

Heavy radioactive and trans-lanthanide elements in the geothermal microecology of the Los Azufres volcanic complex.

Waleed A Abuhani^{1,(a)}, Nabanita Dasgupta-Schubert^{2*}, Luis Manuel Villaseñor Cendejas^{1,(b)}, Steven A. Alexander³ and Sheldon Landsberger⁴

¹ Institute of Physics and Mathematics (IFM), University of Michoacán (UMSNH), C.U., Morelia, Mich. 58060, Mexico

^(a) Current address: Alghad International Colleges for Applied Medical Science, Al Madinah, Saudi Arabia

^(b) Current address: University of Morelia (UEM), Morelia, Mich. 58230, Mexico

² Dept. of Physics and Mathematics (FCFM), University of Michoacán (UMSNH), C.U., Morelia, Mich. 58060, Mexico

³ Dept. of Physics, Southwestern University, Georgetown, TX, USA

⁴ Nuclear Engineering Teaching Lab., University of Texas, Austin, TX, USA

* nita@ifm.umich.mx; nitaschubert@gmail.com

Abstract. The distribution of the heavy metals ^{80}Hg , ^{82}Pb , ^{90}Th and ^{92}U in the biogeochemical microcosm of three geo and hydro thermal sites of the Los Azufres volcanic complex have been determined by the nuclear analytical techniques of Polarised Energy Dispersive X-Ray Fluorescence spectrometry and Instrumental Neutron Activation Analysis. We have shown that the sites chosen can be considered to be ‘real-time’ natural laboratories to simulate the Ordovician-Devonian periods. We observe that (1) the primitive, extremophilic plants of the fumaroles – the mosses and ferns – are efficient agents of pedogenesis; (2) that their rhizospheric soil retains more heavy metal than the hydrothermal sediments. The former implies that large-scale photosynthesis and the consequent burial of soil organic carbon could have substantially contributed to the late-Ordovician climate cooling by CO_2 draw-down, and the latter, that dissolved heavy metals in the hydrothermal seas could have been one of the reasons for the marine extinction of that period. This ‘holistic’ approach at simulating the Paleozoic environment differs from extant purely laboratory-based studies. However, it corroborates the findings of some earlier works.

1. Introduction and Background Information

The Los Azufres volcanic complex (Fig. 1a) is located 220 km WNW of Mexico City and sits at an altitude of some 2000 m to 3000 m on the central sector of the Mexican volcanic belt. This dormant volcanic complex [1], consists of a large 18 km x 20 km early Pleistocene caldera and is characterized by many still-active geothermal zones where hot-springs, fumaroles and bubbling mud-pools (“mud volcanoes”) abound. The thermal fluids are meteoric water and magmatic fluid in origin with temperatures between 300 °C to 320 °C, high contents of the gases CO_2 and H_2S , pH between 5.8 to



7.2 and an average Cl^- content of 3100 mg/kg. The gas phase may be as much as 90% enriched in CO_2 . The average oxygen level is 74% of the value at sea-level and the average yearly precipitation is 14 times higher than the global average. The active geothermal zones form unique microcosms where micro-organisms of the family *archaea* and primitive plants such as mosses (*bryophytes*) and ferns (*pteridophytes*) thrive under these extreme conditions. The sites investigated in this work (Fig. 1b) are Nopalitos-I (N1), Cumbres-I (C1) and Cumbres-II (C2) that are unpopulated, remote and restricted to public thoroughfare. They contain the archetypal fumaroles, hot-springs and hot mud-pools (Fig. 2). Table 1 summarises the physicochemical characteristics of the fumaroles, the hot-springs and the virgin volcanic rock or substrate (VS), also termed “tuff”, investigated in this work.

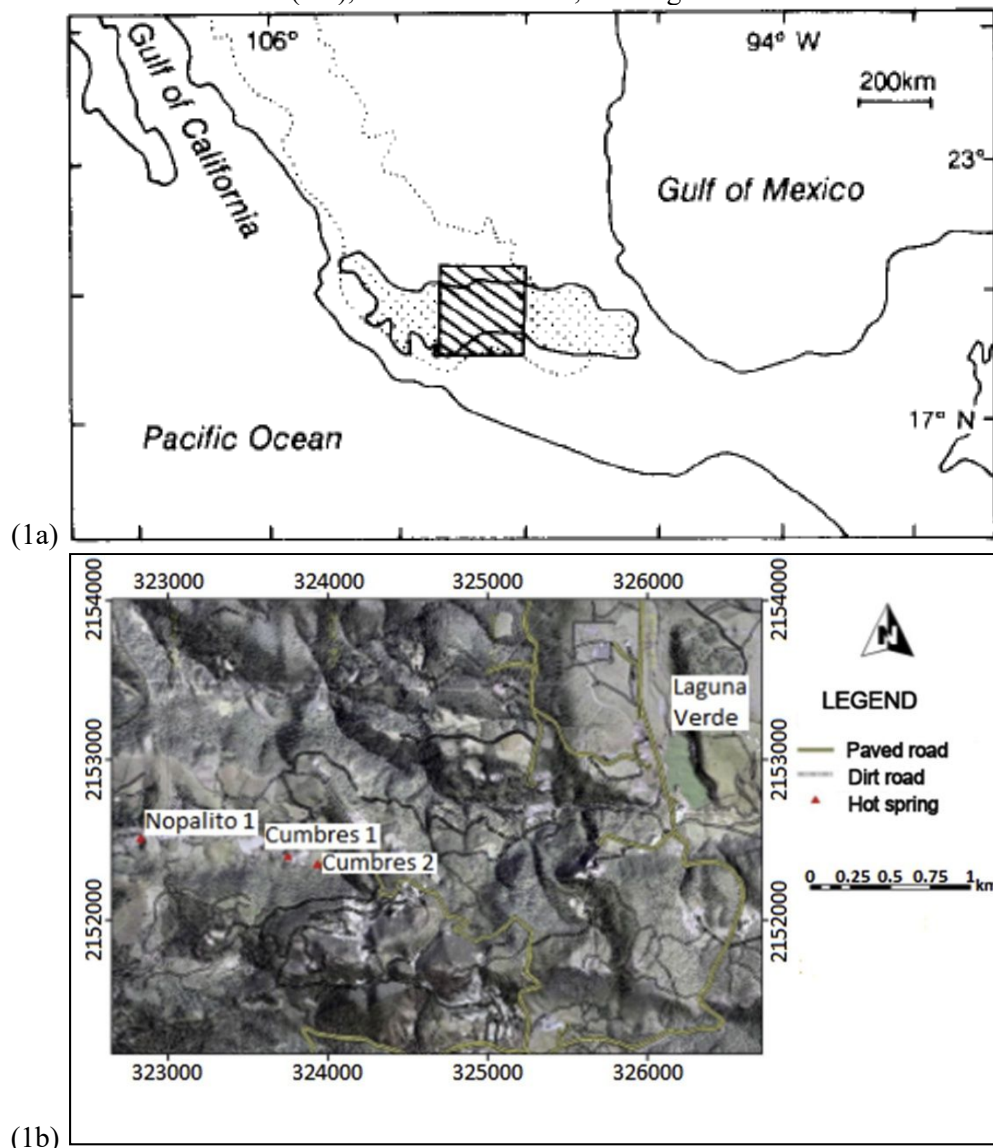


Fig. 1. The maps of the Los Azufres volcanic region in increasing order of detail. (1a) The hatched zone is Los Azufres, while the dotted and continuous lines delineate respectively, the Sierra Madre Occidental range and the Mexican volcanic belt (from Ref. 1, with permission). (1b) A magnified three-dimensional map of the geothermal zone within Los Azufres showing the sites of Nopalitos-I (N1), Cumbres-I (C1) and Cumbres-II (C2) studied in this work. This figure is a topographical one in the UTM (Universal Transverse Mercator) coordinates and shows the x,y coordinates of the sampled sites (Courtesy Emigdio Casimiro of CFE, Los Azufres, Mexico).



Fig. 2. The bubbling hot mud-pool of N1 and its near-by fumarole showing a wisp of escaping vapour, moss close to its mouth and an overhanging fern.

The first plants to colonise land were the *bryophytes* that appeared in the Ordovician period 485.4 to 443.4 million years ago while the first vascular plants - the fern allies (lycophods) and ferns - appeared in the mid-Devonian period about 360 million years ago [4]. The climate in the early-mid Ordovician was warm and wet and the atmospheric CO_2 and O_2 levels were higher and lower respectively than present day levels. An extensive system of terrestrial and oceanic volcanic arcs spewed forth volcanic gases rich in CO_2 , H_2S and SO_2 [5]. The climate in the Devonian period was warm and arid and the atmospheric composition was qualitatively similar to the Ordovician's. It is believed that these early and ubiquitous land plants were instrumental in pedogenesis (soil formation) through biogeochemical weathering of the bedrock, nutrient recycling and organic matter deposition [6]. A recent work [7] surmises that the Ordovician *bryophytes* were responsible for a large atmospheric CO_2 drawdown through biogeochemical weathering and this led to the late-Ordovician ice-age as well as the eutrophication of the oceans that caused the mass marine extinction of that period. That work however, bases its premise on simulations using a modern non-extremophilic moss grown on rocks in the laboratory and numerical earth system modelling with extrapolated data. Yet another work [8], suggests that the mass marine extinction could have occurred as a consequence of the toxification of the marine organisms by heavy metals such as Fe, Mo, Pb, Mn and As in the paleo sea water.

Table 1: Geo-physicochemical properties of the ambients of the fumaroles and the exposed volcanic substrate (VS) as well as the hot-springs of the sites of N1, C1 and C2 (see ref. 2 for details). The abbreviations RH, GV, NCG stand for relative humidity, geothermal vapour and non-condensable gases, respectively. The GV and NSG values serve as a representative example (well AZ-05 of ref. 3)

Fumaroles and VS:

Air temperature: $\sim 45^\circ\text{C}$ (N1), $> 45^\circ\text{C}$ (C1, C2), inside mouth; 19°C (N1, C1, C2), outside mouth; 22°C (VS)

RH (%): 69 (N1), 20 (C1, C2), inside mouth; 20 (VS)

Light intensity (kLux): 1.378 (N1) inside mouth; 1.382×10^2 to 1.117×10^2 (C2); 1.256×10^2 (VS)

Gas conc. (% of total GV): Steam 97.4, NCG 2.6;

NCG gas conc. (% of total NCG): CO_2 97.4, H_2S 2.3, O_2 0.2, Other gases 0.1

Hot-springs:

Average water temperatures: 80°C (N1), 86.5°C (C1), 88.5°C (C2)

Average pH: 2.31 (N1), 1.95 (C1), 2.00 (C2)

Average electrical conductivity ($\mu\text{S}/\text{cm}$): 3770 (N1), 6580 (C1), 5650 (C2)

Range of concs. (mg/L) of dissolved ions and neutral species: Cl^- 3.2 to 52.7; HCO_3^- 0.0; SiO_2 327 to 456; SO_4^{2-} 843 to 4472.

The micro-ecology of the fumaroles investigated in this work showed the colonization of the mouths of the fumaroles by at least 11 species of mosses and the population of the external rims of the fumaroles by predominantly the ferns (5 distinct species were counted). The physicochemical characteristics (Table 1) point to a close resemblance to the Ordovician and Devonian conditions described earlier. The low light intensity within the fumaroles mimics the cloud cover corresponding to the wet weather during the Ordovician while the high light intensity outside them approximates the lighting condition during the dry warm weather of the Devonian. Taken in sum, the geothermal microcosm studied in this work resembles the planetary ambience of the Ordovician and Devonian periods. This microcosm might then serve as a “real-time” natural laboratory to study the elemental distribution in the bio-geosphere through geothermal activity and biogeochemical weathering by these primitive extremophilic plants. We believe that this approach could possibly better serve as proxy of the environmental processes that might have taken place in the mid-Paleozoic era, than laboratory simulations and model-dependent analyses. The work presented here is an excerpt of our comprehensive study of the elemental distribution within the geothermal microcosm of the sites of N1, C1 and C2 of the Los Azufres volcanic complex. Specifically here, we focus on the distribution of the naturally occurring heavy radioactive elements (NOHRE) ^{90}Th and ^{92}U and the trans-lanthanides (TL), ^{80}Hg and ^{82}Pb , between the rhizospheric soil of the plant, the sediment of the hydrothermal springs and the virgin volcanic substrate also termed “tuff” at the aforesaid sites. It is hoped that this would offer some clues towards understanding how biogeochemical processes versus the purely geochemical ones might have shaped the terrestrial distribution of these elements.

The x-ray radiation-based elemental analysis technique of Polarized Energy Dispersive X-ray Fluorescence (PEDXRF) spectrometry [9] is optimally suited for the multi element analysis entailed in this work because it can analyse elements from Na to U in a single run, thus permitting high sample throughput. It has a large dynamic range (concentrations of the level of percents to parts per million) and it is non-destructive requiring only simple sample preparation. The primary x-ray beam is polarized by double orthogonal reflection and the fluoresced photons are collected in the detector placed at an axis orthogonal to the exciting beam. This 3D optics effectively ‘cancels out’ the Bremsstrahlung background of the primary beam thereby substantially improving the instrument’s sensitivity. Solid or liquid samples may be analyzed, the only requirement for the former in powder form, being that the particle size should be within 100 μm .

2. Experimental

All details of the experimental procedures involved in this work and the description of the samples are to be found in Ref. 2.

The physical characteristics of density and total organic matter content (TOMC) of the solid substrates were measured after pelletizing the dried, pulverised and sieved substrate powders, under the same uniform high pressure of 10.4 tonnes. The pellet dimensions and weights were recorded. The standard low temperature Loss on Ignition protocol was used to measure the TOMC.

The bulk of the elemental analysis was performed by the SPECTRO XEPOS III (Spectro Analytics GmbH / Ametek Inc., Kleve, Germany) PEDXRF spectrometer at the University of Michoacan (Morelia, Mexico) while a few elements were also analysed by Instrumental Neutron Activation Analysis (INAA) at the University of Texas (Austin, USA). Selected elements of atomic number $Z < 13$ were analysed by Inductively Coupled Plasma Mass Spectrometry (ICPMS) at the Helmholtz Centre for Environmental Research (Leipzig, Germany). All the elements reported in this work were analysed by PEDXRF while U was also analysed by INAA. As far as PEDXRF is concerned, in a previous work [10] we have shown that, depending on the matrix and the element analysed, sample masses as low as 0.5g (the factory recommended mass is 4g) may be analyzed without significant deterioration of the statistical figures of merit of the analysis. This permitted us to analyse the low plant dry bio-masses of each type of extremophilic moss collected.

The PEDXRF method used in this work was validated ([2] and [10]) by analysing a series of Standard Reference Materials (SRMs) obtained from the US National Institute of Standards and

Technology (NIST) and SPECTRO Analytical Instruments GmbH (Kleve, Germany). The certificate value for Hg (0.032 ± 0.004) mg/kg for the SRM GSS-1 of SPECTRO was below the detection limit of our spectrometer whereas the measured value for Pb (94.00 ± 1.56) mg/kg showed an index of accuracy of (95.92 ± 6.08)% and a precision factor of 98.35% (*cf.* [10] for the definition of terms). The values for Th and U are given in [2].

The experimental measurements were conducted in replicates of ≥ 3 . Errors are quoted as standard deviation (SD) errors on primary measurements and as propagated errors on derived quantities.

3. Results and Discussion

Table 2 shows the average densities and TOMC of the 3 types of substrates that constitute the geothermal microecology: the native volcanic substrate (VS), the hydrothermal spring sediments (S) and the rhizospheric soil (RS) of the extremophilic plants within, or at the rim of, the fumaroles.

Table 2. Average densities and TOMC of the VS, S and RS. The Student's t-test for statistical distinguishability [11] showed that at 98% Confidence Level, the values for the RS are distinct and the values for the S are not, when compared to the values for the VS [2]

Substrate type	Density (g/cm ³)	TOMC (%)
VS	2.01 ± 0.01	2.18 ± 0.25
S	2.11 ± 0.31	1.78 ± 0.34
RS	1.74 ± 0.18	6.79 ± 1.03

The RS has the least density and the highest amount of TOMC whereas the S has exactly the opposite values. Both the RS and the S however are derived from the same source – the volcanic substrate. Two distinct processes shape them. The RS is formed by biogeochemical weathering of the VS whereas the S is formed by the purely geochemical one. The hot hydrothermal waters rich in highly reactive chemical species (Table 1), break down the volcanic bedrock with the resulting insoluble particles settling as sediment. Rain water run-offs and streams carrying particles resulting from the atmospheric weathering of distant VS also contribute to sediment formation. In contrast, biogeochemical processes are suave and involve the action of root exudates such as organic acids, enzymes and other metabolic products to weather the VS, and the deposition of dead organic matter to form humus. Consequently the substrate in the root zone becomes increasingly soil-like - richer in organic matter and porous. This transition is indicated by an increase in TOMC and a decrease in density as manifested by the RS of this work (Table 2). In terms of the time evolution of the process, we note that the differences of density and TOMC between the native VS and the S are not statistically significant but in the same period the differences between the RS and VS are, which shows that the biogeochemical processes in the rhizosphere of the mosses and ferns are more effective in pedogenesis than the abiotic geochemical ones notwithstanding the harsh chemistry of the hot-spring waters. Hence this microecology that mimics the conditions prevailing during the Ordovician-Devonian periods, shows us that extensive land cover by the first mosses and ferns were instrumental in converting the volcanic rocks to topsoil suitable for the evolution of later higher plants. Furthermore, the three-fold increase of organic matter in the RS compared to the VS means that the fumarolic vegetation is a good sink for atmospheric carbon-dioxide through photosynthesis. Thus the advancing cover of the bare land during the mid-Palaeozoic era by the early ancestors of the same plants studied in this work, was directly (through photosynthesis) and perhaps also largely, responsible for the CO₂ draw-down that could have led to overall climate cooling.

Tables 3a and 3b show the distribution of the 4 heavy metals (HM), Hg, Pb, Th and U, between the VS, S and RS of the geothermal sites of N1 and C2. Elevated concentrations of these metals are highly toxic to all living organism and are known to cause teratological disorders [12]. The VS of the C2 site could not be directly analyzed because it was hard and rocky. Its values in table 3a have been arrived

at by approximation: the equilibrium ratio of the elemental concentration in the moss RS to its concentration in the corresponding VS was assumed to be equal at the two sites of N1 and C2. Knowing the former at both sites and the latter at the N1 site, the VS (C2) concentration could be arrived at. (The moss RS concentrations are the result of biogeochemical processes that are likely to be the same at the two sites given the same type of overlying vegetation (mosses). Consequently there would exist a definite relationship - linear at its simplest - between the concentration of the element in the substrate with its concentration in the soil formed from the substrate, the RS). The Earth's crust concentrations were obtained from WebElements (<https://www.webelements.com/>) which is a compilation from several scholarly works. With the exception of U, the VS concentrations at both sites, but particularly at C2, are distinctly higher than the values for the Earth's crust which are the averages over a depth of around 60 km and where atmospheric weathering processes do not reach. This observation is a reflection of the high mineral content of the geothermal vapours as a consequence of their magmatic contact, much of which is retained in their condensed phase. Weathering of the VS by acid rain due to the high CO₂ effusions at this geothermal zone, could account for the lowered U concentrations given that uranyl carbonate complexes are soluble, in contrast to the carbonates of Hg, Pb and Th that are not.

Table 3b shows that elemental concentrations in the RS and S at the two sites. It should be mentioned that the RS values for each site shown in the table are the averages over the RS values for the moss and fern RSs at each site (values not shown). For all four elements, RS(C2) accumulates more of the HM than RS(N1). This is not only because the C2 VS is intrinsically richer in these HM (Table 3a) but also because the overlying foliage contained a larger component of ferns and fern allies, whereas the cavity fumaroles of N1 were largely populated by the mosses [*cf.* Ref.2]. The root structure of these first vascular plants are more massive than the small feathery rhizoids of the mosses and therefore are able to interact more with the soil, enhancing biogeochemical activity. Consequently they are better able to fix the HM in the RS. The fixation of the HM occurs through the precipitation of the HM as insoluble organic or inorganic complexes onto soil particles or organic matter and by the adsorption/absorption on the walls of the roots. In fact this fixation in soil is termed *phytostabilization* apropos of the environmental biotechnology of *phytoremediation* which endeavours to remove or contain environmental contamination by plant cover [13]. With the exception of the values for U and the RS(C2) value for Hg, however, the RS values at both N1 and C2, as exemplified by their grand average values, are lower than their corresponding VS values (Table 3a). These fumaroles are wet areas where a substantial amount of the geothermal vapours condense out. The porosity of the RS soil (Table 2) favours soil drainage, that implies a proportionate leach-out of the soluble HM compounds of the RS. The anomalies in the case of Hg and U are possibly due to the degree of insolubility of their organic/inorganic complexes formed by the rhizospheric biogeochemical activity. The physicochemical characteristics of the C2 fumarolic environment differs in detail from that of the N1 fumaroles, which may affect the Hg compounds to a greater extent causing their relatively higher precipitation.

The same observation applies to the case of the S at the two sites. Because only inorganic processes operate in the hydrothermal waters of the hot-springs, and because the gases emanating from the hydrothermal vents and the surface fumaroles close to them have the same origins, it seems plausible that the HM precipitates in both the S and RS are chiefly inorganic in composition. The comparison between the grand averages of the RS and S concentrations throws up an interesting feature - the HM concentrations in the S are generally less than their corresponding ones in the RS, particularly for Hg and Pb (disregarding the statistical variation). This means that leach-outs notwithstanding, the rhizospheric soil is better able to *retain* the HM than the sediments of the hot-springs. Given the high temperatures and high electrical conductivity of the hydrothermal waters and the high concentrations of inorganic anions and colloidal particles (SiO₂) (Table 1), it is likely that a large fraction of the HM remains as soluble or colloiddally adsorbed species above the sediments.

Mirroring this evidence back to the Ordovician period, it would mean that the Ordovician's warm seas would have been substantially richer in the dissolved or dispersed HM species. This would have

made the HM far more dangerous to aquatic or marine organisms because it is only the solubilized HM that passes through the cell membrane. Thus contrary to the plant cover acting as a the major source of the HM in the run-offs of their leachates to the oceans as stated in [7], it would seem that the prolific terrestrial and underwater volcanic activity of that period could have caused marine extinction by HM toxification, as pointed out in [8].

Table 3a: Average ($n \geq 3$) elemental concentrations of the volcanic substrates VS collected at the sites of N1 and C2, and the average concentration in the Earth's crust (from WebElements). Z is the element's atomic number. *Gr.Avg* stands for grand average.

* Derived concentration (see text).

Element	Z	Elemental mass fractions (mg/kg)			
		Earth's crust	VS(N1)	VS(C2)*	Gr. Avg. VS
Hg	80	0.067	12.85±0.92	14.13	13.49± 0.90
Pb	82	10.00	18.40±3.25	34.11	26.26±11.11
Th	90	6.00	8.35±0.35	17.37	12.86± 6.38
U	92	1.80	0.13±0.002	0.52	0.33± 0.28

Table 3b: Average ($n \geq 3$) elemental concentrations of the rhizospheric soil (RS) and the hot-spring sediment (S) samples collected from the sites of N1 and C2.

Element	RS(N1)	RS(C2)	Gr.Avg. RS	S(N1)	S(C2)	Gr.Avg. S
Hg	9.40±3.68	23.89±22.89	16.64±10.24	5.98±2.16	18.83±3.85	12.40±9.09
Pb	13.18±1.45	28.55±5.69	20.86±10.87	14.13±0.39	21.95±0.85	18.04±5.53
Th	6.08±0.25	11.75±3.55	9.86±4.02	5.95±0.28	12.55±2.05	9.25±3.99
U	0.15±0.02	0.81±0.39	0.60±0.44	0.21±0.02	1.17±1.06	0.69±0.83

4. Conclusion

We have studied the distribution of the heavy metals ^{80}Hg , ^{82}Pb , ^{90}Th and ^{92}U in the geothermal and hydrothermal biogeochemical microcosm of the Los Azufres volcanic complex and have shown that the sites chosen can be considered to be real-time natural laboratories to proxy the Ordovician-Devonian periods. The heavy metals were traced by Polarised Energy Dispersive X-ray Fluorescence spectrometry and Instrumental Neutron Activation Analysis. While the statistical variation is large as would be obvious given the multitude of variables that are involved in such a non-controlable environment, certain trends could nonetheless be clearly observed. We note the following: (1) The primitive, extremophilic plants of the fumaroles – the mosses and ferns – are efficient agents of pedogenesis; (2) that their rhizospheric soil retains more of the heavy metals than the hydrothermal sediments. The former implies that large-scale photosynthesis and the consequent burial of soil organic carbon could have substantially contributed to the late-Ordovician climate cooling by CO_2 draw-down, and the latter, that dissolved heavy metals in the hydrothermal seas could have been one of the reasons for the marine extinction of that period. The aforesaid 'holistic' approach at simulating the Paleozoic environment differs from extant purely laboratory based studies. However, it corroborates the findings of some earlier works.

References

- [1] Ferrari L *et al* 1991 *Journal of Volcanology and Geothermal Research*, **47**, 129-148
- [2] Abuhani WA *et al* 2015 *Journal of Environmental Radioactivity*, **139**, 33-42
- [3] Suarez Arriaga MC *et al* 2000 *Proceedings of the World Geothermal Congress, Kyushu Tohoku*,

- Japan, May 28-June10*
- [4] Stewart WN, Rothwell GW. *Paleobotany and the evolution of plants*. 2nd ed. 1993. Cambridge Univ. Press, Cambridge, UK
 - [5] Parnell J, Foster S. 2012 *Geochemical Transactions*, **13**(1), 7
 - [6] Jenny H, *Factors of soil formation*. 1994. Dover Publications Inc., New York
 - [7] Lenton T *et al* 2012 *Nature Geoscience* **5**, 86-89
 - [8] Vanderbroucke TRA *et al* 2015 *Nature Communications* **6**, 7966
 - [9] Heckel J, Ryon RW 2002 *Polarized beam x-ray fluorescence analysis*. In: Van Grieken R., Markowicz A. (Eds). *Handbook of x-ray spectrometry*, 2nd ed. Marcel Dekker Inc. New York, pp. 603-630
 - [10] Abuhani WA *et al* 2014 *Powder Diffraction* **29**, 159-169
 - [11] Mandel J. 1984. *The Statistical Analysis of Experimental Data*. Dover Publications, New York.
 - [12] Inouye M 1989 *Congenital Anomalies*, **29**(4), 333-344
 - [13] Pilon-Smits E 2005 *Annual Review of Plant Biology*, **56**, 15-39 (2005).