

5. Geochemistry and isotopes in mountain water and environmental research

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5.1 Introduction: Geochemistry and isotope geochemistry and its role in fluid and environmental research

Geochemistry can be defined as the science that uses the principles of the chemistry to explain the dynamics and physical-chemical processes in Earth systems. The geochemistry studies all the physical-chemical and biochemical processes, involving rocks, minerals, and fluids (water and gas). In an un-contaminated environment, these matrixes can mutually interact one each other, deeply modifying their native geochemical composition. In addition, others modifications derive from external sources, as the anthropogenic activities (industrial processes, fossil fuel burning, deforestation and many others human activities). Then, geochemistry contributes also to identify the source and origin of pollutants and their dynamics in the environment. In research on fluid and the environment, geochemistry represents an interdisciplinary science concerned with chemistry of water in the subsurface environment (Appelo and Postma, 1996). The contribution of geochemistry can rely on the use of major, minor and trace elements compositions and of isotope ratios.

In the second half of 20th century, laboratories of Pisa became one of the point of reference in Italy and Worldwide for fluid geochemistry collected in different environmental contexts. In particular, since 1979, the CNR's laboratory facilities in Pisa represent one of the leading laboratories working in fluid geochemistry for geothermal exploration, environmental geochemistry and gas hazard due to natural gas emissions. It is worth to mention the essential contribution for the study and identification of H₂ and CO as two of the most important gas species present in geothermal and volcanic effluents. These gas phases allowed to introduce for the first time a new geothermometer/geobarometer for the estimation of equilibrium T and P present at depth (Bertrami et al., 1985; Chiodini and Cioni, 1989). Also, the pioneering research on carbonyl-sulphide (COS) contents, determined in geothermal fluids in the Larderello field, to develop a new system for P_{CO2} evaluation in the gas equilibration zone, is noteworthy (Chiodini et al., 1991).

The Laboratory of Nuclear Geology instituted in Pisa in 1956-1957 by Prof. Ezio Tongiorgi was the first in Italy and among the first in Europe to apply isotope and nuclear techniques in geology (Gonfiantini, 2011). Carbon-14 dating of archaeological samples came at first, followed soon after by Rb-Sr, and K-Ar rock dating techniques. The development of gas spectrometers application then involved the oxygen stable isotope ratios of shell calcium carbonate for palaeotemperature determinations. The determination of the ¹⁸O/¹⁶O variation in rainwater samples shortly followed, and showed huge seasonal variation (Gonfiantini and Picciotto, 1959). Since then, natural waters, (e.g. rainwaters, freshwaters, ground waters) became a major field of investigation, and the technical improvements for ²H/¹H ratio variations began to be coupled with the oxygen isotope ratio.

During the 1960s, isotope application in hydrology and geochronology in the Nuclear Geology Laboratory put solid roots in Pisa, also benefitting by frequent visiting scientists, and contributed to the developing of theories destined to become a milestone in the stable isotope geology (Craig and Gordon, 1965), and to become one of the world leading center for the rock geochronology (e.g. Ferrara, 1962; Borsi, Ferrara and Tongiorgi, 1966). This experience continued through the Institute of Geochronology and Isotope Geochemistry of Italian National Research Council (CNR), and continues today at the Institute of Geosciences and Earth Resources, that recently benefits of a substantial instrumental upgrade thanks to the NextData project.

Isotopes of a given chemical element share the same number of protons but differ in neutron numbers and, among the 90 naturally occurring elements, only 19 are monoisotopic; natural variations of isotopic composition occur for most of the elements. Basically, isotope composition of elements may vary as a consequence of two processes: radioactive decay, where one (or more) isotopes are the father, the daughter or the intermediate product of a chain, and isotope fractionation linked to chemical reaction and/or phase change.

The pioneering studies of E. Rutherford e F. Soddy at the beginning of 20th century, leading to the discovery of isotopes, are strictly linked with the discovery of natural radioactivity. At the same time, J.J. Thompson showed that some non-radioactive elements may have different masses (e.g., White, 2013). The discovery of radioactivity was fundamental to put back the terrestrial age, fixed at 20-40 Ma by Lord Kelvin: Bertram Boltwood published in 1907 the first age determinations of rocks, spanning from 400 and 2200 Ma (Boltwood, 1907). After the Second World War, thanks to the mass spectrometers made by Nier and Urey, isotope geochemistry had a huge development and isotope studies were gradually extended to many disciplines (White, 2013). Radioactive isotopes with half-life “geological” times, that is of 1 Ga magnitude order (such as ^{40}K , ^{87}Rb , ^{147}Sm , ^{238}U , ^{235}U , ^{232}Th , etcetera) are both geochronometers and natural tracers of processes.

Isotopes of an element with the same number of protons and electrons but variable neutron numbers have a different atomic weight; it is immediate to predict that they will have a different kinetics in chemical reactions, and thus isotope fractionation should occur in non-equilibrium processes. According to the classical physics, which postulates that chemical properties only depend from electron clouds, and are wholly unrelated to nuclear properties, isotope fractionation should not take place in equilibrium reactions. On the contrary, quantum mechanics links vibrational, rotational and translational energies of atomic nuclei with their mass, and accounts for the reason why two nuclei with the same proton number, but different neutron numbers (that is different mass) do not have the same stability in compounds, both gas, liquids or crystals. Bonding energy of two isotopes in a solid is different, and breaking the bond of a lighter isotope in a solid-liquid phase change requires less energy than breaking the same bond made by a heavier isotope. Thus, we should presume that isotope fractionation occurs for any phase change and, more in general, for any chemical reaction. We should just ask ourselves if the isotope fractionation could be detected by sensitivity of the instruments we use.

From the birth of mass spectrometry, Earth Sciences (*sensu lato*) are among the sectors gaining major advantages from isotope composition studies. Isotope geochemistry was the source of astonishing progress: from the opportunity to give an age to rocks and minerals, and hence to fix the age of the Earth and of the Solar system, to the possibility of recognizing heterogeneous

domains in the Earth's Crust and Mantle, to the paleo-climatic reconstructions. In particular, stable isotope of light elements are fundamental to investigate environmental processes such as geo-bio sphere interactions, groundwater and superficial circulation, soil formation and evolution, carbon sequestration and cycling (in the present and in the past), and change of the ecosystem services in relation to the global changes.

Over the years, and through the developing of various isotope systematics, it became clear that variations of isotope composition are maybe the best way to trace the origin of the elements, and the processes in which they were involved. The use of different isotopic systematics on the same system allows identifying and tracing the mass exchange related with natural processes with more and more constraints. In the last thirty years, the field of application of isotope systematics has expanded both for radiogenic isotopes (e.g. Re-Os, Lu-Hf, U-Th decay series) and for several stable isotopes. Most stable isotopes of lights elements (such as B, Li, H, O, C, N, S) are characterized by fractionation with order of magnitude of few per mil units, rarely few percent. After the introduction of HR-MC-ICP-MS (High Resolution Multi Collector Inductively Coupled Plasma Mass Spectrometer), more elements (Mg, Ca, Si, Cr, Zn, Mn, Fe, Hg and many others) were found to be affected by detectable isotope fractionation, triggering the systematic exploration of the periodic table of elements: new disciplines are developed, based on isotope fractionation of "non-traditional stable isotopes" (O'Neal, 2004). Among these elements, for example Mg, Ca, Si, Cr, Zn, Mn, Fe, Hg and many others are included. In facts, more than three quarters of all the elements of the periodic table have two or more isotopes, and only some of them were investigated in the past for isotope studies by the scientific community, due to the common belief that is impossible to measure the small differences in isotope composition due to the fractionation of quite heavy elements (such as Cu, Fe and Sn). Maybe the best synthesis of the evolution of scientific thinking induced by the new analytical machines, such as the Multi Collector ICP-MS is represented by two papers by Prof. O'Neal, who wrote in 1986: "Isotopic variations have been looked for but not found for heavy elements such as Cu, Sn, and Fe. (...). Natural variations in isotopic ratios of terrestrial materials have been reported for other light elements such as Mg and K, but these variations usually turn out to be laboratory artifacts" (O'Neal, 1986). The same author (O'Neal, 2004) completely revisited his thoughts. This demonstrate that starting from early '90 a sort of revolution occurred in isotope geochemistry, erasing preconceptions and opening up new roads, unthinkable just a few years ago.

The growing interactions of different scientific sectors, as well as the advancement in technology of mass spectrometers, has expanded the disciplinary fields that use isotopic tracers to solve several questions (environmental studies, archaeology, cultural heritage and life sciences).

5.2 The use of mass spectrometers coupled to gas chromatography

5.2.1 Introduction

In the last decade, the study of the elemental speciation, defined as the distribution of an element's particular chemical species in a sample, is increased considerably. Scientific interest in the "speciation" was also promoted by its relationship with oxidation state (cationic or anionic species), organometallic nature (i.e. presence of a strong metal-carbon covalent bond) or complex form. The

geochemical behaviour and toxicity can be significantly changed in presence of different species or forms of a single element and, therefore, knowledge of the total concentration of an element may be uninformative and even misleading regarding any positive or negative effects (Easter et al., 2010). Element speciation can be studied and identified by combining a separation technique with an atomic mass spectrometric detection. After the development of the Inductively-Coupled-Plasma-Mass-Spectrometry (ICP-MS), the easiest way to investigate the element speciation was to separate chemical species, using the High Performance Liquid Chromatography (HPLC). This technique is suitable for liquid samples and it is extensively used to study the speciation of elements such as Cr, As and Pb (Al-Rashdan et al., 1991, Markiewicz et al., 2015; Lelli, 2013).

The traditional metal analytes characterised by high ionization efficiencies generally do not appear as volatile complexes. Nevertheless, the coupling of gas chromatography (GC) and ICP-MS has specific and innovative applications in the area of elemental speciation. Main advantages of the GC-ICP-MS technique can be summarised as follows: i) Universal and Specific; ii) Extremely Sensitive; iii) Robust Plasma; iv) Single Tune for Most Elements; v) Compound Independent Calibration (CIC); vi) Isotope Measurement. Furthermore, gaseous sample introduction offers several significant advantages (Easter et al., 2010): i) the transport efficiency approaches 100%; ii) the plasma energy, normally required for desolvation and vaporization, is available for atomization, excitation and ionization, thus leading to enhanced spectrometric signals and improved sensitivity. In addition, isobaric interferences are reduced as a result of the absence of a liquid mobile phase.

Therefore, the GC-ICP-MS technique presents several advantages that demonstrate enhanced analytical capability not only for traditional metal species (e.g. As, Sn, Sb, Hg), but also for non-traditional elements (e.g. P, Cl, S, Br). In general, this technique offers ultra-trace sensitivity for many volatile metallic compounds and it is also competitive for detecting sulphur-containing compounds (Geiger and Raynor, 2009).

5.2.2 Feature of the GC-ICP-MS system

The most important issue related to the coupling of the GC with the ICP-MS instruments is related to the need to maintain the column temperature once it left the oven for the insertion into the ICP torch. This issue has benefited of several improvements since the time of its conception and it based on heated transfer line, connecting the end of the GC column to the ICP injector.

For the IGG's Fluid Geochemistry Laboratory, the instrumental innovation operated in the framework of the NextData project includes:

- *Agilent 7890S Series GC Custom*: the GC is a double column instrument, equipped with two different Thermal Conductivity Detectors (TCD). It is able to use the same carrier gas (e.g. He) in both lines, or use He in the front line and Ar in the back line, thus allowing to expand the number of gas species can be determined in the same run. Sample introduction system was modified, introducing a 10-way valve and giving the chance to introduce samples at controlled pressure (also below the atmospheric pressure);
- *Agilent 7800 ICP-MS*: the ICP-MS is equipped with ionic extraction lenses with off-axis omega lenses, Octapole Collision and Reaction Cell capable of eliminating all the most common interference in collision mode equipped with high efficiency ion driving, Quadrupole

Hyperbolic bar Analyser and off-axis Detector, with dual mode measurement and 10 orders of magnitude of linearity.

- *Agilent transfer line*: the GC-ICP-MS interface is equipped with heater and insulating material, in order to maintain a constant temperature and to prevent condensation, or cold spots, from forming while the sample is being transferred. The GC system directly controls the temperature and power supply for the interface. This makes it easy to adjust the temperature from the GC system. It also eliminates the need for an external power source.

5.2.3 Applications

Many applications involve the use of the GC-ICP-MS system from health and environmental studies (e.g. landfill gas monitoring, trace and ultra-trace impurities in gas used for health reasons, sulphur trace detection in gasoline or n-gas) to that of industrial ones (e.g. Electronic and Semi-Conductor sector).

The contribution of this analytical technique on environmental research is constantly growing, since it offer the opportunity to obtain in the same run the information regarding the total content and speciation of several elements present in gas phase. One example is well represented by the study of high mountain and/or polar environments, in which climate changes over last decades produced alteration/degradation of the permafrost (Schaefer et al., 2011; Lawrence et al., 2012; Schuur et al., 2013; Streletskiy et al., 2015). More or less, 50% of the organic carbon is contained in permafrost soils, which could cause significant carbon-climate feedbacks if emitted to the atmosphere as greenhouse gases (Hobbie et al., 2000; Shaver et al., 2000; Dutta et al., 2006; Vogel et al., 2009; Tarnocai et al., 2009; IPCC, 2013a). The thawing permafrost can make available to microbial degradation the organic carbon, which can be emitted from the soil in the form of CO₂ and CH₄ (Tarnocai et al., 2009; Sadava et al., 2014). CO₂ and CH₄ flux measurements are commonly used as an environmental monitoring tool, to study the dynamic and environmental effect of the thawing permafrost (Christensen T. R. et al., 2004; Vogel et al., 2009; Natali et al., 2011; Taylor et al., 2018). The amount of CO₂ and CH₄ that will be released is uncertain, as well as the rate of the carbon released in form of these gases. Therefore, more researches are needed in order to study the dynamics of the thawing permafrost and to understand how it can affect the environment. Since the first stage of the permafrost thaw, the evolution of the active layer induces several bio-geochemical processes, involving (and linking) both the organic and inorganic media. Therefore, it is likely that together with CO₂ and CH₄ others gas compounds (e.g. CO, COS) could be originated and released from the soil, since carbon (in organic and inorganic form) is present with other chemical elements such as sulphur, oxygen and halogens. Moreover, taking into account the availability of metals and metalloids, as present in solid particle of the permafrost or in pore water, also organometallic species could be originated and released in the environment. Depending of geochemical characteristics of the thawing permafrost (e.g. rocks, minerals, waters), and also of hydrology, morphology and local climate conditions, different bio-geochemical processes can take part of the thawing phenomena. Therefore, the presence and amount of trace and ultra-trace organic gas compounds can vary considerably and their existence can be proof only if a very sensitive and multi-elements analytical technique is available. The GC-ICP-MS system accomplishes these pre-requisites and can provide a valuable help in detecting forming organic and inorganic

molecules difficult to detect in another way. This kind of measurements are ongoing at the Earth Critical Zone Observatory at Grand Paradiso and at the Bayelva basin in Ny-Alesund (Svalbard Islands, Norway). In these studies, the detection of trace and ultra-trace gas compounds are combined to the diffuse flux evaluation of most common greenhouse gases (i.e. CO₂ and CH₄), in order to study the dynamics of thawing permafrost and possible release in the atmosphere of C-S-bearing gas compounds.

5.3 The use of multicollector mass spectrometers

In the frame of the NextData project, an important renovation at the former Thermal Ionization Mass Spectrometers (TIMS) laboratory in Pisa was carried out through the installation of a Multi Collector-High Resolution-Inductively Coupled Plasma-Mass Spectrometer (MC-HR-ICP-MS). In the last two decades, the most significant contribution to the “isotope revolution” was the introduction of this last-generation mass spectrometer, which started as complementary tool of the TIMS, but gradually are substituting it (e.g., Douthitt, 2008). Indeed, TIMS spectrometers were and are still used for isotopic analysis with excellent precision and reproducibility. TIMS however, allows analysis of a limited number of elements (e.g. Sr, Nd, Pb, B, Cr, U-Th decay series) and of limited number of samples, because of the long sample preparation and following technical constrains: 1) isotopic fractionation during evaporation of the sample, which is especially critical for elements that have only one pair of isotopes, 2) low efficiency of ionization of heavy elements (ie U, Hf, Mo, Re, Os et cetera), 3) chemical complexity of the procedures required for the purification of the sample (necessary to avoid isobaric interferences and a further reduction in the efficiency of ionization); 4) long time required for the measurement. All these limits are overcome by MC-ICP-MS. In fact, the high ionization efficiency of the ICP source virtually allow the analysis of almost all elements of the periodic table, and of radiogenic isotopes systematic such as Hf-W and Lu-Hf. New analyses using MC-HR-ICP-MS evidenced isotopic variations in the isotopic composition of a large number of stable isotopes, such as Zn, Cu, Mo, Mg, Hg and Cd. In addition, the high sensitivity of the MC-ICP-MS give the opportunity to measure the isotopic composition of ultra-trace elements even in case of extremely low concentrations (10 ppb), thus widening the horizons in the “more traditional” isotope systematics.

The impact of MC-ICP-MS in environmental research was even stronger than in other traditional disciplines of Earth Sciences. Indeed, these studies usually involve complex open systems, and a significant number of data needed, to constrain and trace sources and processes. Well-established isotope systematics, such as Sr, Nd and Pb, find applications in studying micro-samples, as PM, dusts trapped into glaciers, tephra layers in sediments, soils or glaciers, or to deal with samples having an extremely low amount of analyte, e.g. Nd isotopes in waters having less than 20 ppb of dissolved Nd. The B isotope, or the B-Sr multi-isotope fingerprinting find application in the investigation of surface and groundwater, and in mountain or glacial environment. However, while the B-rich waters (generally >0.5 mg/L) can be either determined via TIMS or MC-ICP-MS (e.g., Pennisi et al., 2019), the B-poor water (<0.1 mg/L), and in particular rainwaters where B is generally in the order of 1-50 ppb, suffers of significant analytical difficulties using TIMS, because of samples size (liter of samples needed) and a time consuming sample preparation. The use of MC-ICP-MS, performing analyses in

the 10-15 ppb B range, have thus opened to the new investigation of meteoric, mountain and glacial waters.

Glacial water research is fundamental to trace glacier induced floods and runoff chemistry from ice-covered drainage basins. High and low ion concentrations in subglacial water could be attributable to slow-flow and fast flow subglacial drainage, respectively. High concentrations indicate longer water-substrate-rock interaction time and the decrease of these concentrations could suggest that the subglacial drainage system became more efficient, thus decreasing the average residence time of the subglacial meltwater (Arendt et al., 2017). Isotopic techniques can play a significant role when coupled to chemical and hydrologic measurements. Environmental isotopes can investigate all phases of the snow-melt runoff processes. Thermonuclear tritium added to the atmosphere as a worldwide pulse has been used to determine the presence of modern recharge in groundwater, while the major interest on O-18 and deuterium lies in their variability in precipitation as a function of latitude, altitude, and atmospheric temperature. Tritium versus O-18 plot can be useful in identifying different types of water and study the mixing and interrelation of waters having different origins. Given the high sensitivity of MC-ICP-MS, new investigations will be added on dissolved elements present in glacial and rainwater from mountain and glacial environment. As a first goal, the use of boron isotopes, coupled to traditional measurements of the stable isotopes of the water molecule, opens new perspectives on the origin of the precipitation and on the anthropogenic components that can eventually be carried in polar or mountain environments.

First analyses on rainwater from the Adige river watershed have recently been performed at IGG-CNR using the new acquired HR-MC-ICP-MS Neptune plus (Dordoni, 2018; Pennisi et al., 2019). The goal of the study was to investigate the anthropogenic contamination of the river. The results indicate that no main contamination exists in the Adige river waters. The boron isotopic composition shows the main B-source in the geogenic component, and a subordinate one in the meteoric component (Dordoni, 2018). New researches, involving isotopic systematics using MC-ICP-MS, are ongoing at the Earth Critical Zone Observatory at Grand Paradiso, and at the Arctic Station in Ny-Alesund, Svalbard (Norway). Isotopic investigation of aqueous samples and chemical and hydrological parameters will be associated to the study of solid samples. In facts, ice streams flow via internal ice deformation, and the transport of sediments provides an important constraint on the basal conditions and processes beneath the former ice stream (Boswell et al., 2018). Transported sediments could be fingerprinted, using isotopic provenance, i.e analyzing the isotopic composition of elements (Sr, Nd, Pb) that provides a robust interpretation of the sourced rock for a better understanding of the whole system.

The high sensitivity of this spectrometer allowed, for the first time in the history of IGG-CNR of Pisa, the measurement of the isotopic composition of boron in meteoric water and solids, which are characterized by a low concentration in this element (< 1 ppb for the fluids presented in this work). This is an important achievement, which push the analytical limits in mass spectrometry forward and opens to new possibilities in the study of the interaction between the atmosphere and hydrosphere.

5.4 A portable mass spectrometer

The Stable Isotopes Laboratory of the IGG-CNR of Pisa is equipped for measurements of the content of nitrogen, hydrogen, oxygen and organic and inorganic carbon (TN, O, H, TOC, TIC) of solid, liquid and gas samples and their isotopic composition.

Isotopic geochemistry is a powerful tool to investigate and study the origin of terrestrial gases and fluids (hydrothermal, geothermal, magmatic) that i) precipitate minerals, ii) interact with the geo- and biosphere, iii) feed aquifers, iv) circulate in the deep and superficial layers of the earth. It is also fundamental to define the magmatic history of a rock, to identify the biological role in the formation or alteration of terrestrial rocks, to see the climatic variations over time (on a geological and recent scale), to study the anthropic impact on the Earth system and on the biogeochemical cycles of the elements.

The current instrumentations of the Stable Isotope Lab do not allow to measure isotopic compositions directly in the field, outside the laboratory itself, which are fundamental to study processes with high temporal resolution, such as broad spectrum environmental monitoring: anthropogenic carbon emissions, industrial pollution, landfill, monitoring of CO₂ capture and sequestration technologies (van Geldern et al., 2014), monitoring of diffuse natural emissions in geothermal and volcanic environments (Rizzo et al., 2014), study of bio-geological surface interactions in the critical zone and ecosystem dynamics (Braden-Behrens et al., 2017).

For this reason, a new portable field instrument (IRIS Delta Ray Thermofisher) has been acquired, consisting of an infrared laser spectrometer for high-performance measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO₂ in air at environmental concentrations in the framework of NexData project.

The isotope laser analyzers are analytical tools of recent development, based on optical spectroscopy principles. The sample, in gaseous and steam form, is introduced into the measuring cell, where it interacts with a laser beam. Each of the gas molecules absorbs light at a specific wavelength and, in proportion to their relative abundance, up to molar fractions of parts per trillion (10⁻¹²). Delta Ray spectrometer is characterized by a simple, robust multi-pass sample cell, with an internal 500 Hz scan rate (averaged to 1, 10 or 60s). It allows a non-destructive, simultaneous ¹³C and ¹⁸O isotope ratio and concentration measurement of CO₂, in a concentration range of 200-3500 ppm. The accuracy of the isotopes analyses is <0.07 ‰ $\delta^{13}\text{C}$ (300 s average, 10 replicates) and <0.1 ‰ $\delta^{18}\text{O}$ (300 s average, 10 replicates).

At the Earth Critical Zone Observatory at Grand Paradiso the research focuses on the dynamic of CO₂ exchange between soil and atmosphere driven by climate and environmental changes. In this framework, Delta Ray analyses enable to deeply investigate the dynamics of photosynthesis and respiration processes at the scale of alpine meadows through the quantification and stable isotope of the CO₂ diffuse fluxes.

At the Bayelva basin the main challenge of IGG-CNR research is devoted to understand the effects of global changes on the glacier melting and on periglacial ecosystems. For this reason, Delta Ray spectrometer allows to evaluate the CO₂ dynamic and the evolution of permafrost in the Arctic region, by the measurements of CO₂ concentration and its isotopic composition.

5.5 Geochronology with Argon-Argon methods

In the last decade, a new generation of rare gas multicollector mass spectrometers entered the market, and, at present, has almost completely replaced the old generation of single-collector mass spectrometers, which, as a design concept, dates back to about 30 years ago (Mark et al., 2009; Coble et al., 2011). Without going into technical details, it is worth noting that the coupling of the isotopes multicollections with significant improvements on the electronic components, resulted in a significant step forward from an analytical point of view in the field of $^{40}\text{Ar} - ^{39}\text{Ar}$ dating, where five argon isotopes, both natural and artificial, are measured. In summary, multicollection improves the accuracy of isotope intensity measurements, because any system disturbances affect simultaneously all isotopes, and reduces analytical times because all isotopes are measured simultaneously instead of in peak-jumping mode (i.e. in temporal succession from the heaviest to the lightest) (Jicha et al., 2016; Phillips et al., 2017).

As part of NextData project, a multicollector rare gases mass spectrometer was purchased and installed at the Ar-Ar Geochronology Laboratory of IGG in Pisa, where a single collector mass spectrometer, acquired with PNRA (Progetto Nazionale di Ricerca in Antartide) funds, has been in operation since 1998.

^{40}Ar - ^{39}Ar dating method, based on the decay ^{40}K to ^{40}Ar , has a wide spectrum of chronological applications because potassium is a major element, commonly found in several rocks and minerals. Moreover, ^{40}K half-life of 1.25 Ga allow to obtain, in relatively K-rich samples of late Quaternary ages, a detectable amount of daughter ^{40}Ar , and therefore an age.

Dating of distal tephra enclosed in marine and continental successions, as well as in ice in polar areas, allows to assign an age to paleo-climatic events noteworthy. The detrital geochronology (eventually coupled with isotopic fingerprinting) performed on cored samples in areas interested by glaciation is a useful tool to trace expansion and retreat of glaciers.

5.6 Application of QQQ-ICP-MS to Earth and Environmental Sciences

The release of ICP-MS (Inductively Coupled Plasma - Mass Spectrometer) with Triple Quadrupole analyzer (QQQ or TQ) in the 2012 represented a real technological revolution, opening up new exciting application scenarios and scientific investigations. The main feature of this instrument is the possibility to control and reduce interferences on target masses in very low resolution conditions ($<1 \text{ M}/\Delta\text{M}$) with extreme effectiveness.

To solve the problem of mass spectrum interference in ICP-MS analyzers, as early as 1999, Q-ICP-MS spectrometers had been developed, in which a reaction/collision cell was placed before the quadrupole (Q) (Dynamic Reaction Cell: DRC). Within it, the ions from the sample were made to collide or combine with injected gases. However, due to the complexity of the ionic population entering the DRC and the high absolute abundance of interferents, this technological solution has proved to be inefficient compared to the ability to reduce interferences during mass high and medium resolution analyzes of sector spectrometers magnetic (HR-ICP-MS).

The technological solution introduced in the TQs involves the positioning of a quadrupole before the collision/reaction cell. In this way, only the ions having the mass/charge ratio of the target mass are allowed to enter the collision/reaction cell. This has the effect of extraordinarily increasing the

effectiveness of the various processes that can be triggered in the reaction / collision chamber to eliminate interference.

Thanks to the very low mass resolution, this procedure allows to maintain a very high signal intensity, which is associated with an almost maniacal abatement of the instrumental background signal. The combination of these features allows the TQs to have the lowest detection limits in elemental analyzes and above all to show a marked vocation towards the accurate determination of isotopic ratios.

Following this, the QQQ-ICP-MS are particularly efficient once associated with laser probes (Laser Ablation: LA), which allow sampling of solid matrices (but also of liquids and gases, if included in solids) with a lateral resolution of 10-100 μm .

The analytical potential of the LA-ICP-MS/MS instrumentations are confirmed by the very low detection limit of the elemental analyzes, which allow the determination at ultra-trace levels (ppb-ppt range) in key minerals for environmental, climatological, petrological, sedimentological, structural studies, such as calcite and quartz, and the development of analytical protocols for the determination of isotopic ratios (systematic U-Pb, Lu-Hf, Rb-Sr, K-Ca, etc.), also in matrices that contain the elements investigated in concentrations very low. Comparisons made suggest an analytical potentiality similar to that of MC-ICP-MS spectrometers. It is interesting, however, to note how the QQQ-ICP-MS and MC-ICP-MS systems have highlighted technological specificities that make them complementary from the point of view of analytical skills, and the availability of both in a research structure leads to the completion of investigative potentials, especially in terms of isotopic chemical analysis. It is more than plausible that not all the interferences of the isotopic systematics analyzed with the MC can be eliminated with the DRC, while the determination of the isotopic composition of the systematic Rb-Sr, feasible with the QQQ, cannot be carried out with the MC. In addition, the new mass spectrometer allows to analyse the same element with the two quadrupole; in this configuration the sensitivity is lower but the oxides and the background are highly reduced.

The LA-ICP-MS/MS instrumentation is ideal for environmental and (paleo) climate investigations, when these require elemental and/or isotopic chemical analyzes of very high precision and accuracy, with a lateral resolution of a few tens of microns. In particular, the combination of this instrument with excimer laser sources (fundamental radiation 193 nm), allows to analyze any solid material, including minerals, glass, soil and sediments (once homogenized by fusion), bones, teeth, otoliths, leaves, wood, epidermal tissues (ice, but with special cells: Reinhardt et al., 2001, but also many others).

The purchase of a QQQ-ICP-MS Series 8900 (Agilent Technologies Ltd), which has been installed at the LA-ICP-MS laboratory of IGG in Pavia, where it can be coupled to solid state LASER sources, among which a 193 nm excimer laser GeoLas102, MicroLas (Göttingen, Germany) and 213 nm Nd YAG deep UV model UP213 (New Wave Research), allowing the following case studies to be addressed:

1. Characterization of trace element concentrations of different growth stages of calcareous algae from the Mediterranean region;
2. Characterization of trace element concentrations of different growth stages of *Artica Islandica* shells recent and fossil;

3. Trace element analyses of volcanic Tephra (on embedded particles with a diameter greater than 10 microns);
4. Analysis of sediments and pelitic - arenaceous soils (after preparation with their fusion);
5. Direct analysis of trace elements and Rb-Sr, Sr-Sr, U-Pb isotopic analysis in carbonate sediments and segregation.

The LA-ICP-MS/MS is potentially useful for other applications in environmental studies already tested with other LA-ICP-MS techniques: 1) Dendrological analysis: variations of trace elements in plant growth rings; 2) Elemental and isotopic analysis of animal teeth and bones; 3) Elemental and isotopic analysis of speleothemes; 4) Elemental analysis (Ti, Al) of quartz released from fluids.

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