Implementation of a Ti(III) reduction method for the determination of nitrogen (δ15N) and oxygen (δ18O) isotopic composition of nitrate

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affected the AMR during Early and Middle Miocene. The CPR presumably caldera-forming eruptions, each potentially expelling 10s to 100s of km^3 of pyroclastic material (tephra), produced widely spread ignimbrites, best exposed in northern and southwestern Pannonian Basin. These eruption products were also likely distributed by tropospheric easterly trade winds towards the southwest, and were finally deposited as ash fallouts in various distal sedimentary archives. These basinal settings ranged from terrestrial to marine, depending on the evolution of discrete basins within the CPR, as well as in the Alps, the Appenines, the Dinarides and the Aegean-Balkan regions. These volcaniclastic deposits could represent synchronous event marker horizons, and therefore represent potentially powerful tools for constraining the space-time evolution of the region. Furthermore, karstic environments such as the Dinarides could have been distal sinks for fallout tephra sourced from voluminous AMR silicic eruptions during Cenozoic. Under specific paleoenviromental and paleoclimatic conditions, these volcanic materials may have served as the main part of the protolith for karst bauxite formation, and therefore the spatio-temporal distribution of these volcaniclastic rocks has significant bearing on understanding continental paleoclimate for the region.

To address outstanding questions regarding regional Early–Middle Miocene silicic volcanism and bauxitization, we examined volcaniclastic deposits, including ignimbrites and fallout tuffs, and karst bauxites, scattered across the AMR. In order to best capture the full potential dispersion of these volcanic events, sampling included localities within the CPR, as well as distal localities in the Dinaride Lake System, the North Alpine Foreland Basin, and northern Appenines. We utilized volcanological, mineralogical and petrological screening, *in situ* and high-precision U-Pb zircon geochronology, zircon chemistry and Lu-Hf isotopic composition, as well as volcanic glass major and trace elemental and isotopic compositions. Our goals are: 1) to define the ages and temporal relationships of Lower and Middle Miocene volcaniclastic horizons; 2) to reliably evaluate the provenance and correlativity of eruption products and their potential origin from individual widespread silicic eruptions, contributing to regional tephrostratigraphic and volcanological reconstructions; 3) to gain insight into petrogenesis for CPR silicic magmas with time; 4) to constrain the timing, origin, provenance and paleoclimatic implications of karst bauxites underlying the Dinaride Lake System.

IMPLEMENTATION OF A TI(III) REDUCTION METHOD FOR THE DETERMINATION OF NITROGEN (δ15N) AND OXYGEN (δ18O) ISOTOPIC COMPOSITION OF NITRATE

IMPLEMENTACIJA TI(III) REDUKCIJSKE METODE U SVRHU ODREĐIVANJA IZOTOPNOG SASTAVA DUŠIKA (δ^{15}N) I KISIKA (δ^{18}O) IZ NITRATA

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Pollution of surface and groundwater by nitrate (NO3–) is one of the most serious environmental problems worldwide. The crucial isotopes for the sources and dynamics of nitrogen (N) in the aquatic environment are the nitrogen and oxygen isotope data of NO3-. The stable isotope of nitrogen (δ15N) in dissolved nitrate has been most commonly used to estimate NO3- sources in groundwater. However, measurement of the stable nitrogen isotope alone does not provide a definitive determination of NO3– origin, so the stable oxygen isotope (δ18O) must be used, i.e., a dual isotope approach. The analysis of NO3- for both δ15N and δ18O has been made possible by the development of various laboratory methods for sample preparation, each with its own advantages and disadvantages. Current methods such as the cadmium reduction method (Azide method) or the bacterial denitrification method require toxic chemicals or anaerobic bacterial cultures for NO3- reduction to N2O gas. In 2019, a new sample preparation method was developed (ALTABET *et al.*, 2019), which is a simple one-step conversion method that utilizes Titanium(III) chloride reagent to reduce NO3– to N2O within septum sample vials:

$$2NO_3{}^-{}_{(aq)} + 8Ti^{+3} + 10H^+ \rightarrow N_2O_{(g)} + 8Ti^{+4} + 5H_2O$$

A single sample preparation takes only a few minutes, followed by a 24-h reaction that generates N_2O headspace gas for δ^{15}N and δ^{18}O analysis by IRMS or laser spectrometer. Briefly, Ti(III) chloride is preconditioned with zinc metal powder about 30 minutes before sample preparation to ensure efficiency by removing Ti(IV). The volume ratio of sample to reagent for groundwater samples is 10:1, 20:1, or 40:1. We found that higher amounts of Ti(III) reagent (10:1 and 20:1 ratios) gave slightly more accurate $\delta^{18}O$ values. The $\delta^{15}N$ values were most inaccurate at ratios of 10:1 and 40:1, but were more accurate at a 20:1 ratio of sample to reagent. Therefore, a 20:1 ratio is considered practical for further measurements. To ensure consistent N_2O yields and ^{15}N and ^{18}O results, the N concentrations in each vial must be identical for all samples, laboratory controls, and standards. This is achieved by adding an appropriate volume of sample, degassed deionized water, 10% hydrochloric acid, and the preconditioned Ti(III) chloride reagent. The $\delta^{15}N$ and $\delta^{18}O$ isotope analyses were performed using the Isotopic N_2O Laser Analyzer (GLA451-N2OI3), which was acquired as part of the CRO7002 project “Using Nitrogen and Oxygen Stable Isotopes in the Determination of Nitrate Origin in the Unsaturated and Saturated Zone of the Velika Gorica Wellfield”, funded by the International Atomic Energy Agency (IAEA). The described method is very competitive (simple, faster and more cost-effective) compared to the existing methods currently used in most laboratories worldwide, and its implementation at the Faculty of Mining, Geology and Petroleum Engineering (University of Zagreb) enabled the development of new research on the estimation of the origin of nitrate in groundwater.

ALTABET, M.A., WASSENAAR, L.I., DOUENCE, C., ROY, R. (2019): A Ti(III) reduction method for one-step conversion of seawater and freshwater nitrate into N_2O for stable isotopic analysis of $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$. Rapid Communications in Mass Spectrometry, 33/15, 1227–1239.

CONTROL VARIABLES OF THE WATER GEOCHEMISTRY IN THE RULL CAVE, ALICANTE, SPAIN KONTROLNE

VARIJABLE U GEOKEMIJI VODE U ŠPILJI RULL, ALICANTE, ŠPANJOLSKA

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The geochemistry of the water stored in underground karstic caves is the product of a complex interaction between climate, soil, unsaturated zone, and the cave inner atmosphere. This geochemical evolution, that begins with rainfall, has a fundamental role in soil configuration, formation of karstic secondary porosity, and the development of caves and speleothems, which constitute key tools for the study of paleoclimate.

The aim of our research is to estimate the controlling factors on cave water chemistry, and to infer some of the processes acting through the infiltration from soil to cave. The studied area is the Rull Cave (SE Spain), developed in marls and limestones under a semi-arid climate. The cave has an average air temperature of 16.2 °C and undergoes annual ventilation cycles, associated with the air density differences between outdoor and indoor atmospheres. During summer, cave air remains stagnant, with higher CO2 concentrations (over 3000 ppm). During winter, through advective gaseous flux, CO2 drops to 478 ppm (PLA *et al.*, 2023). The water inside the cave can be found as drippings, or as gours (cave pools) in chemical equilibrium with the inner atmosphere and its gaseous composition.

To approach the aim of this study, the parameters and elements measured in the water sampled from the largest gour (hereinafter “cave water”) were compared with those of the water that has passed through the soil (hereinafter “soil water”). The comparison was made for April and June 2022, considered representative of the wet and dry seasons, respectively.

Soil water was obtained by carrying out two leaching experiments in the laboratory, inserting rainfall-like water (pH 5.5, electric conductivity≈40 µS/cm) into a column of 600 g of soil sampled above the cave, and collecting the water below. We recreated the soil conditions at the selected months. During April (spring of 2022), heavy rains occurred on a soil that is at 8 °C and has held a high volumetric water content throughout the winter (VWC $> 25\ m^3/m^3$). During June (summer of 2022), the scarce rainfalls occurred on dry soil (VWC $< 5\ m^3/m^3$), at 25 °C.