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FLUORINE GEOCHEMICAL ASSOCIATIONS AND RELATED ENVIRONMENTAL IMPLICATIONS IN THERMAL SPRINGS OF BORMIO (ITALY)

Riassunto. — Il seguente lavoro segnala la presenza del fluoro nelle sorgenti minerali calde e fredde di Bormio. Il fluoro appare associato agli alogeni Cl, Br, ai solfati, alle terre alcaline Ca, (Mg), Ba, Ra. U, Th, Rn, già studiati precedentemente, sono presenti insieme ad altri metalli. La concentrazione media del fluoro supera quella limite raccomandata per acque potabili. Alcune correlazioni binarie suggeriscono due distinte associazioni geochimiche nelle sorgenti: 1) F + alogeni + SO_4 principalmente nelle sorgenti più calde; 2) U, Th, Ra, Rn nella più fredda. La prima associazione deriva probabilmente da rocce triassiche, la seconda da conglomerati permo-carboniferi (Verrucano).

Abstract. — The presence of fluorine in the hot and cold mineral springs of Bormio is described. Fluorine appears to be associated with the common halogens Cl, Br, with SO_4, alkaline earths Ca, (Mg), Ba, Ra. U, Th, Rn, previously investigated, are also present with other heavy metals. Fluorine mean concentration exceeds the recommended control limits of drinking water quality standards. Some binary correlations suggest two distinct geochemical associations in the mineral supply of the springs: 1) F + halogens + SO_4 mostly in the hotter springs; 2) U, Th, Ra, Rn mostly in the coldest one. The former supply probably comes from Triassic rocks whereas the latter is from Permo-Carboniferous conglomerates (Verrucano).

Introduction

The hot and cold mineral springs of Bormio come to the surface near to the Zebrù fault, the boundary line between the crystalline basement and the Mesozoic carbonate rocks. Between the above formations lies the chalks formation (Berbenni & Pozzi, 1966).

De Capitani et al. (1974) pointed out the presence of Ra in geochemical association with U, Th, Rn and others in the coldest spring, in its supergene and bio-system.

The present paper describes the presence of fluorine in the same mineral springs and investigates its geochemical associations and seasonal variations in order to determine the source of the mineral « supply ».

Such waters are widely employed for drinking, hydropinic and therapeutical uses.

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Field measurements and sampling

In four months of the years 1974-75, which had marked differences in the levels of precipitation, the spring of Bormio were analysed either in the field or in the laboratory: the sampling months were March, June, August and September.

Temperature, pH, F, Cl, SO_4 and Br were determined in the field. Samples of vegetation were taken in the same occasions.

Analytical methods

Fluorides were determined by Orion Fluorine sensing electrode and checked by colorimetric method with SPADNS reagent.

Chlorine, Br, Ca, Ba, SO_4 and pH were determined by titration and colorimetric procedures, contained in « Standard Methods », published by the American Public Health Association and the American Water Works Association, by means of a field spectrophotometer; Na and K were determined by flame photometry.

The vegetable matter was analyzed in ash form.

Results

Table 1 gives the physicochemical data and the mean chemical values.

TABLE 1

Mean values in ppm of chemical components between March, June, August and September samplings in the Bormio springs

Thermal Springs	T°C	pH	Na	K	Ca	Ba	SO_4	Cl	F	Br
San Martino	33	8.5	18.23	2.68	171.4	3.25	533	10.65	2.07	≈0.03
Pliniana	38	7.7	25.37	3.63	257.8	3.9	753	14.20	2.82	<0.03
Cassiodora	40.5	7.8	30.60	7.28	219.4	2.9	725	12.78	2.40	≈0.03
Fondovalle	40.4	7.6	22.06	3.13	221.0	4.9	655	17.75	2.60	0.07
Stat. Stelvio	17.6	8.2	7.15	1.50	94.5	4.4	220	7.10	1.03	≈0.03
Cinglaccia	39	7.6	21.44	3.06	223.4	3.3	690	14.20	2.55	≈0.03
Arciduchessa	39.2	7.9	20.70	3.03	213.8	3.9	673	14.20	2.46	0.07
San Carlo	19.1	7.7	20.47	3.13	210.6	2.9	640	12.07	2.43	0.07

The mean concentration value of fluorine in these waters (F = 2.3 ppm) appears to exceed the control limits of 1.2-1.3 ppm of fluoride in drinking water, recommended by the Regione Lombardia for the annual average maximum daily temperature, which is 17° C in the Bormio district.

TABLE 2

Seasonal ranges of chemical and physicochemical values in the Bormio springs (ppm)

Thermal Springs	Ca	Na	K	F	SO_4	pH	T°C
San Martino	171.37	22.26/15.73	3.07/2.45	2.15/2.02	630/450	8.7/8.3	36/31
Pliniana	259.46/256.26	25.74/25	3.71/3.55	2.9/2.75	790/710	7.9/7.5	38.5/38
Cassiodora					760/690	8/7.7	41/40
Fondovalle	221.82/220.22	24.11/20.77	3.32/2.97	2.6	690/620	7.7/7.5	41.8/39.5
St. Stelvio	94.5	7.27/7.03	1.54/1.47	1.05/1	250/170	8.3/8.15	19/16.5
Cinglaccia	224.22/222.62	21.74/21.14	3.13/2.99	2.65/2.5	760/640	7.7/7.5	40/38
Arciduchessa	219.42/208.21	21.37/20.03	3.03	2.6/2.38	740/540	8/7.85	41/37
San Carlo	213.01/208.21	20.55/20.40	3.28/2.99	2.55/2.35	690/610	7.7/7.6	20/18.5

The Br mean concentrations prove to be very close to the detection threshold of the colorimetric method. Nevertheless all the values fall close to the average of 0.01 ppm given for river waters (CORRENS, 1956) and appear to be very similar to those of domestic water supplies.

Moreover the seasonal analyses show, relatively, no appreciable chemical variations for many of the components during periods of thaw or heavy rain; table 2 gives the observed seasonal ranges for several metals, anions, pH and temperature.

TABLE 3

Fluorine contents of land and marine organisms in ppm

Marine organisms		
	Lingula anantina	15,200
	Obolus	27,800-33,100
	Ostrea edulis	30-120
	Mytilus edulis	30-120
Land organisms		
	Limnea, Planorbis and Helix	30
	• Sphagnum	280

Bromine contents of biosphere and petroleum in ppm

Marine organisms		
	Laminaria digitata	1,200
	Sponges	0-26,000
	Gorgonidae (coral)	2,300-2,610
	Vermes	20-3,190
Land organisms		
	Raphanus sativus	8
	Boletus scraber	36
	Curcuma citrullus	262
	• Sphagnum	5
Petroleum		
	Crude petroleum	1.6
	Asphalt	3.42
	Oil distilled	1.98

On the contrary, the SO_4 anion content seems to be effected by a certain seasonal dilution; DE CAPITANI et al. (1974) observed that the seasonal fluctuation in Rn activity is relatively higher than that of the major components discussed here. Besides we have to recall that the coldest spring is the richest one in U, Th,

Ra (De Capitani et al., 1974); thereby all together U, Th, Ra, parents of Rn, must be probably more variable in different seasons, if compared with the low fluctuation of the main components. So, in the mineral springs of Bormio, both the above statements suggest a more superficial geologic horizon of mineral supply of U, Th, Ra than F and others.

In the moss (gen. Sphagnum), growing close to the coldest spring, named the « Statale Stelvio », the halogen content values are: F = 280 ppm, Br = 5 ppm.

A comparison between the fluorine and bromine contents in living matter samples (Correns, 1956) and that in the Bormio vegetation (Table 3) shows an appreciable biological accumulation of these halogens in the latter. The fluorine content in the Sphagnum indicates an appreciable selective absorption aptitude for fluorine. Such an aptitude seems to be lower than in the moss gen. Tillandasia usneoides, which has been reported to contain up to 624 ppm F (Fleischer, 1959).

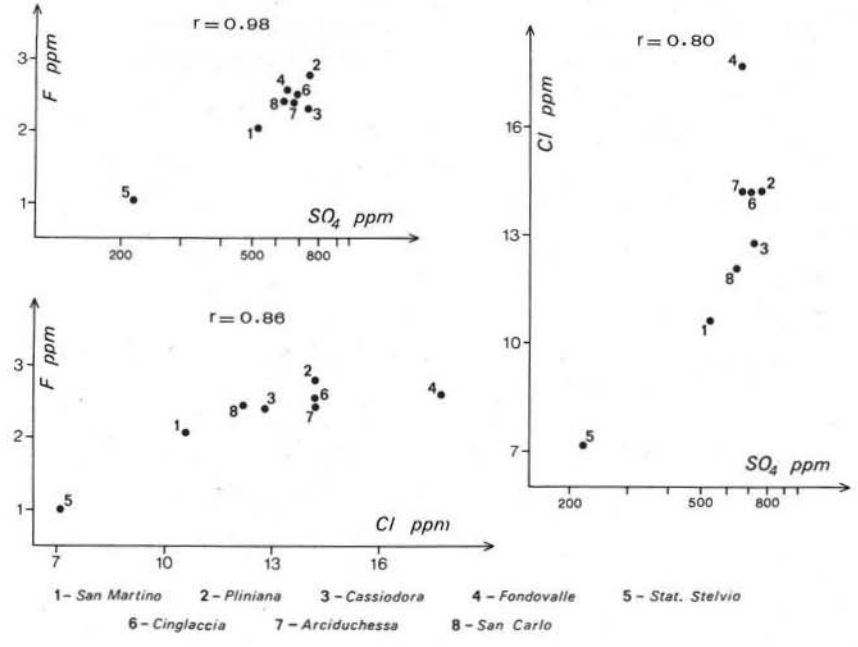

Fig. 1. — The binary correlations Cl/SO_4, F/SO_4, F/Cl show a strong correlation among all the compared anions, as well in the colder as in the hotter springs.

Discussion

Some binary correlations among components and between components and temperature are shown in figg. 1, 2, 3, 4.

The correlation coefficients, r, indicate that the Na/K ratio is independent from the temperature, while Ca appears to be slightly dependent. On the other

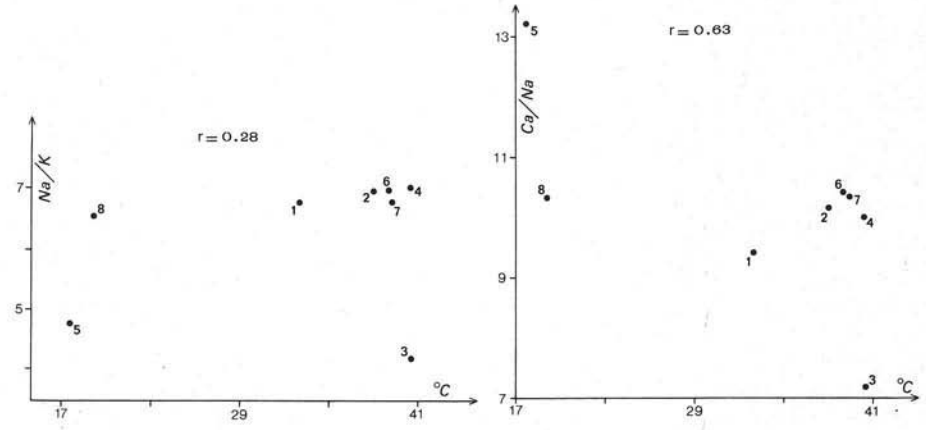

Fig. 2. — The binary correlations between F, Cl, Ca and the temperature show clearly that their strong correlation is lowered by the peculiar deviation of the S. Carlo spring.

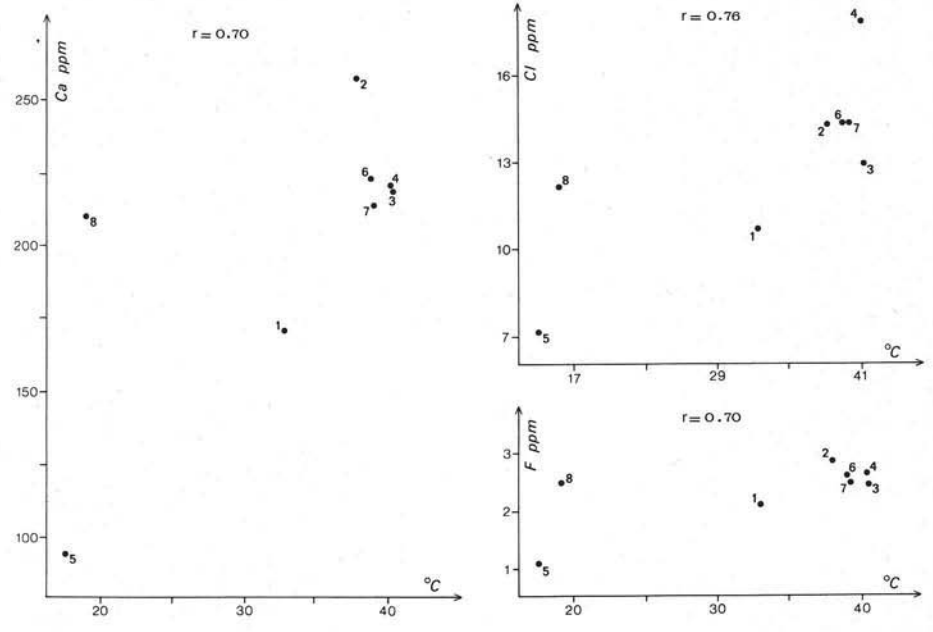

Fig. 3. — The Ca/Na and Na/K ratios are correlated with the temperature. The plots show that the S. Carlo spring, though relatively cold, appears to have the same mineral content of the hotter mineral springs. This fact seems to suggest that the alkaly-Ca contents are independent from the temperature of the springs, while they are probably dependent from the lapped geological formations.

hand, Ba^{2+} seems to be independent from Ca^{2+}, K^{+}, SO_4^{--} contents and from the temperature, whilst Cl^{-}, F^{-}, and SO_4^{--} together appear to be related to T.

Leaving out the question of different solubility products, it is possible to distinguish at least two geochemical associations of elements in the springs of Bormio, corresponding to two different geological sources of their mineral supply:

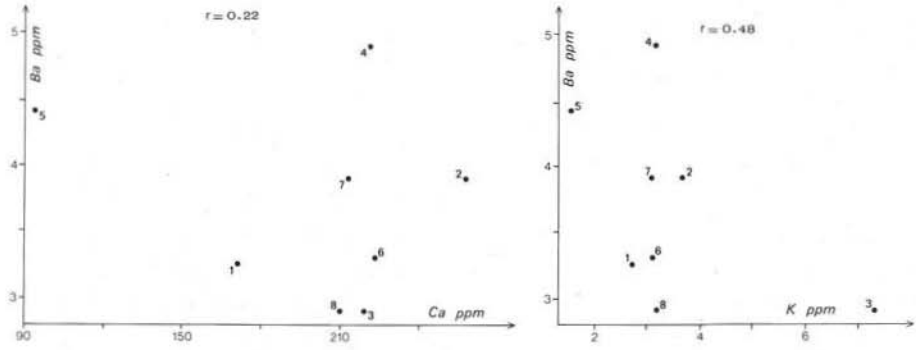

Fig. 4. — The plots show that Ba doesn't appear to be geochemically associated with Ca and K, in these thermal waters.

1) Fluorine + halogens + sulphates geochemical association, with Na/K = = 6.49 and Ca/Na = 9.68, which is characteristic of the hottest springs; it probably originates in the Triassic carbonate rocks and chalks (TONANI, 1957).

2) U + Th + Ra + Rn geochemical association, with Na/K = 4.77 and Ca/Na = 13.22, which is prevalent in the coldest spring and could arise from the Permo-Carboniferous conglomerates and associated rocks of the Verrucano formation.

Conclusion

The hydrogeologic conclusion we can draw is that U, Th, Ra mineral supply of the Bormio Springs comes from a more superficial geologic horizon than halogen-sulphate mineral supply.

Rn, U, Th, Ra show indeed no correlation with temperature of the springs, whereas a clear correlation between the components of the fluorine geochemical association and the temperature leads us to believe that the halogen-sulphate mineralization of the Bormio spring waters takes place at a much greater depth than the U, Th, Ra mineralization.

REFERENCES

AMERICAN PUBLIC HEALTH ASSOCIATION (1969) - *Standard methods for the examination of water, sewage, and industrial wastes.* New York.

BERBENNI P., POZZI R. (1966) - *Le sorgenti termominerali di Bormio: osservazioni idrogeologiche, chimiche e chimico-fisiche.* Giornate della chim. delle acque, Maccari Ed., 79-88.

CORRENS C. W (1956) - *The geochemistry of Halogens.* Phys. and Chem. of the Earth, I, Ahrens, Rankama and Runcorn Ed.

DE CAPITANI L., FIORENTINI POTENZA M., TERRANI M. (1974) - *Geochemistry of Ra in the supergene zone of a radioactive spring.* Atti Soc. It. Sc. Nat., 115, 2, 157-169.

FLEISCHER M., ROBINSON W. O. (1963) - *Some problems of the geochemistry of Fluorine.* Studies in Anal. Geochem., Royal Soc. of Canada Spec. Publ. n. 6.

TONANI F. (1957) - *Il contenuto di fluoro e di boro in acque termominerali toscane.* Atti Soc. Tosc. Sc. Nat., A. LXIV, 184-205.