Soil-gas geochemistry as permeability tracer of thermally altered clays at Orciatico (Tuscany, Central Italy)

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Abstract

The physical properties of clay allow to consider argillaceous formations as geological barriers to radionuclide migration in high-level radioactive-waste isolation systems. As laboratory simulations are short term and numerical models always involve assumptions and simplifications of the natural system, natural analogues are extremely attractive surrogates for the study of long-term isolation.

The thermally altered clays of the Orciatico area (Tuscany, Central Italy) represent an interesting natural model of a heat source which acted on argillaceous materials. The study of this natural analogue was performed through detailed geoelectrical and soil-gas surveys in order to define both the geometry of the intrusive body and the gas permeability of a clay unit characterized by different thermal alteration degrees. In particular, soil-gas radon and carbon dioxide distributions highlighted that the clay sequences, in spite of their thickness and plasticity, if fractured and metamorphosed, form a lesser impermeable barrier for naturally migrating gas.

Keywords: gas permeability, thermally altered clay, gas migration.

Introduction

Clay formations are considered an excellent isolation and sealing material due to their ability to immobilize water and other substance over geological timescales. Some natural phenomena would confirm these excellent properties of clays: two meaningful examples of the isolation capacity of clays are the Dunarobba fossil forest (Tiber valley, Umbria region ï Italy), with its tree-trunks perfectly preserved in the two million year old clay deposit, and hydrocarbon traps all over the world. The common idea is that the low permeability of clays is not necessarily affected by tectonic stress especially for the swelling capability of the clay minerals during rock-structure friction. The evaluation of long-term behaviour of clays under normal and extreme conditions is still the main topic in questions relating the role of clays as geological barrier for the permanent isolation of long-lived toxic residues. High-level-radioactive-waste containers are designed to fail within about 300 years implying a release of the nuclear contaminant into groundwater. Thus, the clay buffer and the indigenous rock/clay formation itself become the ultimate containment barrier (Hueckel and Pellegrini, 2002). One of the main problems relating nuclear waste is the heath output. There are two principal ways in which heat may affect the mechanical and hydraulic performance of a repository. One is short-term and regards heat-induced stress and pore pressure changes that subside after the decay heat output decreases to the background levels. The other mechanism is through irreversible changes in mineralogical soil makeup affecting strength, strain and permeability with a long-term impact.

The Orciatico clay study was part of an EC project (FI-4W7CT9570014) aimed to study natural analogues of the thermo-hydro-chemical and thermo-hydro-mechanical response of clay barriers. The main idea of this project was to achieve information and experimental data regarding the long-term stability of permeability and plasticity of the clays affected by high temperatures. Natural analogues were identified in clay formations near contact with volcanic intrusions. According to Hueckel and Pellegrini (2002), there are shortcomings of natural analogues as simulators of high-level-radioactive-waste disposal, such as: (i) the actual temperature of intrusion, which usually is much higher than that of nuclear waste, requiring a careful identification of the zone of the actual thermal analogy; (ii) effects of mechanical penetration of volcanic rock into clay mass with the corresponding strain; (iii) observability only of the terminal state of the entire thermal cycle; and (iv) superposition of possible effects of post-analogue history, such as unloading due to weathering, with the consequent exhumation of the site, natural erosion process, etc.

Although igneous rock emplacement temperatures were very high, cooler zones could be identified which were more representative of conditions expected during the disposal of heat-emitting radioactive wastes. In the framework of the project, the Orciatico area was investigated from different points of views: thermally-induced mineralogical, whole-rock geochemical and thermo-hydro-mechanical changes were studied; paleotemperatures were determined primarily by vetrinite reflectance and illite cristallinity; present-day porewater chemistry was analyzed. The evolution of mudstone strength stiffness and permeability were also examined and compared to changes in mineralogy.

In this paper, results from different applied techniques are presented: i) from soil-gas surveys performed to identify the distribution and properties of fractures within metamorphosed and un-metamorphosed clays; ii) from six soil samples collected for isotopic analysis in order to estimate the influence of natural radiogenic content of terrains on radon distribution and iii) from geophysical surveys (vertical electrical soundings and dipole electrical tomography profiles) to better delineate the size and shape of the hidden part of the intrusion. Our study identified several observations of direct relevance to performance assessment of the disposal of heat-emitting wastes into clay-rich rocks.

Background Geology

The Orciatico area, a few km NW the town of Volterra, is located on the western edge of the Val dôEra graben. This area is characterized by the presence of a small, outcropping sub-volcanic intrusion, named Selagite (Rodolico, 1934). The emplacement of the Selagite intrusive body was probably controlled by the NNW-SSE trending faults related to the post-tectonic extensional regime. Dating of this unit yields an emplacement age of 4.1 Ma (Borsi et al., 1967), an age which partly overlaps with Tuscan anatectic magmatism but which precedes the Roman magmatism by 3 Ma. According to *Stefanini* (1934), the Orciatico magma was intruded into shallow Pliocene sediments in the form of a sill-laccolith body fed by a narrow NW-SE trending dike. The intrusion has a chilled margin, varying from glassy to slightly porphyritic, and a massive holocrystalline core. Oxides and K-feldspars are the most abundant phases in the groundmass (Conticelli et al., 1992). The country rocks underwent thermal metamorphism, attaining pyroxene-hornfels facies in the resultant aureole (Leoni et al., 1984). Late-stage hydrothermal metamorphism has also been recognized which modified the Sr-isotopic ratios of the country rocks, but not affecting the magmatic body (Ferrara et al., 1988). Figure 1 shows a simplified geological sketch of the Orciatico structure characterized by:

- *Selagite*: a small, shallow alkali-trachyte intrusion emplaced in Pliocene clays (Rodolico, 1934; Stefanini, 1934; Barberi and Innocenti, 1967).
- *Metamorphosed clays* (ñTermantiteò), (Polizzano et al., 1984)*:* the rocks of the metamorphic aureole can be subdivided into three main groups: i) hornfels facies: extremely compact, hard, dark, aphanitic rocks; ii) spherulitic rocks: differing from the

hornfels facies due to a distinctly lower hardness and the presence of numerous dark spherulites embedded in a yellowish matrix; iii) ñpseudo-galestrineò rocks : yellow-grey, underrated fissile shale.

- *Un-metamorphosed clays*: the Pliocene sedimentary formation where the Orciatico laccolith was emplaced is a thick, prevalently marine, clastic sequence. Locally these sediments are represented by plastic, grey-blue, marly-silty clays.

Methodology

Soil-gas sampling and analysis

A total of 1086 soil-gas samples was collected in the Orciatico area. A first survey was performed collecting 486 samples along a regular grid near the village of Orciatico (Fig. 1) with a sampling density of about 500 samples/km^2. The survey was performed during summer (July-September 1997) in a very dry period in order to avoid climatic factors which may affect soil-gas values (Hinkle and Ryder, 1994). Nonetheless, monthly surveys (from April to September 1998) were performed to monitor possible variations of soil-gas concentration due to weather conditions. A total of 600 samples were collected in two small zones within the studied area: the first one called ñ*Casa Petroia*ò area, located in the northern part, characterized by altered clays and the second one, ñ*background*ò area, situated in the unaltered clays.

The studied gases included major (N_2, O_2, CO_2) and trace (^4He, ^{222}Rn) gases and light hydrocarbons (C_1 to C_4). Shallow soil-gas samples were obtained using a 1 m stainless steel probe fitted with a brass valve: this system enabled soil-gas to be collected and stored in metallic containers (with a vacuum 10^{-2} atm) for laboratory analysis or to be pumped for on-site Rn analysis. Radon determination was accomplished in the field with an EDA Inst. RDA-

200 Radon Detector. The determination of helium was performed with a Varian Inst. Mass 4 spectrometer. N_2, O_2, CO_2 and light hydrocarbons (C_1 to C_4) concentrations were analyzed using a Fison Inst. GC-8000 Series gas-chromatograph. The used detectors are: Thermal Conductivity Detector (TCD) for N_2, O_2 and CO_2 in order to achieve a sensitivity up to percentage and Flame Ionization Detector (FID) for light hydrocarbons with a sensitivity of an order of 100 ppb.

Geoelectrical survey

On the basis of 13 probings performed (in the framework of the above mentioned EC project) in order to draw the intrusive body geometry, a total of 20 electrical soundings (VES) and 8 dipole electrical tomography (DET) profiles were carried out across the intrusive body and in the clays characterized by several thermal and mechanical alteration degrees. Electrical sounding method was used for stratigraphic studies: two electrodes were located at a minimum electrodic distance and resistivity measures were achieved. After that, the electrodic distance was changed until to reach the maximum electrodic distance previously defined. Obtained resistivity values versus electrodic distance were considered graphically: points were interpolated getting a curve showing apparent resistivity. Dipole electrical tomography profiles allowed to establish resistivity variations without changing electrodic distance. Furthermore, resistivity values can be interpolated sketching isoresistivity curves.

Results and discussion

Soil-gas surveys

All analytical data obtained using the above-mentioned procedures were statistically and graphically processed to best define geochemical lineaments and anomalies.

Some descriptive statistical data are reported in Table 1 for the first survey (the areal one) and in Table 2 (where mean values are listed) for the monthly samplings (from April to September 1998). The radon contour line map, figure 2, shows that highest radon values (> 25 Bq/l) occur in the south-western part of the studied area (characterized by the presence of Selagite outcrop) and along a narrow belt, with direction NNW-SSE, where metamorphosed clays (named ñTermantiteò) are present. Furthermore, anomalous values occur in unaltered clays especially in correspondence of the boundary of the resistive complex supposed on geoelectrical results. All over the north-eastern sector, in non metamorphosed clays, radon values are very similar to background values reported in literature (10-15 Bq/l). In the same way as radon values, the highest carbon dioxide values (>2 %,v/v) are mainly concentrated at the Selagite-Termantite contact (Fig. 3) and in unaltered clays especially along the boundary of the resistive complex.

Since radon and carbon dioxide values seem directly correlated with the volcanic intrusion and clay thermal alteration, collected data were divided in three subsets considering their location on different lithological areas. Figure 4 shows two merged probability plots (CO_2 and ^{222}Rn) elaborated to highlight different concentrations on Selagite outcrop, Termantite (metamorphosed clays) and intact (unaltered) clays: it is well evident a general decreasing trend of the measured concentrations in the three different sites, showing the lowest values in the un-metamorphosed clays. In fact, soil-gas distribution is partially influenced by lithology as demonstrated by isotopic analysis over six soil samples collected at different depths (Tab. 3) and lithologies (Fig.5): sample I3 was collected in the Selagite, samples I4, I5 and I1 in clays considering different alteration degrees. Soil samples underwent γ spettometry analysis for determining ^{40}K, ^{238}U, ^{226}Ra and ^{228}Th activity concentrations (the analyzed daughter nuclides for the determination of progenitor activity concentrations are listed in Table 4). Figures 6a, b, show two different histograms of a comparison among activity concentrations of progenitor radionuclides: in general, samples have very low activity concentrations excepting sample I3 composed of volcanic material and so, rich of radiogenic elements. The different nature of sample I3 is also evident in Fig. 6b where ^{40}K activity concentrations are displayed. Very small variations are visible in the Fig 7 representing the activity of three samples collected at the same site (I1) but at different depths (Table 3). These results would confirm that there is no considerable differences of concentration activity values among the other samples highlighting that the natural content of radionuclides in Pliocenic clays doesnôt affect soil-gas distribution.

After these first results and considering that the soil-gas survey was performed during summer time (July-September 1997), a monthly monitoring (from April to September 1998) started in order to study seasonal influence and/or local factors (i.e. seasonal vegetation) on soil-gas distributions. Since it was not possible to collect, every month, the same number of samples of the first survey, two small zones within the studied area were chosen (Fig. 2, the dashed boxes): the first one, called the ñ*Casa Pietroia*ò area, where highest Rn and CO_2 values were found during the first survey and the second area characterized by the lowest values and for this reason defined the ñ*background*ò area. Fifty soil-gas samples were collected in each area every month (always in the same points) and measured concentrations are reported in Table 2. Mean values for each month are very similar to the first sampling (Tab.1). Figure 8 shows polynomial regression (5° degree) of radon (dashed line) and carbon dioxide (continuous line) concentrations in the ñCasa Pietroiaò area, during the six months: also in this case, graphs highlight a general decreasing trend of soil-gas values moving away from the Selagite. Soil-gas distributions in the southern area have the same trend. Results from these monthly surveys showed that in spite of seasonal variations related to weather and/or vegetations, soil-gas concentrations remain constant confirming that gas concentrations are directly correlated with clay permeability.

Geoelectrical surveys

Geoelectrical surveys were performed in order to identify the geometry of the trachite-alkaline intrusive body (Selagite) outcropping a few hundred meters NE of the village of Orciatico, and to verify the presence of mineralized zones in the surrounding clays. A total of 20 vertical electrical soundings (VES) and 8 dipole electrical tomography (DET) profiles have been performed across the intrusive body. DET results are represented through pseudo-sections of resistivity (calculated from experimental values at the scale 1:2000).

The vertical electrical soundings defined three electrical layers: the first and third layers have a resistivity between 5 and 10 ohm*m and are attributed to Pliocene clays, while the intermediate layer has a resistivity between 15 and 60 ohm*m and is correlated with the Selagite intrusion, near the outcrop, and with the clays that underwent modification because of the intrusion effects. The metamorphosis degree of clays is function of their distance from the intrusion, and, clearly, highest metamorphosed clays are near Selagite outcrop. The uncommonly low value of medium resistive complex indicates that the intrusion is highly fractured in the southern part and it is strongly altered in the northern sector.

The DET profiles indicate that resistivity values decrease in all directions away from the Selagite intrusion, with a steep gradient near the intrusion and vertically downwards. Particular attention was given to a small area between Fonte Carta and Casa Petroia, where soil-gas (in particular, Rn and CO_2) anomalous concentrations were found. In this area, six profiles were performed to verify the presence of anomalous conductors. All DET profiles are characterized by the presence, in the southern part, of a relatively resistive mean (ρ_a>10 ohm*m) on the surface. The shape and the trend of this resistive mean would confirm the hypothesis that the Orciatico intrusion is a laccolith. In every profiles, it is possible to note the presence of deep conductor terrains; in particular, as regard profile 8 it is important to note the three sub-vertical areas (resistivities about 6 ohm*m) below terrains having resistivities > 20 ohm*m. DET profile 4, performed in the southern sector of the studied area, shows the presence of a resistive body among conductor terrains: the Loke inversion model and its interpretation allowed to create an interpretative section highlighting the presence of a central body (ρ_a=60 ohm*m) surrounded by a halo with ρ_a=35 ohm*m, a branch towards E with resistivity values decreasing plunged into a terrain with ρ_a=6 ohm*m .

Comparison between geochemical and geoelectrical results

As radon and carbon dioxide values decrease gradually from Selagite outcrop towards un-metamorphosed clays, soil-gas data set were projected along two longitudinal lines coinciding with geoelectrical profiles 4 and 3. These two profiles were chosen since the pseudo-sections highlight a quick resistivity decrease both in the vertical and in the horizontal way.

Figure 9a shows polynomial regression (3^{rd} degree) radon and carbon dioxide values plotted against the distance from a reference point. Graphs highlight a decreasing trend of radon soil-gas values (continuous line) towards the NE, from Selagite outcrop until un-metamorphosed clays. The same behaviour is well evident also for CO_2 polynomial regression (dashed line): the overlapping peaks in the radon-carbon dioxide plots should confirm that the soil-gas distribution is linked to clay alteration degree. Indeed, highest CO_2 and Rn values were found between Selagite outcrop and the first resistive limit, in a narrow belt characterized by a high alteration degree and, probably, by an intense shallow fracturing. On the other hand, after the second resistive limit, where clays did not undergo the effects of the intrusive body, radon and carbon dioxide values are in agreement with the mean values reported in literature excepting in the last 200m of the profile where values slightly increase again.

Thoron (^{220}Rn), derived from ^{232}Th, is a very interesting tracer for studying diffusion in the lower layers of the atmosphere. Because of its short half-life (55 sec), ^{220}Rn is sufficiently long-lived to indicate whether the Rn anomaly detected is due to primary U or Th sources, or in an areas devoid of such mineralization to indicate zones of higher-than-background permeability: rapid transport rates (certainly greater than those due to diffusion alone) can bring high levels of ^{220}Rn to the surface of the Earth.

Smith et al. (1976) and Morse (1976) have shown that sampling Rn activity over short periods of time allow the separate identification of ^{220}Rn and ^{222}Rn activities from a single soil-gas sample. During the first three minutes of counting, the count rate drops due to the decay of ^{220}Rn. Thereafter, as ^{218}Po activity continues to grow from the decay of ^{222}Rn, the count rate rises to an equilibrium level which is attained 3-4 hours after sampling. Thus, depending on the relative contributions to the total Rn content by each isotope, the count rate may either rise or fall in the first 3 minutes of counting. The raw data obtained from the digital readout can therefore be processed to yield activities due to total Rn, ^{220}Rn and ^{222}Rn (Durrance and Gregory, 1987).

Determination of activity ratios can give information on the effective permeability of the gas source. A high ^{220}Rn/^{222}Rn activity ratio indicates high ground permeability, and is frequently associated with a high total flux at structural discontinuities. However, ^{220}Rn/^{222}Rn activity ratios can be calculated in two ways. In the first one, calculated isotopic activities are used, but the second method is simpler, employing the ratio of the first and the third minute count (*Morse*, 1976).

Polynomial regression (3rd degree) values of $^{220}Rn/^{222}Rn$ activity ratios were plotted against the distance from a reference point (Fig. 9b). Also in this case, it is possible to distinguish a decrease from Selagite outcrop until the first geoelectrical limit after which values rise until un-metamorphosed clays. Intact Pliocenic clays, far from the intrusive body, have a high activity ratio that can indicate the presence of structural discontinuities not visible at the surface. This should be a considerable hypothesis that would explain why Rn and CO_2 soil-gas value increase in intact clays.

Conclusions

The results of this study provided specific information about soil-gas permeability on the Orciatico clay units characterised by different degrees of thermal alteration. This research represents the first study performed in thermally and mechanically altered clays and results demonstrated that the method gives interesting information also in clays that apparently did not undergo to mineral and geothecnical variations. Radon and carbon dioxide soil-gas anomalies are mostly concentrated in zones where Selagite outcrop and thermally altered clays are present. Soil-gas distributions are interpreted as being due to intense shallow fracturing of clays along the inferred laccolith boundary: the intrusion of the laccolith caused thermo-hydro-chemical and thermo-hydro-mechanical stress and contact metamorphism in the clay. On the contrary, far from Selagite, clays apparently prevent the rising of gases. Indeed, small soil-gas anomalies were found over the estimated intact Pliocenic clays having a permeability due to structural discontinuities not visible at the surface. This study allowed to highlight the role of soil-gas technique for the identification of secondary permeability in a clay sequence: clay can strongly modify its characteristics (i.e., reduction of the properties of isolation and sealing material) when affected by thermal alteration although this effect is not visible through traditional investigative methods. The results of this study suggest a review of the role of clays as geological barrier for the permanent isolation of long-lived toxic residues in the radioactive-waste isolation framework.

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Table and figure captions

Table 1. Main statistics for the first soil-gas survey. Anomaly threshold was calculated both (*) considering the mean * + ½ standard deviation and (**) according to Sinclair (1974).

Table 2. Mean values for the monthly soil-gas surveys (from April to September). A total of 600 samples were collected in two small zones within the studied area: the first one called ñCasa Petroiaò area located in the northern part characterized by altered clays and the second one, ñbackgroundò area, situated in the unaltered clays.

Table 3. Depths of soil samples collected from cores.

Table 4. Analyzed daughter nuclides for the determination of progenitor activity concentrations.

Figure 1. Geological sketch map of the Orciatico igneous body (from Conticelli et al., 1992) and soil-gas surveys. A first survey (July-September 1997) was performed along a regular grid with a sampling density of about 500 samples/km^2 (dark dots). The two dashed rectangles indicate two monitored zones (from April to September 1998).
1) Pliocene Quaternary sediments; 2) Miocene lacustrine and marine sediments; 3) thermally metamorphosed rocks (Termantite); 4) Orciatico orendite; 5) faults and inferred faults.

Figure 2. Radon distribution in soil-gas. Anomalous values (>25 Bq/l) are in correspondence of the boundary of the resistive complex supposed on geoelectrical results. All over the north-eastern sector, in non metamorphosed clays, radon values are very similar to background values reported in literature (10-15 Bq/l).

Figure 3. Carbon dioxide distribution in soil-gas. As well as the radon values, the highest carbon dioxide values (>2 %,v/v) are mainly concentrated at the Selagite-Termantite contact and in unaltered clays especially along the boundary of the resistive complex supposed on geoelectrical results.

Figure 4. Merged probability plots of CO_2 and ^{222}Rn. The plots were elaborated in order to highlight the gas concentration differences on Selagite outcrop, methamorphosed clays and intact (un-methamorphosed) clays. There is a general decreasing trend of the measured concentrations in the three different sites, showing the lower values in the un-metamorphosed clays.

Figure 5. Map of core location. Soil samples were collected in clays characterized by different thermal alteration degrees.

Figure 6. Histograms of activity concentrations of progenitor radionuclides. The ^{40}K activity concentration (b) was considered in a different histogram because of the bigger scale. In both histograms, the only sample (I3/IS1) having highest values was collected in the volcanic intrusion (Selagite).

Figure 7. Histograms of activity concentrations of progenitor radionuclides for I1/IS2, I1/IS3 and I1/IS4 samples belonging to the same core but collected at different depths. Very small variations are evident in this histogram confirming that the natural content of radionuclides in Pliocenic clays doesnȇt affect soil-gas distribution.

Figure 8. Polynomial regression (5° degree) of radon and carbon dioxide concentrations at the "casa Pietroia" area during six month monitoring (April-September 1998). The left axis represents carbon dioxide values (straight line) whilst on the right axis there are radon values (dashed line). Graphs highlight a general decreasing trend of soil gas values towards NE. Results from these monthly surveys showed that in spite of seasonal variations, soil gas concentrations remain constant.

Figure 9. a) Comparison between polynomial regression (3° degree) map and geoelectrical profile 4. Radon graph (continuous line) highlights a general slightly decreasing trend of soil-gas values towards the NE, from Selagite outcrop until un-metamorphosed clays. The same behaviour is well evident also for CO_2 polynomial regression (dashed line). b) The polynomial

regression (3° degree) values of $^{220}Rn/^{222}Rn$ activity ratios compared with geoelectrical profile. Values slightly rise towards un-metamorphosed clays. Intact Pliocenic clays, far from the intrusive body, have a high activity ratio indicating the presence of structural discontinuities not visible at the surface.