



## Geochemistry of the formation waters in the Po plain (Northern Italy): an overview.

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### Abstract

The Po Valley brines represent the base level of the Quaternary aquifer located in a thick clay-sands sedimentary sequence. Geochemistry indicates that these are marine waters, evaporated to the stage of gypsum precipitation and trapped at the bottom of the basin in the late Messinian. Most of the groundwater samples collected from different springs and wells in the plain result from a mixture of these Na–Cl brines and shallow groundwaters laterally recharged by the Alpine and Apennine chains.

Natural outflows of brackish waters are associated with major tectonic features. Mud volcanoes, located in the eastern sector of the Po plain, are constantly monitored as sudden chemical changes are significant precursors of seismic activity. In the western sector, calcite-filled veins isotopically record different degrees of water-rock interaction. These are outcropping fossil conduits, where mixing between shallow groundwaters and deep seated brines has occurred. The temporal continuity of the hydrological circuits allows the reconstruction of past and present groundwater circulation patterns.

This paper summarises and integrates the geochemical data produced over many years in order to obtain a regional picture of brine origins and the natural mechanisms of groundwater flow. © 1999 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction and geological background

The Po plain (Fig. 1) is located in Northern Italy and covers an area of approximately 46 000 km<sup>2</sup>. It is bound to the N by the Alps, to the SW by the Apennine chain and to the E by the Adriatic Sea. The basin formation is related to the early stages of the opening of the Atlantic Ocean, where the Mesozoic carbonate substratum was formed. Starting from late

Cretaceous, the basin was progressively filled with sediments derived from the Alpine and Apennine chains. The stratigraphy includes gypsum deposits of Messinian age, covered by clay layers, followed by a thick sequence of sands with interbedded clays, reaching more than 7 km of thickness in the central part of the basin (Dondi et al., 1982).

In the Mediterranean, Messinian evaporites are widely distributed both as outcropping sediments in small marginal basins (Rouchy, 1981) and in marine cores (DSDP leg 13 and leg 42A) (Hsü et al., 1978). Geophysical, sedimentological and isotopic studies on the evaporites indicate the presence in the

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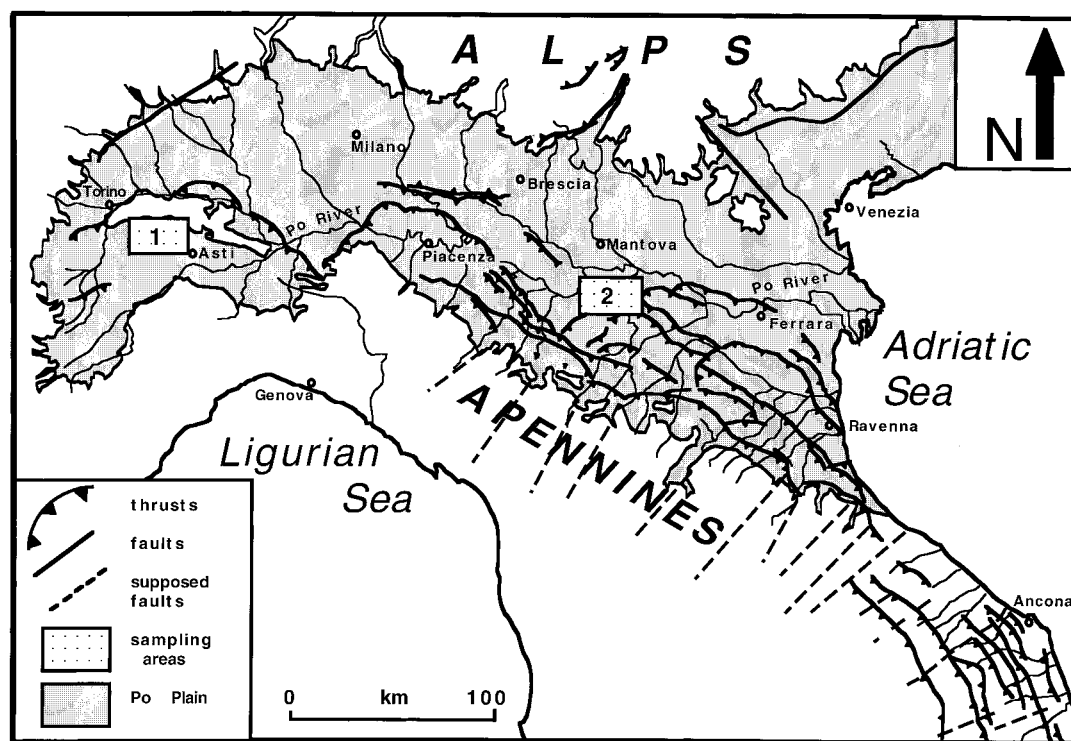


Fig. 1. Map of the Po plain (Northern Italy), showing the main tectonic features and the sampling areas. 1 – Monferrato; 2 – mud volcanoes' region (modified after Dondi et al., 1982).

Paleomediterranean of a number of sub-basins, each of them with a particular morphology, depth and water inputs. An intermittent flow of marine water derived from the Atlantic ocean was recognised through the Messinian. On the other hand, halite precipitation could not occur because of a continuous dilution of the brine by freshwaters, which also played an important role in the extent and orientation of diagenesis (Pierre and Fontes, 1978; Pierre, 1982; Fontes et al., 1987). Progressive filling of these sub-basins led to the formation of aquifers similar to the Po plain in different regions (Fleischer et al., 1977; Deák, 1978; Deák et al., 1987; Samper et al., 1993).

The presence of brackish and salt waters in the Po Valley has been known since Roman times, when they were used for thermal purposes. More recently, they have been extensively studied for 3 main reasons:

1. their association with methane and oil. These products are extracted, among others, by the national company Agip, which conducted extensive drilling to great depths in the central part of the basin and offshore in the Adriatic Sea, and performed complete and detailed geophysical and geochemical studies (E.N.I., 1972; Mattavelli et al., 1983; Ricchiuto et al., 1984; Agip, 1994). Unfortunately, these docu-

ments are often restricted and data are not completely available to the scientific community;

2. their low enthalpy geothermal potential and their natural flow phenomena (Coggiola et al., 1987). Their outflow is closely related to tectonic features, as indicated by geophysical and structural investigations (Pieri and Groppi, 1981; Cassano et al., 1986; Capozzi et al., 1994). The plain itself represents the foreland for both the Alpine and Apennine chains and is undergoing subduction on both sides. On the Apennine front, mud volcanoes erupting brackish waters associated with clay and organic matter are found. Their 'activity' is constantly monitored as these springs undergo drastic and sudden changes in their chemistry and gas content in relation to the regional seismic activity (Martinelli, 1987; Martinelli et al., 1995);
3. water resource and human activities inducing movement of the brines within the plain. The Po plain supports most of the agricultural and industrial activities of Northern Italy, which are associated with shallow groundwater pollution in the multilayer sand aquifer. As a consequence, groundwater for domestic purposes has to be pumped from the deepest layers, resulting in a mixing between fresh and saline waters (Zavatti et al., 1995).

Table 1

Some representative analysis of groundwaters from the Po plain. Data from Coggiola et al., 1987 (A); Ricchiuto et al., 1985 (B); Regione Emilia-Romagna, 1979 (C); Conti, 1996 (D); Martinelli et al., 1989 (F); Chiarle, 1991 (G); Arione, 1984 (H); De Vecchi, 1979 (I); \* = this paper

		Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	Sr <sup>2+</sup> mg/l	Alk mg/l	Cl mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	Br mg/l	I mg/l	Fe mg/l	δ <sup>2</sup> H‰ vs SMOW	δ <sup>18</sup> O‰ vs SMOW	δ <sup>13</sup> C‰ vs PDB	<sup>87</sup> Sr/ <sup>86</sup> Sr
<i>Po plain groundwaters</i>																
<b>AGNADELLO</b>																
Agnadel SL	B	56.0	35.4	927	7.8		60.0	1530	19.2			7	28.27	2.48		
<b>AQUI TERME</b>																
La Bollente	A	136	6.1	700	16.3		39.7	1170	188					9.01		
La Bollente	G							1200		5.1		0.1		7.85	2.45	
<b>BACEDASCO</b>																
F Alberoniana	C	84.2	58.4	220	9.1	0.88	723	141	89.1	0.5	0.48	0.13				
F. Amussia	C	71.7	48.6	76.8	6.25	9.35	423	106	68.9	0.33	0.42					
F. Fedelina	C	72.5	57.1	140	8.23	16.8	593	110	103	0.46	0.46	0.27				
F. Ipogea	C	107	38.9	54.3	1.1	10.9	544	17.6	94.2	0.22	0.05	0.13				
F. Korneriana	C	58.9	63.2	158	1.25	20.1	423	95.3	90.4	0.48	0.88	0.28				
F. Nuova	C	71.7	59.6	105	7.11	18.4	480	77.8	78.9	2.4	0.53	0.03				
F. Piazzale	C	40.5	34	360	3.2		733	309	99.7	0.85	2.29	0.05				
F. S. Lorenzo	C	41.7	45.0	201	11.4	18.1	449	267	19.1	0.75	1.22	0.54				
<b>BALZOLA</b>																
Balzola	A	2630	500	1680	180		60.0	3510	540							
<b>BOBBIO</b>																
Terme	A	8.8	2.6	2220	67.0		169	4970	52.0					8.41		
Sulfurea	A	29.7	4.0	387	140		149	10050	10.0					7.86		
Salsoiodica	A	64.4	4.4	8550	280		172	32520	21.0					5.45	2.9	
S. Martino	C	417	63.8	2450	9.3	50	304	4560	56.4		0.6	0.4				
<b>BORDOLANO</b>																
Bordolano 1	B	1270	823	5520	57.2		450	11100	2550			10	31.83	1.64		
<b>BRISIGHELLA</b>																
Colombarino	C	247	112	61	1.2		701	106	464							
Igea	C	1754	794	14510	58.0		69.0	27950		48	24	78				
Terme	G											11.36		4.31	2.5	
<b>BRUGHERIO</b>																
Brugherio	B	1040	540	18060	112		130	30200	1440			13	16.75	0.2		
<b>CASTEGGIO</b>																
Casteggio	B	40.0	53.0	6300	60		1190	8900	190			11	29.8	0.4		
<b>CASTROCARO</b>																
S. Anna	C	148	97.3	1090	12.0			1950	23.5							
Beatrice	C	290	198	3180	32.0			5820	4.9		3.5					
Salubria	C	209	134	2200	22.4			3970	15.2		2.2					
Casetta e Pozzo 66	C							19860								
Conti	C	886	722	13000	10.6			24020	117		24.8					
<b>CONTIGNACO</b>																
Acqua S. Giovanni	C	85.2	30.7	94.9	5.6		528	31.3	72.3			0.2		4.17		
<b>CORNEGLIANO</b>																
Cornegliano 1	B	806	480	9360	156		659	16100	1060			10	25.3	2.13		
<b>CORREGGIO</b>																
Coreggio 1	B	249	84.0	5110	75		201	8500	48.0			1.5	47.87	6.67		
Correggio C	B	400	145	9775	81.9		12.2	16500	14.4			3.6				
Correggio 17	B	420	145	9640	78		18.0	15900	25.0			2.7	39.33	5.06		
<b>CORTEMAGGIORE</b>																
Pozzo 44	B	2140	686	25300	61.8			46150	7.0			3.1	9.18	1.47		
Pozzo 51	B	6920	2370	52850	299		24.0	103780	3.0			3	51.46	2.5		
Pozzo 51	G							118600		540		96				
Pozzo 77	B	872	300	8230	39		177	15900	48.0			4.3		7.19		

(continued on next page)

Table 1 (continued)

		Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	Sr <sup>2+</sup> mg/l	Alk mg/l	Cl mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	Br mg/l	I mg/l	Fe mg/l	δ <sup>2</sup> H‰ vs SMOW	δ <sup>18</sup> O‰ vs SMOW	δ <sup>13</sup> C‰ vs PDB	<sup>87</sup> Sr/ <sup>86</sup> Sr
Pozzo 81 MALOSSA	B	2700	876	30130	117		79.3	55000	9.6			4.8		0.54		
Malossa 9	B	778	256	9100	28		1700	11700	2500			7	18.37	14.02		
Malossa 11 MONTICELLI	B	802	386	9130	46.8		1560	13490	2510			10		12.88		
Terme	A	730	230	11900			330	18440	130							
Pozzo 13 PONTE TIDONE	C	7260	2710	38900	211	647	23.2	81560		490.3	32.03	46.2				
Ponte Tidone 1 PORRETTA TERME	B	610	454	6800	115		464	11400	1270				34.83	0.32		
Puzzola	C	38.4	9.6	1280	9.67	4.89		1680	15.0							
P. Vecchia RICCIONE	C					4.81	652	1280	12.0							
Isabella	C	1280	1190	10200	170		460	21350	120	104.1	8.1	0.3				
Claudia-Riccione	C	974	959	5870	56.4		598	12800	682	51.8	2.3	1.5				
Margherita	C	85.2	291	6050			492	9460	265		15.2					
Salsoiodica	C	93.4	375	6480			689	10770	90.8		55.8					
Vittoria	C	216	757	10500			228	18630	8.3		57					
Vittoria ROMANENGO	G						457	15800	445			9.48		1.83	1.2	
Romanengo SALICE TERME	B	260	120	8400	78		670	13100	28.0			2.8	18.37	1.42		
Terme SALSOMAGGIORE	A	4360	2160	27840	236		561	56090	7.2					0.85		
Salsomaggiore	A	4390	630	48000	20.0		340	65340	230		40			0.5		
Miscelazione SALVAROLA	C	5360	1440	49190	198	392	101	90620	145	235.6	54.9	29.6				
Pozzo 1	C	50.8	86.3	315	0.9		1050	83.7	200			0.3				
Pozzo 2 S.ANDREA TERME	C	13.2	12.3	5600			2090	8040	33.5	55	33.5					
Acqua purgativa	C	669	785	10560	7.7		110	19560	4.8	235	29.5	3.5				
Acqua purg. legg. SORGARA	C	268	172	5810	85.0		145	9710	16.6			0.4				
Salutare purg. SPILAMBERTO	C	424	260	4250	197			7700	151	2.8	3.2	7.8				
Spilamberto 16	B	68.1	42.7	955	6.3		81	1600	16.7			2	32.87	2.99		
Spialmberto 7	B	510	315	7160	49.5		120	11420	125			4		1.85		
Spilamberto P TABIANO	B	700	6.48	7845	117		244	24200	1060			4	13.3	0.85		
Terme	C	1700	840	1470	87		70.0	2260	50							
Arvel VALMADONNA	C	618	109	1600	8.1	10	452	132	1680	0.07	0.06	3				
Inea VOLPEDO	I	870	250	6900	58.7		525	10600	927					8.56		
Volpedo	A	1170	910	12800	182		30.0	23670	4.0							
<i>Monferrato</i>																
Montafia 3	D	39.5	49.8	262	10.1	0.9	472	566	5.89				9.14	10.97	0.70920	
Brozolo	D	32.3	45.8	95.4	3.43	0.8	401	172	29.7				7.67	13.52	0.71112	
Murisengo	D	110	106	63.3	3.76	0.9	290	119	490				7.91	12.56	0.70882	
Alfiano Natta	D	44.9	77.5	17.4	1.47	0.2	434	18.8	75.8				8.10	14.22	0.70972	
S. Margherita	D	611	324	2270	37.9	15.6	119	4720	3480				10.00	10.73	0.70903	
Rio Freddo	D	46.7	113	28.9	1.3	1	516	19.3	37.1				6.67	14.06	0.70871	
Lussello 1	D	72.3	58.0	3.56	0.56		434	15.2	48.2				8.34	13.69		

Table 1 (continued)

		Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	Sr <sup>2+</sup> mg/l	Alk mg/l	Cl mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	Br mg/l	I mg/l	Fe mg/l	δ <sup>2</sup> H‰ vs SMOW	δ <sup>18</sup> O‰ vs SMOW	δ <sup>13</sup> C‰ vs PDB	<sup>87</sup> Sr/ <sup>86</sup> Sr
Treville 2	D	568	126	54.5	4.87	13	379	155	1620					7.34	11.89	0.70900
Montemagno	D	569	105	38	5.02	12.8	416	51.6	1470					7.68	13.32	0.70898
Calliano	D	581	118	154	6.50	14.2	382	265	1570					7.76	14.80	0.70896
Agliano 3	D	217	213	2220	25.0	8.2	311	3860	1960					8.96	10.32	0.70908
Allere Alta	D	196	43.0	17.4	0.66		466	45.6	175					7.67	12.36	
<i>Po plain mud volcanoes</i>																
NIRANO																
vulcanello	F	95.0	265	4350	42.0		405	7300	200	62.6	40.3					
vulcanello 3/7/87	*												2.02	4.69		
vulcanello 13/7/87	*					4.77							4.03	5.51		0.70894
OSPITALETTO																
Ospitaletto 1 23/5/87	F*	105	101	4800	11	24.0	970	7350	0	37.7	24.7		9.05	5.93		0.70918
Ospitaletto 2	F	190	131	4950	18		490	8090	0							
Ospitaletto	*												3.27	4.62		
REGNANO																
vulcanello	F*	220	84.0	5500	21.5		1880	8020	53.0	58.8	40.5					
vulcanello	G						2010	7900	185					2.93	1.7	
vulcanello 23/5/87	*					8.78										0.70899
vulcanello 1/3/94	*					16.3							2.24	3.58		0.70872

Geochemical studies of natural springs and oil-associated brines have been published over the years (Chiarle et al., 1992; Coggiola et al., 1987; Martinelli et al., 1989; Regione Emilia-Romagna, 1979; Ricchiuto et al., 1985). These studies are often limited to specific sectors of the Po plain or to particular geochemical problems. This paper is an attempt to review the available geochemical data and to complement them with more recent or unpublished data (Arione, 1984; Chiarle, 1991; Chiarle et al., 1991; Conti, 1996; De Vecchi, 1979), in order to obtain a regional picture of the brine origins and their natural mechanisms of movement.

Some representative analyses of groundwaters from springs and wells tapping into the lowest levels of the sedimentary sequence are reported in Table 1, although in the following discussion, all the available geochemical data will be taken into account.

## 2. Geochemical characteristics of deep seated brines

### 2.1. Major elements

Major cations plotted against Cl (Fig. 2) for the most concentrated brines show good agreement with the geochemical characteristics of a marine water evaporated to the stage of gypsum precipitation (Fontes and Matray, 1993). Most of the natural springs and wells sampled fall on a dilution curve between this

end-member and shallow fresh waters. Discrepancies are greater for the most diluted terms, originating by lateral recharge of the aquifers from the Alps and the Apennines. Some cation exchange with clays may be responsible in part for the observed variations in the Na/Ca ratio.

The SO<sub>4</sub> ion does not show a good correlation with Cl. In general, it is observed that waters close to the recharge areas plot above the mixing line between sea water and fresh waters, while more concentrated waters plot below it. Oxidation-reduction phenomena are most likely responsible for this behaviour. In fact, in the deepest levels characterised by a strongly reducing environment, SO<sub>4</sub> is absent. During the upward movement and consequent mixing with shallow fresh waters, sulphide minerals are readily oxidised giving rise to sulphates. Additionally, shallow groundwaters may contain high SO<sub>4</sub> contents themselves, that originate from leaching of Messinian deposits and from human activities (Olivero et al., 1987).

### 2.2. Trace elements

Halogens have been widely used to distinguish primary brines, originating by evaporative concentration of seawater, from secondary brines, derived from evaporite dissolution (Rittenhouse, 1967; Collins, 1969). The Br to Cl ratio is constant during seawater evaporation, and at the onset of halite precipitation it starts increasing. Consequently, leaching of salts would pro-

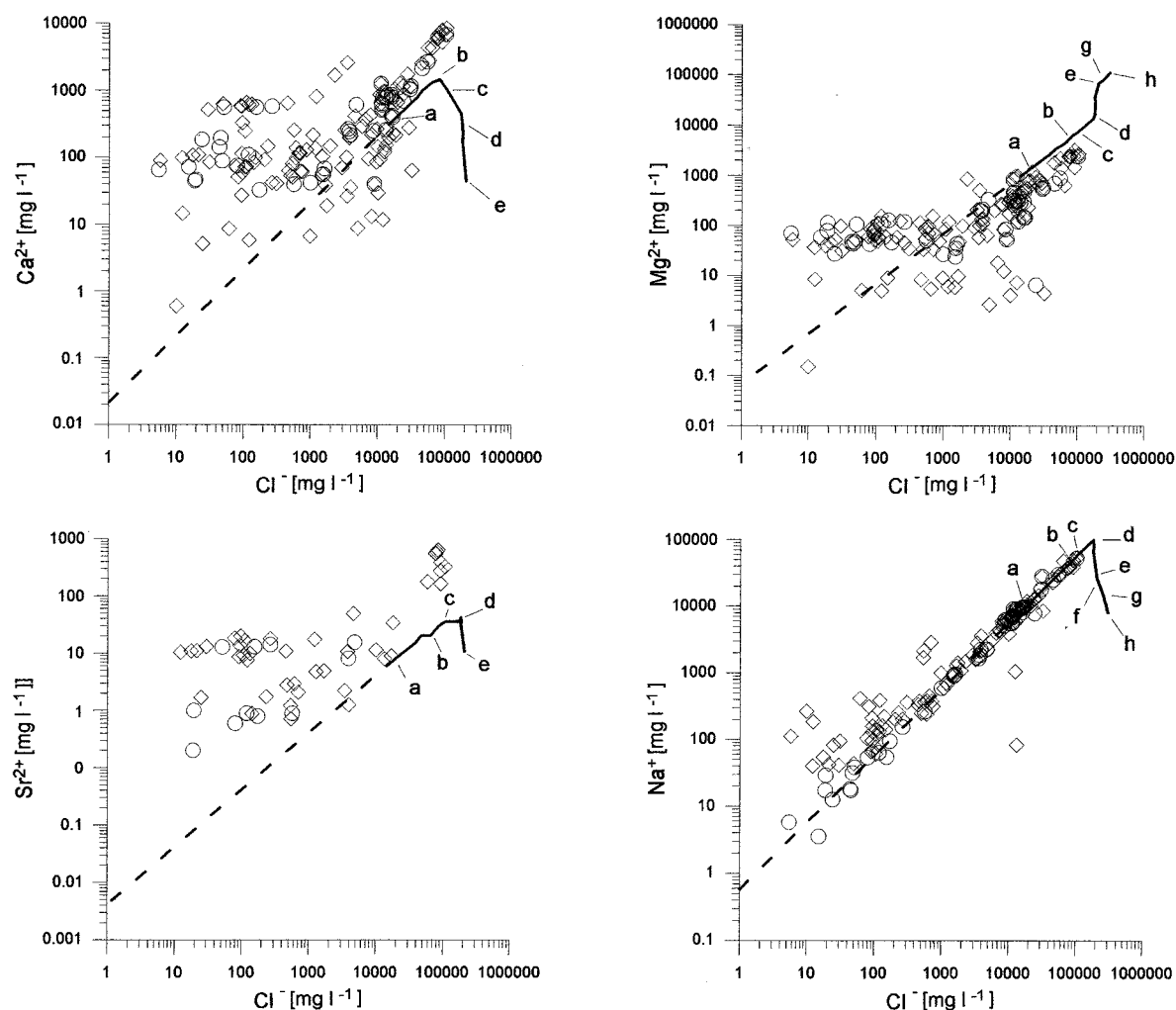


Fig. 2. Chemical composition of deep groundwaters in the Po plain. Major and minor elements are plotted versus  $\text{Cl}^-$  concentration.  $\diamond$  = data points;  $\circ$  = Monferrato waters; solid line = static evaporation of marine water; a = seawater; b = beginning of calcite precipitation; c = beginning of gypsum precipitation; d = beginning of halite precipitation; e = beginning of epsomite precipitation; f = beginning of sylvite precipitation; g = beginning of carnallite precipitation; h = beginning of bischofite precipitation; dashed line = dilution line between sea water and shallow fresh waters. Data from Arione, 1984; Chiarle, 1991; Chiarle et al., 1992; Coggiola et al., 1987; Conti, 1996; De Vecchi, 1979; Martinelli et al., 1989; Regione Emilia-Romagna, 1979; Ricchiuto et al., 1985; Fontes and Matray, 1993.

duce brines with a  $\text{Br}/\text{Cl}$  ratio lower than sea water, while residual brines are generally enriched in Br (Fontes and Matray, 1993). Both Br and I tend to be retained by organic matter and are released during its decomposition.

In the Po Valley brines, I and Br (Fig. 2) show a good correlation with the  $\text{Cl}$  content. The  $\text{Br}/\text{Cl}$  marine ratio is kept constant even in the most concentrated solutions, confirming the absence of halite precipitation. Some waters show slightly higher Br contents, most likely due to the mineralisation of organic matter. Iodine is constantly enriched with respect to

the hypothetical dilution curve. This is related to the presence at depth of high concentrations of organic matter. The relative enrichment of I with respect to Br, if related to the decomposition of organic matter, has been discussed by Chiarle (1991), noting that most of the gas fields are associated with I-rich waters. Gases generated at depth would either directly contribute I to the brines or testify to a higher degree of organic matter mineralisation occurring at higher temperatures.

The few heavy metals and other elements (Fe, Mn, Sb, V, Se and As) that have been analysed all show high concentrations, especially in the anoxic salt

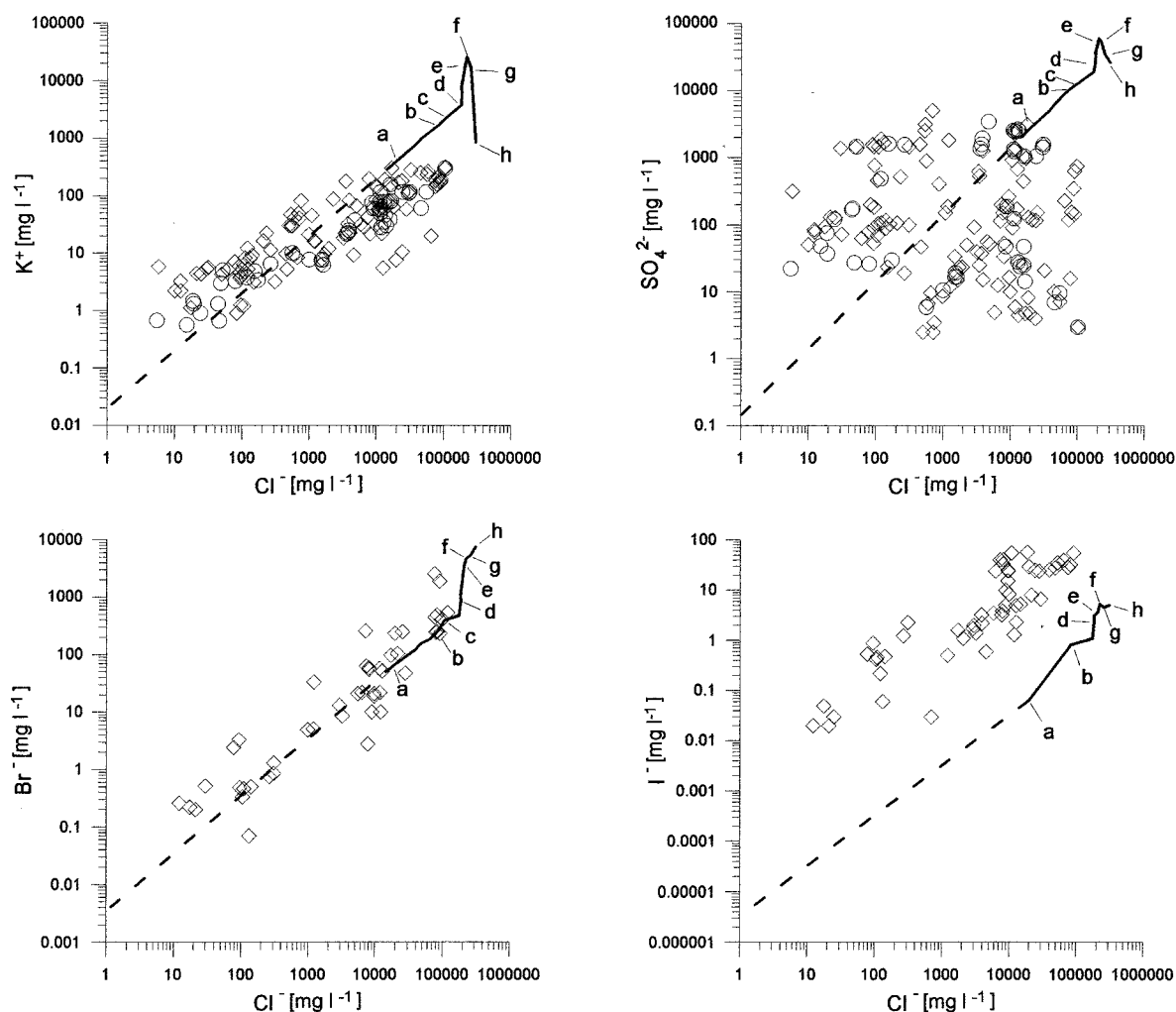


Fig 2 (continued)

waters. Maximum values reach  $96 \text{ mg l}^{-1}$  for Fe,  $16 \text{ mg l}^{-1}$  for Mn,  $36 \mu\text{g l}^{-1}$  for Sb,  $104 \mu\text{g l}^{-1}$  for V and  $412 \mu\text{g l}^{-1}$  for Se (Chiarle, 1991). The presence of As up to  $250 \mu\text{g l}^{-1}$  (Zavatti, 1990), has been the focus of a more detailed investigation because of possible contamination of wells used for human consumption. Arsenic is strongly associated with Fe and it can be co-precipitated with pyrite during  $\text{SO}_4$  reduction or transported in the water when forming complexes with Fe hydroxides. Its distribution in the Po Valley is not uniform in space and time, making any type of forecast difficult. Zavatti et al. (1995) present a model relating the presence of As to Fe hydroxide 'pockets' in sedimentary layers, that are eventually mobilised during pumping.

### 2.3. Stable and radioactive isotopes

Limited stable isotope data of the water molecule are available at present. In the diagram  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  (Fig. 3) groundwaters mostly seem to result from a mixing between shallow fresh waters and seawater, with a  $\delta^{18}\text{O}$  enrichment most likely due to an exchange with host rocks of the deep reservoirs. Mud volcanoes show the more enriched values in  $^2\text{H}$ .

In the diagram  $^{18}\text{O}$  vs  $\text{Cl}^-$  concentration (Fig. 3), the end-members considered for the dilution curves are the isotopic compositions of shallow fresh waters and gypsum crystallisation waters ( $\delta^{18}\text{O} \approx +5\text{‰}$ ) found in the Mediterranean (Pierre, 1982, 1989). Most of the samples can be described by different degrees of di-

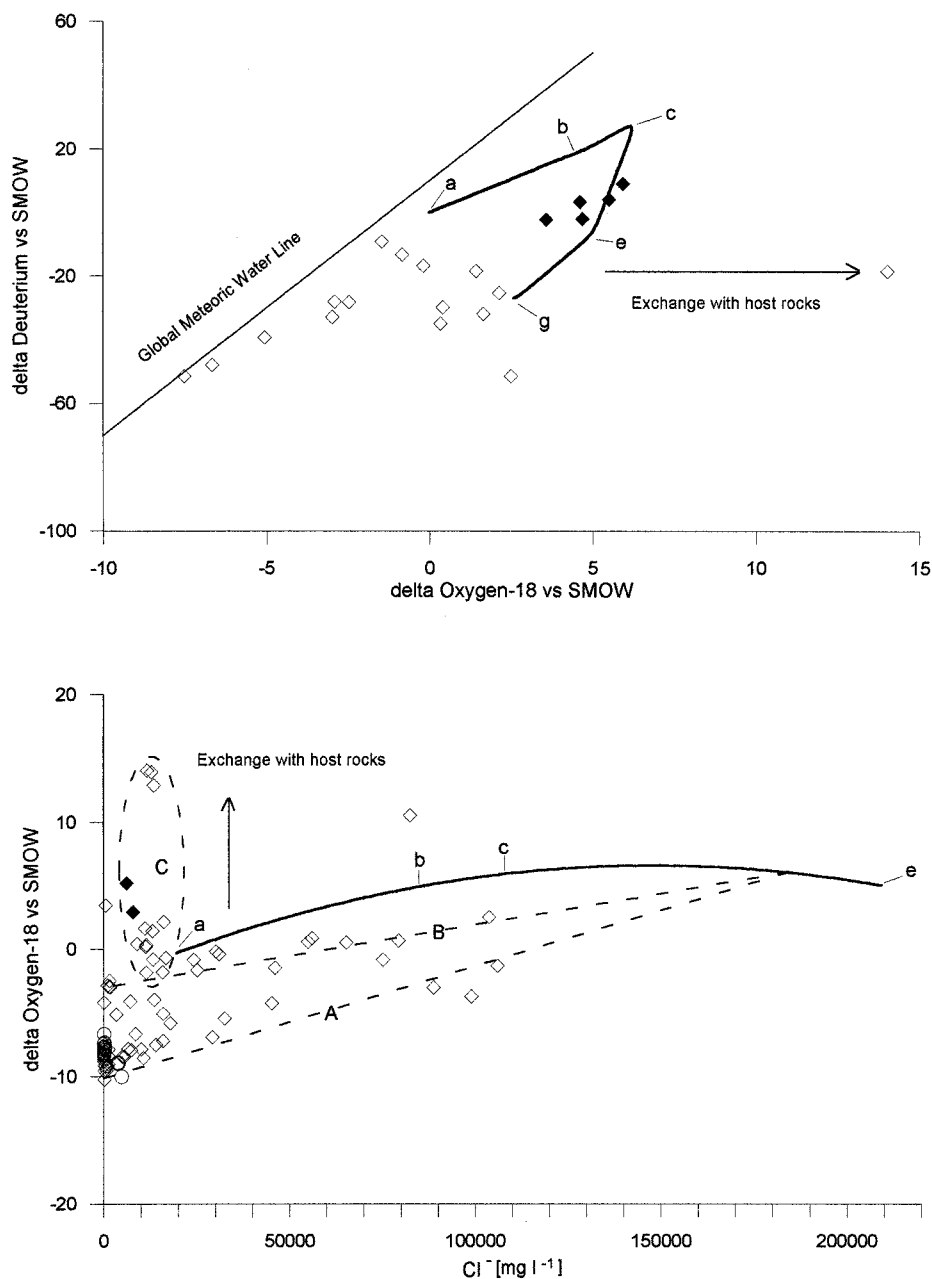


Fig. 3. a)  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  plot and b)  $\delta^{18}\text{O}$  vs chloride concentration in waters.  $\diamond$  = data points;  $\circ$  = Monferrato waters;  $\blacklozenge$  = Po plain mud volcanoes; solid line = static evaporation of marine water; dashed lines A, B and C refer to the mixing and circulation models described in the text and in Fig. 4a.

lution of these end-members, considering a slight shift of the isotopic composition of fresh waters. An  $^{18}\text{O}$  enrichment due to the exchange with host rocks is also observed.

In order to explain the high variability of Cl contents and stable isotope compositions (Fig. 3),

Ricchiuto et al. (1985) distinguish 3 types of groundwater mixing and circulation (Fig. 4a):

1. *Mixing between downward moving freshwaters and brines.* This is the case for example of the Cortemaggiore and Correggio (Table 1) hydro-



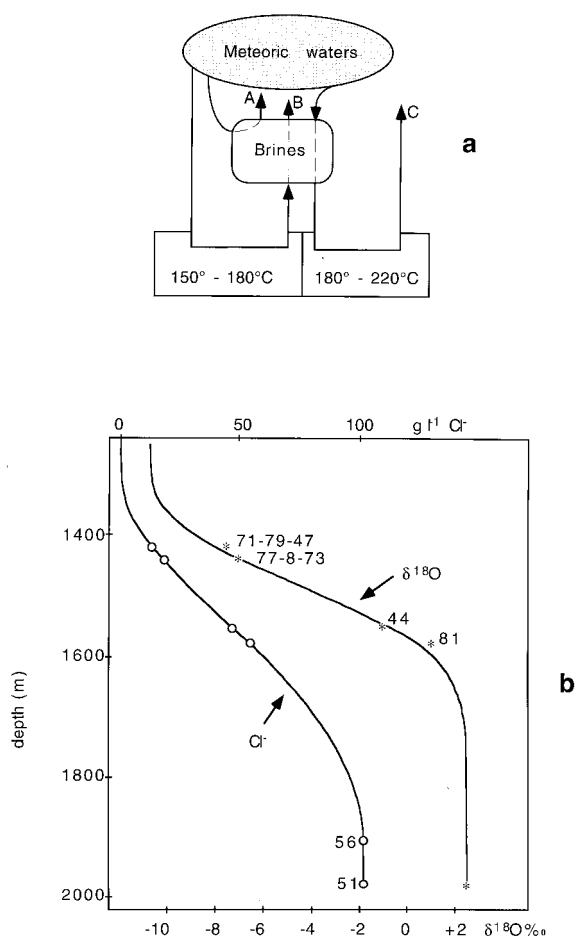


Fig. 4. a) Scheme of the possible mixing phenomena and circulation models derived for the Po plain sector. See text for explanation. b)  $^{18}\text{O}$  and Cl contents vs depth in the Cortemaggiore oil well (data are reported in Table 1). Modified from Ricchiuto et al., 1985.

carbon exploration wells. These waters only partially leach the upper part of the brine reservoir, and fall on the mixing line of Alpine and Apennine freshwater with the saline end-member. The evolution of the Cl<sup>-</sup> and  $^{18}\text{O}$  content with depth in the Cortemaggiore well is shown in Fig. 4b. Temperature measurements inside the boreholes do not exceed 60°C, indicating that the shallow water circulation is cooling the host rock reservoir.

2. *Mixing between upwelling deep warm waters and brines.* This is the case of groundwaters located close to tectonic discontinuities (Agnadello, Brugherio, Spilamberto; Table 1). These waters are enriched in  $^{18}\text{O}$  because of the isotopic exchange

between groundwaters penetrated at depth and the pre-Messinian carbonate host rocks. On the other hand, their Cl<sup>-</sup> content is a function of the degree of mixing with the brines during the upward movement. Using independently these two parameters (degree of isotopic exchange and degree of mixing with brines), temperatures at depth could be calculated, ranging between 150° and 180°C.

3. *Mixing between downward moving freshwaters and brines, subsequently flowing in deeper circuits.* This is the case of fields structurally related to the Alpine and Apennine fronts (Acqui Terme, Salice Terme, Ponte Tidone, Casteggio, Abano Terme; Table 1) or upwelling from the pre-Messinian formations (Malossa; Table 1). Their Cl<sup>-</sup> content is lower than the previous two groups.  $\delta^{18}\text{O}$  can be heavily enriched only if the pre-Messinian host rocks are carbonate (Casteggio, Ponte Tidone, Malossa). If the deep reservoir is mainly made of silicates, only a dilution of basal brines by meteoric waters is observed. The extent of the isotopic exchange indicates temperatures at depth up to 220°C. This value is confirmed, taking into account the various degrees of mixing, by the silica geothermometer.

The mixing of Alpine and Apennine fresh waters with deep waters occurs with an increase of  $^{13}\text{C}$  at constant  $^{18}\text{O}$  (Chiarle et al., 1992), due to a contribution of enriched  $\text{CO}_2$  possibly coming from the decarbonation of the Mesozoic platform undergoing subduction (Borgia et al., 1988), or from the organic matter mineralisation (Conti, 1996). A combined enrichment of both  $^{18}\text{O}$  and  $^{13}\text{C}$  indicates a higher degree of interaction between waters and carbonate rocks.

The origin of S compounds in water is generally leaching and dissolution of the Messinian evaporites (Olivero et al., 1987). Studies with  $\delta^{34}\text{S}$  data indicate that  $\text{SO}_4$  reduction can take place at depth, where elevated temperatures and the presence of organic compounds gives rise to residual  $\text{SO}_4$  heavily enriched ( $\delta^{34}\text{S} = +50\text{‰}$  vs CD) and a sulphide with an isotopic composition close to zero. The complexity of the aquifer geometry (coexistence of porous media and fractures) and of the geochemical system (presence of organic matter and its decomposition products) controls the evolution of S compounds during the movement of brines towards the surface (Chiarle et al., 1992). Moreover, shallow waters show high contents of  $\text{SO}_4$  coming from fertilisers used in agriculture, as indicated also by the presence of a high  $\text{NO}_3$  content.

Groundwater dating by means of  $^{14}\text{C}$  is not possible, as these waters normally show values close to the detection limits because of the age of the brines and also the contribution of enriched  $\text{CO}_2$ . On the other hand,  $^{14}\text{C}$  may be used as a tracer to identify mixing ratio with shallow groundwaters (Chiarle, 1991).

### 3. Natural outflows

Two sectors of the Po plain have been especially investigated in order to identify the natural mechanisms leading to the upward flow of the deep seated brines: the eastern border of the Northern Apennine chain, where mud volcanoes are found, and the western sector (Monferrato) where outcropping Messinian gypsum deposits may be found (Fig. 1).

#### 3.1. Mud volcanoes

Mud volcanoes are a typical manifestation of accretionary complexes and are widely observed all over the world, mainly along continental margins (Higgins and Saunders, 1974; Le Pichon et al., 1990; Davisson et al., 1994).

Faults associated with shale diapirism processes strongly influence mud volcanoes' occurrences (Barber et al., 1986). Extrusion products are clay mud, connate salty waters and gases (mainly CH<sub>4</sub>). Temperatures of extruded fluids generally reflect shallow environments but, in some cases, thermal anomalies have been observed in connection with paroxysmal eruptions. Mud is driven upward by buoyancy forces arising from the bulk density difference between an overpressured muddy mass and an overburden of greater density (Brown, 1990). Mud volcanism is one of the mechanisms through which pore water is expelled during tectonic compacting phases that give rise to confined fluid reservoirs located along tectonic disturbances.

Twelve mud volcanoes were identified in the compressive belt of the Apennine chain during the past century and a large volume of literature described their occurrence and behaviour (Spallanzani, 1795; Stoppani, 1908). More recently, geochemical investigations indicated that confined fluids of mud volcanoes act as natural strain meters and are sensitive to pre-earthquake processes (Martinelli and Ferrari, 1991). Previous studies have pointed out a correlation between the occurrence of seismic events and sudden changes in chemistry, stable isotopes and dissolved gas content measured in expelled fluids (Martinelli et al., 1995).

Radon is continuously produced by <sup>226</sup>Ra natural decay in the host rock and is readily detectable in mud volcanoes' emissions. <sup>226</sup>Ra content ranges from 260 pCi kg<sup>-1</sup> to 470 pCi kg<sup>-1</sup> in the clay fraction and is around 20 pCi kg<sup>-1</sup> in the water phase. Radon was monitored both in the gas and in the liquid phase of mud volcanoes of the Northern Apennines. In particular the Nirano and Ospitaletto mud volcanoes were monitored by systematic manual investigation with an EDA RD-200 Rn detector from July 1986 to December 1989, while the Regnano mud volcano was

continuously monitored using an automatic station equipped by a Pylon decaying chamber detector from 1988 to 1991.

The best results were obtained in the Nirano and Ospitaletto sampling sites. Radon variations in the liquid phase were evaluated to be significant precursors of local seismic activity. Although automatic monitoring of the Rn content in the gas phase at the Regnano test site appears to be the most suitable approach to mud volcano monitoring, results show a poor signal to noise ratio. This discrepancy between results obtained on the gas phase and the liquid phase can be interpreted as due to the difficulty in obtaining a correct evaluation of Rn concentration in the emerging bubbles when the original ratio between all phases at depth is unknown (Mucciarelli et al., 1996). Nevertheless Rn content in the liquid phase appeared to be a reliable precursor of seismic events, confirming the close link between mud volcanoes and tectonic disturbances.

#### 3.2. Calcite fracture fillings

Isotopic studies on spring waters and calcite-filled vein systems related to the main tectonic structures have been carried out in the Monferrato area (Northwestern Apennines, Fig. 1). In this region, the intense deformation linked to the juxtaposition of Alpine and Apennine chains gives rise to several important tectonic planes (N–NE verging thrust fronts, NNW–SSE transpressive faults). The related fracture systems are often filled by carbonate minerals. Both vein fillings and host rocks have been analysed, as the former may reflect the composition of the fluid phase that once permeated the system, while the latter can bring evidence of the extent and the intensity of fluid-rock interactions (Dietrich et al., 1983; Fourcade et al., 1989; Burkhard and Kerrick, 1990; McCaig et al., 1995).

In addition, the geochemical investigation included spring waters linked to the main structural features of the area. Literature (Arthaud and Dazy, 1989; Bortolami, 1989; Chiarle, 1991) commonly relates these waters to Messinian evaporites doming and outcropping in southern Monferrato and in the Langhe Basin. Most of these springs have low flow rates (<5 l s<sup>-1</sup>). The parallel investigation on vein calcites and waters has been carried out in order to eventually define the relationship existing between past and present-day hydrologic systems and the main tectonic features of this sector of the chain (Carter et al., 1994; Davisson et al., 1994).

Oxygen and C isotopic ratios of vein systems' carbonates span over a quite large compositional range: 6.88‰ < δ<sup>18</sup>O < 0.39‰; 9.85‰ < δ<sup>13</sup>C < 0.13‰, both expressed on the PDB scale

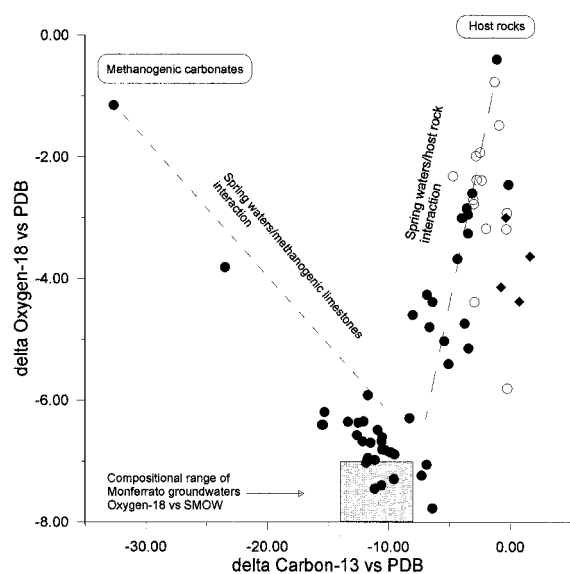


Fig. 5.  $\delta^{18}\text{O}$  vs  $\delta^{13}\text{C}$  plot from carbonate fracture fillings of the Monferrato region and the Po plain mud volcanoes, including the compositional range of Monferrato groundwater samples. ● = carbonate veins; ○ = Tertiary marine limestones; ◆ = Po plain mud volcanoes

(Conti et al., 0000). Spring water compositions fall in a rather smaller range:  $10.00\text{‰} < \delta^{18}\text{O} < 6.67\text{‰}$  (vs SMOW);  $14.80\text{‰} < \delta^{13}\text{C} < 10.32\text{‰}$  (vs PDB). On the other hand, the Sr isotopic ratios in waters are characterized by important variations ( $0.70871 < ^{87}\text{Sr}/^{86}\text{Sr} < 0.71112$ ), the Sr concentration being  $0.004 < [\text{Sr}] \text{ mmol l}^{-1} < 0.228$ .

In the Monferrato region, vein calcites derive their isotopic characteristics from the composition of the mother fluid and from the extent of fluid-rock interactions; additionally another geochemical process,  $\text{CH}_4$  oxidation (Fig. 5), may be identified. The trends defined in Fig. 5 can be interpreted as resulting from a mixing in the veins of an host rock-equilibrated fluid with an exogenous fluid having lighter O and C. The inferred  $\delta^{18}\text{O} = 8\text{‰}$  PDB of the vein end-member implies that most veins precipitated from, or at least were equilibrated with, a fluid bearing a meteoric signature. This fluid was enriched in organic C as classically observed in groundwaters (Deines et al., 1974).

In this area, the host rocks are mainly constituted of Oligo-Miocenic marine sediments. The carbonate fraction of the matrix has been in some cases partially modified by the percolating fluid at veins rims. This is generally the case of extensional fracture systems with high fluid/rock ratios. In other cases, especially during the early stages of vein formation, vein fillings may inherit the isotopic signature of the enclosing rock. This phenomenon is common in compressive regimes characterised by low fluid/rock ratios.

The  $\delta^{18}\text{O}$  in Monferrato waters is close to values inferred for local meteoric water, while their  $\delta^{13}\text{C}$  is consistent with the presence of organic C in the groundwater reservoir. The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of calcite potentially precipitated in equilibrium with such waters at temperatures between  $18^\circ$  and  $25^\circ\text{C}$  has been calculated using the equation derived by McCrea (1950). This calcite ranges between  $\delta^{18}\text{O}$  vs PDB = 7 to 8‰ and  $\delta^{13}\text{C} = 10$  to 12.5‰. These values are very close to the lowest values obtained on vein calcite samples (Fig. 5). Such a similarity suggests that groundwaters identical to present-day spring waters may have contributed to the precipitation of vein calcite. In this case, the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of vein carbonates could be interpreted as a mixing trend between a host rock-equilibrated fluid and a groundwater end-member. It is worth noting that a similar mixing trend appears not only for host-rock limestones with  $\delta^{13}\text{C} \cong 0\text{‰}$ , but also for the highly negative veins samples bearing a methanogenic signature.

Some Monferrato spring waters (Fig. 6) inherit the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio typical of the Messinian evaporites hosting the hydrologic circuit. This is especially the case of outflows located in the less deformed eastern and southern sectors of the region. On the other hand, springs associated with the NE-verging thrust fronts exhibit a sharp geochemical differentiation. It is generally observed that in proximity of the main tectonic features, spring water compositions abruptly change, assuming either isotopic ratios relatively similar to that of the Oligocenic carbonate country-rocks, or highly radiogenic ratios. The complex structural setting of the area could partly account for the observed variations. In fact, hydrological circuits developed along deep-rooted tectonic planes undergo intense fluid-rock interactions because of longer residence times or, in the case of transpressive faults or thrusts, of pressure-solution phenomena.

In the eastern sector of the Po plain mud volcanoes reveal a clear isotopic signature of Messinian deposits as testified by their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr concentrations (Fig. 6).

The comparison between the isotopic ratios of vein filling calcite and those of present-day waters underline the importance of the structural framework in controlling not only the geometry of hydrological systems, but also the kind and extent of fluid-rock interaction processes. Even if the geodynamic settings of the Apennine sector are different from the Po plain sector, some common hydrogeological and geochemical features have been identified. These are the upwelling of important volumes of fluids as a consequence of deformation events and the temporal continuity of this phenomenon. This allows the extrapolation to a regional scale of the main features of the past and recent hydrological systems.

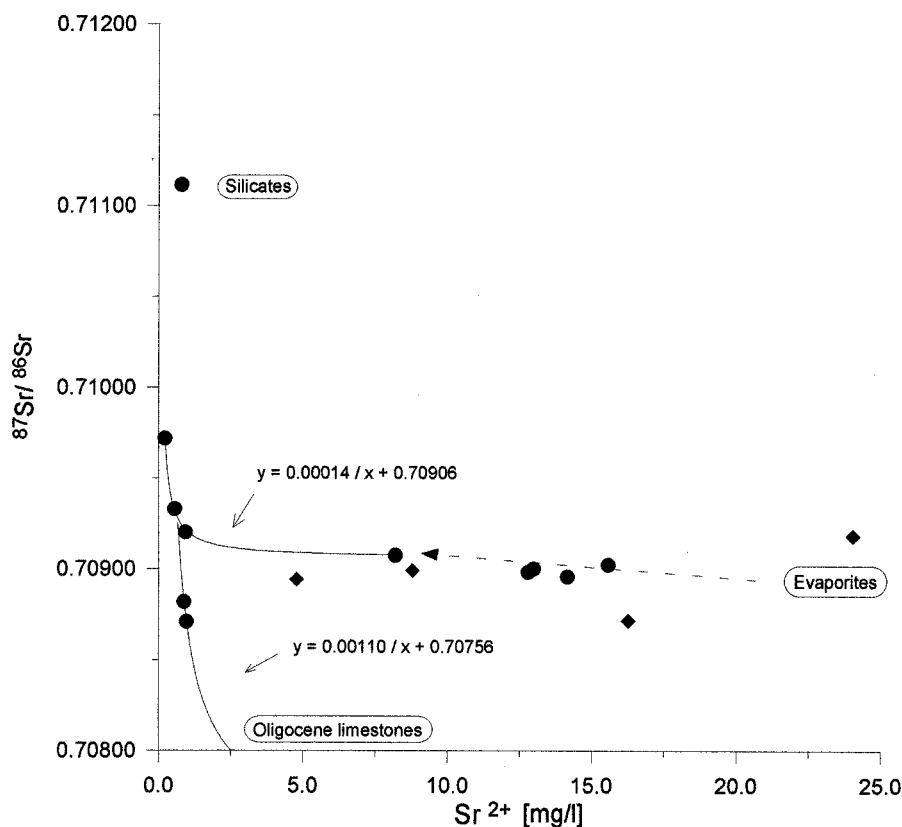


Fig. 6.  $^{87}\text{Sr}/^{86}\text{Sr}$  vs Sr concentration in groundwaters from the Monferrato region and the Po plain. ● = Monferrato springs and wells; ◆ = Po plain mud volcanoes. The values for solid end-members are also indicated.

#### 4. Summary and conclusion

The Po Valley brines represent the base level of the Quaternary aquifer located in the thick clay-sand layer sedimentary sequence. Geochemistry indicates that these are marine waters, evaporated to the stage of gypsum precipitation, trapped at the bottom of the basin in late Messinian. The mobility of these brines is restricted because of their high density. Nevertheless, natural outflows of brackish waters are observed, especially in relationship with tectonic features, such as buried and outcropping thrust faults. Saline waters are brought to the surface either by infiltrating meteoric waters, that can partially leach the upper part of the brines, or by the compressive forces acting along the Po Valley margins, squeezing the brines out from the sediments.

Brines play an important role as a lubricating fluid along major fractures. This can be observed at present in the eastern sector, where mud volcanoes undergo changes in discharge, chemistry and noble gas content, associated with seismic events. In the western sector, spring waters show chemical and isotopic character-

istics relating them to the Messinian gypsum deposits. Given the temporal continuity of the hydrological flow path, as proved by the isotopic composition of calcite in vein-fillings associated with the main deformation structures, it is possible to interpret all these natural outflows as different stages of the same deformation process. What are found as outcropping veins in the western sector is the fossil evidence of the fluid conduits operating in the region in the past and which presently are found at depth in the eastern sector.

An attempt at a 3-dimensional reconstruction of the distribution of the deep seated brines was conducted by Coggiola et al. (1986), based on natural outflows and data obtained from Agip logs of oil extraction wells (Fig. 7). This broad reconstruction does not take into account local disturbances associated with the intense exploitation of deep groundwaters for domestic or industrial purposes and methane or oil extraction.

Human-induced perturbations are a serious concern in the region. Human activities have lowered the pore-water overpressure at depth and are now considered to be responsible for the increase in subsidence of the Po plain and sea water pollution of coastal aquifers.

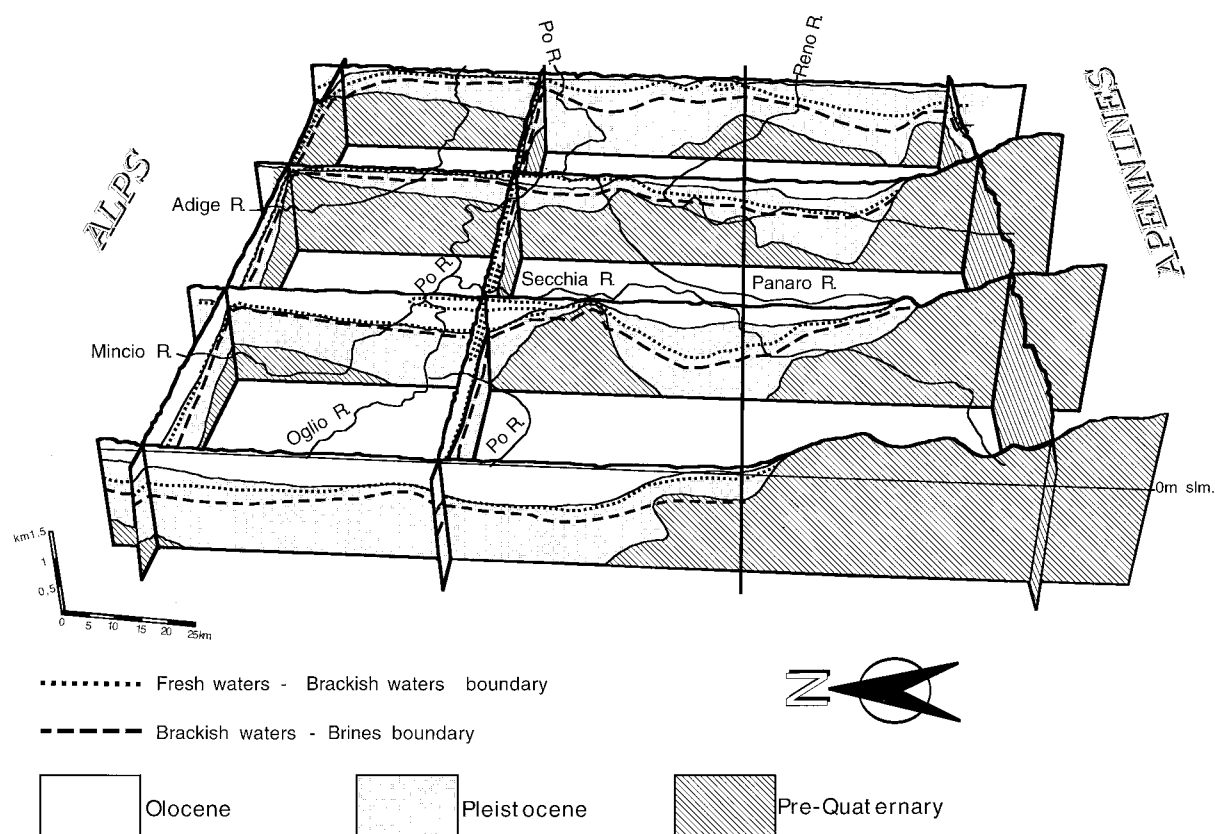


Fig. 7. Three dimensional reconstruction of the distribution of deep seated brines in the Po plain. Fresh water–brackish water boundary =  $1 \text{ g l}^{-1}$  total salinity; brackish waters–brines boundary =  $10 \text{ g l}^{-1}$ . Modified from Coggiola et al., 1986.

These phenomena have been intensively studied for their dramatic consequences on Adriatic cities like Venice, Ravenna and Bologna. A rational planning of the use of both shallow and deep groundwaters is urgently needed and requires attention in the near future by the relevant government agencies.

The distribution and circulation model that has been outlined for the Po Valley brines could also be validated for other sedimentary basins affected by active tectonics in compressive regimes.

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