Research Article

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Carbonate stable isotope constraints on sources of arsenic contamination in Neogene tufas and travertines of Attica, Greece

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Abstract: We presented new C and O isotope data of rock-forming calcite in terrestrial carbonate deposits from Neogene basins of Attica (Greece), coupled with standard mineralogical and bulk geochemical results. Whereas both isotope datasets [$\delta^{18}\text{O}$ from -8.99 to -3.20‰ (VPDB); $\delta^{13}\text{C}$ from -8.17 to $+1.40\text{‰}$ (VPDB)] could be interpreted in principle as indicative of a meteoric origin, the clear lack of a statistical correlation between them suggests diverse sources for the isotopic variation of the two elements. On the basis of broad correlations between lower carbon isotope data with increasing Fe and bulk organic carbon, we interpreted the light carbon isotope signatures and As enrichments as both derived mainly from a depositional process involving increased supply of metals and organic carbon to the original basins. Periodically augmented biological production and aerobic cycling of organic matter in the ambient lake waters, would have led to the precipitation of isotopically light calcite in concert with elevated fluxes of As-bearing iron oxy-hydroxide and organic matter to the initial terrestrial carbonate sediment. The terrestrial carbonate deposits of Attica therefore represented effective secondary storage reservoirs of elevated As from the adjacent mineralized hinterland; hence these and similar deposits in the region ought to be regarded as key geological candidates for anomalous supply of As to local soils, groundwater and related human activities.

Keywords: Terrestrial Carbonates; Tufa; Travertine; Stable Isotopes; Arsenic; Contamination; Neogene; Greece

1 Introduction

Environmental arsenic (As) contamination is known to be related to both anthropogenic sources (e.g. mineral processing, wood preservation and combustion of some coal deposits) [1, 2] and natural processes linked to alluvial or deltaic sedimentation, volcanic processes, thermal spring activity and/or the weathering products of associated deposits [3–14]. Yellowish-brown terrestrial carbonate deposits occur in widespread fashion in many geographical areas throughout Attica. Recently, elevated As contents (61–210 mg/kg As) were identified both in such terrestrial carbonates at a quarry in locality Varnavas (NE Attica) – where the rock is exploited as a popular multi-coloured building stone – and in associated soils (33 to 430 mg/kg As) [7]. Compilation of mineralogical, geochemical and combined multivariate statistical and GIS data on several terrestrial carbonate and soil samples, provide evidence for significant contamination in As, Ni, Cr and Ba in the Neogene basins of Attica. This poses a potential impact of alarming dimensions on both human health and surrounding ecosystems alike [15–17]. The integrated water-soil-plant investigation of the arsenic contamination and especially the elevated contamination of the groundwater [2, 18–22] in the Neogene basins of Attica may indicate a potential human health risk in similar Neogene lacustrine formations [17].

Terrestrial carbonates comprise a wide spectrum of lithologies (speleothems, calcrete, lacustrine limestone, travertines and tufas) which are mainly precipitated under subaerial conditions from calcium bicarbonate-rich waters in a large variety of depositional and diagenetic settings [23]. Travertine consists of calcite and/or aragonite, of low to moderate inter-crystalline porosity and often high framework porosity formed within a vadose or shallow phreatic environment [24]. It is a type

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of chemically-precipitated continental limestone deposit that forms around seepages, points of spring emergence, along streams and calcium-rich rivers, and occasionally in lakes. Most travertines are formed from the solutions of surfacing carbon dioxide-rich groundwater. A wide array of other substrata (basalts, rhyolites, carbonatites, ultramafics, granites, dolomites, evaporites) invariably also act as potential source of elements involved in the formation of travertine [23]. Seasonal climatic factors and tectonic activity, variations in lateral and vertical travertine facies, geographic locality and base topography of travertine formation, fluctuations in the volume of the waters storing travertine, and changes in organic carbon fluxes and flow rate of surface runoff, are all parameters that either singly or in combination is frequently encountered in travertine fields [24]. Travertine formed by hotter water in hydrothermal systems is generally more widespread than tufa that formed in cooler spring waters [25–27].

Travertine deposits have a carbon isotope composition that typically ranges between -1 to 10‰ [24, 26]. Typically, downstream temperature changes, evaporation and mineral phase change (*e.g.* aragonite to calcite) lead to systematic changes in the carbonate $\delta^{18}\text{O}$. Turi [28] argued that during CO_2 degassing, the lighter isotopes would be preferentially lost, leading to heavy isotope enrichment in the deposited travertine in geothermal environments.

Capezzuoli *et al.* [27] describe tufa deposits as terrestrial carbonates which are formed under surface open-air conditions in streams, rivers, and lakes, as products of a combination of physicochemical and microbiologically mediated processes. Consequently, they typically contain biological remnants such as microphytes, macrophytes, invertebrates and bacteria [25]. The majority of tufa deposits forms in limestone terrains and are essentially terrestrial carbonate deposits whereby the carrier CO_2 originates in the soil and epigeal atmosphere. They are the most widely distributed and often display characteristic fabrics. Isotopically, tufas have a $\delta^{13}\text{C}$ range from -12 to 0‰ , reflecting the depleted ^{13}C character of soil-derived CO_2 [24, 29].

The present study presents application of carbonate-carbon and oxygen isotope ratios of representative samples of terrestrial carbonate deposits occupying a significant part of Neogene basins of Attica. We compare the data with published data on travertine and tufa deposits. Thereafter, we assess the origin of these signatures in the context of co-existing As anomalies in the host carbonates, in an attempt to establish the potential value of light stable isotopes in constraining sources of environmental As contamination in the study area and beyond.

2 Geological background

The alpine basement of Attica is composed both of metamorphic and non-metamorphic rocks and covered by post-alpine Neogene to Quaternary formations [30–39]. In Attica, the deposition of the terrestrial carbonates (total surface area of about 30 km^2) is associated with the lacustrine Upper Miocene deposits in the three main Neogene basins (Figure 1), which are distinguished in: 1) the Kalamos - Varnavas basin to the north, forming part of the longitudinal basin of Thiva - Tanagra – Malakassa; 2) the southern basin of Athens; and, 3) the Mesogeia basin in the south-east. The color of terrestrial carbonates varies from yellow-brown in the Kalamos - Varnavas basin to reddish in the Mesogeia basin. Their porosity is varied, with the most compact travertine occurring in the Kalamos region and their stratigraphic thickness generally varies from a few m to several tens of m. The terrestrial carbonates are accompanied by intense surface karstification in the Kalamos - Varnavas basin, whereas the same deposits are associated with fault zones in the Athens and Mesogeia basins. During the Upper Miocene, the climate was still warm and humid and led to the development of the local lignite basins (Malakassa – Oropos, Kalogreza, Peristeri, Rafina) in the Neogene basins of Attica [34].

The basin of Kalamos - Varnavas is the result of tectonic movements with vertical displacements of the Lower Miocene that continue until today. The main structure is the NNE – SSW Attica detachment fault starting from the southern Evoikos Gulf and ending in the Saronic Gulf, which plunged the western plate of the unmetamorphic rocks and raised the eastern plate of the metamorphic rocks from the deepest part of the lithosphere during the transformation of the Eocene-Oligocene [38].

The sedimentary infill of specifically the Kalamos - Varnavas and Athens basins consists of marls and marly limestones with lignite intercalations and travertine, while stratigraphically upwards fluvio-lacustrine deposits of clays, sandstones and conglomerates are developed [36]. In the Mesogeia basin, the first stages of sedimentation began in the Upper Miocene [33], following cooling and formation of high pressure rocks in the fragile upper crust, at 8–9 my BP as determined by the intrusive age of the Lavrion granodiorite [40, 41]. The formation of the basin and the simultaneous removal of the metamorphic rocks are interconnected processes that are controlled by detachment faults [33]. Due to the development of intense hydrothermal activity, the well-known porphyry type, vein and carbonate-hosted massive sulfide Pb-Zn-Ag ores of Lavrion were formed [42–44]. In the Meso-

Figure 1: Geological sketch map of Attica, showing the sampling sites (modified from Kampouroglou, 2016; after I.G.M.E., 2000; 2002; 2003; Papanikolaou *et al.*, 2004).

geia basin, the deposition of marls, travertine, marly limestones and fluvio-terrestrial sediments took place on the basement, depending on the morphology of the basin and provenance. Although any continuity between the Grammatiko Fe–Mn mineralization and the famous Lavrion mining district is not obvious, underground mining at Grammatiko revealed geological and structure relationships between hosting rocks and the ferromanganese formation or gossans [15, 16, 41].

Today, active thermogenic travertine deposits accompanied with surface manifestation of several hot springs [45] are found in the northwestern Euboea Island and the neighboring part of the mainland in eastern Central Greece (Sperchios area). These are linked to an active hydrothermal system controlled by active tectonics, and supplied with heat by a 7–8 km deep magma chamber (Plio-Pleistocene).

3 Methods

For the present study, we collected diverse and representative carbonate rock material: five samples came from the Kalamos-Varnavas basin (north Attica); two samples came from the areas of Kaisariani and Papagou of the Athens basin (south Attica); and three samples represented the Drafi and Artemida areas of the Mesogeia basin (south-east Attica). We initially crushed, homogenized and split the samples, and subsequently pulverized them using an agate mortar, to particle size less than 100 mesh. This fraction was used for major, trace element and stable isotope (carbon and oxygen) analyses of the bulk carbonate fraction (Table 1). The rock samples were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) after Aqua Regia Digestion at the ACME Analytical Laboratories in Canada. We checked the analytical precision for major and trace elements by means of duplicate samples and in-house standards, and found to be within international standards.

Table 1: Major and trace elements, carbon and oxygen isotopic composition in terrestrial carbonates from Neogene basins of Attica.

Location	Kalamos-Varnavas basin				Athens basin			Mesogeia basin			Detection limit	Reference materials		Calcareous rocks*
	Kalamos area		Varnavas area		ELKE	AGI	Artemida area	AR R4	AR R7	Drafi area		STD	DS9	
Sample	VAR	LF	ER1	ER2	KAL	R18	R24	2P	THP	DR R5				
mg/kg														
As	250	61	102	48	800	230	110	63	61	180	0.5	9.1	27	1–2.5
Cu	7	5.1	5.6	4	36	6.8	13	1.0	1	1	0.1	690	110	2–10
Pb	160	43	51	4.8	21	78	84	7	10	3	0.1	14	130	3–10
Zn	220	87	130	9	75	250	110	1	29	10	1	29	310	10–25
Ni	24	26	22	25	410	970	530	1	29	15	0.1	380	43	5–20
Co	11	42	9.2	4.4	34	45	23	1	3	1	0.1	53	8	0.1–3
Mn	560	2400	210	170	470	340	1800	260	310	260	1	400	590	200–1000
Sr	63	60	40	82	27	20	75	120	74	280	1	2	60	460–600
Sb	18	1.9	2.7	0.7	14	3.7	14	2.5	3	7	0.1	0.1	4.5	0.15–0.3
V	10	5	9	5	50	23	12	3	4	4	2	300	40	10–45
Cr	9	12	34	22	970	380	12	6	18	9	1	990	130	5–16
Ba	72	430	42	18	38	9	130	35	27	34	1	150	340	50–200
Sc	0.5	2.2	2.5	0.5	5	4.8	1.8	0.5	0.5	0.5	0.1	79	2.5	0.5–5
wt. %														
Fe	1.1	0.3	0.7	0.4	2.2	1.7	2.6	0.07	0.3	0.4	0.01	22	2.4	0.4–1.0
Ca	36	37	32	33	34	28	28	37	36	35	0.01	0.06	0.7	-
Mg	0.1	0.1	0.1	0.3	0.2	0.3	2.6	0.1	0.1	0.2	0.01	0.09	0.6	-
Al	0.1	0.2	0.2	0.1	0.5	0.10	0.11	0.02	0.2	0.09	0.01	3.2	1	0.4–1.3
Na	0.01	0.003	0.003	0.007	0.01	0.010	0.013	0.01	0.01	0.01	0.001	0.02	0.1	-
K	0.02	0.03	0.03	0.03	0.09	0.02	0.03	0.01	0.04	0.02	0.01	0.05	0.4	-
P	0.01	0.01	0.01	0.006	0.01	0.004	0.019	0.004	0.01	0.003	0.001	0.03	0.1	-
LOI (440°C)	0.30	0.14	0.31	0.15	0.58	0.41	0.65	0.08	0.05	0.15				
O.M.**	0.14	0.10	0.21	0.09	0.27	0.17	0.28	0.07	0.01	0.09				
$\delta^{13}\text{C}_V$ PDB	-3.20	-1.16	-3.35	0.64	-7.37	-8.17	-4.14	0.97	1.40	-1.53				
$\delta^{18}\text{O}_{VPDB}$	-3.20	-8.99	-7.92	-7.70	-6.90	-7.28	-5.68	-8.53	-7.53	-7.84				

* Kabata-Pendias, 2011

** = calculated total organic matter content (see text for details)

Representative rock sections were also mounted in resin, polished and carbon-coated, and examined by means of reflected light microscopy, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). We carried out semi-quantitative spot analyses and SEM imaging at the University of Athens, Department of Geology and Geoenvironment, using a JEOL JSM 5600 SEM instrument, equipped with an automated EDS analysis system ISIS 300 OXFORD, under the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, time of measurement 50 sec and beam diameter 12 μm . The spectra were processed using the ZAF program (3 iterations). We obtained the XRD data using a Siemens Model 5005 X-ray diffractometer, Cu-K radiation at 40 kV, 40 nA, 0.020° step size and 1.0 sec. step time. The XRD patterns were evaluated using the EVA 2.2 program of the Siemens DIFFRAC and the D5005 software package.

We determined the moisture content of the samples by drying them initially at 105°C in an oven overnight. We determined the organic matter content by ignition of the oven-dried samples in a muffle furnace at 440°C for 3 h [46]. We calculated the organic matter content (Table 1) as the difference between the initial and final sample weights divided by the initial sample weight and multiplied by 100 to yield the wt.% fraction [46, 47]. All organic carbon determinations were averages of duplicate determinations. In addition, assuming that the weight loss can derive from organic matter oxidation and H_2O released from Fe-hydroxides, and that all iron is hosted in goethite [48], we calculated the expected organic matter. It is lower than the measured one (Table 1), and with exception of one sample with negligible content (0.05 wt.% O.M.) the (organic matter measured)/(organic matter calculated) ratio showed a variation between 1.40 and 2.43 (average = 1.86 ± 0.42).

Results for C and O isotope ratios of all samples of travertine limestone selected for this study were obtained at the stable isotope laboratory of the Department of Geosciences at the University of Cape Town in South Africa, following standard analytical protocols (see [49], for details). Data from this study and also from literature are hereafter presented in the conventional δ notation relative to V-PDB ([50]; Table 1). It should be noted that the CO_2 gas for isotope measurements was evolved after reaction of sample powders in pure phosphoric acid at 25°C over 6 hours; hence the data represent only the dominant calcitic fraction of the samples.

4 Results

The predominant mineral in the carbonate samples of the Kalamos-Varnavas basin was Mg-poor calcite microcrystals (Table 2; Figure 2) while in the areas of Papagou and Kaisariani (Athens basin), minor dolomite also occurred as a residual mineral in fracture zones, in addition to calcite (Table 3; Figure 3). Quartz, goethite, hematite, siderite, Mn-Fe-Ni-Co (hydro)oxides, apatite (fluor-hydroxylapatite), rutile and rare earth element (REE)-bearing minerals such as xenotime, were also present in varying proportions in the studied samples. In the Kalamos (Kalamos-Varnavas basin) (Table 2; Figure 2) and Kaisariani area (Athens basin), minor siderite in particular showed significant Cr, As (up to 3.0 wt.% As_2O_3) and Ni contents (Table 2-3). Although carbonates from the Mesogeia basin were dominated by pure calcite, in the Artemida area the carbonates record elevated Mg, Fe and As contents (Table 4-5; Figure 4-5). Siderite, goethite, sphalerite, chromite, and lesser rutile and Cu-Zn sulfosalts were also present in smaller amounts in the Artemida area.

Generally, the terrestrial carbonate samples of this and previous related studies [16] showed high average contents in As (70 mg/kg), Cu (19 mg/kg), Zn (169 mg/kg), Ni (79 mg/kg), Co (1 mg/kg), Sb (3 mg/kg), and Cr (50 mg/kg), while average values of Sr (118 mg/kg), Ba (45 mg/kg) and Al (0.29 wt.%) were lower as compared to average global ranges in calcareous rocks [1]. The samples examined here exhibit much higher levels in As and heavy metals like Pb, Zn, Ni, Co, Sb and Cr than common calcareous rocks [1] (Table 1). We observed the highest As contents in samples from the Kalamos area (800 mg/kg) in the Kalamos – Varnavas basin. The Cr content was often accompanied by elevated Ni, Co and Fe contents (Table 1). Calculated organic matter content ranged from 0.01 to 0.28 wt.% and showed a negative correlation with calcium ($r = -0.64$) and a good positive correlation with arsenic ($r = 0.59$; Figure 6a) and total iron ($r = 0.89$; Table 6; Figure 6b). Arsenic showed moderate to good positive correlation with Cu, Ni, Sb, V, Cr and Fe (Table 6).

Carbon and oxygen isotope data of carbonate samples from Kalamos-Varnavas, Athens and Mesogeia basins (Figure 7) are shown in Table 1. The $\delta^{18}\text{O}$ values range from -8.99 to -3.20 ‰ while $\delta^{13}\text{C}$ data show a wider range from -8.17 to 1.40 ‰. The poor statistical correlation between the two isotopic datasets is illustrated on the binary plot of Figure 7. Negative $\delta^{13}\text{C}$ values represented mainly the samples from the Athens and Kalamos – Varnavas basin, whereas the samples from the Mesogeia basin ranged from -1.53 to 1.40 ‰ (VPDB) (Table 1). Correlation between $\delta^{13}\text{C}$

Table 3: Representative microanalyses of calcite, siderite, hematite, goethite, Mn-Fe-Ni-Co (hydro)oxides and rare earth elements (REE) minerals of tufas in the Athens basin (South Attica).

Kalamos						Varnavas					
wt%	Calcite	Siderite	Hematite	Fe-Mn (hydro)oxides	REE	Calcite	Siderite	Goethite	Mn-Fe (hydro)oxides	Fe-Mn (hydro)oxides	REE
SiO ₂	n.d	7.3	0.9	3.8	0.5	4.2	2.4	1.2	2.8	1.0	
Al ₂ O ₃	n.d	4.6	n.d	6.0	0.6	n.d	2.3	2.3	15.5	4.7	
As ₂ O ₃	n.d	2.8	n.d	1.5	n.d	n.d	n.d	1.7	3.4	2.5	
FeO	n.d	40.8	4.5	52.8	n.d.						
Fe ₂ O ₃	n.d	91.1	44.8	81.3	5.8	60.8	n.d.				
Cr ₂ O ₃	n.d	1.9	n.d	n.d	n.d.	n.d	0.4	n.d.	n.d.	n.d.	n.d.
K ₂ O	0.2	n.d.	n.d	n.d.	n.d.	n.d	0.6	n.d.	n.d.	n.d.	n.d.
P ₂ O ₅	n.d.	n.d.	n.d.	n.d.	26.0	n.d.	n.d.	n.d.	n.d.	n.d.	37.6
TiO ₂	n.d	n.d.	n.d	n.d	n.d.	n.d	0.6	n.d.	0.4	n.d.	0.5
CaO	52.1	3.1	1.6	16.1	7.1	47.1	0.8	0.5	2.7	3.6	0.9
MnO	n.d	n.d.	n.d	1.7	n.d.	n.d	n.d	n.d.	44.1	n.d.	n.d.
MgO	n.d	0.5	n.d	n.d	n.d.	n.d	n.d	1.1	n.d.	n.d.	n.d.
NiO	n.d	0.5	n.d	n.d	n.d.	n.d	n.d	n.d.	2.1	n.d.	n.d.
ZnO	n.d	n.d.	n.d	n.d	n.d.	n.d	n.d	n.d.	2.1	n.d.	n.d.
BaO	n.d	n.d.	n.d	n.d	n.d.	n.d	n.d	n.d.	2.2	n.d.	n.d.
SO ₄	n.d	0.4	n.d	0.5	0.6	n.d	n.d	n.d.	n.d.	n.d.	n.d.
Y ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	49.6
Dy ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.8
La ₂ O ₃	n.d.	n.d.	n.d.	n.d.	16.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CeO ₂	n.d.	n.d.	n.d.	n.d.	31.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nd ₂ O ₃	n.d.	n.d.	n.d.	n.d.	9.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	52.3	61.9	93.5	74.4	92.2	52.1	61.7	87.6	77.8	75.3	96.9

Table 4: Representative microanalyses of calcite, siderite and goethite of travertine in the Mesogeia basin (Southeast Attica).

		Artemida				Drafi	
wt%		Calcite		Calcite		Siderite	Goethite
SiO ₂	n.d	0.9	n.d	n.d	n.d	n.d	n.d
As ₂ O ₃	n.d	0.9	n.d	n.d	n.d	n.d	n.d
Cr ₂ O ₃	n.d	n.d	n.d	n.d	n.d	n.d	n.d
FeO	n.d	n.d	n.d	60.8	61.5	70.6	
Fe ₂ O ₃	n.d	9.9	n.d	n.d			
K ₂ O	n.d	0.2	n.d	0.1	n.d	n.d	n.d
SO ₄	n.d	n.d	0.4	0.5	n.d	n.d	n.d
CaO	51.3	41.9	52.1	51.7	1.0	1.2	1.4
MnO	n.d	n.d	n.d	n.d	n.d	n.d	n.d
MgO	0.8	n.d	n.d	n.d	n.d	n.d	n.d
NiO	n.d	n.d	n.d	n.d	n.d	n.d	15.2
ZnO	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Total	52.1	53.8	52.5	52.3	61.8	62.7	87.2

Figure 2: Representative backscattered SEM image of the tufa at the Kalamos area (Kalamos-Varnavas basin) showing dark grey calcite, light grey siderite and Mn-Fe (hydro)oxides. Abbreviations: Cal=calcite; sd=siderite.

Table 5: Mineralogical composition by X-ray diffraction of the terrestrial carbonates in the Neogene basins of Attica.

Location		Sample	Calcite	Dolomite	Quartz	Illite
Kalamos-Varnavas basin	Kalamos	KAL-R18	+	+		
		KAL-R24	+			
	Varnavas	LF_ER1	+		+	
		LF_ER2	+		+	+
		VAR-R5	+			
Mesogeia basin	Drafi	DR-R5	+			
	Artemida	AR-R4	+			
		AR-R7	+			
Athens basin	Kaisariani	ELKE 2P	+	+	+	
	Papagou	AGITHP	+	+

Figure 3: Representative backscattered SEM image of the tufa at the Papagou area (Athens basin) showing black dolomite, dark grey calcite and light grey goethite. Abbreviations: Dol=dolomite; Cal=calcite; Gth=goethite.

values and both total Fe (Figure 8a) and organic matter (Figure 8b) appeared to be broadly negative, pointing to a possible relationship between the cycles of Fe and organic carbon in the primary depositional environment. That relationship will be explored further in the section that follows.

5 Discussion

5.1 Comparison and origin of isotopic signatures

Comparison between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of carbonates from the Neogene deposits of Attica with those for

Figure 4: Representative backscattered SEM image of the travertine at the Drafi area (Mesogeia basin) showing dark grey calcite and sphalerite. Abbreviations: Cal=calcite; Sp=sphalerite.

Figure 5: Representative backscattered SEM image of the travertine at the Artemida area (Mesogeia basin) showing dark grey calcite and chromite. Abbreviations: Cal=calcite; Chr=chromite.

Figure 6: Plot of As (a) and Fe (b) content *versus* organic matter in terrestrial carbonates. Data from Table 1 and Table 6.

the Denizli basin of Turkey, indicate that samples from the Kalamos – Varnavas and Athens basins – whose $\delta^{13}\text{C}$ values range from -8.17 to 0.64‰ – compare better with tufas. Travertine from the Denizli Basin of Turkey (Figure 7) has $\delta^{13}\text{C}$ values ranging from -3.3 to 11.7‰ and $\delta^{18}\text{O}$ values from -16.6 to 15.6‰ , whereas tufa from the same locality has $\delta^{13}\text{C}$ values ranging from -4.0 to 4.7‰ and $\delta^{18}\text{O}$ values from -10.3 to -8.3‰ [51]. By contrast, carbonates of the Mesogeia basin display relatively higher $\delta^{13}\text{C}$ values from -1.53 to 1.40‰ which compare better with travertines forming by hot aqueous fluids in a hydrothermal system. The same carbonates are also similar with those of travertine in the area of Veroia, Northern Greece, whose $\delta^{13}\text{C}$ values range from -5.86 to -0.04‰ and $\delta^{18}\text{O}$ values from -12.12 to -8.25‰ [52] (Figure 7).

On the basis of carbon isotope composition, the terrestrial carbonate deposits studied in this manuscript can therefore be distinguished between travertine-type in the Mesogeia basin and tufa-type in the basins of Kalamos – Varnavas and Athens. The tufa-like samples are composed mainly of calcite micro-crystals, cementing variable

amounts of other minerals, including Fe-Mn-hydroxides that confer on the bulk rock a brownish-yellow color. Our tufas share the same general characteristics of the meteorogenic travertine of lake facies (lacustrine travertine) described by Pentecost [24]. Their low stable isotope data (Table 1) would principally indicate a meteoric origin, whereas variability in $\delta^{18}\text{O}$ would reflect the relative contribution of isotopically light meteoric waters interacting with the limestone at variable water-rock ratios and temperatures. However, the lack of any clear correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in travertine calcite as indicated earlier (Figure 7) suggests a probable decoupling in the origin of the isotopic variations in C and O, which is at apparent odds with classic diagenetic models of carbonate re-equilibration with a common (with respect to C and O), CO_2 -bearing meteoric fluid source.

5.2 Isotopic constraints on As contamination

Mineralogical and geochemical data of the studied tufas in Kalamos-Varnavas and Athens basins and particularly the presence of Fe-Mn-hydroxides, minor base metal sulphides, as well as F-apatite, quartz, Ti-oxides, zircon, sphene, rutile and REE-phosphate minerals [16] provide evidence for a detrital and chemical contribution from the erosion of mineralized rocks at Grammatiko (Fe-Mn oxides) [16]. The same basins would have probably also received variable fluxes of organic matter. The plots of As, Fe and bulk organic carbon against calcite carbon isotope data revealed a positive correlation (Figure 6a, 6b) and may reflect a common link of these components with redox processes in the primary depositional environment. Organic matter is an important component in aqueous environments as it can sequester a wide range of dissolved ions such as iron during diagenesis. Its preservation in a porous tufa is also likely to be influenced by oxygen availability in an aerobic environment [24].

Among the As-minerals in the terrestrial carbonate samples are the bacterio-morphic aggregates of goethite containing up to 3.4 wt.% As_2O_3 , Fe-(hydro) oxides and Mn-Ba-(hydro) oxides (hollandite) containing up to 1.7 wt.% As_2O_3 and siderite with up to 3.0% wt.% As_2O_3 [16]. The proposed mechanisms of arsenic transport and reaction pathways in groundwater include the oxidation of arsenic-containing pyrite [53, 54], the reduction of adsorbed As(V) to As(III) [55, 56], the competitive anion exchange of adsorbed arsenic [57, 58] and the reductive dissolution of arsenic-containing iron oxides [59–61].

Table 6: Correlation matrix of major and trace elements in the terrestrial carbonates from Neogene basins of Attica.

	As	Cu	Pb	Zn	Ni	Co	Mn	Sr	Sb	V	Cr	Ba	Sc	Fe	Ca	P	O.M.
As	1.00																
Cu	0.62	1.00															
Pb	0.29	0.63	1.00														
Zn	0.45	0.67	0.83	1.00													
Ni	0.55	0.74	0.50	0.74	1.00												
Co	0.40	0.84	0.77	0.83	0.78	1.00											
Mn	0.03	0.41	0.54	0.43	0.34	0.60	1.00										
Sr	-0.41	-0.70	-0.65	-0.67	-0.64	-0.81	-0.11	1.00									
Sb	0.76	0.46	0.46	0.43	0.40	0.25	0.36	-0.08	1.00								
V	0.83	0.88	0.53	0.66	0.82	0.75	0.16	-0.78	0.55	1.00							
Cr	0.69	0.64	0.20	0.43	0.71	0.59	-0.12	-0.79	0.17	0.87	1.00						
Ba	-0.16	0.20	0.33	0.20	-0.11	0.30	0.84	0.17	0.21	-0.15	-0.43	1.00					
Sc	0.51	0.74	0.52	0.62	0.73	0.83	0.33	-0.80	0.21	0.80	0.78	0.06	1.00				
Fe	0.68	0.84	0.61	0.80	0.90	0.72	0.30	-0.56	0.62	0.86	0.59	-0.02	0.63	1.00			
Ca	-0.19	-0.48	-0.43	-0.50	-0.77	-0.51	-0.08	0.48	-0.14	-0.54	-0.44	0.30	-0.56	-0.71	1.00		
P	0.24	0.69	0.63	0.55	0.40	0.49	0.40	-0.38	0.48	0.47	0.12	0.39	0.30	0.61	-0.28	1.00	
O.M.	0.62	0.90	0.66	0.70	0.73	0.78	0.44	-0.55	0.55	0.81	0.51	0.22	0.75	0.87	-0.64	0.57	1.00

Figure 7: Plot of $\delta^{18}\text{O}_{\text{VPDB}}$ versus $\delta^{13}\text{C}_{\text{VPDB}}$. Data from Table 1; Koukouvou (2012); Özkül *et al.* (2013).

Variations in surface runoff and thus quantitative transfer of As-enriched Fe/Mn hydroxides into the Neogene basins of Attica would have been primarily a function of changing climatic/tectonic conditions through the lifetime of these basins in combination with source rock composition at the hinterland. The Early Miocene - Late Pliocene is thought to have marked a period of fluvio-lacustrine deposit formation in the study area (marls, marl limestone, travertine or tufa, clays and conglomerates), affected by syn-depositional tectonic activity. The Zefiri - Ag. Paraskevi fault (Figure 1) with a WNW-ESE strike direction is thought to have extended to the southern part of the investigated region (Athens basin) and created a graben in the northern part (Kalamos-Varnavas basin and the larger basin of Assopos). A key consequence of this tectonic regime was a topographically elevated area to the south, which functioned as a physical barrier preventing incursion of marine waters. This natural “dam” was ultimately responsible for the formation of seasonal lakes further north in the Kalamos-Varnavas basin [39]. Paleoflora studies have revealed that the concurrent Late Miocene climate was humid and warm [34]. During wet periods, soil activity was stronger therefore resulting in more negative $\delta^{13}\text{C}$ values [26] akin to those recorded in our studied carbonates. Such climatic conditions would have prob-

ably also favored the formation of marly limestone with lignite intercalations such as those seen in Almyropotamos, Pikermi, Mavrosouvala, and Milesi [62, 63]. The lakes therefore seem to have formed in dynamic response to an integrated environmental, climatic and tectonic realm, and their sedimentary archive thus provides a continuous record of local and regional change [64].

We contend that the oxygen isotope data of sedimentary calcite may record the compound effect of isotopic exchange processes post-depositionally, in contact with CO_2 -poor, isotopically light meteoric waters. We assert, however, that the light carbon isotope signal of the latter requires an alternative interpretation that may be linked chiefly to the aqueous environment of primary terrestrial carbonate deposition. We envisage that during periods of accelerated weathering, the detrital and thus organic input to the basins would be expected to have increased. The increased flux of specifically particulate iron oxyhydroxides may have provided an essential micronutrient promoting primary biological production in the surface waters of the lacustrine basins. This would have probably resulted in amplified aerobic redox cycling of organic carbon in the basin waters and recycling thereof as isotopically light CO_2 .

Figure 8: Plots of Fe (a) and organic matter (b) versus $\delta^{13}\text{C}_{\text{VPDB}}$. Data from Table 1 and Table 6.

It is the contribution of such isotopically light carbon to authigenic calcite formation that we consider to have driven its carbon isotope values lower. This signal of lower $\delta^{13}\text{C}$ calcite would ultimately be transferred to and recorded in the sediment through primary carbonate precipitation. In the same environment, the deposition of isotopically light calcite would have been coupled with increased export of As-bearing particulate Fe-hydroxides to the sediment, resulting in the observed broad relationship between higher abundances of Fe and As, organic carbon and lower $\delta^{13}\text{C}$ calcite. In light of the above arguments, we would also interpret much of the observed As anomaly as linked mainly to primary processes of As-bearing ferric hydroxide deposition, and to a much lesser extent on redistribution of As through later diagenetic fluid-flow. We must also stress, however, that the alternative interpretation of a hydrothermal system having influenced the deposition of travertine in the Mesogeia basin and the elevated As contents measured therein [33] remains potentially plausible, but cannot be conclusively constrained by our new results.

6 Conclusions

The present study sheds new light on the overall paleo-environmental conditions in Neogene lacustrine basins of Attica that led to the formation of As-enriched carbonate deposits such as travertine and tufa. Previous publications argue that the studied deposits formed during warm humid periods of the Upper Miocene, under a tectonically-controlled regime of lake development devoid of any significant marine incursion. Influx of meteoric water to these basins maintained primarily by surface runoff transferred variable fluxes of As-enriched Fe/Mn hydroxides into the basins where travertine precipitation occurred. Metals such as Cu, Ni and Cr, and the metalloid As were sourced primarily from adjacent mineralized rocks at the hinterland. Combination of mineralogical, geochemical and stable isotope data and specifically the good statistical correlation between Fe-oxide abundance, organic matter content and calcite carbon isotopes, point to a mainly primary depositional process of As sequestration in Fe hydroxide, coupled with organic carbon cycling in the basin and coprecipitation of isotopically light calcite. Later diagenetic influx of isotopically low meteoric waters with respect to at least oxygen is by no means precluded, but it is not deemed to have been central to the observed As anomalies themselves. Further attention must thus be placed on identifying and delineating all terrestrial carbonate deposits (tufa and travertine) in Attica as key reservoirs of As with the potential to adversely impact human health and ecosystems.

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