

Soil gas investigations over sulphide ore-bearing fractures - the Fontalcinaldo case study (Boccheggiano and Niccioleta mining district - southern Tuscany, Italy)

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ABSTRACT. — The application of soil-gas analysis to sulphide exploration has been evaluated at Fontalcinaldo (southern Tuscany, Boccheggiano-Niccioleta mining district). Samples were collected for He, Rn and CO₂ analysis and compared with deep sulphide-bearing fractures identified using borehole and geophysical data. The selected gases were chosen because they are proven fault tracers. In addition CO₂ has the added benefit that it can also give indirect information on the presence of buried sulphide deposits, as sulphide mineral oxidation produces sulphuric acid which, in turn, reacts with host-rock carbonate minerals to form carbon dioxide. Elevated He, ²²²Rn and CO₂ concentrations have been found over fault and fracture systems defined on the basis of geological and geophysical mapping; further N-S trending lineations have also been highlighted, including a possible northward extension of the Boccheggiano Fault. The surveys also indicated systematic soil-gas anomalies related to mineral occurrences, with the most consistent patterns (i.e. elevated CO₂ values) occurring over the main sulphide orebodies present in the area. The present research indicates that soil-gas techniques can provide useful information on the presence of ore-bearing fractures, especially during initial reconnaissance exploration or where other geochemical data are

scarce because of unfavourable geological conditions (i.e. impermeable covers).

RIASSUNTO. — Nell'ambito di una ricerca eseguita nel 1990 in cooperazione tra l'Università di Roma e la Rimin Spa nell'area facente capo al distretto minerario delle Colline Metallifere (Toscana Meridionale), sono state applicate metodologie di prospezione dei gas del suolo al fine di individuare la presenza in profondità di mineralizzazioni a solfuri intruse in faglie sepolte al di sotto di una spessa coltre argillosa scarsamente permeabile. Con il presente lavoro si è voluta verificare la possibilità di acquisire informazioni geochimiche relative alla presenza di mineralizzazioni in aree dove lo spessore e la scarsa permeabilità di certi litotipi, come le argille ed i flysch argillosi, possono permettere la migrazione in superficie di specie gassose endogene ma non la migrazione in soluzione dei traccianti comunemente usati nelle tecniche di prospezione tradizionale (stream sediments, analisi di elementi in tracce nei suoli ecc.). È stata quindi effettuata, tra il 1990 ed il 1992, una campagna di prospezione nel corso della quale sono stati prelevati in totale 542 campioni di gas del suolo. Tra le specie gassose analizzate le più significative sono risultate essere He, ²²²Rn e CO₂. Tali gas, come è noto, costituiscono buoni traccianti di fratture sepolte; inoltre la CO₂ risulta essere un valido indicatore

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della presenza in profondità di mineralizzazioni a solfuri. I processi ossidoriduttivi che si innescano in tali ambienti rendono infatti le acque di circolazione fortemente aggressive nei confronti della calcite con consumo di O₂ e liberazione di CO₂. I risultati delle campagne di prospezione hanno evidenziato, mediante l'esame delle mappe di distribuzione dei gas, la buona correlazione delle anomalie di He, ²²²Rn e CO₂ con i sistemi di faglie e fratture individuati mediante le indagini geofisiche. Lo studio degli andamenti delle anomalie suggerisce inoltre la probabile esistenza di lineamenti tettonici orientati nord-sud non riportati nelle carte geologiche e/o sismiche; di questi il più importante sembra essere la prosecuzione verso nord della nota Faglia di Boccheggiano. Per quanto attiene la relazione tra anomalie di fuga e corpi mineralizzati si è potuto riscontrare che incrementi significativi delle specie gassose analizzate, in particolare la CO₂, coincidono con le aree mineralizzate. Oltre a ciò si è potuto verificare che il metodo d'indagine proposto consente di acquisire informazioni sulla presenza di probabili mineralizzazioni sepolte sia in terreni permeabili (Formazione del Calcere Cavernoso) che in sedimenti scarsamente permeabili come quelli flyshoidi (Argille a Palombini). Ciò può rivelarsi particolarmente utile sia nelle prime fasi dell'esplorazione mineraria, in cui particolarmente elevato risulta il rischio di insuccesso in relazione ai costi di prospezione, sia in aree nelle quali le sfavorevoli condizioni idrogeologiche non consentono l'utilizzo dei metodi tradizionali di prospezione.

KEY WORDS: *Tuscany (Italy), geochemical prospecting, soil-gas survey, ore prospecting.*

INTRODUCTION

Soil-gas methods are becoming increasingly accepted in the broad spectrum of geochemical exploration techniques, and numerous recent studies have defined geochemical haloes at the surface which are associated with buried mineral resources (Hinkle and Harms, 1978; Reimer and Bowles, 1979; Lovell *et al.*, 1980; Lovell and Hale, 1983; Ball *et al.*, 1985; McCarthy *et al.*, 1986). In areas undergoing sulphide weathering, O₂ is consumed while CO₂ can be formed by the reaction of acidic

groundwater (usually present around oxidising sulphide deposits) with host-rock carbonate minerals (Lovell *et al.*, 1979; Lovell and Hale, 1983; Lovell *et al.*, 1983; Ball *et al.*, 1985; Peachey *et al.*, 1985; Hinkle *et al.*, 1990; Reid and Rasmussen, 1990). Sulphur gas species derived from sulphide mineral alteration may be also present (Taylor *et al.*, 1982; Hinkle, 1984; Hinkle and Dilbert, 1984; Stedman *et al.*, 1984; Nicholson *et al.*, 1988; Ball *et al.*, 1990; Hinkle *et al.*, 1990; Kesler *et al.*, 1990). Tectonic discontinuities, along which geothermal fluids circulate and deposit sulphide minerals, can provide preferential pathways for gases ascending to the surface (Reimer and Bowles, 1979; Rose *et al.*, 1979; Gregory and Durrance, 1985; Malmqvist *et al.*, 1989; Duddridge *et al.*, 1991).

A co-operative research study between the Earth Sciences Department of «La Sapienza» University of Rome and the Italian mining company Rimini SpA permitted the assessment of the soil-gas method for sulphide ore exploration. Research carried out during 1990 and 1992 consisted of the collection and analysis of soil gas samples near Fontalcinaldo (Boccheggiano-Niccioleta mining district, southern Tuscany), a known pyrite deposit which has an extensive geological data-base for comparison with the soil-gas results.

The objectives of the research were to study:

- The use of He, ²²²Rn and CO₂ as tracers of concealed faults and fractures, which are potential hosts for sulphide mineralisation.
- The use of CO₂ as a tracer of deep-seated sulphide-bearing fractures.
- The acquisition of geochemical data in areas where traditional geochemical methods, based on trace-element migration in groundwater, may fail because of the thickness and low permeability of certain lithotypes. One of the innovative aspects of this work, with respect to similar studies, is the attempt to overcome the limitations imposed by the presence of thick and/or low permeable sediments over the Fontalcinaldo deposit.

GEOLOGICAL SETTING AND MINERALOGICAL FEATURES OF THE RESEARCH SITE

The Fontalcinaldo site is situated about 40 km north of Grosseto, within the mining district that includes the Niccioleta and Boccheggiano-Campiano pyrite mines (fig. 1). The geological setting of the area is a consequence of two different tectonic phases which began during the Oligocene. The initial compressional phase formed the Apennine Chain, while the second period created

Apennine-trending depressions along a series of extensional faults (RIMIN, 1988).

The main tectonic structure visible at Fontalcinaldo is the «Ritorto Fault», a WNW-ESE striking extensional structure which has a dip of 40°-45° towards the NE (fig. 2). The Ritorto Fault represents the western prolongation of the larger Boccheggiano Fault, which is well known for its mineralised veins. This structure juxtaposes a raised block of outcropping «substratum» corresponding to the carbonate «Tuscan Sequence» (primarily

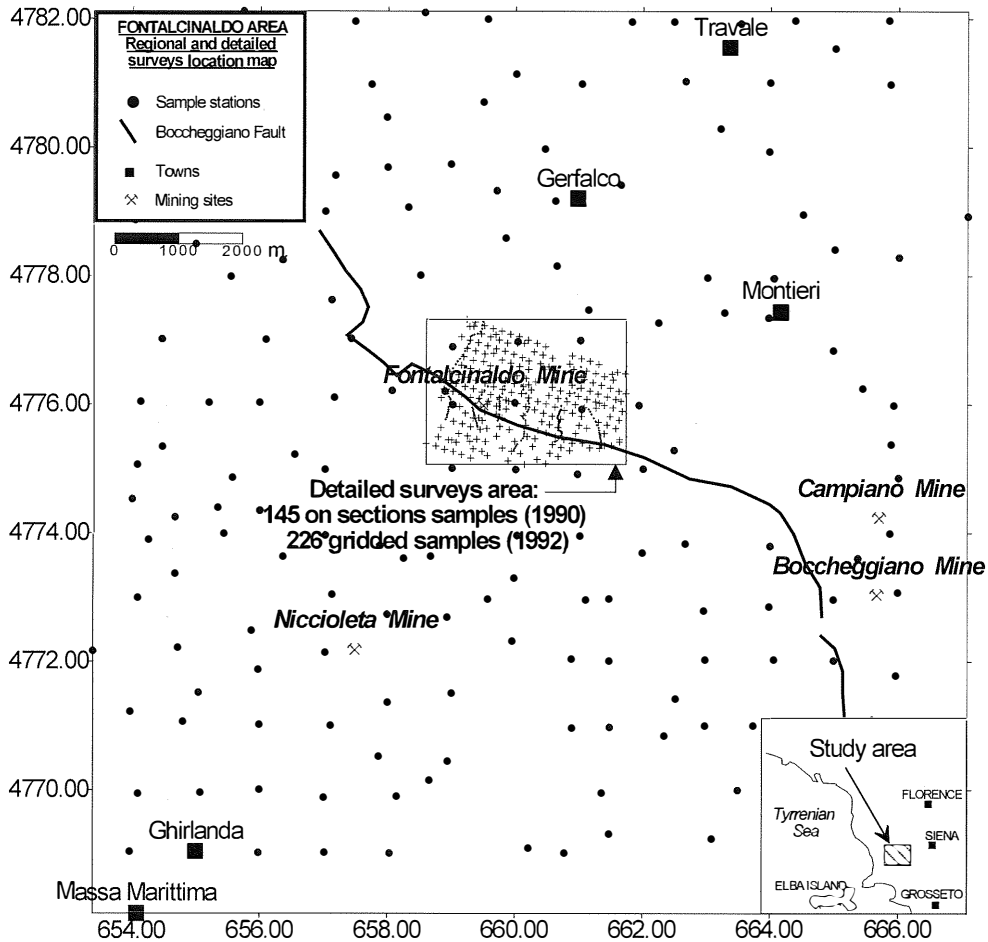


Fig. 1 – Study area and samples location map.

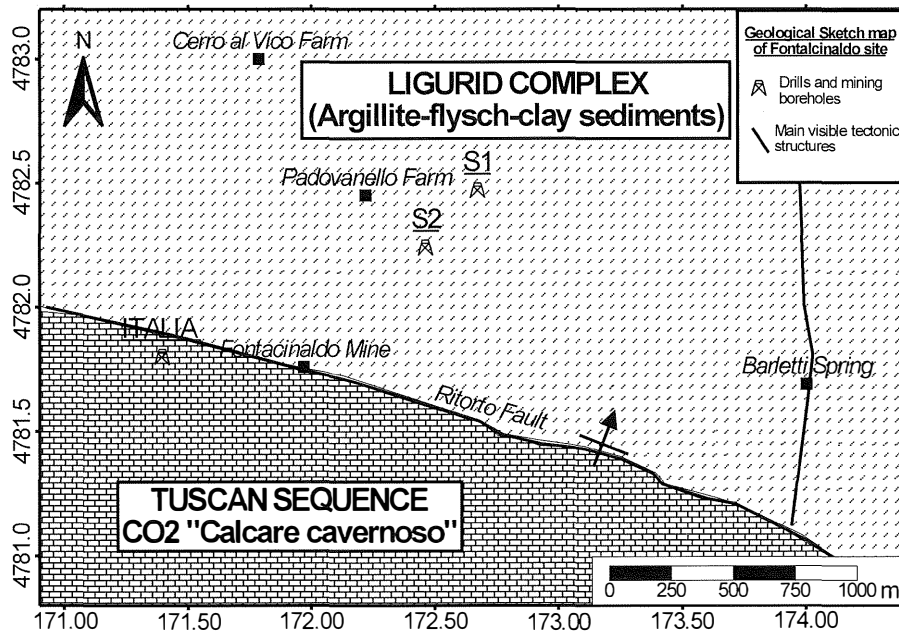


Fig. 2 – Geological sketch map of the Fontalcinaldo area.

the «Calcare Cavernoso» Formation and the underlying Triassic Boccheggiano Schistose sequences) and a collapsed area to the north (the Pavone River Graben) where the same lithological sequence is overlain by the allochthonous Ligurid Complex. These latter sediments mainly consist of the Cretaceous «Argille a Palombini» Formation, a low-permeable clayey flysch which ranges in thickness from 500 metres near the Ritorto Fault to 800 metres at the centre of the graben (RIMIN, 1988). Seismic data also show the presence of sub-parallel normal faults below the flysch which follow the Ritorto Fault direction and which lower the calcareous «substratum» towards the north. Although the extension of these faults to surface is likely, there is no clear geological or geophysical evidence of them occurring in the overlying flysch. This is probably due to erosion which eliminated any previous surface expression or to the plastic-homogeneous nature of these sediments which precludes seismic detection

of any discontinuity (Chiantore V., ISMES, p.c.). N-S and NE-SW trending lineaments are also present in the eastern and north-western portion of the area (RIMIN, 1988).

The sulphide orebodies occur primarily as pyrite lenses along the Ritorto Fault plane (Fontalcinaldo mine), as well as partially infilling the tectonic contact between the Ligurid Complex and the Calcare Cavernoso Formation at an average depth of 20-25 m. Surficial alteration haloes containing oxides and silicates overlay the main ore-bodies (Gregorio *et al.*, 1980).

Minor sulphur mineralisation was intercepted in holes (S1 and S2) drilled over an airborne magnetic anomaly that also corresponds with weak soil-geochemistry anomalies. This mineralisation infills the tectonic breccias of the Ritorto Fault and related fractures at a depth of 500-800 metres below surface and consist mainly of disseminated sulphide minerals (such as pyrite, galena and sphalerite) and iron oxides (magnetite); trace gold and

relatively consistent amounts of Ag minerals are also present (RIMIN, 1988).

SAMPLING AND ANALYSIS METHODOLOGY

The soil-gas surveys were performed during two stages (see fig. 1). In September 1990 a preliminary survey was performed at Fontalcinaldo. One hundred forty five samples were taken every 50-100 meters along 6 N-S oriented sections, perpendicular across the Ritorto (Boccheggiano) Fault (see fig. 3 for details). Bad weather conditions precluded any soil gas collection in 1991.

In June and July 1992 two gridded surveys were performed, both at Fontalcinaldo and in the surrounding areas respectively. In the first, an integration of 1990 data set was accomplished through the collection of 226

reconnaissance soil gas on a grid with a sample spacing of 200 m. In the second, in order to best evaluate background values, an additional set of 171 samples were taken over a 150 km² area (mesh spacing about 1 kilometre).

He, ²²²Rn and CO₂ were selected for analysis. Other species, such as methane and sulphur gases, were not addressed because they usually have very low soil-gas concentrations above sulphide deposits (Taylor *et al.*, 1982; Hinkle, 1984; Hynkle and Dilbert, 1984; Stedman *et al.*, 1984; Nicholson *et al.*, 1988; Ball *et al.*, 1990; Hynkle *et al.*, 1990; Kesler *et al.*, 1990) and sufficiently sensitive instruments were not available at the time of the surveys.

Soil-gas samples were collected by driving a hollow steel probe 0.5 m into the ground, inserting a syringe needle through an upper septum port on the probe and withdrawing the gas. ²²²Rn was determined in the field by

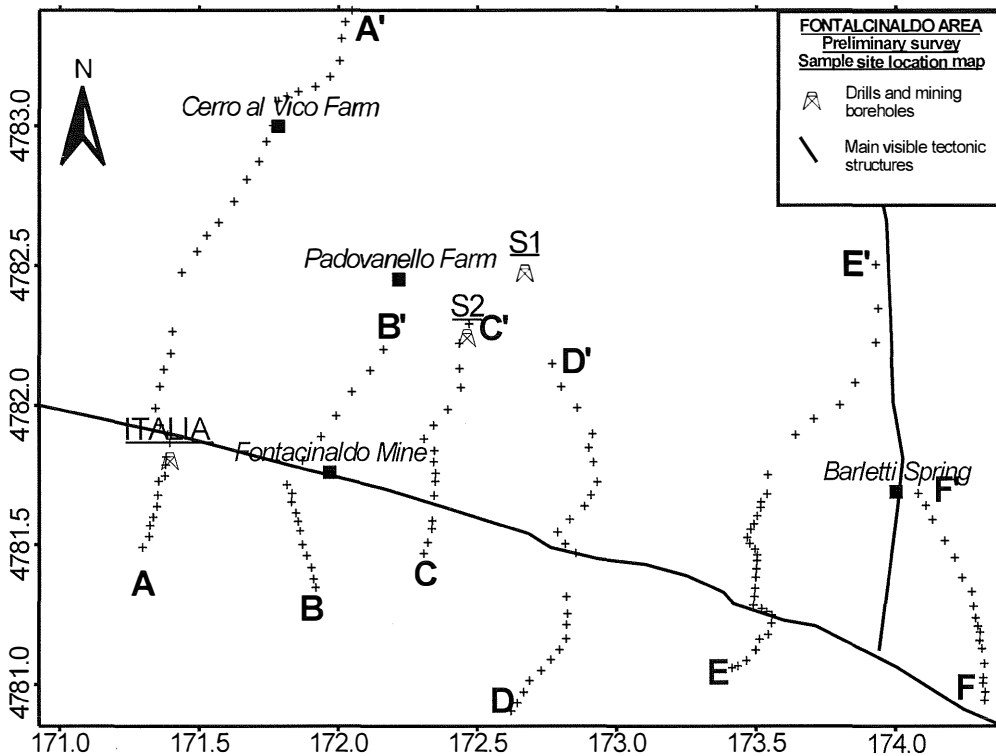


Fig. 3 – Location map for soil-gas samples collected during the preliminary survey.

TABLE 1

Statistical parameters for each gas species including recalculated ^{222}Rn parameters for samples collected over flysch and calcareous sediments.

1990 Soil gas preliminary survey					
Sample distance on sections : 50-100m.					
^{222}Rn (Bq/l)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
35.4	57	144	0	576.8	50
CO_2 %					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
2.35	1.90	140	0.03	12.2	3.9
ΔHe (ppb)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
166	214	139	-340	905	182
^{222}Rn (Bq/l) (Flysch)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
25.98	26.52	101	0	229	32
^{222}Rn (Bq/l) (CO_2 Calcareous sediments)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
		43	0	229	55
1992 Detailed soil gas survey (mesh 200 m x 200 m)					
^{222}Rn (Bq/l)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
16	16	226	0	116	40
CO_2 %					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
2.5	2	226	0	10	3.2
ΔHe (ppb)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
66	113	226	-265	406	136
^{222}Rn (Bq/l) (Flysch)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
12	13	148	0	78	20
^{222}Rn (Bq/l) (CO_2 Calcareous sediments)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
		78	0	229	33
1992 Regional soil gas survey (mesh: 1.5 km x 1.5km)					
^{222}Rn (Bq/l)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
12	21	171	0	145	26
CO_2 %					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
0.9	0.89	171	0	5.2	1.1
ΔHe (ppb)					
Mean	Std. Dev.	Count	Minimum	Maximum	Anomaly Thr.
22	93	171	-205	445	67

introducing soil-gas samples into a portable alpha-particle counter, while other gases were stored in stainless steel samplers and analysed in the laboratory by gas-chromatographic and mass-spectrometric methods. Radon activity is expressed as Bq/l while helium levels are given as the difference (δHe) between sample and atmospheric (5220 ppb) concentrations.

DISCUSSION

Basic statistical parameters and anomaly threshold levels for each gas species analysed are presented in Table 1. The mean and the standard deviation were preliminary used to state the statistical anomaly threshold defined at mean + $\frac{1}{2} \sigma$. Though this subjective model-based technique of threshold determination is arbitrary and in some cases not suitable (because no physical reason exists for considering values greater than one half standard deviation ($\frac{1}{2} \sigma$) above the mean level as «anomalous») it is widely used in exploration geochemistry for the recognition of

anomalous and background samples. (McCarthy and Reimer, 1986; Vakin and Lyalin, 1990; Klusman, 1993). Furthermore the method does not take on account the fact that anomalous and background population can overlay extensively; as these groups are actually two different population the mean and the standard deviation derived from the entire data-set have no statistical validity. Several more objective statistical procedures can be used to recognise geochemical population in a data-set (Lepeltier, 1969; Sinclair, 1974; Miesch, 1981). In this work the statistical approach to threshold estimation is obtained using probability graphs. (Sinclair, 1974; 1991). In the simplest case a single threshold will define two population (background and anomalies values); if, however the two population are not clearly separated they may overlap in an interval defined by two bounding threshold values. Probability plots features such as curves with inflection points or sharp breaks (see fig. 4), define the presence of different populations. As far as the preliminary

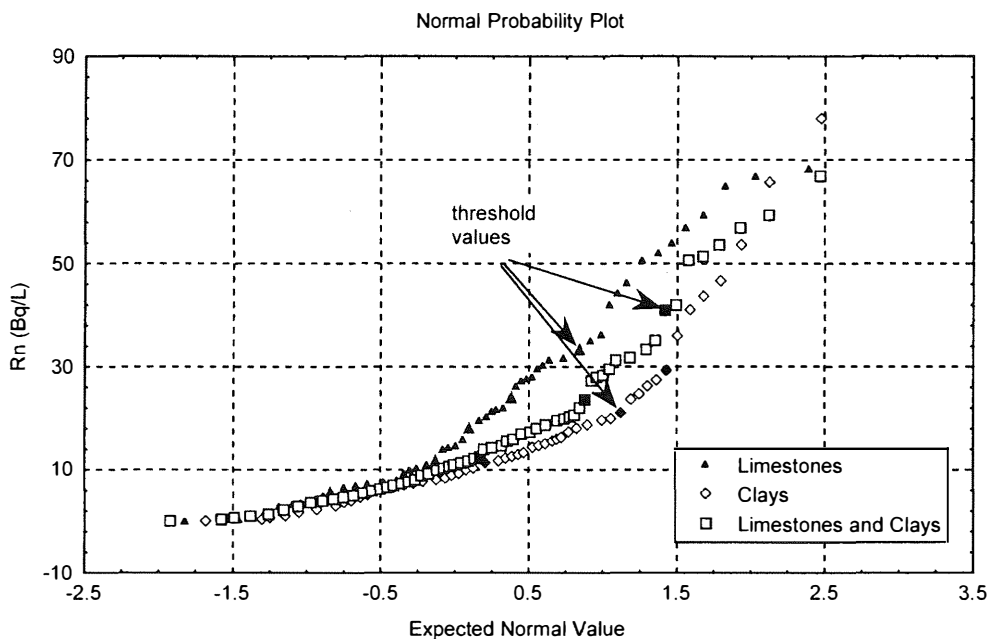


Fig. 4 – Example of normal probability graph used to define anomaly thresholds.

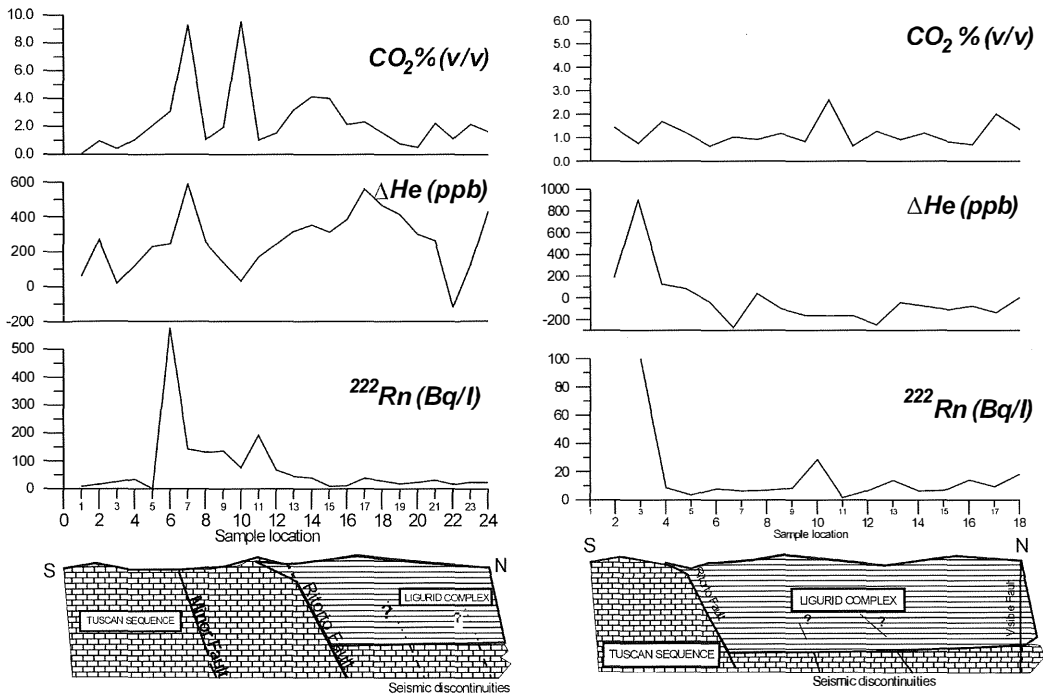


Fig. 5 – Geochemical cross sections D-D' a) and F-F' b) performed during the preliminary survey at Fontalcinaldo.

survey is concerned the values of each transect were plotted and compared with the Ritorto Fault outcrop as well as the surface projection of its related faults (figs. 5 a-b). ΔHe and CO_2 show anomalous peaks, i.e. higher than the respective threshold values of 182 ppb and 3.9%, which may be fault related. Radon levels remain higher than 50 Bq/l over the Calcare Cavernoso Formation but show a sharp decreasing over the flysch, probably related both to a source rock difference and different permeability between the two lithotypes. To highlight the presence of «hidden» radon peaks in clay sediments samples collected over the Argille Palombini formation and Calcare Cavernoso formation were statistically treated as a two separated subset of data. These newly calculated radon values were considered anomalous if they exceeded the threshold of 32 Bq/l over the flysch – as this value also represents the quantity of Rn generated by the

average uranium content present in argillaceous sediments, (Etioppe, 1995) – and 55 Bq/l over limestones. Moreover, in order to best compare the geological and geochemical data, plan view diagrams were produced with geochemical data, the surface trace of the Ritorto Fault and the surface projection of deep seismic discontinuities identified in the carbonate substratum (fig. 6a-b-c). In general He, CO_2 and re-calculated ^{222}Rn anomalies tends to overlay the tectonic structures of the area over both outcropping lithotypes («Calcare Cavernoso» and «Argille a Palombini» formations); in particular the good correlation between anomalous gas patterns and fractures (faults) revealed by geophysics in the carbonate «substratum» suggests the presence of lines of weakness in the flysch which act as preferential pathways for ascending gases. The high CO_2 values recorded along the Ritorto Fault close to Fontalcinaldo mine and «Italia» mining

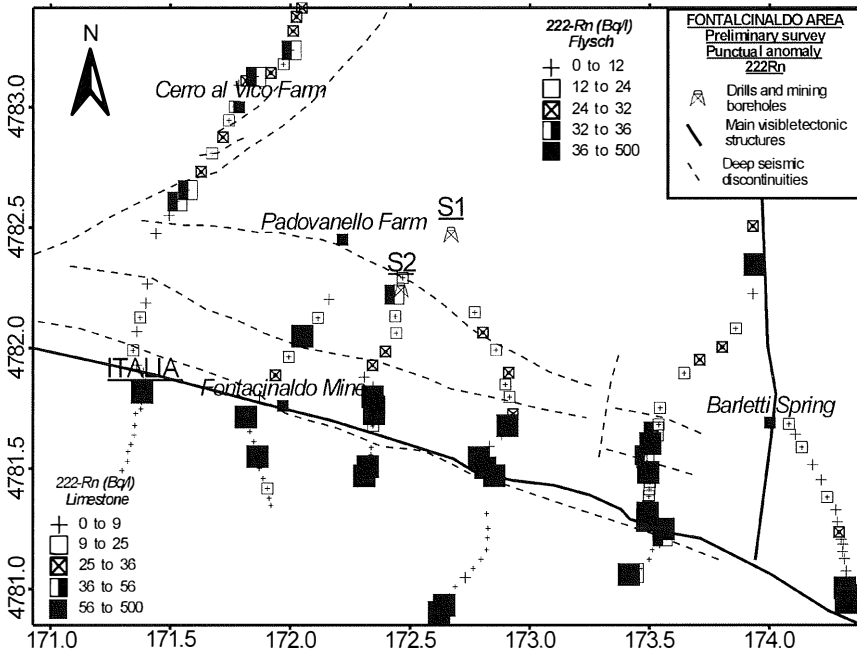


Fig. 6a – Plan view ^{222}Rn -anomaly map showing point values.

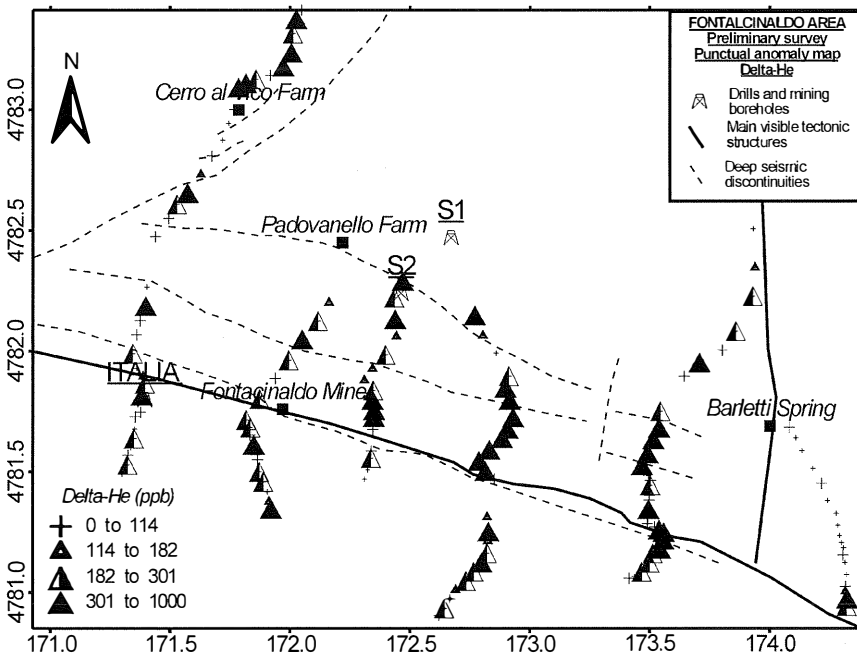


Fig. 6b – Plan view ΔHe -anomaly map showing point values.

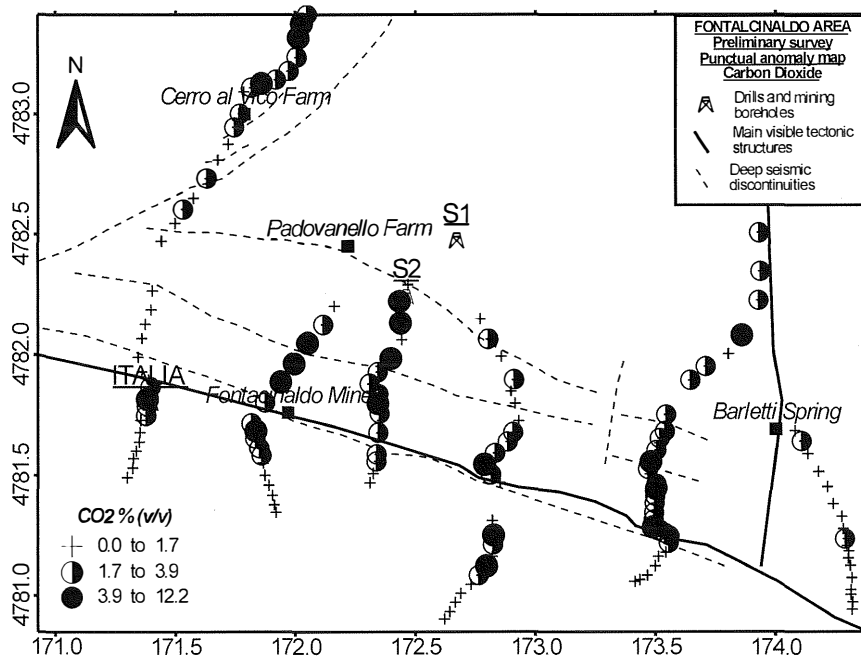


Fig. 6c – Plan view CO₂-anomaly map showing point values.

borehole as well as in correspondence of drillholes S1 and S2 are worth noting, as they imply the reaction of sulphuric acid with limestone and thus may be important from a mineral exploration point of view.

Geostatistically-produced contour maps obtained by processing the 226 samples uniformly collected over the same area in 1992, show He, ²²²Rn and CO₂ anomalies (see table 1) which are associated with either WNW-ESE or N-S tectonic lineaments, as shown in fig. 7a-b-c. Moreover He, CO₂ and ²²²Rn contour maps also suggest the possible existence of N-S tectonic lineaments in the central and north western section which are not delineated in the geological or geophysical maps.

The local presence of a N-S tectonic trend appear to be clearly confirmed by observing regional contour maps as shown in fig. 8a-b-c. Besides to reproducing the regional WNW-ESE tectonic trend (as they are prevalently distributed along the Boccheggiano Fault), He, ²²²Rn and CO₂ distribution show clearly N-S

trending anomalies close to Niccioleta and Campiano mining sites. In particular CO₂ contour lines also indicate the presence of a tectonic lineament north of Campiano that probably corresponds, as deduced from structural field data, to the northern extension of Boccheggiano Fault. The existence of such a structure would play an important role in the regional tectonic style of the study area and might also justify the constant occurrence of the previously mentioned N-S-trending gas anomalies at Fontalcinaldo.

In addition to the classical statistical procedures described above an alternative statistical approach aimed to further aid in the structural interpretation has also been applied. This method consists of fitting consecutive punctual anomaly values on the sample-location maps in order to define «linear anomalies». Lines were drawn between points showing values higher than the thresholds levels; moreover, points showing very different values from the local background were also

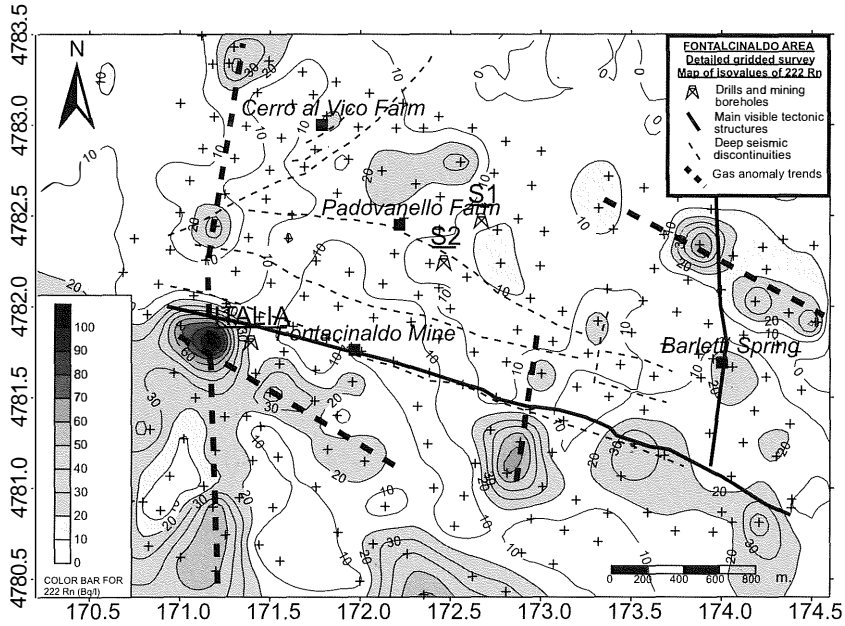


Fig. 7a – Anomaly contour map showing distribution of ^{222}Rn in soil gas samples collected at Fontcinaldo during the detailed gridded survey.

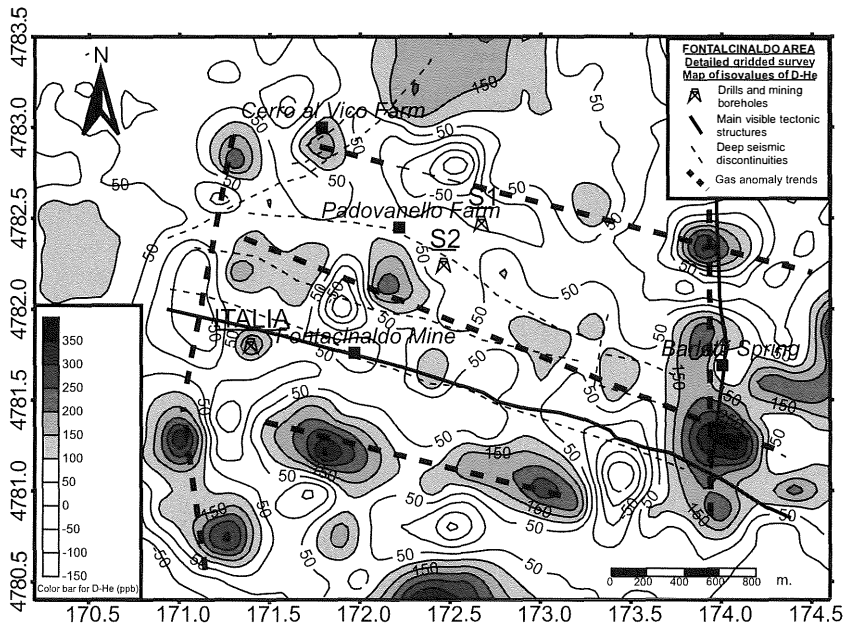


Fig. 7b – Anomaly contour map showing distribution of ΔHe in soil gas samples collected at Fontcinaldo during the detailed gridded survey.

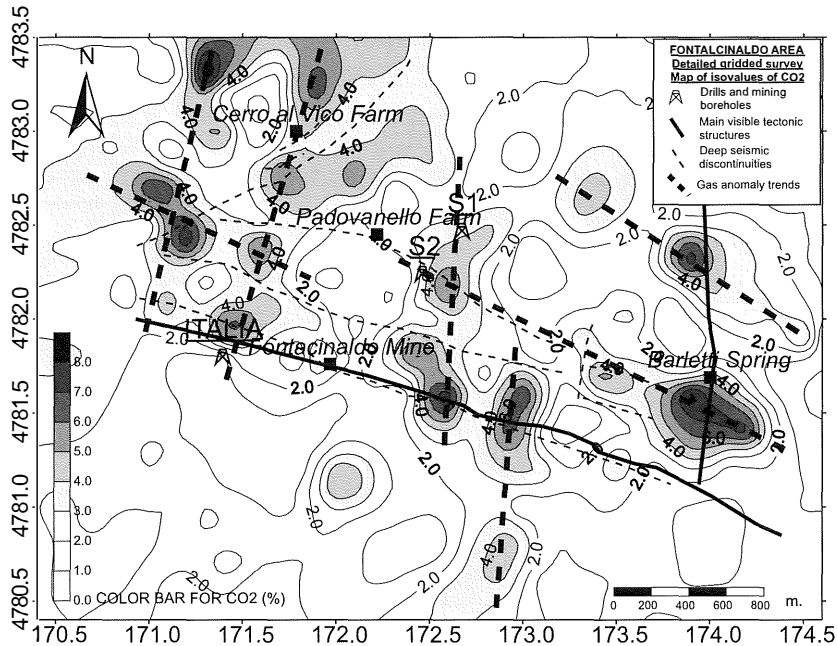


Fig. 7c – Anomaly contour map showing distribution of CO₂ in soil gas samples collected at Fontalcinaldo during the detailed gridded survey.

included even if they were not above the calculated threshold values. The statistical distribution of the resulting lines were then plotted on rose diagrams and compared with the regional and local tectonic trends. These results are shown for ²²²Rn in fig. 9, (CO₂ and DHe are similar); as can be seen a reasonable correlation exists between these trends and those of deep and surficial tectonic lineaments defined by geophysical and geological field studies, moreover a reasonable percentage of anomalous linear trends reveal the presence of probably hidden N-S tectonic structures.

As deduced from the data discussed above, these results also support the conclusion that soil-gas surveys are able to aid in the structural mapping of areas having low permeabilities. The following describes the work conducted to ascertain the presence of sulphide mineralisations which may fill such tectonic structures.

As indicated by the regional contour maps, CO₂, Rn and He anomalies appear to correlate well with the main mining areas (Niccioleta,

Boccheggiano-Campiano, Fontalcinaldo); in particular, high CO₂ anomalies indicate the possible occurrence of sulphuric acid-limestone reactions.

The detailed survey conducted in the Fontalcinaldo area supports the regional profiles. CO₂ increases (6-12% v/v) were recorded over the Ritorto Fault in the southern portion of the area where weak soil-chemistry anomalies have been observed and where sulphide mineralisation has been detected in drillholes S1 and S2 (fig. 7c) high CO₂ values, as well as other gases, were also noted close to P. Cerro al Vico and the Barletti Spring (near the north-western and eastern edges of the area, respectively) over fractures for which mineral occurrence data has not been collected. In this second case the concomitant presence of high CO₂, He and Rn concentrations may suggest the presence of sulphide mineralisation, although further studies which address sulphur gas detection are needed to verify this hypothesis.

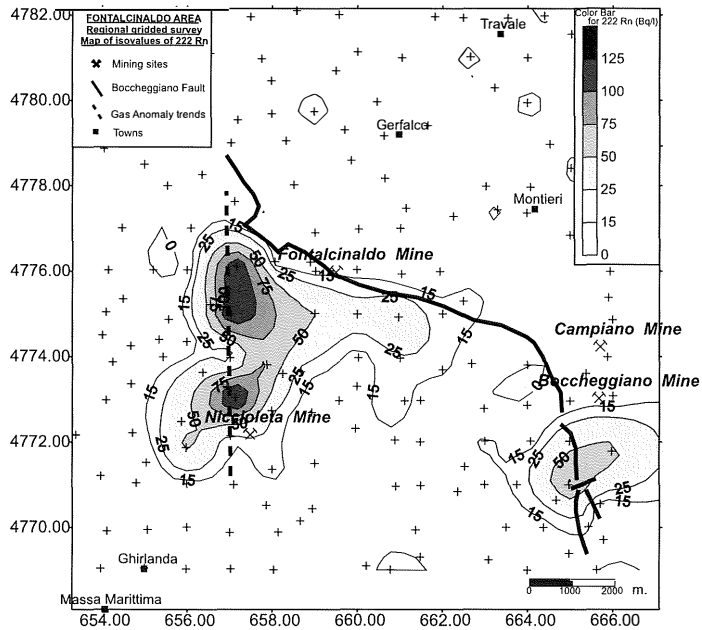


Fig. 8a – Anomaly contour map showing distribution of ^{222}Rn in soil gas samples collected around Fontalcinaldo during the regional gridded survey.

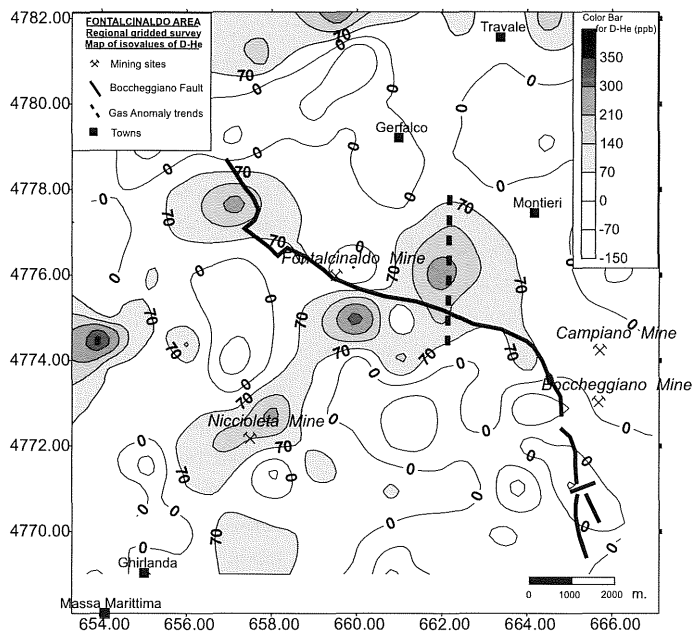


Fig. 8b – Anomaly contour map showing distribution of ΔHe in soil gas samples collected around Fontalcinaldo during the regional gridded survey.

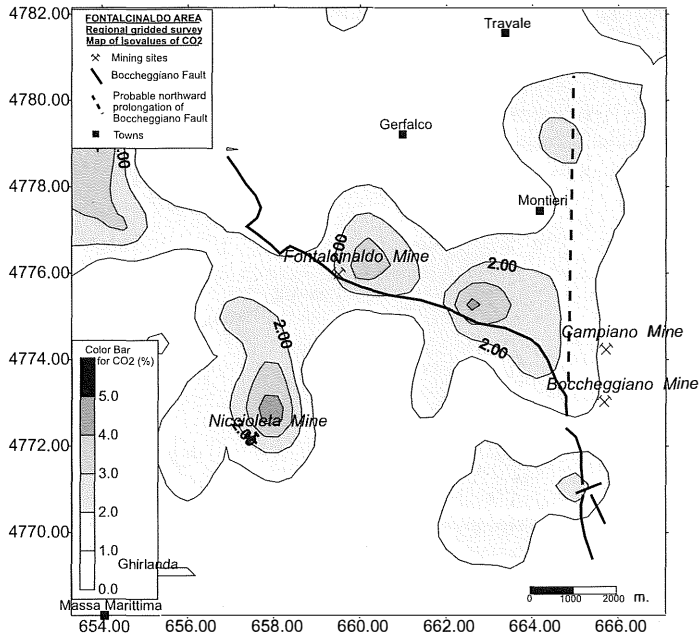


Fig. 8c – Anomaly contour map showing distribution of CO₂ in soil gas samples collected around Fontalcinaldo during the regional gridded survey.

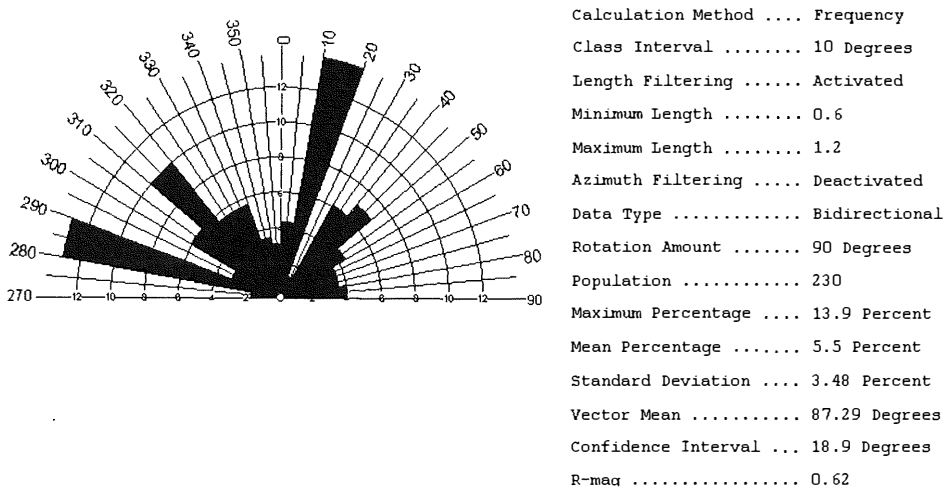


Fig. 9 – Rose diagrams showing statistical distribution of the anomalous trends resulting from ²²²Rn linear anomalies.

CONCLUSIONS

The present study on the application of soil-gas analysis for sulphide-ore exploration at Fontalcinaldo have revealed several important facts. Soil-gas surveys may be able to collect geochemical information in areas where thick, low-permeability clay deposits preclude the use of traditional geochemical methods based on trace-element aqueous migration. At Fontalcinaldo He, Rn and CO₂ show anomalies over both the investigated lithotypes (carbonate Tuscan Sequence and clayey Ligurid Flysch) and the method does not seem to be disturbed by the nature of the terrains. Earlier studies on the application of soil-gas methods to mineral exploration only regarded ore deposits overlain by thin, permeable sediments. In contrast, the soil-gas investigations performed at Fontalcinaldo are related to deposits overlaid by very thick and low-permeability sediments.

Fault and fracture systems act as preferential pathways for the upward migration of deep-seated gases and thus control surficial gas distribution. Traverse and gridded surveys performed at different times and scales give the same type of information on the structural setting of the investigated area, as well as on the possible location of sulphide ore-bearing fractures.

Regional soil-gas distributions appear to be controlled by the Boccheggiano Fault, which bisects the area along a WNW-ESE trend; CO₂ contour lines also suggest the probable occurrence of a northward extension of this fault in the vicinity of Campiano.

Detailed surveys performed at Fontalcinaldo show elevated soil-gas values over both the Ritorto Fault and over known structures in the eastern and western edge of the area. The occurrence over the flysch of gas anomalies running parallel to the Ritorto Fault direction (WNW-ESE) indicates the possible presence of hidden fracture related to deep seismic discontinuities identified in the carbonate substratum. Furthermore, contour maps also highlight the occurrence of N-S trending lineaments, reflecting the role played by the

above-discussed northward prolongation of the Boccheggiano Fault in terms of the local tectonic style.

In addition to the favourable results obtained both on the delineation of hidden tectonic structures and the acquisition of geochemical data in low-permeable clay sediments, soil-gas techniques may provide valuable information on the location of sulphide-ore-bearing fractures. As observed in the regional survey, CO₂, He and Rn seem to correlate well with major mining areas, thereby showing promise in the detection of sulphide deposits. Moreover, increased CO₂ levels have been recorded at Fontalcinaldo over known mineralised fractures in correspondence with the presence of Rn and He. The presence of other anomalies (CO₂ and other gases) detected over faults where no mineral-deposit data are available suggest that further studies on sulphur gas distribution would aid interpretation.

Considering the CO₂ distribution and the limitations placed on the research by the unfavourable geological conditions (depth and disseminated nature of the deposits) the reported results may be considered very promising.

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