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ABSTRACT

The studied area is a 130 km long fast spreading graben in Central Greece. Its complex geodynamical setting includes both the presence of a subduction slab at depth responsible for the recent (Quaternary) volcanic activity in the area and the western termination of a tectonic lineament of regional importance (the North-Anatolian fault). A high geothermal gradient is made evident by the presence of many thermal springs with temperatures from 19 to 82 °C, that discharge along the normal faults bordering the graben.

In the period 2004–2012, 58 gas and 69 water samples were collected and their chemical and isotopic analysis revealed a wide range of compositions.

Two main groups of thermal waters can be distinguished on the basis of their chemical composition. The first, represented by dilute waters (E.C. <0.6 mS/cm) of the westernmost sites, is characterised by the presence of CH₄-rich and mixed N₂–CH₄ gases. The second displays higher salinities (E.C. from 12 to 56 mS/cm) due to mixing with a modified marine component. Reservoir temperatures of 150–160 °C were estimated with cationic geothermometers at the easternmost sites.

Along the graben, from west to east, the gas composition changes from CH₄- to CO₂-dominated through mixed N₂-CH₄ and N₂-CO₂ compositions, while at the same time the He isotopic composition goes from typical crustal values (<0.1 *R*/*R*_A) up to 0.87 *R*/*R*_A, showing in the easternmost sites a small (3–11%) but significant mantle input. The δ^{13} C values of the CO₂-rich samples suggest a mixed origin (mantle and marine carbonates).

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1. Introduction

The studied area, the Sperchios Basin — Evoikos Gulf Graben (Fig. 1), has a complex geological history. Its high geodynamic activity has long been recognised. In fact it was documented in the earliest historical documents as well as in the Greek mythology (Fytikas et al., 1999). The legends tell us, in fact, that the battle between the Greek gods and the Titans occurred in this area, at the foot of Mt. Orthrys. This battle has been interpreted as a memory of intense prehistoric volcanic and seismic activity (Fytikas et al., 1999).

This area has been renowned as having one of the highest geothermal gradients in Greece outside the South Aegean active volcanic arc (SAAVA) (Fytikas and Kolios, 1979). It is a 130 km long actively spreading graben in Central Greece bordered by active faults (1 cm/a – Makris et al., 2001). Its complex geodynamical setting includes the presence of both a thinned crust (20 km thickness below the central part of the northern Evoikos Basin) and a subduction slab responsible for the recent (Quaternary) volcanic activity in the area (Makris et al., 2001). Some studies (Fytikas et al., 1976; Bellon et al., 1979; Papoulia et al., 2006) have suggested that the volcanic products of this area represent the northward continuation of the SAAVA.

Another important geodynamic feature that belongs to the study area is the western termination of the North-Anatolian fault (NAF). This right-lateral transform tectonic lineament of regional importance runs approximately east-west for more than 1000 km along the majority of the Anatolian peninsula and the northern Aegean sea. Previous authors have assumed that the opening of the Sperchios Basin graben together with the Kremasta Fault System accommodates the transcurrent movements of the NAF on the east with those of the Cephalonia Transform Fault on the west as a "bridge of failure" (Kilias et al., 2008). The high geothermal gradient of the area is made evident by the presence of many thermal



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Figure 1. Elevation map of the study area. Main fault of the area are evidenced in red. The ten sampled thermal sites are shown with different symbols. The same symbols are used in all the figures. SB = Sperchios Basin; MB = Maliakos Bay; NEG = North Evia Gulf; AFZ = Atalanti fault zone; OC = Orei Channel. The inset shows the study area within the Hellenic territory: The green line shows the South Aegean Active Volcanic Arc (SAAVA) and the relative main active (Ni = Nisyros; Sa = Santorini; Mi = Milos; Me = Methana) or extinct (So = Sousaki) volcanic systems. The North Anatolian Fault (NAF) is shown in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

springs with temperatures from 24 to 82 °C, that discharge along the normal faults bordering the graben.

The seismic activity of the area has been widely documented throughout history (Makris et al., 2001; Burton et al., 2004). The strongest earthquakes in the past were recorded in 426 BC, 1740 and 1894 (Papazachos and Papazachos, 1997) and were mostly associated with the Atalanti fault zone.

Pertessis (1961), Margomenou-Leonidopoulou (1976) and Antonopoulos (1992) believe that the significant variations of the thermal features of the area are correlated to important seismic events. The former refers to the description that Thucydides gave of the big earthquake of 426 BC that was responsible of a tsunami within the Maliakos Gulf. The historian states that the springs of Thermopiles and Edipsos dried up for three days, and when they had started to flow again at Edipsos they had changed their position. Pertessis (1961) recounts that the Gialtra spring's water became turbid; while Margomenou-Leonidopoulou (1976) refers that many new springs appeared in the area of Edipsos as a consequence of the earthquake of Atalanti in 1894.

Because it is inert along with all of the other noble gases, helium is an excellent natural tracer for fluid migration and can be extremely helpful in unravelling complex chemical processes that affect other more reactive species (e.g. Ballentine et al., 2002). Distinct mantle, crustal, and atmospheric sources are characterized by unique noble gas isotopic compositions, so their sources can be identified and used to constrain the fluid's history. Helium isotopes can also provide unequivocal evidence for the presence of mantlederived volatiles.

Continental crust with negligible additions of mantle volatiles has low ${}^{3}\text{He}/{}^{4}\text{He}$ ratios of 0.02–0.1 R_{A} , reflecting a strong radiogenic ⁴He component with a very low ${}^{3}\text{He}/{}^{4}\text{He}$ production ratio in the crust. The upper asthenosphere, as constrained by samples of midocean ridge basalt (MORB), has a ${}^{3}\text{He}/{}^{4}\text{He}$ ratio of 8 \pm 1 R_{A} that indicates the presence of primordial ³He acquired during the Earth's formation (Ballentine et al., 2002). The European Sub-Continental lithospheric mantle (SCLM) has a ³He/⁴He ratio of 6.3 R_A (Gautheron et al., 2005). ³He/⁴He values between 0.1 and the appropriate mantle end-member (i.e., 6.3 or 8 R_A) are generally interpreted as a mixture of mantle and crustal sources. Lowering of the mantle value occurs through mixing with radiogenic ⁴He as fluids move through the crust (Ballentine and Burnard, 2002). Conventionally, any air-corrected ${}^{3}\text{He}/{}^{4}\text{He}$ ratio $R_{C}/R_{A} > 0.1$ is considered to have an unequivocal mantle component (Ballentine et al., 2002) reflecting recent transport from the mantle. The presence of a significant mantle signature of He has often been used to track the input of mantle fluids in the crust either through the injection of magma batches (Sano and Wakita, 1985; Allard et al., 1997) or along deep-rooted regional transform faults. Examples of the latter mechanism can be found along the NAF in Turkey (Gülec et al., 2002), the San Andreas Fault in California (Kulongoski et al., 2013), the Dead Sea Trasform Fault (Torfstein et al., 2013) and the Karakoram Fault (Klemperer et al., 2013).

The studied area's thermal springs have been the subject of scientific investigations since the Pertessis's studies in the thirties (1937). Very few studies have been devoted to the geochemistry of the gases and those that have were limited to the most important manifestations (Barnes et al., 1986; Minissale et al., 1989; Shimizu et al., 2005). The geochemistry of the discharged waters has been studied more extensively and at least one chemical analysis, generally limited to the major ion composition, has been published for all of the thermal manifestations (Pertessis, 1961; Margomenou-Leonidopoulou, 1976; Garagunis, 1978; Minissale et al., 1989; Gartzos and Stamatis, 1996; Lambrakis and Kallergis, 2005; Duriez et al., 2008; Kelepertsis et al., 2009; Metaxas et al., 2010: Lambrakis et al., 2013).

As highlighted by the previous studies, fluids discharged in this area show a wide range of compositions. This is to be expected considering its complex geodynamic situation. However, despite the long list of previous studies, no comprehensive study of the geochemistry of the gases and the waters of the thermal features of the whole area has been undertaken up until now. In the period 2004–2012, 58 gas (either free or dissolved) and 69 water samples from the thermal manifestations were collected and analysed for their chemical and isotopic compositions. Eleven additional coldwater samples were collected to get insight in the chemical and isotopic composition of local groundwater. The present study contributes new data regarding the sampled manifestations since some measured parameters have never been determined for many sites. Considering that the area is a highly seismic zone, the present data, together with that of the previous authors, could be the necessary basis to study variations induced by the earthquakes of the region.

2. Study area and methods

2.1. Geology of the area

The Sperchios Basin and the Northern Evoikos Gulf form an active spreading graben with an extensional rate of about 1 cm/a, bordered on both sides by a series of extensive fault systems. Together with the nearby Corinthiakos Gulf graben, of parallel orientation and similar Quaternary age, it accommodates a large part of the SW–NE extension of central Greece (Roberts and Jackson, 1991).

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