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Origin of the geogenic gases and preliminary estimation of the carbon release of Greece

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Volatiles are transported from the deep crust or mantle to the surface in geodynamically active areas where seismic, volcanic and geothermal activity is present; the circulation of hydrothermal fluids in the crust is enhanced. In such areas, faults may act as preferential pathways for advective gas-carrying fluid transport. Towards the surface, pressure decrease allows the gases to escape from the fluids into soil gas and eventually into the atmosphere (King, 1986). The migration of carbon-bearing crustal and mantle fluids contributes to Earth's carbon cycle (Berner & Kothavala 2001). However, till now, the mechanisms, magnitudes and time variations of carbon transfer from depth to the surface remain the least understood parts of the global carbon budget. Carbon dioxide and methane are the main contributors of the total amount of C-degassing from geological (volcanic and non-volcanic) sources. From the beginning of the last century, high attention has been paid to the reservoirs of CO_2 and CH_4 in the atmosphere because they represent the most dangerous species in terms of global warning. The increased amount of carbon dioxide and methane in the atmosphere has important implications for the energy balance and the chemical composition of the atmosphere. Mörner and Etiope (2002) calculated that 10^2-10^3 Mt of CO_2 are presumably involved in the carbon cycle every year. This estimation though, is affected by high uncertainty as a number of sources and C-degassing environments that account for this high leakage were not taken into consideration.

Greece belongs to the most geodynamically active regions of the world and as such, it has to be considered an area of intense geogenic degassing. Regarding carbon, the territory is characterized by the high hydrothermal and volcanic activity of the South Aegean Active Volcanic Arc (SAAVA), and by widespread geological seeps of buried carbon dioxide and methane. In the present work, we present more than 700 literature data of free gases spread along the whole Hellenic territory to get insight on geographic distribution and composition of the released fluids. Moreover, we review all the published studies on CO_2 and/or CH_4 output of high degassing areas of Greece that are mainly concentrated along the SAAVA in a first attempt to estimate the total geologic output of the nation.

Helium isotope data propose that the highest mantle contribution (50 to 90%) is found along the SAAVA, whereas the lowest in continental Greece (0-20%), with the atmospheric contribution being mostly negligible. Based on the geographical distribution of the gases, it is evident that the R/R_A ratios and CO_2 concentrations increase in areas characterized by: i) thin crust; ii) elevated heat flow values; iii) recent (Pleistocene-Quaternary) volcanic activity; and iv) deep routed extensional or transtensional regional faults. The highest values are therefore found along the SAAVA and the lowest in the western part of Greece where CH_4 emission is prevailing. Furthermore, it was noticed that the majority of the samples present a prevailing limestone C component, whilst only few samples have a prevailing mantle C component (Sano and Marty, 1995). It seems barely possible though to distinguish CO_2 deriving from crustal and slab-related limestones. Additionally, due to the complex geodynamic history, the mantle C isotope composition could be affected by subduction-related metasomatism and, similarly to the nearby Italian area (Martelli et al., 2008), the C isotope composition could be more positive. In this case, the mantle contribution is probably underestimated.

In terms of geogenic carbon degassing, the best studied and most exhaling area is the SAAVA, which releases 104,090 t/a of CO_2 and 20.26 t/a of CH_4. Continental Greece on the contrary, is much less studied but may release CO_2 in the same order of magnitude in its eastern-central and northern part. The western and south-western parts of Greece are conversely the main area of methane and higher hydrocarbon degassing. Methane output of Greece is much less constrained but the presence on its territory of one of the biggest thermogenic gas seepages of Europe releasing about 200 t/a of CH_4 to the atmosphere underscores its potentially high contribution.

Approximately 114,310 t/a of CO_2 and 221 t/a of CH_4 are released from the whole Hellenic territory (Daskalopoulou et al., submitted). This estimation though, should be considered minimum as there are processes and sources that have not been taken into consideration yet. More specifically, in the submarine manifestations found at greater depths, gases cannot reach the sea surface due to the dissolution process that takes place along the water column; this is especially true for CO_2 that is more soluble in water respect to other gases (eg. Milos - Dando et al., 1995; Kolumbo - Rizzo et al., 2016 etc). Moreover, the geological and geodynamic regime can contribute in the formation of CO_2 reservoirs. This is the case of Florina Basin (Pearce et al., 2004) where more than one CO_2 reservoirs were created, with one of them being exploited by the company Air Liquide Greece. It is worth noting that this reservoir, found at a depth of approximately 300 m, produces 30,000 t/a of CO_2 (Pearce et al., 2004). Moreover, in the same area, water is also used for water supply and irrigation purposes. This water though contains a great amount of dissolved CO_2 great part of which is released to the atmosphere when the water is pumped to the surface. Another source that should be underscored is the quantification of geogenic CO_2 dissolved in big karstic aquifers. Chiodini et al. (1999, 2000) demonstrated that the relatively high solubility of CO_2 in water plays an important role in the quantification of carbon. This approach was proved for central Italy and it might be the case for continental Greece due to the similar geodynamic history. Finally, in ophiolitic sequences where serpentinization takes place, if and when the conditions are adequate (i.e. presence of effective catalysts – Etiope and

Ionescu, 2015) an abiogenic origin for CH_4 seems to be favored even at low temperatures. Ophiolitic sequences crop out widely in Greece along two N-S trending belts, whilst more hyperalkaline springs or dry seeps may be present. However, their flux in generally is very low and therefore their contribution to the total natural CH_4 output has probably to be considered negligible.

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