7.83
RL-16@35	0.13	49.64	0.00	49.44	0.00	99.21	0.02	3.45	0.00	4.36	0.00	7.83
RL-16@36	0.03	49.22	0.00	50.54	0.00	99.79	0.00	3.42	0.00	4.45	0.00	7.87
RL-16@37	0.12	49.17	0.00	49.99	0.00	99.28	0.02	3.43	0.00	4.42	0.00	7.87
RL-16@38	0.10	49.31	0.00	50.01	0.00	99.41	0.02	3.43	0.00	4.41	0.00	7.86
RL-16@39	0.13	49.47	0.00	49.62	0.00	99.22	0.02	3.44	0.00	4.38	0.00	7.84
RL-16@40	0.11	48.31	0.00	50.85	0.00	99.28	0.02	3.39	0.00	4.52	0.00	7.93

4.3.2. Trace Elements

The trace element composition of apatite from the RL-6, RL-10, and RL-16 samples are shown in Table 4 and plotted in Figures 7 and 8. The total REE (Σ REE) of RL-6 ranges from 3209 to 5179 ppm, and the Eu anomalies are >0.10 ($\text{Eu}/\text{Eu}^* = 0.10\text{--}0.16$). The total REE (Σ REE) of RL-10 ranges from 3381 to 4812 ppm, and the total REE (Σ REE) of RL-16 ranges from 2872 to 7030 ppm. The apatite of RL-10 and RL-16 cannot be distinguished by their respective Eu anomalies (Eu/Eu^*) because the Eu anomalies (Eu/Eu^*) of almost all the spots are in the range below 0.1. Apatite is enriched in LREEs and depleted in (HREE), and the LREE/HREE ratio ranges from 3.61 to 24.07. The REE patterns of RL-6, RL-10, and RL-16 are generally flat ($(\text{La}/\text{Yb})_{\text{N}} = 0.78\text{--}8.69$). In general, the RL-10 apatite has transitional geochemical characteristics between RL-6 and RL-16 apatite. The Y/Ho ratio of RL-6 ranges from 28.41 to 40.58, and RL-16 ranges from 37.51 to 65.45, but RL-10 has a narrow variation range from 30.55 to 32.69 (Figure 8). The Sr content of RL-6, RL-10, and RL-16 decrease in turn, and RL-6 ranges from 59.16 to 77.04; RL-10 ranges from 24.42 to 74.24; and RL-16 ranges from 10.29 to 17.48. Yttrium and high-field-strength element (HFSE; U, Th, Ta, and Hf) content have a wide variation range.

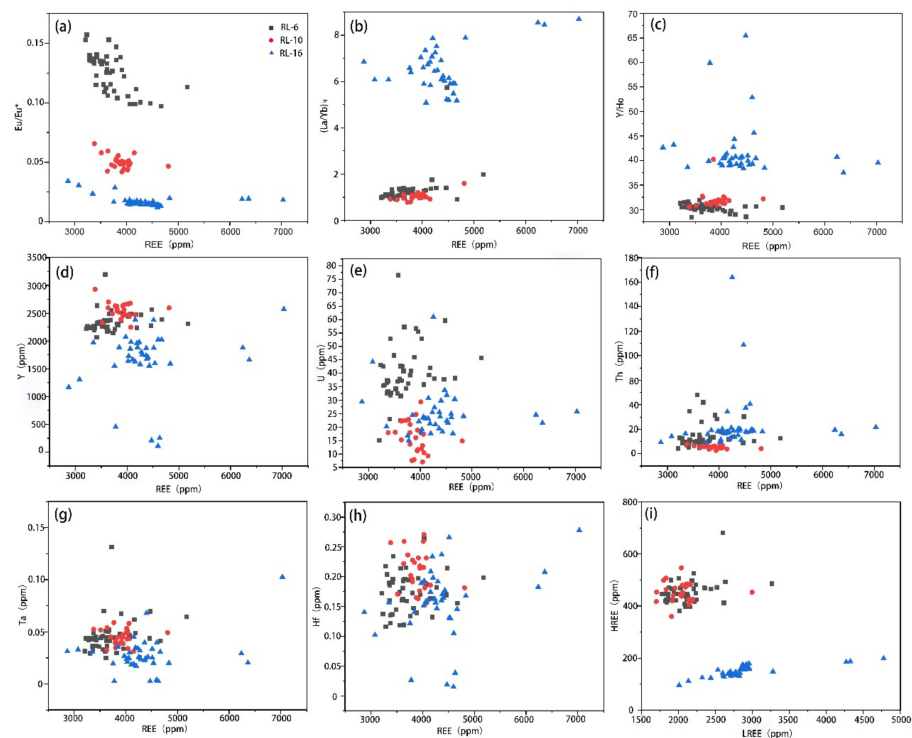


Figure 8. Scatter diagram of apatite in the RL-6, RL-10, and RL-16 samples: (a) REE vs. Eu/Eu^* ; (b) REE vs. $(\text{La}/\text{Yb})_{\text{N}}$; (c) REE vs. Y/Ho ; (d) REE vs. Y ; (e) REE vs. U ; (f) REE vs. Th ; (g) REE vs. Ta ; (h) REE vs. Hf ; and (i) LREE vs. HREE.

Table 4. Trace element composition for apatite of the pegmatite from the Renli Nb-Ta deposit (ppm).

Spot	Sc	Rb	Sr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U	Y/Ho
RL-6@1	0.00	0.15	74.2	2268	294	889	124	568	235	11.7	297	60.2	382	72.3	195	28.1	179	21.9	0.19	0.04	10.1	9.0	36.4	31.4
RL-6@2	0.02	0.18	74.1	2235	283	867	120	551	230	11.7	298	59.7	376	71.0	191	27.9	177	21.9	0.22	0.04	5.9	8.5	35.4	31.5
RL-6@3	0.07	0.16	73.9	2244	288	876	121	551	230	11.6	299	59.9	379	72.6	195	28.3	179	22.2	0.20	0.03	9.7	8.7	35.7	30.9
RL-6@4	0.07	0.09	73.5	2235	294	901	124	574	237	11.8	302	60.1	378	72.1	194	28.4	180	22.5	0.12	0.04	8.8	9.2	36.9	31.0
RL-6@5	0.11	0.14	73.8	2201	293	901	123	573	232	11.6	300	60.2	374	72.3	193	28.2	179	21.7	0.19	0.03	7.2	9.4	37.4	30.4
RL-6@6	0.24	0.18	71.7	2223	283	851	115	522	214	12.1	276	56.9	363	71.1	198	29.7	193	24.5	0.17	0.03	5.1	4.3	15.0	31.3
RL-6@7	0.09	0.07	61.5	2478	383	1160	159	736	291	10.5	364	71.4	442	85.2	223	30.9	189	23.1	0.16	0.06	6.0	18.5	39.3	29.1
RL-6@8	0.09	0.18	64.2	2490	371	1118	154	708	282	10.4	364	70.6	437	84.1	223	31.0	193	23.3	0.19	0.05	7.4	17.3	35.8	29.6
RL-6@9	0.31	0.16	63.3	2471	395	1198	165	762	294	10.9	375	72.3	442	85.3	226	31.2	191	23.3	0.18	0.03	5.0	13.8	38.0	29.0
RL-6@10	0.00	0.13	74.3	2255	292	875	120	570	239	11.8	308	61.9	388	74.0	199	28.6	185	22.8	0.14	0.05	7.0	7.2	33.2	30.5
RL-6@11	0.00	0.09	69.3	2442	369	1118	154	716	277	10.7	346	68.1	422	81.6	215	30.9	198	24.1	0.26	0.05	10.9	18.1	52.9	29.9
RL-6@12	0.19	0.07	69.5	2289	348	1068	149	680	267	10.1	331	64.7	405	76.9	204	28.2	172	20.9	0.15	0.03	7.2	12.4	41.0	29.8
RL-6@13	0.21	0.16	67.7	2183	332	1027	142	656	253	9.7	308	61.0	381	72.5	190	26.8	161	19.2	0.12	0.04	7.5	9.7	37.2	30.1
RL-6@14	0.00	0.18	70.4	2367	316	964	132	612	251	12.3	320	64.3	403	78.5	213	31.1	200	24.7	0.19	0.04	9.0	13.2	42.8	30.1
RL-6@15	0.20	0.12	70.9	2063	312	959	133	610	236	9.9	293	58.1	351	68.2	178	25.4	159	19.1	0.14	0.04	5.9	5.3	23.0	30.3
RL-6@16	0.13	0.25	72.9	2490	320	960	130	596	248	14.0	316	65.2	422	82.8	224	34.0	221	27.6	0.20	0.05	6.9	26.1	42.5	30.1
RL-6@17	0.00	0.21	72.6	2366	305	937	131	612	254	10.7	318	64.2	404	77.9	206	29.7	187	22.8	0.12	0.05	7.7	9.9	36.9	30.4
RL-6@18	0.12	0.18	10.3	1980	471	1441	191	765	426	2.1	464	91.7	416	48.8	90	10.4	55	5.5	0.21	0.07	9.9	19.6	25.0	40.6
RL-6@19	0.16	0.21	68.1	2563	420	1260	171	784	303	11.1	386	75.5	467	89.8	234	32.8	202	24.1	0.17	0.04	9.2	30.3	59.6	28.5
RL-6@20	0.08	0.11	73.0	2274	296	892	120	553	229	11.6	295	60.5	382	74.2	200	29.5	192	24.1	0.16	0.04	7.3	9.0	37.7	30.7
RL-6@21	0.14	0.20	71.5	2237	294	862	115	527	215	12.4	272	55.9	366	70.7	197	30.0	195	24.2	0.14	0.04	8.0	8.6	32.6	31.6
RL-6@22	0.19	0.11	72.1	2261	326	1011	137	628	246	11.4	302	59.8	385	74.2	200	29.5	190	23.5	0.19	0.04	5.9	13.0	43.1	30.5
RL-6@23	0.02	0.16	70.8	2177	310	939	128	589	233	10.5	292	58.2	371	70.8	192	28.2	179	22.3	0.19	0.05	8.5	7.6	31.6	30.8
RL-6@24	0.12	0.15	74.5	2636	554	1572	208	931	339	13.8	410	79.2	494	92.8	241	32.7	189	22.7	0.20	0.06	6.9	34.7	52.9	28.4
RL-6@25	0.33	0.14	71.6	2309	332	1019	140	633	254	10.9	325	63.6	400	75.9	204	29.6	182	22.4	0.16	0.04	6.6	12.7	45.6	30.4
RL-6@26	0.00	0.27	74.1	2551	331	1052	145	677	274	12.3	347	68.6	441	83.2	227	34.8	232	30.4	0.17	0.03	8.1	41.9	57.2	30.7
RL-6@27	0.18	0.22	72.9	2462	356	1076	145	656	267	12.6	341	68.6	433	81.1	217	32.0	206	25.3	0.20	0.07	6.8	28.4	55.4	30.4
RL-6@28	0.10	0.19	77.0	2504	344	1050	142	644	263	13.5	341	69.0	439	83.3	225	33.2	213	25.8	0.14	0.05	8.9	31.5	56.6	30.1
RL-6@29	0.16	0.19	73.4	2367	304	921	127	585	249	12.2	319	64.0	407	77.3	206	31.0	196	24.4	0.17	0.04	7.5	13.4	45.9	30.6
RL-6@30	0.00	0.13	74.1	2265	335	1002	139	639	247	12.5	305	60.7	382	73.3	197	28.4	178	21.7	0.16	0.02	7.2	9.4	34.2	30.9
RL-6@31	0.00	0.15	74.3	2168	296	874	120	551	230	11.8	290	59.2	372	69.9	187	27.8	178	22.0	0.12	0.04	7.5	4.9	22.5	31.0
RL-6@32	0.06	0.16	73.3	2247	321	999	136	625	248	11.4	311	62.0	391	73.7	201	29.6	185	22.5	0.18	0.05	7.7	12.4	42.6	30.5
RL-6@33	0.00	0.15	67.6	2253	426	1258	170	758	277	11.1	337	64.9	400	76.5	201	27.7	164	19.8	0.13	0.05	7.1	15.6	42.6	29.5
RL-6@34	0.32	0.12	71.0	2237	338	1064	146	668	262	10.5	324	63.3	396	75.2	198	27.9	170	20.7	0.13	0.04	7.4	11.8	42.0	29.7
RL-6@35	1.06	0.18	70.6	2211	324	997	138	621	249	10.0	312	61.1	381	73.9	194	27.1	167	19.7	0.21	0.07	7.2	8.2	36.3	29.9
RL-6@36	0.05	0.16	59.2	3196	416	1267	172	745	305	10.7	372	80.1	524	100.0	286	45.8	310	38.9	0.16	0.04	5.4	47.9	76.5	32.0
RL-6@37	0.01	0.18	76.9	2384	369	1056	141	637	255	12.7	321	64.3	403	77.8	209	31.0	202	24.7	0.17	0.04	6.4	10.3	38.2	30.6
RL-6@38	0.07	0.20	71.1	2309	316	985	135	613	245	10.2	315	63.2	398	76.2	206	30.2	189	23.0	0.16	0.03	8.4	10.4	39.3	30.3
RL-6@39	0.00	0.24	75.1	2244	333	1022	142	648	254	11.7	319	63.4	396	74.1	198	27.7	168	20.3	0.22	0.05	7.6	9.8	37.9	30.3
RL-6@40	0.00	0.12	74.4	2376	297	908	124	569	237	11.9	304	62.0	400	78.0	216	32.8	222	28.3	0.14	0.04	8.7	11.3	40.8	30.5
RL-6@41	0.00	0.13	76.3	2346	327	1008	140	641	264	12.3	335	66.1	411	78.2	207	29.4	186	22.4	0.19	0.13	7.5	15.5	46.7	30.0
RL-6@42	0.01	0.13	75.5	2146	328	1006	138	622	246	12.1	306	59.9	372	70.3	189	26.5	163	19.8	0.17	0.03	6.9	8.6	34.4	30.5
RL-6@43	0.10	0.15	72.6	2353	296	897	122	553	232	12.2	302	62.5	400	77.0	210	31.7	204	25.0	0.20	0.04	9.0	9.7	32.5	30.6
RL-6@44	0.00	0.13	70.6	2316	302	920	124	563	227	11.7	296	59.7	386	75.5	207	31.2	203	25.2	0.23	0.04	5.9	9.5	31.9	30.7
RL-6@45	0.12	0.21	76.8	2332	375	1067	142	651	255	13.6	316	62.4	396	76.2	204	30.0	192	23.5	0.19	0.03	6.3	11.3	32.7	30.6
RL-10@1	0.00	0.11	27.0	2540	297	949	142	671	345	6.3	416	83.0	478	80.8	206	29.9	192	23.2	0.23	0.04	8.6	5.5	20.9	31.4
RL-10@2	0.14	0.16	37.2	2634	306	956	143	693	338	6.2	423	84.7	494	85.2	218	32.5	206	25.3	0.26	0.05	8.0	5.9	24.7	30.9
RL-10@3	0.12	0.16	37.7	2666	310	969	145	698	344	5.9	420	85.4	497	84.9	219	32.3	208	25.5	0.19	0.05	8.8	6.0	29.4	31.4
RL-10@4	0.10	0.19	27.0	2451	304	1008	152	724	356	5.5	418	82.1	468	78.5	197	28.4	179	21.4	0.22	0.05	8.2	6.4	7.1	31.2
RL-10@5	0.10	0.20	27.1	2470	305	1015	153	720	355	5.6	417	82.0	472	77.8	196	28.3	177	21.4	0.27	0.04	5.8	6.6	17.7	31.7

Table 4. Cont.

Spot	Sc	Rb	Sr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U	Y/Ho
RL-10@6	0.19	0.15	26.6	2666	265	837	127	603	348	5.8	415	85.7	496	83.6	220	33.4	225	27.7	0.20	0.06	7.8	4.5	12.0	31.9
RL-10@7	0.18	0.16	26.7	2629	308	969	144	691	355	6.6	428	85.3	493	84.3	218	31.9	203	24.7	0.18	0.03	9.3	6.8	22.8	31.2
RL-10@8	0.08	0.13	28.2	2465	472	1456	206	863	365	5.8	390	78.2	448	75.7	199	30.0	200	24.1	0.18	0.05	7.7	7.7	13.1	32.6
RL-10@9	0.00	0.09	26.9	2594	287	898	132	611	354	7.2	446	88.2	494	80.6	203	29.5	186	22.5	0.22	0.04	8.6	4.0	14.8	32.2
RL-10@10	0.06	0.16	27.0	2517	283	854	123	571	316	6.9	396	80.0	468	79.6	208	30.5	200	24.9	0.26	0.05	5.8	4.6	7.5	31.6
RL-10@11	0.00	0.23	52.9	2702	297	943	141	670	339	6.2	416	83.5	488	83.1	217	31.5	205	25.4	0.22	0.05	7.7	5.3	22.2	32.5
RL-10@12	0.12	0.16	74.2	2474	297	962	138	645	325	6.2	390	76.9	450	77.4	202	28.6	184	23.2	0.23	0.04	7.7	4.8	18.8	31.9
RL-10@13	0.28	0.17	27.8	2582	301	968	144	680	334	5.8	401	80.4	471	82.4	214	31.3	202	24.9	0.18	0.05	7.7	3.7	13.6	31.3
RL-10@14	0.02	0.15	29.6	2556	283	897	134	639	330	6.2	404	81.2	473	80.8	210	31.0	202	25.0	0.20	0.04	8.3	2.7	11.2	31.6
RL-10@15	0.26	0.20	27.4	2626	306	1002	149	704	344	6.0	418	82.2	488	84.8	221	31.7	204	24.8	0.16	0.06	8.0	4.9	17.9	31.0
RL-10@16	0.01	0.23	27.8	2679	308	995	150	705	342	6.1	420	83.7	495	85.8	222	32.3	204	24.8	0.23	0.04	8.2	5.0	17.3	31.2
RL-10@17	0.02	0.21	28.2	2245	249	875	135	646	357	5.4	414	80.7	443	69.4	169	24.2	150	16.8	0.22	0.03	7.9	6.2	10.5	32.3
RL-10@18	0.21	0.16	24.4	2594	289	901	130	597	375	6.7	479	95.2	509	79.4	194	28.0	176	21.8	0.16	0.04	4.7	5.8	15.2	32.7
RL-10@19	0.29	0.17	28.8	2385	271	811	112	510	282	6.8	352	73.2	435	75.2	199	30.1	200	25.0	0.26	0.05	8.6	5.8	7.9	31.7
RL-10@20	0.00	0.19	29.2	2930	315	922	136	666	361	7.7	461	93.0	547	95.9	249	36.2	232	28.8	0.19	0.03	10.1	7.9	17.9	30.6
RL-10@21	0.12	0.13	25.3	2471	231	782	119	566	336	7.1	422	84.6	473	77.7	194	28.0	174	21.1	0.17	0.05	6.4	3.8	9.3	31.8
RL-10@22	0.00	0.12	25.8	2332	299	985	149	709	351	5.2	404	78.9	451	75.6	191	26.9	168	20.3	0.16	0.05	8.6	6.4	18.1	30.8
RL-10@23	0.07	0.16	25.6	2450	300	987	149	701	350	5.5	410	80.6	466	78.2	198	28.3	177	21.4	0.21	0.04	9.8	6.3	16.1	31.3
RL-10@24	0.15	0.12	25.9	2653	256	814	124	604	346	5.9	405	84.7	491	83.0	218	33.4	220	26.8	0.24	0.05	8.8	4.6	11.6	31.9
RL-10@25	0.14	0.09	25.2	2488	295	934	139	661	337	6.0	401	80.0	472	79.8	203	29.5	188	23.0	0.14	0.04	7.1	5.6	22.5	31.2
RL-16@1	0.00	0.13	11.2	1886	479	1421	189	744	405	2.0	440	88.2	399	46.9	87	10.2	53	5.2	0.24	0.02	8.4	19.1	24.4	40.2
RL-16@2	0.04	0.12	11.1	1872	486	1435	190	753	405	2.0	443	88.1	399	46.2	87	10.1	53	5.2	0.16	0.07	10.4	20.1	25.5	40.5
RL-16@3	0.04	0.06	11.8	1708	455	1381	181	692	377	2.1	399	80.3	362	41.9	77	9.0	45	4.5	0.16	0.02	12.6	20.1	29.9	40.8
RL-16@4	0.00	0.06	11.5	1667	502	1432	185	702	376	2.3	400	79.7	353	40.3	74	8.8	43	4.3	0.20	0.02	10.5	16.7	23.2	41.4
RL-16@5	0.03	0.00	10.3	1884	392	1262	173	705	402	2.0	447	88.5	401	46.7	87	9.9	52	5.0	0.16	0.03	10.2	12.1	17.6	40.4
RL-16@6	0.09	0.07	11.0	1979	490	1469	197	774	429	2.2	460	90.7	416	48.3	89	10.6	56	5.6	0.13	0.02	9.9	18.2	23.4	41.0
RL-16@7	0.04	0.00	12.0	1598	474	1375	180	684	359	2.3	390	76.5	348	40.9	75	8.7	44	4.4	0.16	0.02	8.5	17.3	21.6	39.1
RL-16@8	0.06	0.13	11.1	1861	486	1458	191	740	396	2.1	429	86.4	396	46.0	87	10.0	54	5.2	0.17	0.02	10.3	20.2	23.7	40.5
RL-16@9	0.00	0.06	11.4	1683	470	1411	187	725	391	2.0	428	83.4	378	42.8	77	8.8	44	4.5	0.16	0.03	10.2	18.6	23.9	39.4
RL-16@10	0.00	0.00	11.8	1580	513	1419	170	570	284	2.7	281	62.1	302	35.6	72	9.5	54	5.4	0.03	0.00	13.0	143.8	61.0	44.4
RL-16@11	0.00	0.09	16.3	456	433	900	84	222	86	3.8	70	15.6	72	7.6	15	1.9	10	1.0	0.15	0.02	14.7	15.9	15.0	59.9
RL-16@12	0.00	0.03	11.2	1634	434	1319	174	680	375	2.0	414	80.1	365	41.9	77	8.7	44	4.3	0.11	0.04	11.2	9.6	18.0	39.0
RL-16@13	0.04	0.03	11.2	2027	485	1458	195	779	435	1.9	488	96.0	436	51.5	99	11.3	60	5.8	0.13	0.03	16.0	18.4	23.6	39.3
RL-16@14	0.06	0.00	11.7	1876	495	1502	196	766	410	2.4	442	87.9	409	47.0	87	10.6	54	5.3	0.17	0.02	9.5	18.1	22.4	39.9
RL-16@15	0.00	0.08	12.0	1632	466	1396	182	699	379	2.1	410	80.2	360	41.9	78	8.7	46	4.3	0.19	0.02	11.7	16.9	23.2	39.0
RL-16@16	0.00	0.00	11.6	1752	466	1397	184	730	407	2.0	443	86.5	389	44.6	83	9.3	48	4.5	0.12	0.02	10.4	13.8	21.0	39.3
RL-16@17	0.05	0.20	11.3	1550	400	1242	162	633	357	2.0	385	75.6	338	38.8	71	7.8	41	3.9	0.28	0.10	9.5	9.4	16.8	39.9
RL-16@18	0.00	0.03	13.2	2572	829	2443	322	1183	628	3.8	642	130.6	586	65.1	115	12.9	64	6.1	0.19	0.02	11.8	21.7	25.7	39.5
RL-16@19	0.06	0.00	11.1	1730	421	1313	173	690	381	2.1	414	82.1	370	42.8	80	9.4	48	4.5	0.14	0.03	9.6	11.5	19.1	40.4
RL-16@20	0.00	0.05	13.3	1168	347	1066	133	462	230	2.6	225	49.4	234	27.4	52	6.5	34	3.3	0.10	0.03	8.2	9.2	29.4	42.7
RL-16@21	0.00	0.07	13.2	1309	364	1145	140	484	245	2.5	244	53.5	259	30.3	60	7.7	40	3.9	0.16	0.04	8.1	14.2	44.2	43.2
RL-16@22	0.14	0.00	12.3	1737	481	1424	186	741	414	2.4	451	87.2	392	44.8	82	9.3	47	4.4	0.01	0.00	11.8	15.0	19.5	38.8
RL-16@23	0.00	0.00	14.0	109	514	1141	111	306	108	2.7	73	10.6	31	2.1	2	0.2	1	0.1	0.04	0.00	13.7	40.6	24.9	52.9
RL-16@24	0.00	0.04	15.3	251	562	1345	144	446	167	3.2	122	19.2	69	5.5	8	0.8	4	0.3	0.15	0.03	11.9	19.9	17.7	45.6
RL-16@25	0.00	0.06	11.1	2027	493	1473	199	777	431	2.2	477	93.6	433	50.1	95	10.7	56	5.8	0.23	0.03	11.9	18.5	30.3	40.4
RL-16@26	0.00	0.10	10.8	1957	477	1473	200	803	445	2.1	492	95.1	431	50.0	92	10.6	55	5.4	0.19	0.03	9.3	17.6	21.3	39.1
RL-16@27	0.18	0.06	11.0	2072	473	1487	199	793	448	2.0	495	95.9	442	52.6	100	11.8	62	6.2	0.17	0.02	9.2	18.1	22.1	39.4
RL-16@28	0.00	0.07	11.9	1591	482	1418	182	699	380	2.0	415	78.9	353	41.3	77	8.9	46	4.4	0.18	0.03	10.9	18.0	24.1	38.5
RL-16@29	0.16	0.24	11.7	1553	438	1334	175	669	365	2.2	399	76.7	346	40.5	73	8.4	42	4.1	0.16	0.03	10.1	11.3	18.3	38.4
RL-16@30	0.00	0.09	11.8	1977	581	1694	215	787	423	2.8	439	90.4	408	46.3	84	9.7	50	4.8	0.18	0.03	7.6	21.1	25.4	42.7

Table 4. Cont.

Spot	Sc	Rb	Sr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U	Y/Ho
RL-16@31	0.03	0.09	11.3	1877	477	1476	195	748	405	2.1	440	87.2	398	46.1	86	10.0	54	5.2	0.21	0.02	10.4	19.5	24.6	40.7
RL-16@32	0.00	0.00	12.0	1661	462	1401	185	718	391	2.1	430	83.9	372	44.3	82	9.3	48	4.7	0.27	0.03	12.6	16.0	21.6	37.5
RL-16@33	0.00	0.01	12.0	2376	780	2190	283	1016	535	3.4	555	115.0	516	58.0	106	12.0	62	5.8	0.21	0.05	9.6	37.5	31.9	41.0
RL-16@34	0.15	0.13	12.1	2386	780	2208	287	1050	556	3.6	576	119.4	536	59.9	107	12.2	62	6.0	0.16	0.03	12.3	34.3	30.8	39.8
RL-16@35	0.06	0.00	11.2	1969	460	1451	196	771	423	2.0	469	92.9	425	51.0	96	11.2	60	6.0	0.02	0.00	10.1	16.4	20.2	38.6
RL-16@36	0.05	0.05	17.5	212	367	669	54	122	41	4.5	27	6.1	29	3.2	7	1.1	8	0.9	0.15	0.03	12.0	88.8	33.8	65.5
RL-16@37	0.00	0.06	10.8	1802	445	1374	183	699	385	2.0	413	82.6	381	44.2	82	9.7	51	4.9	0.11	0.02	12.3	18.8	27.2	40.8
RL-16@38	0.01	0.02	10.7	1465	417	1230	151	521	266	2.1	266	57.8	278	32.9	65	8.3	46	4.5	0.19	0.03	12.0	19.6	33.4	44.6
RL-16@39	0.19	0.06	11.0	1984	472	1443	193	758	411	2.1	455	90.3	423	49.9	96	11.4	61	6.0	0.16	0.04	9.3	13.9	20.4	39.8
RL-16@40	0.00	0.15	11.8	1664	488	1424	183	721	396	2.3	427	82.6	374	43.2	78	8.6	44	4.3	0.19	0.04	11.3	19.7	24.9	38.5

4.4. Apatite U-Pb Ages

The results of apatite U-Pb dating are listed in Table 5 and plotted in Figure 9. There are 45 spots along a discordia in the Tera–Wasserburg Concordia diagram of RL-6, and they yield a lower intercept age of 130 ± 2 Ma (2σ , MSWD = 1.2, Figure 9a, [37]). There are 25 spots along a discordia in the Tera–Wasserburg Concordia diagram of RL-10, and they yield a lower intercept age of 135 ± 8 Ma (2σ , MSWD = 1.8, Figure 9b, [37]). There are 40 spots along a discordia in the Tera–Wasserburg Concordia diagram of RL-16, and they yield a lower intercept age of 134 ± 3 Ma (2σ , MSWD = 1.3, Figure 9c, [37]).

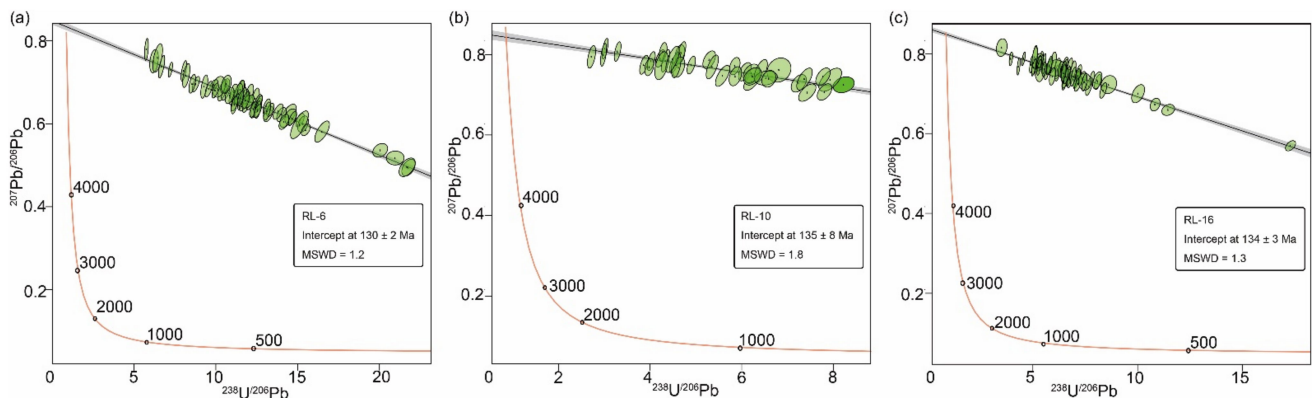


Figure 9. Apatite U-Pb lower intercept ages of the (a) RL-6, (b) RL-10, and (c) RL-16 samples.

Table 5. Apatite U-Pb dating by LA-ICP-MS.

Sample	U (ppm)	2s Error	Th (ppm)	2s Error	$^{207}\text{Pb}/^{206}\text{Pb}$	2s Error	$^{206}\text{Pb}/^{238}\text{U}$	2s Error	$^{207}\text{Pb}/^{235}\text{U}$	2s Error	Rho $^{206}\text{Pb}/^{238}\text{U}$ vs. $^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$ Age	±	2σ (Ma)
RL-6														
RL-6@1	34.6	0.3	13.1	0.3	0.6606	0.0135	0.0881	0.0013	8.1028	0.1336	0.0523	544	±	8
RL-6@2	33.9	0.3	12.6	0.3	0.6638	0.0145	0.0908	0.0015	8.3965	0.1471	0.2789	560	±	9
RL-6@3	34.5	0.2	12.7	0.3	0.6494	0.0149	0.0896	0.0012	8.0408	0.1548	0.2727	553	±	7
RL-6@4	35.6	0.2	13.6	0.3	0.6818	0.0183	0.0867	0.0013	8.1330	0.1774	0.2154	536	±	8
RL-6@5	35.7	0.3	13.6	0.3	0.6510	0.0143	0.0871	0.0010	7.7998	0.1480	−0.0191	538	±	6
RL-6@6	14.1	0.2	6.0	0.2	0.7796	0.0216	0.1733	0.0026	18.5811	0.4627	0.1763	1030	±	14
RL-6@7	35.5	0.4	25.6	0.4	0.6599	0.0215	0.0802	0.0013	7.2703	0.2017	−0.0405	497	±	8
RL-6@8	32.3	0.7	23.9	0.5	0.6823	0.0192	0.0870	0.0016	8.1454	0.1646	0.0812	538	±	10
RL-6@9	35.4	0.3	19.5	0.3	0.6510	0.0165	0.0851	0.0016	7.7193	0.1261	0.1398	526	±	10
RL-6@10	29.8	0.3	9.7	0.3	0.6726	0.0203	0.0873	0.0014	8.2909	0.2204	0.3026	540	±	9
RL-6@11	47.1	0.5	24.6	0.4	0.6088	0.0135	0.0660	0.0009	5.5482	0.1048	0.1460	412	±	5
RL-6@12	36.5	0.4	16.8	0.3	0.6344	0.0166	0.0814	0.0011	7.0860	0.1369	0.0357	504	±	6
RL-6@13	34.9	0.4	13.8	0.2	0.6753	0.0166	0.0829	0.0013	7.7279	0.1663	0.1655	513	±	8
RL-6@14	39.9	0.4	18.6	0.4	0.6238	0.0153	0.0761	0.0014	6.5077	0.1495	0.1842	472	±	8
RL-6@15	21.5	0.3	7.5	0.2	0.7278	0.0202	0.1248	0.0021	12.5101	0.2990	−0.0100	758	±	12
RL-6@16	39.5	0.6	36.6	1.2	0.6195	0.0230	0.0697	0.0020	5.9295	0.1711	0.1646	434	±	12
RL-6@17	33.7	0.5	13.6	0.3	0.6652	0.0154	0.0845	0.0010	7.7980	0.1611	0.1600	523	±	6
RL-6@18	22.2	0.3	26.7	0.5	0.7307	0.0147	0.1388	0.0020	13.9668	0.2275	0.1487	838	±	12
RL-6@19	53.1	0.7	42.1	0.7	0.5994	0.0160	0.0653	0.0011	5.3804	0.1369	0.2736	408	±	7
RL-6@20	34.5	0.4	12.5	0.4	0.6437	0.0140	0.0797	0.0014	7.0790	0.1348	0.1700	494	±	8
RL-6@21	29.8	0.2	11.7	0.3	0.6769	0.0156	0.0904	0.0016	8.3864	0.1964	0.3722	558	±	9
RL-6@22	38.8	0.4	18.2	0.3	0.6418	0.0151	0.0762	0.0011	6.8083	0.0994	−0.0189	473	±	6
RL-6@23	27.4	0.2	10.2	0.2	0.6807	0.0207	0.0963	0.0021	9.0617	0.2102	0.1901	592	±	13
RL-6@24	45.1	1.2	44.7	2.0	0.6171	0.0155	0.0689	0.0013	5.9418	0.1964	0.7627	430	±	8
RL-6@25	43.5	0.5	18.2	0.4	0.6339	0.0130	0.0752	0.0010	6.5538	0.1152	0.3359	468	±	6
RL-6@26	51.7	0.7	41.0	1.5	0.5977	0.0274	0.0664	0.0019	5.5430	0.1670	−0.2308	415	±	12
RL-6@27	52.1	0.4	43.0	0.7	0.5813	0.0209	0.0608	0.0013	5.0184	0.1505	−0.0930	381	±	8
RL-6@28	51.9	0.5	43.7	0.5	0.5854	0.0115	0.0645	0.0010	5.2276	0.0883	0.3909	403	±	6
RL-6@29	39.7	0.4	17.8	0.4	0.6226	0.0140	0.0717	0.0012	6.0812	0.1298	0.2910	446	±	7
RL-6@30	29.0	0.3	12.0	0.3	0.6747	0.0146	0.0944	0.0018	8.7699	0.1681	0.2039	581	±	11
RL-6@31	14.9	0.7	5.3	0.3	0.7513	0.0230	0.1590	0.0064	16.4333	0.7163	0.6630	957	±	34
RL-6@32	38.4	0.5	17.0	0.3	0.6517	0.0156	0.0793	0.0012	7.1340	0.1379	0.1444	492	±	7
RL-6@33	39.8	0.4	22.0	0.4	0.6306	0.0180	0.0760	0.0011	6.6317	0.1439	0.0511	472	±	7
RL-6@34	39.0	0.5	16.6	0.3	0.6352	0.0157	0.0814	0.0013	7.0824	0.1475	0.1249	506	±	8
RL-6@35	31.5	0.2	10.8	0.3	0.6457	0.0177	0.0899	0.0013	8.0507	0.1746	0.0284	555	±	8
RL-6@36	71.7	1.0	70.2	3.0	0.4942	0.0165	0.0459	0.0007	3.1667	0.1001	0.0097	290	±	5
RL-6@37	32.6	0.3	13.3	0.3	0.6644	0.0188	0.0857	0.0012	7.8062	0.1788	0.0230	530	±	7
RL-6@38	34.1	0.2	13.8	0.2	0.6487	0.0172	0.0837	0.0015	7.4785	0.1557	0.0326	518	±	9
RL-6@39	32.5	0.4	12.8	0.3	0.6522	0.0148	0.0823	0.0013	7.5114	0.1517	0.1683	510	±	8
RL-6@40	34.9	0.5	14.7	0.3	0.6473	0.0167	0.0792	0.0012	7.0812	0.1288	−0.3071	492	±	7

Table 5. Cont.

Sample	U (ppm)	2s Error	Th (ppm)	2s Error	²⁰⁷ Pb/ ²⁰⁶ Pb	2s Error	²⁰⁶ Pb/ ²³⁸ U	2s Error	²⁰⁷ Pb/ ²³⁵ U	2s Error	Rho ²⁰⁶ Pb/ ²³⁸ U vs. ²⁰⁷ Pb/ ²³⁵ U	²⁰⁶ Pb/ ²³⁸ U Age	±	2σ (Ma)
RL-6@41	41.8	0.2	21.2	0.5	0.6294	0.0154	0.0725	0.0013	6.2564	0.1336	0.0788	451	±	8
RL-6@42	30.9	0.7	11.5	0.3	0.6685	0.0162	0.0925	0.0020	8.5640	0.2117	0.4642	570	±	12
RL-6@43	28.3	0.2	12.8	0.3	0.6913	0.0142	0.0941	0.0020	9.0087	0.1693	0.4342	579	±	12
RL-6@44	28.8	1.2	13.3	0.4	0.6894	0.0205	0.0981	0.0029	9.4285	0.3742	0.6249	603	±	17
RL-6@45	27.5	0.6	14.4	0.5	0.6955	0.0177	0.0944	0.0022	9.0336	0.2643	0.4968	581	±	13
RL-10														
RL-10@1	19.2	0.1	7.6	0.2	0.7396	0.0171	0.1525	0.0028	15.5448	0.4280	0.5396	915	±	16
RL-10@2	22.2	0.2	7.7	0.2	0.7053	0.0177	0.1354	0.0029	13.1901	0.2517	0.1212	818	±	16
RL-10@3	26.2	0.2	7.7	0.3	0.7247	0.0161	0.1215	0.0027	12.1711	0.3292	0.6569	739	±	15
RL-10@4	16.5	0.1	8.6	0.3	0.7572	0.0186	0.1651	0.0032	17.2035	0.3841	0.2938	985	±	18
RL-10@5	16.1	0.4	8.9	0.2	0.7326	0.0178	0.1615	0.0039	16.5996	0.3538	0.4433	965	±	22
RL-10@6	10.7	0.1	5.8	0.2	0.7900	0.0176	0.2373	0.0047	25.8821	0.5685	0.3547	1372	±	25
RL-10@7	20.5	0.3	10.0	0.6	0.7283	0.0179	0.1382	0.0025	13.9819	0.3217	0.4278	834	±	14
RL-10@8	11.5	0.2	10.0	0.3	0.8006	0.0191	0.2154	0.0039	23.3322	0.6576	0.3786	1257	±	21
RL-10@9	13.2	0.3	5.2	0.2	0.7869	0.0180	0.1890	0.0039	20.3246	0.4274	0.3932	1119	±	22
RL-10@10	6.7	0.1	6.1	0.2	0.8075	0.0198	0.3028	0.0057	33.6970	0.7418	0.2869	1704	±	28
RL-10@11	18.7	0.1	6.6	0.3	0.7371	0.0236	0.1263	0.0034	12.8350	0.3533	0.2646	767	±	19
RL-10@12	14.3	0.5	5.5	0.3	0.7612	0.0246	0.1484	0.0044	15.4642	0.5304	0.5559	892	±	24
RL-10@13	12.7	0.1	5.0	0.2	0.7774	0.0193	0.2207	0.0041	23.6186	0.4341	0.1328	1285	±	22
RL-10@14	10.1	0.1	3.5	0.1	0.7744	0.0192	0.2587	0.0054	27.4632	0.5091	0.2297	1482	±	28
RL-10@15	16.2	0.2	6.6	0.2	0.7475	0.0159	0.1599	0.0029	16.4580	0.3785	0.4966	956	±	16
RL-10@16	14.9	0.2	6.3	0.2	0.7531	0.0188	0.1609	0.0036	16.6342	0.4997	0.6277	965	±	21
RL-10@17	9.9	0.1	8.8	0.3	0.8064	0.0190	0.2343	0.0038	25.8651	0.6291	0.2787	1356	±	20
RL-10@18	14.5	0.2	8.2	0.2	0.7690	0.0242	0.1873	0.0037	19.8275	0.4547	0.0103	1106	±	20
RL-10@19	7.2	0.1	8.0	0.2	0.8144	0.0210	0.3320	0.0058	37.8986	0.7357	0.0523	1847	±	28
RL-10@20	16.1	0.3	10.5	0.3	0.7711	0.0176	0.1711	0.0029	18.1543	0.4484	0.4525	1018	±	16
RL-10@21	8.5	0.1	5.3	0.1	0.7834	0.0193	0.2489	0.0044	26.6856	0.5651	0.2891	1432	±	23
RL-10@22	17.2	0.3	9.3	0.3	0.7590	0.0232	0.1565	0.0029	15.9779	0.3245	0.0706	937	±	16
RL-10@23	13.0	0.3	7.6	0.2	0.7469	0.0215	0.1804	0.0041	18.6170	0.3782	0.1243	1068	±	22
RL-10@24	9.6	0.1	5.6	0.1	0.7844	0.0227	0.2298	0.0044	25.1664	0.5404	−0.0250	1333	±	23
RL-10@25	20.6	0.2	7.9	0.2	0.7447	0.0180	0.1279	0.0020	13.1321	0.2624	0.1494	777	±	11
RL-16														
RL-16@1	22.7	0.3	26.9	0.4	0.7365	0.0194	0.1406	0.0027	14.2526	0.2691	0.0711	848	±	15
RL-16@2	23.4	0.2	28.3	0.4	0.7549	0.0142	0.1385	0.0018	14.3759	0.2293	0.2176	836	±	10
RL-16@3	28.6	0.3	29.7	0.6	0.7387	0.0136	0.1362	0.0025	13.9304	0.2619	0.4542	823	±	14
RL-16@4	21.9	0.2	24.2	0.4	0.7733	0.0145	0.1528	0.0025	16.4573	0.2727	0.3427	916	±	14
RL-16@5	16.7	0.6	17.6	0.6	0.7750	0.0153	0.1905	0.0064	20.2202	0.5954	0.7844	1123	±	35
RL-16@6	21.2	0.2	25.4	0.4	0.7438	0.0158	0.1390	0.0018	14.3927	0.3016	0.1958	841	±	10
RL-16@7	20.0	0.3	24.5	0.4	0.7789	0.0208	0.1685	0.0034	17.7675	0.3686	0.3465	1003	±	19
RL-16@8	22.1	0.2	28.6	0.4	0.7680	0.0170	0.1486	0.0024	15.5202	0.2643	0.1403	893	±	14
RL-16@9	22.5	0.2	26.7	0.3	0.7546	0.0141	0.1628	0.0026	16.8759	0.2822	0.2469	972	±	14

Table 5. Cont.

Sample	U (ppm)	2s Error	Th (ppm)	2s Error	$^{207}\text{Pb}/^{206}\text{Pb}$	2s Error	$^{206}\text{Pb}/^{238}\text{U}$	2s Error	$^{207}\text{Pb}/^{235}\text{U}$	2s Error	Rho $^{206}\text{Pb}/^{238}\text{U}$ vs. $^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$ Age	±	2σ (Ma)
RL-16@10	55.2	1.2	199.5	5.6	0.6591	0.0114	0.0875	0.0019	7.9263	0.1973	0.7213	541	±	11
RL-16@11	13.1	0.8	20.7	0.8	0.8152	0.0182	0.2893	0.0163	32.4016	1.9992	0.9153	1634	±	82
RL-16@12	15.7	0.1	12.8	0.3	0.7849	0.0169	0.1848	0.0030	19.8663	0.3543	0.2589	1093	±	16
RL-16@13	19.7	0.3	23.2	0.5	0.7652	0.0290	0.1874	0.0074	20.2513	1.2949	0.8493	1107	±	41
RL-16@14	19.7	0.2	24.2	0.4	0.7397	0.0177	0.1498	0.0018	15.1754	0.3257	0.2091	900	±	10
RL-16@15	20.1	0.2	22.3	0.3	0.7522	0.0141	0.1768	0.0028	18.4591	0.3329	0.2540	1049	±	15
RL-16@16	17.7	0.2	17.7	0.4	0.7697	0.0134	0.1922	0.0030	20.3765	0.3617	0.3937	1133	±	16
RL-16@17	15.9	0.3	13.7	0.3	0.7911	0.0237	0.1964	0.0042	21.6664	0.5447	0.3116	1156	±	23
RL-16@18	23.7	0.3	30.5	0.5	0.7372	0.0160	0.1491	0.0024	14.9583	0.2168	0.0247	896	±	14
RL-16@19	17.0	0.1	15.5	0.3	0.7743	0.0213	0.1807	0.0029	19.2228	0.3690	−0.0786	1071	±	16
RL-16@20	29.8	4.1	13.0	1.6	0.7030	0.0252	0.1125	0.0128	11.2317	1.6203	0.9769	681	±	73
RL-16@21	38.1	4.6	22.0	2.5	0.6737	0.0352	0.0896	0.0097	8.2989	1.0344	0.9446	552	±	57
RL-16@22	15.8	0.3	18.3	0.5	0.7829	0.0285	0.1951	0.0055	20.9283	0.5350	0.2984	1149	±	29
RL-16@23	21.4	0.2	55.8	0.9	0.7602	0.0233	0.1624	0.0032	17.0932	0.4407	0.1861	970	±	18
RL-16@24	15.2	0.1	26.0	0.3	0.7679	0.0175	0.2314	0.0033	24.4709	0.3909	0.1253	1344	±	18
RL-16@25	20.8	1.4	21.1	1.1	0.7642	0.0164	0.1699	0.0117	17.4631	1.2066	0.9290	1007	±	64
RL-16@26	19.1	0.1	23.9	0.4	0.7634	0.0183	0.1528	0.0023	16.2311	0.3000	−0.0402	916	±	13
RL-16@27	20.1	0.1	25.0	0.4	0.7356	0.0171	0.1472	0.0021	14.9330	0.2918	0.1032	885	±	12
RL-16@28	22.3	0.2	25.3	0.4	0.7467	0.0170	0.1539	0.0027	15.9057	0.3129	0.2983	922	±	15
RL-16@29	17.1	0.2	16.1	0.3	0.7786	0.0143	0.1885	0.0030	20.2667	0.3621	0.4125	1113	±	16
RL-16@30	22.1	0.3	28.2	0.3	0.7561	0.0212	0.1449	0.0025	15.0707	0.2880	0.0467	872	±	14
RL-16@31	22.2	0.2	26.9	0.5	0.7244	0.0153	0.1390	0.0027	14.0507	0.2140	0.1358	841	±	16
RL-16@32	19.8	0.3	22.4	0.4	0.7606	0.0150	0.1805	0.0029	18.5472	0.3440	0.5514	1069	±	16
RL-16@33	29.3	0.3	52.8	0.7	0.7292	0.0155	0.1233	0.0019	12.5220	0.2185	0.1750	749	±	11
RL-16@34	27.8	0.3	47.3	0.6	0.7391	0.0136	0.1278	0.0017	13.0778	0.2164	0.1945	775	±	10
RL-16@35	17.6	0.2	22.1	0.5	0.7430	0.0177	0.1683	0.0035	17.3573	0.4396	0.4180	1002	±	20
RL-16@36	29.5	0.2	119.2	1.1	0.7180	0.0186	0.1304	0.0022	13.1268	0.2351	−0.0181	790	±	13
RL-16@37	24.6	0.9	25.8	0.7	0.7298	0.0175	0.1328	0.0043	13.4743	0.5406	0.8162	803	±	24
RL-16@38	29.0	0.6	25.6	0.6	0.7330	0.0174	0.1246	0.0028	12.6632	0.3029	0.5166	757	±	16
RL-16@39	17.9	0.2	18.4	0.3	0.7750	0.0148	0.1894	0.0035	20.2482	0.3459	0.4434	1118	±	19
RL-16@40	21.7	0.2	25.8	0.4	0.7617	0.0154	0.1586	0.0026	16.4778	0.2950	0.3053	949	±	14

5. Discussion

5.1. Origin of the Apatite from the Renli Deposit

Many studies have considered that the apatite includes magmatic (mixing, inheritance, and composition variation of the host magma) and hydrothermal apatite [38–42]. Among these, magma mixing and inheritance can lead to sudden changes in the composition of apatite, but the REE in apatite is not easily redistributed [4,43]. RL-6, RL-10, and RL-16 apatite show similar chondrite-normalized REE patterns and a gradual decrease in Σ REE. Therefore, magma mixing and inheritance are unlikely.

The levels of LOI of RL-6, RL-10, and RL-16 are less than 1 wt.%, and they do not have porosity, which indicates that post-magmatic alteration or weathering is not obvious [44]. The unsaturated fluid of REE infiltrates through apatite, and monazite inclusions will be formed in apatite [45,46]. Monazite will extract LREE from the more fractionated melts, resulting in the depletion of these elements in apatite [47]. The contents of LREE in RL-6, RL-10, and RL-16 are enriched, and the LREE/HREE ranges from 3.61 to 24.07 (Figure 8i). Therefore, hydrothermal alteration is unlikely. Moreover, the apatites have a subhedral to anhedral structure and the surface of backscattered electron (BSE) images are homogeneous without fractures (Figure 4g–i). The chondrite-normalized REE patterns of RL-6, RL-10, and RL-16 apatite vary systematically and are similar to those of pegmatite in the Renli deposit (Figure 7), suggesting that is the result of gradually magmatic evolution. Cl in apatite will preferentially combine with LREE, resulting in the separation of LREE and HREE [48,49]. However, the separation degree of LREE and HREE is low, especially in the RL-6 and RL-10 samples (Figure 8). In brief, according to apatite texture and composition of apatite, we confirm that the origin of the RL-6, RL-10, and RL-16 apatite is magmatic.

5.2. Time of Nb-Ta Mineralization and Tectonic Environment

Many studies have been conducted on the geochronology of the Renli Nb-Ta deposit. The Zircon U-Pb age obtained by Xiong et al. (2020) from biotite monzogranite was 154 ± 3 Ma, and this represents the crystallization age of biotite monzogranite in the Renli Nb-Ta deposit [14]. The zircon U-Pb age obtained by Xiong et al. (2020) from muscovite monzogranite was 141 ± 2 Ma, and a SHRIMP Zircon U-Pb age obtained by Li et al. (2017) was ca. 137 Ma [13]. Regarding the time of mineralization, a muscovite ^{40}Ar – ^{39}Ar age range obtained by Li et al. (2017) for the Mufushan complex granite ore-bearing pegmatite was 131–128 Ma, and a coltan U-Pb age obtained by Xiong et al. (2020) was ~140 Ma [13,14]. Because of extensive mineralization, many studies confirm that biotite monzogranite and muscovite monzogranite from the Mufushan granite are spatially and genetically related to the Renli Nb-Ta deposit [14]. The new LA-ICP-MS apatite U-Pb ages obtained from the two-mica pegmatite were approximately 130 Ma, which is consistent with the muscovite ^{40}Ar – ^{39}Ar age reported by Li et al. (2017) [13]. South China was in a lithospheric extension system during the period around 140 Ma [50–52]. Therefore, the Renli deposit likely formed in an extensional environment, and the Nb-Ta mineralization of Renli deposit lasted until approximately 130 Ma.

The apatite U-Pb system is characterized by a relatively low closure temperature ranging from 350 to 550 °C, so the system can be easily reset during heating [3]. For the RL-6, RL-10, and RL-16 samples, the LA-ICP-MS U-Pb ages of apatite are almost the same (within the uncertainty range), and the mean value is approximately 130 Ma. The LA-ICP-MS U-Pb age of zircon from the columbite-bearing albite pegmatite is 131 ± 2 Ma, which represents the age of new magmatic–hydrothermal growth and recrystallization in the giant Renli Nb-Ta deposit [19]. The youngest LA-ICP-MS U-Pb age of zircon from columbite-bearing albite pegmatite and the apatite U-Pb age under LA-ICP-MS are similar. Therefore, one possible explanation is that the U-Pb system in apatite crystals is subsequently disturbed throughout the block, which is the result of the inflow of the youngest mantle-related granitic magma and the growth and recrystallization of the new magmatic–hydrothermal solution [3]. This suggests that there was no younger thermal event (above 350 °C) in the Renli area [3].

5.3. Oxidation State of Nb-Ta Mineralization

Apatite is an important accessory mineral in various magmatic rocks, and Ca^{2+} can be occupied by a number of cations, such as Na^+ , Fe^{2+} , Mn^{2+} , Sr^{2+} , rare earth elements ($\text{REE}^{2+}/^{3+}$), and Y^{3+} [4,53–56]. The trace elements in apatite depend on the characteristics of the host rock, so the geochemical characteristics of apatite can be used to interpret the mineralogical and geological conditions [57–63]. Large quantities of elements (Ce, Eu, and Mn) enter apatite, and due to the variable oxidation of these elements, their anomalies in apatite can be used to indicate the redox state of magma [47,64,65].

In this study, the RL-6, RL-10, and RL-16 samples do not have significant Ce anomalies; the Ce anomalies range from 1.02 to 1.22. All the analyzed apatite has strong negative Eu anomalies (Figure 7). Eu anomalies are strongly controlled by feldspar crystallization prior to or simultaneously with apatite crystallization, so it is difficult to explain the oxidation state of the host felsic magma [47,66,67]. The Sr content of apatite has nothing to do with oxidation state [68]. The Sr content of pegmatite is lower than the Sr content of apatite, which also supports the plagioclase crystallization. Previous studies have used Mn anomalies to indicate the redox state of magma, because the radius of Mn^{2+} is more similar to that of Ca^{2+} ; reduced magmas have a higher content of Mn than oxidized magma [47]. Because the Mn contents of the whole rock are >100 ppm, this effect will be obscured during the fractionation of granitoid magmas [47]. In contrast to Mn, the content of Ga in apatite is independent of the host rock; because the radius of Ga^{2+} is more similar to that of Ca^{2+} , reduced magmas have a higher content of Ga than oxidized magmas [69]. We found that the Ga content decreases successively from the RL-6 and RL-10 rock to the RL-16 rock, so the degree of oxidation gradually increases. In addition, compared with rocks with a lower oxidation degree, apatite in the rocks with a higher oxidation degree has a lower $\text{Y}/\Sigma\text{REE}$ ratio, a higher La/Sm ratio, and a higher Ce/Th ratio [47]. The $\text{Y}/\Sigma\text{REE}$ ratio ranges from 0.44 to 0.69 in RL-6 apatite and ranges from 0.05 to 0.46 in RL-16 apatite (Figure 8d). The gradual reduction in the $\text{Y}/\Sigma\text{REE}$ ratio in apatite from the Renli pegmatites indicates an increase in the oxidation degree of the Nb-Ta mineralization in the giant Renli deposit. Compare to pegmatite, the apatite has higher content of Y and HREE, suggesting that the apatite is product of water-poor melts [68]. Highly evolved and volatile rich magmas have a non-chondrite Y/Ho ratio [25]. The mostly Y/Ho ratio of RL-6, RL-10, and RL-16 are >34, which indicate that its host pegmatite is formed in a transitional magmatic-hydrothermal system [1]. In brief, the REE behavior of apatite can be used to constrain the oxidation state of Nb-Ta mineralization, and apatite has great potential as an exploration indicator.

6. Conclusions

- (1) The origin of the apatite is magmatic, and the oxidation degree of the Nb-Ta mineralization increases in the giant Renli deposit.
- (2) The Renli Nb-Ta deposit likely formed in an extensional environment, the Nb-Ta mineralization lasted until approximately 130 Ma, and there was no younger thermal event (above 350 °C) in the Renli deposit.
- (3) The host pegmatite of apatite from Renli deposit is formed in a transitional magmatic-hydrothermal system. The combination of the composition and U-Pb ages of apatite can be used to constrain the magmatic-hydrothermal evolution of granite and pegmatite-type Nb-Ta deposits.

Author Contributions: Conceptualization, Y.C. and Z.X.; methodology, Y.C., Z.X. and H.D.; formal analysis, Z.X. and H.D.; investigation, Y.C., Z.X., Z.Z., C.M., F.Z., L.Z. and J.C.; resources, H.T., J.H., F.Z., L.Z., J.C. and C.W.; writing—original draft preparation, Y.C., Z.X. and H.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by The National Natural Science Foundation of China Project (42130810), National Key Research and Development Program of Hunan Province (2019SK2261), The Science and Technology Innovation Leading Talent Project of Hunan Province (2020RC4003), The Scientific and Technological Talents Support Engineering Project of Hunan Province (202TJ-Q01), and The Science and Technology Innovation Program of Hunan Province (2021RC4055).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jiang, S.Y.; Wen, H.J.; Xu, C.; Wang, Y.; Sun, W.D. Earth sphere cycling and enrichment mechanism of critical metals: Major scientific issues for future research. *Bull. Natl. Nat. Sci. Found. China* **2019**, *33*, 112–118. (In Chinese with English abstract) [[CrossRef](#)]
2. Wang, R.; Che, X.; Wu, B.; Xie, L. Critical mineral resources of Nb, Ta, Zr, and Hf in China. *Chin. Sci. Bull.* **2020**, *65*, 3763–3777. [[CrossRef](#)]
3. Gawęda, A.; Szopa, K.; Chew, D. LA-ICP-MS U-Pb dating and REE patterns of apatite from the Tatra Mountains, Poland as a monitor of the regional tectonomagmatic activity. *Geochronometria* **2014**, *41*, 306–314. [[CrossRef](#)]
4. Zhang, W.; Jiang, S.-Y.; Ouyang, Y.; Zhang, D. Geochronology and textural and compositional complexity of apatite from the mineralization-related granites in the world-class Zhuxi W-Cu skarn deposit: A record of magma evolution and W enrichment in the magmatic system. *Ore Geol. Rev.* **2021**, *128*, 103885. [[CrossRef](#)]
5. Toplis, M.; Dingwell, D. The variable influence of P₂O₅ on the viscosity of melts of differing alkali/aluminium ratio: Implications for the structural role of phosphorus in silicate melts. *Geochim. Cosmochim. Acta* **1996**, *60*, 4107–4121. [[CrossRef](#)]
6. Pan, Y.; Fleet, M.E. Compositions of the Apatite-Group Minerals: Substitution Mechanisms and Controlling Factors. *Rev. Miner. Geochem.* **2002**, *48*, 13–49. [[CrossRef](#)]
7. Cao, M.J.; Evans, N.J.; Hollings, P.; Cooke, D.R.; McInnes, B.I.; Qin, K. Apatite Texture, Composition, and O-Sr-Nd Isotope Signatures Record Magmatic and Hydrothermal Fluid Characteristics at the Black Mountain Porphyry Deposit, Philippines. *Econ. Geol.* **2021**, *116*, 1189–1207. [[CrossRef](#)]
8. Amelin, Y.; Zaitsev, A. Precise geochronology of phosphates and carbonates: The critical role of U-series disequilibrium in age interpretations. *Geochim. Cosmochim. Acta* **2002**, *66*, 2399–2419. [[CrossRef](#)]
9. Gleadow, A.J.; Belton, D.X.; Kohn, B.P.; Brown, R.W. Fission Track Dating of Phosphate Minerals and the Thermochronology of Apatite. *Rev. Miner. Geochem.* **2002**, *48*, 579–630. [[CrossRef](#)]
10. Cherniak, D. Uranium and manganese diffusion in apatite. *Chem. Geol.* **2005**, *219*, 297–308. [[CrossRef](#)]
11. Li, Q.; Li, X.-H.; Wu, F.-Y.; Yin, Q.-Z.; Ye, H.-M.; Liu, Y.; Tang, G.-Q.; Zhang, C.-L. In-situ SIMS U-Pb dating of Phanerozoic apatite with low U and high common Pb. *Gondwana Res.* **2012**, *21*, 745–756. [[CrossRef](#)]
12. Chew, D.M.; Babechuk, M.G.; Cogné, N.; Mark, C.; O’Sullivan, G.; Henrichs, I.A.; Doepke, D.; McKenna, C.A. (LA,Q)-ICPMS trace-element analyses of Durango and McClure Mountain apatite and implications for making natural LA-ICPMS mineral standards. *Chem. Geol.* **2016**, *435*, 35–48. [[CrossRef](#)]
13. Li, P. *Magmatic Activities and Metallogenic Regularity of Rare Metals of Mufushan Area*; Post-Doctoral Outbound Report; Institute of Mineral Resources, Chinese Academy of Geological Sciences: Beijing, China, 2017; p. 301. (In Chinese with English abstract)
14. Xiong, Y.-Q.; Jiang, S.-Y.; Wen, C.-H.; Yu, H.-Y. Granite-pegmatite connection and mineralization age of the giant Renli Ta Nb deposit in South China: Constraints from U-Th-Pb geochronology of coltan, monazite, and zircon. *Lithos* **2020**, *358–359*, 105422. [[CrossRef](#)]
15. Li, P.; Li, J.; Chen, Z.; Liu, X.; Huang, Z.; Zhou, F. Compositional evolution of the muscovite of Renli pegmatite-type rare-metal deposit, northeast Hunan, China: Implications for its petrogenesis and mineralization potential. *Ore Geol. Rev.* **2021**, *138*, 104380. [[CrossRef](#)]
16. Wang, X.-L.; Zhou, J.-C.; Griffin, W.L.; Wang, R.-C.; Qiu, J.-S.; O’Reilly, S.Y.; Xu, X.; Liu, X.-M.; Zhang, G.-L. Detrital zircon geochronology of Precambrian basement sequences in the Jiangnan orogen: Dating the assembly of the Yangtze and Cathaysia Blocks. *Precambrian Res.* **2007**, *159*, 117–131. [[CrossRef](#)]
17. Zheng, Y.-F.; Xiao, W.-J.; Zhao, G. Introduction to tectonics of China. *Gondwana Res.* **2013**, *23*, 1189–1206. [[CrossRef](#)]
18. Zhao, G. Jiangnan Orogen in South China: Developing from divergent double subduction. *Gondwana Res.* **2015**, *27*, 1173–1180. [[CrossRef](#)]
19. Li, P.; Li, J.; Liu, X.; Li, C.; Huang, Z.; Zhou, F. Geochronology and source of the rare-metal pegmatite in the Mufushan area of the Jiangnan orogenic belt: A case study of the giant Renli Nb-Ta deposit in Hunan, China. *Ore Geol. Rev.* **2020**, *116*, 103237. [[CrossRef](#)]
20. Liu, X.; Zhou, F.C.; Huang, Z.B.; Li, J.K.; Zhou, H.X.; Xiao, G.Q.; Bao, Y.H.; Li, P.; Tan, L.M.; Shi, W.K.; et al. Discovery of Renli Superlarge Pegmatite-type Nb-Ta Polymetallic Deposit in Pingjiang, Hunan Province and its Significances. *Geotecton. Metallog.* **2018**, *42*, 235–243. (In Chinese with English abstract) [[CrossRef](#)]

21. Xu, D.R.; Deng, T.; Dong, G.J.; Ning, J.T.; Wang, Z.L.; Zhang, J.L.; Zou, F.H.; Zhou, Y.Q.; Chen, G.W.; Yu, D.S.; et al. Zircon U-Pb geochronological and geochemical characteristics of the Lianyunshan two-mica monzogranites in northeastern Hunan province: Implications for petrogenesis and tectonic setting associated with polymetallic mineralization. *Earth Sci. Front.* **2017**, *24*, 104–122. (In Chinese with English abstract) [[CrossRef](#)]
22. Zhou, F.C.; Li, J.K.; Liu, X.; Li, P.; Huang, Z.B.; Shi, W.K.; Su, J.N.; Chen, H.; Huang, X.Q. Geochemical Characteristics and genetic significance of ore bodies in RenLi Nb-Ta deposit, Hunan province. *Acta Geol. Sin.* **2019**, *93*, 1392–1404. (In Chinese with English abstract) [[CrossRef](#)]
23. Che, X.-D.; Wang, R.-C.; Wu, F.-Y.; Zhu, Z.-Y.; Zhang, W.-L.; Hu, H.; Xie, L.; Lu, J.-J.; Zhang, D. Episodic Nb–Ta mineralisation in South China: Constraints from in situ LA–ICP–MS columbite-tantalite U–Pb dating. *Ore Geol. Rev.* **2019**, *105*, 71–85. [[CrossRef](#)]
24. Shu, L.S.; Jahn, B.-M.; Charvet, J.; Santosh, M.; Wang, B.; Xu, X.S.; Jiang, S.Y. Early Paleozoic depositional environment and intraplate tectono-magmatism in the Cathaysia Block (South China): Evidence from stratigraphic, structural, geochemical and geochronological investigations. *Am. J. Sci.* **2014**, *314*, 154–186. [[CrossRef](#)]
25. Xiong, Y.-Q.; Shao, Y.-J.; Cheng, Y.; Jiang, S.-Y. Discrete Jurassic and Cretaceous Mineralization Events at the Xiangdong W(Sn) Deposit, Nanling Range, South China. *Econ. Geol.* **2020**, *115*, 385–413. [[CrossRef](#)]
26. Xiong, Y.Q.; Shao, Y.J.; Mao, J.W.; Wu, S.C.; Zhou, H.D.; Zheng, M.H. The polymetallic magmatic-hydrothermal Xiangdong and Dalong systems in the W-Sn-Cu-Pb-Zn-Ag Dengfuxian orefield, SE China: Constraints from geology, fluid inclusions, H-O-S-Pb isotopes, and sphalerite Rb-Sr geochronology. *Miner. Depos.* **2019**, *54*, 1101–1124. [[CrossRef](#)]
27. Li, P.; Li, J.K.; Pei, R.F.; Leng, S.L.; Zhang, X.; Zhou, F.C.; Li, S.M. Multistage magmatic evolution and Cretaceous peak Metallogenic epochs of Mufushan composite granite mass: Constrains from Geochronological evidence. *Earth Sci.* **2017**, *42*, 1684–1696. [[CrossRef](#)]
28. Li, C.Y. The Genesis of Chuanziyuan Niobium-Tantalum-Lithium Rare Metal Deposit in Pingjiang Hunan. Master's Thesis, Central South University, Changsha, China, 2016.
29. Wen, C.H.; Chen, J.F.; Luo, X.Y.; Li, S.M. Geochemical features of the Chuanziyuan rare metal pegmatite in northeastern Hunan, China. *Bull. Mineral. Petrol. Geochem.* **2016**, *35*, 171–177. (In Chinese with English abstract)
30. Wen, C.-H.; Shao, Y.-J.; Xiong, Y.-Q.; Li, J.-K.; Jiang, S.-Y. Ore genesis of the Baishawo Be-Li-Nb-Ta deposit in the northeast Hunan Province, south China: Evidence from geological, geochemical, and U-Pb and Re-Os geochronologic data. *Ore Geol. Rev.* **2021**, *129*, 103895. [[CrossRef](#)]
31. Li, P.; Zhou, F.C.; Li, J.K.; Liu, X.; Huang, Z.B.; Zhang, L.P. Zircon U-Pb Ages and Hf Isotopic Compositions of the Concealed Granite of Renli-Chuanziyuan Deposit, NE Hunan and Geological Significance. *Geotecton. Metallog.* **2020**, *44*, 486–500. (In Chinese with English abstract) [[CrossRef](#)]
32. Zhou, F.C.; Liu, X.; Li, J.K.; Huang, Z.B.; Xiao, G.Q.; Li, P.; Zhou, H.X.; Shi, W.K.; Tan, L.M.; Su, J.N.; et al. Metallogenic characteristics and prospecting direction of Renli super-large rare metal deposit in Hunan province, China. *Geotecton. Metallog.* **2019**, *43*, 77–91. (In Chinese with English abstract) [[CrossRef](#)]
33. Thomson, S.N.; Gehrel, G.E.; Ruiz, J.; Buchwaldt, R. Routine low-damage apatite U-Pb dating using laser ablation-multicollector-ICP-MS. *Geochim. Geophys. Geosyst.* **2012**, *13*, Q0AA21. [[CrossRef](#)]
34. Chew, D.; Petrus, J.; Kamber, B. U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb. *Chem. Geol.* **2014**, *363*, 185–199. [[CrossRef](#)]
35. Petrus, J.A.; Kamber, B. VizualAge: A Novel Approach to Laser Ablation ICP-MS U-Pb Geochronology Data Reduction. *Geostand. Geoanal. Res.* **2012**, *36*, 247–270. [[CrossRef](#)]
36. Sun, S.S.; McDonough, W.F. *Chemical and Isotopic Systematics of Oceanic Basalts: Implications for Mantle Composition and Processes*; Geological Society of London Special Publication: London, UK, 1989; Volume 42, pp. 313–345.
37. Tera, F.; Wasserburg, G. U-Th-Pb systematics in three Apollo 14 basalts and the problem of initial Pb in lunar rocks. *Earth Planet. Sci. Lett.* **1972**, *14*, 281–304. [[CrossRef](#)]
38. Li, X.; Zhou, M.-F. Multiple stages of hydrothermal REE remobilization recorded in fluorapatite in the Paleoproterozoic Yinchang Fe–Cu–(REE) deposit, Southwest China. *Geochim. Cosmochim. Acta* **2015**, *166*, 53–73. [[CrossRef](#)]
39. Pochon, A.; Poujol, M.; Gloaguen, E.; Branquet, Y.; Cagnard, F.; Gumiaux, C.; Gapais, D. U-Pb LA-ICP-MS dating of apatite in mafic rocks: Evidence for a major magmatic event at the Devonian-Carboniferous boundary in the Armorican Massif (France). *Am. Miner.* **2016**, *101*, 2430–2442. [[CrossRef](#)]
40. Glorie, S.; Jepson, G.; Konopelko, D.; Mirkamalov, R.; Meeuws, F.; Gilbert, S.; Gillespie, J.; Collins, A.; Xiao, W.; Dewaele, S.; et al. Thermochronological and geochemical footprints of post-orogenic fluid alteration recorded in apatite: Implications for mineralisation in the Uzbek Tian Shan. *Gondwana Res.* **2019**, *71*, 1–15. [[CrossRef](#)]
41. Zeng, L.-P.; Zhao, X.-F.; Li, X.-C.; Hu, H.; McFarlane, C. In situ elemental and isotopic analysis of fluorapatite from the Taocun magnetite-apatite deposit, Eastern China: Constraints on fluid metasomatism. *Am. Miner.* **2016**, *101*, 2468–2483. [[CrossRef](#)]
42. Zhang, X.B.; Guo, F.; Zhang, B.; Zhao, L.; Wu, Y.M.; Wang, G.Q.; Alemayehu, M. Magmatic evolution and post-crystallization hydrothermal activity in the early Cretaceous Pingtan intrusive complex, SE China: Records from apatite geochemistry. *Contrib. Miner. Petrol.* **2020**, *175*, 35. [[CrossRef](#)]
43. Tepper, J.H.; Kuehner, S.M. Complex zoning in apatite from the Idaho Batholith; a record of magma mixing and intracrystalline trace element diffusion. *Am. Miner.* **1999**, *84*, 581–595. [[CrossRef](#)]

44. Palma, G.; Barra, F.; Reich, M.; Valencia, V.; Simon, A.C.; Vervoort, J.; Leisen, M.; Romero, R. Halogens, trace element concentrations, and Sr-Nd isotopes in apatite from iron oxide-apatite (IOA) deposits in the Chilean iron belt: Evidence for magmatic and hydrothermal stages of mineralization. *Geochim. Cosmochim. Acta* **2019**, *246*, 515–540. [[CrossRef](#)]
45. Harlov, D.E.; Andersson, U.B.; Förster, H.-J.; Nyström, J.O.; Dulski, P.; Broman, C. Apatite–monazite relations in the Kiirunavaara magnetite–apatite ore, northern Sweden. *Chem. Geol.* **2002**, *191*, 47–72. [[CrossRef](#)]
46. Harlov, D.E.; Förster, H.-J. Fluid-induced nucleation of (Y+REE)-phosphate minerals within apatite: Nature and experiment. Part II. Fluorapatite. *Am. Miner.* **2003**, *88*, 1209–1229. [[CrossRef](#)]
47. Belousova, E.A.; Griffin, W.L.; O'Reilly, S.Y.; Fisher, N.I. Apatite as an indicator mineral for mineral exploration: Trace-element compositions and their relationship to host rock type. *J. Geochem. Explor.* **2002**, *76*, 45–69. [[CrossRef](#)]
48. Migdisov, A.; Williams-Jones, A.; Wagner, T. An experimental study of the solubility and speciation of the Rare Earth Elements (III) in fluoride- and chloride-bearing aqueous solutions at temperatures up to 300 °C. *Geochim. Cosmochim. Acta* **2009**, *73*, 7087–7109. [[CrossRef](#)]
49. Zhang, W.; Jiang, S.-Y.; Gao, T.; Ouyang, Y.; Zhang, D. Constraints on the Petrogenesis and Metallogenic Setting of Lamprophyres in the World-Class Zhuxi W–Cu Skarn Deposit, South China. *Minerals* **2020**, *10*, 642. [[CrossRef](#)]
50. Li, Z.X.; Li, X.H. Formation of the 1300-km-wide intracontinental orogen and post-orogenic magmatic province in Mesozoic South China: A flat-slab subduction model. *Geology* **2007**, *35*, 179–182. [[CrossRef](#)]
51. Jingwen, M.; Yanbo, C.; Maohong, C.; Pirajno, F. Major types and time–space distribution of Mesozoic ore deposits in South China and their geodynamic settings. *Miner. Depos.* **2013**, *48*, 267–294. [[CrossRef](#)]
52. Zhou, X.; Sun, T.; Shen, W.; Shu, L.; Niu, A.Y. Petrogenesis of Mesozoic granitoids and volcanic rocks in South China: A response to tectonic evolution. *Episodes* **2006**, *29*, 26–33. [[CrossRef](#)]
53. Gaft, M.; Reisfeld, R.; Panczer, G.; Blank, P.; Boulon, G. Laser-induced time-resolved luminescence of minerals. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **1998**, *54*, 2163–2175. [[CrossRef](#)]
54. Marfunin, A.S. *Spectroscopy, Luminescence and Radiation Centers in Minerals*; Springer: Berlin/Heidelberg, Germany, 1979.
55. Morozov, A.M.; Morozova, L.G.; Trefimov, A.K.; Feofilov, P.P. Spectral and luminescent characteristics of fluoroapatite single crystals activated by rare earth ions. *Opt. Spektrosk.* **1970**, *29*, 590–596. (In Russian)
56. Kempe, U.; Götze, J. Cathodoluminescence (CL) behaviour and crystal chemistry of apatite from rare-metal deposits. *Miner. Mag.* **2002**, *66*, 151–172. [[CrossRef](#)]
57. Belousova, E.A.; Walters, S.; Griffin, W.L.; O'Reilly, S.Y. Trace element signatures of apatites from granitoids of Mount Isa Inlier, north-west Queensland, Australia. *Aust. J. Earth Sci.* **2001**, *48*, 603–619. [[CrossRef](#)]
58. Boudreau, A.E.; Kruger, F.J. Variation in the composition of apatite through the Merensky cyclic unit in the western Bushveld Complex. *Econ. Geol.* **1990**, *85*, 737–745. [[CrossRef](#)]
59. Perseil, E.-A.; Blanc, P.; Ohnenstetter, D. As-Bearing fluorapatite in manganese deposits from St. Marcel—Praborna, Val D'aosta, Italy. *Can. Miner.* **2000**, *38*, 101–117. [[CrossRef](#)]
60. Seifert, W.; Kampf, H.; Westernack, J. Compositional variations in apatite, phlogopite and other accessory minerals of the ultramafic Delitzsch complex, Germany: Implications for cooling history of carbonatites. *Lithos* **2000**, *53*, 81–100. [[CrossRef](#)]
61. Wu, M.Q.; Samon, I.M.; Qiu, K.F.; Zhang, D.H. Multi-stage metasomatic Zr mineralization in the world-class Baerzhe Rare earth element-Nb-Zr-Be deposit. *Am. Mineral.* **2022**, in press. [[CrossRef](#)]
62. Qiu, K.F.; Yu, H.C.; Hetherington, C.; Huang, Y.Q.; Yang, T.; Deng, J. Tourmaline composition and boron isotope signature as a tracer of magmatic-hydrothermal processes. *Am. Mineral.* **2021**, *106*, 1033–1044. [[CrossRef](#)]
63. Yu, H.C.; Qiu, K.F.; Chew, D.; Yu, C.; Ding, Z.J.; Zhou, T.; Li, S.; Sun, K.F. Buried Triassic rocks and vertical distribution of ores in the giant Jiaodong gold province (China) revealed by apatite xenocrysts in hydrothermal quartz veins. *Ore Geol. Rev.* **2022**, *140*, 104612. [[CrossRef](#)]
64. Jia, F.; Zhang, C.; Liu, H.; Meng, X.; Kong, Z. In situ major and trace element compositions of apatite from the Yangla skarn Cu deposit, southwest China: Implications for petrogenesis and mineralization. *Ore Geol. Rev.* **2020**, *127*, 103360. [[CrossRef](#)]
65. Mercer, C.N.; Watts, K.E.; Gross, J. Apatite trace element geochemistry and cathodoluminescent textures—A comparison between regional magmatism and the Pea Ridge IOAREE and Boss IOCG deposits, southeastern Missouri iron metallogenic province, USA. *Ore Geol. Rev.* **2020**, *116*, 103129. [[CrossRef](#)]
66. Bea, F.; Mitchell, J.N.; Scoates, J.S.; Frost, C.D.; Kolker, A. Residence of REE, Y, Th and U in Granites and Crustal Protoliths; Implications for the Chemistry of Crustal Melts. *J. Petrol.* **1996**, *37*, 521–552. [[CrossRef](#)]
67. Gawęda, A.; Sikorska, M. Alkali feldspar megacrysts from the High Tatra granite-indicators of magma mixing/mingling processes. *Mineral. Spec. Pap.* **2009**, *35*, 82.
68. Yu, H.C.; Qiu, K.F.; Hetherington, C.J.; Chew, D.; Huang, Y.Q.; He, D.Y.; Geng, J.Z.; Xian, H.Y. Apatite as an alternative petrochronometer to trace the evolution of magmatic systems containing metamict zircon. *Contrib. Mineral. Petrol.* **2021**, *176*, 68. [[CrossRef](#)]
69. Pan, L.-C.; Hu, R.-Z.; Wang, X.-S.; Bi, X.-W.; Zhu, J.-J.; Li, C. Apatite trace element and halogen compositions as petrogenetic-metallogenic indicators: Examples from four granite plutons in the Sanjiang region, SW China. *Lithos* **2016**, *254–255*, 118–130. [[CrossRef](#)]