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Lithium as a Pathfinder Element in the Large Scale Hydrogeochemical Exploration for Hydrothermal Systems

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ABSTRACT

The perspectives offered by using lithium as a pathfinder element in hydrogeochemical exploration for hydrothermal systems, even on a large scale, are discussed in the present paper.

Approximately 200 natural water samples, coming for the most part from Tuscany, have been analyzed. The waters correspond to different geochemical conditions and/or processes, ranging from condensed steam from the Larderello geothermal fields to thermal springs, and from pyrite mine waters to stream waters.

Lithium hydrogeochemical dispersion aureoles in the surface drainage system, originating from hydrothermal systems, are very marked and wide-spread. The Ombrone and Cornia rivers, in the basins of which thermal spring systems come to the surface, show marked lithium anomalies until the point where they merge with the sea.

On the basis of the results achieved lithium appears to be the most specific pathfinder element, among the trace elements, in the hydrogeochemical exploration for hydrothermal systems. This element may, moreover, be utilized in large scale exploration by using a low density sampling, due to its high geochemical mobility in the surface environment.

The results we obtained are furthermore of noteworthy importance with respect to the environmental geology, due to the link existing between the tectonic situation and the circulation of thermal fluids. The above topics are discussed in detail in the paper.

Introduction

The aim of this paper is to discuss the perspectives offered by using lithium as a pathfinder element in geochemical exploration for hydrothermal systems, even on a large scale.

The thermal waters are characterized by a quite different composition from both surface and cold ground waters. The hydrothermal systems can bring to the surface even high flows of thermal waters, then giving rise in the surface drainage system to hydrogeochemical dispersion aureoles of all the compounds showing relatively high content in thermal waters (Tonani 1970).

With an eye to the detectability of the dispersion aureoles thus formed, we have to consider, for each of the elements taken into consideration, the following factors.

a) The contrast value, that is, the ratio between the content in thermal waters and the normal content in stream waters in the region under investigation, conditions the intensity and the maximum dimension of the dispersion aureoles that are formed. This contrast value has to take into account the variability of the contents in the thermal waters, as well as the variability of the content found in the surface waters under varying environmental conditions.

b) The more or less univocal origin of the element, or better still, of the association of the elements under investigation, directly influences the reliability of the decision to be made in the exploration stage. Actually no elements or compounds are ever put into circulation by only one geochemical process, so in our quantitative approach to the problem, as indicated under point a), we must remember that the presence of anomalies of a given element can be connected with more than one geochemical process that brought it there. Studying the geochemical associations between various elements is normally the best way to reach a high specificity in the exploration (Dall'Aglio, Tonani 1972).

c) The stability in the supergene environment of the compounds brought to the surface by hydrothermal systems can even affect the possibility of forming dispersion aureoles. The thermal waters in fact reach the surface after undergoing for a long time physico-chemical processes quite different from those at the surface, particularly where the value of temperature Eh, and of the partial pressures of gases are concerned.

d) Then too, the geochemical mobility of the elements and/or compounds put into circulation affects the maximum dimensions of the hydrogeochemical dispersion aureoles, and thus the size of the sampling grid to be employed in prospecting.

In a previous paper (Dall'Aglio, Tonani 1972) it was shown that, as far as the aureoles of the major constituents are concerned, studying the correlations and regressions analysis between sulphate and the other compounds dissolved in the stream waters allows us to detect marked, wide-spread anomalies in the sulphate, deriving from the hydrothermal systems. These sulphate aureoles have features quite similar to those deriving from oxidizing sulphides. Thus studying the major constituents only does not give us a high specificity in the prospecting for hydrothermal systems.

Some elements (Br, I, B, etc.) showing high contents in thermal waters are characterized by a high geochemical mobility and they are found to be in very high content in the sea. Marine and evaporitic formations therefore show a high content of these elements, giving rise to high content in waters leaching such formations. Furthermore, B can reach high content in volcanic rocks and in the waters which leach them. Even if the above-mentioned elements do not provide

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very highly specific indications in the hydrogeochemical prospecting for hydrothermal systems, studying their associations with the major constituents can highly improve the efficiency of the prospecting methods (DALL'AGLIO, TONANI 1972).

Among the elements that are unstable in the supergene environment we recall the elements that have a high mobility under reducing conditions. Iron and manganese are in fact often present in thermal waters as bivalent ions, but as soon as they arrive at the surface they oxidize quickly and precipitate as hydroxides. The volatile compounds of sulphur at a reduced state oxidize quickly and easily, under the conditions found at the surface. Ammonium too is generally present at high levels in the thermal waters but in the surface environment oxidizes to nitrite-nitrates. Ammonium can also be put into natural waters, as the result of biological activity, industrial pollution, and the use of fertilizers. Ammonium therefore is not a very specific pathfinder compound for the detection of thermal systems, especially in large scale hydrogeochemical prospecting.

Therefore all these unstable compounds in the supergene environment cannot in themselves give rise to widespread dispersion aureoles on the surface drainage system, even if the reduced sulphur compounds do contribute to the forming of sulphate anomalies. The rare alkali metals, lithium, rubidium, and caesium deserve to be dealt with separately. These elements have high content in the thermal waters, and in addition are characterized by high geochemical mobility in the supergene environment, with Li, Rb, Cs in decreasing order. Lithium, in particular, seems to be well suited to detect thermal systems, because of its high mobility and because its origin is one of the most specific we know of; it shows in fact content of several ppm in thermal waters, in contrast with the few ppb in normal surface waters; that is, in thermal waters it is from 100 to 10,000 times higher than in normal surface waters. There do not seem to be, moreover, any important and wide-spread processes capable of bringing its content to such high values in waters, except the process of the relatively high temperature water-rock interaction along the route of the thermal water (following paragraph).

We have recently worked out an analytical method for lithium by flame emission scanning (DALL'AGLIO, VISIBELLI 1974). This method is characterized by such a high sensitivity and specificity that we can detect this element even in fresh water samples, and it has allowed us to overcome all the difficulties met with up to now in the analysis of lithium in natural substances. In the past these difficulties were a serious handicap to improving our knowledge of the hydrogeochemistry of this element.

In the last few years we have carried out a systematic study of the hydrogeochemical behaviour of lithium under different environmental and geochemical conditions, on the basis of the analysis of hundreds of water samples. In this paper we shall confine our interest to the perspectives of hydrogeochemical prospecting, even on a large scale, for hydrothermal systems, by using lithium as a pathfinder element.

Hydrogeochemistry of lithium

The geochemistry of lithium is well known in its essential aspects. There have also been recent important publications (HORSTMAN 1957; RONOV ET AL. 1970; TARDY ET AL. 1971) that deal with the supergene geochemistry of this element. Nonetheless there are many aspects in which our knowledge of the behaviour of lithium in the supergene and in the transition environment is lacking. In particular, as far as the lithium distribution and circulation in continental waters is concerned, there is only fragmentary and incomplete information, although recent publications have dealt with some aspects of the problem (FABRICAND ET AL. 1968; KHODKOVA, GEMP 1970; SREEKUMARAN ET AL. 1968; MOROZOV 1969; REEDER ET AL. 1972).

This lack of information on lithium geochemistry is also due to the fact that until very recently there were no analytical methods sensitive and specific enough to detect this element in fresh waters, without preconcentrating the sample first, and/or depending on peculiar and highly expensive equipment. As already mentioned, this analytical problem has been solved by flame emission scanning.

The ionic and cristallochemical properties of lithium are quite unique. Its small ionic radius (0.68 Å) is distinctly different from that of the other alkali-metals, so that lithium itself cannot enter the lattice structure of the minerals of other alkali-metals. Among the most abundant elements, the only ones that have an ionic radius value like lithium are Mg, Fe, and, to a lesser degree, Al, but the differences in the electric charge, and thus in the ionic potential (Z/r), tend to restrict the geochemical analogies between lithium and these elements. The geochemistry of lithium thus tends to be clearly different from that of the other alkali-metals, whereas lithium turns out to be partially similar to magnesium, and this is valid in the internal cycle as in the external one.

The general pattern of the distribution of lithium between igneous rocks, sedimentary rocks and the hydrosphere outlines the tendency of lithium to accumulate in the hydrosphere. Its overall geochemical mobility is thus high, the same as that of Ca (GOLDBERG 1963, WEDEPOHL 1968). Among the rare alkali-metals it is by far the most mobile. The behaviour of lithium on its way through the process of weathering has been studied by RONOV ET AL. (1970) by TARDY ET AL. (1971) and by HORSTMAN (1957), on the basis of the lithium distribution in the sedimentary rocks. The observations

of the above authors agree in pointing out the importance of the process of water-clay minerals interaction in determining the eventual distribution of lithium. Clay minerals (kaolinite, montmorillonite, illite, etc.) can in fact selectively remove lithium from natural waters, and therefore they can reach high lithium contents (i.e. from several hundreds to several thousands ppm). Within this process the behaviour of lithium is affected by that of magnesium: these two elements in fact enter the clay structure together. As far as the behaviour of lithium in the initial stage of weathering is concerned, that is within the water-rock interaction at the beginning of the hydrological cycle, the results are scarce and at times contradictory. The leaching of volcanic rocks brings into solution Na and K as well as Li (KHODKOVA ET AL. 1970). This is also clearly shown by a set of hydrogeochemical data we gathered in northern Latium. Water samples leaching alkali-potassic Quaternary volcanites, show a lithium content from 10 to 100 ppb (BRONDI ET AL. 1975). This has been indirectly confirmed by TARDY ET AL. (1971, pg. 406): « Dans les minéraux argileux d'alteration, la rétention du lithium est faible (inférieure à 60 ppm) et du même ordre que les teneurs initiales dans les roches ».

In the first stage of the hydrological cycle the igneous rocks tend to become poorer in lithium, which will tend to enrich the waters. The waters which continue in the hydrological cycle, and come into contact with the clay minerals in the sediments, eventually tend to become poorer, in a selective way, in lithium and the other elements that can be precipitated by clay minerals. When fresh waters, at the end of their continental circulation, flow into the sea, they generally show a low lithium content, i.e. in the order of a few ppb (LIVINGSTONE 1963). The lithium content of the waters flowing into the sea should depend largely on the ratio between the intensity of the leaching process in the first stage of the hydrological cycle and the exchange with hydrolized minerals in the second stage of continental circulation. Morphological and climatic conditions can be more important factors than the geolithological feature in conditioning the relationship between the intensity of the two processes quoted above, and thus conditioning the eventual lithium content of the waters.

It should, however, be pointed out that lithium does not have insoluble secondary minerals and it eventually behaves as a mobile element in the supergene environment. For instance, as the evaporitic minerals precipitate, it tends to become highly enriched in brines (DALL'AGLIO, ORLANDI 1975). In particular, as soon as it has entered into circulation in stream waters, there are no important processes capable of removing in any appreciable way the lithium from the waters.

Unlike the low contents of the surface waters (generally less than 10 ppb) the contents in thermal waters are extremely higher. Contents over 1000 ppb are normal for thermal springs, even at not so high temperatures (40 °C), and there are frequently contents in the order of 10 ppm (10,000 ppb) (WHITE 1970). The lithium content in thermal waters changes according to the kind of rocks leached (ELLIS 1967), but the variability caused by different kinds of rocks is of secondary importance as compared to the differences observed between thermal and cold waters.

So in the case of lithium a very small difference in the temperature at which the water-rock interaction takes place, manages to raise the content of the waters to a factor of from 100 to 10,000 times. This is probably a consequence of the peculiar ionic properties of lithium. The lithium ion, characterized by a low ionic radius value and low electric charge, is driven away from the lattice structure which it entered, or else does not enter it at all. This is confirmed by the observations reported by HORSTMAN (1957), as to the great decrease of the lithium content in the shales and in the recrystallized inclusions in contact with the Bounder batholith; this decrease is much greater than that observed for other elements in the same conditions.

Once the thermal waters reach the surface and are put into stream waters, the lithium content should not undergo any appreciable decrease except for dilution processes. The aim of the present paper is therefore to study the extent and the detectability of the hydrogeochemical lithium aureoles originating from hydrothermal systems.

Analytical methods

The analyses of lithium were carried out by flame emission scanning of the spectrum zone near the Li analytical line 6708, using the P.E. Mod 303 spectrophotometer. The method used has been discussed by DALL'AGLIO and VISIBELLI (1974).

A few milliliters of water are enough to perform high quality lithium analysis; the sensitivity is equal to 0.1 micrograms of Li per liter, and the specificity is good because the analytical line 6708 measurements are unaffected by background signals by using scanning.

The major constituents were determined according to classical methods, but using mobile laboratories precisely designed for hydrogeochemical studies (BRONDI ET AL. 1966). These laboratories allow us to carry out some analyses and some treatments of water samples on the spot, i.e. measurements of pH, Eh, analysis of Ca, Mg and HCO_3, filtering the samples, etc.

The analytical methods employed are as follows:

Ca and Mg : titration with EDTA and/or atomic absorption spectrophotometry (P.E. 303);

Na and K   : flame emission photometry by using a two channel photometer especially designed by C.N.E.N. for hydrogeochemical analysis;

HCO_3^- = acidimetric titration on the spot;

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Presentation of data

185 water samples were tested, coming for the most part from Tuscany, and corresponding to different situations and/or geochemical processes, or more precisely

— 173 stream water samples
— 7 thermal water
— 3 condensed steam
— 2 water leaching pyrite ore bodies.

The stream water samples were gathered to study the characteristics of the lithium hydrogeochemical dispersion aureoles caused by hydrothermal systems. The samples of stream waters, as well as the analytical data dealing with the major constituents, were kindly supplied by Dr Cioppi of the Institute of Mineralogy, Petrography and Geochemistry of Florence University, who carried out a hydrogeochemical study of the zone.

In order to complete our information on the extent of the hydrogeochemical aureoles, the sampling made by Dr Cioppi was extended downstream in the most important rivers of the zone.

In order to improve our knowledge of the way lithium is transported in the hydrothermal systems three samples of condensed steam were analyzed, coming from the productive wells of Larderello and Mt. Amiata area (Bertoli, St. Vincenzo 2, and Bagnore wells), as well as a thermal water sample from the Camorsi deep well.

Within the present work a restricted number of thermal springs were examined, firstly because complete information is available on the hydrogeochemistry of many thermal sources in Italy and abroad (BALDI ET AL. 1974; WHITE 1970); and because the purpose of the present work is to focus mainly on the study of the lithium hydrogeochemical dispersion aureoles caused by hydrothermal systems in the surface drainage system.

Finally, water samples from the pyrite mines of Niccioleta and Boccheggiano were analyzed. This was done in order to test the efficiency of lithium in discriminating between sulphate anomalies caused by thermal systems and anomalies caused by oxidizing sulphides (DALL'AGLIO, TONANI, 1972).

A map of the sampling carried out is shown in Figure 1 and the analytical data obtained are given in Tables 1 and 2.

TABLE 1. — *Lithium content of the water samples supplied by Dr. Cioppi. The analyses of the major constituents are reported in the Dr. Cioppi paper (1974).*

Sample No.	Lithium content moles litre × 10⁻⁶	Date of sampling	Sample No.	Lithium content moles litre × 10⁻⁶	Date of sampling	Sample No.	Lithium content moles litre × 10⁻⁶	Date of sampling	Sample No.	Lithium content moles litre × 10⁻⁶	Date of sampling
13000	7.10	3.72	13044	8.60	3.72	13094	1.10	3.72	13150	0.20	3.72
13002	0.85	3.72	13046	13.0	3.72	13096	0,72	3.72	13152	2.90	3.72
13004	7.40	3.72	13047	4.10	3.72	13098	4.80	3.72	13154	3.20	3.72
13005	9.20	3.72	13048	8.10	3.72	13100	0.34	3.72	13156	9.80	3.72
13006	2.50	3.72	13050	0.34	3.72	13101	3.00	3.72	13158	3.50	3.72
13008	0.23	3.72	13052	14.00	3.72	13102	0.37	3.72	13160	2.20	3.72
13009	0.55	3.72	13054	8.40	3.72	13104	0.16	3.72	13162	1.30	3.72
13010	1.50	3.72	13056	9.60	3.72	13106	0.79	3.72	13164	1.90	3.72
1301\	0.65	3.72	13058	0.42	3.72	13108	0.52	3.72	13166	1.30	3.72
13012	0.83	3.72	13060	0.30	3.72	13110	3.00	3.72	13168	0.53	3.72
13013	0.65	3.72	13062	0.33	3.72	13112	5.70	3.72	13170	1.10	3.72
13014	0.36	3.72	13063	0.65	3.72	13114	3.60	3.72	13172	1.20	3.72
13016	0.91	3.72	13064	2.10	3.72	13116	1.10	3.72	13174	1.00	3.72
13017	0.04	3.72	13066	1.70	3.72	13118	0.59	3.72	13176	1.80	3.72
13018	2.10	3.72	13068	2.10	3.72	13120	0.92	3.72	13178	1.30	3.72
13020	0.42	3.72	13069	1.00	3.72	13122	71.00	3.72	13180	0.79	3.72
13021	0.36	3.72	13070	0.73	3.72	13124	11.00	3.72	13182	1.30	3.72
13022	0.37	3.72	13071	1.00	3.72	13126	9.60	3.72	13184	2.60	3.72
13023	0.37	3.72	13072	0.75	3.72	13128	15.00	3.72	13186	1.80	3.72
13024	0.10	3.72	13074	1.70	3.72	13129	46.00	3.72	13188	4.60	3.72
13025	0.29	3.72	13075	0.65	3.72	13130	11.00	3.72	13190	3.40	3.72
13026	0.39	3.72	13076	1.40	3.72	13132	14.00	3.72	13192	2.50	3.72
13028	1.70	3.72	13077	0.55	3.72	13134	3.30	3.72	13194	11.00	3.72
13029	0.79	3.72	13078	2.20	3.72	13136	10.00	3.72	13196	6.30	3.72
13030	1.60	3.72	13080	0.75	3.72	13138	2.50	3.72	13198	0.46	3.72
13032	1.60	3.72	13082	2.20	3.72	13140	1.90	3.72	13200	0.10	3.72
13034	0.14	3.72	13084	2.40	3.72	13142	1.90	3.72	13202	11.00	3.72
13036	9.6	3.72	13086	0.26	3.72	13144	6.90	3.72	13204	0.34	3.72
13038	2.3	3.72	13088	0.48	3.72	13146	0.83	3.72	13206	5.60	3.72
13040	13.0	3.72	13090	3.40	3.72	13148	6.80	3.72	13208	6.40	3.72
13042	0.14	3.72	13092	6.30	3.72						

TABLE 2. — *Lithium content and chemical composition of the water samples collected and analyzed by the authors.*

Sample No.	Date	pH	°C	Ca	Mg	Na	K	Bic	SO₄	Cl	SiO₂	F	B	Li
						meq/l						moles/l × 10⁻⁶		
12827	9.4.73	5.9	36	30.00	11.00	4.30	0.22	12.00	32.00	2.10	320.00	130.00	2100.00	83.00
12828	10.4.73	7.5	17	23.00	5.60	0.40	0.03	2.70	27.00	0.27	100.00	49.00	58.00	3.70
12829	10.4.73	7.9	14	19.00	5.90	0.39	0.03	3.30	22.00	0.57	110.00	30.00	10.00	1.70
12830	10.4.73	7.4	15	21.00	6.10	0.32	0.03	3.80	22.00	0.33	140.00	31.00	14.00	1.50
12831	10.4.73	8.0	10	3.30	1.30	0.63	0.02	3.60	1.20	0.60	110.00	9.00	17.00	1.20
12832	10.4.73	7.9	95	5.00	0.41	2.60	1.12	2.60	10.00	0.60	2400.00	220.00	1700.00	360.00
12833	10.4.73	6.1	20	14.00	3.80	1.30	0.06	17.00	0.58	0.39	350.00	12.00	30.00	4.50
12834	10.4.73	6.3	—	0.02	0.001	0.02	0.003	14.00	0.12	0.46	5.00	7.00	2900.00	1.50
12835	11.4.73	6.3	41	7.30	2.00	4.20	0.07	13.00	0.45	0.53	1900.00	13.00	150.00	7.60
12836	11.4.73	6.6	38	47.00	20.00	19.00	1.10	50.00	27.00	9.70	460.00	120.00	1000.00	190.00
12837	11.4.73	7.9	12	7.60	6.70	4.50	0.24	6.70	9.70	2.60	70.00	19.00	130.00	31.00
12942	9.11.73	8.2	14	8.10	12.00	44.00	1.40	4.10	12.00	52.00	110.00	30.00	84.00	9.50
12943	9.11.73	8.4	13	7.00	2.80	1.50	0.09	4.10	6.3	1.20	90.00	35.00	64.00	9.00
12944	9.11.73	8.8	14	3.20	2.90	1.30	0.10	3.05	3.60	0.81	240.00	32.00	20.00	3.50
12945	9.11.73	8.5	14	8.30	3.40	1.64	0.10	4.80	76.00	1.30	130.00	37.00	82.00	12.00
12946	9.11.73	7.8	10	6.30	2.00	0.74	0.04	4.30	5.00	0.62	140.00	40.00	320.00	1.60
12947	10.11.73	8.0	10	13.00	4.20	0.47	0.04	4.50	13.00	0.42	140.00	570.00	26.00	1.40
12948	10.11.73	6.4	41	40.00	13.00	6.10	0.50	24.00	33.00	5.30	460.00	130.00	650.00	180.00
12949	10.11.73	7.8	10	8.40	2.80	3.70	0.21	5.20	6.40	2.70	180.00	67.00	300.00	78.00
12950	10.11.73	8.0	12	12.00	4.40	0.25	0.06	5.00	11.00	1.20	110.00	42.00	74.00	11.00
12951	10.11.73	7.6	11	5.60	1.40	2.30	0.19	6.00	2.50	1.50	210.00	10.00	700.00	7.70
12952	10.11.73	8.3	12	9.20	6.60	7.10	0.42	8.30	13.00	4.10	120.00	25.00	300.00	47.00
12953	10.11.73	7.8	12	4.60	1.30	1.70	0.17	5.60	1.40	1.20	230.00	10.00	30.00	3.50
12954	10.11.73	7.9	11	5.80	1.30	1.00	0.03	6.30	1.10	0.65	180.00	27.00	56.00	0.29
12955	10.11.73	8.0	12	6.20	1.40	1.30	0.04	5.80	2.20	0.82	190.00	220.00	48.00	0.48
12956	11.11.73	7.6	13	3.60	1.50	1.30	0.11	4.40	1.20	1.20	140.00	60.00	48.00	0.59
12957	11.11.73	8.0	13	14.00	4.80	2.30	0.39	8.70	12.00	1.60	280.00	45.00	66.00	5.80
12958	11.11.73	8.0	12	4.50	1.20	1.30	0.14	4.80	1.80	0.88	170.00	16.00	38.00	1.00
12959	11.11.73	8.2	12	8.20	4.40	2.60	0.14	6.60	7.50	1.90	210.00	16.00	24.00	4.10

Table 2 continued

Table 2 continued

| Sample-No.	Date	pH	°C	Ca	Mg	Na	K	Bic	SO₄	Cl	SiO₂	F	B	Li
						meq/l						moles/l × 10⁻⁶		
12960	11.11.73	8.0	12	6.80	14.00	50.00	1.40	4.50	9.70	67.00	140.00	60.00	110.00	4.60
12961	11.11.73	9.9	—	0.02	0.001	0.001	0.001	16.00	0.54	0.40	35.00	14.00	1200.00	0.02
12968	13.2.74	8.1	11	6.60	1.70	1.10	0.07	5.00	3.40	0.92	120.00	22.00	32.00	1.40
12969	13.2.74	8.1	11	4.60	1.60	1.20	0.16	4.10	2.60	0.70	220.00	25.00	38.00	1.80
12970	13.2.74	8.1	9	4.10	1.80	1.90	0.15	3.70	3.20	0.84	170.00	21.00	42.00	2.60
12971	13.2.74	7.6	8	3.70	1.30	1.70	0.13	3.50	2.50	0.70	150.00	18.00	6.00	2.30
12972	13.2.74	8.2	8	6.10	3.90	6.00	3.90	4.20	9.80	2.00	110.00	18.00	24.00	8.00
12973	13.2.74	8.2	8	3.20	0.84	0.84	0.07	3.40	1.10	0.42	130.00	12.00	56.00	1.90
12974	13.2.74	8.3	9	3.90	1.20	0.47	0.04	3.80	1.80	0.54	180.00	16.00	100.00	2.30
12975	13.2.74	8.2	8	3.80	1.50	0.61	0.04	3.60	2.50	0.60	120.00	12.00	2.00	2.30
12976	14.2.74	8.1	—	0.06	0.04	0.01	0.004	6.50	0.02	0.02	20.00	13.00		0.07
12977	14.2.74	8.0	12	3.80	0.90	0.66	0.04	3.50	1.30	0.52	100.00	18.00	52.00	1.60
12978	14.2.74	8.0	11	4.70	1.10	1.40	0.05	4.30	1.40	1.40	150.00	18.00	20.00	0.65
12979	14.2.74	7.8	22	16.00	5.80	2.40	0.16	6.10	16.00	1.90	270.00	72.00	1000.00	44.00
12980	14.2.74	8.0	14	4.00	5.30	1.20	0.07	4.30	5.20	1.00	150.00	31.00	250.00	11.00
12981	14.2.74	7.8	12	5.40	1.90	2.40	0.08	4.50	2.30	3.00	160.00	24.00	3.00	0.88
12982	14.2.74	7.8	11	7.20	2.50	1.70	0.09	4.40	5.20	1.70	150.00	28.00	270.00	11.00
12983	14.2.74	7.9	11	5.70	2.00	1.50	0.07	4.80	2.90	1.50	130.00	19.00	0.10	1.00
12984	14.2.74	7.7	11	7.50	2.40	1.40	0.08	4.20	5.70	1.40	130.00	32.00	250.00	13.00
12985	14.2.74	7.8	12	7.80	2.80	1.50	0.09	4.00	6.30	1.40	150.00	31.00	260.00	14.00
12986	14.2.74	7.8	12	5.80	2.10	2.60	0.07	4.80	2.30	3.30	150.00	21.00	10.00	0.99
12987	14.2.74	8.1	14	13.00	28.00	120.00	3.10	3.70	20.00	150.00	100.00	41.00	260.00	14.00
12988	14.2.74	8.2	11	4.60	1.40	1.20	0.16	4.20	2.40	0.73	240.00	26.00	32.00	1.70
12989	14.2.74	8.3	11	4.60	1.60	1.20	0.16	4.20	2.50	0.72	240.00	26.00	48.00	1.70
12990	14.2.74	7.9	11	4.00	1.00	0.80	0.084	4.40	1.20	0.60	65.00	18.00	10.00	1.50
12991	20.2.74	7.8	—	4.50	0.57	1.10	0.09	3.80	1.40	0.92	120.00	20.00	24.00	0.96
12992	21.2.74	8.1	—	5.20	0.40	0.21	0.02	5.10	0.57	0.38				0.04
12993	21.2.74	8.1	—	4.40	1.00	0.66	0.15	3.20	2.80	0.42				14.00
12994	21.2.74	8.1	—	5.20	0.48	0.52	0.06	4.10	1.50	0.38				3.70
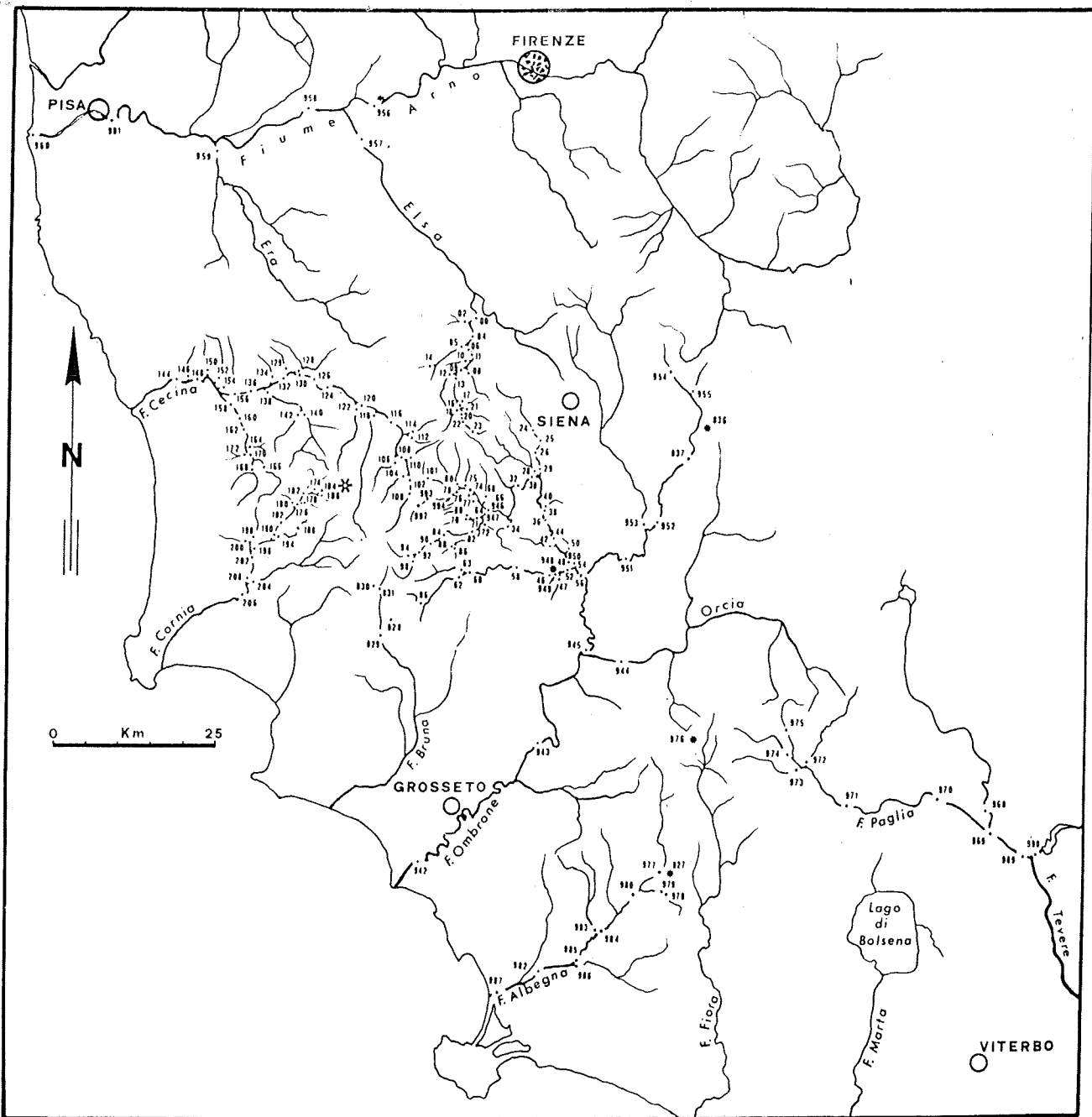
FIG. 1. — *Sampling sites and identification numbers of water samples examined (first two or three digits of each number omitted).*

Discussion of results

In the diagram of Figure 2 the lithium content of all the water samples analyzed is plotted versus the total salinity of waters. Figure 3 shows the lithium versus Mg content diagram, and Figure 4 shows the lithium-sulphate diagram.

The pattern is quite similar in all the above diagrams, and in fact there are no significant correlations between lithium and the constituents taken into account. This is a consequence of two circumstances, namely:

a) as discussed below, the lithium content in waters does not show, in general, clear correlations with other compounds dissolved in waters. Its hydrogeochemical behaviour is, in fact, quite unique with respect to other elements;

b) the set of data examined is heterogeneous as regards the geochemical processes undergone by the different waters examined.

The analytical data on thermal fluids gathered in the Larderello area clearly show some important features of lithium circulation in hydrothermal systems. The three condensed steam samples show extraordinarily

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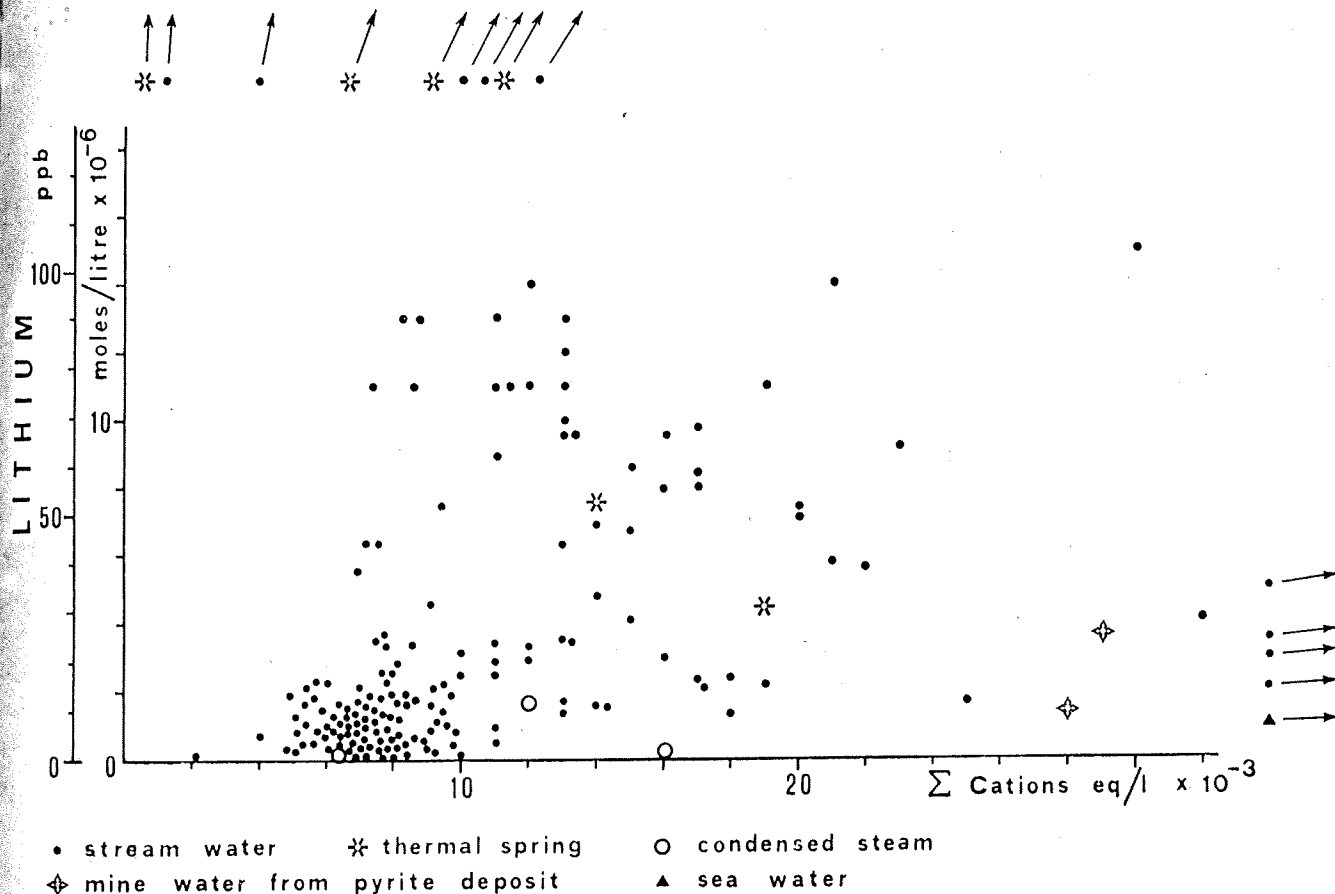
FIG. 2. — *Lithium content versus total salinity values. Water samples from Tuscany and Latium.*

low lithium content (1.5; 0.07; and 0.02 micromoles/l respectively). These small amounts of lithium can be carried along with the low content of water carried by the vapour. Furthermore, the Li/Na and Li/K is found to be similar to those found in the reservoir waters of the same area. This low content can however also be reached by contamination of the samples. The indication which clearly comes from this data is that lithium is not at all transported in the vapour phase. The total lithium flow towards the surface in a hydrothermal system may be relatively less than for the volatile compounds such as B or NH_4. In a vapour dominated system the lithium is not transported to the surface by the biphase transfer of heat and fluids, while the volatile compounds tend to be transported and selectively enriched as compared to the other compounds. Even if this partial limitation exists, the overall lithium flow towards the surface, even in a vapour dominated system in general must be high because there is also an intense circulation of thermal waters in the vicinity of the vapour dominated systems.

The water samples leaching the pyrite deposits of Boccheggiano and Niccioleta show a very high sulphate content in contrast to a very low lithium content. The representative points of these samples in the diagram

of Figure 4 fall within an area completely distinct from that of clusters of other points. Lithium is thus found to be an excellent pathfinder element, just as good as boron, for discriminating between sulphate anomalies coming from oxidizing sulphide deposits and those coming from thermal systems (DALL'AGLIO, TONANI 1972).

As far as the problem of detecting dispersion aureoles in the surface drainage system is concerned, we must first examine the best criteria to adopt in selecting the anomalous samples. Especially in geochemical surveys on a regional scale, with a low sampling density (1-10 samples per 100 km²) variations in climatic, geological and environmental conditions, in general, can cause broad fluctuations in the content of the element under investigation, and these fluctuations can even mask the anomalous values of the dispersion aureoles. Studying the simple and multiple correlations can contribute to reducing decisively the casual variations of the element under investigation, thus leading to a greater overall efficiency in selecting the anomalous samples and therefore in the geochemical exploration (DALL'AGLIO 1971; DALL'AGLIO, TONANI 1972). The above considerations cannot be applied to the set of data under investigation, due to the following circumstances.
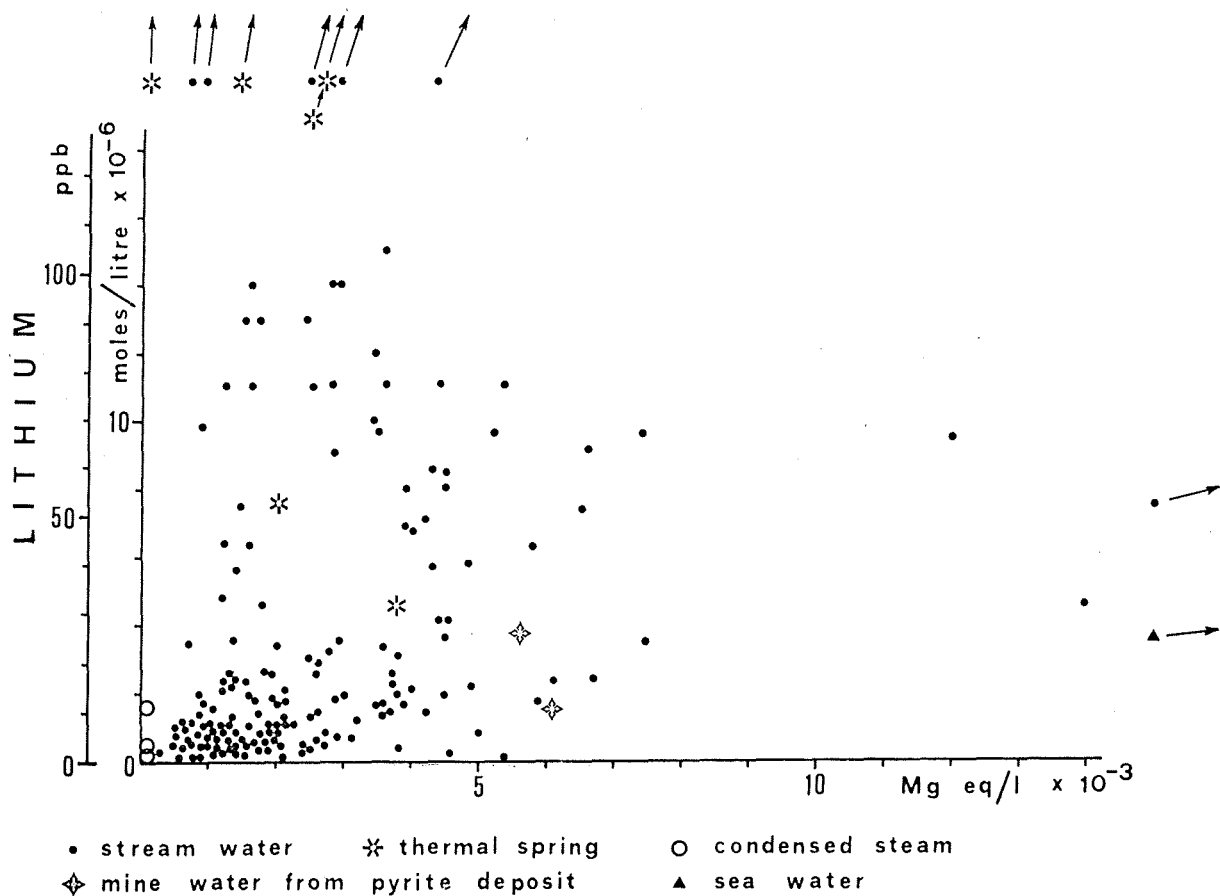
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FIG. 3. — *Lithium versus magnesium content of all water samples examined.*

On the basis of the limited information on the hydrogeochemistry of lithium, it is possible to state that there are in general no significant correlations between lithium and other constituents dissolved in the waters.

The distribution of this element in the ground and surface waters of northern Latium has shown how the correlations between lithium and other constituents are valid only within sets of samples from the same environmental situation. Thus within the samples of waters gathered in the same basin, and otherwise uniform from the geolithological viewpoint, significant correlations were ascertained between lithium content on the one hand and total salinity, Na, K and Mg contents, on the other. If, instead, we examine natural waters under conditions even a little different from each other, there are no significant correlations between lithium and the other constituents dissolved in water samples. This lack of correlation is valid even within the single process of water-rock interaction at low temperature and pressure considered by itself, and is accentuated if we examine in the same set of data the thermal waters and the dispersion trainees in the surface drainage system from which they originate. In the thermal waters lithium in fact is greatly enriched as compared to the ground waters, whereas the other components, which have similar properties as far as stability and geochem-

ical mobility in the supergene environment are concerned, do not show enrichment factors of the same order. This derives from the unique ionic properties of the lithium, which have already been mentioned above.

The diagrams given in Figure 2 and Figure 3 provide clear evidence as to the above-mentioned lack of correlation between lithium and other constituents. In a situation of this kind, it will be useful to consider the associations between lithium and other elements originated by particular geochemical processes as for the associations of high sulphate and low lithium content in the case discussed above, of waters leaching oxidizing sulphides; but it may even prove harmful to select the anomalous samples on the basis of the correlations between lithium and the other elements, within the set of samples investigated here.

For the above reasons the selection of anomalous lithium samples was made on the sole basis of the frequency distribution of the lithium content in waters. The geographic distribution of the samples at various anomaly levels, thus selected, are shown in Figure 5. This map shows that the distribution of the anomalous samples delineates the presence of marked and widespread lithium anomalies. Going from south to north the results can be summarized as follows.
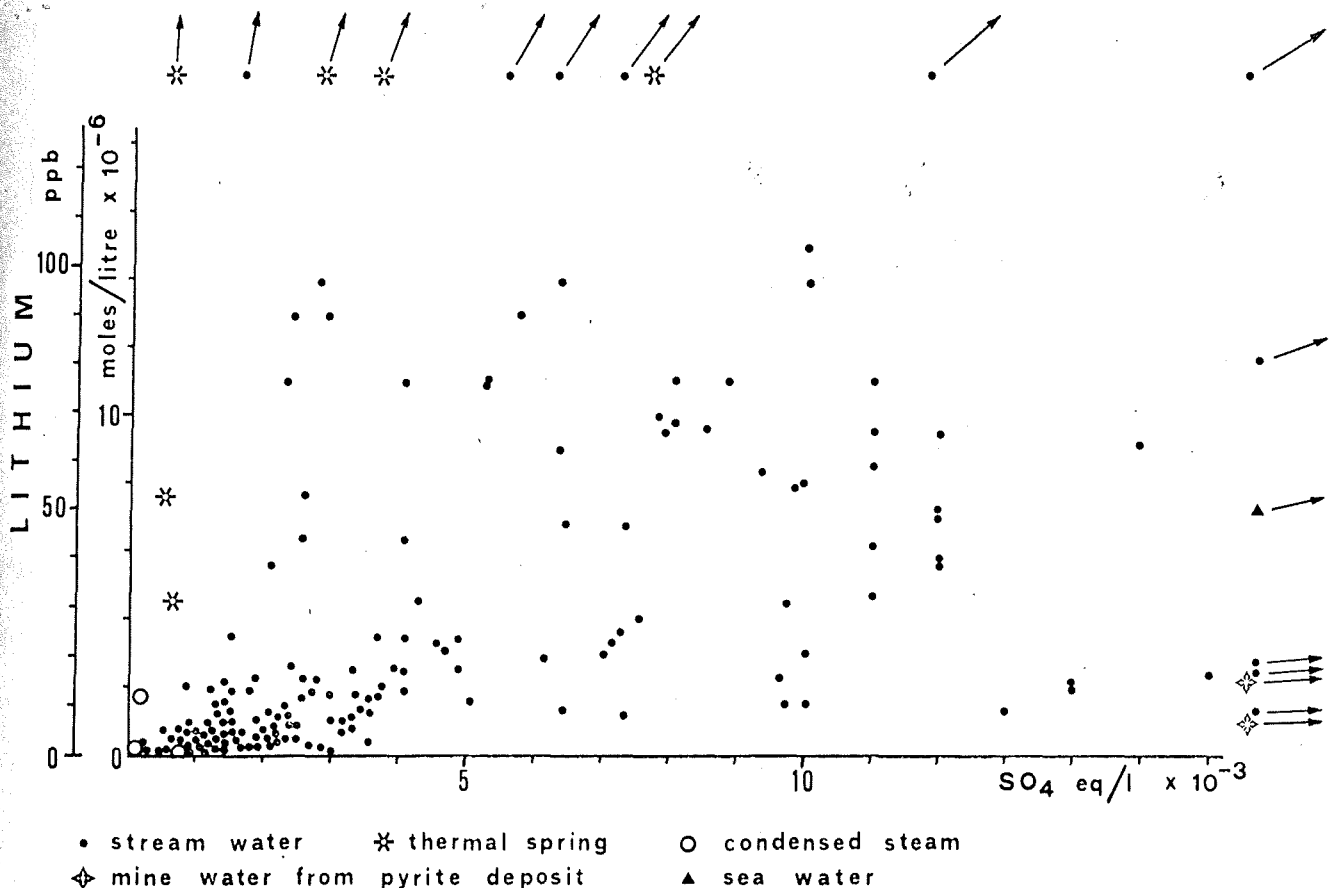
150

Fig. 4. — *Lithium versus sulphate content of all water samples examined.*

— The Albegna river shows a noteworthy dispersion aureole originating from the thermal spring of the Saturnia Baths. This aureole continues to have high content up to where it flows into the sea, although the Albegna river has a high discharge rate.

— The Paglia river does not show any significant anomalies for lithium, even although the geothermal field of Monte Amiata lies in the upper part of its basin. In fact the ENEL wells initially producing a mixture of steam and water were closed some years ago. The existing electric power plants are freely discharging only condensed steam into the atmosphere and/or into the surface drainage system. As mentioned above lithium is not transported into the vapour phase and thus the absence of lithium anomalies in the Paglia river are explained. It would have been extremely interesting to check if before the geothermal field was put into production there had been lithium anomalies. There probably were, if we consider how easily the thermal waters can get to the surface in a zone with high geothermal flow and characterized, further more, by far from arid climatic conditions.

— The Ombrone river shows an intense lithium anomaly as far as the sea. Into this river flow a large number of thermal systems, from that of Rapolano to the hydrothermal system located to the south of Siena, just before the Merse flows into the Ombrone river. In addition to this it receives the Travale geothermal field discharge, mainly made up of condensed steam.

— The water from the pyrite mines of Niccioleta and Boccheggiano are discharged into the Bruna river. As already mentioned these waters do not show anomalous lithium content.

— The Cornia river shows a marked lithium aureole caused by thermal springs present in the upper part of the basin.

— The Cecina river shows a consistent anomaly originating from the Larderello area. Also the Larderello 2 and 3 electric plants discharge into the Possera creek.

— Low lithium anomalies are found in the Era and Elsa rivers until their mergence with the Arno river. These anomalies probably originate in the hydrothermal systems which come to the surface in the upper part of the basins of these two rivers.

A detailed analysis of the pattern of the anomalies found shows that where these anomalies diminish it is because of a simple process of dilution.

Conclusions

The purpose of the present work has been to critically evaluate the effectiveness of lithium as a pathfinder in hydrogeochemical prospecting, for hydrothermal systems also on a large scale. 185 water samples were analyzed, corresponding to different geochemical processes, ranging from condensed steam from geothermal fields to thermal springs, and from pyrite mine waters to stream waters.
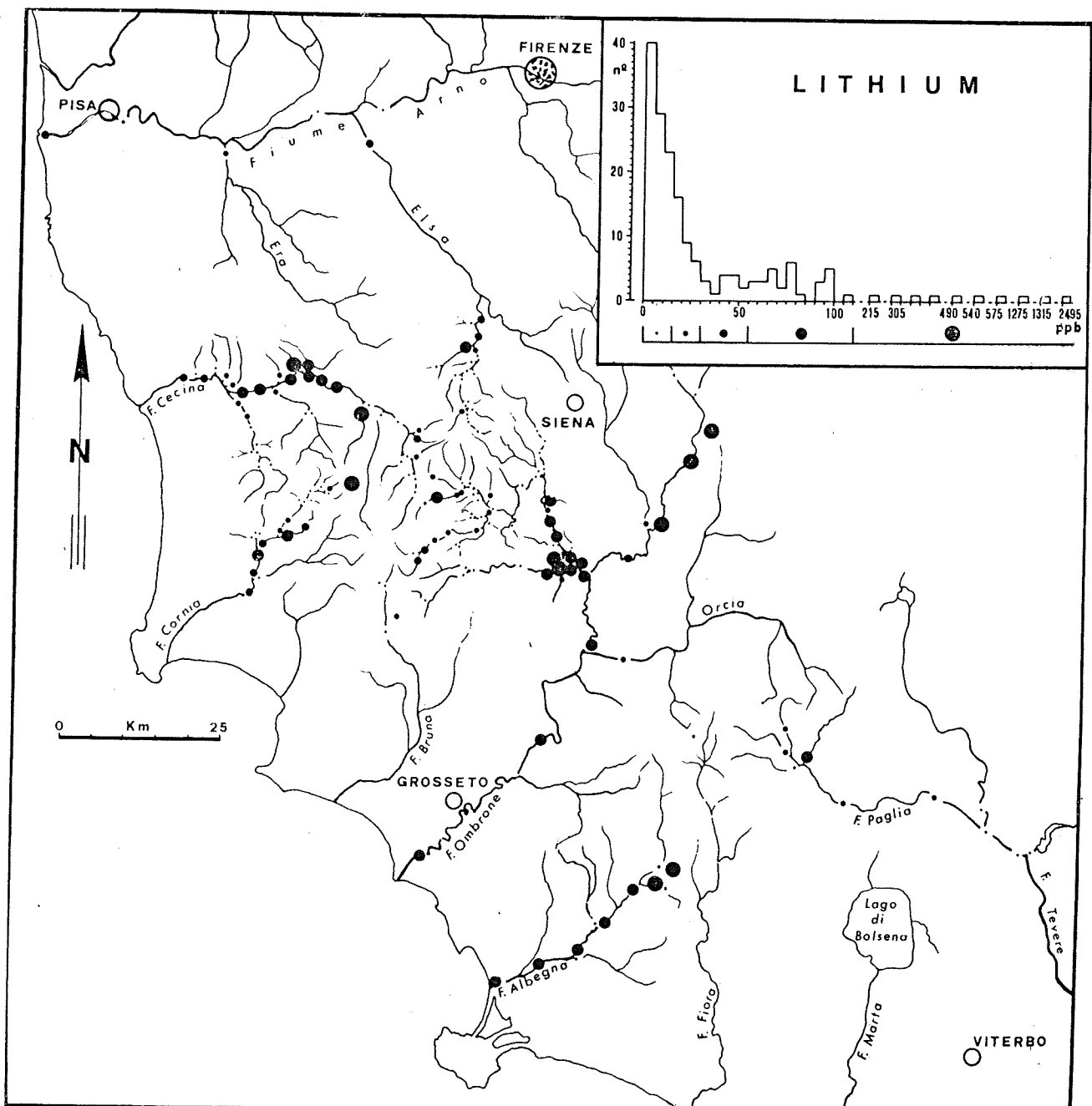
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FIG. 5. — *Areal distribution of the lithium anomalous samples of water.*

The results obtained can be summarized as follows.

— All the data gathered indicate that lithium tends to be enriched in the water mostly, and almost exclusively, when the water-rock interaction takes place at a temperature higher than the ambient one. All the thermal waters show in fact high lithium content, i.e. in the order of ppm even if the thermality is low. This happens for all the types of rocks that the waters go through on route, though there are differences in the lithium contents of the thermal waters, depending on the lithium content in rocks which are leached. This peculiar characteristic is probably a result of the particular ionic and crystallochemical features of lithium; this element shows, in fact, a much smaller ionic radius value than the other alkali, similar to that of Mg and Fe. In many minerals, and especially in the clay minerals, lithium

can therefore replace Mg, and to a lesser degree Fe, too; but the difference in charge makes it unstable in the lattice structure. Therefore a small rise in temperature is enough to cause the lithium to leave the lattice structure of the minerals which it previously had entered and/or not to enter them at all from the surrounding thermal solutions.

— The condensed steam samples analyzed showed extremely low lithium content, even much lower than 1 ppb, i.e. lithium is not at all transported by the vapour phase.

— The water samples from the Niccioleta and Boccheggiano pyrite mines show low lithium content, 26 and 10 ppb respectively.

— The surface stream waters and the cold ground waters have low lithium content, i.e. under 10 ppb in general.

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— The lithium hydrogeochemical dispersion aureoles in the surface drainage system, coming from the thermal waters that get to the surface, seem to be quite marked and persistent. This derives from the high contrast value, i.e. the ratio between the lithium content in the thermal waters and in normal cold waters, and from the high geochemical mobility that lithium shows once it has begun circulation in the stream waters. The decrease in the content, as the aureole source gets farther away, is due solely to processes of dilution by waters poorer in lithium. In the area we investigated an analysis of the lithium at the mouths of the rivers provides a sufficiently approximate measure of the ratio between the thermal water flow and the total water discharge rate.

— The study of the distribution of lithium in natural waters can be a valid aid, not only in prospecting for geothermal fields, but also in basic geological and geochemical studies.

The tectonic situation in a given area, the presence and the extent of active faults, which are the most common circulation routes for thermal waters, can be inferred by the study of lithium circulation in the natural waters, also taking into account the geological feature of the region under investigation.

The results here presented constitute, moreover, a contribution to environmental geochemistry as follows:

a) The role of lithium in the biogeochemical processes has been little known up till now but it appears to be very important. A better knowledge of lithium distribution and circulation in waters constitutes a first approach to this problem.

b) In the specific field of forecasting earthquakes by hydrogeochemical methods, lithium can play an important role as a pathfinder element (DALL'AGLIO 1974).

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