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Hydrogeochemical exploration for gold in the Osilo area, Sardinia, Italy

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Abstract—A study to test the use of hydrogeochemical methods for gold prospecting was carried out in the Osilo area, northern Sardinia. The study area, covering about 30 km^2, is characterised by Tertiary andesitic rocks. Gold concentrations up to several ppm, associated with abundant pyrite, arsenopyrite, stibnite, tetrahedrite and electrum, and subordinate galena, sphalerite and chalcopyrite, are present in quartz veins associated with a polyphase, incipient and pervasive alteration of the andesitic rocks.

Forty-eight water samples (17 streams, 29 springs and 2 boreholes) were analysed for Au and a wide range of major and trace elements, both in solution (<0.4 μm) and in suspension. Background values for dissolved Au were below the detection limit of the methods used (between 0.3 and 0.5 ng L^{-1} Au). Gold concentrations in solution up to 3 ng L^{-1} were found in waters draining the mineralised vein system. The observed dispersion of Au in surface waters was restricted to about 500 m from the auriferous veins. Dissolved Au anomalies do not vary significantly in water samples, taken monthly over a one year period, suggesting that the dispersion of Au is unaffected by seasonal conditions in the Osilo area. For samples where Au was detected both in solution and in suspension, the Au content of the suspended matter was usually lower than that in solution.

The best indicators of Au mineralisation, apart from Au itself, both in solution and in suspension, were As and Sb which showed a dispersion clearly related to the known auriferous veins.

INTRODUCTION

Direct hydrogeochemical prospecting for Au is not considered to be a promising method owing to the low concentration of gold in natural waters, though recent work (Hamilton *et al.*, 1983; Hall *et al.*, 1986; McHugh, 1988; Bergeron and Choinière, 1989; Benedetti and Boulègue, 1989; 1991; Andrade *et al.*, 1991; Cook *et al.*, 1992; McHugh and Miller, 1992; Grimes *et al.*, 1993; Schmitt *et al.*, 1993) detected Au anomalies, in spring and surface waters, up to several tens or even hundreds of nanogrammes per litre (ng L^{-1}) in association with different Au deposits. For soil pore-waters in a tropical rain forest environment, an average dissolved Au concentration of 3.6 μg L^{-1} (with a maximum of 84.4 μg L^{-1}) has been reported from the Ashanti Au district (Bowell *et al.*, 1993a), while Séa *et al.* (1993) reported values up to 17 μg L^{-1} for auriferous laterites of Misséni.

A preliminary study in the U.K. (Cidu and Edmunds, 1990), to evaluate the possibility of direct hydrogeochemical prospecting for Au, concluded that dissolved Au occurs usually at the ng L^{-1} level in areas of known Au mineralisation in the climatic conditions of the U.K., with highest Au concentrations of 10 ng L^{-1}, and background values below the detection limit of 0.5 ng L^{-1}.

The aim of the present study was to test the feasibility of hydrogeochemical prospecting for epithermal Au deposits in Sardinia, both directly, using methodologies able to determine Au in solution and suspension at the sub-ng L^{-1} level (Cidu *et al.*, 1994), and indirectly by analysing a large set of minor and trace elements in solution and in the suspended matter, potentially associated to Au mineralisation, to determine the most promising hydrochemical markers of Au in similar environments.

GEOLOGICAL SETTING

The study area, covering about 30 km^2, is located in the district of Logudoro, northern Sardinia (Fig. 1), a few kilometres south of the village of Osilo. The area consists of hills (with altitudes between 665 m at Monte Pedrosu and 160 m at the Rio Mascari stream)

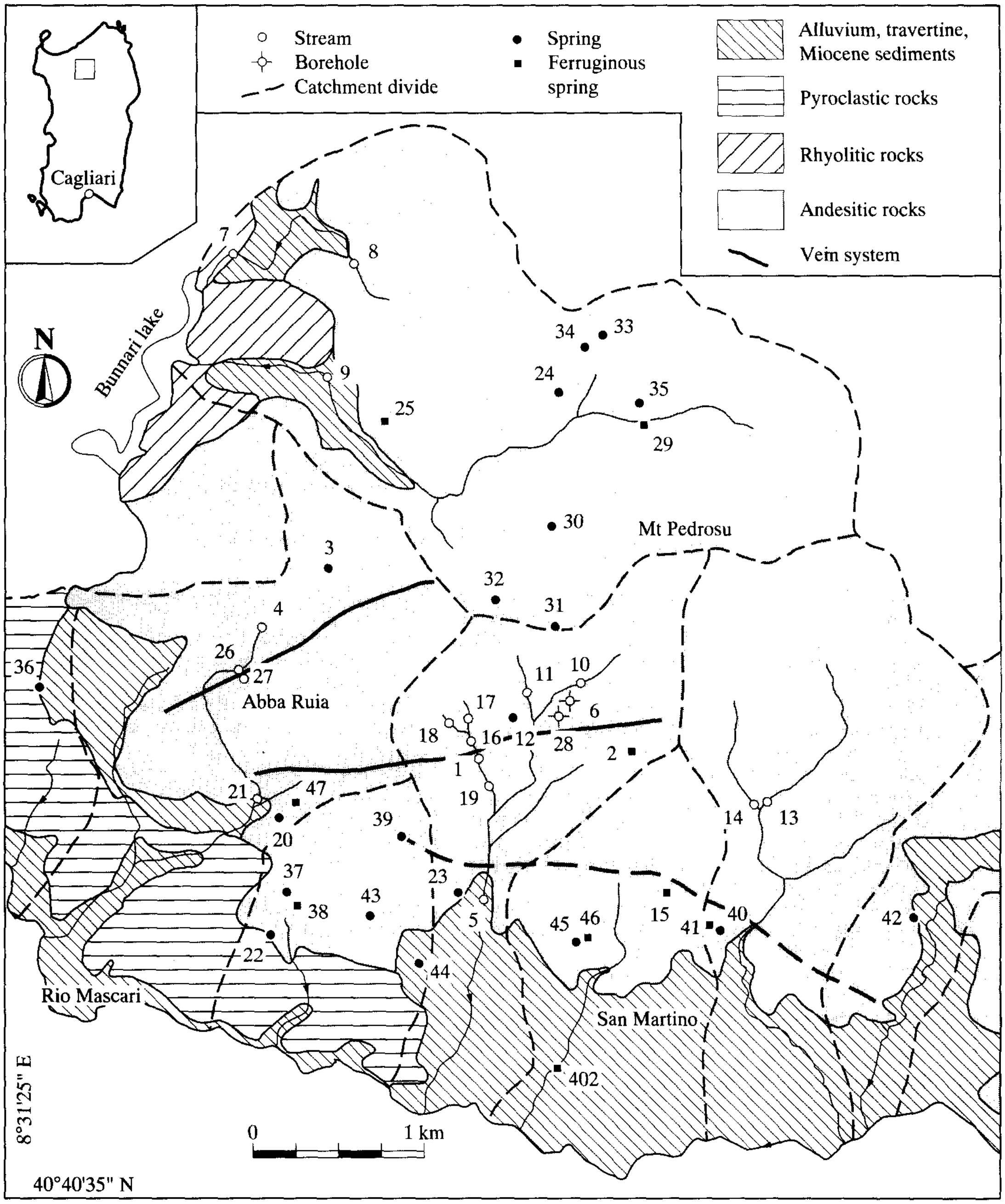

Fig. 1. Geological sketch map of the Osilo area with sample location.

covered with poorly developed soils and scanty vegetation.

Geology

In Sardinia, Tertiary volcanism took place when the Sardinia-Corsica microplate separated from the European continental margin during the Lower Oligocene; the earliest products were probably owing to crustal melting related to the early rifting phase. Subsequently, the opening of the Balearic Basin activated a subduction zone to which the main calc-alkaline volcanic cycle is related (Bellon *et al.*, 1977; Savelli *et al.*, 1979; Beccaluva *et al.*, 1980).

In Logudoro, 3 eruptive episodes, with ages ranging from 24 to 13 Ma, have been recognized; volcanic rocks are composed of basalts, basic andesites, andesites, dacites and rhyolites (Dostal *et al.*, 1982).

The Osilo area is characterised by Tertiary andesites, which show widespread alteration (potassic, propylitic or argillic), but of different degree and areal distribution. Geophysical studies indicate the volcanic massif of Osilo to be a well defined structure extending downwards to about 9 km (Pecorini *et al.*, 1988). Subordinate marine and lacustrine sediments

(Lower to Middle Miocene), and recent travertines outcrop above the volcanic rocks in the southern part of the area (Fig. 1).

Mineralisation

Mineralisation closely related to the Tertiary calc-alkaline volcanic rocks in Sardinia was known previously, but considered to be of minor interest, until recent studies showed occurrences of Au, Cu, Ag and other metals (Pretti, 1988).

In the Osilo area, an epithermal system of the low-sulphidation type, with ESE-WNW and ENE-WSW trending quartz veins, and associated with a polyphase, incipient and pervasive alteration of the andesitic rocks, was recognised (Fiori *et al.*, 1990). The mineralised quartz veins have a thickness of between 30 and 100 cm. They are usually brecciated and re-cemented by comb and saccharoidal quartz in small veins and geodes. Au is present up to several ppm (Fiori *et al.*, 1990), and the mineral assemblage consists of abundant pyrite, arsenopyrite, stibnite, tetrahedrite and electrum, and subordinate galena, sphalerite and chalcopyrite.

Hydrogeology

In the Osilo area, the mean annual temperature is 16°C, precipitation 800 mm, with 75 rainy days per year, a dry period usually extending from May to October, and high evapotranspiration. Surface drainage is made up of intermittent streams following lines of structural weakness.

The hydrogeology is dominated by the presence of aquifers in andesitic rocks. Piezometric surfaces generally follow the surface morphology with preferential discharges to thalwegs where the topographic surface cuts through the water table. The regional groundwater flow is from north to south, except in the northernmost catchment where east to west trending flow prevails.

In the studied area, there are a number of springs characterised by low average flow rates. Most of the springs originate from andesitic aquifers (Fig. 1), having shallow circulation and relatively short residence times, with recharge to the aquifers directly from rainfall. The boreholes and some of the springs are related to important faults which are loci of alteration and contain Fe- and Mn-oxides as well as disseminated sulphide minerals (Pretti, 1988). These waters can be distinguished clearly in the field due to the precipitation of brownish deposits of Fe-oxy-hydroxides at their emergence. These ferruginous waters are sometimes found in the immediate vicinity (within about 10 to 50 m) of non-ferruginous springs unrelated to faults (e.g. sample Nos. 38 near 37; 41 near 40; 46 near 45).

The San Martino thermal spring (sample No. 402) is a high-PCO_2 water representative of regional circulation in andesitic and pyroclastic facies, where inflow of CO_2 from deep origin occurs (Caboi *et al.*, 1993). Therefore, this sample must be regarded as a unique water.

SAMPLING AND ANALYTICAL METHODS

Sampling campaigns were performed in late April 1992 and February 1993, which represent roughly low and high flow conditions, respectively. Due to the semi-arid nature of Sardinia, spring and stream waters were collected in order to obtain a good coverage of the area. Forty-eight water samples were collected: 17 stream waters, 29 springs and 2 boreholes. The sample locations are shown in Fig. 1.

Five sampling sites (sample Nos. 6, 20, 21, 25 and 28) were monitored over a one year period to establish the seasonal variability; these samples were collected once a month, and on two occasions in duplicate for Au analysis by graphite furnace atomic absorption spectroscopy (GFAAS). Water flow was continuous, albeit fluctuating over the whole period; only the stream No. 21 was dry for part of the monitoring time.

Filtration on a 0.4 μm pore-size membrane filter (Nuclepore type 111130) was carried out, as close as possible to the sampling site, using an all-plastic filtration system (a domestic garden sprayer with a Millipore Swinnex-47 filter holder), or alternatively using an all-plastic filtration assembly (Sartorius SM 16510) under N_2 pressure.

Aliquots of filtered, unacidified water were collected, either in high-density polyethylene bottles (Nalgene), for the analysis of the major anions and PO_4^{3-}, or in a glass vial, for determination of total organic carbon (TOC). Sample preservation, for major cations and trace elements, was carried out on site, immediately upon filtration. For the determination of most metals, an aliquot was collected, in acid cleaned Nalgene bottles, and acidified using HNO_3 (final concentration 1% HNO_3, v/v), while for the determinations of As and Sb, and SiO_2, aliquots were acidified using HCl acid (final concentration 0.1% HCl, v/v). A sample of unfiltered water for the analysis of Hg, was collected in an acid-cleaned glass vial and stabilised to 0.1% H_2SO_4, v/v, and with some $KMnO_4$ crystals. Reagents used were BDH Aristar grade quality (or, at least, equivalent).

For dissolved Au analysis, 2 L samples were filtered and collected in acid-cleaned Nalgene bottles. Samples for Au-analysis by inductively-coupled plasma mass spectrometry (ICP-MS) were stabilised, immediately upon filtration, with 20 mL of concentrated HNO_3 and 60 mL of concentrated HCl to reduce adsorption of Au onto the container walls. Samples for Au analysis by GFAAS were stored unacidified, and acidified prior to preconcentration with 20 ml of a solution containing 5% (v/v) Br in concentrated HCl, which is highly efficient at liberating any adsorbed Au.

The acidification steps convert the Au present into ionic Au-chloride and/or -bromide complexes necessary for the subsequent preconcentration step.

Flow, temperature, conductivity, pH, Eh, dissolved O_2 (by gas-sensing electrode), alkalinity (by titration with 0.1 M HCl versus methylorange or bromphenolblue), and CN^- (by ion-selective electrode) were measured on site. Anion species (Cl^-, $SO_4{}^{2-}$ and $NO_3{}^-$) were analysed by chromatography, while NH_3 and F^- were determined using an ion-selective electrode. The TOC was determined by the combustion-infrared method. Phosphate and SiO_2 were determined by spectrophotometry; major cations by flame emission spectrometry, Al by GFAAS, other metals by inductively-coupled plasma optical emission spectroscopy (ICP-OES), ICP-MS or GFAAS techniques. Arsenic and Sb, and H_3 were determined by atomic absorption spectroscopy (AAS) after hydride or Hg-vapour generation.

Two independent analytical methodologies were used for the determination of Au (Cidu *et al.*, 1994):

(a) at the University of Cagliari: a preconcentration method based on anion exchange (Dowex AG 1X-8 resin), elution into an acetone-HNO_3 mixture, and finally extraction into 4-methylpentan-2-one (methylisobutyl-ketone, MIBK) was used. The MIBK phase was analysed on a Perkin Elmer Zeeman/3030 GFAAS, equipped with autosampler and pyrolytically coated graphite tube with platform;

(b) at the British Geological Survey: a preconcentration method based on solvent extraction into MIBK, destruction of the organic phase and uptake in 4% aqua regia, followed by analysis on a VG PlasmaQuad ICP-MS was used; instrumental drift was corrected using Pt as internal standard.

Recoveries, determined for each batch of samples using 2 L spiked solutions (with Au contents between 0.5 and 10 ng L^{-1}), were similar for both methods used, 84 ± 14% ($n=52$) and 83 ± 12% ($n=34$) respectively.

Two-litre blank solutions (high-purity water, Milli-Q, acidified as samples) were extracted together with each batch of samples and analysed using the procedures outlined above. Detection limits for Au (defined at 3 times the standard deviation on the blanks) varied between 0.3–0.5 ng L^{-1} Au depending on the blank variability. Day-to-day differences in instrument performance contribute to a significant spread in detection limits. A few water samples were analysed for Au by GFAAS after preconcentration by anion exchange, using a 1 l sample; for these samples, a detection limit of 1 ng L^{-1} Au was found and data are reported accordingly.

At the University of Antwerp, the suspended matter (defined as material retained on a 0.4 μm pore-size membrane filter), was analysed by instrumental neutron activation analysis (INAA) for Au and about 50 other elements. The analysis scheme comprised three irradiations, in different irradiation channels of the "Thetis" reactor (Institute for Nuclear Sciences of the State University at Ghent, Belgium) and subsequent measurements on a high-purity Ge semiconductor detector (Blommaert *et al.*, 1980).

The blank content for Au in the suspended matter was found to be 0.18 ± 0.08 ng per pellet (one pellet consisting of a 47 mm diameter 0.4 pm Nuclepore membrane filter and a 55 mm diameter Whatman 541 paper filter). As a consequence, the absolute detection limit for Au in the suspended matter is 0.25 ng per pellet, but owing to the activity, induced during neutron irradiation, of other components of the suspension this can, sometimes, increase up to 0.5 ng per pellet. This translates, for filtered volumes of between 6 and 0.5 L, to a detection limit for Au of between 0.04 and 1 ng L^{-1}.

RESULTS AND DISCUSSION

Background hydrogeochemistry

Table 1 reports selected parameters and chemical components determined in solution for waters from the Osilo area. The waters exhibit considerable variation in their degree of mineralisation: total dissolved solids (TDS) range from 310 to 1510 mg L^{-1}, with the exception of the San Martino spring (No. 402) which has a TDS of 3.2 g L^{-1}. The San Martino spring was the only sample clearly distinguished from the others as a marked $NaHCO_3{}^-$ composition, owning to the high-PCO_2. The other water samples show a general trend from Ca(Mg)–HCO_3 to Na(Ca)–Cl–SO_4 composition with increasing TDS values, but cannot be characterised easily on the basis of the major components. This is probably owing to differences in the alteration degree of andesitic rocks.

Ferruginous waters, defined here as containing more than 1 mg L^{-1} of Fe in solution, were generally near-neutral ($6.2 < pH < 6.8$, but for sample No. 41 having a pH of 4.5), non-reducing ($140 < Eh < 370$ mV) and contained, in most cases, dissolved O_2. The 0.4 μm pore-size membrane filter did retain only a small amount of the total iron present in any form in these waters. No increase in particulate Fe content was found when using membrane filters with pore-sizes down to 0.015 μm, suggesting that Fe is present in true solution or as small colloidal particles.

In most natural waters, the measured Eh cannot be assigned to a single thermodynamically meaningful redox couple (Stumm and Morgan, 1981; Hostettler, 1984; Lindberg and Runnells, 1984; Drever, 1988). However, in the case of the ferruginous waters, the measured Eh probably closely resembles the true Fe redox state (Doyle, 1968). At the Eh–pH conditions of the Osilo waters, ferrous iron in solution will be the dominant valency, mostly as Fe^{2+} and $FeHCO_3{}^+$ species, while for waters with an Eh < 300 mV also the

Table 1. Selected parameters and chemical data determined in solution (<0.4 μm) for waters from the Osilo area

No.	Temp °C	pH	Eh mV	O_2 mg L^{-1}	TOC mg L^{-1}	CN μg L^{-1}	TDS mg L^{-1}	Ca mg L^{-1}	Mg mg L^{-1}	Na mg L^{-1}	K mg L^{-1}	Alk mg L^{-1}	Cl mg L^{-1}	SO_4 mg L^{-1}	Fe μg L^{-1}	Mn μg L^{-1}	Zn μg L^{-1}	Co μg L^{-1}	Ni μg L^{-1}	Cu μg L^{-1}	As μg L^{-1}	Sb μg L^{-1}
1	14	7.9	459	10.9	1.8	<10	575	70	30	87	2.3	264	161	70	17	12	8	0.2	0.5	4.0	2.8	0.7
2	18	6.2	311	3.5	nd	nd	663	58	25	110	5.9	89	172	185	1842	1840	85	18	5.2	5.0	20	0.8
3	22	5.8	479	8.5	nd	nd	376	28	11	59	7.8	22	116	100	163	555	55	7	3.9	3.0	3.0	0.7
4	15	7.6	427	10.9	6.1	<10	311	24	13	55	2.3	53	81	74	40	6	9	0.1	<0.5	1.6	3.4	0.5
5	22	8.0	286	11.1	3.7	<10	809	110	42	109	5.9	183	189	236	3	4	8	0.2	<0.5	3.0	7.7	1.0
6	18	6.6	234	0.3	6.4	24	955	115	43	131	6.6	206	190	326	10985	1106	16	4.9	2.2	9.4	69.2	10.4
7	13	8.0	507	11.6	11.2	nd	1136	141	64	172	4.3	303	405	180	209	86	42	0.3	<0.5	2.8	0.8	0.1
8	17	7.4	509	10.1	nd	nd	696	88	35	111	0.8	156	200	166	114	251	21	<0.1	<0.5	2.3	<0.5	<0.1
9	16	7.3	466	9.8	16.9	<10	639	87	29	82	3.5	41	148	244	21	177	22	1.7	2.6	3.9	<0.5	0.2
10	12	7.5	495	10.9	5.3	<10	821	115	38	93	2.0	87	197	310	3	2	7	0.2	<0.5	2.0	<0.5	0.1
11	19	7.7	375	9.1	6.8	nd	1382	187	85	189	5.1	324	424	314	27	4	14	0.3	<0.5	3.0	<0.5	0.2
12	16	7.2	458	6.6	<1	<10	1170	92	73	227	2.0	388	405	160	3	1	11	0.1	<0.5	2.5	<0.5	<0.1
13	18	8.0	374	9.9	2.1	<10	753	95	41	95	4.7	303	189	159	23	6	9	0.2	<0.5	2.7	1.0	0.2
14	17	7.7	380	7.6	nd	<10	795	111	39	99	3.9	153	172	267	13	2	11	0.2	<0.5	1.7	1.0	0.8
15	17	6.6	215	2.8	1.3	<10	670	82	29	97	3.1	159	137	200	7900	594	33	8.5	4.7	5.4	245	6.1
16	17	8.2	381	11.0	<1	<10	564	74	31	85	2.0	266	143	73	26	21	11	0.2	<0.5	2.9	17	0.7
17	17	7.6	400	8.5	3.5	56	598	85	35	85	2.0	310	150	66	28	58	12	0.4	<0.5	2.1	2.9	0.5
18	21	8.0	393	10.1	2.7	28	571	69	31	94	2.0	2.61	136	79	42	9	13	0.1	<0.5	3.8	1.1	0.7
19	24	8.7	339	11.5	7.8	<10	560	66	30	91	2.3	258	145	75	12	6	6	0.1	<0.5	2.0	23	1.4
20	16	7.7	379	9.1	1.7	<10	613	72	29	110	6.2	325	145	51	3	2	7	0.1	<0.5	9.9	34	2.4
21	17	7.7	386	9.8	2.5	<10	583	46	28	111	6.2	134	166	124	51	77	13	0.4	<0.5	5.5	9.7	1.1
22	15	6.6	278	3.6	5.9	420	1426	140	65	265	14.8	479	379	292	300	317	8	0.7	<0.5	3.9	6.8	0.7
23	18	7.5	406	3.2	6.1	28	626	93	45	61	2.7	454	99	68	3	1	7	1.0	<0.5	0.6	2.7	0.4
24	15	6.7	299	5.1	8.3	<10	837	127	34	78	3.1	117	113	368	15	710	149	1.7	4.1	1.5	0.9	<0.1
25	16	6.6	215	6.9	10.7	<10	683	88	26	100	4.7	131	140	205	1555	1147	144	8.7	3.4	0.4	1.3	<0.1
26	13	7.6	352	9.9	2.3	22	452	36	19	86	3.5	90	152	76	19	16	3	0.1	<0.5	1.8	1.7	0.6
27	14	7.1	276	6.7	11.3	35	452	37	20	87	2.7	81	151	79	213	22	13	0.1	<0.5	1.3	1.6	0.6
28	17	6.5	140	0	8.7	14	976	138	39	129	7.2	284	194	285	9617	2000	8	4.6	1.8	1.8	73	5.2
29	11	6.6	210	4.0	3.6	<10	1512	267	56	129	4.2	240	288	600	6516	1744	65	4.1	1.9	8.0	1.9	<0.1
30	13	6.0	400	5.0	5.3	<10	582	44	26	107	2.4	57	232	105	98	62	4	0.3	<0.5	1.1	0.7	<0.1
31	12	6.8	350	8.0	4.2	<10	338	37	19	50	1.5	111	105	41	28	5	13	<0.1	<0.5	0.3	<0.5	<0.1
32	13	6.9	370	5.0	3.0	14	547	79	35	63	2.5	267	115	100	29	122	9	0.1	<0.5	<0.3	<0.5	<0.1
33	14	6.3	310	3.5	6.4	22	824	143	39	76	2.0	130	140	335	9	5	5	0.2	<0.5	1.1	<0.5	<0.1
34	16	6.6	245	7.0	4.0	<10	456	62	16	52	2.9	95	84	143	483	887	65	6.9	3.4	0.4	<0.5	<0.1
35	13	6.3	350	6.0	5.0	<10	996	160	52	76	2.5	149	156	435	437	865	20	8.8	8.2	0.5	<0.5	<0.1
36	16	6.8	350	3.0	3.4	<10	665	86	14	122	9.2	387	136	32	19	2	17	0.1	<0.5	0.3	13	1.4
37	17	6.8	330	2.0	3.6	<10	1044	97	41	277	6.4	405	324	120	15	19	6	0.1	<0.5	3.1	11	0.8
38	18	6.6	250	1.0	9.5	<10	1439	134	68	270	16.2	498	376	295	1823	634	2	1.3	<0.5	2.7	68	0.8
39	16	7.2	340	4.5	5.0	<10	772	71	37	155	4.8	439	202	52	10	29	0.5	0.1	<0.5	1.6	1.3	0.2
40	9	6.5	200	8.0	3.8	<10	313	12	11	60	7.4	23	80	85	938	114	9	0.8	<0.5	1.0	16	0.5
41	12	4.5	370	7.0	2.5	17	341	8	7	64	8.2	82		89	3948	333	33	9.0	2.3	0.9	118	0.5
42	13	7.0	310	5.5	3.5	<10	915	108	49	153	5.0	387	265	120	16	1	6	0.1	<0.5	1.2	<0.5	0.2
43	16	7.1	195	6.5	3.2	<10	1491	115	67	295	19.9	440	395	350	292	213	170	0.4	<0.5	<0.3	25	0.5
44	14	6.8	320	4.0	3.8	<10	966	107	48	158	4.5	374	295	135	7	25	5	0.1	<0.5	0.8	1.8	0.6
45	15	6.7	320	4.5	4.1	<10	822	81	51	126	9.4	342	200	153	6	2	3	0.1	<0.5	2.2	0.8	0.5
46	14	6.9	246	3.8	nd	<10	969	70	42	179	13.6	221	230	285	2096	465	6	1.5	1.5	0.5	65	0.5
47	18	6.2	264	5.2	nd	<10	720	40	29	138	11.8	107	229	159	18665	1682	56	16	4.5	0.4	260	1.9
402	19	6.6	231	3.5	nd	<10	3199	389	95	805	50.7	2750	256	225	2583	1356	44	2.9	1.7	2.1	46	0.3

TOC, total organic carbon; TDS, total dissolved solids; Alk, alkalinity; nd, not determined.

$Fe(OH)_3{}^0$ species becomes important, controlled by solid ferric-oxy-hydroxides (Hem, 1985).

Where ferruginous and non-ferruginous springs occur in close proximity, they do not exhibit a clear difference in their general chemical composition, but ferruginous waters contain higher As (Fig. 2 (a)), and Co (Fig. 2 (b)) concentrations than non-ferruginous waters.

Gold in solution and suspension

Table 2 summarises the Au content in solution and in the suspended matter in the studied water samples. All Au values are blank subtracted and corrected for recovery.

Most, randomly taken, duplicate samples for the analysis of dissolved Au, showed values below the detection limit of both methods used, suggesting that no spurious Au values are determined. No significant differences in the dissolved Au contents, obtained by both methods, can be observed taking into consideration the variability associated with concentrations near the detection limits. A single method (anion-exchange prior to GFAAS) reproducibility of better than 20% is observed in duplicate 2 L samples (Table 2) for Au contents in the range of 0.4 to 1.8 ng L^{-1}, which is not too different from the reproducibility of the recoveries at these very low concentrations (for 1 ng L^{-1} Au spiked solutions, recovery is 88 ± 15%, $n = 15$; for 2 ng L^{-1} Au spiked solutions, recovery is 83 ± 13%, $n = 15$).

Therefore, the consistent use of solute Au values obtained by one of the methods allows significant statements to be made as to the distribution of dissolved Au in the investigated area.

Background values for dissolved Au are less than the detection limit of the methods used, and therefore lower (at least by one order of magnitude) detection limits are necessary to evaluate the regional background. Most samples, where Au in solution is detected in a range of 0.6 to 3 ng L^{-1}, were taken in the neighbourhood of the known Au bearing mineralised veins (Fig. 3). These samples included both

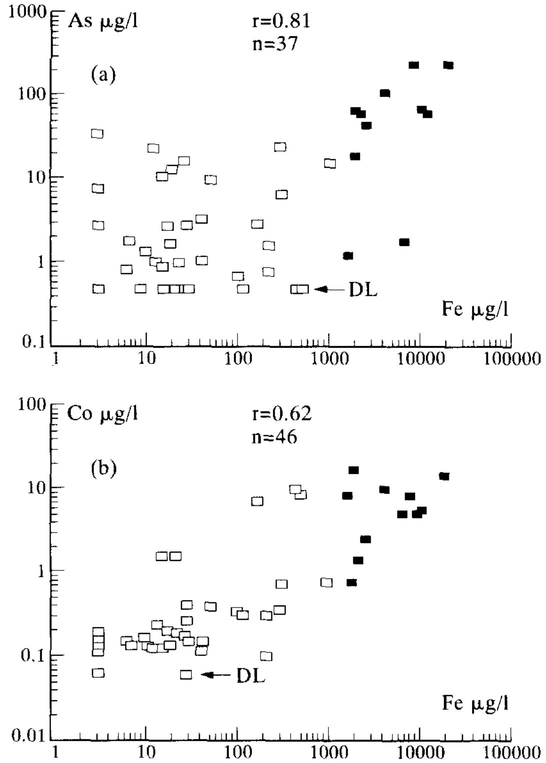

Fig. 2. Plots of arsenic (a) and cobalt (b) versus iron concentrations in solution. Detection limits (DL) for arsenic and cobalt were 0.5 and 0.06 μg L^{-1}, respectively. Black squares indicate the ferruginous waters. In both cases, the correlation coefficient (*r*) corresponds to probability higher than 0.9995.

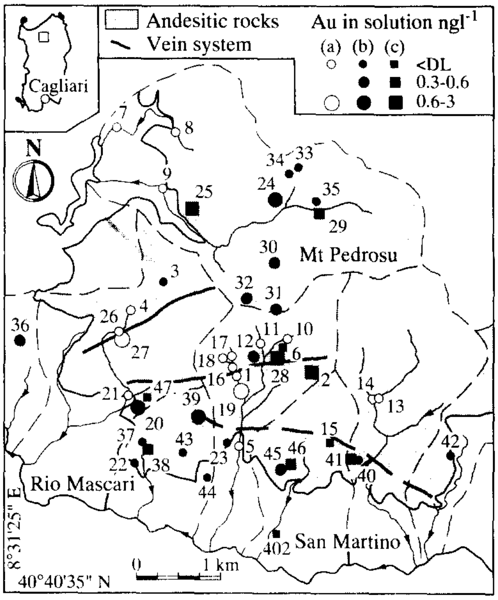

Fig. 3. Map showing the distribution of Au in solution. Symbols: (a) stream, (b) spring, (c) ferruginous water; same symbols in the following maps.

ferruginous and non-ferruginous waters. Au concentrations up to 1.7 ng L^{-1} are also found in the northernmost catchment area where Au mineralisation was unknown (Au prospecting was not carried out in this area until recently and has confirmed bedrock Au).

The amount of suspended matter retained on the membrane filters was, in most cases, very low, even for filtered volumes of up to 6 L. Au concentrations in suspension range from not-detectable to 1.2 ng L^{-1}. Whenever Au is detected both in solution and in suspension, the Au content of the suspended matter is generally lower than that in solution, in agreement with previous observations (Gosling *et al.*, 1971; Plyusnin, 1988; Schmitt *et al.*, 1993). Concentrations of Au in suspension are not directly correlated with those in solution. However, an obvious influence on the suspended matter content of Au, or for that matter on any of its constituents, is the amount of suspended matter per litre. One way to circumvent this problem is to normalise the concentration of a trace element to a major component of the suspension, to highlight any influence other than mechanical weathering. Concentrations of Au in suspension do not show a significant correlation ($r=0.30$, $n=23$) with the amount of aluminium in suspension, therefore aluminium can be used as a major component independent of Au. If the raw Au in suspension data are plotted (Fig. 4 (a)), a few anomalies can be seen. When normalising the Au content to the respective aluminium content (Fig. 4 (b)) some of the anomalies disappear, and maxima are observed at sampling sites closest to the mineralised vein.

Suspended Au is detected in some of the samples from all 5 monitoring sites showing, however, a wide range in concentration (up to a factor of 43); the range becomes narrower when normalised to the corresponding Al (Table 2).

Spring sample No. 20, situated about 400 m from the Au-bearing vein, is the only sample site which always has a detectable dissolved Au content over the duration of the monitoring period. The dissolved Au concentration is independent of the flow (1.5 ± 0.3 L^{-1}), pH (8.0 ± 0.2) and Eh (379 ± 27 mV) conditions, and also of other components in solution which seem to be rather stable (Fig. 5), so that no relationship between dissolved Au concentration and other physical or chemical parameters can be inferred or excluded. Dissolved Au concentrations over the monitoring period at the other monitoring sites are, sometimes, below the detection limit. Concentrations between 0.4 and 0.8 ng L^{-1} Au are found in these samples, with values replicated at least 3 times over the monitoring period, but a large variability was observed in the ferruginous waters (the spring No. 25 and the boreholes Nos. 6 and 28, see Table 2). This behaviour may be owing to coprecipitation and/or adsorption of Au onto ferric-oxy-hydroxides. The ability of ferric-oxy-hydroxides to coprecipitate or adsorb Au has been documented through experimental studies (Mann, 1983; Machesky *et al.*, 1991; Schoonen *et al.*, 1992; Greffie *et al.*, 1993), and may

Table 2. Gold concentration in solution and in suspension, and Au/Al ratio in the suspended matter for water samples from the Osilo area

No.	Gold solution (< 0.4 μm) GFAAS ng L^{-1}	ICP-MS ng L^{-1}	Gold suspension (> 0.4 μm) INAA ng L^{-1}	Au/Al suspension (10^{-3})	No.	Gold solution (< 0.4 μm) GFAAS ng L^{-1}	ICP-MS ng L^{-1}	Gold suspension (> 0.4 μm) INAA ng L^{-1}	Au/Al suspension (10^{-3})
1 a	<1	nd	0.38	0.012	22	<1	<0.5	<0.02	
1 b	<1	<0.5	0.22	0.002	23	<0.5	<0.5	0.03	0.008
2	3	nd	0.72	0.107	24	<0.5	0.5	0.11	0.009
3	<1	nd	1.1	0.019	25 a	<1	1.7	0.29	0.043
4	<1	<0.5	0.16	0.001	25 c	nd	nd	1.2	0.3
5	<1	<0.5	<0.05		25 g	0.7	nd	0.28	0.033
6 a	<1	<0.5	<0.02		25 i	0.4-0.6	nd	0.23	0.01
6 b	<0.5	<0.3	0.59	0.155	25 j	0.4	nd	<0.035	
6 c	<0.5	nd	0.34	0.097	25 k	<0.5	<0.3	<0.03	
6 d	<0.5	nd	0.12	0.06	25 l	<0.3	nd	<0.08	
6 e	0.5	nd	<0.03		25 m	<0.5	nd	<0.06	
6 f	0.4	nd	0.64	0.237	25 n	<0.5	nd	<0.08	
6 g	0.5	nd	0.065	0.043	26	<1	<0.5	0.11	0.012
6 i	0.4	nd	0.068	0.03	27	<1	0.7	0.15	0.003
6 j	<0.3	nd	0.18	0.316	28 b	<0.5	<0.3	0.062	0.030
6 k	0.7	<0.3	<0.015		28 c	nd	nd	0.038	0.038
6 l	0.4	nd	<0.06		28 d	<0.5	nd	0.14	0.045
6 m	<0.5	nd	<0.06		28 e	<0.5	nd	0.15	0.016
6 n	0.7-0.9	nd	<0.07		28 f	0.5	nd	0.26	0.113
7	<1	<0.5	0.18	0.005	28 g	0.4	nd	<0.03	
8	<1	<0.5	1.2	0.016	28 i	0.3	nd	0.22	0.088
9	<1	<0.5	0.03	0.003	28 j	0.4	nd	0.071	0.008
10	<1	<0.5	0.10	0.003	28 k	0.7	<0.3	<0.015	
11	<1	<0.5	0.35	0.001	28 l	0.3	nd	0.098	0.265
12	<1	0.5	0.08	0.016	28 m	<0.5	nd	<0.06	
13	<0.5	<0.5	0.17	0.004	28 n	0.8	nd	<0.08	
14	<1	<0.5	0.40	0.008	29	<0.5	0.4	0.14	0.002
15 a	<0.5	<0.5	0.054	0.002	30	0.4	<0.3	0.50	0.014
15 g	nd	nd	0.057	0.066	31	0.4	<0.3	0.15	0.003
16	<1	<0.5	0.06	0.007	32	0.6	<0.3	<0.08	
17	<0.5	<0.5	<0.09		33	<0.5	<0.3	0.26	0.050
18	<0.5	<0.5	0.09	0.002	34	<0.5	<0.3	<0.08	
19	<1	0.7	0.24	0.005	35	<0.5	<0.3	<0.08	
20 a	<1	0.6	0.07	0.017	36	<0.5	0.3	<0.05	
20 b	0.8	0.7	0.72	0.126	37	<0.5	<0.3	<0.05	
20 c	1.2	nd	0.30	0.047	38	0.6	0.4	<0.1	
20 d	1	nd	0.14	0.016	39	0.5	0.7	<0.06	
20 e	1.5	nd	0.053	0.009	40	<0.5	<0.3	<0.06	
20 f	0.9	nd	0.098	0.021	41	<0.5	0.4	<0.08	
20 g	1.2	nd	0.064	0.012	42	<0.5	<0.3	0.25	0.048
20 i	1.2	nd	0.26	0.02	43	0.4	<0.3	<0.08	
20 j	1.4-1.8	nd	0.16	0.038	44	<0.5	<0.3	<0.08	
20 k	0.8	<0.3	<0.03		45	0.4	<0.3	<0.08	
20 l	1.6	nd	<0.07		46	0.6	nd	<0.12	
20 m	0.8	nd	<0.08		47	<0.5	nd	0.14	0.067
20 n	0.9	nd	0.082	0.025	402 a	<1	<0.5	1.1	0.073
21 a	<1	<0.5	<0.09		402 b	<1	<0.5	0.5	0.05
21 b	0.7	<0.3	0.48	0.001					
21 f	0.7	nd	0.3	0.004					
21 k	<0.5	<0.3	0.062	0.001					

Detection limit of <1 ng L^{-1} Au refers to analyses on a 1 L sample. Letters signify different sampling times.

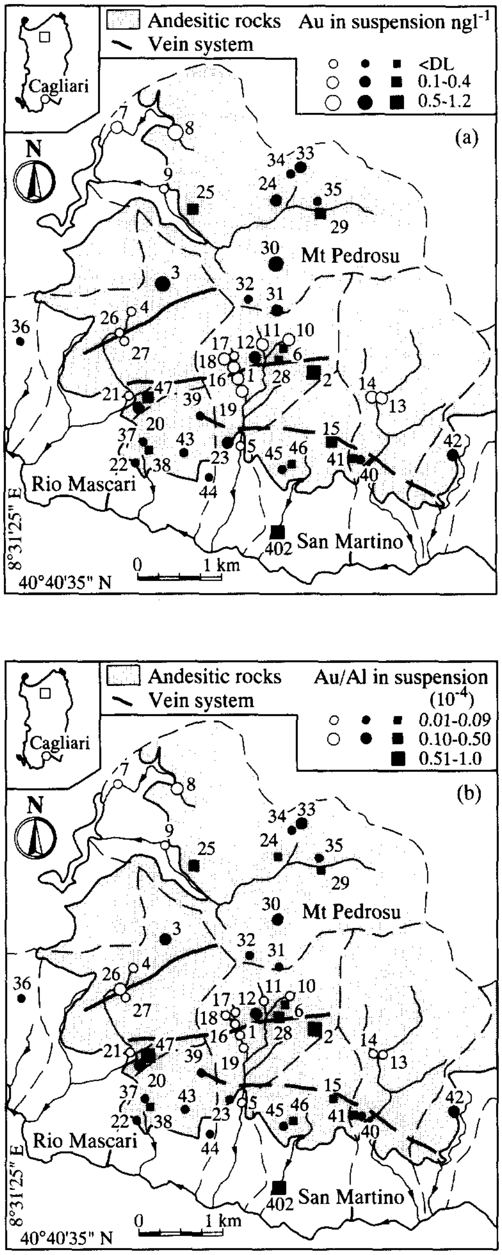

Fig. 4. Map showing the distribution of Au (a) and Au normalised to the corresponding aluminium (b) in the suspended matter.

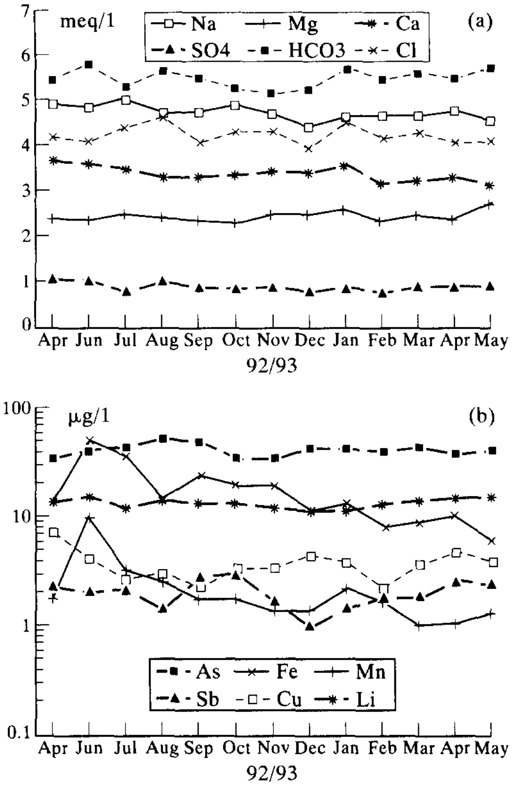

Fig. 5. Concentrations of major (a) and trace elements (b) in the spring sample No. 20 over the monitoring period.

therefore exert an important control on the transport of Au in the aquatic environment, particularly when Fe-rich groundwaters are discharging.

Also, reduction of Au(I) species by Fe^{2+}, yielding metallic Au and an amorphous ferric-oxy-hydroxide precipitate, can act as a migration barrier to dissolved Au. The relationship between the ratio of dissolved to particulate Au ($Au_{dissolved}/Au_{suspended}$) and particulate Fe is shown in Fig. 6 for the Osilo waters. High values of the ratio of dissolved to suspended Au are only observed in the Fe-poor waters where equilibrium concentrations (ca. 10 $\mu g\ L^{-1}$) of Fe are present. In the ferruginous waters, which are precipitating ferric-oxy-hydroxides as evidenced by high suspended Fe contents, the ratio is always low, the implication being that any dissolved Au (when present) has been coprecipitated with, or adsorbed onto, neoforming ferric-oxy-hydroxides. This highlights the importance of analysing the suspended material in Fe-rich waters where most of the Au is likely to occur in association with ferric-oxy-hydroxides. When this is not possible, the implication of this process is that any Au in solution in Fe-rich waters represents a minimum content. The ratios of dissolved to particulate As and Sb also show a similar relationship with the suspended matter Fe content.

The observed dispersion of Au in surface waters, either in solution or in suspension, is restricted to about 500 m from the mineralised vein system. The low dispersion of Au in waters means that hydrogeochemical prospecting is unlikely to be beneficial in regional exploration programmes, where sampling densities are small, but is extremely valuable in being able to precisely locate the Au mineralisation.

Relationships between dissolved gold and other parameters

As pointed out by Bowell (1992), natural waters are rarely in equilibrium with metallic Au implying that solubility calculations represent an upper limit of Au

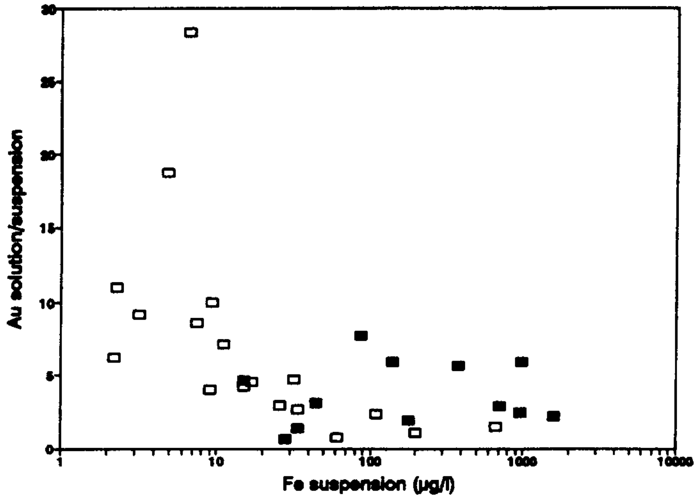

Fig. 6. Relationship between the ratio of Au in solution to Au in suspension and iron concentration in suspension. Black squares indicate the ferruginous waters.

solubility. The geochemical cycling of Au will be more a function of Au concentration in the host rocks and its dissolution reaction kinetics. Once Au is in solution, homogenous reactions will proceed faster, allowing speciation calculations to determine the most likely species of Au in solution.

The pH and redox conditions are considered important parameters for Au mobilisation in natural waters since these will determine the stability of the possible complexing species. However, in the aerobic waters from the Osilo area, no correlation between pH, Eh and dissolved Au was observed (Table 3). Under these oxidising, near-neutral, generally low-salinity conditions, Au in solution will be in its 3^+ valency. Moreover, disproportionation reactions (Au^+ to Au^{3+} and metallic Au) are a likely process.

Cyanide was pointed out by Renders and Seward (1989) to be one of the best complexing ligands for Au (as $Au(CN_4^-)$). Where Au was detected in solution no significant correlation with their corresponding CN^- concentrations was observed (Table 3). However, the few data available on CN^- concentration (mostly below the detection limit of 10 $\mu g\ L^{-1}$, Table 1) do not prove or exclude a correlation between the two components.

A number of inorganic ligands have been invoked to account for the complexation of dissolved Au in oxidising environments. Hydroxy complexes such as $Au(OH)_3^0$ and $Au(OH)_4^-$, Cl^- complexes such as $AuCl_4^-$, mixed hydroxy-Cl^- complexes such as $Au(OH)_3Cl^-$, NH_3 complexes such as $Au(NH_3)_4^{3+}$, are among the most important. No correlation could be observed in these waters between the dissolved Au content and either Cl^-, Br^- or NH_3.

Other possible complexing species, important in near-neutral- to alkaline-reducing conditions, such as $S_2O_3^{2-}$, SO_3^{2-} and S^{2-} (Webster, 1986; Renders and Seward, 1989; Benedetti and Boulègue, 1991; Jaireth, 1992) were not determined. They are thought to be either absent or at extremely low concentrations due to the oxidising nature of the waters. If we assume equilibrium among the different S-species in solution, then concentrations of HS^-, $S_2O_3^{2-}$ and SO_3^{2-} can be calculated from their redox reactions (data from Wagman *et al.*, 1982). This yields extremely low concentrations (mol L^{-1}: $<10^{-46}$ [HS^-]; $<10^{-50}$ [$S_2O_3^{2-}$]; $<10^{-38}$ [SO_3^{2-}]) for the reduced S-species, implying that they do not play a role in the transport of Au in these waters, however, this does not exclude that these species play an important role in the primary dissolution of Au in the mineralised veins.

Organic matter is postulated to be a prime complexing agent for Au (Baker, 1978; Bergeron and Harrison, 1989; Benedetti and Boulègue, 1989; 1990; Gatellier and Disnar, 1989; Vlassopoulos *et al.*, 1990; Bowell *et al.*, 1993a; 1993b; Colin *et al.*, 1993; Séa *et al.*, 1993), although other authors conclude that humic and fulvic acids act only as reductants of oxidised Au species leading to the formation of colloidal Au particles (Ong and Swanson, 1969; Machesky *et al.*,

Table 3. Correlation coefficients (*r*) between dissolved gold and other components in solution. Probability (*p*) for the corresponding number (*n*) of samples ($p < 0.90$ not reported)

H^+	Eh	O_2	TOC	CN^-	TDS	Cl^-	SO_4	Fe	Mn	Zn	Co	Ni	Cu	Pb	As	Sb	
r	−0.06	−0.04	−0.06	0.23	0.75	−0.14	−0.12	−0.05	−0.03	0.43	0.20	0.74	0.76	0.26	−0.15	−0.07	−0.07
n	22	22	22	20	6	22	22	22	22	22	22	21	9	20	14	19	15
p										>0.90		>0.99	>0.90				

1992). Au in solution does not show a significant correlation with the total organic carbon (TOC) content (Table 3).

Since the observed Au contents are very low, the lack of any pattern for the Osilo waters does not exclude the existence of the relations pointed out in the literature which, however, were mostly observed in experimental studies at rather high Au and complexing agent concentrations.

Pathfinder elements

According to Boyle (1979), the most effective indicators in natural waters of most types of Au deposits are Zn, Ag, As, Sb and Cu, while Bi, Ni, Co, U and Hg may be useful indicators where the Au deposits contain these elements. However, for each specific area the effective pathfinders are likely to be different, mostly depending on the mineral assemblages of the mineralisation, gangue and host rocks.

In the Osilo area, a wide range of metals was determined, both in solution and in suspension, in parallel with the investigation of aqueous and suspended Au, to test their potential use as pathfinder elements for hydrogeochemical Au prospecting. Anomalous concentrations (up to 2 orders of magnitude higher than the local background values) of As and Sb in solution are observed in waters closely associated with the known Au-bearing

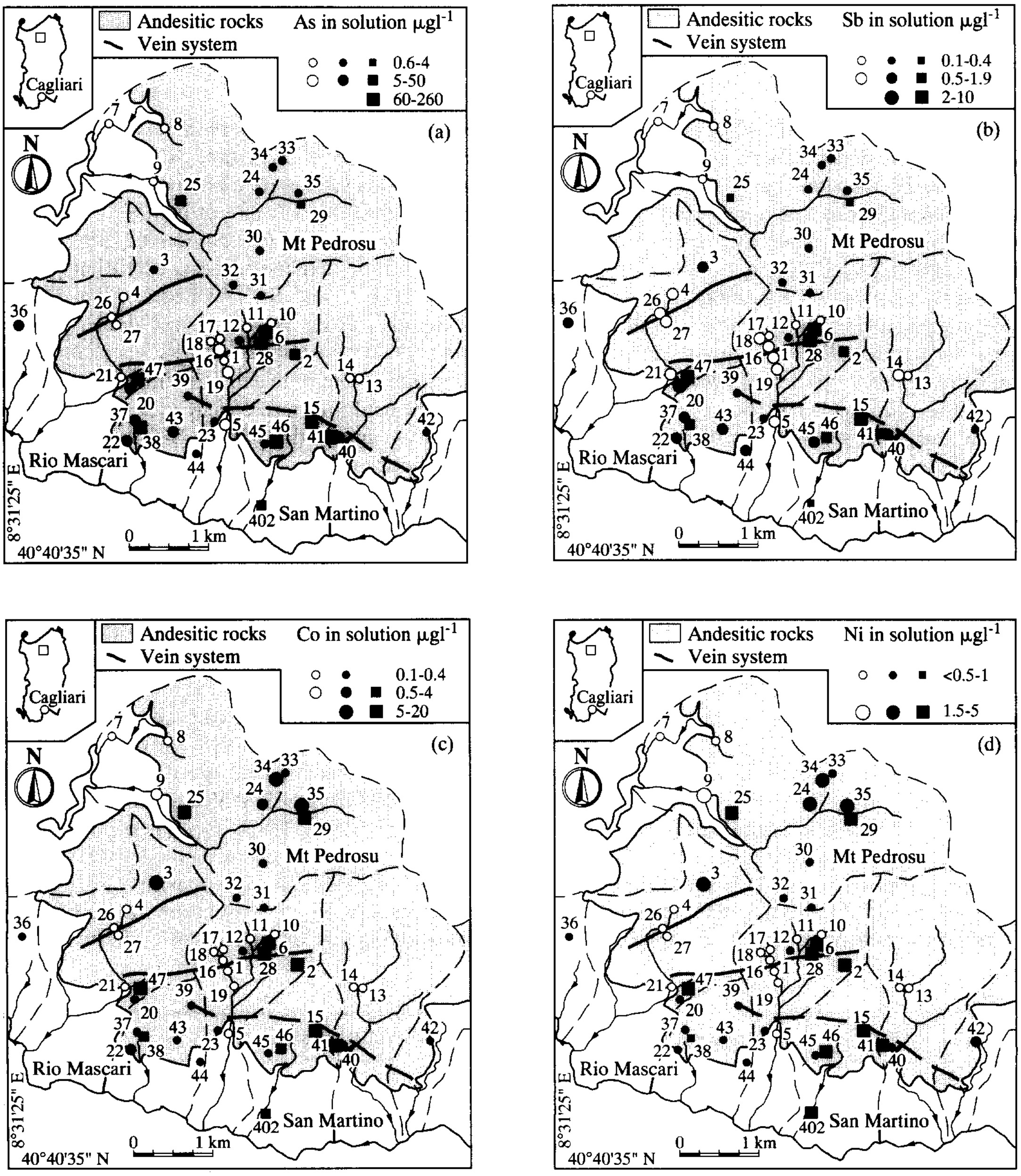

Fig. 7. Maps showing the distribution of arsenic (a), antimony (b), cobalt (c) and nickel (d) in solution.

veins (Figs 7 (a) and (b)). These samples include the boreholes and ferruginous springs, and streams which follow the regional N-S flow pattern. A similar behaviour is observed for Co and Ni in solution (Figs 7 (c) and (d)), moreover, their concentrations outline the northernmost catchment as an anomalous area, where Au is also detected in solution.

Concentrations of As, Sb and Co in the suspended matter were generally much lower than the corresponding concentrations in solution, and Ni was mostly below the detection limit. Nevertheless, the dispersion patterns of As, Sb and Co in suspension correspond remarkably well with those observed in solution (Figs 8 (a)–(c)).

Silver concentrations in solution were below the detection limit (0.2 $\mu g\ L^{-1}$), while Ag in suspension (in the range of 5 to 14 ng L^{-1}) was detected only in sample Nos. 6, 20, 21, and 39, which also show detectable Au. Thallium concentrations in solution (in the range of 0.2–7.7 $\mu g\ L^{-1}$, compared with a DL of 0.1 $\mu g\ L^{-1}$), were observed in sample Nos. 15, 22, 38, 40, 41, and 402, mostly ferruginous waters related to the southern mineralised vein.

The distribution of other potential pathfinders, both in solution and suspension, considered in this

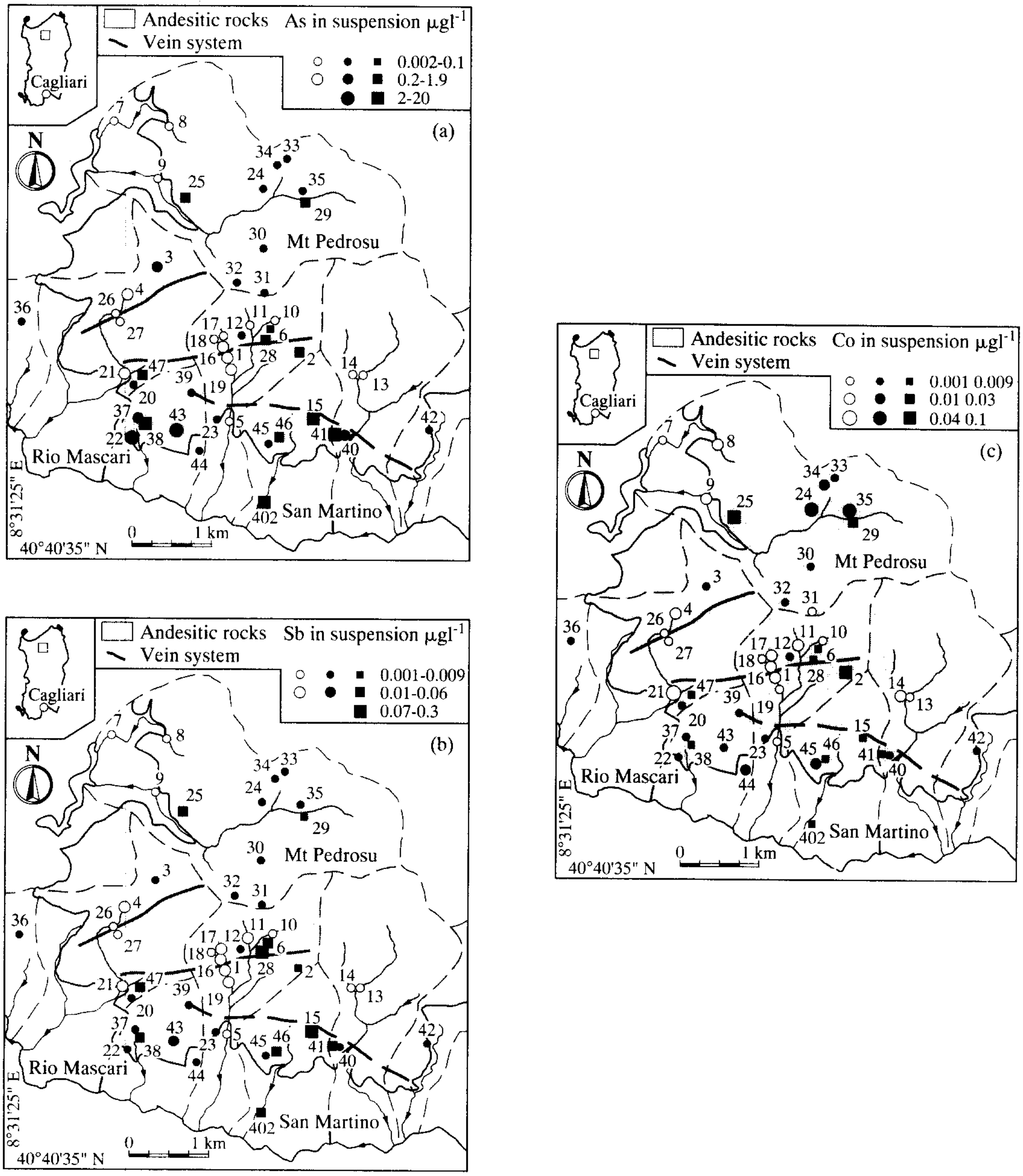

Fig. 8. Maps showing the distribution of arsenic (a), antimony

study do not show a correlation with the Au mineralisation, in agreement with the mineral assemblage (mainly Fe, As and Sb sulphides) of the Au-bearing veins. In particular, Hg concentrations in solution are always below the detection limit (1 μg L^{-1}), and not-detected in suspension. Bismuth in solution is below the detection limit (0.08 μg L^{-1}). Lead, Cr and Cd contents in solution are generally low (0.4–10, <0.3–8, <0.4–1.6, and <0.1–0.3 μg L^{-1}, respectively).

CONCLUSIONS

An integrated and comprehensive strategy for evaluating the role of hydrogeochemistry in the exploration of Au deposits, including the analysis for Au and pathfinder elements both in solution and suspension, was tested in the Osilo area of northern Sardinia. The two different methods used for the determination of Au in solution gave similar extraction efficiencies, low detection limits (0.3 to 0.5 ng L^{-1}), and good reproducibility (20% at the 0.5 ng L^{-1} Au level).

Solute Au concentrations up to 3 ng L^{-1} were confined to the vicinity of known Au-bearing veins. A second potential area of Au occurrence was outlined in the northernmost catchment. Solute Au concentrations did not show seasonal variations for a spring water, sampled monthly over a one year period.

Au concentrations in solution did not correlate with those in suspension. Au content in the suspended matter showed a much clearer relationship to the mineralisation when normalised to a major element (e.g. Al). The adsorption and/or coprecipitation of soluble Au by ferric-oxy-hydroxides, as reported in experimental studies, is shown to be an important control on Au solubility for Fe-rich groundwaters, and highlights the importance of analysing Au both in suspension and in solution.

In the Osilo area, the best indicator of the Au mineralisation was Au itself. However, other excellent pathfinders, both in solution and suspension, were As, showing a marked dispersion spatially associated with the known auriferous veins and Sb, with a somewhat smaller dispersion, while Co and Ni were found to be associated only locally with Au.

The results from the Osilo area show that solute Au concentrations above the detection limit are confined to areas of mineralised bedrock. Dispersion of Au in these waters, both in solution and suspension, is very low, allowing for the precise localisation of Au bearing structures. The pathfinder elements As and Sb are particularly useful, on a somewhat larger scale, in outlining anomalous areas.

An improvement of analytical methods, aimed at achieving lower detection limits for Au determination, may contribute to delineate wider dispersion haloes, allowing the application of hydrogeochemical prospecting on a regional scale. However, the present study shows that hydrogeochemical methods can be effective prospecting tools for Au deposits by combining techniques able to determine Au both in solution and suspension at the sub-ng L^{-1} level, with parallel analysis for elements potentially associated with Au deposits.

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REFERENCES

Andrade W.O., Machesky M.L. and Rose A.W. (1991) Au distribution and mobility in the surficial environment, Carajas region, Brazil. *J. Geochem. Explor.* **40**, 95-114.

Baker W.E. (1978) The role of humic acid in the transport of gold. *Geochim. Cosmochim. Acta* **42**, 645-649.

Beccaluva L., Deriu M. and Macciotta G. (1980) Riflessioni sul significato del vulcanismo oligo-miocenico della Sardegna nell'ambito dell'evoluzione geodinamica del Mediterraneo occidentale. In *Volume dedicato a S. Venzo*, pp. 159-161. STEP, Parma.

Bellon H., Coulon C. and Edel J.B. (1977) Le déplacement de la Sardaigne. Synthèse des données géochronologiques, magnétiques et paleomagnétiques. *Bull. Soc. Geol. Fr.* **19**, 825-832.

Benedetti M. and Boulègue J. (1989) Au in supergene environments: role of gold-organic matter interactions. *28th Int. Geol. Cong. Transactions Washington D.C., Abstracts* **1**, 25.

Benedetti M. and Boulègue J. (1990) Transfer and deposition of Au in the Congo watershed. *Earth Planet. Sci. Lett.* **100**, 108-117.

Benedetti M. and Boulègue J. (1991) Mechanism of Au transfer and deposition in a supergene environment. *Geochim. Cosmochim. Acta* **55**, 1539-1547.

Bergeron M. and Choinière J. (1989) L'or dans les eaux souterraines: implications pour l'exploration. *J. Geochem. Explor.* **31**, 319-328.

Bergeron M. and Harrison Y. (1989) Le transport chimique de l'or dans les environments de surface: formation d'un colloide et complexation organique. *Can. J. Earth Sci.* **26**, 2327-2332.

Blommaert W., Vandelannoote R., Van't Dack L., Gijbels R. and Van Grieken R. (1980) Relative evaluation of neutron activation, X-ray fluorescence and spark source mass spectrometry for multi-element analysis of geothermal waters. *J. Radioanal. Chem.* **57**, 383-400.

Bowell R.J. (1992) Supergene Au mineralogy at Ashanti, Ghana: implications for the supergene behaviour of gold. *Mineral. Mag.* **56**, 545-560.

Bowell R.J., Foster R.P. and Gize A.P. (1993a) The mobility of Au in tropical rain forest soils. *Econ. Geol.* **88**, 999-1016.

Bowell R.J., Gize A.P. and Foster R.P. (1993b) The role of fulvic acid in the supergene migration of Au in tropical rain forest soils. *Geochim. Cosmochim. Acta* **57**, 4179-4190.

Boyle R.W. (1979) The geochemistry of Au and its deposits. *Bull. Geol. Surv. Can.* **280**, 584 pp.

Caboi R., Cidu R., Fanfani L., Zuddas P. and Zanzari A.R. (1993) Geochemistry of the high-PCO_2 waters in Logudoro, Sardinia, Italy. *Appl. Geochem.* **8**, 153-160.

Cidu R. and Edmunds W.M. (1990) Preliminary studies of hydrogeochemical method for Au prospecting - results from the United Kingdom. *Trans. Instn. Min. Metall. Sect. B* **99**, 153-162.

Cidu R., Fanfani L., Shand P., Edmunds W.M., Van't Dack L. and Gijbels R. (1994) The determination of Au at the ultratrace level in natural waters. *Anal. Chim. Acta* **296**, 295-304.

Colin F., Vieillard P. and Ambrosi J.P. (1993) Quantitative approach to physical and chemical Au mobility in equatorial rainforest lateritic environment. *Earth Planet. Sci. Lett.* **114**, 269-285.

Cook N. J., Wood, S. A. and Zhang Y. (1992) Transport and fixation of Au, Pt and Pd around the Lac Sheen Cu-Ni-PGE occurrence in Quebec Canada. *J. Geochem. Explor.* **46**, 187-228.

Dostal J., Coulon C. and Dupuy C. (1982) Cainozoic andesitic rocks of Sardinia (Italy). In *Andesites* (ed. R.S. Thorpe), pp. 353-369. John Wiley and Sons, New York.

Doyle R.W. (1968) The origin of the ferrous ion - ferric oxide Nernst potential in environments containing dissolved ferrous iron. *Am. J. Sci.* **266**, 840-859.

Drever J.I. (1988) The geochemistry of natural waters. 2nd edition. Prentice Hall, Englewood Cliffs, New Jersey.

Fiori M., Grillo S.M., Marcello A. and Pretti S. (1990) Depositi epitermali e metalli preziosi in Sardegna. Prime notizie sul sistema filoniano di San Martino (Osilo-Codrongianus). *L'ind ustria mineraria* **2**, 11-14.

Gatellier J.-P. and Disnar J.-R. (1989) Organic matter and gold-ore association in a hydrothermal deposit, France. *Appl. Geochem.* **4**, 143-149.

Gosling A.W., Jenne E.A. and Chao T.T. (1971) Au content of natural waters in Colorado. *Econ. Geol.* **66**, 309-313.

Greffie C., Parron C., Benedetti M., Amouric M., Marion P. and Colin F. (1993) Experimental study of Au precipitation with synthetic iron hydroxides: HRTM-AEM and Mössbauer spectroscopy investigations. *Chem. Geol.* **107**, 297-300.

Grimes D.J., Mchugh J.B., Ficklin W.H. and Meier A.L. (1993) Anomalous gold, antimony, arsenic, and tungsten in ground water and alluvium around disseminated Au deposits along Getchell trend, Humboldt County, Nevada. *Extended abstract in Integrated methods in exploration and discovery* (ed. Fletcher D.I.), *Soc. Econ. Geol.*

Hall G.E.M., Vaive J.E. and Ballantyne S.B. (1986) Field and laboratory procedures for determining Au in natural waters: relative merits of preconcentration with activated charcoal. *J. Geochem. Explor.* **26**, 191-202.

Hamilton T.W., Ellis J., Florence T.M. and Fardy J.J. (1983) Analysis of Au in surface waters from Australian Goldfields: an investigation into direct hydrogeochemical prospecting for gold. *Econ. Geol.* **78**, 1335-1341.

Hem J.D. (1985) Study and interpretation of the chemical characteristics of natural waters - 3rd edition. *U.S. Geol. Surv. Water-Supply Paper* **2254**, 263 p.

Hostettler J.D. (1984) Electrode electrons, aqueous electrons and redox potentials in natural waters. *Am. J. Sci.* **284**, 734-759.

Jaireth S. (1992) The calculated solubility of platinum and Au in oxygen-saturated fluids and the genesis of platinum-palladium and Au mineralization in the unconformity-related uranium deposits. *Mineral. Deposita* **27**, 42-52.

Lindberg R.D. and Runnells D.D. (1984) Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science* **225**, 925-927.

Machesky M.L., Andrade W.O. and Rose A.W. (1991) Adsorption of gold(III)-chloride and gold(I)-thiosulphate anions by goethite. *Geochim. Cosmochim. Acta* **55**, 769-776.

Machesky M.L., Andrade W.O. and Rose A.W. (1992) Interactions of Au (III) chloride and elemental Au with peat-derived humic substances. *Chem. Geol.* **102**, 53-71.

Mann A.W. (1983) Hydrogeochemistry and weathering on the Yilgarn Block, Western Australia - ferrolysis and heavy metals in continental brines. *Geochim. Cosmochim. Acta* **47**, 181-190.

McHugh J.B. (1988) Concentration of Au in natural waters. *J. Geochem. Explor.* **30**, 85-94.

McHugh J.B. and Miller W.R. (1992) A hydrogeochemical survey using Au in water, northern Nevada. *U.S. Geol. Surv. Open-File Rep.* **92-303**, 11 pp.

Ong H.L. and Swanson V.E. (1969) Natural organic acids in the transportation, deposition and concentration of gold. *Quart. J. Colorado School Mines* **64**, 395-425.

Pecorini G., Balia R., Ciminale M., Loddo M., Patella D. and Tramacere A. (1988) Studio geofisico del bacino del Logudoro (Sardegna) e delle aree circostanti. *Boll. Soc. Geol. It.* **107**, 547-560.

Plyusnin A.M. (1988) Formation of aqueous dispersal-flows at Au deposits in bald-mountain landscapes. *Geochem. Int.* **25** (8) 78-82.

Pretti S. (1988) Mineralization related to Tertiary volcanism in Sardinia: opportuneness of a re-examination. *Proc. "Zuffar'days" Symp. Cagliari*, October 10-15 1988, pp. 89-100.

Renders P.J. and Seward T.M. (1989) The stability of hydrosulphido- and sulphido-complexes of Au(I) and Ag(I) at 25°C. *Geochim. Cosmochim. Acta* **53**, 245-253.

Savelli C., Beccaluva L., Deriu M., Macciotta G. and Maccioni L. (1979) K/Ar geochronology and evolution of the Tertiary "calc-alcalic" volcanism of Sardinia (Italy). *J. Volcanol. Geotherm. Res.* **5**, 257-269.

Schmitt H.R., Cameron E.M., Hall G.E.M. and Vaive J. (1993) Mobilization of Au into lake sediments from acid and alkaline mineralized environments in the southern Canadian Shield: Au in lake sediments and natural waters. *J. Geochem. Expl.* **48**, 329-358.

Schoonen M.A.A., Fisher N.S. and Wente M. (1992) Au sorption onto pyrite and goethite: a radiotracer study. *Geochim. Cosmochim. Acta* **56**, 1801-1814.

Séa F., Tanguay M.G., Trudel P. and Bergeron M. (1993) Solubilité de l'or dans les eaux interstitielles de la latérite coiffant le gîte aurifère de Misséni, au Mali. *Can. J. Earth Sci.* **30**, 1553-1565.

Stumm W. and Morgan J.J. (1981) *Aquatic Chemistry.* Wiley-Interscience, New York.

Vlassopoulos D., Wood S.A. and Mucci A. (1990) Au speciation in natural waters: II. The importance of organic complexing Experiments with some simple model ligands. *Geochim. Cosmochim. Acta* **54**, 1575-1586.

Wagman D.D., Evans W.H., Parker V.B., Schumm R.H., Halow I., Bailey S.M., Churney K.L. and Nuttall R.L. (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units. *J. Phys. Chem. Ref. Data* **11**, suppl. 2, 393 pp.

Webster J.G. (1986) The solubility of Au and silver in the system Au-Ag-S-O_2-H_2O at 25°C and 1 atm. *Geochim. Cosmochim. Acta* **50**, 1837-1845.