

Stable isotope studies of the water cycle and terrestrial environments: introduction



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This Special Publication is devoted to Earth surface environmental reconstructions and environmental changes that may be deciphered and modelled using stable isotopes along with mineralogical/chemical, sedimentological, palaeontological/biological and climatological methodologies. The volume is divided into two sections, both of them using stable isotopes analysis (δD , $\delta^{18}O$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$ and clumped isotopes Δ_{47}) in various samples and phases as the main research tools. The first section is devoted to studies focusing on the distribution of isotopes in precipitations, groundwaters, lakes, rivers, springs and mine waters, and their relationship with terrestrial environments at regional to continental scale. In relation to this, the second section includes case studies from a range of continental settings, investigating cave deposits (stalagmites and bat guano), animal skeletons (dinosaurs, alligators, turtles and bivalves), present and past soils (palaeosols) and limestones. The sections focus on the interaction between the surficial water cycle and underground water storage, with deposits acting as archives of short- to long-term climatic and environmental changes. Examples from the Early Cretaceous–present time come from Europe, Asia, Africa and America.

The contributions included in this volume present a broad range of studies grouped into ‘Water Cycle and Terrestrial Environments’. In the first part of the volume, investigated sites are situated in Europe (France, Croatia, Romania, Austria and Finland), Asia (India and Iran), Africa (Ethiopia) and the Americas (USA, Canada and Brazil). Samples were collected from rain, river and tap water (France, Romania, Canada, India and Ethiopia), springs (Romania), karst lakes (Croatia), and mining waters

(Finland and Romania). In the second section, investigated environments and materials span from recent, Quaternary ones and then back in time to the Eocene and the Upper–Lower Cretaceous. Studied material includes stalagmites, bat guano deposits, bivalves, soil calcretes, littoral limestones, dinosaur and crocodylian teeth, and turtle osteocutes.

The concept and design of this Special publication was initially rooted in several scientific sessions and open discussions focusing on topics such as isotopic studies in the water cycle and terrestrial environments; these sessions being held each year between 2009 and 2019 within the framework of the European Geoscience Union (EGU) in Vienna. Contributions presented at the European Society for Isotope Research (ESIR) are also included.

Water cycle

Lécuyer *et al.* (2020) compiled, at a regional scale, monthly δ^2H and $\delta^{18}O$ values of precipitation from IAEA European stations. Local Meteoric Water Lines (LMWL) allow the slope (S) for each station to be determined. The study correlates S with longitude (Φ), relative air humidity (RH) and air temperature variations. A slope with a value of S close to 9 is expected to reflect hydrogen and oxygen isotope fractionation close to equilibrium during condensation of water vapour, in this way isotopic equilibrium during condensation is estimated.

Nagavciuc *et al.* (2020) analysed the influence of the Carpathian Mountains, Romania, on the variability of stable isotopes in precipitation by employing a combination of measured and modelled data.

From: Bojar, A.-V., Pelc, A. and Lécuyer, C. (eds) *Stable Isotope Studies of the Water Cycle and Terrestrial Environments*. Geological Society, London, Special Publications, **507**, <https://doi.org/10.1144/SP507-2021-32>

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Publishing disclaimer: www.geolsoc.org.uk/pub_ethics

The $\delta^{18}\text{O}$ values and their spatial distribution were estimated using the ECHAM5-wiso model. The simulations indicate the lowest $\delta^{18}\text{O}$ values over the Romanian Carpathians Mountains and the highest ones over the extra-Carpathian area, with the maximum in the southeastern part of Romania.

Daux *et al.* (2021) analysed the first country-scale survey of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in tap waters sampled across France, and compared the values with those modelled in precipitation by the isotope-enabled model ECHAM6-wiso. The aim of the study is to provide data that could be used in archaeology and forensics, as well as to evaluate whether modelled data could be surrogates for field measurements.

Marche *et al.* (2020) monitored precipitations in the western Newfoundland at Corner Brook, Canada. The isotope data from the study were validated with precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data from Truro in Nova Scotia, Bay D'Espoir in Newfoundland and Goose Bay in Labrador. The similarity of data among these four sites is explained by the geographical and climatic factors such as latitude, distance from the coast and seasonal atmospheric fluctuations.

Varlam *et al.* (2020) presented a long-term record of precipitation data, spanning between 2012 and 2018 for the Râmnicu Vâlcea, Romania. The station is situated in a hill region, southwards of the South Carpathians Mountains. The paper discusses the influence of meteorological mechanisms, including large-scale moisture circulation and the North Atlantic Oscillation, on the isotopic imprint.

Bojar *et al.* (2020a) combined stable isotopes, and major anion and cation distributions in spring and borehole water with field-derived geological information. The investigated area belongs to a region with high continentality index, Mehedinți County, Romania. The siliciclastic aquifer is situated in Quaternary deposits of the Moesian unit. The acquired data allowed the design of a hydrological model for various sources of drinking water, from historical known springs to present drill holes.

Bădăluță *et al.* (2021) investigated isotopic composition and chemistry of water from Prut, Suceava, Moldova and Bistrița rivers and their tributaries situated in the northern sector of Moldavia, Romania. Their results are compared with precipitation data from the Suceava station and regional meteorological records. The authors propose a water-quality distribution map for rivers and tributaries.

Joshi *et al.* (2020) designed a hydrogeological model for the area delimited by the Sutlej and Yamuna rivers, northwestern India. Groundwater resources and interactions are quantified by analysing the isotopic composition of groundwater, rivers, precipitation and canal water. Spatial and vertical changes are displayed, the study representing a baseline for recharge processes in NW India, which is

critical for an improved management of the groundwater system.

Sironić *et al.* (2020) investigated the source of dissolved inorganic carbon (DIC) in springs, lakes and tributaries of the Plitvice Lakes, Croatia, which represent a complex karstic lake system. Geology, flow rates and seasonal changes influence the ^{14}C activity and the $\delta^{13}\text{C}$ values of DIC, the variations being compared with those measured 30 years earlier. The site represents a unique laboratory for modelling the carbon isotope composition in DIC over time and through space using a semi-empirical model.

Papp *et al.* (2020) provide a review of stable isotope investigations at mining sites. The authors present case studies for locations situated in Romania including Apuseni (Zlatna, Roșia Montană), East Carpathians (Ilba, Baia Borșa, Rødna, Băița Bihor, Cacova Ierii, Delnița), South Carpathians (Lupeni, Ciudanovița) as well as a high latitude site from Finland (Kittilä). The authors show that stable isotopes are an important method for understanding the hydrological systems in mining areas in terms of water dynamics and contaminants transport.

Terrestrial environments

The investigated deposits will be presented in chronological order, from younger to older ones.

Quaternary

Bojar *et al.* (2020b) presented a decadal-scale high-resolution stable isotope record ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of speleothem calcite grown between 1945 and 2018 in an artificial tunnel network located in the city of Graz, Austria. The speleothem isotopic composition is correlated using time series (TS) analysis of mean air temperatures (MAT) and mean annual precipitations (MAP) that were recorded in a neighbouring meteorological station. The authors conclude that the $\delta^{18}\text{O}$ values of calcite increase along the growth axis, and correlate with high temporal resolution MAT, MAP and weighted mean annual $\delta^{18}\text{O}$ of precipitations.

Cleary and Onac (2020) provided an up-to-date review of cave bat guano as climatic and environmental archives, and discussed this along with their associated $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^2\text{H}$ records. The $\delta^{13}\text{C}$ values of guano record vegetation dynamics, $\delta^{15}\text{N}$ variations relate to precipitation patterns, while guano-derived $\delta^2\text{H}$ studies could offer additional information related to mean annual temperature or diet. The investigated sites are the Bat, Eagle Creek, Mammoth and Fern caves in the USA, and the Măgurici, Zidită, Gaura cu Muscă, Gura Ponicovei and Topolnița caves in Romania, amongst others.

Stable isotope-water cycle-terrestrial environment

Tabor *et al.* (2021) measured isotopic and temperature variations in the Shinfa River watershed situated in the lowlands of Ethiopia, along with variations in the isotopic composition of authigenic calcite formed on river pebbles and different bivalve species collected from the same site. The authors explain the differences in measured and calculated isotopic compositions, and conclude that the stable oxygen isotopic compositions of calcite samples offer a minimum assessment of the environmental extremes that occur in the region.

Bayat *et al.* (2020) investigated the isotopic compositions, microfibrils and diagenetic overprint of pedogenic carbonates formed during the Holocene in both gravelly (calcareous alluvium: Isfahan and Mashhad, central Iran) and non-gravelly deposits (calcareous loess: Shahrekord, northeastern Iran). The data indicate a strong relationship between the $\delta^{13}\text{C}$ of carbonates and rainfall, and between the $\delta^{18}\text{O}$ value of carbonates and aridity indices.

Eocene

Veras *et al.* (2021) presented a section belonging to the Eocene Tambaba Formation that crops out on the Atlantic beach sector in central Brazil. Stable isotope investigations, in association with cathodoluminescence and minor element distribution in reef limestones, allows an assessment to be made of the extent of diagenetic overprint and correlation with the recovery interval following the Paleocene–Eocene Thermal Maximum event.

Cretaceous

Yamamura *et al.* (2021) investigated oxygen isotope compositions of multiple taxa from the Kaiparowits Formation of Campanian age occurring at the Rainbows and Unicorns quarry, south-central Utah (USA). In order to assess a greater palaeoecological context, information from isotopic compositions of serially sampled dinosaurs tooth enamel phosphate were completed with $\delta^{18}\text{O}$ values of apatite phosphate from crocodylians and turtles living at the same site. The seasonal precipitation pattern and temperature of the continental formation is compared to modern analogue settings, such as the monsoonal climate of Hanoi, Vietnam and Cuiaba, Brazil.

Suarez *et al.* (2020b) refined previous studies devoted to the amount of precipitation, atmospheric CO_2 and temperature distributions for the late Aptian–Albian deposits belonging to Cedar Mountain Formation situated in Utah, USA. The techniques used for this study include both traditional and clumped isotope techniques, and microscopic and mineralogical investigations, along with wavelength-dispersive X-ray fluorescence for elemental concentration.

Suarez *et al.* (2020a) reconstructed palaeohydrological dynamics by measuring the O-isotopic composition of turtle-shell phosphate and comparing it with pedogenic carbonate isotopic compositions of Early Cretaceous (Aptian–Albian) deposits from several North American palaeolatitudes. The estimated isotopic composition of $\delta^{18}\text{O}_w$ values of groundwater and the deviation from the regional trend document, for example, temporal shifts in the Hadley Cell circulation and associated precipitation flux/evaporation flux.

Acknowledgements The guest editors, Ana-Voica Bojar (Austria), Andrzej Pelc (Poland) and Christophe Lécuyer (France) are grateful to the Geological Society of London for the invitation to organize this Special Publication. Bethan Phillips is thanked for guidance and time spent for an efficient and straightforward book processing. Tamzin Anderson, Sarah Gibbs, Samuel Lickiss, Maggie Simmons, Angharad Hills, Karen Coldwell are thanked for their careful editorial work.

The papers from this book have greatly benefited from the comments and suggestions of the referees, therefore we would like to thank them for their expertise and time: Romain Amiot (France), Victor Barbu (Romania), Reese Barick (USA), Emily Beverly (USA), Tiziano Boschetti (Italy), Philippe Boulvais (France), Daniel O. Breecker (USA), Landon Burgener (USA), Gabriela Cristea (Romania), Octavian G. Duliu (Romania), Tatiana Gaona-Narvaez (USA), Beata Gebus-Czupyt (Poland), Vasile Ersek (UK), Agnieszka Galuszka (Poland), Istvan Forisz (Hungary), Robert van Geldern (Germany), Ines Krajcar Bronic (Croatia), Deborah Leslie (USA), Naomi Levin (USA), Franz Neubauer (Austria), Tonu Martma (Estonia), Tatiana Gaona Narvaez (USA), Franz Ottner (Austria), Aurel Perşoiu (Romania), Natalia Piotrowska (Poland), Gregory Price (UK) Kazimierz Rozanski (Poland), Zachary Sharp (USA), Lauren Simkins (USA), Edward Simpson (USA), Jan Smit (The Netherlands), Grzegorz Skrzypek (Australia), Vinodt Tewari (India), Thomas Tütken (Germany), Irina Vagner (Romania), Ştefan Vasile (Romania), John Webb (Australia), Jacob Clement Yde (Norway) and Carmen Zaharia (Romania).

The authors acknowledge the valuable contributions of Daniel Le Heron, volume editor.

Author contributions A-VB: conceptualization (equal), writing – original draft (lead); **AP:** conceptualization (supporting), writing – original draft (supporting); **CL:** conceptualization (supporting), writing – original draft (supporting).

Funding This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Data availability All data generated or analysed during this study are included in this published article (and its supplementary information files).

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