Heavy Metals in groundwater around massive sulphide deposits : exploration and environmental aspects

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Objectives

To determine water-rock interactions around VMS deposits with application to two VMS ore deposits from Iberian Pyrite Belt:

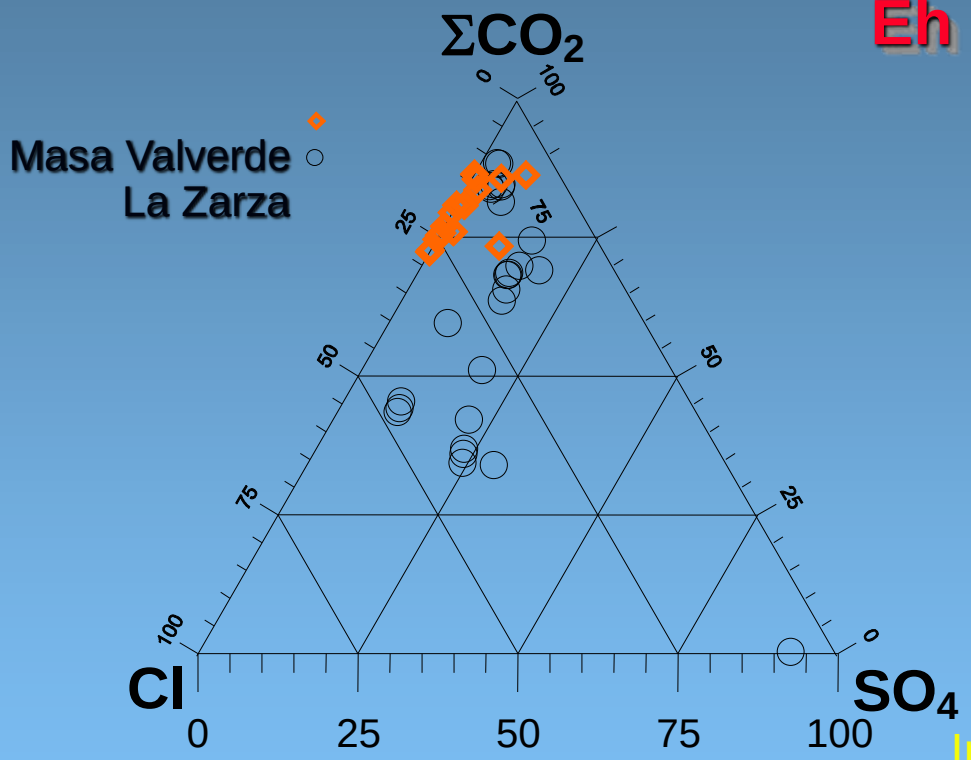
- the effect of a deeply buried orebody on the composition of groundwaters
- metal speciation and solubility controlling role of complexants

Applications in exploration and baseline studies

La Zarza and Masa Valverde VMS

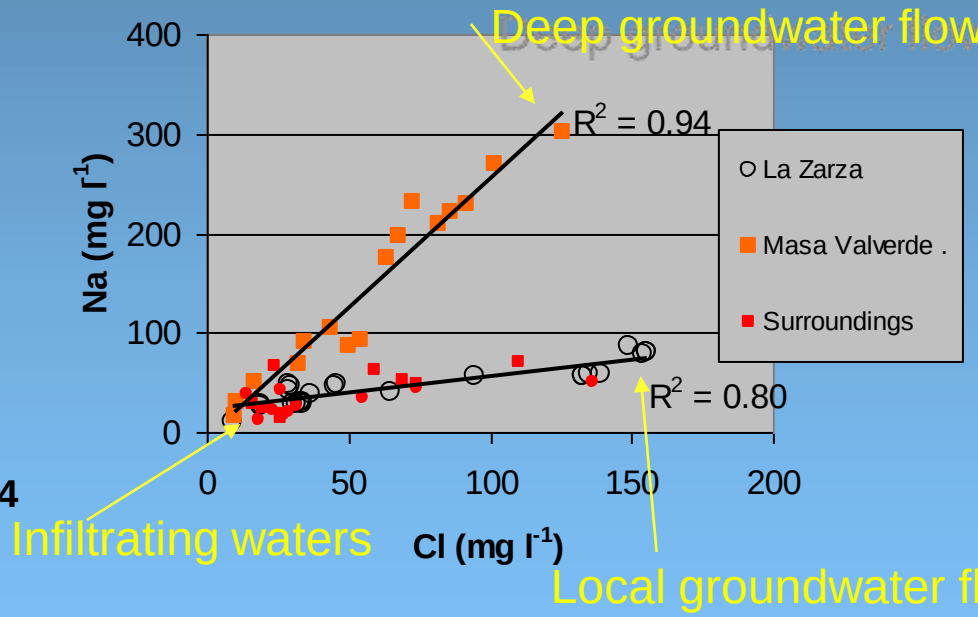
La Zarza	Masa Valverde
Nearly outcropping to more than 500 m depth	Buried at 400-600 m depth
Mined between 1853 and 1991 Remaining reserves: 110 Mt	Unworked Reserves : 100 Mt
Low to very low permeability of host-rock Located in an area of hydrogeological recharge	Low to very low permeability of host-rock Located in a hydrogeological discharge zone

Hydrogeology and Chemistry



Eh Masa Valverde : -285 to -230 mV

La Zarza : -30 to + 400 mV



Different chemical characteristics strengthened by occurrence of two mixing trends

Metal determination: VIP and ICP-MS

IDRONAUT s.r.l

Voltammetric In-situ Profiling System (VIP):

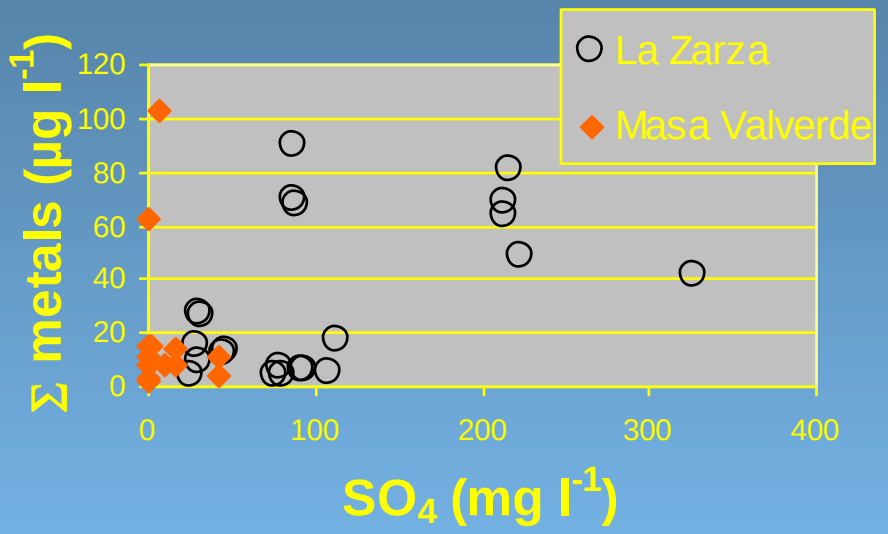
Submersible voltammetric probe
+ Calibration deck unit
+ Surface deck unit + PC

Specifity: measures only the concentration of the mobile fraction of trace metals (free metal ions + small labile complexes <few nm)

- Analysis by VIP for Cu, Pb, Zn, Cd, Mn
- Analysis by ICP-MS for Cu, Pb, Zn, Cd, Fe, Mn, Co, Ni, Al, As

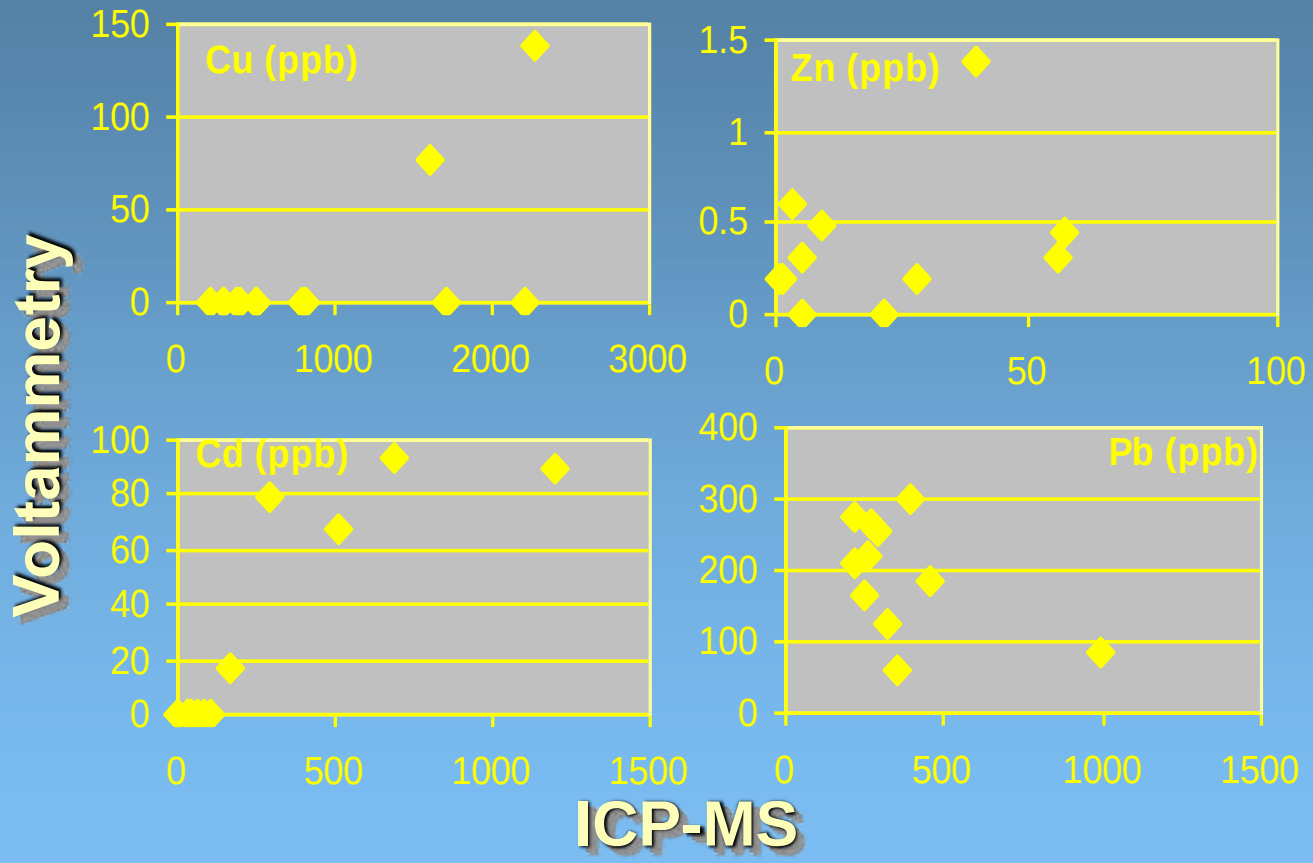
Metal contents

Σ(Zn+Cu+Pb+Cd+As+Ni+Co) in a concentration range of the same order at both sites, despite :
- very reducing conditions at Masa Valverde
-very low solubility of sulphide minerals



Impossible distinction between La Zarza and Masa Valverde G.W. using any particular metal

Metal Speciation: Comparison VIP / ICP-MS



La Zarza G.W. :

% of concentration measured by VIP with respect to ICP-MS:

Cu : less than 6%

Zn : 0.5 to 21 %

Cd : less than 27 %

Pb: 8 to 100%

Cu, Zn and Cd present as macromolecules and/or adsorbed on colloids/small particles

Pb presents as free ions + small labile complexes

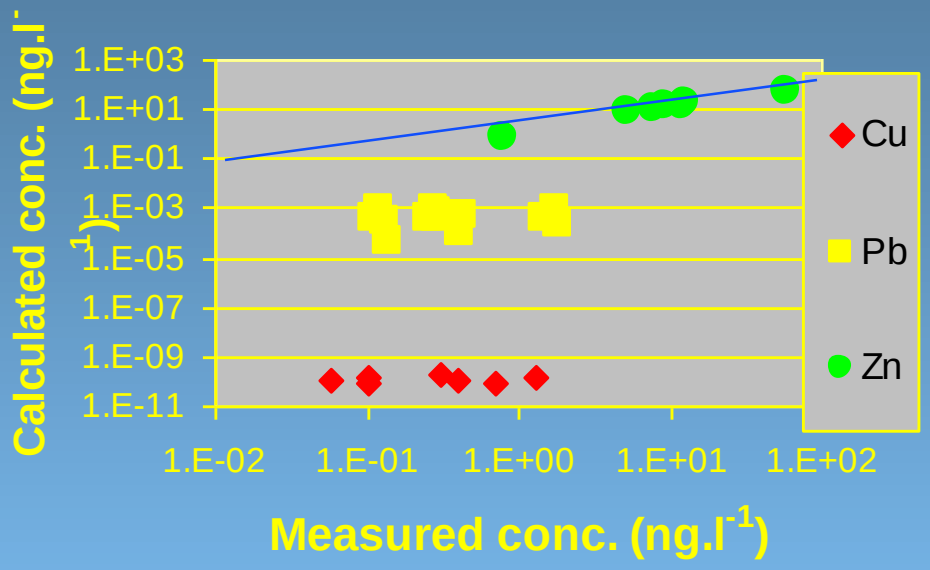
Metal Speciation: Geochemical Modelling

Masa Valverde G.W.

Using EQ3NR:

- Estimation of undectable H2S from equilibrium with respect to pyrite

- Estimation of Cu, Pb, Zn concentrations expected from equilibrium with respect to chalcopyrite, galena and sphalerite



Cu and Pb present as macromolecules and/or adsorbed on colloids/small particles

Zn presents as free ions + small labile complexes

Conclusions and Perspectives

Two major observations :

- **Similar total metal concentrations at both disturbed and deep buried unworked deposits**
- **Enhancement of total metal concentrations in GW by the formation of complexes or by metal adsorption on colloids or small particles**

Conclusions and Perspectives : Mineral exploration

These results:

- **Enlarge the field of potential applications for deep orebody exploration using hydrogeochemical methods at local scale**

  not only restricted in case of acid mine drainage

  despite low solubility of sulphide minerals

- **Contribute to support the possible role of G.W.-rock interactions in the formation of surface geochemical anomalies identified by enzyme leach, MMI selective digestions and others...**

Conclusions and Perspectives : Environmmental assessment

These results:

- **Confirm the importance of a natural baseline study in order to determine realistic achievable targets for remediation.**
- **Pose the problem of suitable methods for estimating natural background total metal concentration at abandoned mine sites:**

  Predictive modeling constitutes an upper limit in the case of acid mine drainage and a lower limit in the absence of significant oxidation.