



**D8.11 REPORT INDICATING THE FULL
IMPLEMENTATION OF NEW LABORATORY
FACILITIES CONSTITUTING THE ITALIAN
ENVIRONMENTAL ISOTOPE NETWORK**

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1. INTRODUCTION: HOW TO FILL THE “GAP”

Isotope Geochemistry has become a fundamental tool in the study of natural processes, and numerous applications have proved valuable in a diversity of research fields, mainly Environmental Science, in which sources and transport of pollutants, the impact of climate change, and the behaviour of contaminants in soil, atmosphere, and waters remain open questions to be answered with the fundamental tools of isotopes, as well as any discipline belonging to Earth System Sciences, such as Geology, Biology, Agronomy, Ecology, and food authenticity and traceability. In this context, variations of isotope ratios occurring in the Earth provide a great wealth of information and are powerful tools to trace many kinds of processes, especially when more isotope systematics are joined to build up a more comprehensive “*isotope fingerprinting*”.

In Italy, there are numerous national institutions, universities and private entities conducting diverse isotope systematics using instrumentations able to guarantee high performances with high accuracy and reproducibility in isotope measurements. In this context, the Institute of Geosciences and Earth Resources (IGG) pioneered the development of Isotope Geochemistry and currently hosts a fundamental wealth of knowledge concerning this branch of science, as well as the most complete and up-to-date equipment for a wide variety of isotope studies (e.g., *Agostini et al., 2020*). However, a meeting point between these institutions seems to be missing and a range of isotope studies are not performed in Italy due to the lack of most recent mass spectrometers, implying that there are still important gaps to be filled. For example, in the field of stable isotopes, no instruments able to apply the clumped isotope technique are present in Italy, as well as when considering radiogenic and non-conventional stable isotopes, in which the most modern techniques, such as LA-MC-ICP-MS, allow *in situ* analyses, which no longer present the problems of matrix effects or isobaric interferences, thank the introduction of collision cell, and eventually with a mass filter, able to remove most or all isobaric interferences (e.g., *Lewis et al., 2022*).

In addition, the scope of Task 8.9 is to build the Isotope Virtual Research Environment (hereafter VRE), a pioneering Italian isotope database dedicated to stable, non-conventional stable, radiogenic isotopes and a set of tools to analyse such data, that will go to fill the gap due to the absence of a complete isotope data collection. The ISOTOPE VRE will rely on a national database on environmental isotopes missing so far in Italy that will collect the data and information scattered across various sources and institutions, currently hindering data, and information retrieval.

For all these reasons, with the scope of filling gaps, integrate the isotope data produced by Task 8.9, and to be competitive and functional with the new challenges affecting the Earth Sciences, a set of new instruments were deemed necessary to purchase, with the aim to reinforce the systematics already present, and to increase the number of isotope applications, both for face new scientific challenges and to supply missing isotope data to the database.

In the following section we are describing into details the instruments acquired in the frame of WP 8.9. Here, we would like to remark that an integral part of the new analytical system also consists of the tools acquired as part of WP 8.1, including a FE-SEM configured for the automated mineralogical-geochemical mapping of inorganic and organic matrices (Fig. 1).



Figure 1 – The Zeiss Sigma 360 FE-SEM installed at IGG-CNR in the frame of WP 8.1

The new FE-SEM (FE-SEM Zeiss Sigma 360 equipped with EDS-WDS-microXRF) has a configuration strongly aimed at the chemical-textural characterization of materials, from inorganic to organic, and is a good/excellent system for imaging. It is equipped with three detectors/sources for microanalysis: 1) new generation EDS (SDD) of 100 mm²; 2) WDS parallel beam with 5 crystals covering from Be to U; 3) Micro-XRF source for light to heavy elements up to concentrations of a few tens of µg/g. The FE-SEM, for its peculiar characteristics, represents an instrument which will be able to provide valuable contributions to research in many fields/sectors of the Earth Sciences, for analysing complex inorganic/organic matrices, such as those characterizing the Critical Zone field, as well as providing information for the interpretation of geochemical and isotopic data. Information on the acquisition of the FE-SEM and its specific and technical characteristics are detailed in the “Report on the acquired instrumentation to fill the knowledge gaps in the construction of the CZ VRE service” (D8.6 – WP8, Gennaro et al. 2024). The instrument was installed and tested by May 31, 2024. It is currently in the calibration phase with regards to the mineralogical libraries necessary for the automated acquisition procedures. In the coming months, specialized training will be conducted on the software and the development of the analytical routines.

2. ACQUIRED INSTRUMENTS IN THE FRAMEWORK OF THE ITINERIS PROJECT (WP 8.9)

To complement the already important instrumentation present in IGG, and with the aim of keeping up with the new frontiers of isotopic geochemistry, it became necessary to acquire the following instrumentation:

1. A Multi-Collector System, that is a High Resolution (HR)- Laser Ablation (LA)-MC-ICP-MS for stable, non-conventional and radiogenic isotopes and equipped Laser Ablation system 193 nm, a pre-cell mass filter and collision cell (aka collision/reaction cell), and a single quadrupole ICP-MS;
2. A Clumped isotope system for stable isotope analyses and their molecular aggregates (namely clumped isotopes), coupled with carbonate samples preparation peripheral and Elemental Analyzer for solid matrices;
3. An Isotope Ratio Mass Spectrometer (IRMS) for C, O, H, N, and S isotope analyses equipped with a on-line gas preparation and introduction system for head-space gas analyses;

4. Cathodoluminescence system that provides information on the genesis, provenance and alteration of the materials by luminescence technique;
5. A Time-Of-Flight (TOF) ICP-MS, with time-of-flight technology equipped with laser ablation system and fast wash-out cell.

2.1 Instrument purchase and state of the art

A four lots tender was opened for the supply of instruments and subsidiary equipment were published on 04/07/2023 as an open procedure on ASP platform (ID. 3643371, Prot. N. 0202811 of 30/06/2023):

1. LOT 1 CIG A01D2D0AA2: LA-MC-ICP Mass Spectrometry and a single quadrupole ICP-MS
2. LOT 2 CIG A01D30EDCB: Spectrometer for Clumped Isotopes
3. LOT 3 CIG A01D31EB00: Isotope Ratio Mass Spectrometer (IRMS)
4. LOT 4 CIG A01D32D762: Cathodoluminescence system

An additional tender was opened for acquisition of a TOF-ICP-MS on 06/10/2023 (Prot. N. 0296151).

During Bimester 6, the commission was nominated for offer evaluation (Prot. N. 0259969 of 06/09/2023), and, after several sessions (Report Prot. 0289627 of 03/10/23), no awarding was reached due to a lack of proposals meeting valid technical criteria for lots 1, 2 and 3, and due to a lack of any offer for lot 4 (DAC Prot. 0307963 of 17/10/2023). The CO₂ Laser with accessories (tender ID N. 3558378) was awarded to the ESI (Elemental Scientific Instruments) company with awarding act N. 0218736 of 13/07/2023, and contract stipulated Prot. N. 02434214 of 27/07/2013. The instrument was delivered on the date 05/10/2023 and then installed in the same days. The procurement tender for the supply of a TOF-ICP-MS spectrometer was published on 10/10/2023, as an open procedure on ASP platform (ID. 0309971, Prot. N. 0309971 of 18/10/2023), with the deadline for receiving offers fixed at 07/11/2023.

During Bimester 7, a new tender started for the supply of spectrometers and subsidiary equipment (open procedure tender over UE-threshold on ASP Platform, ID 3800003) and a new commission was appointed (Prot. N. 0369176 of 28/11/2023). The commission finalised its work with an assignment proposal (Prot. N. 412363 of 21/12/2023). The Thermo Fisher company was declared winner for LOT 1, LOT 2 and LOT 3, Prot. 412504 of 21/12/2023, whereas lot 4 was not assigned, due to a lack of technical requirements in the offer. About the procurement tender for the supply of a

TOF-ICP-MS spectrometer, the received offers from participating companies in the tender were carefully checked for the meeting of administrative and technical requirements. For cold cathode equipment with an optical microscope an exploratory market investigation started on 14/12/2023 (Prot. N. 398133) and the deadline for receiving offers from companies participating to the tender was set on 29/12/2023. In the meantime, laboratory managers focused on the planning of technical needs such as Power, Heating and/or Cooling systems to meet the pre-requirements needed for the installation of the new instruments.

During Bimester 8, the executive director of the contract (DEC) was appointed (Prot. N. 51055 of 15/02/2024) and the contract of supplying LOT 1 (Prot. N. 55059 of 19/02/2024), LOT 2 (Prot. N. 55065 of 19/02/2024), and LOT 3 (Prot. N. 55071 of 19/02/2024) with Thermo Fisher Company were prepared, signed, and registered. As regards LOT 4 (Cathodoluminescence System) a direct negotiation was started on 24/01/2024 with a potential supplier (O.E., Operatore Economico), found after an exploratory market survey (Tender N. 3952173, Prot. N. 23304 of 24/01/2024). As the offer was received, the check for the meeting of administrative and technical requirements started. In the procurement tender for the supply of a TOF-ICP-MS spectrometer, the commission (Prot. N. 0008013 of 12/01/2024) started the evaluation of the offers.

During Bimester 9, relative to the acquisition of laboratory instruments, the matching of all the requirements was verified (Certification of Effectiveness Prot. N. 78663, 07/03/2024). The CCT (Collegio Consultivo Tecnico) was appointed with Prot. N. 110570 del 03/04/2024. As regards LOT 4 (Cathodoluminescence System), a direct negotiation was started on 24/01/2024 with a potential supplier (O.E.), found after an exploratory market survey (Tender N. 3952173, Prot. N. 23304 of 24/01/2024). As the offer was received, the check for the meeting of administrative and technical requirements started. The deadline for receiving offers was postponed to 11/03/2024. The offer from a potential supplier was received, and the check for the meeting of administrative and technical requirements was performed. In the procurement tender for the supply of a TOF-ICP-MS spectrometer, the commission evaluated the technical part of the offers, and the choice of the potential supplier. Therefore, the administration started the meeting of the administrative criteria of the selected potential supplier. Finally, we proceed with the planning of technical needs for the installation of the new instruments in the laboratories, producing a requirement technical feature and preparing the timeline for their installations.

In Bimester 10 (April-May 2024) all the tenders were completed, the contract signed, and dates of delivery and installation were defined. Work is currently in progress in bimester 10 and 11 to adapt the technical installations for the laboratory rooms that will house the instrument, to meet the technical criteria needed for electricity power supply, room conditioning, fume extraction and safety devices. Delivery of the instrument is set at bimester 12.

Installation of instruments 1 to 5 is currently in progress. An appendix to this deliverable will be released once all the instruments have been set up, tested and routinely operating.

2.2 Instruments description

2.2.1 Thermo Scientific Neoma MC-ICP-MS and Thermo Scientific iCAP Qnova series ICP-MS

Most solid materials for isotope analysis require an initial sample preparation step with the aim to bring them into solution. For many sample matrices, a dissolution procedure is necessary to avoid problems of sample inhomogeneity. In addition, depending on the type of sample matrix, digestion processes, as well as element separation in ion-exchange chromatographic columns represent fundamental steps before introducing samples in the mass spectrometer. In situ isotope analyses of conventional stable isotopes are quite widespread, and a growing number of studies present in-situ isotope data, obtained either by Secondary Ion Mass Spectrometry (SIMS, e.g., *Ireland, 2004*) or coupling a Laser Ablation System with a Multi-Collector ICP-MS (e.g., *Gerdes and Zeh, 2006*). However, both these techniques show strong limitations, impacting with in-situ isotope studies. In fact, SIMS data are usually restricted to light isotopes, whereas most common applications of LA-MC-ICP-MS involve heavy radiogenic isotope systems (*Ireland, 2004; Gerdes and Zeh, 2006*). In addition, in any case matrix effects are very strong and need to be corrected, leading to possible misinterpretation, and needing a set of standard calibrated through column chemistry (e.g., *Bell et al., 2009; Cannaò et al., 2020*), and frequently isobaric interferences are very hard to correct, or impossible to remove, resulting in a dramatic increase of errors as well as external reproducibility. On the contrary, the latest generation of MC-ICP-MS is equipped with Laser Ablation (LA), pre-cell mass filter, and collision cell, favouring in situ isotope analyses of both radiogenic and non-conventional stable isotopes. As previously mentioned, there are circumstances when even the highest resolution is not enough to perform the best possible analyses (e.g., Rb-Sr), because of isobaric interferences that cannot be overcome using a simple ICP-MS system.

The just purchased Thermo Scientific Neoma MS/MS MC-ICP-MS allows to better separate isobaric interferences by reaction with gas in a dedicated collision/reaction cell (Fig. 2).

Figure 2 – Neoma MS/MS MC-ICP-MS (from www.thermofisher.com)



These novelties make Neoma MC-ICP-MS system able to overcome the problems encountered in other methodologies such as SIMS or conventional MC-ICP-MS, because they are able to the complete removal of any unwanted matrix elements in the pre-cell filter, as well as the prevention of any undesirable secondary reactions in the following collision/reaction cell of which the instrument is equipped with (Fig. 3). This implies a more stable ion beam, leading to an increase of sensitivity and signal stability. These characteristics ensure the same analytical accuracy reached by TIMS, and the removal of isobaric interferences, which is not only necessary for in situ isotope measurements, but also will allow running isotope analyses of solution, i.e., both water samples as well as dissolved matrices, with no need of chemical separation.

This instrument guarantees the ability to work at low, medium and high-resolution modes, with 100% transmissivity as well as resolution power > 300 in low resolution mode. Neoma is also equipped

both with at least 9 high-ohmic amplifier slots with associate resistors with resistivity comprised between 10^{11} and 10^{13} Ohm, and at least one SEM (Ion Counting).

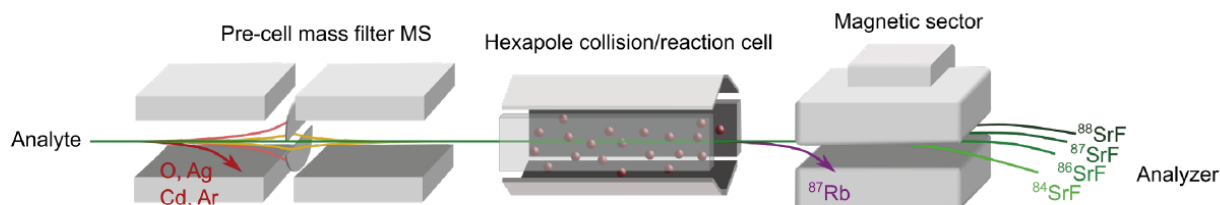


Figure 3 – Schematic of Pre-cell mass filter and collision/reaction cell of Neoma MS/MS MC-ICP-MS (from www.thermofisher.com)

These features allow to better measure of Li, B, Ca, Mg, Fe, Sr, Nd, Hf, U, Th, and Pb in solution with a minimum concentration of 20 ppb (part per billion) or less, with external reproducibility at least 1‰ for B and Li stable isotopes, 0.5‰ for Ca, Mg, and Fe, and 0.1‰ relative to Sr, and Nd isotope compositions. In addition, two optional components were made added: the Extra High Resolution (XHR) and the Retarding Potential Quadrupole (RPQ). The XHR element increases the resolving power to 15000, by ensuring an excellent peak position stability, and allowing hydrate removal from systems such as Mg and Ca, whereas the Retarding Potential Quadrupole improves abundance sensitivity by an order of magnitude, which are fundamental in systems such as U.

The ESI NWR 193 laser ablation system with a 193nm excimer Coherent laser source (Fig. 4) coupled with the Thermo Scientific Neoma MS/MS MC-ICP-MS offers a powerful analytical tool that combines the advantages of both techniques.

This setup provides high spatial resolution sampling (up to $1\mu\text{m}$), allowing precise targeting of small areas within heterogeneous materials. The direct solid sampling capability of laser ablation minimizes sample preparation and reduces contamination risks, while enabling in-situ analysis that preserves the spatial context of elements and isotopes, which is crucial for geochemical studies. The combined technique allows for rapid analysis and mapping studies, and it is versatile enough to be applied to a wide range of geological materials, and other materials such as metals, ceramics, and glasses. Moreover, this method is minimally invasive, consuming only a small amount of the sample, making

it suitable for valuable or irreplaceable samples (e.g., meteorites and cultural heritage materials), where traditional destructive methods are not acceptable.

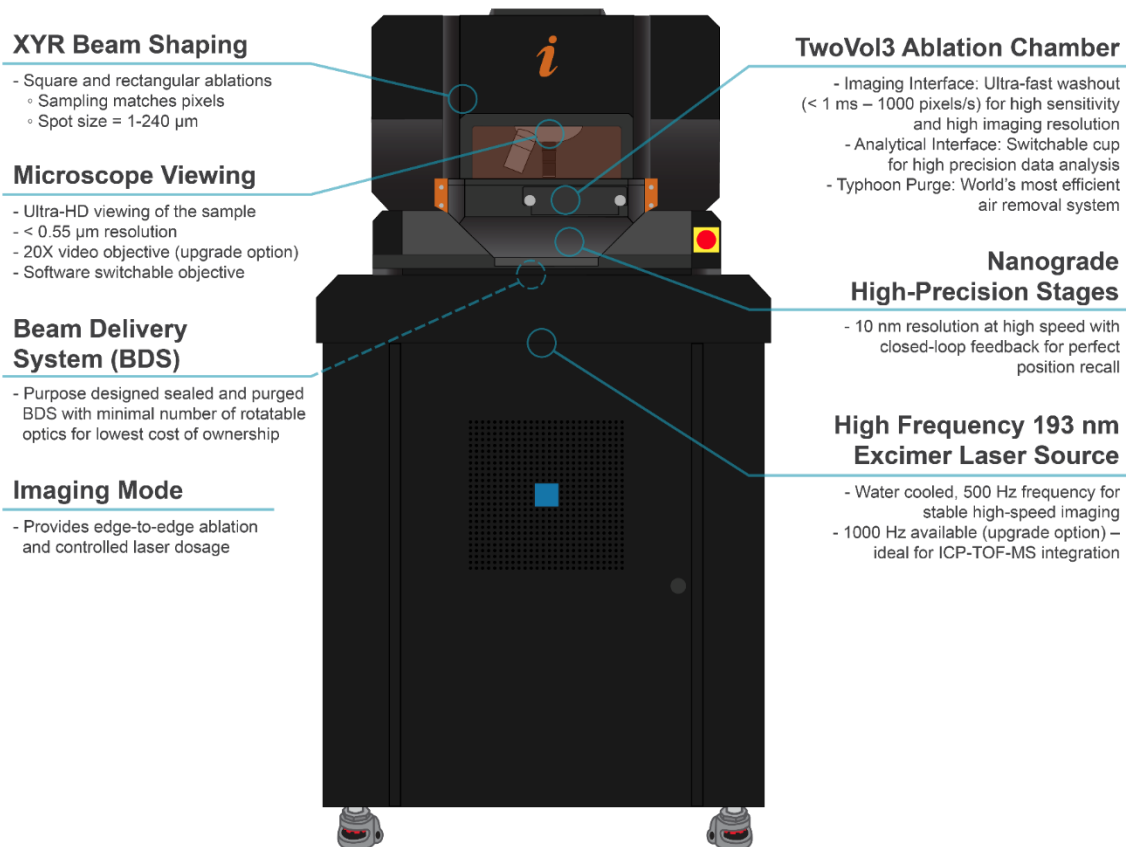


Figure 4 – Main features of the ESI NWR 193 laser ablation system from Elemental Scientific Lasers (from <https://www.icpmslasers.com/products/imageGEO193/>)

In addition to LA-MC-ICP-MS, the Neptune-TIMS Laboratory of CNR-IGG will be equipped with a single quad iCAP Qnova series ICP-MS (Fig. 5). The availability, in the same laboratory of a MS/MS-LA-MC-ICP-MS, along with a conventional MC-ICP-MS and a single quad ICP-MS, will allow cross calibration among LA analyses and solution analyses, as well as among matrix removal obtained through column chemistry (and measured via MC-ICP-MS) and matrix removal after LA through Mass Filter and Collision Cell.



Figure 5 – iCap Qnova series ICP-MS (from www.thermofisher.com)

Laser Ablation analyses constitute the biggest analytical advancement, allowing in-situ analysis of several isotopic systematics, e.g. Sr, Nd, Pb, B, Li, Mg, Fe, Ca and others. The MS/MS will allow this through matrix and isobares removal thanks to mass filter and reaction cell. These analyses, however, need to be performed with standard-sample bracketing, and the accuracy of analyses is strictly dependent from standard availability. Given the limited availability and unsuitability of most in-situ isotope standard, it is necessary to develop a series of in-house standards, which should have a matrix close to unknown samples. The setup and calibration of these standards will require sample digestion, column chemistry and analysis of purified solutions through conventional MC-ICP-MS.

2.2.2 Thermo Scientific 253 Plus 10 kV IRMS

One of the major challenges of this institute is to trace geological process, fluid/rock interactions and carbon cycle, investigating processes linked to carbonate precipitation. Carbonate clumped isotope thermometry is based on measurements of the degree of ordering of ^{13}C and ^{18}O into bonds with each other in lattices of carbonate minerals. This method is based on a recent innovation in gas source mass

spectrometry and generally unfamiliar principles of isotope geochemistry (*Eiler and Schauble, 2004; Huntington et al., 2009*), and provide unique information on geological samples and processes that are unobtainable with any other geochemical tool. In more details, carbonate clumped isotopes geochemistry enables reconstructing the temperature of carbonate mineral formation as well as the $\delta^{18}\text{O}$ composition of the precipitating fluid in the temperature range between ambient temperatures and 200-250°C. This methodology allows to investigate the temperature history of surface and subsurface environments, carbonation processes, CO₂ mineral sequestration, biomineralization processes, and the alteration history of meteorites, as well as the origin of possible kinetic effects.

Figure 6 – Thermo Scientific 253 Plus10 kV IRMS (from www.thermofisher.com)



For this reason, a clumped system, which will be the first system in Italy to measure isotopologue was acquired. The new Thermo Scientific 253 Plus10 kV IRMS isotope ratio mass spectrometer (Fig.

6) with proven 10-kV technology offers the highest sensitivity, best peak shape and best peak stability of any commercially available IRMS and delivers very high precision for the determination of $^2\text{H}/^1\text{H}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, and $^{34}\text{S}/^{32}\text{S}$. This instrument is unique in its capability to achieve high precision measurements from the smallest amounts of sample and smallest ion beams even from complex isotopologue systems while providing the widest dynamic range in class. It is equipped with low noise 10^{13} -ohm resistors, which are fundamentals for measurements of CO_2 ⁻⁴⁷, CO_2 ⁻⁴⁸, and CO_2 ⁻⁴⁹ abundances. This system is interfaced with an automated unit for the preparation of carbonate samples and gases and their purification through cryotrap. The Protium IBEX Clumped Isotope System ensures the carbonate samples -not only calcite but also dolomite, magnetite, and siderite - preparation for analyses, allowing work on samples with large size comprise between 3 to 15 mg, and using a series of variable temperature cryo-traps for chemical purification processes to clean CO_2 from solid or gaseous sources.

The new Thermo Scientific 253 Plus10 kV IRMS allows to perform analyses both in Dual-Inlet (DI) and Continuous Flow (CF) mode, with internal precision of 0.005‰ for $^{13}\text{C}(\text{CO}_2)$, 0.01‰ for $^{18}\text{O}(\text{CO}_2)$, and 0.09‰ for $^2\text{H}(\text{H}_2)$ in Dual-Inlet mode, and 0.06‰ for $^{13}\text{C}(\text{CO}_2)$, 0.08‰ for $^{18}\text{O}(\text{CO}_2)$ in Continuous Flow mode, respectively. Interfaced with the instrument is the Elemental Analyzer (EA) which includes a dual oven reactor system for sequential on-line determination of C and N weight percent data from solid and liquid samples. The EA system is equipped with reactors capable of reaching temperatures of 1100°C for sample processing. In summary, the most significant advancement provided by this new instrument is the high range of sample size (μg - to mg-level) that can be analysed, reducing cost per sample, and providing high-precision elemental and isotopic analysis. Innovation in the instrument will provide helium saving technology and integration of temperature ramped gas chromatography delivering quick analysis times and low-cost analysis alongside outstanding quality data, especially on small sample amounts. These features allow you to push boundaries for research and routine analyses in geological carbon cycle as well as in ecology and biology.

2.2.3 Thermo Scientific DELTA Q IRMS and GAS BENCH III online gas preparation system for head-space analyses

The IRMS system is mainly dedicated to carbon (C) and oxygen (O) isotope measurements on solid carbonates, as well as to C isotope measurements of dissolved inorganic carbon (DIC) in water, both for paleoclimatic/paleoenvironmental reconstructions and for environmental research. In more details, the stable C and O isotope compositions of natural carbonatic archives (e.g., speleothems and lacustrine deposits) are important proxies for past environmental and climatic parameters, such as soil/vegetation state and hydrology (rainfall amount, seasonality and source among others). Therefore, the high-resolution analyses of these materials allow the reconstructions of the past climatic and environmental evolution. Hence, the need for an instrument that allows accurate and cutting-edge measurements, and a high analytical output. The Thermo Scientific DELTA Q Isotope Ratio Mass Spectrometer (IRMS) represents the next evolutionary leap forward in isotope analysis ensuring high analytical capability. able to allow very-high-resolution studies and levels of accuracy allowing the detailed resolution of small variations, formerly not possible to investigate due to the higher errors of instruments with a lesser sensitivity (Fig. 7). The instrument is characterised by high sensitivities up to 8000 molecules per CO₂ ion in Dual-Inlet (DI) mode, and up to 1000 molecules per ion in Continuous Flow (CF) modality. It is equipped with GasBench Plus system composed by TriPlus RSH SMART autosampler which offers exceptional precision, flexibility, and producibility in a robotic sample-handling solution. This configuration permits the isotope determinations of air and/or carbonate CO₂, CO₂ from DIC (Dissolved Inorganic Carbonate), and ¹⁸O and D analyses from aqueous samples by CO₂/H₂O, H₂/H₂O and DOC (Dissolved Organic Carbonate) equilibration. The Thermo Scientific DELTA Q Isotope Ratio Mass Spectrometer (IRMS) guarantees external precision of 0.08‰ for ¹³C_(CO2) and ¹⁸O_(CO2) and 2.0‰ for ²H_(H2).



Figure 7 – Thermo Scientific DELTA Q IRMS and GAS BENCH III (from www.thermofisher.com)

2.2.4 NewTec Scientific MT1000

The Cathodoluminescence (CL) has proved to be an important tool in geological research with a varied spectrum of applications (mineralogy, gemmology, mineral deposits, crustal processes, petrology, geochronology, structural geology, hydrogeology, and environmental studies). Cathodoluminescence studies are fundamental to correctly apply other current analytical methods as Scanning Electron Microprobe (SEM) and Electron Microprobe Analysis (EPMA), and it is particularly important in the study of the distribution of several trace elements (e.g. Rare Earth Elements, REE) also contributing to the knowledge of mineral genesis. The NewTec Scientific

MT1000 is a precise, user friendly, instrument for analysing and qualifying the mechanical and/ or thermomechanical properties of materials under high vacuum atmosphere with a load capacity of 10kN and temperature up to 1000°C. The instrument is constituted with an optical microscope equipped with a low-light camera to which is linked a vacuum chamber with motorized sample holder and/or reflective lighting (Fig. 8).

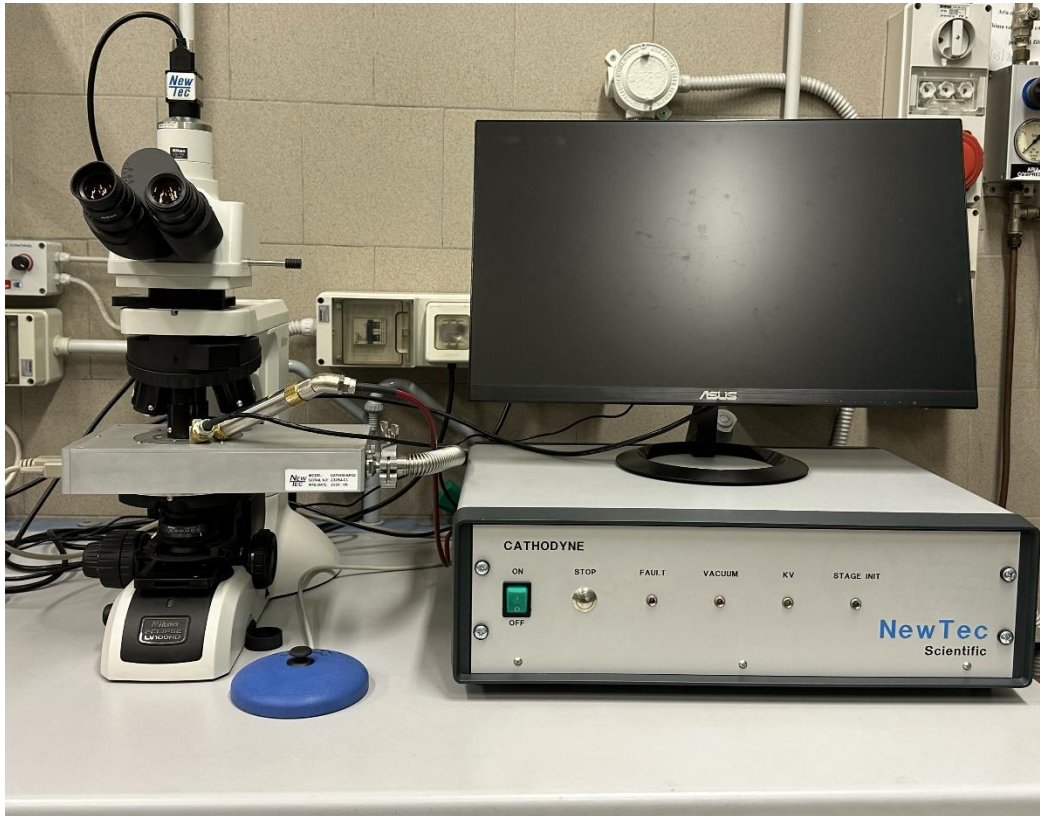


Figure 8 – NewTec Scientific MT1000 installed at IGG-CNR

One of the most important applications of this technique is the visualisation of growth textures, alteration, replacement and other internal textures in minerals that are not discernible with other analytical techniques. These results provide information about the real structure of minerals and materials and can be used for the reconstruction of geological processes of mineral formation and subsequent alteration. The information obtained from CL imaging in combination with spectral measurements of the CL emission allows for a more thorough understanding of structural states of solids and/or trace-element incorporation. In addition, the data collected by analysing different materials and specific characteristics of genesis, alterations and micromorphology, this system can

improve and help fill knowledge gaps on processes related to the deep carbon cycle, mineral carbonation and Critical Zone. Furthermore, regardless of weathering and micromorphology, accurate analysis can help improve understanding of weathering processes and mechanisms.

2.2.5 Nu Vitesse Time of Flight (TOF) ICP-MS

Time-of-Flight (TOF)-Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a powerful analytical technique that enables the measurement of the entire periodic table at fast acquisition times. In this framework, the Nu Vitesse Time of Flight (TOF) ICP-MS system (Fig. 9) can analyse a wide variety of geological, environmental, as well as biological matrices with ultrafast and high spatial resolution analysis, with the fundamental advantage of a quasi-simultaneous determination of the whole Li-U mass spectrum.



Figure 9 – Nu Vitesse TOF ICP-MS (from <https://www.nu-ins.com/products/hr-mc-icp-ms/vitesse>)

The instrument is equipped 193 nm excimer laser ablation system, having extremely high laser pulse frequency, laser beam focusing capability down to sub-micrometer scale, and ultra-fast wash-out specimen holding cell. This instrument provides a further step-forward in in-situ analyses because it allows the building of elemental as well as isotopic mapping of most of the isotope systematics described in the previous chapters. This will allow not only to improve the already existing, Lu-Hf

and Pb-Th-U isotope systems, but also to develop new isotope systematics, especially in the field of light stable isotope. The Nu Vitesse Time of Flight (TOF) ICP-MS ensures fastest wide mass range data acquisition for applications such as laser ablation imaging and nanoparticle analysis, high sensitivity to probe micron sized trace element features in solid samples and determine the elemental composition of individual nanoparticles, high analyte selectivity with a segmented reaction cell optimised for multi-element analysis, and high capability in removing interferences using unique quad QCT option.

3. ISOTOPE DATABASE: STATE OF ART

The creation of the “Italian Isotope Database” aims to provide to the scientific community isotopic data sharing set in a Virtual Research Environment (VRE) able to offer a series of powerful tools to understand and interpret environmental processes. In the VRE, the Italian Isotope application, named “Isotope Studio” (briefly: IS) and developed specifically for the Working Package 8.9 of the “ITINERIS” project, has the following main goals:

1. Collect data in a dedicated relational database “Italian Isotope Database”.
2. Provide users with the most common tools for data analysis and interpretation “Isotope Studio”.

Isotope Studio is designed and implemented as a web application deployed in the dedicated D4science ISOTOPE VRE. From the end-user perspective, a D4Science VRE is a single web application, accessible via any web browser and containing several applications as sub-items. The architecture of the software under development is based on three main layers. The first one is represented by the relational database, designed for heterogeneous data collection, with the software dedicated to access it. The second layer is a web services API (Application Programming Interface) designed to allow automatic interactions with other applications in a “Service Oriented” perspective. These APIs are compliant with the constraints of the REST architectural style. The third layer is a single page web application providing end-users with a friendly, reactive, and powerful interface allowing them to easily access the main functionalities of the application, as, for instance, data retrieving and elaboration. The software relies only on Open-Source software and technologies. For this purpose, we chose PostgreSQL as relational database, Java 11 as base language for developing data access and the REST API, Angular 14.3.0 with Bootstrap as development platform for the web user interface.

At present, the IS application allows the following operations to be carried out:

1. **DATA PLOTTING:** the user can visualise data through four distinct types of plots commonly used in the field of Geosciences:
 - **Binary plot:** it is a graphical representation of mixtures of any two components. Binary diagrams are usually used to represent the composition of a combination of two components.
 - **Ternary plot:** it is a three-variable graph used to represent the composition of a mixture or system composed of three components. Ternary diagrams are typically displayed as equilateral triangles, with each apex representing one of the three components. The interior of the triangle represents all combinations of these components, and data points are plotted within this triangular space. Ternary diagrams or plots are graphical representations of mixtures of any three components, typically expressed as percentages whose sum must be 100%.
 - **Spider diagram:** it is quite common in the field of Geosciences to express the compositional differences between the studied samples and given geochemical reservoirs (or endmembers) in the form of so-called spider diagrams (also known as multi-element diagrams). Spider diagrams allow to represent the total (or most) of one or more sample compositions on a single graph. Commonly, there are logarithmic diagrams in which elemental concentrations are “normalised” (divided) by those in the selected standard, allowing comparison of concentrations that can differ by several orders of magnitude.
 - **Schoeller-Berkaloff diagram:** they are used to show the relative concentrations of anions and cations typically expressed in milliequivalents per litre. Multiple samples from different wells may be plotted on a single diagram to distinguish similar patterns in the ratios of anions and cations. Water concentrations are a function of the groundwater geochemistry and the chemical composition of the aquifer rock material.

2. **MIXING MODEL:** Mixing Model is widely used to improve process understanding throughout Earth and Environmental Science. The term “*Mixing Calculation*” refers to the computation of the proportions (mixing ratios) in which two or more selected endmembers are mixed in a sample. The calculation of mixing ratios is a key task in

diverse fields of Earth Science, which include marine and atmospheric science such as hydrology, ecophysiology, biogeochemistry, and petrology. More details are available in CNR Internal Report “A Two and Three End-Members Mixing Models based on Element Ratios and Isotopic Composition using ITINERIS Isotope Database (Isotope Studio)” (*Di Giuseppe et al. 2024*).

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