CHEMOMETRIC EVIDENCE FOR SR AND RB ISOTOPES DUE TO THE SPECIFIC SOIL CHEMISTRY IN DIFFERENT GEOGRAPHICAL REGIONS

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Abstract

Strontium and rubidium are the commonly used metals for isotope-ratio analysis. Moreover, this geochemical marker varies between different rock types and formations. The $^{87}Sr/^{86}Sr$ ratio has been shown to vary widely in surface rocks, so any Sr released into soils, rivers, and groundwater has an isotopic signature that reflects its source. Sr and Rb isotopes have also been used to trace agricultural products, which have incorporated Sr, along with Ca, from soils incorporating the Sr-isotope ratios of the underlying rocks. The specific conditions in the soil represent characteristic conditions of the environment which is reflected in a certain way in the plants. Despite uncertainty about the organic compounds in a sample, the content of selected elements (trace and rare earth elements, REEs) reflects the growing conditions in the environment. For that instance, in the present research, we will give focus on the inorganic compounds' identifications, due to the more stable response to the lithogenic nature of the soil-plant interaction.
For the present study, the target isotopes were ^{88}Sr, ^{87}Sr, ^{86}Sr, and ^{85}Rb. The isotope analysis was conducted with the application of ICP-MS, following the protocol provided in the EPA METHOD 6020. In the validation process, no significant interference occurred that could affect the sensitivity of the measurement of the selected isotopes. Data analysis has been applied to the comparative issues between Sr and Rb content in soil from North Macedonia and selected regions in China. Moreover, the same chemometric model was applied for data analysis for selected plant species for both regions. Data analyses has improved the significant differences within the element contents and ratios as well between both geographical regions.

Keywords: Isotopic measurement, Rubidium, Strontium, Soil chemistry, Geochemical markers, ICP-MS.

1. Introduction

Strontium and rubidium are the commonly used metals for isotope-ratio analysis (Ucuncuoglu, 2020; Balabanova & Fan, 2024). Moreover, this geochemical marker varies between different rock types and formations (Knoepp, DeBano & Neary, 2005). The $^{87}Sr/^{86}Sr$ ratio has been shown to vary widely in surface rocks, so any Sr released into soils, rivers, and groundwater has an isotopic signature that reflects its source (Sparks, Singh & Siebecker, 2022). Sr and Rb isotopes have also been used to trace agricultural products, which have incorporated Sr, along with Ca, from soils incorporating the Sr-isotope ratios of the underlying rocks (Sharp, 2017).
The specific conditions in the soil represent characteristic conditions of the environment which is reflected in a certain way in the plants (Kelly, Heaton, & Hoogewerff, 2005). Despite uncertainties about the organic compounds in a soil-plant interaction system, the content of selected elements (trace and rare earth elements, REEs) reflects the growing conditions in the environment. For that instance, in the present research, we will give focus on the inorganic compounds' identifications, due to the more stable response to the lithogenic nature of the soil-plant interaction.
Multi-isotope or single-isotope ratios (e.g., strontium, lead and rubidium) can provide unique, representative fingerprints that make it possible to discriminate the origin of plant food samples (Katerinopoulou, Kontogeorgos, Salmas, Patakas, & Ladavos, 2020). Over the past decade,

with the development of new advanced analytical techniques we can successfully retrieve elemental and isotopic compositions, of any given food sample and determine the geographic origin successfully (Liu, Chen, Liao, Zhao, Yang, & Wang, 2021). The growing concern of the consumers stimulated scientific research and publications in recent years, including multi-element and isotope-ratio methods of analysis in food authentication after statistical evaluation of the data (Fan, Yan, Wang, Liang, Kong, Li & Balabanova, 2021; Balabanova & Fan, 2024). The $^{87}Sr/^{86}Sr$ ratio therefore varies between different rock types and formations. Since Rb is an alkali metal and Sr is an alkaline earth, these elements behave differently in geological processes, creating large variations in Rb/Sr, and, so, large variations in $^{87}Sr/^{86}Sr$ (Sparks, Singh & Siebecker, 2022). The $^{87}Sr/^{86}Sr$ ratio has been shown to vary widely in surface rocks, so any Sr released into soils, rivers, and groundwater has an isotopic signature that reflects its source (Ayuso & Foley, 2018). Sr isotopes have also been used to trace agricultural products, which have incorporated Sr, along with Ca, from soils incorporating the Sr-isotope ratios of the underlying rocks (Fairweather-Tait & Dainty, 2002; Nakano, Yokoo, Nishikawa, & Koyanagi, 2004; Katerinopoulou, Kontogeorgos, Salmas, Patakas & Ladavos, 2020).

The aim of this case study was to evaluate strontium and rubidium lithogenic occurrence in soil *vs.* the geochemical impact to the herbal plant yellow wort (*Blackstonia perfoliata*). Total content and isotope ratios were determined regarding regional occurrence in the area of the Republic of North Macedonia, compared to selected areas from China. Furthermore, the elements' isotope ratios were correlated with the average data for the corresponding elements in soil samples (top layer). Samples of yellow wort (*Blackstonia perfoliata*) were used for comparative analysis to the same species obtained in market in China.

2. Material and methods

2.1. Sample collection and preparation: Sample collection has been conducted in the South-eastern region in the country. For collection of each plant species, we have choose 5 network points, from each location two differ samples were collected. In total, 2 samples from each location, we collected 10 samples for each species. The samples have been cleaned form dust, air-dry to constant mass, then homogenized and subjected to acid digestion. For digestion of samples, the microwave digestion system (model Mars, CEM) was applied. Precisely was measured 0.5 g of each sample and placed in Teflon digestion vessels. In total, 5 mL concentrated nitric acid, HNO_3 (69%, 108 m/V), and 2 mL hydrogen peroxide, H_2O_2 (30%, m/V) were added. The Teflon vessels were carefully closed and placed in a microwave digestion system. Samples were digested in two steps for total dissolving at 180°C. After the digestion method was finished, digested samples were quantitatively transferred into 25 mL volumetric flaks, following the protocol of EPA METHOD 3052.

2.2. Chemometric analysis: The isotope analysis was conducted with application of inductively coupled plasma with mass spectrometry (ICP-MS), following the protocol provided in the EPA METHOD 6020. ICP-MS technique was used due to the high sensitivity (LOD <0.1 ppb), as well for the improved accuracy and reproducibility in isotope measurements.

Target masses for strontium were 86, 87 and 88, while for rubidium was selected the 85 mass as the most abundant isotope. In the validation process, no significant interference occurred that could affect the sensitivity of the measurement of both elements. Two modes of analysis have been applied: a) No gas mode (only argon gas is applied) and b) Helium mode (helium gas was applied as interference removal gas). Optimization settings have been optimized as presented in Table 1.

Table 1. The optimized conditions of the instrument ICP-MS, model 7850, Agilent Technologies

Peristaltic pump	10-roller, 3 channels	
Nebulizer	MicroMist (borosilicate glass)	
Spray chamber	Scott-type double-pass (quartz)	
Torch	Dimension 2.5 mm id injector, Shield Torch system: Horizontal and vertical position: ±2 mm, in 0.1 mm steps : Sampling depth: 3 to 28 mm, in 0.1 mm steps	
Ion lens	Extraction lens, off-axis Omega lens	
Octopole reaction system	He collision cell gas line	
Mass analyzer	Quadropole, frequency 3 MHz hyperbolic - mass range 2-260 u	
Vacuum system	Three-stage differential vacuum system	
Isotope ratio Precision $^{07}Ag/^{109}Ag$	<0.05% RSD	
Stability 20 min/2 hr	<2.0% RSD/<3.0% RSD	
Background m/z 9	<0.2 cps	
Interference reduction factor (Performed in a matrix of 2% HNO_3 + 0.5% HCl.) $^{59}Co/^{51}ClO$ >30		

3. Results and Discussion

3.1. ICP-MS method validation: Standard QA/QC variables were used to prove the validity of the method. All set parameters indicate satisfactory analytical sensitivity, accuracy, and precision of analysis. During the measurements, dual gas phases were used for the analytes: a) normal mode using basic carrier gas argon, and b) helium mode, using optional helium gas. From the parameters obtained, it can be determined that the Normal (No gas) analytical mode provides greater sensitivity and linearity of the applied method. Calibration data for the analyzed isotopes has been optimized within the range of 5 µg/L to 100 µg/L (Figure 1). The generated curves were within the satisfactory analytical indication (R>0.999). Cps signals of 10 µg/L calibration standard were used as precision indicator. Satisfactory stability was obtained for CCV Recovery >80% (Figure 2).

Table 2. Data summary of the instrumental condition and validation of the applied methodology

| Element	Isotope	ORS mode	Integration Time (s)	Linear range (µg/L)	Slope	Intercept	R	LOD (µg/L)	LOQ (µg/L)
Sr	86	Normal	0.1	1-50	1.526	10.93	0.9998	0.27	0.872
Sr	86	Helium	0.5	1-100	0.0092	-6.271	0.9994	0.15	0.519
Sr	87	Normal	0.1	1-100	2.125	391.2	0.9999	0.12	0.401
Sr	87	Helium	0.5	0.5-50	1.150	2.483	0.9992	0.096	0.321
Sr	88	Normal	0.1	5-50	1.680	10.27	0.9995	0.77	2.572
Sr	88	Helium	0.5	1-50	2.019	-5.94	0.9991	0,10	0.334
Rb	85	Normal	0.1	1-100	0.058	-0.0063	0.9994	0.29	0.969
Rb	85	Helium	0.5	0.1-10	0.0079	0.0022	0.9991	0.0033	0.011
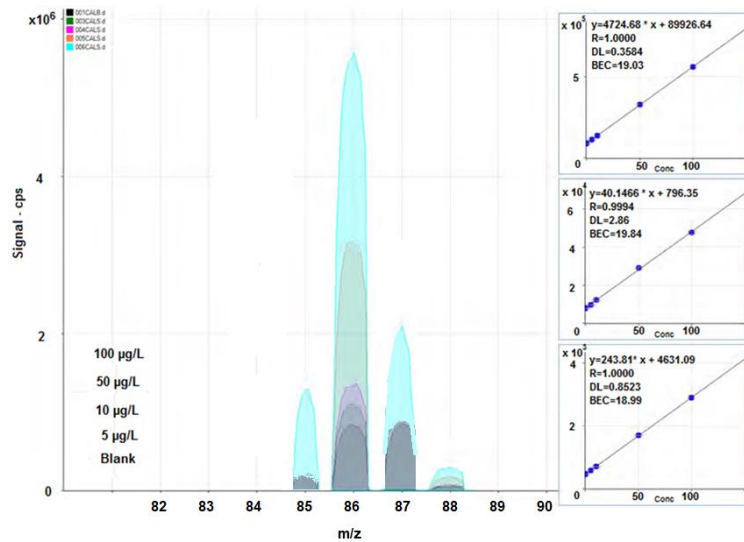
Figure. 1. Calibration data for the analyzed isotopes, within the range of 5 µg/L to 100 µg/L.
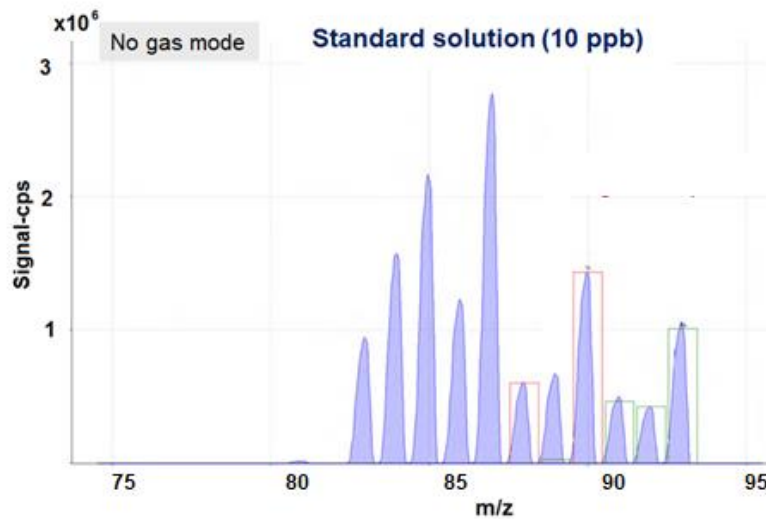

Figure 2. Cps signals of 10 µg/L calibration standard

3.2. Data Analysis: The total content of rubidium and strontium was determined in herbal species collected in North Macedonia. A comparative analysis was made on the species Yellow wort (Blackstonia perfoliata), available in Macedonia vs. China (Table 2). In order to determine the potential of soil enrichment with rubidium and strontium due to the influence of the contents of these elements in the bioaccumulation, the average values for these two elements in the soil are given in comparison in both countries. From the data on the content of rubidium and strontium in the soil, it indicates a greater enrichment of these elements in the soils in North Macedonia, compared to the soils in China.

Table 2. Total content of rubidium and strontium in herbal samples-comparative analysis (N=10)

Sample	Data description	Rb (mg/kg)		Sr (mg/kg)	
		Range	Average	Range	Average
Yellow wort - NMK	Blackstonia perfoliata	12.6-133	54.3	10.8 – 210	77.4
Yellow wort - Ch	Blackstonia perfoliata	0.78 – 77.8	21.4	29.7 – 413	116
Soil data – North Macedonia, NMK	Data for automorphic soil for North Macedonia (Stafilov & Šajn, 2016)	58.9 - 1930	534	21 - 1400	140
Soil data - China, CH	Data for agricultural soil in China (Nakano, Yokoo, Nishikawa & Koyanagi, 2004).	39-573	201	67.3 – 116	98.6

Geochemical markers of isotopic ratios of rubidium and strontium were determined in order to determine the correlation of the bioaccumulation of rubidium and strontium in relation to the specific soil chemistry in different regions (North Macedonia vs. China), for the Blackstonia perfoliata herbal specie. According to the obtained results, there is a significant difference in the isotopic ratios of rubidium and strontium isotopes (Table 3). This indicates that these parameters can represent significant segments in determining the geographic origin of species.

Table 3. Data summary for the Rb and Sr isotopes ratios

Sample	N	^{85}Rb/^{86}Sr	^{86}Sr/^{87}Sr	^{87}Sr/^{88}Sr
Yellow wort - NMK	10	1.471 ± 0.26	0.811 ± 0.16	2.087± 0.22
Yellow wort – Ch [2]	10	2.852 ± 0.85	0.872± 0.25	1.903± 0.18

The target isotopes ^{88}Sr, ^{87}Sr, ^{86}Sr, and ^{85}Rb and isotopic ratios ^{86}Sr/^{87}Sr and ^{87}Sr/^{88}Sr) showed a significant difference in the same species and different geographical regions. This indicates that isotopic ratios of rubidium and strontium can be used as a geochemical marker to determine the geographical authenticity of herbal species. However, isotopic ratios, by themselves, do not represent an isolated geochemical marker. This indicates the multi-cluster nature in determining the geographic origin of plant foods.

4. Conclusions

Geochemical markers represent a significant factor in determining the geographical authenticity of plant foods. This research was aimed at the possibility of using rubidium and strontium isotopes as typical indicative markers in correlation with soil chemistry. The analysis indicated that the natural and anthropogenic indication of these two elements, strontium and rubidium in the soil does not provide significant geochemical marking for the plant species. Strontium and rubidium are important lithogenic markers of important chemical processes in the soil. This research has shown that the total content of elements is not a stable indicator of the typical geochemistry of soils in different geographical regions. However, the isotopic relations in the soil-plant system showed high stability in the expression of geochemical markers in different geographical areas. In this way, this chemometric marker can be used in the authentication of plant foods.

Acknowledgements

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