

Isotopic identification of CO₂ from a deep origin in thermomineral waters of southeastern Spain

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Received 20 February 1997; accepted 14 April 1998

Abstract

The overexploitation of the Alto Guadalentín detrital aquifer has led to an unusually high gas content in the waters, which is released as the hydrostatic charge decreases. The predominant gas proved to be CO₂. Isotopic studies show that δ¹⁸O values are in the range −8.8 to −6.5‰ SMOW, δD ranges between −45 and −40‰ SMOW, excess deuterium lies between +8.0 and +27.4, and δ¹³C values lie between −8.1 and −3.8‰ PDB. This reveals that there is an enrichment in ¹⁸O as well as mixing processes between meteoric and deep circulating waters. Tectonic and seismotectonic studies indicate crustal thinning in the studied region and numerous normal, reverse and strike-slip faults marked by positive thermal anomalies. There is also evidence of present day tectonic activity. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Detrital aquifer; Thermal waters; Neotectonics; CO₂; ¹⁸O–D–¹³C stable isotopes

1. Geological framework

The Alto Guadalentín aquifer is a detrital aquifer situated in southern Spain, with a surface area of 236 km² (Fig. 1). The climate of the area is subarid Mediterranean, with an average annual rainfall of 283 mm and an average annual temperature of 16.8°C. The study area lies within the Betic Cordilleras (Fig. 1), in the eastern sector of the Internal Zones, or the Alborán Domain (Balayá and García-Dueñas, 1987). Materials surrounding the

aquifer and its substratum (Fig. 2) belong to the Nevado–Filábride Complex (schists and quartzite from the Paleozoic substratum as well as quartzite, micaschists, metabasite and marble from sediments originating from the Permian to the Upper Triassic) and to the Maláguide Complex (sandstone, quartzite, shale, conglomerates and limestone, from the Permo-Triassic). Deposited materials on the substratum include marl, marl with gypsum, marl with sandstone, sandy marl, sandstone, marly sandstone, conglomerates, puddingstone, limestone, calcarenite and riocacite (all from the Miocene); lying over all the above are Plio-Quaternary conglomerates, sandstone, silt and clay.

The Alto Guadalentín aquifer is in the Guadalentín Valley, an intramountain Neogene basin formed dur-

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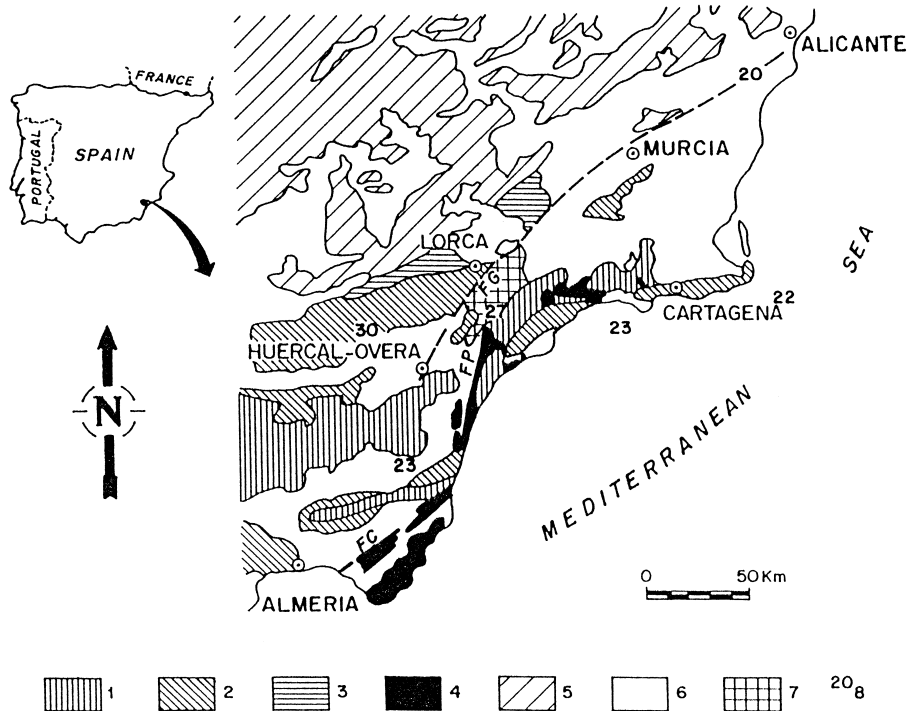


Fig. 1. Location and geological setting of the study area. FG: fault system of the Guadalentín; FP: fault system of Palomares; FC: fault system of Carboneras; 1, 2 and 3: Alborán domain (Internal Zones); 1: Nevado-Filábride; 2: Alpujárride; 3: Maláguide; 4: Neogene volcanism; 5: Southern Iberian domain (External Zones); 6: Miocene and Quaternary sediments; 7: Alto Guadalentín aquifer; 8: depth of the Moho (km). (Modified from Banda et al., 1993).

ing the Tortonian. The aquifer is limited to the northeast by the fault system of the Guadalentín or of Lorca-Alhama de Murcia, and to the southeast by the Palomares fault system (Fig. 1). Both fault systems are related to the collision of the Iberian and African plates, as well as to the tectonic activity of the Internal Zones in the western Mediterranean during the Neogene (Coppier et al., 1989).

Study of the depth variation of the Moho (Fig. 1) and of changes in seismic-wave velocities, obtained from the analysis of seismic refraction profiles (Díaz et al., 1993; Banda et al., 1993; García-Dueñas et al., 1994), reveals a different-natured crust on both sides of the Guadalentín–Palomares–Carboneras fault systems. The first of these profiles, passing W–E through Cartagena, cuts through the Guadalentín fault

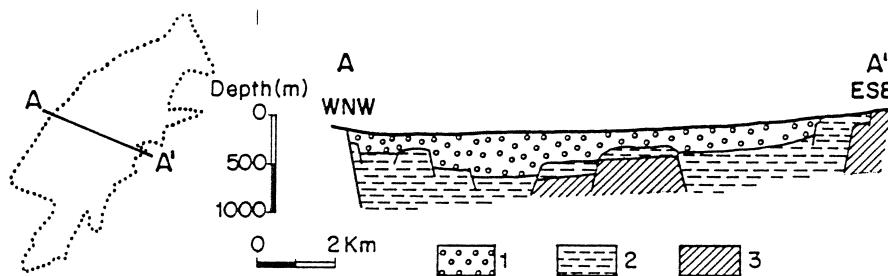


Fig. 2. Schematic cross-section. 1: aquifer; 2: Miocene substratum; 3: metamorphic substratum.

system and reveals an abrupt increase in the depth of the Moho, to 20–30 km, contrasting with 38 km or more outside this region. Thus, the crust is thinner and denser in the eastern part, where the highest seismic wavelength velocities are found.

The second profile, carried out between W Almería and Cartagena, cuts through the Palomares fault system and portrays a similar situation; the depth of the Moho is 28 km to the west of the system and 23 km to the east. This shear zone, therefore, affects the entire crust and places different lithospheric blocks in contact with each other. Seismic wave velocities show two different fragments of crust on either side of the Guadalentín and Palomares fault systems. To the west, the crust is formed by 4 layers with an overall thickness of roughly 38 km, while, to the east, the crust is denser and thinner, formed by only 3 layers with rapidly diminishing thicknesses towards the southeast. The increased density is particularly pronounced in the zone situated at a depth of 10 to 23 km and is probably due to a major intrusion of mantle-derived material in this zone. In this eastern domain, a high-velocity layer (8.0–8.2 km s⁻¹) with a thickness of 6 km under the crust-mantle boundary was distinguishable, followed by a zone of lower velocity (7.8 km s⁻¹) and a thickness of 27 km, with an abrupt velocity increase (8.3 km s⁻¹) at a depth of 63 km (Mueller and Ansoerge, 1986). Therefore, it appears that this strike-slip-fault region of the Internal Zones of the Betic Cordilleras separates two different crustal domains, situated vertically in an abnormal mantle.

The data from oil wells in the Neogene basins of the eastern Betic Cordilleras have provided evidence of a major positive thermal anomaly with relatively high temperature gradients varying between 41 and 56°C km⁻¹ (Albert, 1979). At Cartagena, heat flow measurements of thermal flow indicate high values, almost 95 mW m⁻². From the depth of the Moho in this region (22 km), temperature estimates of about 880°C have been obtained. This contrasts with the Iberian Meseta, where 720°C was calculated for a depth of 40 km (Albert, 1979). Apart from the evidence above, the deep character of the Guadalentín and Palomares fault systems is also shown by numerous thermal springs along the fault lines. The waters of the Alto Guadalentín aquifer are warm and have a high content of certain components (Table 1).

This situation appears to be favoured by the great depth of the fractures affecting the substratum and by the alteration of the hydraulic head of the aquifer due to overexploitation. This allows the rise of groundwater enriched in CO₂-gas. All these facts indicate that the crust to the east of the Carboneras–Palomares–Guadalentín fault system is thinner and different in nature from that of the rest of the Betic Cordilleras. These slip-strike zones affect the entire thickness of the lithosphere and lead to contrasting crustal domains, of different natures and structures.

2. Physicochemical characteristics of CO₂-rich waters

Physicochemical characteristics of the 337 groundwaters samples studied between 1989 and 1992 are shown in Table 1. Table 2 includes the most relevant physicochemical variables analyzed in the samples taken for isotopic determinations. The wells selected (Fig. 3) were those with a high bicarbonate content, which reflects the presence of the CO₂, and/or where the CO₂ was detectable. All the wells are situated above, or very close to, areas

Table 1
Hydrochemical data of the samples taken at different times in the aquifer (STD: standard deviation)

Parameter	Mean	Maximum	Minimum	STD
T (°C)	26.3	32.1	19.0	3.1
pH	6.84	8.06	5.99	0.4
Eh (mV)	18	51	-75	15
C (μS cm ⁻¹ , 25°C)	3423	6810	1087	1319
Cl ⁻ (mg l ⁻¹)	635	1460	99	325
SO ₄ ⁻ (mg l ⁻¹)	1006	2672	120	631
HCO ₃ ⁻ (mg l ⁻¹)	732	2124	285	404
Ca ²⁺ (mg l ⁻¹)	368	761	70	176
Mg ²⁺ (mg l ⁻¹)	215	453	30	85
Na ⁺ (mg l ⁻¹)	313	886	85	191
K ⁺ (mg l ⁻¹)	60	106	27	15
NO ₃ ⁻ (mg l ⁻¹)	22	171	1	21
NO ₂ ⁻ (mg l ⁻¹)	0.07	0.20	0.02	0.03
NH ₄ ⁺ (mg l ⁻¹)	0.9	2.8	0.3	0.5
SiO ₂ (mg l ⁻¹)	36	153	14	18
Sr ²⁺ (mg l ⁻¹)	12	32	1	6
Li ⁺ (μg l ⁻¹)	174	471	17	99
B ⁻ (μg l ⁻¹)	428	1290	98	249
F ⁻ (μg l ⁻¹)	194	874	18	114

Table 2

Selected physicochemical characteristics of the waters containing CO₂ (August 1991)

W	T	pH	C	PCO ₂	Cl ⁻	SO ₄ ⁼	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SiO ₂
14	24.5	6.12	4310	1.029	758	1703	1700	715	381	364	75	17
15	23.1	6.41	4130	1.029	860	1134	800	405	310	384	63	22
20	26.9	6.60	3190	0.254	595	1010	1000	441	277	278	59	26
21	26.8	6.54	3100	0.219	615	875	885	398	239	255	62	21
29	28.7	6.41	2710	0.343	743	405	1000	435	193	172	61	22
30	29.6	6.13	2140	0.900	450	260	1350	364	184	133	62	23
33	25.2	6.21	3180	0.792	442	1053	1550	488	257	193	64	36
35	29.1	6.08	3500	1.201	370	1310	1700	597	336	187	66	29
36	29.8	6.19	4012	0.970	400	1318	1760	585	354	165	65	28
37	29.3	6.12	4100	0.116	465	1185	1795	645	282	195	65	31
39	30.2	6.31	1590	0.454	200	380	1000	232	143	133	58	30
42	30.5	7.07	1200	0.044	220	300	540	157	77	135	61	24
53	27.6	6.20	4255	0.901	475	1326	1704	455	377	278	50	48

W: well; T: temperature in °C; C: conductivity in $\mu\text{S cm}^{-1}$ (25°C); PCO₂ in bars; and ions in mg l^{-1} .

where the metamorphic substratum lies near the surface (horst zones), according to the results of electrical geophysical data (Cerón, 1995).

There was a notably high concentration of bicarbonate (between 900 and 2100 mg l^{-1}), high PCO₂ (between 0.044 and 1.289 bars) and, in some cases, high concentrations of CO₂ (more than 1600 mg l^{-1}); high temperatures were recorded for almost all the sampling points, above 25°C (except at points 14 and 15 with 24.5 and 23.1°C, respectively), and the pH was acidic, varying between 6.08 and 6.60 (except in sample 42, where it was 7.07). Other physical char-

acteristics were a certain degree of turbidity and sharp taste (because of the carbon dioxide). The results of gas analyses carried out by the Regional Government of Murcia at certain aquifer points with manifestations of CO₂ (Fig. 4) are presented in Table 3. The predominant gas was CO₂, with total gas volumes exceeding 83%, except in well 5, where CO₂ and N₂ were equally dominant, and samples 3 and 4, in which the main gas was N₂; H₂S was not detected in any sample.

One aspect considered, was the way in which such overexploitation has influenced the aquifer. Ini-

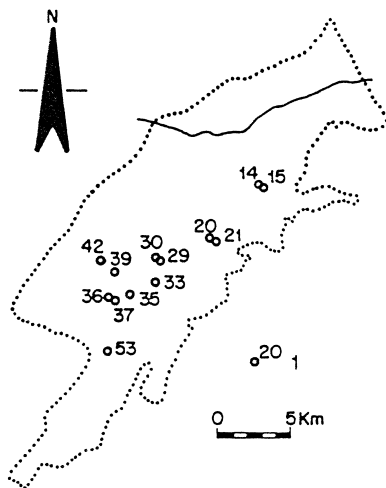


Fig. 3. Situation of the wells chosen for the isotopic analysis. 1: wells and their number.

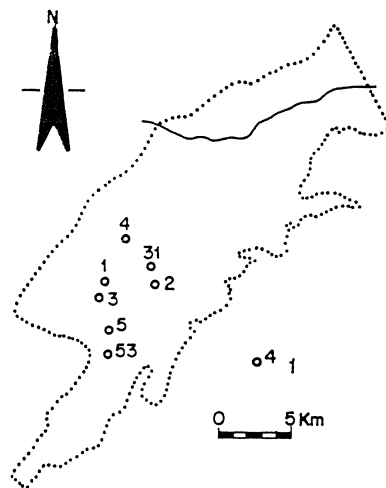


Fig. 4. Situation of the wells chosen for the gas analysis. 1: wells and their number.

Table 3

Gases found (% V) in water samples from the Alto Guadalentín aquifer (source: Regional Government of Murcia)

Well	T (°C)	CO ₂	N ₂	O ₂	CH ₄	H ₂	He
1	30	83.00000	14.00000	2.10000	0.00220	0.00050	0.00570
31	33	84.00000	14.00000	1.30000	0.00200	0.00540	0.02600
53	27	86.00000	11.00000	2.30000	0.00100	0.00270	0.00390
2	29	83.00000	15.00000	1.70000	0.00100	0.03100	0.00810
3	27	4.70000	77.00000	18.00000	0.00100	0.00100	0.00750
4	24	23.00000	63.00000	14.00000	0.00100	0.01100	0.00720
5	27	49.00000	43.00000	7.00000	0.00100	0.00130	0.00750

tially, the aquifer water was pumped in superficial zones, when the original piezometric level was near the surface. As we indicate in the present work, the increase in agricultural activity in the area—based essentially on irrigation with groundwater—resulted in an overexploitation of the aquifer. With this overexploitation, the piezometric level continued to fall, reducing the hydrostatic pressure to a level below that of PCO₂, making the gas rise from the substratum and the deepest zones of the aquifer to the surface. In reality, the gas content in the water is greater in the sectors where the metamorphic substratum is less deep. This would explain the relatively recent appearance of CO₂ in some sectors of the aquifer where this gas had never before been detected. This situation, provoked by human activity, led us to characterize the CO₂ as a contaminant (Cerón and Pulido-Bosch, 1993, 1996). At the same time as this process occurred, the wells pumped water from the deepest zones of the aquifer, thus increasing the salinity content (consequently, increases in CO₂ are accompanied by higher levels of salinity). In relation to this observation, the monitoring of a well near point 39 (from 1975 until 1990, when the well was abandoned) confirms the notable increase in the bicarbonate concentration and conductivity (the amount of the increase was more than 350 mg l⁻¹ and 400 μS cm⁻¹, respectively), when the water level fell below a depth of 150 m.

3. Isotopic data

The origin of CO₂ can be established by isotopic analysis of ¹³C, which indicates the presence of mantle-derived CO₂ ($-8 < \delta^{13}\text{C}\text{‰} < -4$; Blavoux

et al., 1982; Wexteen et al., 1988), or CO₂ derived from biogenic activity in the soil ($-22 < \delta^{13}\text{C}\text{‰} < -25$; Bakalowicz, 1979), it may also be the result of the metamorphism of carbonate rocks ($\delta^{13}\text{C}\text{‰} > -2$; Barnes et al., 1978). On the other hand, Oxburgh et al. (1986), O’Nions and Oxburgh (1988), Griesshaber et al. (1992) and Darling et al. (1995) highlight the significance of helium as an indication of an upper mantle source of gases.

Oxygen-18, deuterium and carbon-13 content in groundwater samples from the Alto Guadalentín was determined at the CSIC Isotope Hydrology Laboratory of Granada using standard techniques (Epstein and Mayeda, 1953; Coleman et al., 1982). The results (Table 4) are expressed as per mille deviations from the internationally accepted standard V-SMOW (Gonfiantini, 1978). The analytical error is $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$, $\pm 1\text{‰}$ for δD , and $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$. Fig. 5 presents the values found for $\delta^{18}\text{O}$ and δD ; the straight lines correspond to the Global Meteoric Line ($\delta\text{D} = 8\delta^{18}\text{O} + 10$) and the meteoric line of the eastern Mediterranean ($\delta\text{D} = 8\delta^{18}\text{O} + 22$). With respect to δD , the samples have similar values, within the interval -40 to -45 .

The distribution of the samples along a horizontal line parallel to the axis of the $\delta^{18}\text{O}$ characterizes the effect produced by high temperatures of the geothermal fields, which make the water react with the minerals of the rock involved, increasing the ¹⁸O content of the heated waters (Gonfiantini et al., 1973; Fontes, 1976). The fact that the rocks are practically devoid of hydrogenated minerals—except hydroxyl radicals of the micas and amphiboles—favours the situation in which there is no particular effect on the D content. Therefore, the waters of geothermal areas are characterized by an increase in

Table 4

Results of the isotopic composition of groundwater from the Alto Guadalentín aquifer

W	$\delta^{18}\text{O}_{(\text{vs. V-SMOW})}$ [‰]	$\delta\text{D}_{(\text{vs. V-SMOW})}$ [‰]	d [‰]	$\delta^{13}\text{C}_{(\text{vs. PDB})}$ [‰]
14	-7.0	-43	+13.0	-6.7
15	-8.8	-43	+27.4	-6.2
20	-7.3	-44	+14.4	-7.7
21	-7.8	-41	+21.4	-7.5
29	-7.8	-43	+19.4	-7.9
30	-7.8	-40	+22.4	-8.1
33	-7.4	-42	+17.2	-4.8
35	-7.7	-42	+19.6	-5.3
36	-6.5	-44	+8.0	-3.8
37	-6.5	-42	+10.0	-5.4
39	-7.2	-45	+12.6	-6.4
42	-6.7	-44	+9.6	-4.0
53	-7.6	-41	+19.8	-5.2

W: well. Precision: $\delta^{18}\text{O} = \pm 0.1\text{‰}$, $\delta\text{D} = \pm 1\text{‰}$, $\delta^{13}\text{C} \pm 0.2\text{‰}$, Deuterium excess: $d = \delta\text{D} - 8\delta^{18}\text{O}$.

^{18}O , with no alteration of the D content (Craig, 1961).

On the other hand, Horita and Wesolowski (1994) demonstrate that the hydrogen isotope fractionation factor between liquid water and water vapour decreases rapidly with increasing temperature, and that hydrogen isotope ratios of liquid water and water vapour become indistinguishable at 220–230°C, thus there is no fractionation of hydrogen isotopes. Above the crossover temperature, water vapour is more enriched in deuterium than the coexisting liquid water; values of the hydrogen isotope fractionation

factor reach a minimum at about 300°C, and approach zero again at the critical temperature of water (374.1°C). In this case, the fractionation mechanism seems unlikely as the estimated reservoir temperature is of the order of 100–130°C (Cerón, 1995).

Giggenbach (1992) described another mechanism producing an ^{18}O increase in thermal waters associated with andesitic magmatism, without a proportional increase in deuterium in geothermal systems along convergent plate boundaries around the Pacific. These waters are recycled seawater and have a narrow range of δD values. They enter the subduc-

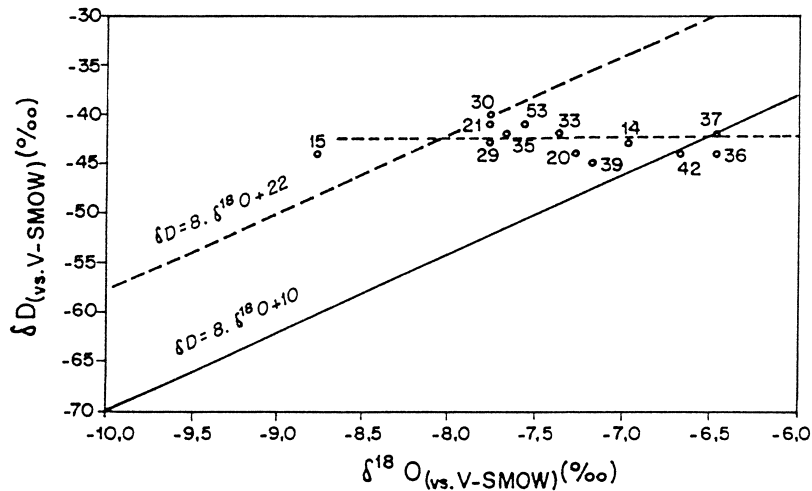


Fig. 5. Relationship between $\delta^{18}\text{O}$ and δD of the samples taken in the Alto Guadalentín aquifer.

tion system in the form of porewater, or as interstitial waters of hydrated clay minerals of accumulated marine sediments and are carried to the source region of arc magmas lying over the subducting slab. However, the different geological setting of the Alto Guadalentín aquifer precludes this process.

Finally, Ferrara et al. (1965) and Fontes (1976) describe another type of reaction that can also change the isotopic content of a gaseous or liquid phase. This implies the contact of thermal waters with great quantities of CO₂, whereby the groundwaters become poor in ¹⁸O.

The representative points are distributed over a horizontal line (Fig. 5), which indicates that the waters are subject to a geothermal exchange with the rock involved, producing an enrichment of the water in ¹⁸O. On the other hand, high CO₂ contents of some samples can cause isotopic changes that would lead to an enrichment of ¹⁸O in the CO₂ phase. In relation to other Mediterranean geothermal areas, the δ¹⁸O and δD contents of the samples taken from the Alto Guadalentín aquifer are relatively similar to the waters of the Tuscany and Larderello areas (Italy). In Tuscany, the waters have high CO₂ contents and would be subject to an isotopic exchange which leads to a depletion of H₂O in ¹⁸O and, to minor extent, to an enrichment of the CO₂ (Ferrara et al., 1965).

The intersection of the straight line defined by the samples with the Global Meteoric Line gives, before the exchange occurs, mean values for ¹⁸O and D of $-6.55\text{‰} (\pm 0.1)$ and $-43\text{‰} (\pm 1)$, respectively; the value for the deuterium excess would be $+9.4\text{‰}$ which suggests that groundwaters in the studied area are recharged predominantly by the Atlantic-derived precipitation (Cruz-San Julián et al., 1992).

The data obtained for ¹³C (Table 4) range between -8.1 and -3.8‰ . According to other authors (Blavoux et al., 1982; Barnes et al., 1978; Craig, 1961; Maisonneuve and Risler, 1979), these values indicate an insignificant CO₂ supply of deep origin.

4. The CO₂ and the seismotectonic characteristics of the area

In the Alto Guadalentín aquifer, CO₂-rich thermal waters are at present developing through the Guada-

lentín and Palomares faults, which allow the rise of the CO₂ from deeper parts of the crust. Sanz de Galdeano (1990) has discussed the possible tectonic continuity of the Guadalentín and Palomares faults with the NE of the Iberian Peninsula.

In the whole area, there are currently known to be numerous seismic focus associated with the distribution of the above-mentioned fault systems. Moreover, there exist reverse faults that affect Quaternary materials, as well as alluvial fans and contemporary riverbeds that have been displaced by the action of strike-slip faults (Silva et al., 1993). This demonstrates the different functioning of these systems during relatively recent periods and is indicative of phases of compression and extension.

5. Final considerations

The importance of the fault systems of Guadalentín and Palomares for the aquifer of the Alto Guadalentín is evident, as is the presence of thermal waters with high contents of CO₂-gas. Isotopic studies show that δ¹⁸O is found in the range of -8.1 to -6.5‰ vs. SMOW, δD is between -45 and -40‰ vs. SMOW, deuterium excess is between $+9.6$ and $+27.4$, and δ¹³C varies between -8.1 and -3.8‰ vs. PDB. This reveals an enrichment in ¹⁸O together with mixing processes between meteoric waters and deep circulating waters, which present high temperatures.

The manifestations of CO₂ in the Alto Guadalentín aquifer appear to be related to currently tectonically active fault systems. CO₂ and other gases have been mobilized, essentially as a consequence of the decreasing hydrostatic pressure in the detrital aquifer due to a long-term overexploitation of the groundwaters. The increase in exploitation of this resource has caused a marked fall in the piezometric level, which has reached a depth of 100 m in wide areas.

Acknowledgements

The authors wish to thank to Drs. Gonfiantini and Grieshaber for their comments, suggestions and criticisms of the earlier version, which have greatly helped to improve the paper. This research was

financially supported by the Spanish DGICYT, Projects AMB92-0211, AMB95-0493 (J.C.C. and A.P.-B.) and PB94-0050 (C.S.G.).

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