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Accurate determination of trace amounts of phosphorus in geological samples by inductively coupled plasma atomic emission spectrometry with ion-exchange separation

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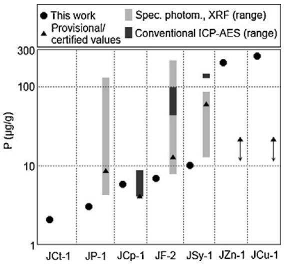
HIGHLIGHTS

- We set up an effective ICP-AES procedure for determining trace P in rock samples.
- Some certified values of P for reference rock samples were proved to be doubtful.
- Accurate and reliable data were presented for a suite of geological reference rocks.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to determine trace amounts of phosphorus in geological and cosmochemical rock samples, simple as well as reliable analytical schemes using an ICP-AES instrument were investigated. A (conventional) ICP-AES procedure could determine phosphorus contents at the level of several 100 $\mu g\,g^{-1}$ with a reasonable reproducibility (<10% for 200 $\mu g\,g^{-1}$; 1σ). An ICP-AES procedure coupled with matrix-separation using cation and anion exchange resins could lower the quantification level down to 1 $\mu g\,g^{-1}$ or even lower under the present experimental conditions. The matrix-separation ICP-AES procedure developed in this study was applied to twenty-one geological reference samples issued by Geological Survey of Japan. Obtained values vary from 1250 $\mu g\,g^{-1}$ for JB-3 (basalt) to 2.07 $\mu g\,g^{-1}$ for JCt-1 (carbonate). Matrix-separation ICP-AES yielded reasonable reproducibility (less than 8.3%; 1σ) of three replicate analyses for all the samples analyzed. In comparison of our data with certificate values as well as literature or reported values, there appear to be an apparent (and large) discrepancy between our values and certificate/reported values regardless of phosphorus contents. Based on the reproducibility of our data and the analytical capability of the matrix-separation ICP-AES procedure developed in this study (in terms of quantification limit, recovery, selectivity of an analyte through pre-concentration process, etc.), it is concluded that certified values for several reference standard rocks should be reevaluated and revised accordingly. It may be further pointed that some phosphorus data reported in literatures should be critically evaluated when they are to be referred in later publications.

1. Introduction

Most geological and cosmochemical samples have moderately low contents of phosphorus, being in the range of 10^{-3} to 10^{-6} g g^{-1}. Phosphorus in such rocky samples is mostly present as apatite [$Ca_5(PO_4)_3(F,Cl,OH)$] and melilite [$Ca_9MgNa(PO_4)_7$]. These phosphate minerals are well known to be major carriers of rare

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earth elements (REEs), thorium and uranium (e.g., [1,2]). REEs have similar chemical and physical properties, including low solubility and immobility in the terrestrial crust, and are generally in the +3 valence state over a wide range of oxygen fugacity. However, cerium can be partly or wholly in the +4 state at the oxygen fugacity of the Earth's surface while europium can be partly in the +2 state at the low oxygen fugacity in the Earth's interior. This gives abundance anomalies for these elements in a so-called REE abundance pattern, a plot of relative REE abundances normalized to chondritic values, which is highly informative in studying geological and cosmochemical evolution processes (e.g., [3,4]). Therefore, REEs and phosphates as their carrier mineral phases are highly concerned in geochemistry and cosmochemistry.

Several instrumental methods have been successfully applied to geological samples for the determination of phosphorus. Spectrophotometric (colorimetric) method has been often applied for determining phosphorus (e.g., [5]). It usually provides precise results, but its sensitivity is not sufficient for low abundance of phosphorus. Neutron activation analysis (NAA) provides high analytical sensitivity, because of high neutron cross section of ^{31}P(n,γ)^{32}P reaction and a reasonably long half-life of ^{32}P (14.5 d) [6]. However, complex and prolonged radiochemical procedures for the radiochemical purification of ^{32}P from interfering radioactive impurities are required and, hence, it is ineffective for routine analysis of phosphorus. X-ray fluorescent analysis (XRF) is convenient because no need is required for the separation of phosphorus from matrix elements (e.g., [7,8]). XRF generally provides reasonably reliable data for relatively high contents of phosphorus, but it cannot work equally when a low content of phosphorus needs to be determined. In XRF, reference samples in place of reagent standards are used for quantification, which may yield a serious problem when certified values for such reference samples are not reliable.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) has been often used in analyzing geological samples for major, minor and trace elements [9–12]. ICP-AES has such analytical advantage as high sensitivity for a variety of elements, wide linear dynamic range of calibration, freedom from chemical and ionization interferences, and capability of simultaneous or sequential multi-element determination. In determining phosphorus, ICP-AES can give us higher sensitivity than XRF and spectrophotometry in principle. This method, however, has some disadvantages such as serious matrix effects with major constituent elements in samples, stray light or scattering due to strong emission lines, and continuous emission backgrounds, which become severe problems in the determination of trace elements [13,14]. In order to minimize such disadvantages caused by matrix effects, so-called matrix matching procedure is performed, where concentrations of major constituent elements in unknown sample solutions are matched with those in standard solutions as closely as possible. The background change at the wavelength of interest can be monitored by changing concentrations of major elements concentrations. In order to assess the background contribution in this way, different sets of standard solutions need to be prepared in accordance with individual sample matrices. For analyzing geological and cosmochemical samples having complicated and variable matrix compositions, it is not practical to apply these procedures to routine and rapid analyses of those samples for trace phosphorus.

In the present work, we aimed to develop the ICP-AES procedure for the determination of phosphorus in geological samples. To reduce or eliminate above-mentioned analytical problems involved in conventional (dissolution and injection) ICP-AES procedure, we introduced a simple separation procedure using ion exchange resins to reduce the matrix element abundance before assaying to ICP-AES. In order to evaluate the analytical capability of ICP-AES with ion-exchange separation, geological reference rocks (in powder) were analyzed by the proposed ICP-AES procedure (hereafter, matrix-separation ICP-AES in this paper). Some samples were also analyzed by ICP-AES without matrix separation (hereafter, mentioned as conventional ICP-AES). By comparing data obtained by matrix-separation ICP-AES with those by conventional ICP-AES as well as literature/reported values for geological reference rocks, we evaluate the analytical capability of both types of ICP-AES procedures conducted in this work. In addition, we also evaluate literature/reported values of phosphorus by comparing all available data including our new data. Furthermore, new data are presented for several geological reference rocks which were recently issued and for which few (or no) data of phosphorus have been reported.

Table 1
ICP-AES instrumentation and operation conditions applied in this study.

ICP-AES instrument	SSI-Nanotechnology model SPS 7800
Plasma conditions	
RF frequency	27.12 MHz
RF power	1.2 kW
Coolant gas flow	14.5 L min^{-1}
Auxiliary gas flow	0.4 L min^{-1}
Carrier gas flow	0.4 L min^{-1}
Observation height	15 mm above work coil
Nebulizer	Concentric type
Sample uptake rate	2.0 mL min^{-1}
Monochromator	Order separator + Echelle spectrometer
Order separator	
Mount	Seya-Namioka mounting
Focal length	20 cm
Grating	Holographic concave grating
Grating line number	1200 grooves mm^{-1}
Echelle spectrometer	
Mount	Czerny-Turner mounting
Focal length	30 cm
Grating	Echelle plane diffraction grating
Grating line number	3600 grooves mm^{-1}
Integration	3 s
Repetition	5 times
Selected wavelengths	
Analyte	P(I) 213.618 nm
Internal standard	Be(I) 234.861 nm
Concentrations of working solutions	
P	2.00 μg g^{-1}
Be	0.200 μg g^{-1}

2. Experimental

2.1. Instrumentation and operating conditions

An ICP-AES instrument of SPS 7800 (SSI-nanotechnology products, Chiba, Japan) with a concentric type nebulizer was used in this study. The instrumental components and operating conditions applied are summarized in Table 1. An analytical wavelength (213.618 nm) for phosphorus given in Table 1 was chosen in consideration of an emission signal intensity (which should be maximal) and spectral interferences (which should be minimal) [8,15]. The conditions were kept constant throughout this work even for the case of the matrix-separation ICP-AES procedure. A straight line joining points for blank and working standard solutions was drawn for a calibration curve. Beryllium was adopted as an internal standard element [16]. In choosing an internal standard element, germanium and boron were also evaluated in addition to beryllium. Emission lines at 238.861 nm, 208.957 nm and 209.426 nm were used for beryllium, boron and germanium, respectively, in the evaluation experiment. Among these three elements, beryllium gave the highest sensitivity. An emission line of beryllium at 234.861 nm may be interfered by iron, which has emission lines at 234.810 nm