

In situ Imaging of Multi-elements on Pyrite Using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry



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Abstract: A method of *in situ* multi-elements 2D imaging on single pyrite was developed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Nine elements and 50 thousands valid data were acquired in a 1 mm × 1 mm scanning area, with the total analyzed time of 1.5 h. The data showed that the signals of Fe and S were uniformly distributed on the pyrite, and the ratio data of Fe/S was centralized with a lower relative standard deviation of 11.6%, indicating the good homogeneity of the pyrite and stability of this method. Compared with the surrounding black shale, the detected trace elements on the pyrite showed different degrees of enrichment or losses, might be the response of the redox environment during this pyrite forming or the later secondary reforming process. This method will help the popularization and application of LA-ICP-MS in single mineral particles analysis, and provide more direct and accurate visual data for the study of paleoenvironment, source rock and fluid accumulation.

Key Words: Laser ablation; Inductively coupled plasma-mass spectrometry; Pyrite; Trace elements; *In situ* imaging

1 Introduction

Pyrite is the most common sulfide mineral in the earth crust, and one important iron-bearing mineral in the organic-rich sediments^[1]. As an authigenic mineral, sedimentary pyrite could provide much information on redox conditions and hydrographic conditions of the bottom water. So, it is the most important objects for the research of paleo-ocean environments and early-diagenetic processes^[2]. In recent years, extensive researches are focusing on the mechanism of organic-rich sediments accumulation and the process of paleo-ocean oxidation in the Proterozoic era^[3–5]. Thus, almost all of the information provided by pyrite are widely concerned, including the morphology^[6], the size distribution^[7], the contents of trace elements^[6, 8], and the isotopic compositions

of iron and sulfur^[9,10], etc. However, it is worth noting that pyrite can also be formed during post-deposition. Most of the pyrites in sediments, especially the macroscopic pyrite grains, are secondary mineral. These pyrites could not reflect the original geochemical features, but recorded some information of secondary reconstruction. Unfortunately, current geochemical studies of pyrite did not clearly distinguish these different types. The data are usually come from all of the pyrites in sediments. Subtle studies of single pyrite grain are still lacking. As a consequence, the *in situ* analysis of trace elements from single pyrite is of great importance for the studies of pyrite formation mechanism, depositional redox identification, secondary reforming process, and the further research of paleo-environment, source rock evaluation, and fluid accumulation effect, and so on.

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As a solid sampling technique, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can achieve the *in situ* microanalysis of the major, minor, and trace elements, and is widely used in geology, biology, medicine, and other fields^[11–13]. With the rapid development of quasi-nanoscale microanalysis and the requirement of high spatial resolution, the sampling areas of LA-ICP-MS are tend to be more microscopic and more stereoscopic^[14,15]. In fact, this technique was successfully applied in the analysis of single cell^[16,17], single mineral^[18], trace elements distribution mechanism^[19], mineral growth mechanism^[20], and crystalline material characterization^[21], etc. In this study, a rapid analysis method of *in situ* multi-elements imaging in single pyrite with high resolution was developed using a 193-nm ultra-short pulse excimer laser ablation system and quadrupole rods inductively coupled plasma mass spectrometry. Then, the enrichment characteristics of nine elements were imaged and semi-quantitative statistical analyzed.

2 Experimental

2.1 Sample information

Ablated pyrite was from the black shale of the Doushantuo Formation, which was from the drill core of ZK102 in Tongren City, Guizhou province, China. The target sample was cut to the size of 76 mm × 26 mm with a thickness of 2 mm using a core cutter. The target sample was then polished until the pyrite grains exposed on the surface, followed by a thorough washing with deionized water and acetone to ensure the surface clean.

2.2 Instrument conditions and analysis parameters

The pyrite grains were examined using a ZX10 polarizing microscope (Carl Zeiss AG Corporation, Germany). Morphology features of selected pyrite grain were pictured with reflected light.

LA-ICP-MS analysis was performed using an Analyte Excite 193 nm ultra-short pulse excimer laser ablation system (Photo Machines Corporation, USA) and an iCAP Q

inductively coupled plasma mass spectrometry (Thermo Fisher Corporation, USA). Solid glass standard sample NIST 612 was used in tuning of instrument conditions and analysis parameters. The rate of oxidation products ($^{232}\text{Th}^{16}\text{O}^+ / ^{232}\text{Th}^+$) was tuned to be less than 0.3% to reduce the oxide interference. Because both the contents of Th and U in the standard sample NIST 612 were 37 mg kg⁻¹, the mass ratio of $^{232}\text{Th}^+ / ^{238}\text{U}^+$ was tuned to be closed to 1.00, with an relative standard deviation (RSD) of lower than 5% in 10 min, to reduce the mass discrimination effect.

Square spot with a diameter of 20 μm and line scan mode was adopted. The ablation line spacing was set to 20 μm. It was confirmed that, the time required to remove the light spot from the end of one line to the beginning of next line was about 0.5 s, and the time required to reduce the signal counts from > 300000 to blank (< 0.1% maximum signal counts) in HelExII sample cell with He was about 2 s, and the time required to transfer the aerosol particles from the sample cell of LA to ICP-MS and then to achieve the element signal counts was about 2 s. Therefore, a pause of 5 s was set after each line ablation. Moreover, each analysis time of ICP-MS was 5 s more than the corresponding LA line ablation time. These parameters setting could ensure the complete record of the ablated samples in ICP-MS, and remove the cross-contamination of different line ablation. Detailed instrument conditions and operating parameters are shown in Table 1.

2.3 Data analysis

The sample position recorded in LA and the elements signal counts recorded in ICP-MS were linked by the analysis time. Igor Pro 6.1 software (Wave Metrics Corporation, USA) was used for two-dimensional (2D) imaging of multi-elements and element ratios. Origin 8.5 software (OriginLab, USA) was used to select interesting regions and read the counts of each element for the further semi-quantitative statistical analysis.

3 Results and discussion

3.1 Multi-elements imaging

Table 1 Parameters of LA-ICP-MS

Laser ablation system		Inductively coupled plasma mass spectrometry system	
Wavelength	193 nm	RF power	1375 W
Pulse repetition rate	5 Hz	Cool gas/Ar	14.0 L min ⁻¹
Output energy ratio	50%	Auxiliary gas/Ar	0.8 L min ⁻¹
Pulse energy	5 mJ	Nebulizer gas/Ar	0.9 L min ⁻¹
Energy density	7 J cm ⁻²	Carrier gas/He	10 L min ⁻¹
Ablation model	Energy	Dwell time	0.01 s
Laser pit size	20 μm	CCT model	Standard (STD)
Scan rate	10 μm s ⁻¹	Data acquisition	Time-resolution mode (TRM)
Scan model	Line	Isotopes	³⁴ S, ⁵³ Cr, ⁵¹ V, ⁵⁷ Fe, ⁶⁵ Cu, ⁶⁶ Zn, ⁷⁵ As, ⁸² Se, ⁹⁵ Mo
Ablation line spacing	20 μm		

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