Gas migration from two mine districts: The Tolfa (Lazio, Central Italy) and the Neves-Corvo (Baixo Alentejo, Portugal) case studies

Voltattorni[1*] N., Lombardi[2] S., Beaubien[2] S.E.

[1]Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata 605, 00143 Rome, Italy

[2]Earth Science Department, University "La Sapienza", Piazzale A. Moro 5, 00185 Rome, Italy

*corresponding author: nunzia.voltattorni@ingv.it

Abstract

Detailed soil gas surveys were conducted at two mine districts to understand gas migration mechanisms from deposits buried at different depths. The Tolfa (Lazio, Central Italy) and Neves-Corvo (Baixo Alentejo, Portugal) mine districts have different characteristics: the former is relatively shallow (30-100 m) whereas the latter is at a depth of 400-500 m and covered by low-permeability metamorphic rocks. The studied gases included major (N_2, O_2, CO_2) and trace (^4He, ^{222}Rn) gases, hydrocarbons (CH_4, C_2H_6 and C_3H_8) and S compounds (H_2S, COS, SO_2).The measured concentrations (some examples of max values at Tolfa: Rn 233 Bq/L, CO_2 9.5 % , CH_4 12.3 ppm, COS 3.7 ppm; and at Neves-Corvo: Rn 130 Bq/L, CO_2 24.3%, CH_4 0.1 %) indicate that gases migrate preferentially through zones of brittle deformation by advective processes, as suggested by the relatively high rate of migration needed to obtain anomalies of short-lived ^{222}Rn in the soil pores. Considering the different depths of the two ore deposits, obtained results can be considered as features of near-field (Tolfa) and far-field (Neves-Corvo) gas migration.

1. Introduction

It is well known that deep-origin gas can migrate towards the surface via both pressure-driven advection, along large-scale fracture domains, and concentration-driven diffusion, along smallerscale domains (Gascoyne and Wuschke, 1997; Thunvik and Braester, 1987; Abu-ElSha'r and Abriola, 1997). These processes can transport a deep, anomalous gas signature (in terms of composition, concentration, flux rate, etc.) to the near-surface environment where it can be studied as a proxy for subsurface processes (e.g. Voltattorni et al., 2010). Given good vertical continuity of migration pathways, the method can even be applied for mineral exploration where thick and/or low permeability sediments overlie deep buried targets (e.g. Astorri et al., 1999).

Soil gas surveys have been used to study a wide variety of different geological issues, including risk assessment such as faults, earthquakes and volcanic activity (Azzaro et al., 1998; Guerra and Lombardi, 2001; Zhou et al., 2010; Lombardi and Voltattorni, 2010; Walia et al., 2010), environmental problems like nuclear waste and anthropogenic CO_2 storage (Voltattorni et al., 2009, 2010; Kharaka et al., 2010; Fritz, 2011; Harvey et al., 2012), and resource exploration (e.g. geothermal, Phuong et al, 2012; Granieri et al., 2014). Exploration for minerals has been conducted for U deposits (Pereira et al., 2010; Boyle, 2013; Silva et al., 2014) and both base and precious metal deposits (Gao et al., 2011; Noble et al., 2013) using gas geochemistry.

Geochemical anomalies at the surface ("haloes") can be associated with buried mineral deposits (Hinkle and Harms, 1978; Reimer and Bowles, 1979; Ball et al., 1990; Astorri et al., 1999; Franklin et al., 2005; Hannington et al., 2005; Kelley et al., 2006). In areas undergoing sulphide weathering, O_2 is consumed and CO_2 formed (Hinkle et al., 1990; Reid and Rasmussen, 1990). Other species that may be associated with a mineral deposit include S gases (COS, H_2S and SO_2) derived from sulphide mineral alteration (oxidation and leaching) and hydrocarbon gases formed via thermal cracking of organic matter (where ore deposits are associated with hydrothermal activity and/or a high geothermal gradient) (Machel, 1989; Whiticar and Suess, 1990; Seewald et al., 1994; Polito et al., 2002).

Tectonic discontinuities and geothermal fluids can provide preferential pathways for gas ascending to the surface. Since the 1970's, He and Rn soil gases have been used in mineral prospecting as fault tracers where ore deposits undergo tectonic control. The study of Rn and/or

He is particularly useful for detecting crustal discontinuities even when faults are buried or cut non-cohesive clastic rocks, which makes surface recognition difficult using traditional field methods (Duddridge et al., 1991; Durrance and Gregory, 1988; Ciotoli et al., 1998; Ciotoli et al., 1999; Lombardi and Voltattorni, 2010).

The study of gas concentrations in the unsaturated soil horizon was performed over two mine districts with different characteristics. The Tolfa ore deposit (central Italy) is relatively shallow (30-100 m) and abandoned whereas the Neves-Corvo deposit (Portugal) is located at a depth of 400-500 m (covered by metamorphosed rocks with a low permeability) and mining active. Considering the different depths of the two deposits, the main aim of this study was to understand if the ability of soil gases to move towards the surface was related to the country rocks or to the presence of preferential pathways for movements, such as faults and fractures.

2. Materials and Methods

2.1 Soil gas sampling and analysis

Shallow soil gases were sampled using a 1 m long stainless steel probe fitted with a brass valve. This system enabled soil gas to be collected and stored in metallic containers (with a vacuum of 10^{-2} atm) for both laboratory analysis and to be pumped for on-site Rn analysis. The studied gases included major (N_2, O_2, CO_2) and trace (^4He, ^{222}Rn) gases, hydrocarbons (CH_4, C_2H_6 and C_3H_8) and sulphur compounds (H_2S, COS, SO_2). Soil gas surveys were performed during the dry summer season to avoid climatic factors which may affect soil gas values (Hinkle, 1994).

Radon determination was performed in the field using an EDA Instruments RDA-200 Radon Detector. The analytical error is $\pm$ 0.5 Bq/L. The determination of He was performed with a Varian Mass 4 spectrometer whose detection limit is $\pm$ 100 ppb. Hydrocarbons, N_2, O_2, CO_2, and sulphur compounds were determined using a Fison Instrument GC-8000 Series gas-chromatograph. Analytical precision is $\pm$ 100 ppm for CO_2, O_2 and N_2, $\pm$ 0.01 ppm for hydrocarbons and S compounds.

Two areas were investigated, one (Fig.1) in central Italy (Tolfa area, Lazio region) and a second (Fig.2) in the southern part of Portugal (Neves-Corvo, Baixo Alentejo region).

The soil gas survey in the Tolfa area was performed during two stages (Pizzardi, 1998). A preliminary regional survey of 235 points was performed along a regular grid (5 samples / km^2) near the villages of Tolfa and Allumiere. The second survey was carried out at the "Roccaccia-Pozzi" area where there are many abandoned mines. A total of 156 soil gas samples were collected in this small area (around 2 km^2) to test the gas-geochemical technique in an area having known mineralised veins and mine tailings (Ferrini et al., 1970; Ferrini, 1975).

Two horizontal geochemical profiles (traverses) were sampled at the Neves-Corvo mine district, based on geological profiles (Leca et al., 1983) crossing the two main ore deposits. A total of 146 soil gas samples were collected, with spacing ranging from 50-100 m in the peripheral sectors to 25-50 m in proximity of the ore bodies.

2.2 Geospatial Analysis

Different geospatial analysis techniques were applied to collected data to construct prediction maps of soil gas concentration in the two areas. Exploratory Data Analysis (EDA) evaluates the basic characteristics of the raw data and their statistical distribution by using numerical (i.e., calculation of summary statistics and statistical distribution of each variable), and graphical methods (i.e., histograms.) that summarize the data in a diagrammatic or pictorial way (Tukey, 1977; Good, 1983; Sinclair, 1991; Reimann and Filzmoser, 2000). We calculated background and anomalous contributions of data, taking into account that these can correspond to one or more populations (characterized by different statistical parameters) that can be referred to different geochemical processes (Zhang et al., 2005; Rantitsch, 2004; Ciotoli et al, 2007, 2014). Normal Probability Plots (NPP) were used to determine the occurrence of different geochemical populations and to define anomaly threshold values (Sinclair, 1991), which helped us to infer the main controlling processes, particularly when the study area has a large variety of factors such as soil types, geologic units, fractured zones, etc. Pearson's correlation analysis (Edwards, 1976) is a statistical measure of the strength of a linear relationship between paired data. This analysis was performed in order to find possible gas associations. Moreover, using Pearson's correlation coefficient data and the single linkage, R-mode cluster analysis (or hierarchical clustering) was applied in order to classify the gases into categories or clusters based on their nearness or similarity (Vega et al., 1998). The factor analysis is another important tool for the evaluation of geochemical data, consisting of a series of statistical processes explaining the dependence of multivariable models with the use of less number of artificial variables. In this analysis the variability among observed elements in terms of a potentially lower number of unobserved variables called factors and their effect on elements can be examined separately (Davis, 1986; Howarth, 1993; Tüysüz and Yaylalı, 2005). In this method, rather than the original data, dependence among the artificial variables is examined and computed from covariance and correlation coefficient matrices. In other words, eigenvalues and eigenvectors of covariance and correlation coefficient matrices are interpreted. Eigenvalues of correlation matrix were computed by applying the main component analysis to elements under interest. In the meantime varimax rotation was performed to strengthen the factor loads.

Exploratory Spatial Data Analysis (ESDA) technique involves applying statistical techniques in the spatial context to examine the data in more quantitative ways and to gain a deeper understanding of the investigated phenomena (i.e., sampling pattern, post and classed-post maps, spatial outliers, presence of trends, etc.). In particular, it is focused on the evaluation of the distinguishing characteristics of geographic data, and specifically on spatial autocorrelation and spatial heterogeneity (Anselin, 1998; Bailey and Gratell, 1995).

Collected data were processed using the following software: Grapher 9 and Surfer 12 (Golden Software. Inc.) and Statistica 6 (StatSoft. Inc.).

The datum and the projection for geographical coordinates are UTM WGS84.

3. Background Geology

3.1 The Tolfa mine district (Lazio, Central Italy)

The Tolfa mine district (Fig.1), located in the Tolfa Mountains area, is characterised by two major geological units. The Lower Unit (Carboniferous – Upper Cretaceous) is represented by the Tuscan Series and consists of weakly-metamorphosed continental sediments overlain by a sequence of marine carbonates. This unit is directly overlain by the Upper Unit (Cretaceous-Paleogene), which is mostly an allochthonous flysh complex with dominant limestones and marly limestones.

During the early Pliocene the region was inundated by the sea (Fazzini et al., 1972) and clayey and sandy sediments were deposited. Starting about 4.2 million years ago the area was uplifted by the intrusion of an acidic pluton into the sedimentary rocks (Lombardi et al., 1974). This intrusive event created a system of hydrothermal vein deposits, which formed along major faults. Mineralization in the Tolfa Mountains area can be divided into three stages. The first involved contact metasomatism of the host limestones during pluton intrusion, resulting in the formation of garnet-bearing calc-silicate hornfels. During drilling performed for geothermal research, the contact limestone was seen as deep as 330 m and hornfels were observed at even greater depths (Alberti et al., 1970). The second stage was the formation of phanerocrystalline carbonates within major faults, with fine-grained carbonates commonly found along the outer walls of the veins while medium to coarse-grained calcites are generally located in the interior parts. The third stage involved the deposition of sparry calcite along veinlets that are up to 40 cm wide and which are commonly found throughout the phanerocrystalline carbonate stocks. Rare quartz and fluorite are found in small veinlets scattered in the stocks. Their occurrence is related to the late-stage event (Masi et al., 1980).

Although all mines are now abandoned, the Tolfa area is characterised by a wide range of different mineral associations and resources, including Hg, alunite, kaolinite and feldspar mines;

metal sulphides (galena, marcasite, pyrite); mineral and thermomineral springs (T= 56°C, Cinti et al., 2011).

3.2 The Neves-Corvo mine district (Baixo-Alentejo region, Portugal)

The Neves-Corvo mine district (Fig. 2a) is in the Baixo-Alentejo region of Portugal, located about 50 km SSW of Beja between the towns of Castro Verde and Almodovar. Discovered in 1977, it forms a part of the well-known Iberian Pyrite Belt (IPB), which consists of massive polymetallic sulphide deposits contained within Devonian-Carboniferous volcanic and sedimentary rocks (Tornos, 2006; Albouy, 1981). The IPB is the largest and most important volcanogenic massive sulphide metallogenic province in the world. The original, pre-erosional amounts of sulphides concentrated in about 90 known deposits are estimated at more than 1.7 billion tonnes. Of this amount, about 20% has been mined and 10-15% lost to erosion (Barriga et al., 1997).

The Neves-Corvo mine (Fig. 2b) is the most important European Cu-Sn mine and a world class massive sulphide deposit. It is composed of five main ore bodies, each of which exhibit stockwork mineralization in the footwall host rock and are commonly located above a main felsic volcanic episode (Leca et al, 1983, Barriga and Carvalho, 1983). The Neves-Corvo mine is one of the largest deposits in the IPB, with approximately 300 Mt of total sulphide-rich rock (ore and sub-ore). Another main feature of this deposit is the clear lateral and vertical metal zonation patterns exhibited. As a general rule the Cu-rich sulphides occur at the base of the deposits and are overlain, when present, by Zn sulphides. The "barren" massive sulphides usually appear towards the upper part of the deposits. Tin occurs in close spatial association with the richest parts of the Cu mineralization. Pyrite is the most abundant sulphide, followed by chalcopyrite and spharelite. Cassiterite occurs locally in significant economic concentrations (Barriga et al., 1997; Serranti et al., 2002; Relvas et al., 2006).

4. Results

4.1 The Tolfa mine district (Lazio, Central Italy)

Descriptive statistics of soil gas results from the regional survey are reported in Table 1. Radon concentrations greater than the anomaly threshold (21 Bq/L) are represented by more than 48 % of the data (that is, 111 values over a total of 236 collected measurements, are considered anomalous (Fig. 3)..The maximum value (233 Bq/L) was found inside the mine area where a lava vein outcrops. The Rn frequency distribution is positively skewed, as indicated by the histogram in figure 4. Helium values range from a minimum of 4100 ppb to a maximum of 5600 ppb. The non-normal distribution (Fig. 4) is highly influenced by the numerous values (> 70% of total data set) less than the concentration in air (5220 ± 4 ppb; Holland and Emerson, 1990). The lowest values were found primarily on vulcanite outcrops and flysh covering where hydrothermal phenomena occur.

The highest CO_2 value (9.5 %, v/v) was found at a major hydrothermal spring ("Bagnarello"). Remaining data, almost 70% are below the CO_2 mean value for Italian soils (1.6 % v/v; Ciotoli et al., 2004) and only 20% of the data are greater (up to 5 %, v/v) than the anomaly threshold (2.1 %, v/v).

More than 60 % of oxygen values are below the anomaly threshold (19.1 %). The negative skewness (-1.4) as well as the high IQR value (3.2) indicate that the distribution is non-normal (Fig. 4) and strongly influenced by the large number of low concentrations.

Regarding the hydrocarbon gases, the anomaly threshold of CH_4 is 2.7 ppm v/v with a maximum value (12.3 ppm v/v) located east of Allumiere near a kaolin mine. Anomalous values of ethane (C_2H_6, anomaly threshold: 0.2 ppm) and propane (C_3H_8, anomaly threshold: 0.2 ppm) were irregularly distributed.

Anomalous values of SO_2 (anomaly threshold: 0.1 ppm) and COS (anomaly threshold: 1.0 ppm) are interesting considering the high solubility of the S compounds. The high concentrations (maximum SO_2 and COS values: 0.3 and 3.7 ppm respectively) could be caused by the presence of superficial mineralization.

Table 1 also shows the results of the detailed sampling performed in a small area (Fig.1, the small shaded square) where mining was most active previously. There are several abandoned mines and a considerable extent of mining waste piles. Radon, He, CO_2, and C_2H_6 median concentrations for the detailed survey are all greater than those observed in the regional survey concentrations (maxima: 400 Bq/L, 11300 ppb, 5.2 % and 1.0 ppm respectively; Fig.5).

Results of Pearson's correlation analysis (level of significance $p \leq 0.05$) are given in Table 2. Significant correlations among gases are highlighted with bold values. In the Tolfa area, CO_2 is weakly correlated with Rn ($r = 0.32$). Potential weak correlations are among hydrocarbons and S compounds. Correlation cannot establish cause-and-effect relationships so cluster analysis was used to define compounds with similar behaviors and close relations. and the results are illustrated in a dendrogram in Fig. 6a. The cluster analysis of 12 gas species identified two main groups highlighting the couple Rn-CO_2 and COS-SO_2-O_2.

The results of factor analysis (including Eigenvalue, % of total variance and cumulative %) are in Tab. 3. Figure 6b shows the Factor1-Factor2 plot that highlights four different groups: Rn and CO_2, COS and SO_2, C_3H_8 and C_2H_6, C_2H_2 and C_2H_4. These analyses confirmed the two couples obtained by dendrogram and other gas associations.

Figure 7 shows the contour maps of radon (a), helium (b), carbon dioxide (c), oxygen (d) and methane (e). Gas concentrations were considered anomalous when higher than anomaly threshold fixed on the normal probability plot distribution of this dataset. The highest Rn values are observed at the "La Bianca" zone, where hydrothermal springs are present (Fig.7a). Anomalous Rn values are also over volcanic outcrops especially in the northern sector. In contrast, minimum He values (< 5300 ppb) occur throughout the mineralized areas (abandoned mine area, Fig. 7b). The CO_2 (Fig. 7c) and O_2 (Fig. 7d) anomalies show an inverse relationship, such that high concentrations of the former commonly correspond with low concentrations of the latter. The lowest O_2 values are where superficial S deposits abound and redox phenomena favour CO_2 production (e.g. la Roccaccia and la Bianca areas). The CH_4 distribution (Fig. 7e) is connected neither with volcanic outcrops nor local structural patterns. An anomaly was found to the west of Tolfa village near a kaolin mine as well as in the south-western sector of the studied area.

Figure 8 shows the distribution maps of ethane (C_2H_6), propane (Fig. 8b - C_3H_8), sulphur dioxide (SO_2) and carbonyl sulphide (COS). The anomalous ethane concentrations (Fig. 8a) correspond mainly with the contact between vulcanites and unaltered Tolfa flysh. Moreover, high concentrations were found in the proximity of thermal springs, lava domes and veins. The SO_2 (Fig. 8c) and COS (Fig. 8d) anomalies show a spotty distribution, especially within the altered flysh zone.

Fig. 9 shows the results from the detailed survey in the small area where ore extraction was most active in the past. Anomalous Rn, and CO_2 values are mainly along the Marangone River where fractures are inferred based on the presence of large veins at the surface. Gas anomalies were also found in correspondence with abandoned mines where there is abundant mining waste. Carbonyl sulfide and SO_2 anomalous values were found both over the abandoned mining area and outside the metasomatized area. The distribution of sulphur compounds is probably due to the dispersion of minerals caused by erosion phenomena and interaction with groundwater as well as S oxide-reductions that produce gaseous compounds.

4.2 The Neves-Corvo mine districts (Baixo-Alentejo region, Portugal)

Two horizontal geochemical (soil gas) profiles (or traverses) were performed following the directions (Profile 1: N 36°; Profile 2: N 60°) of two geological cross-sections (Leca et al., 1983) that intersect the two main ore deposits (Fig. 2b). Descriptive statistics of the soil gas results are reported in Table 4. Only 28 Rn measurements out of a total of 146 sampling points were obtained.

The frequency distribution of the few available Rn samples is positively skewed. The maximum Rn value (130 Bq/L) was found along Profile 2 that corresponds with mineralized bodies located between 1500 and 2000 m of depth.

Helium values range from 4900 ppb to 12600 ppb on Profile 1 (P1) and from 4900 ppb to 5500 ppb on Profile 2 (P2). The data suggest a non-normal distribution influenced by the highest anomalous results, as confirmed by the histograms in figure 10. Values higher than He concentration in air (5220 ± 4 ppb; Holland and Emerson, 1990) are only 21.9 % of total data and they were found along both profiles in proximity of deep mineralized bodies. Almost 85 % of the CO_2 values are below the anomaly threshold (0.9 %). However, the positive value of skewness ($\geq$ 6.5) suggest that the highest values (from 6 to 24%) strongly influence the frequency distribution. Except for one particularly low value (3.5 % at P2) the O_2 concentrations range from 12 % to a max of 22%. The numerous low O_2 values result in a negatively skewed non-normal distribution.

Methane results at P2 show three extreme outliers (30.8, 349 and 1172 ppm). As a consequence of these high values, both skewness and SD values are particularly high (8.3 and 131.3, respectively). Ethane and propane, on the contrary, show low values and are almost homogeneous.

The analysis of S compounds highlighted a major abundance of CS_2 in comparison with the other two species COS and SO_2. Only 8 % of total data has values greater than detection limit reaching concentrations up to 0.5 ppm.

Correlation analysis (Table 5) shows there are no meaningful correlations (level of significance $p \leq 0.05$) among gases on P1 whereas Rn is strongly correlated with CO_2 ($r = 0.80$) and CH_4 ($r = 0.67$) at P2. A significant linear relationship ($r = 0.95$) exists between CO_2 and CH_4. Oxygen has a strong negative linear relationship with Rn, CO_2 and CH_4 (-0.65, -0.85 and -0.87, respectively). Figure 11 shows the dendrograms for both profiles. The only significant gas association for P1 is the couple CO_2- C_3H_8 that is not confirmed by factor analysis. Cluster analysis for P2 variables highlighted one main group that gathers Rn, CO_2 and CH_4 and a minor group formed by the couple C_3H_8-SO_2. The results of factor analysis (including Eigenvalue, % of total variance and cumulative %) are given in Tab. 5. The Factor1-Factor2 scatter plot confirm the two gas associations suggested by the dendrogram, and also highlights the group composed by S compounds (COS and CS_2) and hydrocarbons (C_2H_4 and C_2H_6).

Figure 12 shows the running averages (window width = 3) of He, O_2, CH_4 and CO_2 raw data from the Profile 1. Methane, He and CO_2 have different trends. Only O_2 has an inverse relationship with CO_2. Max He concentration was found in slightly to the east of a fault intercepting the mineralised body, at around 2600 m from the beginning of the Profile 1. The distribution of CS_2 and SO_2 (not shown in figure 12) are generally related to the fracture patterns of the geological cross-section.

The running averages of data (Rn, CO_2, He and CH_4) from Profile 2, are shown in figure 13. Radon and CO_2 show a similar trend. A good correspondence between the highest radon values (> 50 Bq/L) and concentration anomalies of CO_2, He and CH_4 can be observed between 1500 and 2000 m along the profile in an area limited by two known faults. This gas association was also evident in the correlations, dendrograms and factor analysis.

4.3 Comparison between the Tolfa and the Neves-Corvo results

Gas leakage does not occur along the entire length of any given fault but is instead focused at isolated points or small areas sometime far from faults (Annunziatellis et al., 2008). This implies a complex permeability distribution along the fault planes, as well as the influence of local mineralizations on the distributions of some gas species. Further, the depth of the ore deposits may play a crucial role in the potential migration of soil gases. Figure 14 shows the comparison of median values from the two investigated mine districts. The graphs indicate that the median value of CO_2 is higher at Tolfa probably because of the oxidation of abundant local sulphurs. The median values of CH_4 are very similar (1.9 ppm Tolfa regional; 1 ppm Tolfa detailed; 1.1

ppm Neves-Corvo_P1; 1.2 Neves-Corvo_P2) suggesting a common origin probably linked to reducing conditions of soils. Median values of ethane (C_2H_6) and propane (C_3H_8) are comparable among the four sites confirming the hypothesis that they can be derived from both buried ore deposits (due to their thermo-catalytic origin) and gas migration pathways (faults and fractures). Both the median value of radon activity (∽25 Bq/L) and He (∽5200 ppm) are comparable among the investigated areas highlighting the influence of active tectonic structures at both the mine districts.

Figure 15 shows box plots of S compounds. Median values are comparable among sites although the Neves-Corvo profiles have a lower number of extreme values in comparison with Tolfa. This is possibly due to the different depth of buried deposits: the Neves-Corvo ore deposit is deeper than Tolfa deposit and covered by low-permeability metamorphic rocks whose humidity acts as barrier to the migration of the very soluble SO_2 and COS.

5 Discussion

5.3 The Tolfa mine district (Lazio, Central Italy)

As a first approach, statistical analysis highlighted different gas associations suggesting different gas origins and/or interactions that would influence the presence of deep/shallow soil gas species at surface. The couple Rn-CO_2 constitutes a typical carrier-trace gas association (Etiope and Lombardi, 1995). Radon is a short-lived (3.8 days) radioactive gas produced from the ^{238}U decay chain. In diffusive systems it displays a poor mobility (Dubois et al., 1995) that, associated with its short half-life, limits its migration from the source rock. The CO_2 acts as carrier gas for Rn transport from deeper source and the spatial coincidence of radon and CO_2 concentrations provides evidence of this transport mechanism. The superposition of high Rn values and CO_2 anomalies in the Tolfa mine district, is evident only in the northern sector between the fault and the volcanic outcrop. These soil gas distributions are interpreted as being due to intense shallow fracturing caused by thermohydro- chemical and thermo-hydro-mechanical stress during magma intrusion. Anomalous soil Rn activities determined near the surface and not associated to CO_2 depend upon many factors, including the Rn emanating power of the local rock and soil (Morawska and Phillips, 1993).

Anomalous CO_2 enrichment and O_2 depletion in soil gas over buried mineral deposits have been documented in several case studies (Hinkle and Dilbert, 1984; McCarthy et al., 1986; Reid and Rasmussen, 1990; Klusman, 1993; Zhang, 2000). The origin of these signatures is controversial (Kelley et al., 2006). Several authors have proposed that the anomalies originate from the oxidation of sulfides, which consumes O_2 and produce CO_2 through generation of acid and dissolution of carbonate (Glebovskaya and Glebovskii, 1960; McCarthy et al., 1986). However, considering the low CO_2 concentrations found at the Tolfa area, biological processes, such as the microbial decomposition of organic matter or root respiration, can have a strong influence on the composition of soil gas (Amundson and Davidson, 1990). Alpers et al. (1990) studied the stable isotopic composition of CO_2 (max value: 9.5%) in soil gas over the Crandon deposit, and found that the anomalous concentrations were consistent with derivation by microbial decomposition of organic matter and root respiration.

According to Polito et al. (2002), the detection of coincidental CO_2 enrichment, O_2 depletion and light hydrocarbon anomalies are strong advocates against the possibility that the anomalies are simply the result of microbiological activity in the soil or in the shear zone. Firstly, methanotrophic and methanogenic bacteria cannot productively co-exist in the same environment given their respective sensitivities to oxygen (or the lack thereof). Second, the presence of higher hydrocarbons ($>C_{2+}$) in soil-gas above ore deposits cannot be explained by the presence of methanogenic bacteria in the soil, because C_{2+} hydrocarbons are not usually produced by bacteria (Oremland 1981; Oremland *et al.* 1988). Moreover, CH_4, C_2H_6 and other light hydrocarbons are known to be present in fluid inclusions of the ore body (Bray et al., 1991; Ho et al., 1992; De Ronde et al., 1992; Graney and Kesler, 1995; Polito et al., 2001). The soil gas distributions at Tolfa area, however, showed no spatial correlations among gas species and, for this reason, we need to apply different gas origins. The low CH_4 concentrations and the distribution of the few anomalies outside the metasomatised area, suggest that the origin of this gas species is probably linked to local biological activity. On the other side, the probable thermo-catalytic origin of ethane and propane means that their presence at the surface is an indication of gas migration along faults.

No significant anomalous He values were found that can be related to the presence of mineralizations as described by many authors (Dyck, 1976; Pogorsky and Quirt, 1981; Gregory and Durrance, 1985; Butt and Gole, 1985; Hinkle, 1994; Gong et al., 2000). The high diffusibility of He would suggest that migration into and out of the pores in response to partial pressure differences would be so rapid that at most the He content of the micropore gas may represent a mean of the fluctuations shown by the inter-crumb voids in the soil (Butt et al., 2000). Furthermore, the high porosity of volcanic soils (where minimum helium values were found) can retain water and act as a barrier to the migration of the low-solubility He (Butt et al., 2000).

Sulphur compounds (H_2S, COS, CS_2 and SO_2) are of most interest in mineral exploration because they potentially have a more direct link to mineralization (Kelley et al., 2006). These volatile species derive not only from sulfide minerals but possibly also from reactions with each other. However, although the mechanisms of their formation appear to be complex, the fact remains that anomalous concentrations of S compounds occur over oxidizing ore deposits (Hinkle et al., 1990). Therefore, the statistical associations found for the Tolfa area would confirm the superficial gas origin, probably due to the presence of local mineralizations.

5.2 The Neves-Corvo mine districts (Baixo-Alentejo region, Portugal)

The depth (4-500 m) of the Neves-Corvo mineralised bodies show different soil gas trends. A likely explanation of the CO_2, CH_4 and O_2 distributions is linked to the oxidation of local sulphurs to H_2SO_4 that reacts with carbonate minerals of host rocks generating carbon dioxide and consuming oxygen (Polito et al., 2002). Methane is also generated in these soil reducing conditions. Both the geochemical profiles present strong variations of He concentrations with several anomalous peaks. Helium is certainly provided through the U and Th decay, the host rocks of the orebody being relatively enriched in U and Th (Pauwels et al., 1999). Indeed, Neves-Corvo is the only IPB orebody having a heterogeneous isotopic composition that includes highly radiogenic stanniferous ore with $^{206}Pb/^{204}Pb$>18.40 in cassiterites (Barriga et al., 1997). This implies the inclusion of U traces in the cassiterite crystal structure. The highest He concentrations often correspond to locations where mineralization was identified at depth.

Since He migrates easily from deep rocks to the surface because of its small diameter, it can be considered as an indirect tracer of the presence of mineralization at depth, whereas the Rn signal can only trace relatively shallow anomalous zones due to its low gas velocity. In order to better understand the obtained results, we considered the study of Pauwels et al. (1999) that analyzed soil gas concentrations at three sites located in the southwest Iberian Pyrite Belt (Los Frailes, Sierrecilla and Herrerias). Radon concentrations are very similar (max value: Pauwels et al., 110 Bq/L; Neves-Corvo, 130 Bq/L) and both found associated to carbon dioxide that represents the main carrier gas for Rn in this area. CO_2 results are unusually high compared with Pauwels et al. (1999) that found a max CO_2 value around 2.5 % whereas our max values is 11.8 % at Profile 1 and 24.3 % at Profile 2. Isotopic analysis of CO_2 would help in the understanding the origin of this gas. However, we can exclude biological activity especially considering that both highest values were found where ore deposits were identified at depth.

Notwithstanding, the superimposition of anomalous Rn, CO_2, He and CH_4 values (Profile 2) reveals the presence of fractures cross-cutting the ore bodies at depth.

6 Conclusions

Soil gas measurements of 12 gaseous species were performed in two mine districts having different characteristics. The Tolfa deposit is relatively shallow buried (30-100 m) while the

Neves-Corvo deposit is located at a depth of 400-500 m and covered by low-permeability metamorphic rocks. Results showed that the eventual gas release on the surface is controlled by different processes. In particular, at both investigated areas, Rn migrates preferentially through zones of enhanced permeability (faults/fractures) as suggested by the relatively high rate of migration needed to obtain anomalies of short-lived ^{222}Rn in the soil pores. Further, the association Rn-CO_2 confirm the presence of high gas microseeps, as well as the known behavior of CO_2 acting as carrier for trace gases (i.e., Rn and He). At both mine districts, the presence of CH_4 is due to soil reducing conditions while C_2H_6 and C_3H_8 derive from both buried ore deposits (due to their thermo-catalytic origin) and gas migration pathways (faults and fractures). Sulphur compounds (e.g., COS, SO_2) are extremely soluble and are the only gas species that seem to be influenced by the depths of the ore deposits.

The Tolfa mine district can be considered as a case study of "near-field" migration from a superficial resource with anomalous gas values directly linked to the metasomatised areas and the principal tectonic structures that, in the past, strongly influenced the ascent of mineralised fluids. Excepting for soluble gas species, similar results were obtained in the Neves-Corvo mine district that represents a "far-field" migration from a deep source.

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Figure and table captions

Figure 1. Schematic geological map of the Tolfa mine district and location of sampling sites. The area is characterised by thermal alteration and by the presence of many inactive mines.

Figure 2. a) Schematic geological map and location of the main massive sulphur volcanogenic deposits at the Iberian Pyrite Belt (IPB – Portugal). b) Geological map of the Neves-Corvo mining region in the Alentejo Province (Portugal) and location of the geochemical profiles (adapted from Batista et al., 2012).

Figure 3. Normal Probability Plot calculated for radon soil gas. The plot highlights the anomaly threshold determinated according to Sinclair (1991)

Figure 4. Histograms of the soil gas raw data from Tolfa mine district. All gas species highlight a non-normal distribution due to the presence of outliers.

Figure 5. Comparison of median gas values between the regional and detailed surveys at the Tolfa mine district. Results from the detailed survey (conducted in the area that had the greatest mining activity) are higher than the regional survey results because of the presence of lava domes, veins, and mine wastes.

Figure 6 Dendrogram (a) depicting the hierarchical clustering of elements (Single Linkage; Pearson's correlation coefficient). Three couples were obtained at Tolfa area: Rn-CO_2, O_2-COS and COS-SO_2. The Factor1-Factor2 diagram (b) highlights four different groups.

Figure 7. Rn (a), He (b), CO_2 (c), O_2 (d) and CH_4 (e) soil gas distribution maps from the Tolfa mine district. Anomalous Rn values are over the mineralized areas and volcanic outcrops, whereas maximum He values are outside the mineralized areas.

Figure 8. C_2H_6 (a), C_3H_8 (b), SO_2 (c) and COS (e) soil gas distribution maps from the Tolfa mine district. Both hydrocarbons and sulphur compound anomalies have a spotty distribution.

Figure 9. Rn - CO_2 and SO_2 – COS soil gas distribution maps from the Tolfa detailed survey. Anomalous gas values are mainly along the Marangone river .

Figure 10. Histograms of the soil gas raw data from the two geochemical profiles performed at Neves-Corvo mine district. All gas species highlight a non-normal distribution due to the presence of outliers.

Figure 11. Dendrogram (a) of elements from Profile 1 at Neves-Corvo area. Three gas associations are highlighted: CO_2 - C_3H_8, O_2 - CH_4 and C_2H_4 – C_2H_6. The latter is the only gas association confirmed by factor analysis (b). The results of cluster analysis from Profile 2 (c) highlighted one main group that gathers Rn, CO_2 and CH_4 and two minor groups: the couple C_3H_8-SO_2 and the group C_2H_4-COS-C_2H_6-CS_2. The Factor1-Factor2 diagram (d) confirm all these gas associations.

Figure 12. Running average (window width = 3) of He, O_2, CH_4 and CO_2 from the Profile 1 performed over the Neves-Corvo ore deposit area... Soil gases show different trends. There is a clear inverse relationship between O_2 and CO_2.

Figure 13. Running average (window width = 3) of He, Rn, CH_4 and CO_2 from the Profile 2 performed over the Neves- Corvo ore deposit area.

Figure 14. Comparison of median values from Tolfa and Neves-Corvo areas. Generally speaking, soil gas median values are comparable among the four sites excepting for CO_2 higher at Tolfa.

Figure 15. Box plots for comparison of the Tolfa and Neves-Corvo distribution data sets. Median values of sulphur compounds are comparable among sites.

Table 1. Main statistical parameters of the Tolfa regional and detailed soil gas surveys. Skewness, standard deviation (SD) and inter-quartile range (IQR) values are useful to evaluate the data dispersion degree and, consequently, the frequency distribution of the different gas species. b.d.l. - below detection limit. The anomaly threshold values were fixed according to Sinclair (1991).

Table 2. Correlation coefficients for soil gas samples of the Tolfa regional survey. Significant correlations among gases are highlighted with bold values..

Table 3. Factor loadings and Eigenvalue values for Tolfa data. Three factors were discriminated.

Table 4. Main statistical parameters of the Neves-Corvo geochemical profiles. SD - Standard deviation, IQR - Inter-Quartile Range, b.d.l. - below detection limit.

Table 5. Correlation coefficients for soil gas samples of the Neves-Corvo profiles. Significant correlations among gases are highlighted with bold values.

Table 6. Factor loadings and Eigenvalue values for Neves-Corvo data. Three factors were discriminated for Profile 1 data whereas only two factors for Profile 2 data.