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USING A FORENSIC – BASED LEARNING APPROACH TO TEACH GEOCHEMISTRY

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ABSTRACT. Science occupies an important and unique role in the criminal justice system and the geochemistry has an important role in investigating cases attributable to crimes against the environment. In this paper, the authors proposed a forensic-based learning methodology in teaching geochemistry using the fluorine compounds and their chemical, mineralogical and geochemical properties. With the assignment of a hypothetical, although realistically, issue, students will develop communication, problem-solving, critical thinking, collaboration, and self-directed learning skills based on recommended topics. Proposals for assessments and learning objectives are discussed in the present paper.

1. Introduction

The forensic science is an interdisciplinary discipline that in its broadest definition is the application of science to law (Saferstein 2018). Each year, our life is strongly influenced by governments needs to regulate the activities that most intimately influence our way of life. Consequently, science merges more closely with civil and criminal law. What has been said is one of the reasons why the forensic science has attracted an increasing number of students in recent years at any grade level, from elementary school up through graduate school (Harper-Leatherman and Huang 2019).

This is contrary to the fact that most students believe that science and in particular geochemistry have no significant impact on their lives. This is very wrong, since, among all the scientific disciplines, geochemistry has a fundamental role in the identification of potentially dangerous environmental contaminants, both from natural sources and anthropic activities, as well as allowing the determination of the release time in cases attributable to environmental crimes.

During the last decades, students have grown up in a world where the borders between fictional and non-fictional crime scenarios started to blur. These crime scenarios, and their related investigations, are ever present in our lives through the communication medias, the classic and modern literature (*e.g.*, Sir Arthur Conan Doyle, Umberto Eco, Agatha Christie, and Patricia Cornwell) and the media either as documentaries or as film and TV dramas (*e.g.*, CSI: Crime Scene Investigation) (Saferstein 2018; Harper-Leatherman and Huang

2019).
One of the greatest benefits of using forensic science framing is that students can readily understand the context within which forensic scientists perform their tasks. Although students understanding of and capacity to analyze may be limited, and sometimes even wrong, students still understand the overall issues at play, the general meaning of what the problem is, how to solve it, and the conclusions (Harper-Leatherman and Huang 2019).
In-class active learning methods can be, actually, more effective than in-class traditional methods, such as simply listening to a teacher speak. In view of the nature of forensic science as a hands-on, open-ended, problem-solving discipline, teaching geochemistry using a forensic science framework, usually falls squarely in the active learning spectrum (Devetak and Glazar 2014).
In view of the above, the authors implemented a forensic-based learning methodology in the present paper.

2. Presentation of a problem as the start of a learning process

Groundwater is perceived as the safest among all the planet's drinking-water available sources. As a result, half of the global population blindly relies on groundwater sources for both drinking – water and survival. Since groundwater plays such a crucial role in the existence of the majority of the global human population, its availability, safety, and purity become issues of critical concern for many governments across the globe (Gupta and Ayoob 2014).
Among all the pollutants, fluorine and in particular fluoride anion, the main form of this element in the nature, plays a fundamental role in the environment, since, is one of the chemicals in drinking – water that is responsible for effects in people. Fluoride anion, has beneficial effects on teeth at low concentrations, but excessive exposure to fluoride, or in combination with exposure to fluoride from other sources, may originate a number of adverse effects. These latter, depending on the level and period of exposure increases, range from mild dental fluorosis to crippling skeletal fluorosis. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world. Fluoride is known to occur at elevated concentrations in a number of parts of the world and in such circumstances can have, and often has, a significant adverse impact on public health and well-being (Gupta and Ayoob 2014).
The World Health Organization (W.H.O.) recommended for fluoride, the limit in drinking water of 1.5 mg F^-/L, which is also the upper limit for fluoride in drinking water for several other countries such as Canada, China, India, Australia, and the European Union. In U.S.A., this limit is much higher (4 mg F^-/L). Moreover, such limit is lower in case water is used for feeding infants (Fawell *et al.* 2006).
As part of the beginning of the learning process, an issue on a problem related to the environmental impact of fluorine is assigned to students to be worked out through the experience of solving an open-ended problem.
The issue assigned is the following: "*It was reported to the Department of Environmental Protection that anomalous quantities of fluoride in the groundwater exceeded the threshold limit values established by law. The case affects an urban and industrial area where there are industrial discharges, urban activities, school facilities, agricultural activities,*

and waste dumps. Given the impact of the groundwater contamination on drinking water wells in the above-mentioned area and the resulting public pressure, the Department of Environmental Protection needs to quickly began to investigate about the origin and the cause of the groundwater contamination. Students use geochemistry inquiry skills to identify, research, construct and refine questions for investigation, propose hypotheses, and predict possible outcomes".

Within this framework, the forensic-based learning methodology can be used to enhance content knowledge while simultaneously fostering the development of communication, problem-solving, critical thinking, collaboration, and self-directed learning skills. There can be a number of further educational approaches that could be used to deliver geochemistry contents within a forensic science framework, most of which encompass some degree of active learning. Examples include problem-based learning, case-based learning, game-based learning, role-playing, storytelling, and guided inquiry, among others. These active learning methods, presumably, can assist students to develop an enhanced understanding of geochemistry, which can increase their higher-order thinking skills. The decision on which approach is most appropriate is dependent on a number of factors: the cognitive level of the students, the teaching environment, the available time and resources, the desired learning outcomes, and the skills and desires of the teacher (Harper-Leatherman and Huang 2019). In addition, students will work in small groups and each student will be involved in clarifying terms, defining problem(s), brainstorming, structuring and hypothesis, learning objectives, independent study and synthesis. Students will receive a geological map where the polluted groundwater area is located.

The learning process will be also integrated by teaching units designed to lead the student into the framing the theoretical picture of the problem.

3. Learning Units – Chemistry, Mineralogy, Geochemistry And Toxicity Of Fluorine Compounds

As briefly introduced in the previous paragraph, the methodology used is a student-centered, inquiry-based instructional model in which students may engage with an authentic, ill – structured problem that requires further research (Jonassen and Hung 2008). The construction of forensic-based learning units can be a formidable task and a variety of arguments may be presented as learning units where the chemistry, mineralogy, geochemistry and toxicity of fluorine can be described.

It is well known that fluorine is the lightest member of the halogen family, elements in Group 17 (VIIA) of the periodic table, and it is the most active chemical element, reacting with virtually every element (Pfennig 2015).

There are approximately 300 fluorine – bearing minerals in the 03/2020 list of species approved by the International Mineralogical Association (IMA). A fluorine – bearing mineral is defined as containing at least one atom of fluorine on a dominant crystallographic site in the crystal lattices and may occur in almost all rock types. To give students an overview of the various mineral species, it is proposed that the learning unit covers the following topics:

- Fluoride minerals (fluoride minerals with the halite-type structure, fluoride minerals with the fluorite-type and derivative structures, fluoride minerals with the sphalerite-type and derivative structures, silicfluoride and borfluoride minerals, Rare Earth Fluoride Minerals).
- Fluorine in Rock-Forming Minerals (amphiboles, apatites, micas, scapolites and sodalites).

Considerations may be made on the incorporation of fluoride anions in hydrous rock-forming minerals that occurs mainly via the isovalent substitution for the hydroxyl anion: $(F)^- = (OH)^-$. Other substitutions such as $(Mg,Fe)^{2+} + F^- = Al^{3+} + O^{2-}$, may also be described. In addition, complex substitutions such as $[BO_3F]^{4-}[SiO_4]^{4-}, [F,OH]_4^{4-} = [SiO_4]^{4-}$ and $(Al,Fe)^{3+} + F^- = Ti^{4+} + O^{2-}$ may be proposed to explain the incorporation of F^- into nominally anhydrous minerals such as olivines, garnets and titanite (Mi and Pan 2018).

The chemistry of the organofluorines, and their compounds (fluorocarbons, fluoropolymers, hydrofluorocarbons, fluorocarbenes, and perfluorinated compounds) may be dealt with in the learning unit.

It is advisable to use a broad scale approach in teaching the geochemistry of fluorine and its compounds. It is recommended that the following theoretical arguments are covered during the course:

- Fluorine compounds in sedimentary systems.
- Fluorine compounds in magmas and hydrothermal systems.
- Fluorine compounds in metamorphic systems.
- Fluorine compounds in seawater.

In the field of surface chemistry, the chemical weathering provides terrific examples of how the occurrence, distribution, and mobility of fluoride in aqueous reservoirs depend on the interplay of a number of geochemical processes and in particular on the chemical speciation of the element, that determine its removal or release into the solution.

The chemical speciation (*i.e.*, the distribution of an element amongst defined chemical species in a system) and the speciation analysis (Templeton *et al.* 2000; Ure and Davidson 2001), namely, the process leading to the quantitative estimation of the content of different species, play a main role in the environmental pollution. It is well known, the total concentration of an inorganic or organic component (metal or ligand) in a multicomponent natural system (fresh water, sea water, soil, etc.) provides insufficient information to deeply understand its behavior in those contests. In fact, the bioavailability, absorption, transport and toxicity of a given pollutant are critically dependent on its chemical form in a given environment. Therefore, to get information on the activity of specific elements in the environment, more particularly for those in contact with living organisms, it is necessary to determine not only the total content of the element but also to gain an indication of its individual chemical and physical form.

For this reason, the chemical speciation now involves different sectors of the sciences, from chemistry, to biology, to biochemistry, to geochemistry and environmental sciences.

The chemical speciation of all the elements present in all compartments of our environment and the environmental pathways of these elements are of high importance in relation to their toxicity towards flora and fauna. Their concentration levels, mobility, transformation and

accumulation processes in the ecosystem depend on parameters such as pH, redox conditions, oxidation states, temperature, the presence of organic matter, and microbiological activity. All these factors strongly influence the biogeochemical cycles of elements in our environment (Florence and Batley 1980).
All these variables, together with the reaction kinetics, that strongly influence the chemical weathering processes, need to be addressed to students.
Further proposed arguments should describe the important role of colloids in controlling pollutant cycling and transport, as they may retain or release ions through adsorption and desorption processes. These phenomena mainly occur at the surface of OH groups, and they may be found on metal (hydr)oxides, clays minerals and amorphous silicates, where they may form two types of complexes with ions at the solid/water interface: inner – sphere complexes and outer – sphere complexes (Preedy 2015).
It is important to underline how the main authigenic fluorine – bearing minerals that may precipitate from saturated solutions in the aquatic environments are fluorite, fluorapatite and, depending on the alkalinity of the media, carbonate fluorapatite (Preedy 2015). As mentioned above, the main fluorine – bearing minerals in the natural environment are amphiboles, micas, fluorite and apatite, among others. All these mineral species show marked differences concerning to their solubility in water. For instance, fluorite is much more soluble than fluorapatite and micas in the range of pH of natural water and their solubilities are almost constant across the entire pH range. On the contrary, the solubilities of fluorapatite and micas are highly pH dependent in wide range of pH. Fluorapatite is more soluble under acidic pH, but it is still one to two orders of magnitude less soluble than fluorite (Preedy 2015). Despite their low solubilities, the dissolution of biotite and muscovite in granitic and gneissic rocks has been considered an important source of fluoride in water that is in contact with such rocks. It is commonly accepted that dissolution of fluorite is the main cause of elevated concentrations of fluoride in groundwater in many parts of the world (Viero *et al.* 2009).
All the above may be represented by an illustration that describes the hydrogeochemical cycle of fluorine compounds (Fig. 1). In particular, the volcanic emissions, evaporation, marine aerosols, and industrial pollution contribute to the transfer of fluorine compounds in the atmosphere creating a cycle. The deposition, both wet and dry, transfers fluorine compounds to the biosphere and geosphere. In the geosphere, uptake and release of fluorine compounds are controlled by various water-rock interactions and by inputs from anthropogenic sources (*e.g.*, waste dumps). In abiotic environments (volcanic and other geothermal emissions) the presence of organic fluorine compounds is very frequent. Rainfall constitutes an important component of the cycle. Fluorine sources in rainfall include marine aerosols, volcanic emissions, and anthropogenic introduction of chlorofluorocarbons (CFCs) and industrial emissions. Industrial aerosols are especially produced from coal burning, brick making and aluminum smelting and fluorine exposure is also linked to domestic coal burning. It is also remarkable the ability of a few plants to sequester and convert fluoride into the highly toxic fluoroacetate and other fluorocarboxylic acids (Edmunds and Smedley 2013).

It is widely accepted that the fluoride is essentially required for mineralization of bone and teeth, maintenance of fertility, hematopoiesis, and activation of certain enzymes, such as adenylate cyclase, acid and alkaline phosphatases, and isocitrate dehydrogenase. Students should be informed that a low level of fluoride intake decreases susceptibility to dental caries

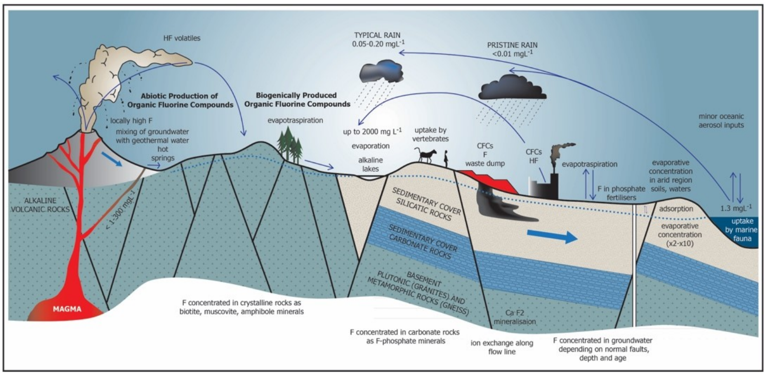

FIGURE 1. The hydrogeochemical cycle of fluorine compounds, (modified from Edmunds and Smedley (2013)).

in human beings. Anticaries action of the fluoride is mediated by its incorporation into the tooth enamel as fluor(hydroxyl) apatite which has high levels of fluoride and low levels of carbonate and high acid resistance. In addition, fluoride can inhibit bacterial metabolism of carbohydrates, hence it decreases production of acids (Preedy 2015).
In addition, it is worth adding that large doses of fluoride exert toxic effects in almost all living creatures. Fluoride is a general tissue poison, even more poisonous than lead and just slightly less poisonous than arsenic. The toxic potential of fluoride can be very well assessed by the fact that a small single dose causes acute toxic effects and death may occur following a single oral fluoride intake. Depending upon the quantity of intake and the chemical form of the fluoride compound, fluoride toxicity can occur in acute, subacute, and chronic form. Acute fluoride toxicity, although rare in occurrence, results mostly after accidental ingestion of large doses of fluorine compounds, such as sodium fluoroacetate and fluoroacetamide used as a rodenticide, sodium fluorosilicate used as an insecticide, and sodium fluoride used as an acaricide. Because of the decrease in use of these fluoride compounds for various household and agricultural purposes, acute fluoride poisoning is now seldom reported. Prolonged intake of low but toxic doses of fluoride compounds induces chronic fluoride toxicity, often referred as "fluorosis". Chronic fluoride toxicity is more common and important for human and domestic animals and is often characterized by pathological changes in teeth (dental fluorosis) and bone (osteofluorosis). Ingestion of fluoride compounds (through food and water) appears the major route of fluoride uptake. When drinking water contains excess fluoride and serves as a major source of excess fluoride intake, the chronic fluoride toxicity produced is referred as "hydrofluorosis". Water fluoride has been reported to cause osteo and dental fluorosis also in a wide range of domestic animals (Fawell *et al.* 2006).

The proposed methodology and learning units foster interdisciplinary knowledge, integrating and augmenting student profiles by the development of transversal skills. Indeed, it appears inescapable that students should possess the requisite knowledge for studying the planned learning units (*e.g.*, hydrogeology, structural geology, geology, chemistry, mineralogy, petrology).

As suggested by Blumberg (2005), throughout the proposed learning processes, the students naturally raise questions that they would like clarified. Toward the end of each learning unit, the students refer to their written list of questions to generate and refine learning arguments, or topics that the students need to research on their own outside of class for further understanding. The students refine the questions, group and classify then to make the job of searching for answers more manageable. The questions can either require additional information on the specific problem or take the form of more general knowledge questions, which are preferred for promoting student learning.

4. Conclusions

The incorporation of forensic science, a very popular field, into the geochemistry curriculum can lead to increase student interest and engagement. Having seen forensic science applications in popular culture, even if not accurately portrayed, this discipline may help students to directly understand the potential application of what they are studying (Harper-Leatherman and Huang 2019).

By the end of the proposed learning processes, students:

- Understand how knowledge of chemical, mineralogical, geochemical, hydrogeological and geological systems is used to design different processes;
- Use science inquiry skills to design, conduct, evaluate and communicate investigations into reactions and the identification of inorganic and organic fluorine compounds, including the mineral species described in the previously learning units;
- Represent data in meaningful and useful ways, including using appropriate maps, graphic representations and correct units and symbols;
- Organize and analyze data to identify patterns and relationships;
- Interpret a range of scientific and media texts, and evaluate processes, claims and conclusions by considering the quality of available evidence; and use reasoning to construct scientific arguments.
- Communicate, predict and explain geochemical phenomena using qualitative and quantitative representations in appropriate modes and genres.

As with any pedagogic approach, it is important to align learning outcomes, teaching and learning activities and assessment tasks, particularly where the intention is to encourage deep, rather than surface, approaches to learning (Biggs and Tang 2003).

As suggested Blumberg (2005), feedback is an essential component of assessment. Current trends in assessment emphasize using different types of assessments including embedded and authentic assessments. Embedded assessment means that assessment of student progress and performance are integrated into the regular teaching/learning activities, whereas non-embedded assessments occur outside of the usual learning process. Assessment should be designed for the purposes of improving the performance of students and teachers. Assessment should not be confused with evaluation which is often done for the purposes of making pass or fail type judgments about students.

On a weekly basis, the observations of student performance in the forensic – based learning activities should offer formative feedback to help students to improve. These types of assessments offer insights into how well the students are learning and are consistent with

the original learning outcomes. These same assessment forms taken together can be used to look at repeated observations or reviews to determine trends and patterns. Such trends and patterns can become the basis for making summative evaluations (Blumberg 2005).
In conclusion, the example of the behaviour of fluorine in groundwater and the related relationships with sciences as chemistry, mineralogy, and geochemistry may be successfully used as a forensic – based methodology accompanied by a variety of arguments proposed as learning units.

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