Deconvolution of the composition of fine-grained pyrite in sedimentary matrix by regression of time-resolved LA-ICP-MS data

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ABSTRACT

Pyrite is a common mineral in sedimentary rocks and is the major host for many chalcophile trace elements utilized as important tracers of the evolution of the ancient hydrosphere. Measurement of trace element composition of pyrite in sedimentary rocks is challenging due to fine-grain size and intergrowth with silicate matrix and other sulfide minerals. In this contribution, we describe a method for calculation of trace element composition of sedimentary pyrite from time-resolved LA-ICP-MS data. The method involves an analysis of both pyrite and pyrite-free sediment matrix, segmentation of LA-ICP-MS spectra, normalization to total, regression analysis of dependencies between the elements, and calculation of normalized composition of the mineral. Sulfur is chosen as an explanatory variable, relative to which all regressions are calculated. The S content value used for calculation of element concentrations from the regressions is calculated from the total, eliminating the need for independent constraints. The algorithm allows efficient measurement of concentrations of multiple chalcophile trace elements in pyrite in a wide range of samples, including quantification of detection limits and uncertainties while excluding operator bias. The data suggest that the main sources of uncertainties in pyrite composition are sample heterogeneity and counting statistics for elements of low abundance. The analysis of regression data of time-resolved LA-ICP-MS measurements could provide new insights into the geochemistry of the sedimentary rocks and minerals. It allows quantification of ratios of elements that do not have reference material available (such as Hg) and provides estimates on the content of non-sulfidic Fe in the silicate matrix. Regression analysis of the mixed LA-ICP-MS signal could be a powerful technique for deconvolution of phase compositions in complex multicomponent samples.

Keywords: Pyrite, LA-ICP-MS, regression, detection limits, analytical geochemistry, chalcophile elements, Paleo-ocean proxy; Understanding Paleo-ocean Proxies: Insights from In Situ Analyses

INTRODUCTION

Pyrite is a common mineral in sedimentary rocks and can host a wide range of trace elements (e.g., Abraitis et al. 2004; Gregory et al. 2015). Trace element compositions of pyrite have been applied to various geochemical problems ranging from tracing chemistry of paleo oceans, nutrient availability and evolution of the atmosphere and biosphere (Huerta-Diaz and Morse 1990; Large et al. 2014, 2015b, 2015a; Gregory et al. 2015; Zhou et al. 2017; Rickard et al. 2017), and to the release of economically important elements during metamorphism (Pitcairn et al. 2010; Large et al. 2012; Tomkins 2013; Goldfarb and Groves 2015). The content of pyrite and its trace element composition in sedimentary rocks can be measured by selective digestions by acids (Huerta-Diaz and Morse 1990; Raiswell et al. 1994); however, such methods yield average compositions of pyrite and cannot resolve different generations of the mineral. The challenges for in situ analysis of pyrite in sedimentary rocks include fine-grain size, low concentration levels of many key elements, abundant inclusions of matrix minerals, and intergrowth with other sulfides (Fig. 1).

LA-ICP-MS is a powerful analytical technique commonly applied for the analysis of pyrite (e.g., Large et al. 2009). Typical analyses are performed by a round laser spot with diameter 20–30 μm but in many sedimentary rocks the size of pyrite is smaller than lateral spatial resolution of the laser (Fig. 1). Analysis could be performed with smaller spot sizes, however, this is rarely practical due to decrease of signal and increase of downhole elemental fractionation (Gilbert et al. 2014a).

Analysis of sedimentary pyrite by LA-ICP-MS results in the acquisition of complex mixed data with variable contributions from phases other than pyrite (Fig. 2). There are two principal methods of recalibration of the mixed compositional data: subtraction and regression (Stepanov et al. 2012). When applied to pyrite, both methods involve analysis of matrix of the rock with minimal pyrite content and mixtures of the pyrite and matrix (Large et al. 2014). For the subtraction method, the integration interval with high pyrite content is selected from the transient