

## Na-carbonate waters of extreme composition: Possible origin and evolution

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Na-carbonate (NaCW) waters are not concentrated in well defined areas, but usually widespread in areas where other water types (e.g., Ca-carbonate) are dominant. NaCW are the product of long-term water-rock interaction with dissolution of Na-silicates in presence of phyllosilicates, silica phases, and calcite. NaCW circulating in calcite-bearing sediments very probably have a Ca-carbonate parent with moderate to low  $P_{\text{CO}_2}$ , which changes its composition assuming increasing Na character as the water-rock interaction proceeds. However, the moderate to low  $P_{\text{CO}_2}$  values of the potential parent Ca-carbonate waters do not account for the high Na content of many NaCW. The higher  $P_{\text{CO}_2}$  required may be due to oxidation of organic matter of the sediments and, perhaps, to further addition of  $\text{CO}_2$  coming from deeper crustal levels, from the mantle, or from other sources. Na-Ca exchange involving a Na-exchanger could be an alternative genetic hypothesis. At present, however, at least for some areas (e.g., Northern Apennines, Italy), this hypothesis is not supported by mineralogical evidence.

### INTRODUCTION

#### Definitions

The Na-carbonate waters (NaCW) are here defined as waters having  $[\text{Na total}] \geq ([\text{K total}] + 2[\text{Ca total}] + 2[\text{Mg total}])$ ,  $([\text{HCO}_3 \text{ total}] + 2[\text{CO}_3 \text{ total}]) \geq ([\text{Cl}^-] + 2[\text{S total}])$  and  $[\text{Na total}] > [\text{K total}]$ , where the values in square bracket are molar concentrations. The waters considered in this paper have moderate values of pH ( $<9.7$ ); thus alkalinity (Alk) is practically only due to carbonate alkalinity, i.e.,  $\text{Alk} \cong [\text{HCO}_3 \text{ total}] + 2[\text{CO}_3 \text{ total}]$ . The Na-carbonate character for each water sample may be expressed by the minimum value of the indexes  $na = [\text{Na total}] / ([\text{Na total}] + [\text{K total}] + 2[\text{Ca total}] + 2[\text{Mg total}])$  and  $calc = ([\text{HCO}_3 \text{ total}] + 2[\text{CO}_3 \text{ total}]) / ([\text{HCO}_3 \text{ total}] + 2[\text{CO}_3 \text{ total}] + [\text{Cl}^-] + 2[\text{S total}])$ .

The Na-carbonate waters are not very frequent; they are commonly present in areas where other

water types (e.g., Ca-carbonate) are dominant. Some analyses of different types of NaCW (mostly from Italy) are reported in Table 1 together with indications about the rocks involved in water-rock interaction.

In the following pages we will focus on waters of extreme composition, i.e., with *na* and *calc* higher than 0.85. In the Northern Apennines (Italy), waters with *na* and *calc*  $> 0.85$  are widespread and thus, frequently, we shall implicitly refer to them.

#### Data processing

For water speciation and for other calculations we have used a recent version of PHREEQC (Parkhurst and Appelo, 1999), a flexible and user-friendly software. The software is adequate for low ionic strength solutions (Debye-Hückel expression), and suitable at higher ionic strength for sodium chloride dominated systems. The limits of

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Table 1. Analyses of Na-carbonate waters from different localities

Ref.	Water type/Sample	Rock formation/Locality	T °C	pH	Alk mEq/L	total S as SO <sub>4</sub> mEq/L	Cl mEq/L	Ca mEq/L	Mg mEq/L
	<i>Low P<sub>CO<sub>2</sub></sub></i>	<i>Carbonate-pelitic and sandstone-pelitic rocks</i>							
2	BIS 13 (*,s)	Bisagno Valley, Liguria, Italy	10.8	9.43	9.71	0.26	0.24	0.57	0.10
2	BIS 13b (*,s)	Bisagno Valley, Liguria, Italy	12.8	9.20	5.90	0.14	0.16	0.21	0.07
2	SC-102 (s)	Bisagno Valley, Liguria, Italy	11.7	9.56	7.66	0.06	0.08	0.10	0.04
2	SC-103 (*,s)	Bisagno Valley, Liguria, Italy	11.7	9.19	7.79	0.08	0.18	0.64	0.18
3	F1/98 (*,s)	Fugazzolo, Parma province, Italy	7.6	8.54	7.08	0.36	0.12	2.47	0.43
3	F3/98 (*,s)	Roccaferrara, Parma province, Italy	9.9	9.37	8.40	0.09	0.10	0.07	0.11
3	F6/98 (*,s)	Bedonia-Rio Monti, Parma province, Italy	11.8	9.20	5.87	0.05	0.11	0.08	0.08
3	K01/98 (*,s)	Montemisoso, Parma province, Italy	7.9	9.68	8.08	0.30	0.21	0.16	0.03
3	K06/98 (*,s)	Lagumi (Ventasso), Parma province, Italy	6.6	8.37	5.51	1.57	0.09	1.06	0.68
3	(*s) F8/98	Vezzolo, Reggio Emilia Province, Italy	11.9	9.26	11.4	0.90	0.56	0.06	0.11
3	F10/98 (*,s)	Maiola, Reggio Emilia Province, Italy	12.2	9.18	11.9	0.54	6.50	0.08	0.09
3	F14/98 (*,s)	Morsiano, Reggio Emilia Province, Italy	11.5	7.93	8.32	0.75	4.35	2.55	0.65
3	F13/98 (*,s)	Varano Melegari, Parma province, Italy	14.9	9.22	9.51	0.89	0.37	0.09	0.17
4	(1) (*,w)	Bagno di Romagna-S.Agnese, Forli Province, Italy	44.0	8.46	11.4	0.00	1.08	0.15	0.15
4	(2) (*,w)	Bagno di Romagna-BR5 Forli Province, Italy (ca. -108 m)	36.2	8.18	9.54	0.05	1.00	0.12	0.11
4	3 (*,s)	Bagno di Romagna-Chiardovo Spring, Forli Province, Italy	12.2	8.86	5.95	0.37	0.56	0.41	0.20
4	(4) (*,s)	Bagno di Romagna-Chiardovo pipe, Forli Province, Italy	16.6	8.64	6.22	0.41	0.41	0.18	0.17
5	12 c (w)	Hornsey Rd, London, England (ca. -120 m)	13.7	7.65	4.80	2.46	1.83	1.30	1.19
5	14 c (w)	Food Res. Ins., London, England (ca. -90 m)	12.4	7.40	5.43	0.94	3.55	2.16	2.14
		<i>Crystalline and volcanic rocks</i>							
9	G5 (s)	Gotthard Tunnels (1100 m from Airolo portal), Switzerland	16.5	9.35	2.40	0.50	0.01	0.11	0.02
9	Ga4 (s)	Gotthard Tunnels (1810 m from Airolo portal), Switzerland	16.5	9.35	3.00	0.48	0.00	0.04	
9	Ga5 (s)	Gotthard Tunnels (4060 m from Airolo portal), Switzerland	20.7	9.67	0.50	0.31	0.00	0.42	0.00
9	Ga6 (s)	Gotthard Tunnels (4280 m from Airolo portal), Switzerland	22.9	9.26	0.50	0.32	0.00	0.36	0.00
9	Ga14 (s)	Gotthard Tunnels (1084 m from Airolo portal), Switzerland	16.1	9.33	3.60	0.94	0.02	0.05	0.02
10	SIB2 (w)	Siblimgen borehole (-337 to -345 m), N Switzerland	22	8.2	4.47	3.22	0.73	0.65	0.09
10	SIB6 (w)	Siblimgen borehole (-1154 to -1164 m), N Switzerland	47	8.8	4.38	2.96	0.7	0.60	0.115
10	SIB7 (w)	Siblimgen borehole (-1493 to -1499 m), N Switzerland	57	8.2	4.61	2.66	0.76	0.55	0.066
6	1 (s)	Marroneto, Tuscany, Italy	14	6.33	1.15	0.24	0.14	0.52	0.16
6	17 (s)	Capanacce, Tuscany, Italy	12	7.8	15.0	1.70	0.41	1.00	0.50
		<i>Uncertain</i>							
1	31 (?)	Acqui 1, Italy	30.1	7.38	7.81	5.69	1.35	2.34	3.29
1	50 (*,?)	Acqui 2, Italy	14.5	8.55	5.95	0.53	0.31	0.50	1.32
	<i>High P<sub>CO<sub>2</sub></sub></i>								
7	97 (s)	Casciana Terme (Acqua S.Lepoldo), Tuscany, Italy	17	6.5	47.0	20.0	14.0	13.0	15
7	103 (s)	Casciana Terme (Acqua S.Lepoldo bis), Tuscany, Italy	16	7.4	75.0	16.0	22.0	17.0	17
7	249 (s)	Gambassi (Acqua di Luiano), Tuscany, Italy	7	6.1	131	22.0	61.0	14.0	83
7	283 (s)	Poggibonsi (Acqua S.Giorgio), Tuscany, Italy	17	6.0	30.0	3.4	9.8	9.1	5.2
8	407 (w)	Logudoro-Sardinia, Italy (well, -0.5 m)	16	6.5	25.3	3.3	12.4	4.44	2.1
8	AB (s)	Abbarghente, Logudoro-Sardinia, Italy	21	6.3	45.2	6.6	10.9	2.82	2.780
8	489 (s)	Logudoro-Sardinia, Italy	15	6.5	31.0	1.28	3.8	2.56	1.6
8	SM (s)	S.Martino-Logudoro, Sardinia, Italy	24	6.4	42.5	5.0	9.1	10.4	4.46

the software depend on the following points: (i) the data are taken from different reference sources and thus the data may lack internal consistency; (ii) for some reactions the temperature dependence of the equilibrium constant is not known. These limits, however, do not invalidate our semi-quantitative approach and results. If thermodynamic data were not found in the PHREEQC data base, for some compounds or reactions data from EQ3/6 (Wolery, 1992) and SUPCTR 92 (Johnson *et al.*, 1992) were used. The saturation degree of pure phases in the water has been quan-

tified by the parameter  $S.I. = \log(K/Q)$ , where  $K$  is the equilibrium constant of the considered dissolution reaction of the phase and  $Q$  is the activity product of the aqueous species involved in the reaction.

#### MAIN GEOCHEMICAL FEATURES AND GENETIC HYPOTHESES

NaCW may have both high (e.g., Larderello geothermal field, central Italy: Duchi *et al.*, 1992) and low temperature (e.g., Northern Apennines,

Table 1. (continued)

Ref.	Water type/Sample	Rock formation/Locality	Na mEq/L	K mEq/L	$\Sigma$ ions mEq/L	Si $\mu$ mole/L	na	calc	log $P_{CO_2}$
<i>Low <math>P_{CO_2}</math></i>			<i>Carbonate-pelitic and sandstone-pelitic rocks</i>						
2	BIS 13 (*,s)	Bisagno Valley, Liguria, Italy	9.58	0.015	20.5	128	0.93	0.95	-3.86
2	BIS 13b (*,s)	Bisagno Valley, Liguria, Italy	6.01	0.015	12.5	188	0.95	0.95	-3.78
2	SC-102 (s)	Bisagno Valley, Liguria, Italy	7.79	0.008	15.7	161	0.98	0.98	-4.11
2	SC-103 (*,s)	Bisagno Valley, Liguria, Italy	7.49	0.028	16.4	166	0.90	0.97	-3.67
3	F1/98 (*,s)	Fugazzolo, Parma province, Italy	4.62	0.015	15.1	108	0.61	0.94	-3.04
3	F3/98 (*,s)	Roccaferara, Parma province, Italy	7.80	0.015	16.6	182	0.98	0.98	-3.84
3	F6/98 (*,s)	Bedonia-Rio Monti, Parma province, Italy	5.72	0.034	11.9	171	0.97	0.97	-3.79
3	K01/98 (*,s)	Montemisoso, Parma province, Italy	7.83	0.010	16.6	110	0.97	0.94	-4.25
3	K06/98 (*,s)	Lagumi (Ventasso), Parma province, Italy	5.00	0.31	14.2	118	0.71	0.77	-2.97
3	(*s) F8/98	Vezzolo, Reggio Emilia Province, Italy	11.8	0.042	24.8	210	0.98	0.89	-3.59
3	F10/98 (*,s)	Maiola, Reggio Emilia Province, Italy	18.2	0.038	37.4	252	0.99	0.63	-3.5
3	F14/98 (*,s)	Morsiano, Reggio Emilia Province, Italy	10.6	0.099	27.3	130	0.76	0.62	-2.33
3	F13/98 (*,s)	Varano Melegari, Parma province, Italy	9.58	0.033	20.6	284	0.97	0.88	-3.61
4	(1) (*,w)	Bagno di Romagna-S.Agnese, Forli Province, Italy	12.1	0.12	25.0		0.97	0.91	-2.54
4	(2) (*,w)	Bagno di Romagna-BR5 Forli Province, Italy (ca. -108 m)	10.2	0.12	21.2		0.97	0.90	-2.37
4	3 (*,s)	Bagno di Romagna-Chiardo Spring, Forli Province, Italy	6.34	0.047	13.9		0.91	0.87	-3.41
4	(4) (*,s)	Bagno di Romagna-Chiardo pipe, Forli Province, Italy	6.69	0.045	14.1		0.94	0.88	-3.14
5	12 c (w)	Hornsey Rd, London, England (ca. -120 m)	7.13	0.24	19.0		0.72	0.53	-2.27
5	14 c (w)	Food Res. Ins., London, England (ca. -90 m)	5.13	0.25	19.6		0.53	0.55	-1.97
<i>Crystalline and volcanic rocks</i>									
9	G5 (s)	Gotthard Tunnels (1100 m from Airolo portal), Switzerland	2.94	0.064	6.04	168	0.94	0.83	-4.33
9	Ga4 (s)	Gotthard Tunnels (1810 m from Airolo portal), Switzerland	3.27	0.046	6.83	130	0.98	0.86	-4.23
9	Ga5 (s)	Gotthard Tunnels (4060 m from Airolo portal), Switzerland	0.43	0.005	1.67	148	0.50	0.62	-5.47
9	Ga6 (s)	Gotthard Tunnels (4280 m from Airolo portal), Switzerland	0.52	0.010	1.71	186	0.58	0.61	-4.91
9	Ga14 (s)	Gotthard Tunnels (1084 m from Airolo portal), Switzerland	4.92	0.038	9.58	187	0.98	0.79	-4.43
10	SIB2 (w)	Siblimgen borehole (-337 to -345 m), N Switzerland	7.87	0.12	17.1	350	0.90	0.53	-2.81
10	SIB6 (w)	Siblimgen borehole (-1154 to -1164 m), N Switzerland	7.53	0.97	17.3		0.82	0.54	-3.30
10	SIB7 (w)	Siblimgen borehole (-1493 to -1499 m), N Switzerland	7.53	0.12	16.3		0.91	0.57	-2.56
6	1 (s)	Marroneto, Tuscany, Italy	0.85	0.16	3.22	1100	0.50	0.75	-1.54
6	17 (s)	Capannacce, Tuscany, Italy	15.1	0.062	33.8	220	0.91	0.88	-1.94
<i>Uncertain</i>									
1	31 (?)	Acqui 1, Italy	8.19	0.13	28.8	375	0.59	0.53	-1.70
1	50 (*,?)	Acqui 2, Italy	4.92	0.082	13.6	323	0.72	0.88	-3.08
<i>High <math>P_{CO_2}</math></i>									
7	97 (s)	Casciana Terme (Acqua S.Lepoldo), Tuscany, Italy	48	0.68	157.7	409	0.63	0.58	-0.18
7	103 (s)	Casciana Terme (Acqua S.Lepoldo bis), Tuscany, Italy	81	1.00	229.0	200	0.70	0.67	-0.9
7	249 (s)	Gambassi (Acqua di Luiano), Tuscany, Italy	130	0.54	441.5	1000	0.57	0.61	0.55
7	283 (s)	Poggibonni (Acqua S.Giorgio), Tuscany, Italy	29	0.37	86.9	329	0.66	0.70	0.15
8	407 (w)	Logudoro-Sardinia, Italy (well, -0.5 m)	34.4	0.5	82.4	531	0.83	0.62	-0.42
8	AB (s)	Abbarghente, Logudoro-Sardinia, Italy	54	1.25	123.6	899	0.89	0.72	0.05
8	489 (s)	Logudoro-Sardinia, Italy	33.2	0.46	73.9	568	0.88	0.86	-0.33
8	SM (s)	S.Martino-Logudoro, Sardinia, Italy	39.3	2.45	113.2	347	0.69	0.75	-0.06

Italy: Toscani *et al.*, 2001; Po plain, Italy: Gorgoni *et al.*, 1982) and salinity. Salinity may range from very low (e.g., some waters from the Gotthard Tunnels, Switzerland: Michard *et al.*, 1966) up to some hundred of milliequivalent/L (mEq/L) of total dissolved ions ( $\Sigma$ ions) (e.g., waters from Gambassi and Casciana, Central Italy: Bencini *et al.*, 1977). Some waters may have high calcium and sulphate contents: Ca up to 13–17 (mEq/L) and  $SO_4$  up to 16–22 mEq/L at Casciana and Gambassi. These high values are most likely due to calcium sulphate dissolution; actually, in

Tuscany as well as in several other Italian regions Permian-Triassic or Messinian evaporites may occur at depth and sometimes at the surface (for geochemical data see, for instance, Cortecchi *et al.*, 1981, and Longinelli, 1979/1980).

Oxygen and hydrogen stable isotope data are not available for all the waters reported in Table 1. However, the available  $\delta^{18}O$  and  $\delta D$  values mostly indicate a recent meteoric origin (Fig. 1), the main variations being related to altitude and continental effects (cf., Longinelli *et al.*, 2000). This, however is not true for some NaCW from

Table 1. (continued)

Ref.	Water type/Sample	Rock formation/Locality	<i>S.I.</i> <sub>cc</sub>	<i>S.I.</i> <sub>chal</sub>	B μmole/L	NH <sub>4</sub> tot mEq/L	NO <sub>3</sub> mEq/L	δ <sup>18</sup> O (‰) V-SMOW	δ <sup>2</sup> H (‰) V-SMOW
		<i>Low P<sub>CO2</sub></i>	<i>Carbonate-pelitic and sandstone-pelitic rocks</i>						
2	BIS 13 (*,s)	Bisagno Valley, Liguria, Italy	1.25	-0.27			92		
2	BIS 13b (*,s)	Bisagno Valley, Liguria, Italy	0.61	-0.26			1.6		
2	SC-102 (s)	Bisagno Valley, Liguria, Italy	0.54	-0.21			3.2		
2	SC-103 (*,s)	Bisagno Valley, Liguria, Italy	1.14	-0.13			6.4		
3	F1/98 (*,s)	Fugazzolo, Parma province, Italy	1.09	-0.21	47				
3	F3/98 (*,s)	Roccaferreira, Parma province, Italy	0.26	-0.08	77	28			
3	F6/98 (*,s)	Bedonia-Rio Monti, Parma province, Italy	0.19	-0.12	60				
3	K01/98 (*,s)	Montemiscoso, Parma province, Italy	0.79	-0.34	80	8		-9.1	-60.8
3	K06/98 (*,s)	Lagumi (Ventasso), Parma province, Italy	0.44	-0.16	39	19			
3	(*,s) F8/98	Vezzolo, Reggio Emilia Province, Italy	0.23	-0.04	173			-9.6	-65.7
3	F10/98 (*,s)	Maiola, Reggio Emilia Province, Italy	0.29	0.05	452	83		-9.2	-66.9
3	F14/98 (*,s)	Morsiano, Reggio Emilia Province, Italy	0.60	-0.17	100	61		-9.0	-60.8
3	F13/98 (*,s)	Varano Melegari, Parma province, Italy	0.37	0.05	173	28			
4	(1) (*,w)	Bagno di Romagna-S.Agnese, Forli Province, Italy	0.36				23	-8.5	-55.1
4	(2) (*,w)	Bagno di Romagna-BR5 Forli Province, Italy (ca. -108 m)	-0.08				6.0	-8.5	-55.4
4	3 (*,s)	Bagno di Romagna-Chiardovo Spring, Forli Province, Italy	0.61				29	-8.2	-54
4	(4) (*,s)	Bagno di Romagna-Chiardovo pipe, Forli Province, Italy	0.14				16	-8.3	-54.9
5	12 c (w)	Hornsey Rd, London, England (ca. -120 m)	-0.16				40	-7.7	-54
5	14 c (w)	Food Res. Ins., London, England (ca. -90 m)	-0.14				40	-7.8	-50
		<i>Crystalline and volcanic rocks</i>							
9	G5 (s)	Gotthard Tunnels (1100 m from Airola portal), Switzerland	0.16	-0.22			6.5	-13.5	
9	Ga4 (s)	Gotthard Tunnels (1810 m from Airola portal), Switzerland	-0.24	-0.33				-13.2	-93.3
9	Ga5 (s)	Gotthard Tunnels (4060 m from Airola portal), Switzerland	0.38	-0.44				-12.5	-87.4
9	Ga6 (s)	Gotthard Tunnels (4280 m from Airola portal), Switzerland	0.09	-0.25				-12.2	-83.5
9	Ga14 (s)	Gotthard Tunnels (1084 m from Airola portal), Switzerland	-0.07	-0.17				-12.5	-81
10	SIB2 (w)	Siblimgen borehole (-337 to -345 m), N Switzerland	0.16	0.12					
10	SIB6 (w)	Siblimgen borehole (-1154 to -1164 m), N Switzerland	0.91						
10	SIB7 (w)	Siblimgen borehole (-1493 to -1499 m), N Switzerland	0.51						
6	1 (s)	Marroneto, Tuscany, Italy	-2.33	0.73	12.0				
6	17 (s)	Capanacce, Tuscany, Italy	0.29	0.05	150.1	42			
		<i>Uncertain</i>							
1	31 (?)	Acqui 1, Italy	0.18	0.07	92.5				
1	50 (*,?)	Acqui 2, Italy	0.45	-0.23	38.8			-11.6	-82.8
		<i>High P<sub>CO2</sub></i>							
7	97 (s)	Casciana Terme (Acqua S.Lepoldo), Tuscany, Italy	0.36	0.27	1.7				
7	103 (s)	Casciana Terme (Acqua S.Lepoldo bis), Tuscany, Italy	1.49	-0.93	2.1				
7	249 (s)	Gambassi (Acqua di Luiano), Tuscany, Italy	0.10	0.81	3.1				
7	283 (s)	Poggibonsi (Acqua S.Giorgio), Tuscany, Italy	-0.33	0.17	3.0				
8	407 (w)	Logudoro-Sardinia, Italy (well, -0.5 m)	-0.21	0.39					
8	AB (s)	Abbarghente, Logudoro-Sardinia, Italy	-0.38	0.56				-7.0	-38.6
8	489 (s)	Logudoro-Sardinia, Italy	-0.35	0.43				-7.0	-40.1
8	SM (s)	S.Martino-Logudoro, Sardinia, Italy	0.31	0.15				-7.9	-41.9

\*Sulphide-bearing waters; waters from: s = spring, w = well, ? = unknown; Alk = total alkalinity; *S.I.*<sub>cc</sub> and *S.I.*<sub>chal</sub> Saturation Index for calcite and chalcidony respectively. Samples BIS 13 to (4) are from Northern Apennines.

References: 1, Marini *et al.*, 2000a; 2, Marini *et al.*, 2000b; 3, Toscani *et al.*, 2001; 4, Cortecchi *et al.*, 1999; 5, Elliot *et al.*, 1999; 6, Duchi *et al.*, 1987; 7, Bencini *et al.*, 1977; 8, Caboi *et al.*, 1993; 9, Pastorelli *et al.*, 2001; 10, Michard *et al.*, 1996.

Lithology and mineralogy of interacting rocks (when reported in the papers).

BIS13-K06: marly sediments and interbedded pelites (illite, smectite-illite mixed layers, albite, silica phases, minor K-feldspar, micas, chlorite, very rare kaolinite) (Venturelli and Frey, 1977; Fontana *et al.*, 1994). F8-F10: calcareous sandstones, marly pelites and sandy pelites. F14-(4): quartz-feldspatic sandstones with interbedded siltites and pelites (silica phases, plagioclase and K feldspar in decreasing amount, and illite, chlorite, some smectite). 12c, 14c: limestones with nodular and tabular flints (minor quartz, montmorillonite, mica, apatite, paligorskite, feldspar, marcasite, cristobalite; kaolinite and mixed layers restricted to the lower chalk) (reported in Edmunds *et al.*, 1987). G5, Ga4: amphibole gneiss of the Tremola series. Ga5, Ga6: orthogneiss. Ga14: Permocarboiferous schists. SIB2-SIB7: crystalline basement. 1-17: mostly trachydacites (plagioclase, K-feldspar, orthopyroxene, clinopyroxene, quartz, and minor mica and olivine) (Ferrari *et al.*, 1996). 31, 50: ultramafic rocks, metasediments, Triassic-Jurassic rocks (?) (Marini *et al.*, 2000a). 97,103: limestones and pelitic cherts. 249: carbonaceous flysch, pelites. 283: limestones, quartz-feldspatic sandstones. 407, AB: calcalkaline ignimbrites (plagioclase, and in place K-feldspar, orthopyroxene, clinopyroxene, rare biotite, glass, amphibole; kaolinite and smectite as alteration products). 489: limestones. SM: andesites (plagioclase, orthopyroxene, clinopyroxene, amphibole, occasional olivine and smectite as alteration product).

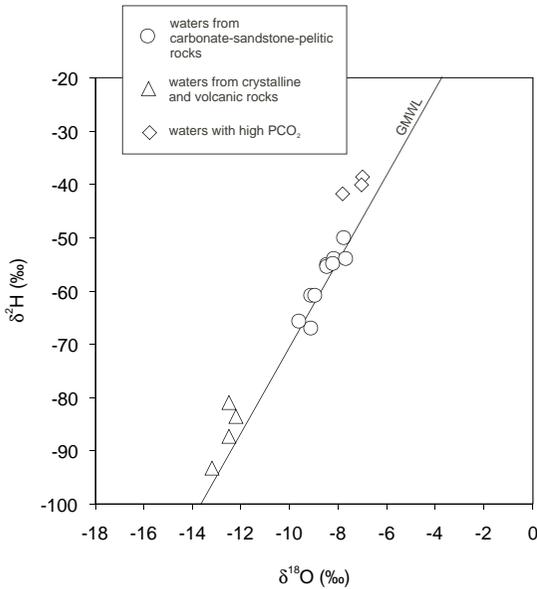


Fig. 1. Oxygen and hydrogen isotopes in  $H_2O$  of some Na-carbonate waters. References: waters from carbonate-pelitic and sandstone-pelitic rocks, Italy and England, Cortecchi *et al.*, 1999, Elliot *et al.*, 1999, Toscani *et al.*, 2001; waters from crystalline rocks, Switzerland, Pastorelli *et al.*, 2001; high  $P_{CO_2}$  waters from Sardinia, Italy, Caboi *et al.*, 1993. GMWL, global meteoric water line,  $\delta^2H = (8.20 \pm 0.07) \delta^{18}O + (11.27 \pm 0.65) (\text{‰})$  (Rozansky *et al.*, 1993).

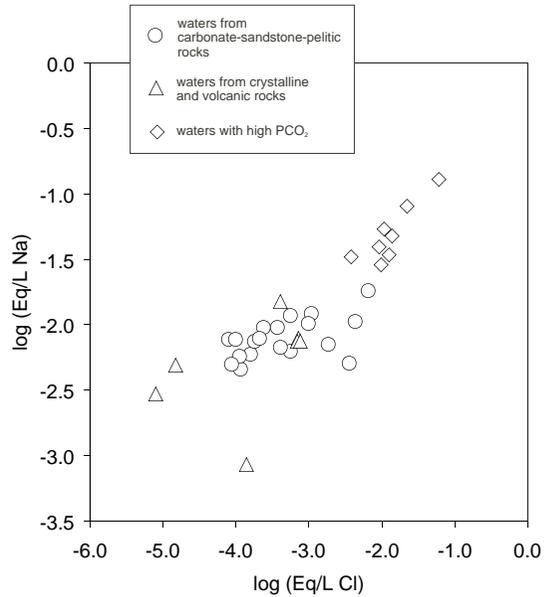


Fig. 2.  $\log[Na]$  vs.  $\log[Cl]$  (Eq/L) for the waters reported in Table 1.

the Po plain, Italy (Gorgoni *et al.*, 1982) not reported in Table 1. The few tritium data support a long-term circulation at depth (Gorgoni *et al.*, 1982; Toscani *et al.*, 2001). The waters reported in Table 1 may be distinguished into two main groups:

(1) Waters with  $P_{CO_2}$  higher than  $10^{-0.5}$  bar, high salinity ( $\Sigma\text{ions} > 80$  mEq/L), low pH (usually  $< 7$ ) and, sometimes, high sulphate and chloride contents; most waters of this groups come from Tuscany, where  $CO_2$  emissions from the ground are common (Gianelli, 1985; Minissale, 1991), and from Sardinia. These waters also exhibit some correlation between Na and Cl (Fig. 2) which indicates addition of NaCl component. The NaCl component may be referred to (i) contribution of NaCl-rich formation waters, (ii) dissolution of halite present in (a) evaporites or (b) as

residual salts in sediments (e.g., Calzetti, 1999) and to (iii) NaCl release from fluid inclusions during water-rock interaction (e.g., Michard *et al.*, 1966). The importance of the different sources varies from place to place. For instance, in Tuscany, NaCl is probably mostly leached from evaporites and, perhaps, fluid inclusions of the crystalline basement.

(2) Waters with  $P_{CO_2}$  less than  $10^{-1.5}$  bar, low salinity ( $\Sigma\text{ions} < 40$  mEq/L), variable but commonly high pH (up to 9.7), and moderate to very low sulphate and chloride concentrations; many waters of this group have extreme composition ( $na$  and  $calc > 0.85$ ) with very low calcium, magnesium, potassium, chloride and sulphur contents (e.g., Toscani *et al.*, 2001).

Field evidence indicates that NaCW are not related to a well defined lithology; they circulate in and emanate from different rock types and in areas where other types of waters may be dominant (e.g., Ca-carbonate or Ca-sulphate waters). It is noteworthy, however, that waters with the lowest salinity circulate in crystalline rocks (see Gotthard Tunnels) whereas most waters coming

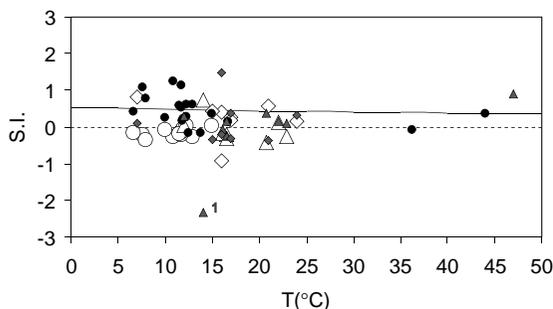


Fig. 3.  $S.I.$ <sub>chalcedony</sub> (open symbols) and  $S.I.$ <sub>calcite</sub> (filled symbols) vs. temperature ( $^{\circ}\text{C}$ ) for the waters reported in Table 1. Circle = waters from carbonate-pelitic and sandstone-pelitic rocks; triangle = waters from crystalline and volcanic rocks; diamond = high- $P_{\text{CO}_2}$  waters. The continuous line indicates the difference  $S.I.$ <sub>qtz</sub> -  $S.I.$ <sub>chalcedony</sub> vs. temperature ( $S.I.$ <sub>qtz</sub> -  $S.I.$ <sub>chalcedony</sub>  $\cong -3.13 \times 10^{-3}T(^{\circ}\text{C}) + 0.51$ ). Only sample 1 from Marmoreto, Tuscany, is strongly undersaturated in calcite.

from carbonaceous-pelitic formations are of extreme Na-carbonate composition ( $na$  and  $calc > 0.85$ ) and contain reduced sulphur.

On average, the Saturation Index for calcite ( $S.I.$ <sub>calcite</sub>) is about 0.3, but many waters deviate considerably from this value. Most NaCW coming from carbonate-sandstone-pelitic rocks are saturated to oversaturated in calcite, whereas low- $P_{\text{CO}_2}$  waters from crystalline and volcanic rocks and high- $P_{\text{CO}_2}$  waters from several lithologies may be undersaturated in this phase. The waters are in general undersaturated in quartz and saturated in chalcedony. Both  $S.I.$ <sub>calcite</sub> and  $S.I.$ <sub>chalcedony</sub> are not apparently related to the temperature (Fig. 3) of the waters suggesting that, as observed in many areas worldwide, dissolution/deposition of these phases does not need high temperature.

The hypotheses on the origin and evolution of NaCW commonly have been only considered in relation to local situations. The most common hypotheses are summarised below.

(1) The excess of dissolved inorganic carbon in respect to Ca (and Mg) is related to addition of  $\text{CO}_2$  which is generated by oxidation of organic matter during bacterially-mediated reduction of S(VI) (e.g., Cortecchi *et al.*, 1999).

(2) Significant dissolution of Na-silicate is made possible by addition of deep-seated  $\text{CO}_2$  during some stage of the water-rock interaction. This interpretation is suggested, for instance, for some thermal waters in Tuscany, Italy (Bencini *et al.*, 1977), in Mt. Amiata geothermal field (Duchi *et al.*, 1987), at Bagno di Romagna (Emilia-Romagna Region, Italy; Cortecchi *et al.*, 1999), and for some  $\text{CO}_2$ -rich waters of Sardinia ( $P_{\text{CO}_2}$  up to about 1 bar; Caboi *et al.*, 1993).

(3) The Na enrichment is due to interactions of water with alkali-rich volcanic rocks (e.g., Duchi *et al.*, 1987, for the Mt. Amiata volcanic area, and Duchi *et al.*, 1991, for the volcanic area of southern Latium, Central Italy) or, in general, with magmatic and metamorphic rocks (e.g., Michard *et al.*, 1996; Grasby *et al.*, 2000; Pastorelli *et al.*, 2001).

(4) NaCW are generated by prograde dissolution of silicate minerals—including albite—under conditions of saturation with respect to other silicate phases. Recently, this process has been proposed to explain the origin of sulphide-bearing NaCW occurring in the Bisagno valley, north of Genoa, Italy (Marini *et al.*, 2000b) and of some strongly reduced waters in the Northern Apennines (Toscani *et al.*, 2001).

(5) The sodic character is due to ionic exchange involving Na-rich clay which releases Na and acquires Ca (and Mg) (e.g., London and Berkshire basins, UK: Elliot *et al.*, 1999; northern Apennines and Po plain, Italy: Gorgoni *et al.*, 1982; Venturelli *et al.*, 2000).

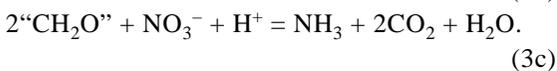
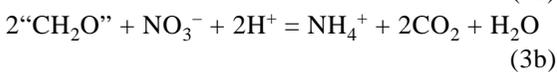
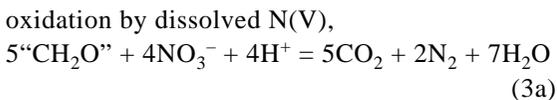
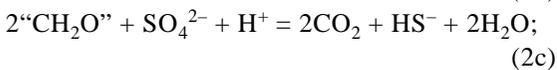
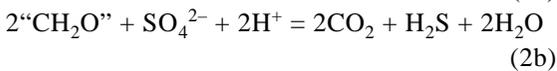
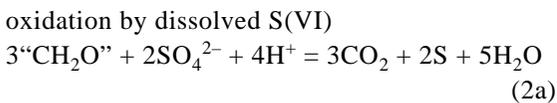
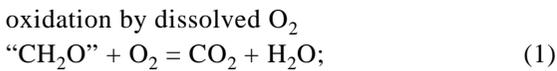
Any of the processes listed above may contribute to the production of NaCW in the different areas; frequently, however, they are not sufficiently constrained. Thus, in the following pages we consider different hypotheses and put constraints on their reliability taking into account speciation in solution and water-rock interaction processes compatible with the geological situations. More specifically, we will try to answer the following questions. (i) Can Na-carbonate waters be produced by interaction with carbonate-rich rocks? (ii) Which is the role of the silicate phases? (iii) Which is the role of carbon dioxide?

## DISCUSSION

### Carbon dioxide

An increase in the carbon dioxide partial pressure during water-rock interaction influence the process of mineral dissolution. Carbon dioxide may be generated by several processes. For instance, in central Italy emission of large amounts of CO<sub>2</sub> from soil, fractures and springs may be due to mantle degassing (Minissale, 1991), to thermal breakdown of carbonate at depth—as a consequence of a high geothermal gradient (Gianelli, 1985) generated by intrusions of magmatic bodies at depth—or to both processes (Marini and Chiodini, 1994).

Carbon dioxide may also be produced by oxidation of organic compounds generated from organic matter entrapped into the sediments at the time of their deposition. The compound CH<sub>2</sub>O is used as simplified representation of organic matter. Neglecting the speciation (aqueous, gas, solid) of the different substances, the following reactions may be written:



If oxygen fugacity and the activity of the dissolved species are appropriate, oxidation of organic matter may be thermodynamically sponta-

neous and, if reducing bacteria are present, sulphur reduction and CO<sub>2</sub> production may be fast.

In the underground waters, which have acquired oxygen from the atmosphere and which are then subtracted to any interaction with an oxygen-bearing gas phase, the content of dissolved O<sub>2</sub> cannot exceed about 0.3 mmole/L (actually [O<sub>2</sub>] ≅ 1.5 × 10<sup>-3</sup> P<sub>O<sub>2</sub></sub>, at 0°C and 1 bar total pressure, and in the atmosphere P<sub>O<sub>2</sub></sub> ≅ 0.2); thus, assuming that in reaction (1) all oxygen is consumed for carbon oxidation, the increase in dissolved C(IV) will be no more than about 0.3 mmole/L. On the contrary, CO<sub>2</sub> generation *via* reactions (2) and (3) may vary largely depending on the concentration of S(VI) and N(V) as well as, of course, on the amount of organic matter present. Actually, whereas the content of oxidised nitrogen is usually low to moderate (<<1 mmole/L), sulphur may reach high values in some sulphate-bearing waters (cf., Toscani *et al.*, 2001). In the case sulphate is the oxidant, high CO<sub>2</sub> production would be coupled with high S(-II) generation (reactions (2b) and (2c)). The role of these processes for the origin of NaCW will be discussed later.

### Dissolution of albite, analcime, nepheline

Albite (or albitic plagioclase) is very common in the pelitic portions of the sedimentary rocks involved in water-rock interaction. Analcime and nepheline may occur in some volcanic rocks (e.g., in the potassic rocks of the Roman Province, Italy; see Table 1); analcime is typically an alteration product of leucite (e.g., Cundari and Graziani, 1964), nepheline is a primary phase. These minerals may constitute main Na sources in the waters, whereas the carbon source may be carbon dioxide of variable origin as discussed before, and carbonate minerals. Simulation of the interaction between albite, analcime, nepheline, ±calcite and pure water is summarized in Table 2(A). At log P<sub>CO<sub>2</sub></sub> = 0, the maximum obtained value of Na (S.I.<sub>Na-mineral</sub> = 0), is about 4.3, 1.6 and 0.6 mequivalent/kg water (mEq/kgW) for nepheline, analcime and albite dissolution respectively. It is noteworthy that, at least for albite and nepheline, these values, are *hypothetical* upper limits of Na

Table 2. Composition of water (mEq/kg water) interacting with albite, analcime, nepheline and calcite at defined saturation index (S.I.), at different  $P_{\text{CO}_2}$  and  $T = 25^\circ\text{C}$

(A)							
$\log P_{\text{CO}_2}$	-3.5	-1.5	0	$\log P_{\text{CO}_2}$	-3.5	-1.5	0
<i>S.I.albite</i> = 0				<i>S.I.albite</i> = 0, <i>S.I.calcite</i> = 0.3			
Na	0.14	0.20	0.55	Ca	1.3	6.5	24.5
Alk	0.54	0.81	2.20	Na	0.14	0.17	0.18
pH	6.8	5.9	5.0	Alk	1.82	7.03	25.2
<i>S.I.analcime</i> = 0				<i>S.I.analcime</i> = 0, <i>S.I.calcite</i> = 0.3			
Na	0.49	0.63	1.60	Ca	1.3	7.0	24
Alk	1.95	2.51	6.39	Na	0.49	0.51	0.72
pH	7.0	6.2	5.4	Alk	3.29	8.50	26.8
<i>S.I.nepheline</i> = 0				<i>S.I.nepheline</i> = 0, <i>S.I.calcite</i> = 0.3			
Na	1.60	1.89	4.32	Ca	1.35	7.0	22
Alk	6.39	7.56	13.3	Na	1.62	1.68	2.62
pH	7.2	6.4	5.7	Alk	7.82	13.2	32.72
				pH	8.4	7.1	6.1

(B)							
$\log P_{\text{CO}_2}$	-3.5	-1.5	0	$\log P_{\text{CO}_2}$	-3.5	-1.5	0
<i>S.I.albite</i> , <i>S.I.Ca-montmorillonite</i> and <i>S.I.chalcedony</i> = 0, <i>S.I.calcite</i> = 0.3				<i>S.I.albite</i> and <i>S.I.Ca-montmorillonite</i> = 0, <i>S.I.calcite</i> = 0.3			
Ca	0.050	0.098	0.30	Ca	0.44	3.0	15.4
Na	13	120	715	Na	2.1	6.6	16.2
Si	0.37	0.28	0.23	Si	2.9	9.4	23.0
Alk	13	120	716	Alk	2.5	9.7	31.6
pH	9.3	8.2	7.4	pH	8.6	7.2	6.2
<i>S.I.albite</i> , <i>S.I.kaolinite</i> and <i>S.I.chalcedony</i> = 0, <i>S.I.calcite</i> = 0.3				<i>S.I.albite</i> and <i>S.I.kaolinite</i> = 0, <i>S.I.calcite</i> = 0.3			
Ca	0.032	0.044	0.10	Ca	0.48	3.6	17.5
Na	38	408	2495	Na	1.9	5.3	11.8
Si	0.46	0.28	0.16	Si	3.7	10.6	23.6
Alk	38	408	2495	Alk	2.4	8.9	29.4
pH	9.6	8.4	7.9	pH	8.6	7.2	6.2
<i>S.I.albite</i> , <i>S.I.illite</i> and <i>S.I.chalcedony</i> = 0, <i>S.I.calcite</i> = 0.3				<i>S.I.albite</i> and <i>S.I.illite</i> = 0, <i>S.I.calcite</i> = 0.3			
Ca	0.13	6.4	24	Ca	1.3	6.4	24
Na	0.22	0.24	0.49	Na	0.14	0.14	0.18
Si	0.29	0.28	0.28	Si	0.41	0.41	0.54
Alk	2.2	7.4	26.1	Alk	1.8	7.0	25.2
pH	8.4	7.1	6.1	pH	8.4	7.1	6.1

The values  $S.I. = 0.3$  for calcite and  $S.I. = 0$  for chalcedony agree with the average values for the investigated waters. Illite =  $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}(OH)_{10}$  and Ca-montmorillonite =  $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ .

(A) Note that, on the basis of mineral stoichiometry, we have: for albite dissolution  $Na = Al = 1/3Si$ , for analcime  $Na = Al = 1/2Si$ , for nepheline  $Na = Al = Si$ .

concentration; in fact, at temperature lower than about 100°C the silicate dissolution is a slow process which could lead to mineral saturation only after long time (see, for instance, Chou and Wollast, 1984; Chou *et al.*, 1989). In spite of it, comparison between the computed and the actual NaCW data leads to the following remarks: (i) also assuming, as a boundary condition, that only the Na that is in excess to Cl derives from silicates, the actual difference [Na]-[Cl] in some NaCW is higher than [Na] obtained by our simulation; (ii) moreover, the computed Si and Al (not reported in Table 2) are too high in comparison with the concentrations observed in the investigated low-temperature waters with pH comparable to those obtained by simulation. These results exclude the possibility that *only* dissolution of silicate phases and addition of carbon dioxide to the aquatic systems is responsible for the high Na content in many of the investigated waters.

In the sediments, other sodic minerals could occur, e.g., as Na-bearing smectites; however, the Na contribution due to their dissolution would be generally low ( $\text{Na} < 0.1 \text{ mEq/kgW}$ ) also under condition of water saturation in these phases and at a high pressure of  $\text{CO}_2$ .

#### *Albite, analcime, nepheline dissolution under conditions of stability of other phases*

As discussed above, dissolution of albite, analcime and nepheline at those conditions cannot *alone* explain the high Na content of most waters. On the other hand, under conditions of saturation in other minerals, such as kaolinite, smectite and silica phases, water with high Na and alkalinity may be produced since dissolution of albite is enhanced by Si and Al removal. It is noteworthy that crystallization of these phases is facilitated if they are already present in some amounts in the rocks interacting with the waters.

From Table 1 it is evident that phyllosilicates (mostly smectite, illite, kaolinite and mixed layers), silica phases and calcite are widespread, often abundant or dominant, in the rocks interacting with the investigated waters. Thus, as an example, the results of a simulation of water rock-

interaction involving albite, calcite, chalcedony, Ca-montmorillonite, illite, kaolinite, and water at variable  $P_{\text{CO}_2}$  is reported in Table 2(B). The main results are the following: (i) a silica phase or illite saturation (and thus precipitation) is necessary to maintain low silica in solution; (ii) under conditions of albite, chalcedony,  $\pm$ Ca-montmorillonite,  $\pm$ kaolinite saturation and slight calcite oversaturation ( $S.I._{\text{calcite}} = 0.3$ , average values for the investigated waters), the Na contents, alkalinity and the Na/Ca ratio reach high values also at moderate  $P_{\text{CO}_2}$ . The dissolving Na-silicate involved in the examples of Table 2(B) is only albite, but similar results may be obtained considering analcime and nepheline.

#### *Prograde water-rock interaction and the origin of NaCW*

The data of Table 1 are plotted in Fig. 4 together with trends obtained by simulations of water-rock interaction. On average, the waters have  $S.I._{\text{calcite}} \approx 0.3$  and  $S.I._{\text{chalcedony}} \approx 0$ ; thus in all the simulations these values of saturation index have been assumed. The trends of the elements in solution have been obtained at 5 and 25°C at defined  $P_{\text{CO}_2}$  ( $10^{-2}$ ,  $10^{-1}$  and 1 bar) and assuming that (i) calcite, Ca-montmorillonite and chalcedony quickly react generating Ca-carbonate water ( $S.I._{\text{calcite}} = 0.3$ ,  $S.I._{\text{Ca-montmorillonite}} = S.I._{\text{chalcedony}} = 0$ ), (ii) saturation in these phases and oversaturation in calcite are maintained during interaction with albite up to variable  $S.I._{\text{albite}}$  values (from  $-4.5$  to saturation). Also simulation with kaolinite in place of Ca-montmorillonite has been performed; however, since the obtained results were very similar, only the trends calculated on the basis of Ca-montmorillonite are reported in Fig. 4.

From Figs. 4A and B, we draw the following conclusions. Among the waters which surely interact with calcite-bearing rocks, the low- $P_{\text{CO}_2}$  group could be generated starting from Ca-carbonate waters characterised by  $P_{\text{CO}_2}$  of about  $10^{-2}$ – $10^{-1}$  bar, whereas for the most saline waters the initial  $P_{\text{CO}_2}$  would be equal or higher than 1 bar. The simulation described above imposes the lim-

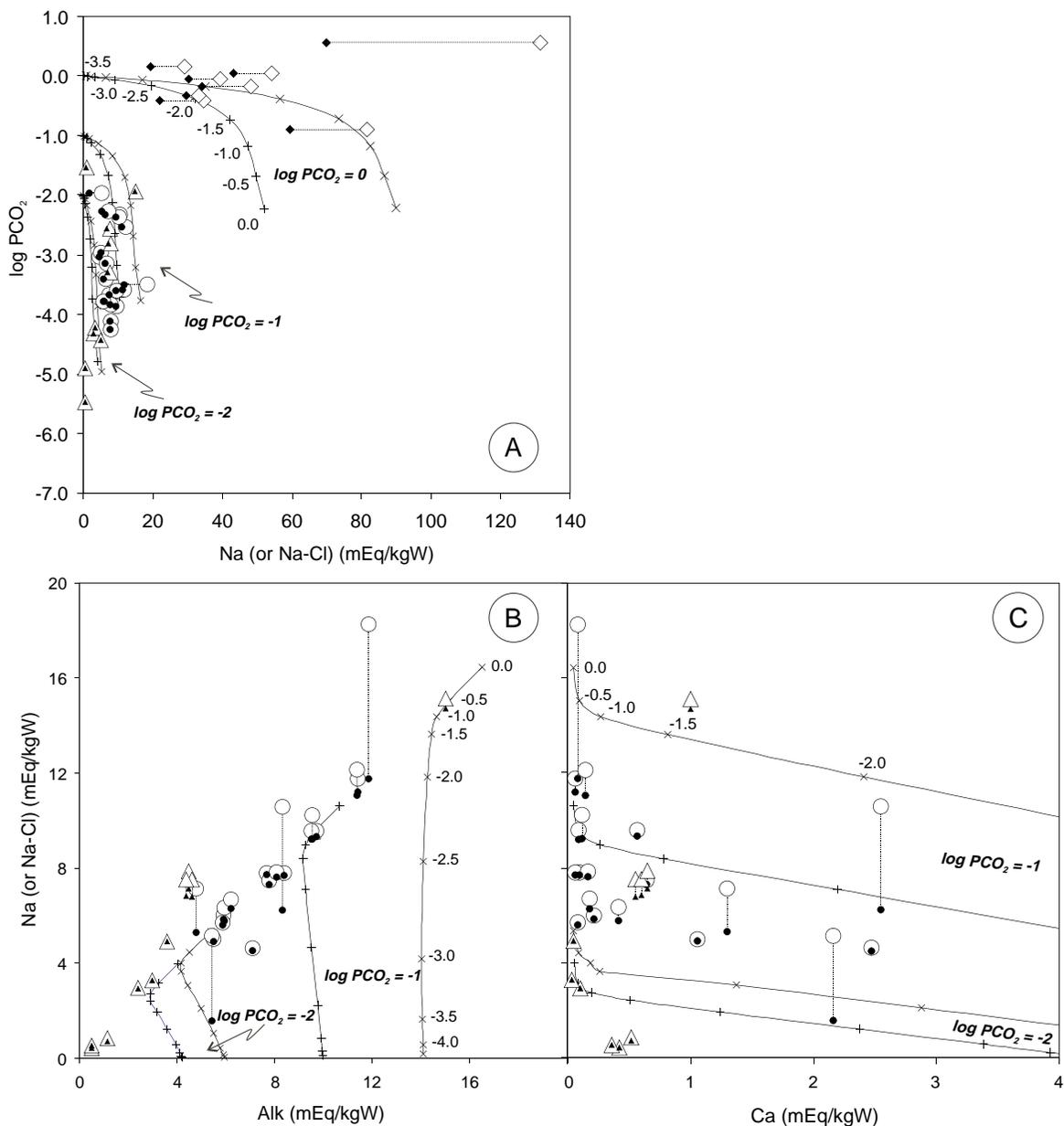


Fig. 4.  $\log P_{CO_2}$  vs. [Na], [Na] vs. [Alk] alkalinity and [Na] vs. [Ca] diagrams for the investigated waters. Shape of symbols as in Fig. 1. Open circle = actual [Na] data; filled symbols = [Na]-[Cl] for the same waters; dotted line = line connecting [Na] and [Na]-[Cl] data for the same sample. The continuous lines indicate the evolution of water interacting with calcite, Ca-montmorillonite, chalcedony and albite at different  $P_{CO_2}$  ( $\log P_{CO_2}$  0, -1, -2) and temperature (5°C, ×; 25°C, +). The trends start from waters oversaturated in calcite ( $S.I._{calcite} = 0.3$ ) and saturated in Ca-montmorillonite and chalcedony and indicate the evolution of waters maintaining oversaturation in calcite ( $S.I._{calcite} = 0.3$ ), saturation in Ca-montmorillonite and chalcedony ( $S.I._{chalcedony} = 0$ ) and interacting with albite ( $S.I._{albite}$  ranging from -4.5 to 0). Numbers close to the lines indicate the value assumed by  $S.I._{albite}$ ; numbers in bold italics refer to the initial  $\log P_{CO_2}$ . As a first approximation,  $mEq/L \equiv mEq/kg$  water is assumed.

iting condition  $[\text{Na}]/\text{alkalinity ratio} \rightarrow 1$  for  $[\text{Ca}] \rightarrow 0$ . Some waters, however, have  $[\text{Na}]/\text{alkalinity}$  ratio significantly higher than unity and  $([\text{Na}]-[\text{Cl}])/\text{alkalinity}$  less than or around 1. This is reasonably due to the contribution of halite occurring in evaporites and as residual salt in sediments (Calzetti, 1999), or to mixing with NaCl-rich formation waters. In the diagrams, the difference  $[\text{Na}]-[\text{Cl}]$  represents an approximate lower limit for the Na derived from silicate dissolution.

*NaCW from carbonate-pelitic and sandstone-pelitic rocks* Most NaCW from carbonate-pelitic and sandstone-pelitic rocks are of extreme composition (*na* and *calc* both  $> 0.85$ ) with very low concentration of components other than Na and alkalinity. Because of the very simple water chemistry, the Na and Ca contents, the alkalinity and the  $P_{\text{CO}_2}$  of the investigated waters may be easily compared with the those obtained by the simulated water-rock interaction.

The simulation indicates that, to obtain the actual Na content found in NaCW from carbonate-pelitic and sandstone-pelitic rocks, the potential Ca-carbonate parent waters of NaCW would have a  $P_{\text{CO}_2}$  in the approximate range  $10^{-2}$ – $10^{-1}$  bar (Fig. 4A). These values, however, are too high if compared with those of the most common Ca-carbonate waters in the studied areas ( $P_{\text{CO}_2}$  in the range  $10^{-3.2}$ – $10^{-1.8}$  bar; see for instance Venturelli *et al.*, 2000, and Marini *et al.*, 2000b). Assuming that the discrepancy is not mostly due to unreliable thermodynamic data, we conclude that NaCW have a Na content higher than expected if they are generated from Ca-carbonate waters with initial  $P_{\text{CO}_2} \approx 10^{-3.2}$ – $10^{-1.8}$  bar and without any further addition of  $\text{CO}_2$ . Theoretically, the Na excess could be produced by dissolution of silicates with Na/Si ratio higher than that in albite, e.g., analcime and nepheline; these phases, however, are not apparently present in the carbonate-sandstone-pelitic rocks interacting with the waters of Table 1 and thus their contribution may be excluded. Actually, addition to the aquifer of  $\text{CO}_2$  coming from the rocks interacting with the waters or from other sources is the most simple explanation of the suspected Na excess.

As discussed above, oxidation of organic matter—which is present in variable amounts in the sediments—may be the source of the added  $\text{CO}_2$ . The effect of a  $P_{\text{CO}_2}$  increase is modelled in Fig. 5, which reports the result of progressive water-rock interaction at  $5^\circ\text{C}$  after organic matter oxidation by dissolved oxygen and sulphate at a water-mineral interaction stage characterised by  $S.I._{\text{albite}} = -3.5$ . Details about the conditions of the simulation are reported in the captions of Fig. 5. At the beginning of the oxidation process, the assumed dissolved  $\text{O}_2$  and S(VI) are  $\approx 0.3$  and  $\approx 0.9$  mmole/L, respectively, the last value being an approximate upper limit for total sulphur in the investigated NaCW from carbonate-sandstone-pelitic rocks.

Oxidation of organic matter at expense of sulphate in presence of sulphate-reducing bacteria (cf., Toscani *et al.*, 2001) may also produce elemental or strongly reduced sulphur (mostly as  $\text{H}_2\text{S}$  and  $\text{HS}^-$ ). In this case, the actual low, S(-II) in the investigated waters (see foot note of Table 1) may be due to prevalent  $\text{S}^0$  production or to S(-II) oxidation during the rise of the water toward the surface.

Although oxidation of organic matter by oxygen and sulphate may produce  $\text{CO}_2$  and  $\text{H}_2\text{S}$  components, the  $P_{\text{CO}_2}$  increase obtained according to the simulation is not sufficient to shift the  $[\text{Na}]-\log P_{\text{CO}_2}$  trend up to the most sodic waters (see Fig. 5). Thus, the wide distribution of the waters in the diagram of Fig. 5 needs additional  $\text{CO}_2$  sources. As an example, we now consider only the NaCW from the northern Apennine chain.

As discussed in the literature, the Tuscany and Emilia-Romagna regions are characterised by the occurrence of dry emission of  $\text{CO}_2$  and  $\text{CH}_4$ , thermal springs very rich in  $\text{CO}_2$ , thermal springs rich in  $\text{N}_2$ , and mud volcanoes with emission of dominant  $\text{CH}_4$  (Bencini *et al.*, 1977; Bencini and Duchi, 1981; Mattavelli *et al.*, 1983; Mattavelli and Novelli, 1987; Minissale and Duchi 1988; Duchi and Minissale, 1995; Minissale *et al.*, 1997; Minissale *et al.*, 2000). South of the Arno river, the dominant gas is  $\text{CO}_2$  (usually more than about 91.5 mole %); north of the Arno river,  $\text{CO}_2$  emis-

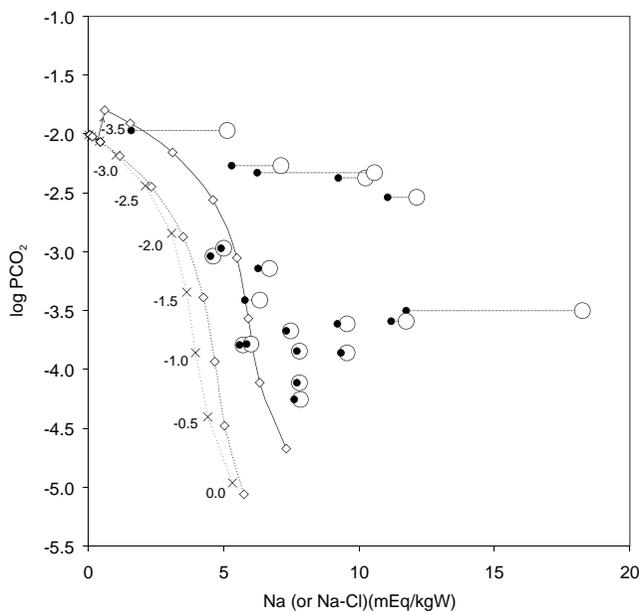


Fig. 5.  $\log P_{\text{CO}_2}$  vs.  $[\text{Na}]$  trends for water interacting with calcite, Ca-montmorillonite, chalcidony, and albite at  $5^\circ\text{C}$  (numbers close to the lines indicate  $S.I._{\text{albite}}$ ). Open circle, actual  $[\text{Na}]$  data for waters from carbonate-pelitic and sandstone-pelitic rocks; filled circle,  $[\text{Na}]-[\text{Cl}]$  data for the same waters. As a first approximation,  $\text{mEq/L} \equiv \text{mEq/kg}$  water is assumed. (i) Dotted line with  $\times$ . Water with  $\text{pH} \cong 7.43$ , alkalinity  $\cong 5.96$   $\text{mEq/kgW}$ , and  $[\text{Ca}] \cong 2.98$   $\text{mmole/KgW}$  ( $S.I._{\text{calcite}} = 0.3$  and  $\log P_{\text{CO}_2} = -2$ ) interacts with calcite, Ca-montmorillonite, chalcidony and albite under conditions of  $S.I._{\text{calcite}} = 0.3$ ,  $S.I._{\text{Ca-montmorillonite}} = S.I._{\text{chalcidony}} = 0$  and  $S.I._{\text{albite}}$  ranging from  $-4.5$  to  $0$ . (ii) Dotted line with  $\diamond$ . Water with  $\text{pH} \cong 7.40$ ; alkalinity  $\cong 5.63$   $\text{mEq/kgW}$ ,  $\text{Ca} \cong 3.73$  and  $S(\text{VI}) \cong 0.9$   $\text{mmole/kgW}$  ( $S.I._{\text{calcite}} = 0.3$  and  $\log P_{\text{CO}_2} = -2$ ,  $S.I._{\text{gypsum}} = -1.35$ ) interacts as at point (i). Continuous line with  $\diamond$ . Water of the point (ii) interacts as at point (i) up to  $S.I._{\text{albite}} = -3.5$ . At  $S.I._{\text{albite}} = -3.5$ , organic matter is oxidised by dissolved oxygen ( $\cong 0.3$   $\text{mmole/kgW}$ ) and sulphate ( $\cong 0.9$   $\text{mmole/kgW}$ );  $P_{\text{CO}_2}$  increases up to  $10^{-1.8}$  bar (see arrow along the continuous line), and  $P_{\text{H}_2\text{S}}$  becomes  $\cong 10^{-2.64}$  bar. During this process;  $\cong 2.1$   $\text{mmole/kgW}$  of  $\text{C}(\text{IV})$  are added to the water and  $\cong 0.9$   $\text{mmole/kgW}$  of  $\text{S}(\text{VI})$  are reduced to  $\text{S}(\text{II})$ . For simplicity of the diagram, the two redox processes are considered to occur instantaneously.

sion are scarce or lacking.

Along the northern Apennine chain and north of the Apennine watershed the dominant gas is  $\text{CH}_4$ , whereas is low to very low, in the approximate range  $10^{-1.6}$ – $10^{-2.9}$  bar for 1 bar total gas pressure. Although the concentration of  $\text{CO}_2$  in the gas mixture is low, interaction of diffused emission with ground waters could be sufficient to increase the silicate dissolution. This is modelled in Fig. 6, which shows in detail how high the concentration of Na become if the water is open to appropriate  $\text{CO}_2$  input also under moderate  $\text{CO}_2$  partial pressure. For the trends shown in Fig. 6, the  $\text{CO}_2$  input is very high also in the case  $P_{\text{CO}_2}$  is

maintained at low values: in detail, for the trends of Figs. 6A and 6B, at  $S.I._{\text{albite}} = 0$ , the carbon added by  $\text{CO}_2$  dissolution is about 75% and 90% of total dissolved C, respectively. Taking into account the great amount of carbon which would need to be added from the external environment, investigation on carbon isotopes of the dissolved carbonic species and gaseous emissions could be useful to support or invalidate the hypothesis of an open system for carbon.

The simulations discussed above are approximate and, at best, may give semiquantitative indications. A more sophisticated kinetic approach is not possible in our case since kinetic param-

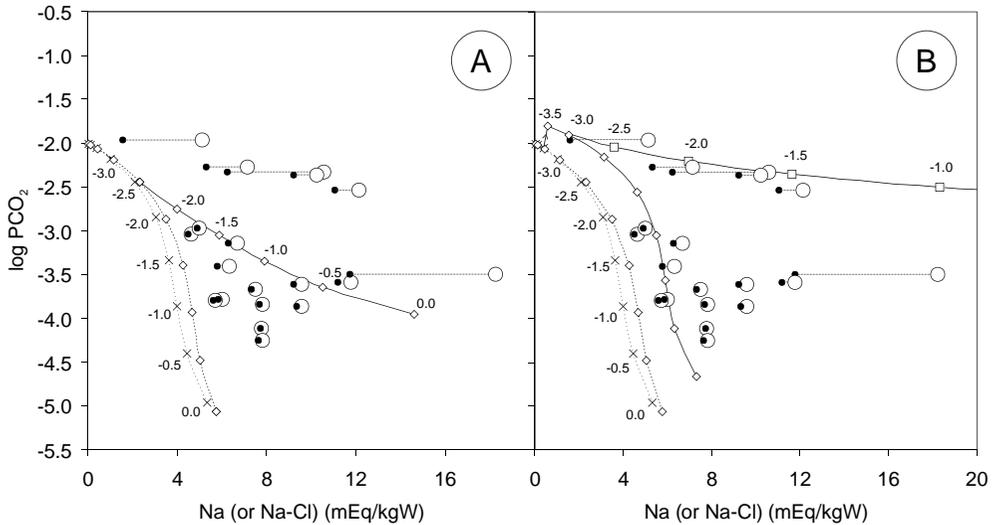


Fig. 6.  $\log P_{\text{CO}_2}$  vs.  $[\text{Na}]$  trends for water interacting with calcite, Ca-montmorillonite, chalcidony, and albite at 5°C (numbers close to the lines indicate  $S.I._{\text{albite}}$ ). Shape of symbols as in Fig. 1. Open circle, actual  $[\text{Na}]$  data for waters from carbonate-pelitic and sandstone-pelitic rocks; filled circle,  $[\text{Na}]-[\text{Cl}]$  data for the same waters. As a first approximation,  $\text{mEq/L} \equiv \text{mEq/kg}$  water is assumed. (A) Dotted lines as in Fig. 5, points (i) and (ii). Continuous line with  $\diamond$  indicates the water evolution down to  $P_{\text{CO}_2} = 10^{-3.95}$  bar starting from the dotted line with diamond at  $S.I._{\text{albite}} \cong -2.5$  and progressive addition of  $\text{CO}_2$  (range of  $P_{\text{CO}_2} : 10^{-2.45} - 10^{-3.95}$  bar). (B) Dotted lines as in Fig. 5, points (i) and (ii); continuous line with  $\diamond$  as in Fig. 5. Continuous line with square indicates the water evolution down to  $P_{\text{CO}_2} = 10^{-2.8}$  starting from the continuous line with diamond at  $S.I._{\text{albite}} \cong -3$  and progressive addition of  $\text{CO}_2$  (range of  $P_{\text{CO}_2} : 10^{-1.9} - 10^{-2.8}$  bar).

eters, such as the mineral surface area, are not available for the involved rocks.

*NaCW from crystalline and volcanic rocks in absence of calcite* As far as the waters from the crystalline and volcanic rocks are concerned, an origin from a Ca-carbonate parent could not be the rule; this in spite of the common saturation or oversaturation in calcite. Actually, also in absence of calcite in the mineral assemblage, saturation in calcite and high pH may be easily reached during dissolution of Ca-plagioclase in water with dissolved  $\text{CO}_2$  coming from atmosphere and soil, and under condition, for instance, of kaolinite saturation. For instance, considering the initial  $P_{\text{CO}_2} = 10^{-3}$  bar, for  $S.I._{\text{anorthite}} = -7$  and  $S.I._{\text{kaolinite}} = -6$ , the resulting value of  $S.I._{\text{calcite}}$  is about 0.4.

#### Na-Ca cation exchange

The role of cationic exchange in the genesis of Na-carbonate waters has been suggested by

several authors (see above). In particular, for waters from the Northern Apennines, cation exchange with release of Na and uptake of Ca by phyllosilicates, according to the general reaction



where R indicate the clay exchanger, has been suggested by Venturelli *et al.* (2000) and criticised by Toscani *et al.* (2001).

Under moderately dry conditions (relative humidity less than about 50%), Na,K-montmorillonites are characterised by  $d_{001}$  around 12 Å, whereas Ca,Mg-montmorillonites have a d-spacing of 14–15 Å (e.g., Alietti and Brigatti, 1979). Although no systematic research on montmorillonites of the Northern Apennine formations has been carried out, it is noteworthy that no 12 Å-montmorillonites have been found so far. Accordingly, recent cationic exchange experi-

ments performed on Apennine clay sediments suggest a calcic character for smectites (Calzetti, 1999).

### CONCLUDING REMARKS

(1) The waters considered in this paper are representative of different types of NaCW. In different areas, NaCW coexist with the most common Ca-carbonate waters generated by fast interaction with calcite-bearing sediments.

(2) NaCW have widely variable composition as evidenced by their Na, Cl, and  $\text{SO}_4$  contents, their alkalinities, Na/Ca ratio and  $P_{\text{CO}_2}$ . NaCW from Tuscany and Sardinia (Italy) may have high  $P_{\text{CO}_2}$  and salinity.

(3) NaCW represent the product of interaction between recent or old waters and different rock-types containing Na-silicates. Simple dissolution of Na-silicates also under high  $P_{\text{CO}_2}$  is not sufficient to produce the high Na contents and high alkalinity which characterise many waters. Dissolution must occur under saturation/oversaturation of clay-minerals, silica phases and calcite; actually, these phases are usually present in the interacting rocks.

(4) At least NaCW generated by interaction with calcite-bearing rocks have Ca-carbonate parents, which, by interaction with albite, clay, and silica phases, acquire Na and lose Ca (mostly calcite deposition). The Na vs. alkalinity and Na vs. Ca evolution is significantly dependent on the initial water conditions (see Fig. 4).

(5) Assuming that the simulation trends have quantitative significance, the  $P_{\text{CO}_2}$  of the Ca-carbonate parent is usually too low to obtain high Na values. Further addition of  $\text{CO}_2$  during the water-rock interaction is necessary. For instance, additional  $\text{CO}_2$  may be produced by oxidation of organic matter present in the sediments and/or by mantle and crust degassing.

(6) As far as the waters from northern Apennines are concerned, at present, cationic exchange involving a Na-exchanger, such as smectite, is not supported by mineralogical evidence.

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