

IN SITU IMAGING OF MULTI-ELEMENTS ON THE PYRITE USING LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

H. J. Wang^{1,2}, S. C. Zhang^{1,2}, Y. T. Ye^{1,2,3}, X. M. Wang^{1,2}, W. X. Zhou^{1,2,4}, J. Su^{1,2}

¹China National Petroleum Corporation, Beijing, China

²Research Institute of Petroleum Exploration and Development, Beijing, China

³Peking University, Beijing, China

⁴Guizhou University, Guiyang, China

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^[2]. However, most of the macroscopic pyrite grains in sediments, are secondary mineral, which can only recorded some information of secondary reconstruction. Current geochemical studies of pyrite did not clearly distinguish these two 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 solid sampling technique, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can achieve the *in-situ* micro-analysis of the major, minor, and trace elements^[3]. In this study, one rapid analysis method of *in situ* multi-elements imaging in single pyrite with high resolution was developed using LA-ICP-MS.

Results

Owing to the great differences between the pyrite and black shale matrix, it is difficult to select suitable internal standard and reference material for normalization and quantitation. Here, we use the signal counts of each element from ICP-MS to image. Iron (Fe) and sulfur (S) are the main constituent elements of pyrite. Meanwhile, Cr, V, Cu, Zn, As, Se and Mo in pyrite would provide the information of the depositional context and secondary alteration^[4]. Therefore, previous elements and the count ratio of Fe/S were given significant attention in the ablated pyrite (Fig.1). The signal counts recorded in ICP-MS were of positive correlation with the element contents in the pyrite. Thus, we could achieve the semi-quantitative analysis for the element distributions according to signal counts.

Statistical analysis results showed that, in the pyrite, the average signal counts value of ⁵⁷Fe and ³⁴S are $(2.89 \pm 0.22) \times 10^6$ and $(8.64 \pm 0.68) \times 10^5$, respectively, with an average value of Fe/S ratio was 3.26 ± 0.38 . On the contrary, in the surrounding black shale, the average signal counts value of ⁵⁷Fe and ³⁴S are $(0.027 \pm 0.008) \times 10^6$ and $(0.49 \pm 0.05) \times 10^5$, respectively, with an average value of Fe/S ratio was 0.59 ± 0.18 . Accordingly, the contents of Fe and S in the pyrite were 100 times and 17.6 times higher than the black shale, respectively. In the other words, the enrichment of iron in pyrite was almost 5.5 times of sulfur, when compared with the black shale surrounding. The molar ratio of Fe/S in the black shale was about 11:1.

As shown in Fig.1, trace element concentrations in pyrite differed greatly with black shale surrounding. The 2D mappings of each element demonstrated a sharp outline of the pyrite, although different trace elements present different distributions. Fe, S, As, Se, Mo and Cu were strongly enriched, while Zn and Cr were less enriched. V was depleted in pyrite grains,

but had high content in the black shale matrix. This phenomenon was consistent with the measurement result reported by Large *et al.*^[4] The enrichments of Fe, S and Cr in pyrite were relatively uniform, yet As, Se, Mo, Cu and Zn showed obvious regional enrichment characteristics. Redox change or diagenetic modification would be responsible for these elements behavior.

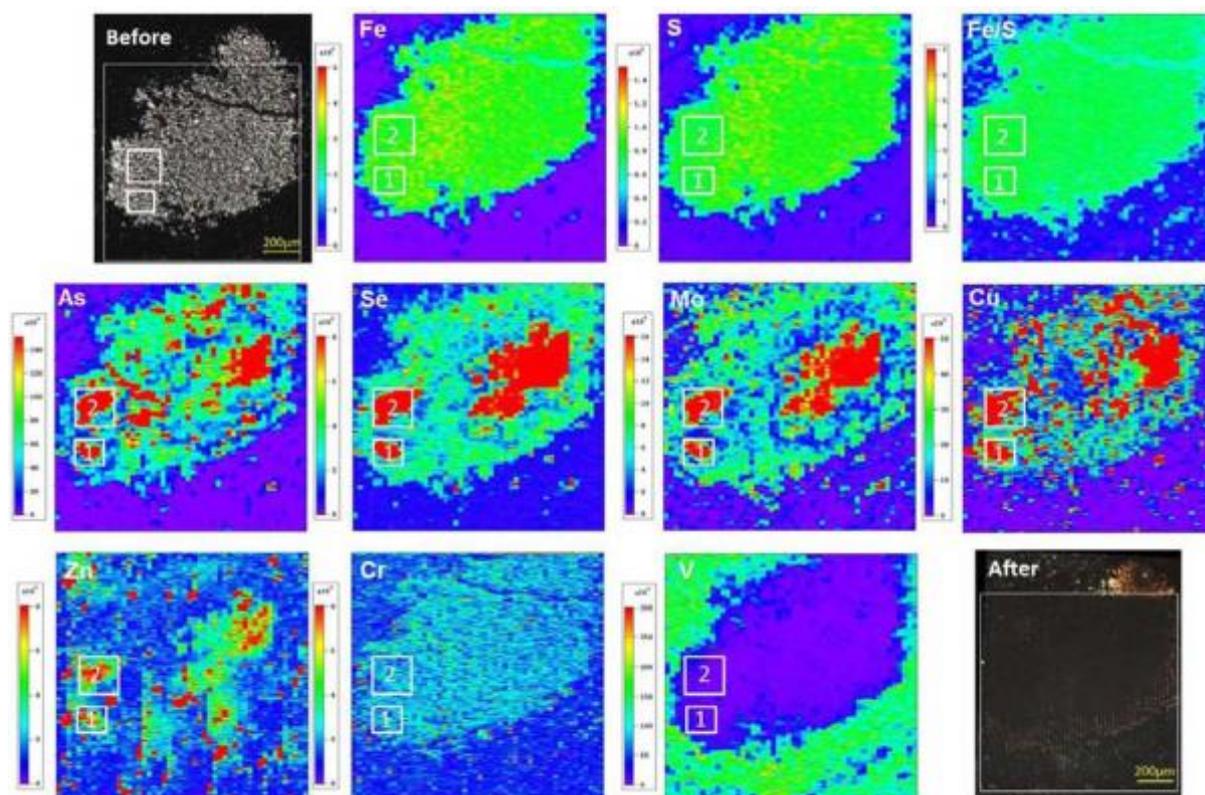


Figure 1 *In situ* imaging of nine elements and Fe/S ratio in one pyrite. Red represents high contents, while purple means low contents. The pyrite was from the black shale of the Doushantuo Formation. Nine elements and nearly 50 thousands valid data were acquired in a 1 mm × 1 mm scanning area within the total analyzed time of 1.5 h.

Conclusions

A method of rapid *in situ* scanning and multi-elements 2D imaging on single mineral particle was developed using LA-ICP-MS. The low RSD of the count ratio of Fe/S means good homogeneity of this pyrite and good stability of this analysis method. *In situ* micro-analysis of multi-elements on single pyrite provide more direct and accurate visual data for these diminary redox conditions and post-depositional alterations. This method will further help the popularization of LA-ICP-MS in the studies of paleoenvironment, source rocks evaluation, and fluid accumulation.

Reference

- [1] Raiswell R, Canfield D E. *Am. J. Sci.*, **1998**, 298(3): 219-245.
- [2] Schippers A, Jørgensen B B. *Geochim. Cosmochim. Acta*, **2002**, 66(1): 85-92.
- [3] Burger M, Gundlach-Graham A, Allner S, *et al. Anal. Chem.*, **2015**, 87(16): 8259-8267.
- [4] Large R R, Halpin J A, Danyushevsky L V, *et al. Earth Planet. Sci. Lett.*, **2014**, 389: 209-220.