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NEW DATA ON THE HYDROGEOCHEMISTRY OF SELENIUM

RIASSUNTO. — Le conoscenze circa la distribuzione e circolazione del Selenio in natura hanno ricevuto, negli ultimi anni, un interesse sempre maggiore. Questo elemento, infatti, risulta tossico per la flora e la fauna per concentrazioni relativamente elevate, ma nello stesso tempo svolge un ruolo essenziale per lo sviluppo dell'attività biologica, ed una sua carenza fa sentire pesanti effetti negativi.

Anche se le linee essenziali della geochimica del Se sono ben note, molte lacune permangono circa la conoscenza della sua distribuzione e circolazione nell'ambiente supergenico; in particolare per quel che riguarda il suo comportamento idrogeochimico si hanno solo notizie frammentarie ed incomplete.

In questo lavoro vengono presentati nuovi dati sulla distribuzione del Se nelle acque naturali. Sono state in primo luogo condotte ricerche per la messa a punto di un nuovo metodo analitico con caratteristiche di elevata sensibilità e specificità. Una procedura basata su estrazione del complesso APDC-Se in cloroformio, riestrazione in fase acquosa, e successiva determinazione con fornello di grafite in assorbimento atomico, ha consentito di raggiungere sensibilità di pochi ng per litro. Questa metodologia è stata in seguito applicata ad una serie di acque naturali corrispondenti a condizioni geologiche e geochimiche molto diverse tra di loro; da acque superficiali scorrevole ad acque termali e fluidi geotermici.

I risultati conseguiti permettono di meglio chiarire alcuni importanti aspetti dell'idrogeochimica del Se.

In condizioni normali questo elemento presenta nelle acque tenori estremamente bassi (ordine dei pochi nanogrammi per litro). Acque molto mature e provenienti dalla lisciviazione di mineralizzazioni ed uranio possono contenere tenori più elevati, superiori a 1 ppb.

I dati sin qui ottenuti non permettono di giungere a conclusioni univoche sulla circolazione del Se nei processi idrotermali, nel mentre sottolineano l'importanza del Se nello studio degli inquinamenti.

ABSTRACT. — The geochemical behaviour of selenium is well known in its main lines since the studies by Goldschmidt and coworkers in the 1930's.

But very few data regarding the distribution and circulation of this element in natural waters are till-now available.

This gap in our knowledge is due to the low selenium contents found in normal natural waters (\ll 1 ppb), and to the lack of analytical methods sensitive and specific enough to measure such low levels.

This work was therefore planned along two main lines. As a first step, a relatively simple analytical method was devised which made it possible the measurement of few nanograms of selenium per liter.

This method is based on the extraction of the Se-APDC complex in chloroform, the re-extraction of the selenium in bidistilled water, and the subsequent determination by AAS in a graphite furnace.

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As a second step, this method was successfully applied to the analysis of natural waters corresponding to different geological and geochemical conditions, such as water samples from Italian rivers, ground and thermal waters, geothermal fluids, and water samples from calcrete areas in western Australia.

The data thus obtained make possible a better understanding of several aspects of the geochemical behavior of this element, of vital interest from the environmental standpoint.

Indeed, selenium is an element whose level in the environment is extremely critical: it is highly toxic in high amounts, but, at the same time, is essential for life.

1. Introduction

Although the geochemistry of selenium is generally well known in its main lines, there is still a lack of information about its behavior in the supergene environment, particularly as regards its distribution and circulation in natural waters.

During the 1930's, GOLDSCHMIDT and coworkers carried out a great deal of experimental and speculative work, which became the basis for a more complete understanding of the geochemical cycle of selenium. The following are the main points of GOLDSCHMIDT's scheme, which is still considered basically valid:

- 1) during magmatic activity, selenium is closely associated with sulphur, both as sulphide and as elemental sulphur;
- 2) during weathering processes, selenium behaves differently from sulphur and separates from it. Sulphur is oxidized to sulphate ion, geochemically very mobile, whereas selenium is oxidized to elemental state or to the selenite ion; and both these compounds exhibit a much lower geochemical mobility than sulphate ion does;
- 3) during the sedimentary process there is a selenium enrichment in the shales and in the iron and manganese deposits. This is due primarily to the adsorption of the selenium present in the natural waters by clays, and Fe and Mn hydroxides.

If a closer look is taken of what is known of the hydrogeochemistry of Se, it can be seen that no significant progress has been made for many decades. This is mainly due to the lack of analytical methods capable of furnishing reliable data on the very low contents (well below the 1 ppb level) of selenium in normal, natural waters.

Only recently there was a growing interest in the hydrogeochemistry of selenium. New analytical techniques have been adopted based on neutron activation (KHARKAR et al., 1968; EWERS, 1976), on atomic absorption (FERNANDEZ, 1973) and on new enrichment methods (CHAU, RILEY, 1965).

The environmental geochemistry of selenium is, on the other hand, of particular and ever-growing interest because the amount of this element in water and soil is proving to be of fundamental importance for the agriculture and for the man's own health. While a high selenium content in the environment and in the food chain has proven to be definitely toxic for many animals, including man, a selenium deficiency has likewise been found to have a considerable negative impact on agriculture, as well as on the health of animals.

The aim of this paper is to contribute to a better understanding of the hydrogeochemistry of selenium. Research was conducted along two main lines. In the first place, an analytical method was devised (which is based on the selective extraction of selenium, and its determination by means of a graphite furnace) capable of furnishing meaningful data down to a few nanograms per liter. Subsequently, a large number of natural water samples corresponding to a high variety of geochemical conditions was analyzed by this method.

The analytical results made it possible to draw some conclusions of general interest, such as, e.g., that the geochemical mobility of selenium, in a broad range of environmental conditions, is low; however, at the same time, they led to a number of new questions dealing with the pathway of circulation of selenium, and to the geochemical factors regulating the migration of this element in natural waters. Future studies will lead to a better understanding of the behavior of this interesting element. In our laboratory an extensive and indepth study of the geochemistry of selenium has been planned. Besides flameless atomic absorption methods, neutron activation techniques will soon be employed.

The necessity of using highly specific and sensitive analytical methods in geochemical studies must once again be stressed. This applies also to the area of environmental geochemistry. In fact, analytical methods, which do little more than determine the threshold levels set by law, are not sufficient; what is necessary is to be able to measure accurately the amounts of certain elements corresponding to the normal geochemical levels occurring in nature. Only in this way it is possible to broaden, on the one hand, basic geochemical knowledge of the element under study, and, on the other hand, to discriminate between the contribution by the natural processes, and by pollution. This is the only approach which can furnish a scientific basis to research in environmental geochemistry.

2. Analyses of selenium in natural waters

2.1. General

The level of selenium in sea water is approximately 0.1 ppb, and fresh waters show, in general, much lower levels.

In order to more closely examine the normal hydrogeochemical behavior of selenium, it was first necessary to develop an analytical method which would have a far greater sensitivity than reported on by several authors, which would be sufficiently selective, and which would not require time-consuming procedures and expensive apparatus.

Most methods reported on in the literature for the analysis of selenium are based either on the neutron activation technique (KHARKAR *et al.*, 1968), or on the selenium separation, through the development of H_2Se , or by solvent extraction, and subsequent analysis by means of atomic absorption techniques.

FERNANDEZ (1973) proposed a method based on the development of H_2Se using

NaBH_4 and HCl with the introduction of the developing gases directly into the flame of the atomic absorption spectrophotometer. The detection limit was 150 ng/l when EDL discharge lamps were used. THOMPSON and THOMERSON (1974) proposed the introduction of the H_2Se bearing gases into a quartz tube mounted on an air-acetylene flame to obtain the atomisation of selenium. The detection limit is 180 ng/l. GOULDEN and BROOKSBANK (1974) proposed an automatic H_2Se developing system, reaching a detection limit of 100 ng/l.

CARBIN and BARNARD (1976) improved the H_2Se developing technique and obtained an absolute sensitivity of 12 ng corresponding to 120 ng/l, starting from 100 ml sample aliquot.

Lastly, HERMAN (1977) reported on a completely automatized system for the development of H_2Se with a detection limit of 50 ng/l.

As far as the solvent extraction is concerned, MULFORD (1966) proposed the extraction of selenium with ammonium-pyrolidin-dithio-carbamate (APDC) dissolved in methyl-isobutyl-ketone (MIBK) at pH values from 3 to 6.

CHAMBERS and Mc CLELLAND (1976) proposed using APDC in chloroform. At a pH value lower than 5, the extraction was found to be quantitative.

2.2. Choice of method

The authors preferred the solvent extraction technique since it allows for higher enrichment factors than would be obtained with the hydride development technique.

Preliminary tests on the use of APDC either in MIBK or CHCl_3 yielded positive results. It was decided to use CHCl_3 because this solvent, unlike MIBK, has higher density than water and it can thus be easily separated in a separatory funnel.

Once all the selenium contained in the water sample has been extracted in an organic phase, a second re-extraction of selenium in bidistilled water is recommended. The advantages are twofold:

- a) the obtainable, global enrichment factor is much higher, and
- b) much better results can be obtained with the graphite furnace, because there is no interference by the organic substances (APDC + CHCl_3).

Br_2 has proven to be highly efficient in destroying the APDC-selenium complex. This however led to the presence of organic substances — derived from the decomposition of APDC — in the water added in order to re-extract the selenium. These substances would interfere with selenium determination in the furnace.

In view of these problems, an effort was made to find a way of extracting selenium selectively. Tests have shown that at a pH of 0.5-1, the APDC chelates the selenium both quantitatively and selectively, with respect to the other metallic ions in solution.

With the use of the smaller amount of APDC necessary for chelating all of the selenium present in the sample to be analyzed, there were no precipitates in the water used for the re-extraction. Fifty μl of the 0.1% APDC solution are enough to chelate 500 ng of selenium. If the amount of selenium in the aliquot to

be analyzed is greater, it is advisable to decrease the volume of water without increasing the APDC amounts.

A small amount of Br_2 goes into the final aqueous phase and this is enough to produce a quenching effect on the atomic absorption signal produced by selenium. This interference was eliminated by washing out the excess Br_2 with CHCl_3 .

The global enrichment factor is 200 under routine conditions, and it may be further increased without producing any serious problems.

The sensitivity obtained is in the order of 2.3 ng/l.

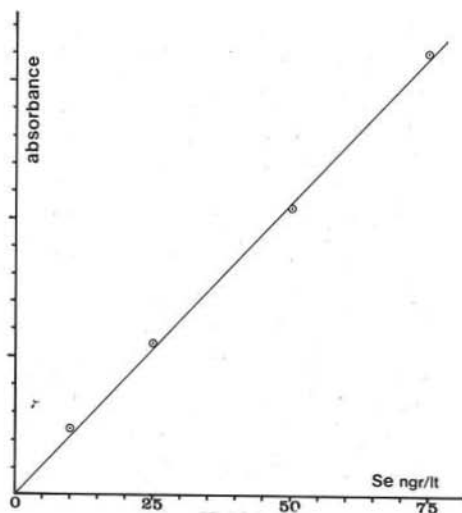


Fig. 1. — Calibration curve for Se analysis by flameless atomic absorption, according to the extraction procedure described in the text.

5 microliters of Br_2 — dissolved in CHCl_3 in a volumetric ratio of 1:4 — are then added, and the whole is then shaken for 10 seconds. 1 ml of bidistilled H_2O is added and then shaken again for 2 minutes.

At this stage, all the selenium originally contained in the sample will be concentrated in the 1 ml of H_2O .

0.5-0.7 ml are then removed from this re-extracted one milliliter, and washed in a small diameter test tube (for an easier pipetting) for 30 seconds with 100 microliters of CHCl_3 . At this point, the washed solution is ready to be analyzed by AAS.

2.3. Operating procedure

An aliquot of 100 or 200 ml of the sample to be analyzed is placed in a 500 ml separatory funnel: HCl 1:2 is added until a pH of 0.5-1 is reached (check with indicator paper pH 0.5); 50 microliters of freshly prepared APDC solution at 0.1% are then added and the whole mixture is shaken for one minute. 2.4 ml of CHCl_3 are added, and extraction is then carried out by shaking for 15 minutes.

The mixture is then left to rest for 2 minutes after which the CHCl_3 containing the organo-metallic complex is collected and placed in a 10 ml test tube.

1.5 ml of CHCl_3 are added to the aqueous solution left in the separatory

funnel, which is then shaken again for 5 minutes and, after it has been allowed to rest, the organic phase is collected in the same 10 ml test tube.

This washing technique should be repeated once more and the organic phase should again be added to the same test tube.

Upon completion of the above operation, all the selenium originally present in the water sample aliquot is transferred into the 5-7 ml of APDC- CHCl_3 solution.

5 microliters of Br_2 — dissolved in CHCl_3 in a volumetric ratio of 1:4 — are then added, and the whole is then shaken for 10 seconds. 1 ml of bidistilled H_2O is added and then shaken again for 2 minutes.

At this stage, all the selenium originally contained in the sample will be concentrated in the 1 ml of H_2O .

0.5-0.7 ml are then removed from this re-extracted one milliliter, and washed in a small diameter test tube (for an easier pipetting) for 30 seconds with 100 microliters of CHCl_3 . At this point, the washed solution is ready to be analyzed by AAS.

The reagents used are:

- 1) a 1000 ppm Se stock solution (FISCHER) which is diluted to the desired concentrations with distilled water passed through Milli-Q Systems for High Purity Water (Millipore);
- 2) HCl of Aristar-BDH or Carlo Erba RPE grade;
- 3) Baker Analyzed Reagent grade CHCl_3 ;
- 4) BDH Br_2 ;
- 5) BDH APDC, $\text{CH}_2 \cdot (\text{CH}_2)_2 \cdot \text{CH}_2 \cdot \text{N} \cdot \text{CSS} \cdot \text{NH}_4 = 164.29$.

Fig. 1 shows the working curve obtained with the above described procedure starting from a 200 ml aliquot of standard solutions.

3. Results

With the very sensitive and reliable analytical method at hand, the authors sought to examine a series of natural water samples corresponding to a wide range of conditions and/or geochemical processes, in order to clarify some ambiguous aspects of Selenium's hydrogeochemistry.

In the first place, the waters of some of Italy's most important rivers were analyzed. All together, the data thus obtained are a very important reference point as they refer to highly variable conditions, as regards the hydrogeological and lithological conditions of the different watersheds, the climatic conditions and, lastly, the different degree of urbanization and industrialization of the areas within the various river basins.

Samples of thermal water having different characteristics were also examined from the point of view of their thermality as well as their hydrogeochemical features. Samples of the thermal waters from the Campi Flegrei, Viterbo, Sasso Pisano, Saturnia, Rapolano and Stigliano areas were analyzed. Geothermal fluids from Cesano 1 well (Rome), the Camorsi well (Larderello), the Lustignao well (Larderello), and the condensed water from the Miniera 1 well (Larderello), were also studied.

As far as the geochemistry of selenium is concerned, there is still a great number of points that have to be understood within the subject of hydrothermal circulation also.

Samples of water collected in the desertic area of western Australia were studied, since in this area the waters are very strongly oxidizing and the levels of organic substances are very low, conditions which both should facilitate the solubilization of selenium. It has been demonstrated that these conditions are favorable to the enrichment of uranium and vanadium in natural waters.

Uranium-rich ground-water samples from the Apulia Tavoliere (plains) were also examined.

Water samples corresponding to the transition environment, such as the « Acqua Rossa » spring (Viterbo), and drainage waters from the Niccioleta and Bocchegiano (Grosseto) pyrite mines, were also analyzed.

TABLE 1
Se content in natural waters

El. conductivity values are given in $\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-4}$

Sample N°	Sampling site	Date of collection	t. °C	pH	Eh(V)	Elect. Cond.	U(ppb)	Se(ng/l)
ITALIAN RIVERS								
14726	Arno (Pisa)	18.7.77	27.5	7.7	.310	1.4	.53	90
14727	Entella (Chivari)	18.7.77	23.5	8.5	.410	2.7	.22	60
14728	(Ticino (Pavia)	19.7.77	10.5	7.6	.380	1.6	.27	20
14730	Po (Pavia)	19.7.77	21	7.7	.380	2.8	1.06	60
14734	Pescara (Pescara)	26.7.77	20	7.5	.390	6.3	.94	<2
14769	Bormida (Alessandria)	3.12.77	5	6.5	.220	5.8	.78	170
14872	Marta (Viterbo)	10.3.78	10	8.5	.260	56	n.d.	<2
A	Tevere (P.te Milvio)	25.2.78	10.5	7.5	.330	82	n.d.	<2
B	Tevere (P.te Marciani)	25.2.78	10.5	7.7	.320	81	n.d.	25
C	Aniene (Prato della Signora)	25.2.78	13	7.3	.330	110	n.d.	<2
12945	Orcia(upstream conf.Orcia river)	9.11.73	14	8.5	n.d.	118	n.d.	10
THERMAL WATERS								
14713	Stufe di Nerone-Bacoli(Napoli)	12.7.77	87	6.7	.360	380	.34	<2
14714	Pisciarelli B1 300 m S.E. di A	13.7.77	87	2	.570	89	4	<2
14715	Pisciarelli B2 " " "	13.7.77	83	1.3	.560	110	5.5	<2
14716	Fanghiera (Agnano Terme)	13.7.77	64	6.4	.210	110	.37	<2
14717	Pisciarelli A (Agnano)	13.7.77	63	3.3	.570	47	.79	<2
14721	Terme Putuelane (Pozzuoli)	13.7.77	67	6.9	.320	100	135	55
14724	Terme Salute (Pozzuoli)	14.7.77	31	6.5	.330	30	38.5	110
14871	Tuscania (Viterbo)	10.3.78	23	6	.050	29	0.5	<2
14873	Bullicame (Viterbo)	10.3.78	64	6.7	.320	28	0.04	<2
14874	Bagnaccio (Viterbo)	10.3.78	65	6.8	.050	26	1.2	5
12826	Bagnaccio (Viterbo)	9.4.73	65	6.3	.040	26	1.2	<2
14876	Stigliano (Roma)	10.3.78	48	6.8	.030	39	1.2	<2
12827	Saturnia (Grosseto)	9.4.73	36	5.9	.510	34	n.d.	<2
12836	Rapolano (Siena)	11.4.73	38	6.6	.070	65	n.d.	3
12948	Petriolo Terme (Siena)	9.11.73	41	6.4	.030	43	n.d.	<2
D	Sorgente Sasso Pisano	7.3.78	59	n.d.	n.d.	n.d.	n.d.	<2
GEOTHERMAL FLUIDS								
E	Cesano 1 (Roma)	10.1.75	n.d.	8.5	n.d.	n.d.	40	20
F	Pozzo Lustignao 8 (Lard., -1945mt)	7.3.78	240	n.d.	n.d.	n.d.	n.d.	2
G	Codensa Miniera 1 (Larderello)	3.3.78	n.d.	n.d.	n.d.	n.d.	n.d.	3
12832	Pozzo Camorsi 3(acqua Trasc.)(Lard.)	10.4.73	95	8.0	.040	13	n.d.	15
WESTERN AUSTRALIA								
14010	Calcrete basins	7.7.73	19	7.6	.240	11	7.2	330
14011	" "	7.7.73	24	7.6	.270	12	17	185
14012	" "	7.7.73	23	7.3	.280	26	164	8
14013	" "	7.7.73	25	7.3	.310	48	86	15
14018	" "	8.7.73	22	8.0	.330	170	298	76
14019	" "	8.7.73	19	8.4	.280	92	104	158
14021	" "	8.7.73	23	9.9	.280	300	574	110
14022	" "	8.7.73	22	9.5	.260	180	226	55
14923	Lake Water 5 Miles S-E Yalgoo	10.7.73	24	9.3	.270	350	141	200
ITALIAN GROUND WATERS								
14308	Tavoliere (FG) ground water	9.9.75	20	7.3	.290	160	73	385
14310	Tavoliere (FG) artesian water	9.9.75	22	8.5	.450	43	12	155
14312	Tavoliere (FG) ground water	9.9.75	18	7.3	.330	84	30	35
14875	Acqua Rossa spring (Viterbo)	10.3.78	19	6.2	.320	11	0.38	<2
12828	Boccheggiano pyrite mine (Grosseto)	10.4.73	17	7.5	.040	22	n.d.	3
12830	Niccioleta (Grosseto)	10.4.73	15	7.4	.040	21	n.d.	10
14881	U mine (Val Rendena)	7.7.73	12	7.9	n.d.	3.4	50	1940
14882	" " " "	7.7.73	17	7.9	n.d.	4	25	10

And finally, the waters coming from the uranium-bearing mineralizations in the Permian formations of the Rendena Valley (Trentino Region) were sampled and analyzed.

The data obtained are given in Table 1.

4. Discussion

4.1. General

The pH-Eh diagram of fig. 2 illustrates the supergene behavior of selenium, compared with that of S, U and Fe.

In addition to what is shown in the figure, it must be stressed that the stability field of selenium (VI) is not reached under normal conditions, and the formation of the selenate ion — which does not form insoluble compounds and is not adsorbed — only occurs under metastable conditions (SATO, 1960).

The mobilization of selenium, however, is not necessarily dependent on its passing to state VI. Selenium can go into solution — infact — as selenite ion, SeO_3^{2-} , but this ion is easily adsorbed by a large number of substances, especially by Fe hydroxides, clays and organic substances. Under alkaline conditions (pH 8), the adsorption of the selenite ion decreases; and above a pH of 11, it is not adsorbed at all. At low pH values, Se becomes immobile whether by precipitation of the elemental Se or by adsorption of the selenite. Lastly, it should be mentioned that the ferroselite (FeSe_2) is very stable (HOWARD, 1977); its field of stability was not shown in fig. 2.

The hydrogeochemical behavior of Se can be better understood if it is divided into two separate processes: a) the leaching of the Se from the minerals in which it is contained, and b) its partitioning between solid and liquid phases once the selenium has passed into solution.

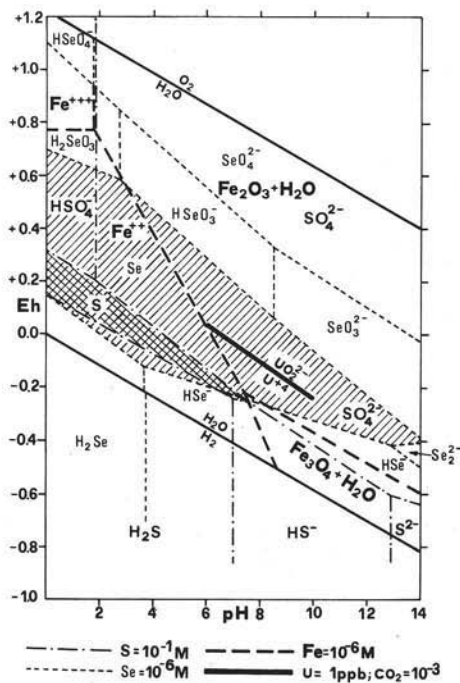


Fig. 2. — Equilibrium distribution of the species of: Sulfur, Selenium, Iron and Uranium at 25° C and 1 atmosphere total pressure for activities as specified above. Selenium and Sulfur data from DYACHKOVA and KHODAKOVSKIY (1966), Iron from GARRELS and CHRIST (1965), Uranium from DALL'AGLIO and TONANI (1960).

mostly immobile. This is what happens, for example, in the weathering of sulphides. Selenium will only be able to enter into solution when the pH increases — owing e.g. to the buffer effect of carbonate minerals —, and when all of the Fe and Mn has been oxidized and precipitated as hydroxides. If the weathering takes place under basic conditions, then Se is more likely to enter into solution as a selenite ion.

Once the selenite is in solution, its fate depends mainly upon the predominance of one of the antagonistic processes of adsorption and desorption.

This dynamic equilibrium depends not only on the pH value, but also on the composition of the substances with which the waters come into contact, as well as on the hydrodynamic conditions.

A comparative examination of the elements given in fig. 2 clearly reveals their different behavior. In the supergene environment, Se and S behave quite differently, due to the very different stability fields of the sulphates and selenates.

The difference of Eh which correspond to the passage of U (IV) - U (VI) and that of Se^0 - Se (IV) should be noted.

4.2. *Surface Waters*

The results presents by KHARKAR et al. (1968) are of significant interest in acquiring a better understanding of the hydrogeochemical behaviour of Se.

- a) The Se content of about ten important rivers in different continents, i.e. in waters whose hydrogeochemical history has varied considerably between one and another, is remarkably close to a value of 0.1-0.2 ppb.
- b) The amounts of Se which can easily be « adsorbed and desorbed » by the various clays represent a high percentage of the circulating selenium.

These observations, together with the circumstance that under natural conditions, the valence state 6^+ is seldom reached, clearly indicate that Se, which occurs mainly in the form of selenite in the supergene environment, is subjected to a series of very intense processes of adsorption and desorption. It is the result of this dynamic equilibrium that can lead to the content value of 0.1-0.2 ppb found in all the analyzed rivers.

The data relative to the surface waters examined here are not homogeneous. In the first place, it must be noted that, as far as Italian rivers are concerned, the Se values tend to be very low (in the range of a few nanograms per liter) in those rivers which are not highly polluted. The case of the Tiber river upstream from Rome and that of the Marta, Ombrone and Pescara rivers are significant.

In the other rivers examined, the Se level seems to indicate a certain degree of pollution rather than the presence of particular geochemical processes within the individual basins. It is not by chance that the Bormida at Alessandria and the Arno at Pisa show the highest Se levels among the samples studied.

Italian rivers show lower Se values than canadian surface waters do (TRAVERSY et al., 1975).

LAKIN (1973) in his comprehensive review of the geochemistry of Se reports on a series of some very high selenium values found in the surface waters from Colorado. During the course of the present project, samples of waters collected a few years ago from calcrete areas of western Australia were analyzed. The very arid climatic conditions of these areas, characterized by low concentrations of organic matter, and by evaporitic conditions, *sensu lato*, might enable the natural waters

to reach very high levels of selenium, as it was demonstrated for vanadium and uranium (DALL'AGLIO et al., 1974).

The data obtained and presented in table 1 show that the selenium contents are, on the average, relatively high, but these values do not appear to be correlated with the V and U content values, or with the increasing salinity along the calcrete basins.

In this case also it seems that the basic process regulating and limiting the Se level in natural waters is the adsorption by the clay minerals.

4.3. Ground Waters

As was mentioned above, the water of the Acqua Rossa spring (northern Latium) and the discharge waters of the Boccheggiano and Niccioleta pyrite mines (Tuscany) were also analyzed. These waters correspond to a transition environment, which goes from reducing to oxidizing conditions, with the subsequent precipitation of Fe and Mn and the simultaneous solubilization of uranium (See fig. 3).

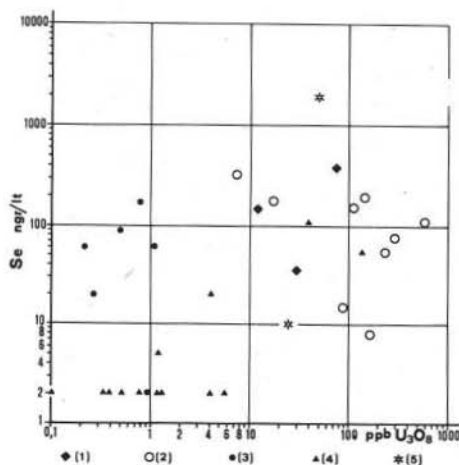


Fig. 3. — Selenium versus Uranium content. (1) Ground waters from Apulia Region (Italy). (2) Water samples from calcrete areas (Western Australia). (3) Italian rivers. (4) Italian thermal waters. (5) Ground waters from uranium mineralization (Val Rendena, Italy).

14310 was collected from an artesian well. These water samples are characterized by a chloride-sulphate chemism and high salinity. These waters strongly interacted with sedimentary formations of marine origin.

The above-mentioned samples were analyzed for selenium as they had very high uranium contents.

The two water samples collected in the uranium bearing Permian formations of the Rendena Valley yielded widely differing results. The first sample, with almost 2 ppb Se, comes from uranium, and probably also selenium, mineralized sandstones,

The «Acqua Rossa» has a Se content below the detection limit, whereas the other two waters given values of 3 and 10 nanograms/liter respectively.

The latter two waters derive from the oxidation of hypothermal pyrite deposits which, despite the lack of direct information, should have a high Se content. The low content found in these waters can be attributed to the coprecipitation or adsorption of the Se by Fe and Mn hydroxides.

The underground waters of the Apulian Tavoliere have revealed high Se levels. These waters were sampled in the northeastern part of the area, between the Triolo and Celone torrents (Foggia).

While samples 14308 and 14312 were taken from the free water table, sample

whereas the second comes from the Permian volcanics in which there are no U ore bodies and has a Se content of only 10 nanograms per liter.

4.4. *Thermal Waters*

Within the framework of this investigation, a great variety of thermal waters were analyzed and the results are given in table 1.

The Se content of the thermal waters of the Flegrean area showed no sign of being positively correlated to the temperature; as a matter of fact, the only two samples that yielded significant analytical data were the Terme della Salute ($t = 31^{\circ} \text{C}$) and the Terme Puteolane ($t = 67^{\circ} \text{C}$), i.e. springs characterized by rather low temperatures.

Other thermal springs (Saturnia, Bagnaccio, Bullicame, Rapolano, Stigliano) were found to have very low selenium contents (a few nanograms/liter).

Very interesting results were obtained from the analysis of samples of geothermal fluids. The water from the Camorsi well has a Se content of 17 ng/l, whereas in the water of the Lustignao well Se is below the detection limit. The brine of the Cesano well 1 contains 20 ng/l. Noteworthy is that the condensate of Mine 1 of Larderello yielded 3 ng/l.

From all the data presented here it would seem that Se is not one of those elements like, for example, As and Hg which are mobilized selectively during hydrothermal processes; the data given here, however, are not conclusive in this regard.

It has to be taken in mind that H_2Se is stable under reducing condition, being a gas even at room temperature. This gas may escape into the atmosphere during the « Flashing process ».

Hence, it will be necessary to study samples fully representative of the volatile phase too, if valid conclusions regarding this topic are to be drawn.

4.5. *Association between U and Se in natural waters*

A peculiar aspect of selenium is its geochemical association with U which is found in many types of uranium-bearing mineralization. An even more exceptional circumstance is represented by the association of these two elements in the waters leaching uranium-bearing mineralizations (LAKIN, 1973).

Fig. 1 clearly show that in a pH-Eh diagram, there are consistent differences between U and Se, as regards the stability fields of insoluble forms and mobile species. Thus, uranium passes into a hexavalent form while the Se^0 form continues to be stable. Under oxidizing conditions, in the field of stability of selenite, it must be remembered that uranium (VI) shows a much greater geochemical mobility over the entire range of pH values encountered in nature.

Fig. 3 shows a correlation diagram between Se and U, relative to the sample analyzed. On the whole there is a positive correlation, but if one goes into greater detail, contradictory trends can be noted. Although a positive correlation seems

to exist for the thermal waters examined, and for the waters from the Italian rivers, there is a negative correlation between Se and U in the Australian waters. This last case lends itself to geochemical considerations of a general character.

In fact, in this area there are no polluting processes which might mask the natural processes regarding the circulation of Se. If one moves along the calcrete basin, one sometimes notices a definite decrease in the Se content, whereas elements such as vanadium and uranium continue to increase.

This tendency indicates that the geochemical mobility of Se is much lower than that of uranium and, hence, a geochemical association between these two elements in natural waters is not always feasible.

5. Conclusions

Selenium is one of the most interesting elements from the environmental standpoint, because, although it is highly toxic in high concentrations, it is also essential to the life of plants, animals and humans (Frost, 1977).

As far as its distribution and circulation in natural waters are concerned, it must be first pointed out that only very few data are available for Italy. In more general terms, it may be remembered that there are still many unexplained aspects of the hydrogeochemical behavior of this element. A quantitative evaluation of the environmental contamination by human activity must include precise information regarding the normal Se back-ground level under natural conditions.

Research on the hydrogeochemistry of selenium was undertaken because of all these reasons.

In the first place, a new analytical method was devised in order to measure Se contents in natural waters. This method, which is characterized by very high sensitivity (2 ng/l), is based on the extraction of Se-APDC chelate in chloroform, re-extraction in bidistilled water, and the subsequent determination by AAS with a graphite furnace (P.E. Mod. 503 and HGA-72). This made it possible to measure the Se content of samples of natural waters corresponding to different geochemical conditions.

The results obtained indicate that Se contents in the natural waters of Italy are generally very low where no pollution exists. Ten major Italian rivers were analyzed. All of them contain less than 0.1 ppb except for the Bormida river at Alessandria which has a content of 0.170 ppb. Of significance is the case of the Tiber River that has Se contents below the detection limit (2 ng/l) upstream from Rome, and 25 ng/l downstream Rome.

The data obtained also show that, under particular geochemical conditions, much higher levels can be reached. As far as Italy is concerned, almost 2 ppb were found in the uranium mineralization drill-hole in the Permian sandstones of the Rendena Valley, and fractions of ppb in the watertable waters in the

Apulia Tavoliere. Waters samples from the western desert of Australia have yielded 0.1-0.3 ppb Se.

Studies were conducted on thermal waters corresponding to a wide range of conditions: from the slightly thermal springs of northern Latium, to the thermal springs of the Campi Flegrei, to geothermal fluids. The analytical results show that the Se contents are never very high, but these data cannot be considered to be conclusive, because Se can form volatile compounds (H_2Se) under reducing conditions, and the samples studied were not representative of the volatile phase.

As far as the geochemical mobility of Se in the supergene environment is concerned, the data gathered indicate, in general, low values. Se is unable, in fact, to form the selenate ion which display a very high mobility. The water samples collected in the desert areas of western Australia show that there is no increase in selenium as the evaporitic processes continue.

These conditions have proven to be almost ideal in bringing about a noticeable increase in the level of other metals such as vanadium and uranium, owing to the scarcity of organic substances and the high pH and Eh values.

Under natural supergene conditions, Se (IV) is stable and can pass into solution especially when the pH values are high, but it is easily adsorbed by solid phases, particularly by the clay minerals with which it comes in contact. The Se contents found in natural waters are the result of two contrasting processes, on the one hand the dissolution of selenite is not hindered by the existence of very insoluble salts, and, on the other hand, the Se in solution is easily adsorbed by clay minerals, organic matter, and Fe and Mn hydroxides.

The Se contents may vary considerably according to which of the two contrasting processes prevails. This requires a direct measurement of Se in order to find out its concentration in the various environments. The availability of a suitable analytical method should facilitate the future acquisition of more data.

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