#### **Research Advances**

# New In-Situ LA-ICP-MS U-Pb Ages of Uraninite from the Mianhuakeng Uranium Deposit, Northern Guangdong Province, China: Constraint on the Metallogenic Mechanism

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# Objective

Hydrothermal uranium deposits in South China have become one of the main uranium producers over the past several decades. Numerous uranium deposits are densely distributed in the Guidong and Zhuguangshan plutons of the Nanling region, which constitute the largest uranium mineralization area in China (Cai Yuqi et al., 2015). The Mianhuakeng (MHK) uranium deposit, one of the largest granite-type uranium deposits in South China, is located in the central-southern part of the Zhuguangshan pluton, northern Guangdong Province, and is characterized by high grade ores (U: 0.01%–1.2%), large reserves (>10000 t) and a large vertical extent of mineralization (ca. 1000 m).

Abundant studies have carried out on the genesis of the MHK deposit. However, the accurate uranium mineralization age is still poorly constrained. A uraninite in-situ LA-ICP-MS U-Pb geochronological study was carried out for the first time in this paper, in order to obtain a precise and accurate mineralization age for the MHK deposit, and to further evaluate the mechanism of uranium mineralization.

#### Methods

Two uranium ore samples (No. MHK1519 and CJ16153) were collected from the mining tunnel at the -150 m level and the KZK39-3 drill core at the -268.95 m elevation in MHK deposit, respectively. Thin sections of the samples were examined for mineral assemblages, mineral chemical compositions and micro-structures using polarizing microscopy, EPMA, SEM and MRS (Micro-Raman spectroscopy) at East China University of Technology and University of Science and Technology of China. Prior to U-Pb isotope analysis, thin sections were re-polished (trimming off 1–2  $\mu$ m) and cleaned with

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ethanol to remove the superficial carbon coat and impurity. The uraninite with homogeneous chemical composition and without fractures or cracks, mineral inclusions and oxidative signs were marked for U-Pb isotope dating, which were conducted by LA-ICP-MS with a beam diameter of 16 µm at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Uraninite standard GBW04420 (a China national standard) was used as external standard for U-Pb isotope calibration (Zong Keqing et al., 2015). Samples were analyzed in runs of ten analyses including six unknowns and four standards of GBW04420. Uraninite standard yielded a weighted average <sup>206</sup>Pb/<sup>238</sup>U age of 70.0±0. 6Ma (n=32, MWSD=0.10) in accord with the recommended (70 Ma). Dates were reduced using ICPMSDataCal 8.3 and Isoplotv. 3.23. Uncertainties for each analysis and weighted average ages were quoted at  $1\sigma$ .

## Results

Uraninite with prominent Raman spectra of UO<sub>2</sub> demonstrates bright white granular, cloddy, irregular or veined form on the BSE images (Figs. 1a and 1b). In-situ LA-ICP-MS uraninite U-Pb dating (Appendix 1) for the sample CJ16153 yielded a weighted average  $^{206}$ Pb/<sup>238</sup>U ages of 59.5±1.0 Ma (*n*=10, MSWD=0.39, Fig. 1c), and the sample No. MHK1519 gave a weighted average  $^{206}$ Pb/<sup>238</sup>U ages of 60.0±0.5 Ma (*n*=21, MSWD=1.13, Fig. 1d). Ages from samples MHK1519 and CJ16153 were identical within the error range, indicating that the uranium mineralization of the MHK deposit occurred at ca. 60Ma.

The new uraninite U-Pb ages (ca. 60Ma) for the MHK deposit are not completely in agreement with the conventional U-Pb ages of uraninite (54 Ma, 68 Ma, 70 Ma and 81 Ma) reported by previous studies. Because previous results involved relatively large analytical errors

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230.5 (b) MHK1519 (a) 700 Uraninite 600 altered uraninite 20 200 594. 40 100 0 400 500 600 Raman shift(cm 200 300 600 700 800 900 (c (d) MHK1519 CJ16153 0.0125 200µ 0.01 1.3Ma Mean=60.0±0.5Ma 0.0115 n=21 spots MSWD=1.13 95% conf. D0.010 20.0105 Pb Pp 0.0095 0.009 Mean=59.5±1.0Ma 0.0085 n=10 spots MSWD=0.39 95% conf. 0.0075L\_\_\_\_\_ 0.045 0.008 0.085 0.055 0.065 0.075 0.095 0.055 0.065 0.075 0.085 0.095 Ph 'n ίΠ

Fig. 1. Images of reflected light (a), Raman spectra (b) and concordia diagrams (c, d) of in-situ LA-ICP-MS uraninite U-Pb ages of ore samples from the MHK deposit. Red points on the BSE image represent the analysis spots. Qtz, Quartz; Py, Ppyrite; Ur, Uraninite.

(8%-20%) or inconsistent <sup>206</sup>Pb/<sup>238</sup>U apparent ages, and

uraninite generally contains fine-grained sulfides (e.g., pyrite and galena) or altered uranium zones (Figs. 1a and 1b), which may influence the U-Pb isotope system of uraninite for U-Pb isotope dating, the conventional ages cannot factually represent the uranium mineralization age of the MHK deposit, but rather mixture ages. Our new insitu LA-ICP-MS uraninite U-Pb ages (ca. 60Ma) are likely much more representative of the age of uranium mineralization for the MHK deposit.

The  $\delta^{13}C_{PDB}$  values of syn-ore calcite (without concomitant barite, graphite and pyrrhotite) are from -9.9% to -5.3%, which miraculously agree with the carbon isotope composition of carbon from the mantle  $(\delta^{13}C_{PDB}$  values: -9‰--3‰), suggesting that the CO<sub>2</sub> related to uranium mineralization was originated from the lithospheric mantle during large-scale extensional processes (Hu et al., 2008).

## Conclusions

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The new U-Pb ages (ca. 60Ma) suggest that the uranium mineralization of the MHK deposit occurred at Paleocene. In the study area, the MHK deposit was accompanied by Paleocene basic rocks (e.g., the basite in Central-south Jiangxi Province and the Sanshui volcanic basin of Northern Guangdong Province) and down-faulted basins (e.g., the Renhua and Nanxiong basins), which is consistent with the notion that the uranium mineralization developed during the Paleocene lithosphere extension of South China.

Pb

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Spot No.	<sup>207</sup> Pb/ <sup>206</sup> Pb		<sup>207</sup> Pb/ <sup>235</sup> U		<sup>206</sup> Pb/ <sup>238</sup> U		<sup>207</sup> Pb/ <sup>206</sup> Pb		<sup>207</sup> Pb/ <sup>235</sup> U		<sup>206</sup> Pb/ <sup>238</sup> U	
	Ratio	$1\sigma$	Ratio	$1\sigma$	Ratio	$1\sigma$	Age (Ma)	$1\sigma$	Age (Ma)	$1\sigma$	Age (Ma)	10
MHK1519 sample												
MHK1519-01	0.0464	0.0014	0.0618	0.0020	0.0096	0.0002	20.5	79.6	60.9	1.9	61.5	1.2
MHK1519-02	0.0482	0.0018	0.0643	0.0026	0.0095	0.0002	109.4	89	63.3	2.5	61.1	1.1
MHK1519-03	0.0478	0.0020	0.0604	0.0024	0.0093	0.0002	100.1	87	59.5	2.3	59.7	1.4
MHK1519-08	0.0491	0.0017	0.0655	0.0023	0.0095	0.0002	153.8	77	64.4	2.1	60.7	1.4
MHK1519-13	0.0497	0.0022	0.0648	0.0027	0.0096	0.0003	189	104	63.8	2.5	61.3	1.8
MHK1519-15	0.0512	0.0021	0.0659	0.0029	0.0093	0.0003	250.1	96	64.8	2.8	59.9	1.7
MHK1519-16	0.0463	0.0020	0.0598	0.0023	0.0097	0.0002	16.8	100	59.0	2.2	62.0	1.5
MHK1519-17	0.0513	0.0017	0.0656	0.0022	0.0093	0.0002	253.8	78	64.5	2.1	59.9	1.3
MHK1519-19	0.0526	0.0035	0.0657	0.0043	0.0093	0.0003	309.3	152	64.6	4.1	59.4	1.9
MHK1519-21	0.0515	0.0043	0.0670	0.0052	0.0095	0.0003	261.2	191	65.9	5.0	60.8	1.7
MHK1519-22	0.0483	0.0024	0.0618	0.0037	0.0091	0.0002	122.3	109	60.9	3.5	58.4	1.6
MHK1519-23	0.0508	0.0019	0.0668	0.0025	0.0095	0.0002	231.6	90	65.7	2.3	60.7	1.2
MHK1519-24	0.0477	0.0016	0.0613	0.0021	0.0092	0.0002	83.4	77.8	60.4	2.0	58.9	1.0
MHK1519-25	0.0466	0.0017	0.0614	0.0026	0.0092	0.0002	27.9	94.4	60.5	2.5	58.8	1.2
MHK151927	0.0469	0.0037	0.0658	0.0049	0.0097	0.0002	42.7	177.8	64.8	4.7	62.5	1.
MHK1519-28	0.0508	0.0020	0.0668	0.0031	0.0093	0.0002	231.6	89	65.6	2.9	59.9	1.:
MHK1519-29	0.0469	0.0018	0.0596	0.0023	0.0092	0.0002	42.7	88.9	58.7	2.2	58.9	1.4
MHK1519-31	0.0474	0.0013	0.0607	0.0017	0.0090	0.0001	77.9	63	59.9	1.6	58.0	0.8
MHK151932	0.0463	0.0018	0.0601	0.0023	0.0093	0.0002	13.1	88.9	59.3	2.2	59.8	1.0
MHK1519-33	0.0470	0.0018	0.0646	0.0033	0.0095	0.0002	50.1	150.	63.6	3.2	60.8	1.4
MHK151934	0.0518	0.0023	0.0670	0.0030	0.0093	0.0002	276	104	65.8	2.8	59.8	1.2
CJ16153 sample												
CJ16153-03	0.0475	0.0046	0.0705	0.0071	0.0094	0.0003	76	224	69.2	6.8	60.0	1.9
CJ16153-04	0.0485	0.0019	0.0621	0.0030	0.0093	0.0004	124.2	89.8	61.1	2.9	60.0	2.
CJ16153-05	0.0469	0.0016	0.0613	0.0026	0.0093	0.0002	42.7	81.5	60.4	2.5	59.6	1.
CJ16153-08	0.0469	0.0016	0.0626	0.0026	0.0095	0.0003	55.7	68.5	61.6	2.5	60.9	1.
CJ16153-09	0.0483	0.0014	0.0632	0.0020	0.0095	0.0002	122.3	66.7	62.2	1.9	60.8	1.
CJ16153-10	0.0484	0.0016	0.0621	0.0022	0.0093	0.0002	120.5	77.8	61.2	2.1	59.8	1.
CJ16153-11	0.0512	0.0012	0.0639	0.0017	0.0090	0.0002	250.1	53.7	62.9	1.6	58.1	1.2
CJ16153-14	0.0480	0.0019	0.0599	0.0023	0.0092	0.0003	98.2	75.5	59.1	2.2	59.0	1.
CJ16153-15	0.0491	0.0014	0.0644	0.0026	0.0093	0.0003	153.8	68.5	63.3	2.5	59.8	1.9
CJ16153-16	0.0465	0.0024	0.0637	0.0042	0.0091	0.0002	33.4	109.3	62.7	4.0	58.6	1.