SYNTHESIS REPORT

FOR PUBLICATION

Contract n°: BRPR - CT97 - 0374

Project n°: BE96-3162

Title : Development of a methodology for detecting deep metal ore deposits through physico-chemical analysis of fluids in shallow boreholes

Project coordinator: BRGM FR

Partners:

Idronaut	IT
Universidad Politecnica de Madrid	ES
INIMA	ES

Reference period: from 01/03/1997 to 29/02/2000

Starting date: 01 March 1997 Duration: 36 Months

Date of issue of this report: 25/05/2000

Project funded by the European Community under the Industrial & Materials Technologies Programme (Brite-EuRam III)

SYNTHESIS REPORT
FOR PUBLICATION

Summary page

The consortium

- **Partner organisations**
- **Consortium description**

Technical achievements

Exploitation plans and follow-up actions

References

Collaboration sought

Summary Page

Keywords: Geochemistry, mineral exploration, groundwater, Iberian Pyrite Belt, deep ore deposit

A new geochemical methodology has been developed for the exploration of deep metalliferous ores. It involves detecting modifications to the chemical composition of groundwater induced by the vicinity of an orebody. Its validation is based on geochemical, hydrogeological, mineralogical, geological and environmental investigations carried out over and around two massive sulphide deposits located in the South West Iberian Pyrite Belt (SWIPB): La Zarza and Masa Valverde.

The methodology has also required the development of high-performance sampling and analytical tools. Thus a Voltammetric In situ Probe (VIP) for *in situ* metal (Cu, Pb, Zn, Cd, Fe, Mn) detection has been miniaturized to 75 mm diameter, and a new device has been built for sampling water in small-diameter exploration boreholes at selected depths to 450 m without any risk of metal contamination during the procedure. The field sampling programme for groundwater analysis at the two sites was undertaken using these tools. The analyses concerned both major and trace elements. Metals (Cu, Pb, Zn, Cd, Fe, Mn) were determined *in situ* in some boreholes by using the VIP, but analysis for these metals, as well as for As, Ni and Co, were also performed by ICP-MS in the laboratory after sampling. Comparison between the VIP and ICP-MS results indicates that a large part of the metals in groundwater are present in form of complexes with organic matter and/or adsorbed onto colloids and/or small particles.

Orebody and host-rock characterization was carried out on the basis of petrographic and mineralogical observation, as well as chemical analysis. Compiled hydrogeological and metal-source maps of the sites highlight possible water and metal transfers from and towards the deposits and their subsequent influence on the chemical composition of groundwater in the vicinity of the deposits.

Application of the EQ3/6 software code to the chemical composition of the groundwaters in the proximity of and in the vicinity of the La Zarza and Masa Valverde deposits has made it possible to demonstrate the minerals with which the waters interact, and to confirm the important influence that organic matter or even thiosulphates and colloids have on the measured metal concentrations, significantly enhancing the measured concentration by up to several orders of magnitude. These results also indicate that the VIP probe is not yet totally operational for exploration, as it measures only truly dissolved metals, which are not detectable in some samples. Provided further modifications/developments are performed on the VIP probe, it will be a very useful tool for exploration as it measures the metals of interest for the methodology and represents a significant time saving, thus enabling an increased amount of data to be obtained.

The synthesis of all the results has led to the identification of indicators of deposit proximity. These are particularly useful for the implementation of the exploration methodology.

The Consortium

Partner organisations

Coordinator	**BRGM**
Contact person	H. Pauwels
Address	3, av. Claude Guillemin BP 6009 45060 ORLEANS France
Telephone	+33 (0)2 38 64 34 06
Fax	+33 (0)2 38 64 36 52
e-mail	h.pauwels@brgm.fr

Partner	**INIMA** (Servicios Europeos de Medio Ambiente, S.A.)
Contact person	M. Arena-Cuevas
Address	Arturo Soria, 336, 6ª Planta 28033 Madrid Spain
Telephone	+34 91 384 73 64
Fax	+34 91 383 15 11
e-mail	marenas@inima.com

Partner	**IDRONAUT**
Contact person	F. Graziottin
Address	Via Monte Amiata, 10 20047 Brugherio Italy
Telephone	+39 (0)39 87 96 56
Fax	+39 (0)39 88 33 82
e-mail	Idronaut@idronaut.it

Partner	**UPM (Universidad Politecnica de Madrid)**
Contact person	R. Castroviejo
Address	Rios Rosas, 21 28003 Madrid Spain
Telephone	+34 91 336 69 77
Fax	+34 91 336 7971
e-mail	Ricardoc@minas.upm.es

Partner	**SEIEMSA (Sociedad de Estudio, Investigationes y explotaciones Mineras, SA, Spain)**
Contact	Ceased its technical activities in 1998

Consortium description

Five partners from three European countries were initially involved in this project.

BRGM

BRGM, as the leader of the project, was responsible for the co-ordination of the project.

BRGM is a French National Research Centre and the parent company of servicing, engineering and mining subsidiaries. It incorporates a Mineral Resources Division involved in R&D projects, Public Service activities and overseas government exploration projects. It also incorporates five other divisions: Geoinformation, Development Planning and Natural Hazards, Water Resources, Environment and Process, and Analytical Laboratories, as well as the Regional Geological Surveys. Applied research at BRGM is devoted to the various domains of the Earth sciences, ranging from metallogeny and geochemical exploration to the environment and water resources.

Within the project, BRGM was mainly involved in adapting the sampling tools, in the fieldwork for groundwater sampling and subsequent laboratory analysis, and in the modelling of groundwater/rock interactions.

IDRONAUT

IDRONAUT SRL, an Italian industrial company established in 1982, has from the very beginning been involved in the following industrial and research fields with a staff of experienced engineers and technologists:

- marine chemistry
- electrochemistry
- electronics
- telemetry
- computer science
- software
- micro-mechanics
- chemical and physical oceanography

IDRONAUT is a small company (staff of 14, mostly dedicated to research) that manages to finance its research and development of innovative instrumentation through the sale of its products. Its Italian customers are the major research agencies such as ENEA, CNR, JRC Euratom CEC, ENEL, CISE, marine biology and oceanography laboratories and universities. Foreign sales are made through a worldwide dealer network. IDRONAUT is also a member of the MAROBOT and EUROLANDER Community, which organizes discussion meetings, and is regularly invited to participate in other meetings such as OSATES and ECOPS.

For the project, IDRONAUT in collaboration with the CABE Group (Analytical and Biophysical Environmental Chemistry Group, University of Geneva) was involved in the development of the analytical equipment; in particular the miniaturization of an existing voltammetric in situ probe (VIP) from 100 mm to 75 mm diameter to enable its use in 90-mm-diameter boreholes and the extension of its analytical capabilities; IDRONAUT also participated in the fieldwork.

INIMA (Servicios Europeos de Medio Ambiente, S.A., Spain)

INIMA, Servicios Europeos de Medio Ambiente S.A., is present in all the strategic sectors and mostly in those related with the most advanced technologies. INIMA offers more than 20 years experience in the environmental field, a global approach to environmental problems, a multidisciplinary treatment, close relationships with organizations, institutions and companies, services adapted to the client's real needs, quality guarantees and an integrated management of solutions. INIMA has a multidisciplinary team of 158 employees, including engineers (mining, civil, agronomy, industrial, etc.), biologists, geologists, chemists, physicists, and economists, all of whom are professionals with a broad experience in environment-related tasks.

INIMA's activities involve, amongst others, environmental consulting, applied geology, water treatment and management, hydrogeology, geothermal power plant studies and design, biomass and other renewable energy, waste, and air pollution.

For the project, INIMA undertook the hydrogeological investigation of the sites and the assessment of the influence of interference from different metals sources on the chemical composition of the groundwaters.

UPM (Universidad Politecnica de Madrid)

UPM is a State University with over 4000 employees and 34 High Schools, Centres and Institutes covering all the areas of modern technology. Its School of Mines is one of the oldest in Europe (1777) and has a long tradition in mining and geology. Its Department of Engineering Geology (*Departmento de Ingenieria Geologica*) is at the forefront of research in the mineral exploration and mining geology fields and as such has been involved in many national and international projects.

For the project, UPM was concerned predominantly with the solid-phase investigations (geological, mineralogical, geochemical, etc.) of the ore and host rock, as well as the interpretation of the deposit model, and participated in the definition of the hydrogeological model.

SEIEMSA (Sociedad de Estudio, Investigationes y explotaciones Mineras, SA, Spain),

SEIEMSA was an industrial small Spanish company involved in mineral exploration. Its commercial activities were restricted to promoting mineral exploration and satellite image processing software. However, it ceased its technical activities at the end of the first year of the project.

It was involved in exploration at one of the selected sites for the project, and would have been a end-user of the methodology after having verified the technical feasibility of the methodology under exploration conditions. It provided data and materials necessary at the beginning of the project, but the cessation of its activities deprived the project of technical facilities and mining exploration boreholes for the development of the methodology.

All four partners have been involved in preparing the application guidelines for the hydrogeochemical methodology.

Technical Achievements

A phased multidisciplinary approach (geochemistry, hydrogeology, analytical chemistry, mineralogy, geology, gitology, etc.) was designed to advance our knowledge of metal behaviour and transfer in the groundwaters around the two selected volcano-sedimentary sulphide polymetallic deposits (La Zarza and Masa Valverde) of the South Iberian Pyrite belt (SIPB) so as to enable the identification of indicators of deposit proximity and formulate practical guidelines for hydrogeochemical prospecting applied to the detection of deep blind polymetallic orebodies. The developed methodology has been demonstrated as a complementary tool that can, through the identification of the presence or absence of metals, help define geophysical (gravimetric, electrical) anomalies indicating the possible presence of ore.

The main result of the project concerns the confirmation of rather high metal concentrations in groundwater in the vicinity of both orebodies due to interactions between the water and the orebody. At La Zarza, the main reaction is the oxidation of sulphide minerals, whereas at Masa Valverde, located in a hydrological discharge area, the metal concentrations are provided by the dissolution of sulphide minerals even though their solubility is very low. The actual metal concentrations in the groundwater are far higher, up to several orders of magnitude for some, than could expected from the solubilities of the concerned minerals. This is due either to the formation of complexes (with organic matter and/or thiosulphates) and/or to adsorption onto colloids and/or small particles. This enhancement of metal concentrations in groundwaters enables their detection using available laboratory analytical techniques and consequently the use of groundwater chemical composition for the prospecting of blind and deep ore deposits, even in low redox conditions.

The main deliverables arising out of the project are as follows:

1- Modification of a voltammetric in-situ probe (VIP) developed through a collaboration between IDRONAUT (Italian SME) and the CABE group (Analytical and Biophysical Environmental Chemistry Group, University of Geneva) for in situ analysis of Cu, Pb, Zn, Cd with a lower detection limit of 50 pM (0.01 ppb) (Fig. 1). First, the mechanics were fully redesigned and the electronics and firmware partially redesigned so as to reduce the external diameter of the probe from 100 mm to 75 mm for use in the upper part of exploration boreholes equipped with suitable perforated tubing. Second, the analytical capabilities were enhanced to include the detection of Mn(II) and Fe(II) in fresh water. However, at present the VIP is able to measure only "truly dissolved" metals which, for some metals, constitutes only a small part of the total metal concentration. Provided that further modification/development is performed on the VIP so that it can measure total metal concentration, this will be a very useful tool in exploration.

Fig. 1: Photograph of the miniaturized VIP before being lowered in a borehole

Fig. 2: Photograph and drawing of the sampler

2- A <50-mm-diameter water-sampling tool for small-diameter boreholes that was developed for groundwater sampling at selected depths in exploration boreholes (60 mm in diameter) (Fig. 2). It has so far been tested with success down to a depth of 450 m. Its main advantages are: 1) a precise selection of the sampling depth without risk of failure (as occurs with traditional samplers due to triggering of the sampling procedure during the lowering); 2) a limited metal contamination of the waters due to interaction with sampler material; 3) the possibility of adjusting the sampling volume to that required for the analysis in only a single sampling pass.

3- A better geological and geochemical knowledge of the La Zarza deposit with determination of the alteration minerals to support the interpretation of the groundwater chemical composition data through water-rock interaction modelling.

4- Two hydrogeological maps (one each for the La Zarza and Masa Valverde sites) compiled with the following information: topography, hydrological basin(s), fractures and areas of high fracture density, water points (38 inventoried for La Zarza and 54 for Masa Valverde), rock and fracture permeabilities, and surface and ground water flow lines. Their interpretation, combined with the chemical composition of the groundwater, has made it possible to define three types of groundwater flow at the scale of the Iberian Pyrite Belt: a shallow groundwater flow that carries O_2 and leads to ore-deposit oxidation, an intermediate groundwater flow and a deep groundwater flow both each more reducing and sodium-rich than the famer.

5- Two risk maps of interference by metals from mine activities (one each for the La Zarza and Masa Valverde sites) compiled to provide a groundwater quality assessment in the investigated areas, and in particular to determine possible metal contamination of the collected groundwater samples from process other than interaction with the deposit.

6- The identification of deposit proximity criteria based on element ratios in the groundwaters. In the case of SO_4-bearing waters, these proximity criteria are revealed in (Cu/H^2, Pb/H^2), (Cu/H^2, Cd/H^2) and (Ni/H^2, Mn/H^2) diagrams (Fig. 3). They can be used when oxidation occurs due to infiltration of O_2-bearing waters, whatever the oxygen supply and whatever the mixing end-member (intermediate or deep groundwater flow). They enable the distinction between waters containing metals due to the immediate vicinity of polymetallic deposits from those containing metals derived from other sources (natural environment or recent and past mining activities).

   In the case of SO_4-free waters, the low redox conditions enable iron to be always at detectable concentrations, whereupon the criteria may be defined relative to iron concentration. It has been clearly demonstrated that, in the proximity of an orebody, other metal concentrations are increased relative to that of iron, with the more significant increases concerning Cu, Pb and Cd. Significant As, Pb and Cu increases relative to Mn have also been observed with deposit proximity.

.

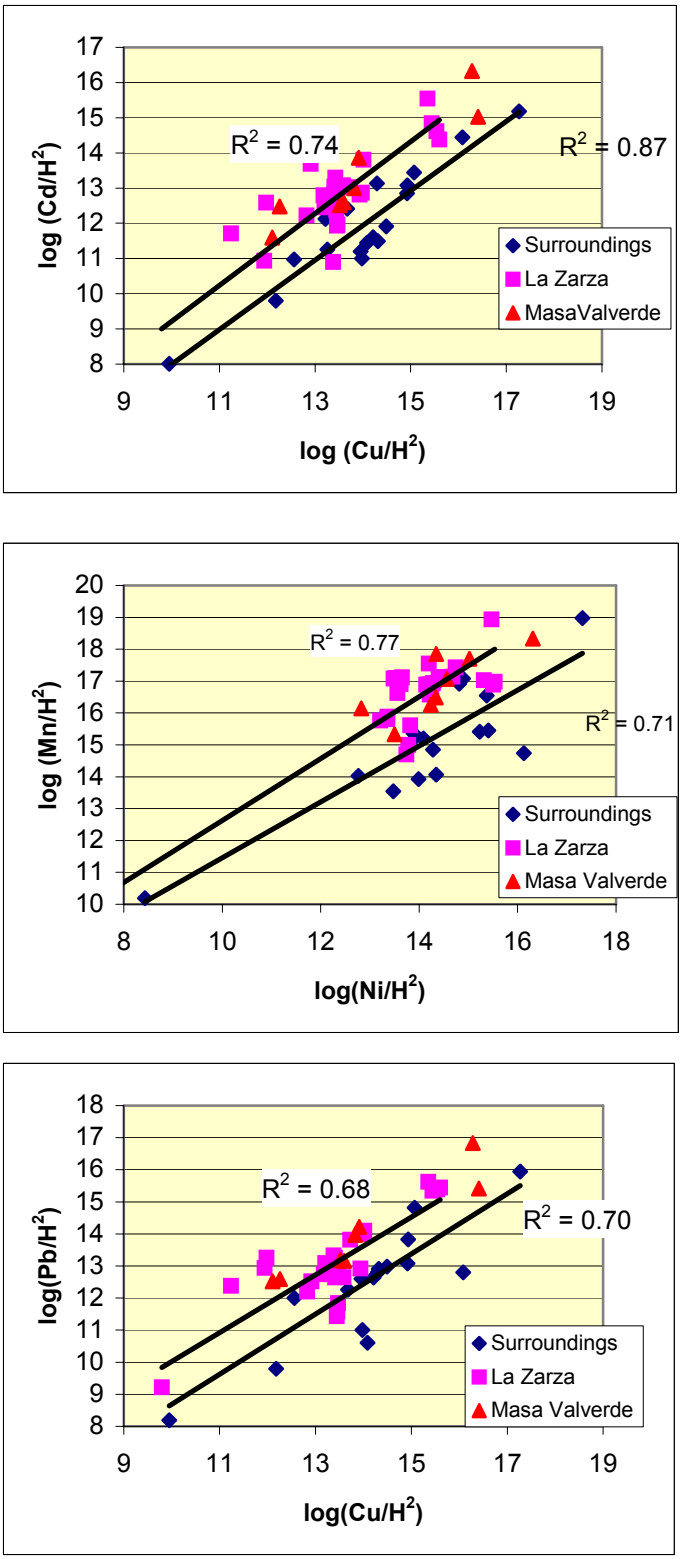

Fig. 3: (log(metal/H^2), log (metal/H^2)) diagrams illustrating differences in the chemical composition of SO_4-bearing groundwaters in the immediate vicinity of La Zarza and Masa Valverde with respect to groundwaters sampled farther from the orebodies

7- The hydrogeochemical methodology application guideline for the exploration of deep metalliferous orebodies. The different steps required in order to use groundwater composition to detect deep metalliferous orebodies can be summarised as follows:
   a. Determination of the hydrogeological position of the investigated site.
   b. Evidence of any risk of metal interference due to anthropic activity.
   c. Physico-chemical log in the concerned borehole(s) using a multiparameter probe such as the IDRONAUT OCEAN SEVEN 302 probe.
   d. Sampling and analysis of the groundwatters for selected major and trace metal elements.
   e. A sufficiently complete database including metal concentrations in the groundwaters in order to apply proximity criteria.

Exploitation Plans and Follow-up Actions

The most immediate applications of the project are obviously oriented towards mineral exploration, but nevertheless they do have a significant environmental aspect.

Publication of the project results in scientific and professional journals will show the level of expertise acquired from the project by the partners. It is therefore important, if the results are to be properly exploited, that they be presented to an international audience. An article for the *Journal of Geochemical Exploration* is presently being prepared.

A direct application of the project methodology, once validated, already exists for targets similar to La Zarza and Masa Valverde within the South Iberian Province where mining is still a topical subject. The project team hopes to be able to carry out the validation (preferably within the South Iberian Province) within the coming months in collaboration with one or more industrial partners, either in the form of a joint venture or as an industrial partnership research project. With this objective, the UPM team is actively maintaining contacts with the staff of various organization and industries from southern Spain and Portugal.

A medium-term objective is to apply the methodology in a context very different from the South Iberian Province. This could be associated with a R&D project at BRGM and/or with international research projects dedicated to testing new exploration methodologies and to identifying the processes by which metal ions are moved through a thick and highly variable overburden cover to form anomalies that are detectable at the surface using new technologies. Improving our understanding of such processes implies determining, through groundwater analysis, the mobile elements released through reactions (such as oxidation) with the sulphide body.

The developed methodology could also have important environmental applications. Increasing attention has been given over recent years to the problems of acid-mine drainage and to the processes and pathways by which metals are transported away from active and abandoned mine sites. The study of the chemical composition of groundwaters around undisturbed deposits also has important implications for baseline studies prior to the exploitation of ore deposits and for setting water-quality limits in the remediation of acid-mine drainage sites. It is technologically easier and more cost-efficient to remediate a site to the level of contamination occurring prior to mining rather than to try and attain higher quality standards —the project partners intend to set up a R&D project on this problem.

The compiled hydrogeological and metal interference risk maps can be used to evaluate the groundwater and/or surface water contamination risk at any site within the two study areas, and could easily be extended to a larger area. INIMA, Servicios Europeos de Medio Ambiente, S.A., expects to be the partner responsible for this activity on behalf of the Spanish Administrations responsible for environmental issues: mainly the *Junta de Andalucía* and the *Confederación Hidrográfica del Guadiana*.

The sampling and analysis tools could also find possible openings in the environmental domain:

- The groundwater sampler was recently used on behalf of DRIRE for sampling related to a hydrocarbon contamination assessment at former mines (Alsace, France) that have been flooded, but whose waters threaten to invade aquifers that are tapped for drinking water.

- Where the VIP is concerned, IDRONAUT's objective is to market it. Interest in the VIP probe has significantly increased since the sale of the first VIP systems to the University of Geneva (2 systems), the University of Goteborg (1 system) and the University of Quebec (1 system). Two further VIP Systems were sold to *Magistrato alle Acque* of Venice (Consorzio Venezia Nuova) in March 2000, and another two systems will be soon installed at the Savona Harbour Authority. In addition, two orders have been received from the University of Ancona and the University of Lancaster (UK), and another two orders are expected to be placed within the next two months.

  Two new project proposals have been submitted, within the context of the "Fifth Framework Programme" (1998-2002) of the European Commission, for the further development of the VIP system within the following Thematic Programmes:

  – Energy, Environment and Sustainable Development,
  – Competitive and Sustainable Growth.

References

Concerning the exploration methodology, the results have been presented at the following workshops:

- Pauwels H., Arenas M., Castroviejo R., Cueto R., Deschamps Y., Foucher J-C., Graziottin F., Samper J (1998) **Development of a methodology for detecting deep metal ore deposits through physico-chemical analysis of fluids in shallow boreholes.** Eurothen' 98 Proceedings of the first annual workshop Athens 12-14 Jan 1998. A. Kontopoulos, I. Paspaliaris, A. Adjemaian, G. Katalagarianakis editors, Laboratory of Metallurgy, National technical University of Athens. 57-63.

- Pauwels, H., Arenas, M., Castroviejo, R., Cueto, R., Deschamps, Y., Foucher, J-C, Graziottin, F., Jerez F., López, Molina A., Samper J., Sinna A., Tercier M-L.., 1999: **Development of a methodology for detecting deep metal ore deposits through physico-chemical analysis of fluids in shallow boreholes.** Eurothen'99, Proceedings of the second annual workshop Cagliari 12-14 Jan 1998. pp. 47-56.

- Pauwels H., Arenas M., Castroviejo R., Cueto R., Deschamps Y., Elorza F.J.., E. Garcia, Graziottin F., Jerez F., Lassin A., Lopez A., Molina A. Samper J (1998) **Development of a methodology for detecting deep metal ore deposits through physico-chemical analysis of fluids in shallow boreholes.** Eurothen' 2000 Proceedings of the first annual workshop Lisbon 19-21 Jan 2000.

Concerning the VIP, the following publications have been printed

- M-L. Tercier-Waeber, J. Buffle, F. Graziottin, and M. Koudelka-Hep, **"Novel Voltammetric Probe for *In-Situ* Trace Element Monitoring"**, Sea Technology, pp. 74-79 (May 1999).

- M-L. Tercier-Waeber, J. Buffle, F. Confalonieri, G. Riccardi, A. Sina, F. Graziottin, G.C. Fiaccabrino, and M. Koudelka-Hep, **"Submersible voltammetric probes for *in situ* real-time trace element measurements in surface water, groundwater and sediment-water interface"**, Meas. Sci. Technol., 10, pp. 1202-1213 (1999).

- M.-L. Tercier-Waeber, J. Pei, J. Buffle, G.C. Fiaccabrino, M. Koudelka-Hep, G. Riccardi, F. Confalonieri, A. Sina, and F. Graziottin, **"A Novel Voltammetric Probe with Individually Addressable Gel-Integrated Microsensor Arrays for Real-Time High Spatial Resolution Concentration Profile Measurements",** Electroanalysis, vol. 12, No. 1, pp. 27-34 (2000).

Collaboration Sought

As mentioned in the "Exploitation plans and follow-up actions" section, the project team is seeking to establish collaboration, either through a joint venture or an industrial partnership research project, with an industrial organization in the South Iberian Belt (Spain or Portugal) in order to validate the methodology.