

## Chapter 2

# Historical Development of *Redox Complex*

**Abstract** The *Redox Complex* (ORP, magnetic susceptibility, spectral reflectance, and soil geochemistry) is a complex of unconventional exploration techniques, used for indirect detection and evaluation of various metal targets, which is based on the *Geochemical Principle of Metal Ions Vertical Migration*. This complex is successfully applied in various fields: oil and gas and metal ores exploration; studies of oil and metal contaminants in soils; and the search for metallic archeological burials. The use of these techniques is intended to complement the conventional prospecting complex with the purposes of reducing areas and/or the selection of the most favorable targets, resulting in an increase in economical–geological effectiveness of investigations. The *Redox Complex* is implemented without physical or chemical affectation to the environment. The combined application of redox potential and magnetic susceptibility of soils to geological prospecting, which is its antecedent, is determined by the possibility of detecting the reducing column that is formed directly on metal and hydrocarbon occurrences and reaches the upper part of the section. Within this column, the conversion of nonmagnetic iron minerals to more stable magnetic varieties is favored, which explains the observed inverse correlation between the attributes and justifies integration of methods. The results of research in control areas confirm the fact, previously noted, that ORP in soil is insensitive to variations in topography and tectonics, being the potential background level a function, only, of the type of geological environment. The only noisy sources known to date are the dry marshy areas or other accumulations of organic material and alluvium with high content in metals, which are reducing surface geochemical targets that produce characteristic intense anomalies ( $<-100$  mV) of steep and symmetrical gradients, occasionally identifiable from direct observation in the field. Although available applications are still, statistically, insufficient for experimental foundation of empirical regularities mathematically formulated, however, they allow, in principle, the establishment of a set of possibilities and limitations of *Redox Complex* for each area of application.

**Keywords** Geological prospecting • Soil redox potential • Magnetic susceptibility • Reduced chimneys • Hydrocarbon deposits • Metallic mineral occurrences

## 2.1 Introduction

The historical—practical evolution of redox potential (ORP) in soils, used in combination with kappametry for the purpose of hydrocarbon and metal ores exploration (Pardo y Stout 1999), since its innovation and introduction in 1992 (Alfonso et al. 1993) until 2001 (Pardo y Carballo 1996; Pardo y Domínguez 1997; Pardo et al. 1997, 2000, 2001a, b; Pardo y Stout 1999, 2001), required a new theoretical and experimental stadium led to multiparametric complementation, the development of the theoretical basis of the technical complex, and the implementation of its quantitative interpretation. Empirical support was needed for that, with minimal (still insufficient) volume of observations on known targets or control areas, which would be conducted in two research projects for 2001–2002 (Pardo 2002) and 2003–2004 (Pardo 2004). The areas were selected to characterize response to different types of environments and deposits with different characteristics: of lying (occurrence), geometry, and composition; so it could do more representative analysis for design quantitative interpretation parameters.

## 2.2 Historical Development of *Redox Complex*

Progress in the historical development of *Redox Complex* has followed the path from empirical observation, through experimentation and application of mathematical expressions that model the observed regularities, to an approach to the theory. The main stages of this development are:

### 1991–1993

- Invention, design, and introduction of in situ soil Redox Potential measurement.
- Innovation, design, and introduction of airborne gamma-spectrometric (AGE) scenarios for oil: The integrated index  $K/eTh$ .

### 1996–2001

- Establishment of the genetic relationship between ORP reduced by local background and magnetic susceptibility of the soil from the *Principle of Metal Ions Vertical Migration*. Introduction of Uredox–Kappa complex to geological prospecting.
- Invention, design, and introduction of ORP temporal measurement from the mathematical formulation of the transient behavior.
- Establishment of the genetic relationship between ORP reduced by local background and Soil Geochemistry from the *Principle of Metal Ions Vertical Migration*. Introduction of Uredox–Kappa–Soil Geochemistry complex to geological prospecting.

**2002–2005**

- Establishment of the genetic relationship between spectral reflectance reduced by local background in soil samples and soil geochemistry, from the *Principle of Metal Ions Vertical Migration*. Innovation, design, and introduction of satellite scenarios for oil and metallic minerals.
- Introduction of normalization (standardization) by local background of the magnetic susceptibility and soil geochemistry.
- Final *Redox Complex* integration: Satellite scenarios, redox potential, magnetic susceptibility, spectral reflectance, and soil geochemistry (attributes reduced or normalized by local background).
- Invention, development (modeling), and automated deployment of mathematical expressions that link various attributes with lying, geometry, and composition parameters of prospecting targets.
- Innovation, design, and introduction of *Redox System* for geological applications (oil and minerals), environmental, and archeological studies.

**2010–2013**

- An approach to the theory of the processes controlling metal mobilization, transport, and accumulation in surficial environment on buried ore bodies and hydrocarbon deposits.

Considering its beginnings, applications to geological prospecting of ORP in soils method are determined by the possibility of detecting the reducing environment column that is formed directly on metal and hydrocarbon occurrences and reaching the top of the section. Within this column, the conversion of nonmagnetic iron minerals to more stable magnetic varieties is favored, which explains the observed inverse correlation with magnetic susceptibility and justifies the integration of both methods. The use of these techniques is intended to complement the conventional prospecting complex with purposes of reducing areas and/or selection of the most favorable targets, resulting in an increase in economical–geological effectiveness of investigations.

Redox Potential (ORP) in soils in situ measurement was a little-known method in the 1990s, determination that was conventionally performed on aqueous or semi-aqueous media (water, sludge, and soil solutions). Its application alone or in combination with soil kappametry for geological exploration had not been since reported. The beginnings of the development and introduction of this method in Cuba were dating from 1992 to 1993 (Alfonso et al. 1993), where it was used in combination with other nonconventional techniques to reveal surface areas of reducing environment on hydrocarbon occurrences. Subsequently, it has been applied in combination with soil kappametry on various metallic and hydrocarbon targets (Pardo y Carballo 1996; Pardo et al. 1996; Pardo y Domínguez 1997; Pardo et al. 1997, 2000, 2001a, b; Pardo y Stout 1999, 2001; Pardo et al. 2003). For its part, the soil kappametry with purposes of geological prospecting has its antecedents in the detection of dispersion haloes on metal occurrences, although it was also known in oil exploration (Saunders et al. 1991). This technique was directed to the detection

of anomalies in the magnetic susceptibility in a given soil horizon, from measurements in samples for other method (soil geochemistry samples or samples for analysis of hydrocarbon gases).

The geological assumptions underlying the combined application of soil ORP and magnetic susceptibility (Kappametry) methods for geological exploration are:

- Prospecting for oil and gas.

It is recognized (Saunders et al. 1991) the fact of the vertical migration of light hydrocarbons (microseepages as ultra-small gas bubbles) from the hydrocarbon deposit in depth, through fractures, layer planes, and faults to the soil top level. For long periods of time, the alterations related to microseepages may take place in the upper levels of the soil from a range of reactions either in gaseous or aqueous phase. Microbial action on the light hydrocarbons was produced as by-products carbon dioxide and hydrogen sulfide, determining a column of chemically reducing environment on the occurrence. Moreover, this environment favors the conversion of nonmagnetic iron minerals (hematite) in magnetic oxide (magnetite) and magnetic sulfides (pyrrhotite and griegite), a fact that underlies the correlation of ORP anomalies (lows) with those of the magnetic susceptibility (highs). On the other hand, concentrations of carbon dioxide in groundwater form carbonic acid which can react with the clay minerals to create secondary mineralization of calcium carbonate and silicification, resulting in more dense and resistant to erosion surface materials (leading to geomorphic anomalies). According to Saunders et al. (1993), simultaneously, the destruction of clay minerals by carbonic acid and organic acids can release potassium, which is subsequently leached. Conversely, thorium remains relatively fixed in its original distribution within the insoluble heavy minerals; hence, it observed characteristic anomalies (lows) of the relationship K/eTh on hydrocarbon deposits.

- Metallic mineral prospecting.

It is the known (Hernán Vázquez 1997) process of vertical migration of metal ions from an occurrence in depth to the surface, determining the formation of a reducing environment column thereon. The metal transport involves diffusion or hydromorphic transport mechanisms linked to weathering events, among others, a process that also affects newly transported cover (exotic). As in the previous case, the reducing environment promotes the conversion of nonmagnetic iron minerals into more stable magnetic varieties.

## 2.3 Methodological Aspects

According to Pardo y Stout (1999), for the soil ORP in situ measurement two electrodes connected to a digital millivolt meter of high input impedance (sensitivity 0.1 mV; commercial) are used: one inert platinum, and other reference copper (nonpolarizable electrode; commercial), located immediately next into a hole of 10–30 cm deep. The ionic communication which closes the circuit is ensured through the porous ceramic of the reference electrode (Fig. 2.1).



**Fig. 2.1** Measurement of Redox Potential in soils

The measurement with the disclosed device has a transient behavior, determining the potential by an algorithm from five readings with a time difference between them of a minute. The quality of field observations is assessed using the absolute error in the determination of the potential, considering 10 % of control measurements made in the same holes used for routine measurements. The acceptable accuracy for the described applications should not exceed 15 mV.

The Magnetic Susceptibility measurement is made with a Kappameter KT-5 (sensitivity  $1 \cdot 10^{-5}$  SI), making seven readings distributed over the floor and walls of the hole, which are averaged. The quality of the field observations is assessed from the relative error in determining the mean value of kappa, considering 10 % of control measurements in the same holes. The accepted accuracy must not exceed 15 % (Fig. 2.2).

Thus, the method of Redox Potential in soils and its combined application with kappametry for the purposes of geological prospecting offered a priori some advantages:

- The possibility of indirect detection of deep or conceal metal occurrences and hydrocarbon reservoirs (structural and stratigraphic traps) with high planimetric accuracy on their location.
- Unlike spontaneous potential method, the measurements are not affected by other processes such as electrofiltration, electrodiffusion, electrokinetic coupling, and bioelectric activity of vegetation.
- Integration with the measurement of soil magnetic susceptibility increases the informational value of the attribute and hence its geological effectiveness.



**Fig. 2.2** Measurement of the Magnetic Susceptibility in soils

- As a complement to other conventional geochemical techniques (e.g., soil geochemistry), it raises its spatial resolution, thereby increasing the success rate of exploratory drilling.
- Measurements are not apparently affected by surface transport processes.
- The simplicity and low cost of field operations.

## 2.4 Research Objects

Research in control areas, in a first project (Pardo 2002), was developed on four objects of hydrocarbons, six of metallic minerals, three of environmental studies, and two of archeology. In a second project (Pardo 2004), investigations were carried on two objects of hydrocarbons, one of metallic minerals, three of the environment studies, and one of the archeologies. In all cases, the technical complex used (*Redox Complex*) considered redox potential, magnetic susceptibility, spectral reflectance, and soil geochemistry. Mineralogical study was only occasionally used in cases where necessary. Chemical analyzes by ICP spectroscopy considered useful and accompanying metallic elements of each occurrence, metal elements characterizing hydrocarbons, the main pollutants of the studied industries, and a typical spectrum of metallic elements for archeology. Thus, the *Redox*

*Complex* was successfully used in different types of hydrocarbon reservoirs (Varadero—Varadero Sur, Cantel, Pina, Jatibonico, and Cristales Oil fields) and metallic minerals (Antonio, Little Golden Hill, Florencia—Cuerpos Norte y Sur, Jacinto—Vetas Beatriz and El Limón, Camagüey II, Cuba Libre—Río Negro, and Camarioca Este ore deposits), which are representatives of a variety of geological environments, structural types, genetic types, composition, structure–textural features of the reservoir and/or ore, lying (occurrence) conditions, and relief. Applications for environmental and archeological studies, respectively, considered the perimeter zones of industries: Fábrica de Baterías Secas Pilas Yara, Siderúrgica Antillana de Acero, Refinería Níco López, Distribuidora de Hidrocarburos Güines, Distribuidora de Hidrocarburos Artemisa, Fábrica de Sulfometales, Fábrica de Pinturas Capdevilla, and Presa de Colas Delita; and the archeological sites: Jardín Exterior del Castillo de la Fuerza, Caimito, and Ingenio Guáimaro.

For the purposes of hydrocarbons (heavy and light, with depths between 300 and 2000 m) works were developed by isolated profiles, step 200 m, extending between 2 and 5 km. For purposes of metallic minerals (Kuroko VMS, Epithermal low and high sulfidation, Refractory chromite, Cyprus VMS, and Nickeliferous crust) works were developed by isolated profiles, step 20 m, extending from 200 to 600 m. For the purposes of environmental studies (surficial and occasionally at groundwater table contaminations of Fe, Mn, As, Pb, Zn, and hydrocarbons) works were developed by isolated profiles, step 20 m, with approximate length of 200 m. For the purposes of archeology (Fe and Au (As) metallic burials) works were developed by isolated profiles, step 0.5 m, with approximate length of 10 m.

## 2.5 *Redox Complex* Economic–Technical Data

Current estimates of productivity and cost of *Redox Complex* (in situ measurements of soil ORP and magnetic susceptibility and soil sampling) applications in mineral and environmental for terrains with difficulty category II–IV, observation step 20–25 m, respectively, are 25–17 PP/DC (500–340 m) and \$250.00–480.00/km. Estimates of spectral reflectance, respectively, are 120 samples/DC and \$3.50/sample (\$175.00/km). The chemical analysis (samples analyzed in Central Laboratory of Mineral, LACEMI) has a response speed exceeding 30 days, with an average cost of \$70.00–90.00/sample. Similarly, for hydrocarbon exploration, estimates of *Redox Complex* in vehicle-transported itineraries, step 200–250 m, are 20 PP/DC and \$250.00/km, while profiling (pedestrian), 200–250 m step, difficulty category II, are 15 PP/DC and \$400.00/km. Estimates of spectral reflectance and chemical analysis remain the same. All the above estimates do not consider the costs of mobilization–demobilization campaign, food, accommodation, and transportation of executioner staff.

## 2.6 Results

The results of research in control areas (Pardo 2002, 2004) confirm the fact, noted above, that the technique of soil ORP is insensitive to variations in topography and tectonics, being the potential background level a function, only, of the type of geological environment. The only sources of noise known to present are dry swampy wetlands or other accumulations of organic material and alluvium high in metals, which are reducing surface geochemical objectives that produce characteristic intense anomalies ( $<-100$  mV) of steep and symmetrical gradients, occasionally identifiable from direct observation in the field.

Although the available applications (Pardo 2002, 2004) are still, statistically, insufficient as experimental foundation of empirical regularities mathematically formulated, however, they allow, a priori, the establishment of a set of possibilities and limitations of *Redox Complex* for each area of application:

### • Hydrocarbon Exploration

#### (a) Possibilities:

- Recognition and detailed mapping of the occurrence vertical projection and assessment, in an indirect and approximate way, of the oil quality.
- Approximate determination of the depth of the occurrence and the possible structural trap type.
- Approximate volumetric assessment of the occurrence from the detailed mapping results.

#### (b) Limitations:

- Existence of several overlapping hydrocarbons levels (includes gas caps).
- Failure to seal or it is much fractured.
- Presence of surface reducing zones of various kinds.
- Prevalence of the lithological response of magnetic susceptibility and spectral reflectance.
- Existence of a recent transported cover (less than 10 years).

### • Metallic Mineral Exploration

#### (a) Possibilities:

- Recognition and detailed mapping of the occurrence vertical projection and rough assessment of its composition and quality.
- Approximate determination of the depth, dip, and vertical extent of the main ore body.
- Rough assessment of resources.



(b) Limitations:

- Existence of overlapping primary ore bodies.
- Presence of surface reducing zones of various kinds.
- Prevalence of the lithological response of magnetic susceptibility and spectral reflectance.
- Existence of a recent transported cover (less than 10 years).

• **Environmental Studies**

(a) Possibilities:

- Recognition and detailed cartography of the contaminated area, allowing to establish its nature (surface or subsurface) and grade.
- Approximate determination of the depth of the subsurface contaminant source.

(b) Limitations:

- Presence of surface reducing or oxidizing zones of various kinds.
- Prevalence of the lithological response of magnetic susceptibility and spectral reflectance.
- Existence of a recent transported cover (less than 10 years).

• **Archeological Studies**

(a) Possibilities:

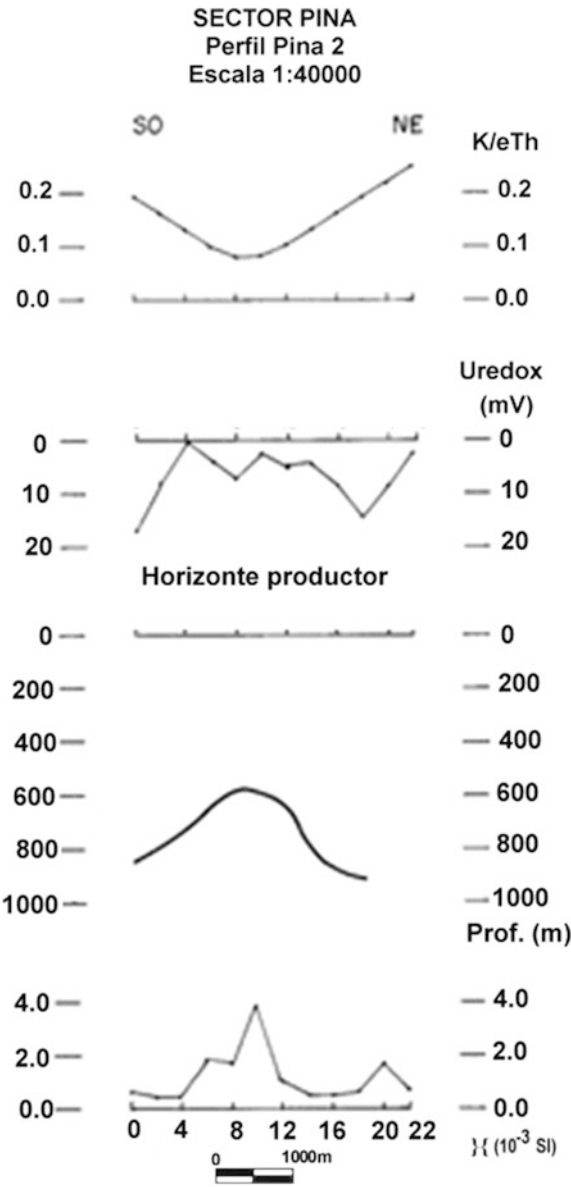
- Planimetric position of metal burials and assessment of its composition.
- Approximate determination of the depth of objects.

(b) Limitations:

- Presence of surface reducing or oxidizing zones of various kinds.
- Prevalence of the lithological response of magnetic susceptibility and spectral reflectance.
- Existence of a recent transported cover (less than 10 years).

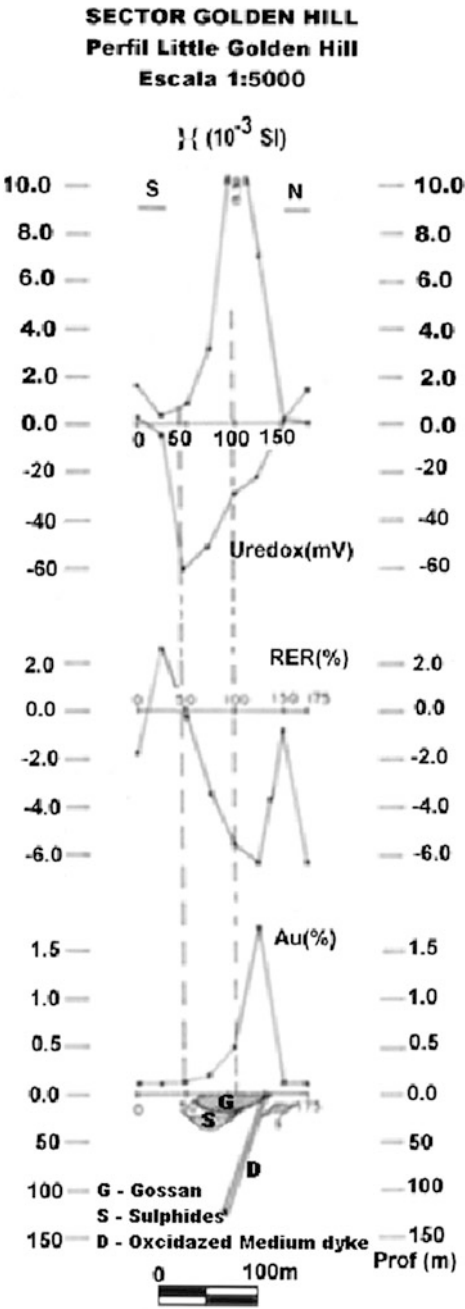
Below are presented, in graphical form, the most representative results of the application of *Redox Complex* in some studied control areas and it is commented on the regularity in the spatial behavior of the different measured attributes.

Oil and Gas



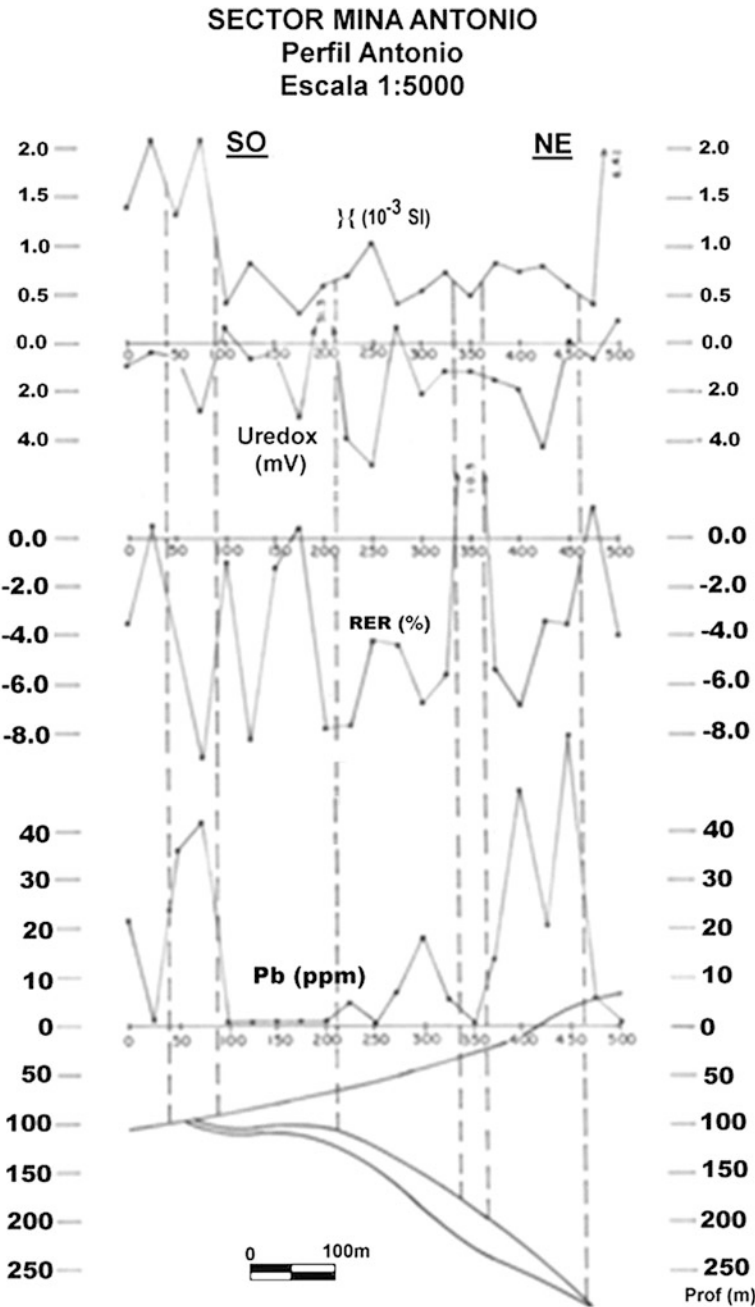
At the *Pina* light oil field, spatial correspondence of a minimum of K/eTh relationship with a maximum of magnetic susceptibility and a disjointed decreased field values in the reduced ORP, linked to the apical part of the producer structure, is observed. Spectral reflectance was not determined.

Metallic Minerals



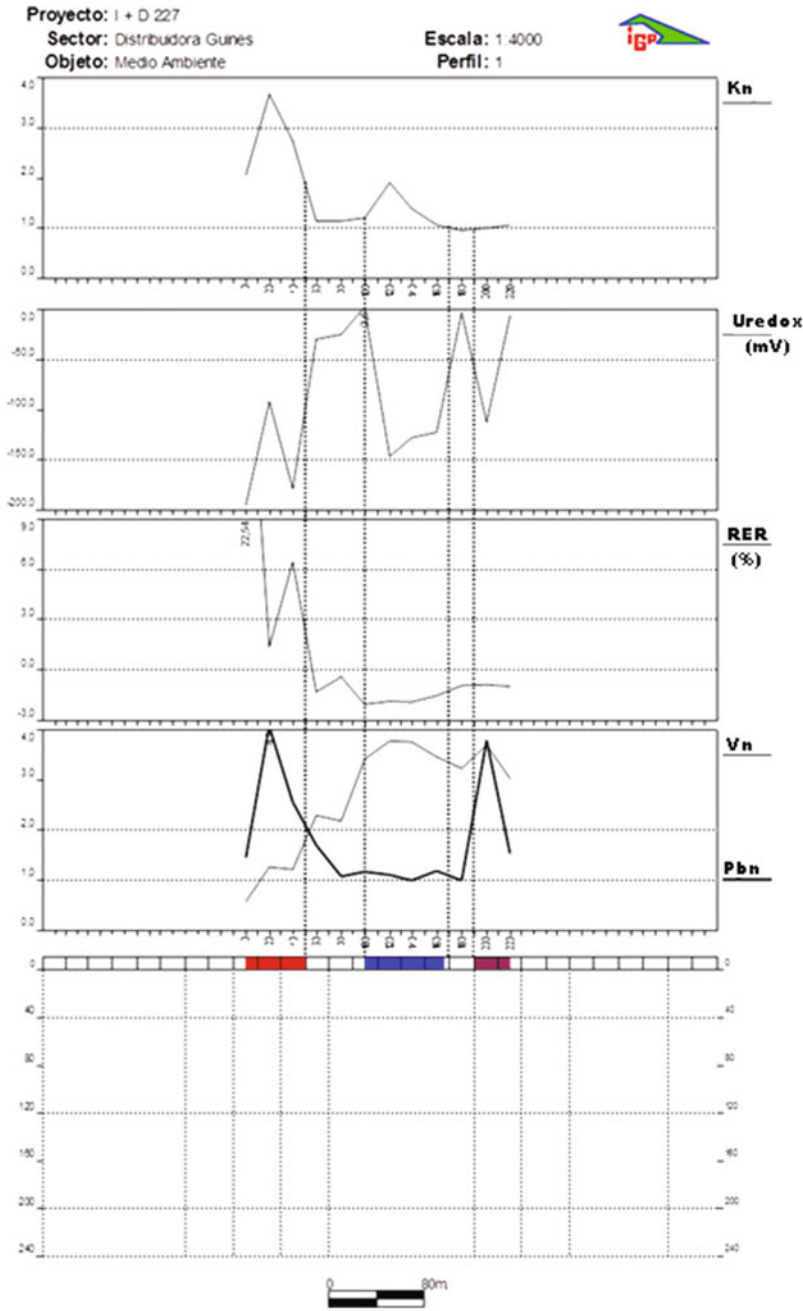
At the *Little Golden Hill* epithermal high-sulfidation gold deposit, spatial correspondence of a maximum of magnetic susceptibility and minimum values of

reduced spectral reflectance (darkening of the ground) to the oxidation zone of the deposit is observed. The reduced ORP low corresponds to the massive sulfide area in the depth (gossan below).

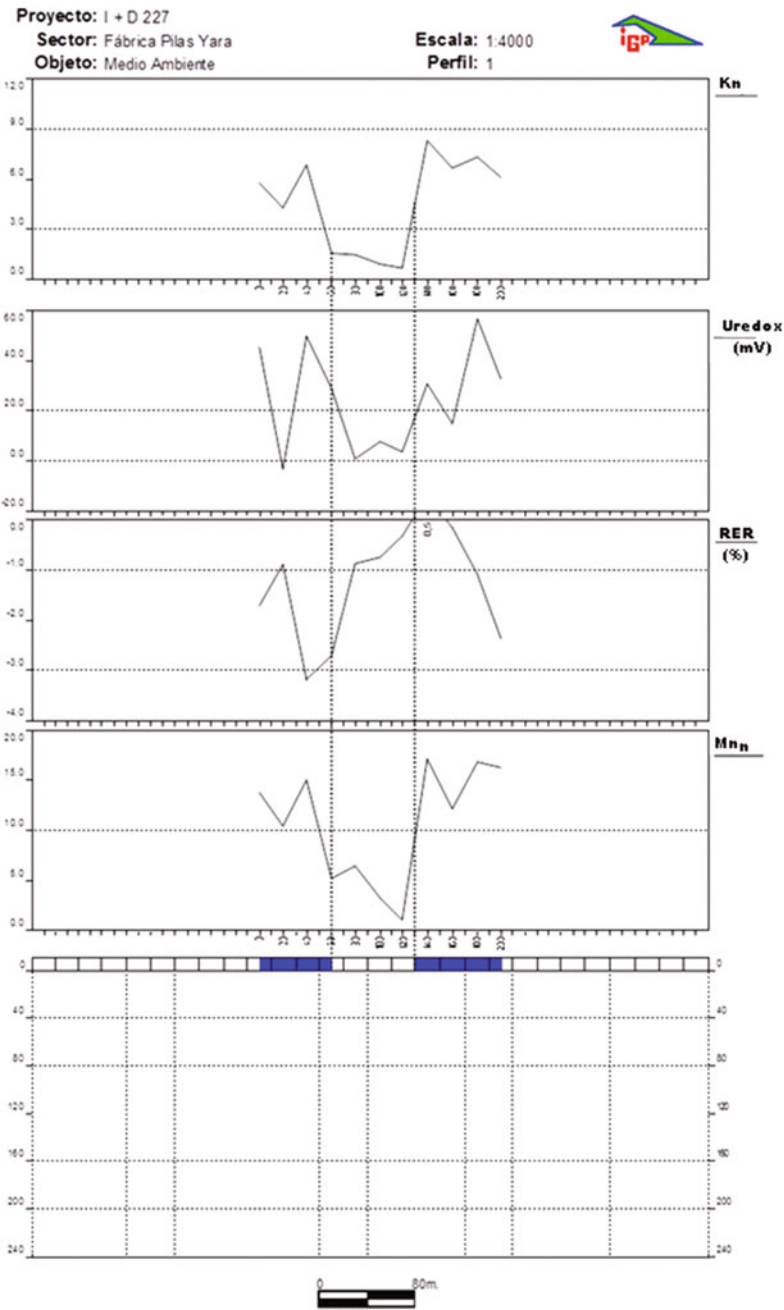


At the *Antonio* polymetallic Kuroko-type volcanogenic massive sulfide deposit, spatial correspondence of magnetic susceptibility highs with lows of reduced ORP and lows of reduced spectral reflectance, associated with increments of Pb in soil (from the deep), is observed.

Environmental studies

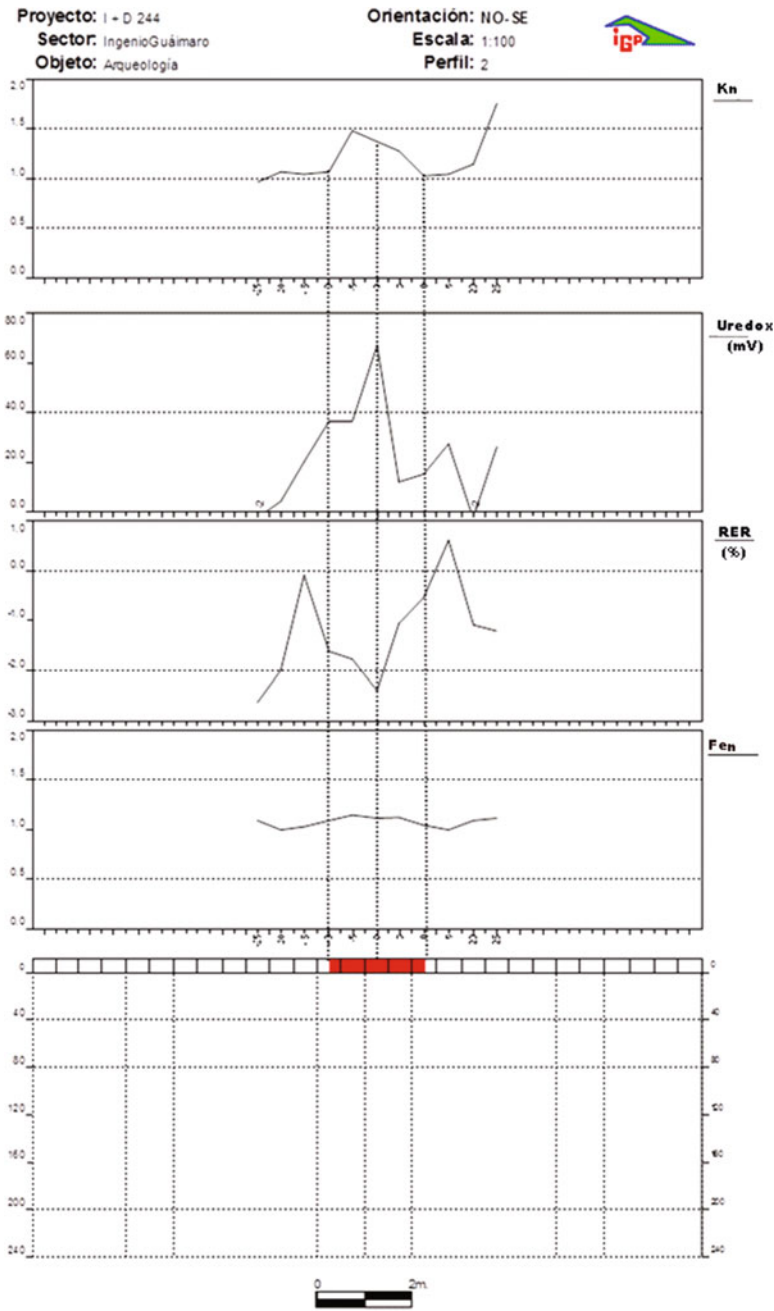


At the *Distribuidora de Hidrocarburos Güines*, not observable surface contamination, and presumably contamination at the level of the water table (from 100 m in the profile), is expressed by the spatial correspondence of maxima of the standard magnetic susceptibility, minimum values of reduced ORP, maxima and minima of the reduced spectral reflectance, and a corresponding increment (normalized) of the metallic elements hydrocarbon indicators: light (Pb) and heavy (V).



At the *Fábrica de Baterías Secas Pilas Yara*, unobservable manganese and other surface metal contamination is expressed by the spatial correspondence of maxima normalized magnetic susceptibility, maximum values of reduced ORP (oxidation zones), an undifferentiated character of reduced spectral reflectance, and a corresponding (normalized) increment of the main contaminant (Mn).

Archeology studies



At the *Ingenio Guáimaro* (Valle de los Ingenios, Sancti Spiritus), burial of a Jamaican Train is recognized by the spatial correspondence of a maxima normalized magnetic susceptibility, a maxima of reduced ORP (oxidation zone), a minima of reduced spectral reflectance, and the corresponding (normalized) increment of indicator element (Fe).

## 2.7 Conclusions

The combined application of redox potential and magnetic susceptibility of soils to geological prospecting, which is the antecedent of *Redox Complex*, is determined by the possibility of detecting the reducing environment column that is formed directly on metal and hydrocarbon occurrences and reaches the top of the section. Within this column, the conversion of nonmagnetic iron minerals to more stable magnetic varieties is favored, which explains the observed inverse correlation between the attributes and justifies integration of methods.

The multiparameter complementation and development of a theoretical basis of the technical complex, based on empirical support (still insufficient) of observations on known targets or control areas, identify the *Redox Complex* (ORP, magnetic susceptibility, spectral reflectance, and soil geochemistry) as a unconventional exploration technical complex, used for the indirect detection and evaluation of various metallic objects. It is based on the *Geochemical Principle of Metal Ions Vertical Migration* and successfully applied in various fields: oil and gas and metallic minerals exploration; studies of oil and metal contaminants in soils; and the search for metallic archeological burials. The use of these techniques is intended to complement the conventional prospecting complex with purposes of reducing areas and/or selection of the most favorable targets, resulting in an increase in economical–geological effectiveness of investigations.

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Unconventional Methods for Oil & Gas Exploration in  
Cuba

The Redox Complex

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2016, XII, 69 p. 18 illus., 4 illus. in color., Softcover

ISBN: 978-3-319-28015-8