



1      Chemical characteristics of groundwater around two massive  
2      sulphide deposits in an area of previous mining contamination,  
3      Iberian Pyrite Belt, Spain

4      Hélène Pauwels <sup>a,\*</sup>, Marie-Lou Tercier-Waeber <sup>b</sup>, Miguel Arenas <sup>c</sup>,  
5      Ricardo Castroviejo <sup>d</sup>, Yves Deschamps <sup>a</sup>, Arnault Lassin <sup>a</sup>, Flavio Graziottin <sup>e</sup>,  
6      Francisco-Javier Elorza <sup>d</sup>

7      <sup>a</sup>Centre Scientifique et Technique, BRGM Research Division, B.P. 6009, 3 Avenue Claude Guillemin, 45060 Orleans Cedex 2, France

8      <sup>b</sup>CABE, Department of Inorganic, Analytical and Applied Chemistry, University of Geneva Sciences II, 30 quai Ansermet,  
9      1211 Geneva 4, Switzerland

10     <sup>c</sup>Inima S.A., Arturo Soria No. 336, 6a Plant <sup>a</sup>, 28033 Madrid, Spain

11     <sup>d</sup>ETSI Minas, U.P. Madrid, Rios Rosas No. 21, 28003 Madrid, Spain

12     <sup>e</sup>Idronaut Srl, Via Monte Amiata 10, 20047 Brugherio (Mi), Italy

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15    **Abstract**

16    A detailed chemical study of groundwater was carried out to elucidate the processes controlling the oxidation and dissolution  
17    of sulphide minerals at two massive sulphide deposits in the Iberian Pyrite Belt (IPB), i.e. the mined La Zarza deposit and the  
18    unmined Masa Valverde deposit. It was found that major-element compositions varied according to the hydrological regime, La  
19    Zarza being in a relatively high area with groundwater recharge (and disturbance due to the human factor) and Masa Valverde  
20    being in a relatively low area with groundwater discharge. The variations mainly concern pH, Eh, SO<sub>4</sub> and Na concentrations.  
21    Metal concentrations were determined (a) by ICP-MS after filtration, and (b) in some cases by voltammetric measurement of  
22    Cu, Pb, Zn, Cd and Mn using the Voltammetric In situ Profiling (VIP) System, which allows detection of only the mobile  
23    fractions of trace elements (i.e., free metal ions and small labile complexes a few nanometers in size). If one compares the  
24    results obtained by each of the two methods, it would appear that the groundwater shows significant enhancement of metal  
25    solubility through complexing with organic matter and/or adsorption onto colloids and/or small particles. In areas of sulphide  
26    oxidation, however, this solubility enhancement decreases according to Cu>Zn>Cd>Pb. Under very low redox conditions, the  
27    attained metal concentrations can be several orders of magnitude (up to 10<sup>8</sup>–10<sup>9</sup> for Cu and 10<sup>2</sup>–10<sup>3</sup> for Pb) larger than those  
28    expected from equilibrium with respect to sulphide minerals as calculated with the EQ3NR geochemical code; Zn con-  
29    centrations, however, are close to equilibrium with respect to sphalerite. The implication of these results is discussed with  
30    respect both to mineral exploration and to environmental issues. © 2002 Published by Elsevier Science B.V.

31  
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34    \* Corresponding author. Fax: +33-2-3864-3518.

E-mail address: h.pauwels@brgm.fr (H. Pauwels).

## 36 1. Introduction

37 It is well established that natural baseline water  
 38 purity can be affected by undisturbed mineralization;  
 39 historic documents provide numerous examples of  
 40 natural metal-rich surface waters due to the presence  
 41 of unworked ore deposits (Runnells et al., 1992). The  
 42 high metal concentrations and acidity observed in  
 43 waters from such areas depend on several parameters  
 44 and processes, such as the depth and permeability of the  
 45 ore deposits, the type and abundance of the metal-  
 46 bearing sulphides, and the buffering capabilities of the  
 47 host rock. Consequently, metal and pH anomalies have  
 48 been proposed as tools for mineral exploration (de  
 49 Geoffrey et al., 1967; Archer and Main, 1971; Shartsev  
 50 et al., 1975; Cameron, 1977, 1978; Simpson et al.,  
 51 1996; Taufen, 1997).

52 From the environmental standpoint, however, high  
 53 metal contents and low pH are toxic to flora and fauna  
 54 and, under certain circumstances, this natural baseline  
 55 water quality can even threaten aquatic ecosystems  
 56 downstream from the ore deposit (Cameron et al.,  
 57 1998). For this reason, recent investigations on natural  
 58 background concentrations in mineralized districts  
 59 have been directed at setting water-quality limits for  
 60 future remediation of acid-mine drainage (Duttweiler  
 61 Kelley and Taylor, 1997; Leybourne et al., 1998),  
 62 because it is both more cost-efficient and technologi-  
 63 cally easier to remediate a site to its natural level of  
 64 contamination prior to mining rather than to attempt to  
 65 impose higher quality standards.

66 Whether the objective has been mineral exploration  
 67 or environmental assessment and improvement, studies  
 68 have focused mainly on surface water or very shallow  
 69 groundwater where chemical compositions are acqui-  
 70 red primarily through oxidation of the deposits. Far less  
 71 attention has been paid to deeper groundwater and the  
 72 effects that orebodies at depths of tens, if not hundreds,  
 73 of metres have on its composition. In the present paper,  
 74 we record and compare the geochemistry of ground-  
 75 water around and away from two massive sulphide  
 76 deposits in the Iberian Pyrite Belt, Spain, which is an  
 77 area of historic mining contamination.<sup>1</sup>

<sup>1</sup> The potential damage that can result from mining contami-  
 nation is exemplified by the disastrous accident of 25 April 1998  
 when spillage from the Los Frailes mine released 5 million m<sup>3</sup> of  
 toxic metal-rich acid waste and severely impacted the Doñana  
 National and Natural Parks.

The main purpose of the study was to determine the  
 water–rock interactions at each site, i.e. La Zarza,  
 which was mined until 1991, and Masa Valverde, which  
 is undisturbed and deeply buried. Emphasis was placed  
 on determining the effect of the deeply buried orebody  
 on groundwater composition, despite the very low  
 oxygen availability and lack of significant oxidation.  
 This included an investigation of metals speciation and  
 the solubility-controlling role of complexants. We also  
 examine the potential role of groundwater chemical  
 composition as an exploration tool, even in areas of  
 previous mining contamination, and the relevance of  
 baseline studies in helping to plan remediation and  
 monitoring prior to mining.

## 2. Study areas

### 2.1. General setting

The La Zarza and Masa Valverde massive sulphide  
 deposits are located in the Iberian Pyrite Belt (IPB),  
 which is 250 km long by 25–70 km wide and forms  
 part of the South Portuguese Zone of the Iberian Massif  
 (Fig. 1). The IPB is made up of Late Devonian to Early  
 Carboniferous rocks, in places overlain by Tertiary–  
 Quaternary units and alluvium (Van den Boogaard,  
 1967; Schermerhorn, 1971; Strauss and Madel, 1974;  
 Routhier et al., 1980; Oliveira, 1990). The three main  
 lithostratigraphic units are: (1) phyllites and quartzites  
 (PQ, Late Devonian) comprising metamorphosed shale  
 and quartz sandstone with rare conglomerate, and an  
 upper sequence containing bioclastic carbonate lenses  
 and nodules; (2) a thick (100–600 m) Late Famennian  
 to Middle Viséan volcano-sedimentary sequence (VS)  
 comprising bimodal shallow submarine volcanism  
 with three rhyolitic sequences (Rb/Sr = 385 ± 40 Ma;  
 Hamet and Delcey, 1971) interlayered with basic  
 volcanics and purple, blue and black shales, and (3) a  
 thick turbiditic formation (Culm facies) that is dia-  
 chronous over the underlying rocks (Late Viséan to  
 Westphalian). The Culm forms a southwestward pro-  
 grading detrital cover beginning with shaly and ash-  
 layer deposits (0–200 m) followed by turbidite facies  
 (greywackes).

The structure of the IPB, acquired during the Varis-  
 can orogeny (initiated during the Late Viséan and  
 culminating during the major Middle Westphalian

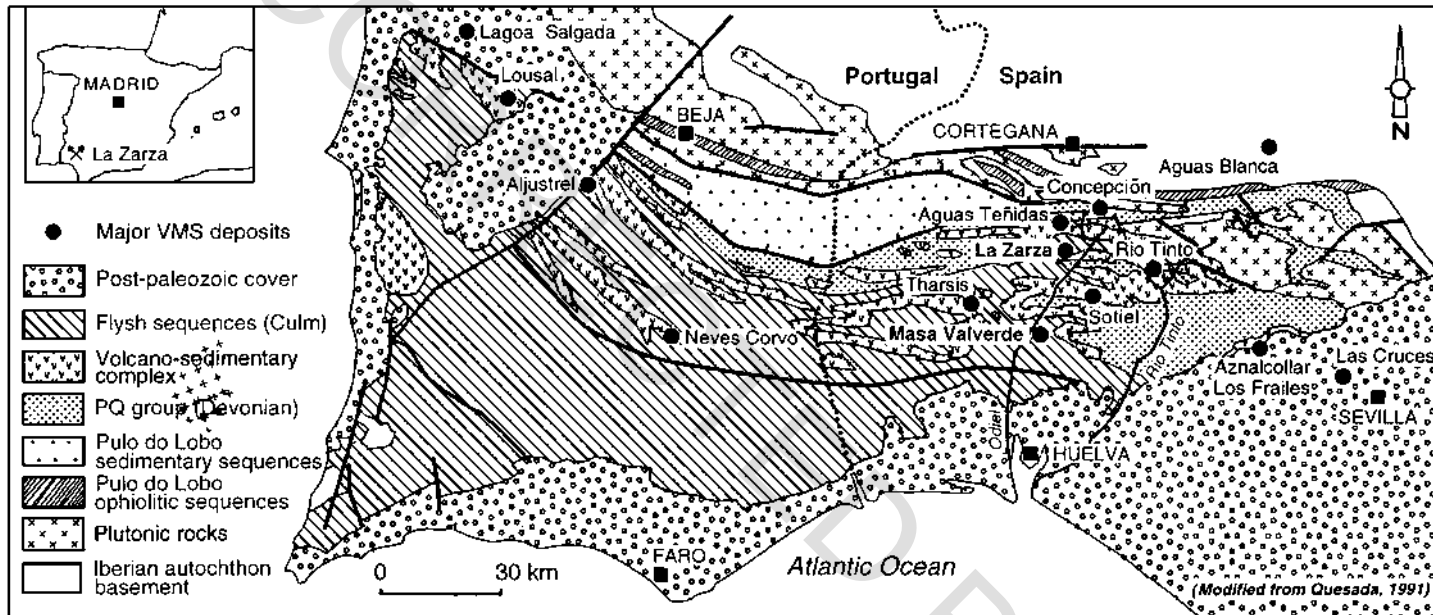


Fig. 1. Simplified geological map of the Iberian Pyrite Belt and location of the main deposits (modified from Quesada, 1991).

123 phase), can be defined as “a thin-skinned foreland  
124 thrust and fold belt” (Silva et al., 1990; Quesada,  
125 1991). The south-verging deformation is marked by  
126 three successive phases of compression under epizo-  
127 nal–metamorphic conditions that resulted in a north to  
128 south overthrusting accompanied by diachronous dep-  
129 osition of the Culm flysch sediments at the thrust front  
130 (Oliveira, 1990).

131 The volcanogenic massive sulphides (VMS) are  
132 hosted by the VS sequence, and either lie directly on  
133 acid volcanic facies units or are hosted by black shales,  
134 both situations being lateral to the acid volcanic  
135 centres. The 80 known deposits of the IPB contain  
136 more than 1700 Mt of sulphide ore (mined + reserves)  
137 totalling 14.6 Mt Cu, 13 Mt Pb, 34.9 Mt Zn, 880 t Au  
138 and 46,100 t Ag (Leistel et al., 1998). Byproducts and  
139 trace metals (e.g., Sn, Cd, Co, Hg, Bi and Se) are also  
140 reported in concentrations ranging from tens to hun-  
141 dreds of ppm. The VMS include several major deposits,  
142 such as Rio Tinto (>234 Mt), Neves-Corvo (>210 Mt),  
143 Aljustrel (>220 Mt), Aznalcollar (>90 Mt), La Zarza  
144 (150 Mt), Masa Valverde (100 Mt) and Tharsis (110  
145 Mt).

146 The La Zarza and Masa Valverde deposits are both  
147 located within the watershed of the Odiel River, which  
148 flows for 128 km through southern Spain to join the  
149 Tinto River and form a common estuary at the town of  
150 Huelva (Fig. 1). The area has a mean annual rainfall of  
151 700 mm with an effective rainfall of close to 150–225  
152 mm (inferred from data recorded during the period  
153 1964–1996). The dry period lasts from April to  
154 October.

155 The host-rock permeability of both deposits is low  
156 to very low ( $10^{-6}$  to  $10^{-8}$  cm s<sup>-1</sup>). Piezometric  
157 data were acquired from 38 water points (springs and  
158 domestic wells) over an area of about 140 km<sup>2</sup> around  
159 the La Zarza deposit, and from 54 water points over  
160 an area of about 110 km<sup>2</sup> around the Masa Valverde  
161 deposit. Groundwater circulation occurs at distinct  
162 levels: shallow circulation through the porous, low-  
163 permeability weathered facies of the VMS volcanic/  
164 volcano-sedimentary host rocks and/or sedimentary  
165 cover; deeper circulation mainly through fractures and  
166 joints. Local flow is subparallel to the topographic  
167 surface, whereas deeper regional flow is north to  
168 south over a distance of around 50 km from the  
169 Cortegana area (altitude 800 m) southwards to the  
170 sea.

A high level of contamination in the soils and  
171 surface waters has been imparted by mining activities  
172 that (a) began in the Chalcolithic era and continued in  
173 Roman times (end of the 4th century AD, mainly for  
174 copper and silver, and (b) were resumed in the middle  
175 of the 19th century with the extraction of pyrite (for  
176 sulphuric acid) and base metals (copper) from about  
177 80 mines. Overall, the Iberian Pyrite Belt has pro-  
178 duced about 280 Mt of pyrite and base-metal ores,  
179 together with significant tonnages of manganese ores.  
180

## 2.2. La Zarza

The La Zarza deposit is primarily a stratiform  
183 massive sulphide orebody produced by submarine  
184 exhalative deposition. The upper and middle parts of  
185 the pyritic orebody are zinc- and lead-rich, whereas  
186 the lower part is copper-rich. The massive orebody  
187 overlies a feeder stockwork rooted in hydrothermally  
188 altered acid volcanics and volcanoclastics. The bulk  
189 composition shows the ore to be the characteristic  
190 Zn–Pb–Cu type of Phanerozoic VMS associated with  
191 a bimodal volcanism. The mined deposit is a contin-  
192 uous lens-shaped body, about 2700 m long with an  
193 E–W strike, and is for the most part blind. Its  
194 apparent thickness varies from 30 to 200 m with a  
195 minimum downdip extension of 550 m in the central  
196 part (Figs. 2 and 3). This geometry is the result of a  
197 system of tight south-verging folds and thrust slices  
198 associated with the main phase of D1 synmetamorphic  
199 deformation. The deep part of the orebody occupies  
200 the hinge of a shear megasyncline with an E–W axis,  
201 which is overturned to the south and is accompanied  
202 by multiple ductile–brittle shears (thrust slices with a  
203 southerly vergence, sinistral transverse thrusts) caus-  
204 ing offsets and duplication of the ore layer.  
205

La Zarza, mined between 1853 and 1991, produced  
206 40–45 Mt of pyrite ore (average grade of 47% S,  
207 0.7% Cu, 1.5% Zn and 0.6% Pb) for sulphur produc-  
208 tion (Strauss et al., 1981). Precious metals (Au, Ag)  
209 are also known to occur. Open-pit mining (in the so-  
210 called “Corta San Pablo”, etc.) was followed by  
211 underground mining that extended for about 2000 m  
212 in an E–W direction, with levels down to 300 m  
213 below the surface. When mining ceased for economic  
214 reasons in 1991, the remaining in situ massive sul-  
215 phide potential at depth was estimated at 110 Mt,  
216 making it one of the largest known resources in the  
217

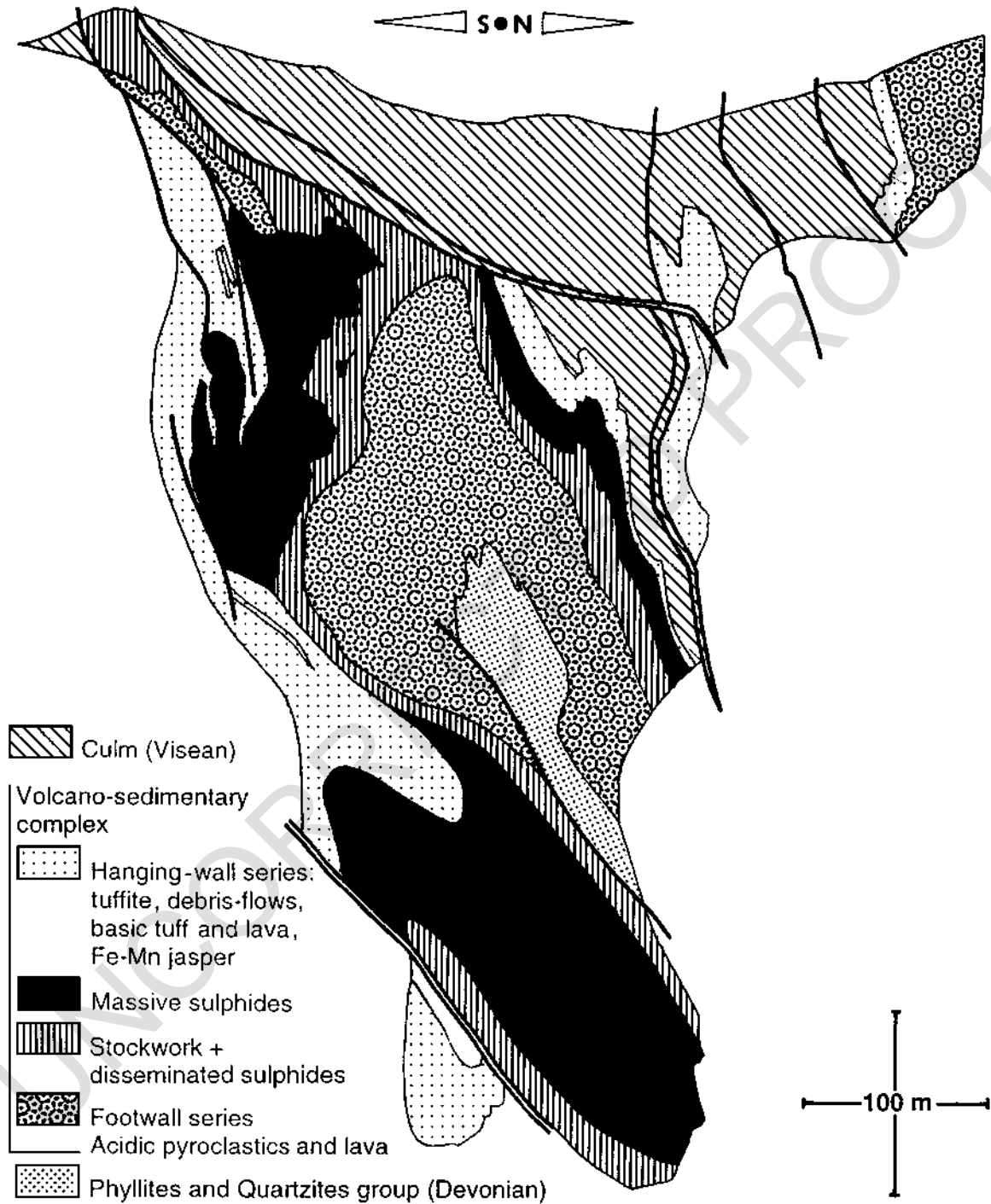


Fig. 2. Cross-section of the La Zarza deposit.

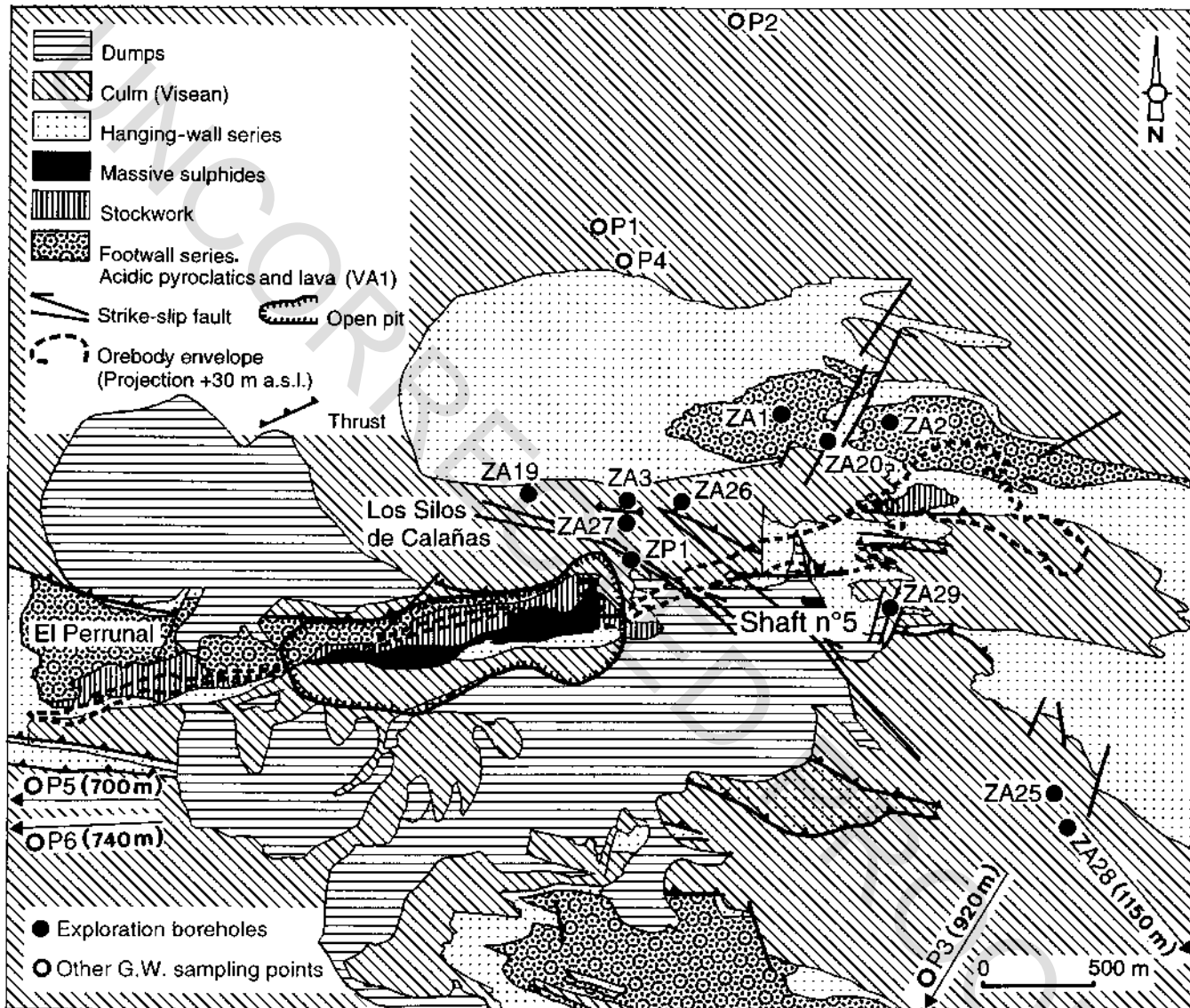


Fig. 3. Simplified geological map of the La Zarza area showing the location of groundwater sampling points. All the plotted exploration boreholes have been sampled.

218 region. The mine was maintained until January 1996,  
 219 when pumping was stopped and the underground  
 220 workings allowed to flood.

221 Hydrologically, La Zarza is located in a relatively  
 222 high topographic area (almost all the exploration  
 223 borehole collars are between 250 and 280 m a.s.l.)  
 224 at the junction of three drainage basins. The piezo-  
 225 metric levels reflect the topography, which (a) sug-  
 226 gests a predominance of local flow, and (b) indicates  
 227 that the deposit to be located in an area of hydro-  
 228 geological recharge.

229 Compilation of data from the Metallogenic Map  
 230 of Spain (IGME), aerial photographs, and field  
 231 campaigns throughout the 140 km<sup>2</sup> area around La  
 232 Zarza, has revealed the presence of several potential  
 233 contamination sources, including four stratiform poly-  
 234 metallic sulphide deposits, several small manganese  
 235 deposits, and gossans. Moreover, mining activities at  
 236 La Zarza have left both old and recent tailings,  
 237 “morrongos” (calcined sulphides), an old abandoned  
 238 mine railway, and various shallow exploration shafts  
 239 and adits.

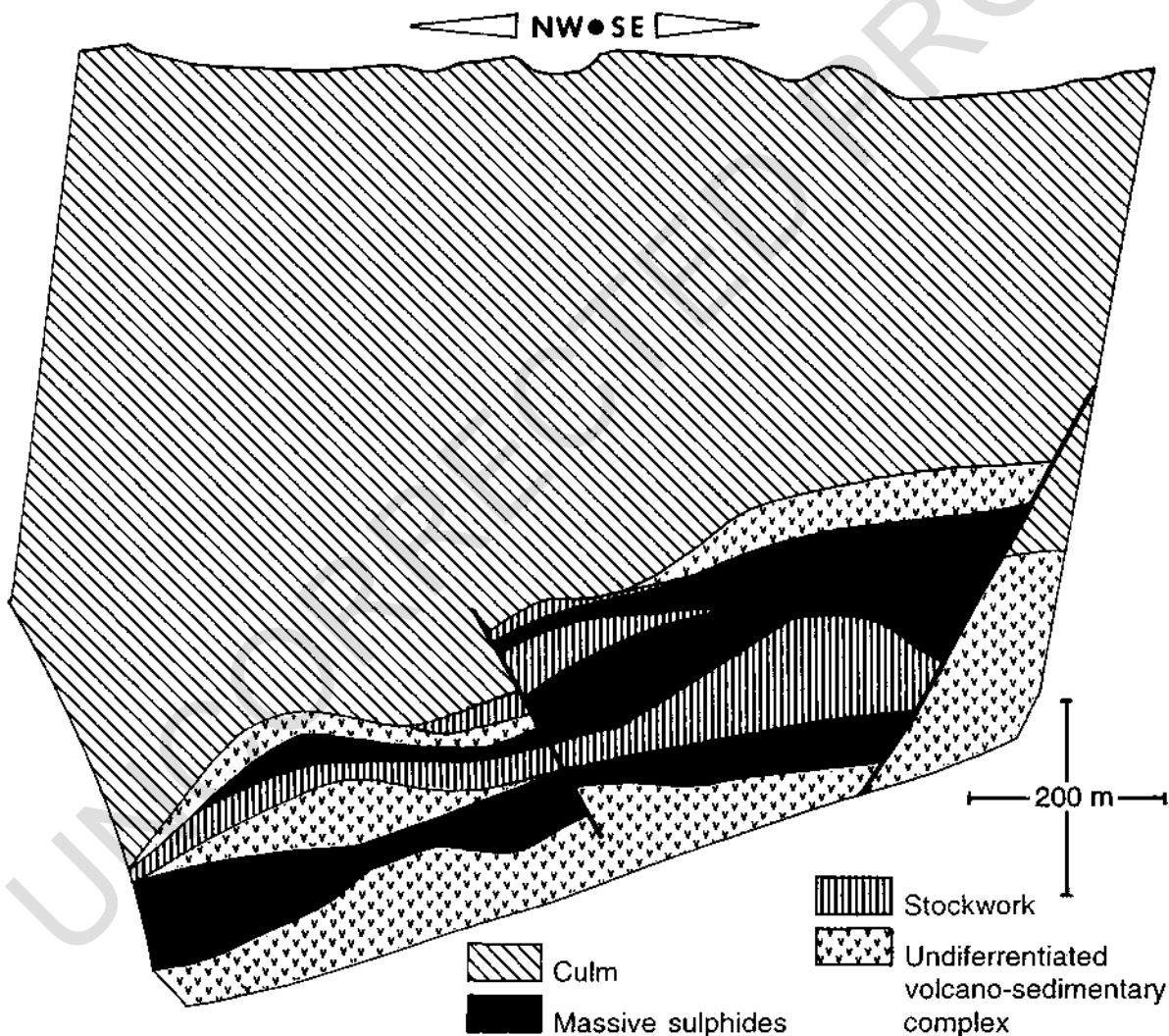


Fig. 4. Cross-section of the Masa Valverde deposit.

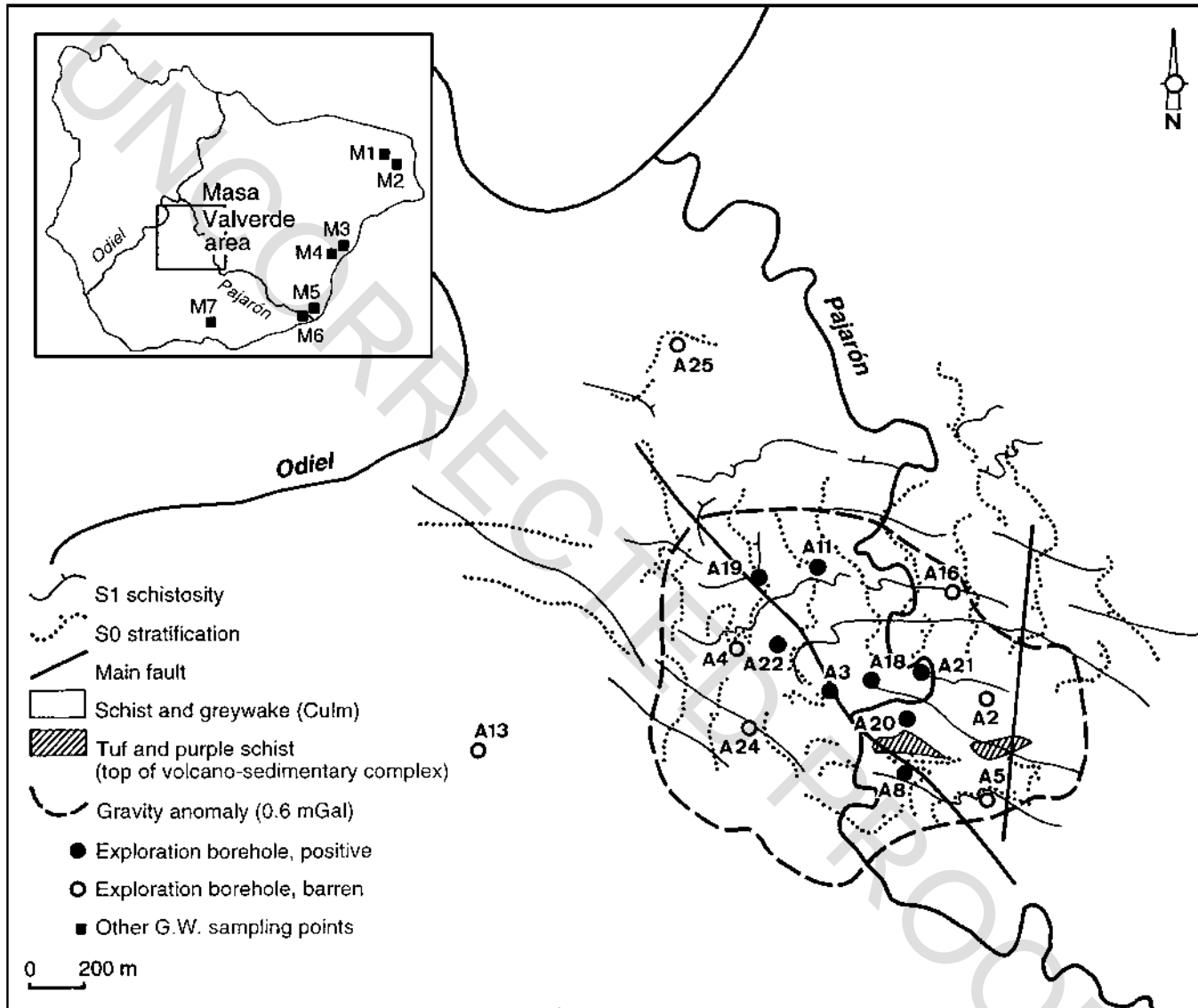


Fig. 5. Location of groundwater sampling points in the Masa Valverde area. All the plotted exploration boreholes have been sampled.



240

## 241 2.3. Masa Valverde

242 The Masa Valverde deposit, located some 18 km  
 243 southwest of La Zarza (Fig. 1), is also a blind  
 244 submarine VMS orebody comprising some 100 Mt  
 245 of pyrite and base-metal sulphides. It was discovered  
 246 in 1985–1986 by drilling a strong gravity anomaly  
 247 located over Culm metasediments. The ore is hosted  
 248 by a strongly deformed volcano-sedimentary se-  
 249 quence of dominant silicic composition and is buried  
 250 below 400–600 m of Culm schist and metagrey-  
 251 wacke. Information on the geology, lithostratigraphy,  
 252 geometry and ore composition was obtained from 25  
 253 boreholes drilled by Empresa Nacional Adaro de  
 254 Investigaciones, Mineras from 1986.

255 The regional deformation shows some similarities  
 256 with La Zarza, although the resulting geometry is  
 257 different. The deposit structure corresponds to a 500-  
 258 to 600-m-deep antiformal stack of slabs bearing stock-  
 259 work and stratiform massive sulphide bodies, with  
 260 axes plunging to the northwest. The deposit is cut off  
 261 at the top by a thrust plane below the Culm metasedi-  
 262 ments, is terminated to the east and southwest by two  
 263 high-angle faults (Figs. 4 and 5), and is still open to  
 264 the north and northeast.

265 The average composition of the ore is typical of the  
 266 Zn–Pb–Cu type (Lydon, 1992), i.e. a VMS relatively  
 267 enriched in Pb–Zn. The close spatial association  
 268 between the massive sulphides and stockwork feeders  
 269 indicates that the deposit was probably proximal.  
 270 Estimated resources at Masa Valverde, which has  
 271 not yet been mined, are 100 Mt of mainly pyritic  
 272 ore containing 0.4% Cu and 1.5% Pb–Zn, with some  
 273 enriched zones of complex ore (11 Mt at 5% Zn–Pb  
 274 and 0.54% Cu) and copper-rich ore (1.3 Mt at 1.91%  
 275 Cu and 1.7% Zn–Pb) (Costa and Parilla, 1992).

276 Hydrologically, the Masa Valverde deposit is in a  
 277 relatively low topographic area below the Pajarón  
 278 River valley and very close to the Odiel River (the  
 279 exploration borehole collars are between 80 and 160  
 280 m a.s.l.). The piezometric levels do not reflect the  
 281 surface topography—some wells are even artesian—  
 282 which suggests that the deposit is located in a dis-  
 283 charge zone as well in an area capturing the deep  
 284 regional flow. Compilation of data from the Metal-  
 285 logenic Map of Spain (IGME), aerial photographs,  
 286 and field campaigns throughout the 110 km<sup>2</sup> area  
 287 around Masa Valverde, has revealed several potential

contamination sources. These include 20 metalliferous 288  
 occurrences comprising small surface workings of 289  
 pyrite and polymetallic (copper-rich) veins, and some 290  
 manganese deposits. 291

## 3. Sampling and analysis 292

Three sampling surveys (April 1998, June 1998, 293  
 and February 1999) were carried out to acquire data 294  
 on the groundwater chemistry around La Zarza and 295  
 Masa Valverde (Figs. 3 and 5). During the April and 296  
 June surveys, groundwater samples were collected 297  
 from exploration boreholes at both deposits, as well 298  
 as from two springs and three wells. During the 299  
 February 1999 survey, groundwater samples were 300  
 collected only from springs and domestic wells. The 301  
 20 water points sampled in the La Zarza area were 11 302  
 exploration boreholes, 5 springs and 4 wells, and the 303  
 25 water points sampled in the Masa Valverde area 304  
 were 16 exploration boreholes, 7 domestic wells or 305  
 boreholes, and 2 points in surface watercourses. In 306  
 general, the springs, domestic wells and domestic 307  
 boreholes are located farther from the deposits than 308  
 the exploration boreholes. 309

The groundwater was collected with a small- 310  
 diameter device that enables samples to be taken at 311  
 selected depths in exploration boreholes. The device 312  
 consists of: (1) a 450-m-long Rilsan sampling tube 313  
 combined with an injection tube, (2) a 40-mm- 314  
 diameter PVC sampling head equipped with a non- 315  
 return valve, and (3) a pressurised bottle of neutral 316  
 gas (nitrogen). Before lowering the sampling head, 317  
 the tubes are filled with gas at a pressure higher than 318  
 the hydrostatic pressure at the selected sampling 319  
 depth so as to prevent premature opening of the 320  
 valve. Once the head is at the selected depth, the 321  
 tubes are depressurised to below the hydrostatic 322  
 pressure whereupon the water to gradually enters 323  
 the two tubes. The water is then lifted through the 324  
 sampling tube by injecting gas down the injection 325  
 tube at a pressure below the sampling depth hydro- 326  
 static pressure. A succession of several pressurisa- 327  
 tion–depressurisation cycles allows the device to be 328  
 rinsed before each sampling and also facilitates 329  
 collection of the volume required for the planned 330  
 analysis. An experiment performed by circulating 331  
 distilled water through the full 450-m-length of the 332

333 device demonstrated the absence of significant met- 381  
334 allic contamination in the water. 382

335 All the groundwater samples were filtered at 0.45 383  
336  $\mu\text{m}$  and stored either without additives for anion and 384  
337 silica determinations, or acidified to pH 2 with ultra- 385  
338 pure  $\text{HNO}_3$  for major cation and trace-element deter- 386  
339 minations. Temperature, pH, Eh, and conductivity 387  
340 were determined on site using Mettler instruments 388  
341 and an Orion pH electrode with automatic temper- 389  
342 ature compensation. In addition, 12 profiles of these 390  
343 physico-chemical parameters were run in situ in 391  
344 exploration boreholes using a submersible Idronaut 392  
345 Ocean Seven 302 multiparameter probe. Total alka- 393  
346 linity was also measured on site by titration with 394  
347 HCl, and the equivalent point determined according 395  
348 to Gran (1952). The presence of  $\text{H}_2\text{S}$  in the samples 396  
349 was tested by adding a few drops of Cd acetate and, 397  
350 if a precipitate appeared, determining its concentra- 398  
351 tion by titration with  $\text{HgCl}_2$ . 399

352 Major cation (Na, K, Ca and Mg) concentrations 400  
353 were determined by capillary electrophoresis (CIA 401  
354 Waters) with precision ranging from 5% for concen- 402  
355 trations over  $2 \text{ mg l}^{-1}$  to 10% for concentrations 403  
356 between  $0.5$  and  $2 \text{ mg l}^{-1}$ . Anion ( $\text{Cl}$ ,  $\text{SO}_4$  and  $\text{NO}_3$ ) 404  
357 concentrations were determined by HPLC (Dionex) 405  
358 with a precision better than 5%. Iron and silica 406  
359 concentrations were determined colorimetrically with 407  
360 a precision of 5%. Total metal concentrations were 408  
361 measured by ICP-MS with detection limits of  $0.004$  409  
362  $\mu\text{g l}^{-1}$  for Sb,  $0.01 \mu\text{g l}^{-1}$  for Co and Mo,  $0.03 \mu\text{g}$  410  
363  $\text{l}^{-1}$  for Cu and Cd,  $0.05 \mu\text{g l}^{-1}$  for Pb and Mn,  $0.07$  411  
364  $\mu\text{g l}^{-1}$  for As,  $0.2 \mu\text{g l}^{-1}$  for Al, and  $0.3 \mu\text{g l}^{-1}$  for 412  
365 Ni. The analytical precision was 5% for Cd, Pb and 413  
366 Sb, and 10% for other metals. 414

367 Voltammetric measurements of Cu, Pb, Zn, Cd and 415  
368 Mn trace elements were also performed with the 416  
369 Voltammetric In situ Profiling (VIP) System as 417  
370 described by Tercier-Waeber et al. (1998a). Briefly, 418  
371 the VIP System consists of a submersible voltammet- 419  
372 ric probe, an Idronaut Ocean Seven 302 multipara- 420  
373 meter submersible probe (optional and not used for 421  
374 this project), a calibration deck unit, a surface deck 422  
375 unit and an IBM-compatible PC. The voltammetric 423  
376 probe can be used for in situ measurements down to a 424  
377 depth of 500 m, with data being transferred by tele- 425  
378 metry. The standard design of the VIP voltammetric 426  
379 probe was modified for our specific application; 427  
380 specifically, the Delrin housing was replaced by a

titanium housing, the diameter was reduced from 100 381  
to 75 mm, and pressure and temperature sensors were 382  
incorporated in the probe. The heart of the probe is an 383  
Agarose Membrane-covered mercury-plated Ir-based 384  
microelectrode used either singly or in array (as for 385  
this project). It is integrated, together with an auxiliary 386  
and reference electrodes, in a pressure-compensated 387  
flow-through cell. These sensors present important 388  
advantages for in situ trace-metal measurements in 389  
natural waters (Belmont-Hébert et al., 1998; Tercier- 390  
Waeber et al., 1998b). In particular, the voltammetric 391  
signals measured at micro-sized electrodes are directly 392  
proportional to the concentration of the mobile frac- 393  
tion of trace metals (defined as free metal ions and 394  
small labile complexes with sizes less than a few 395  
nanometers). In addition, organic and inorganic col- 396  
loidal and particulate materials are efficiently ex- 397  
cluded from the agarose gel and do not interfere 398  
with the voltammetric measurements (i.e., fouling 399  
problem is avoided). The first point is important 400  
because the trace-element mobile fraction is the frac- 401  
tion that is most easily bioavailable, and thus is the 402  
fraction required for ecotoxicological assessment. 403  
Moreover, due to sample degradation, plus the risk 404  
of contamination during sample storage and separa- 405  
tion procedures, etc., the mobile fraction is difficult to 406  
measure without analytical artefact when using clas- 407  
sical techniques; it thus requires direct in situ meas- 408  
urement. Management software allows the user to 409  
control and configure the voltammetric probe operat- 410  
ing parameters and functions, such as electrochemical 411  
parameters, data acquisition, calibration and mainte- 412  
nance operations. 413

414 During the April 1998 sampling survey, eight 415  
water samples were collected from four boreholes. 416  
After filtration, the samples were stored at a temper- 417  
ature of less than  $+4 \text{ }^\circ\text{C}$  without any additives and 418  
sent to the University of Geneva for laboratory vol- 419  
tammetric analyses using the VIP System; this being 420  
the first attempt to measure metal concentrations in 421  
groundwater with the VIP, it was necessary to ensure 422  
that a signal would be obtained. During the June 423  
1998 sampling survey, voltammetric measurements 424  
were performed in the field. With three holes the 425  
VIP probe was lowered directly into the holes and 426  
the measurements made in situ. For two other holes, 427  
where the 56-mm internal diameter was too small for 428  
the probe, the input of the VIP voltammetric flow-

429 through cell was connected to the outlet of the water  
 430 sampling device, and measurement occurred merely  
 431 a few minutes after the groundwater had circulated  
 432 from the sampler to the probe without any contact  
 433 with the atmosphere—five samples were analysed in  
 434 this way. The detection limits with the VIP System  
 435 were 5, 10, 15, and 25  $\text{ng l}^{-1}$  for Cd, Pb, Cu and  
 436 Zn, respectively, and 50  $\mu\text{g l}^{-1}$  for Mn.

#### 437 4. Results

438

439 *4.1. Physico-chemical parameters and major-element*  
 440 *concentrations in groundwater at the La Zarza and*  
 441 *Masa Valverde deposits*

442 Groundwater at the La Zarza and Masa Valverde  
 443 deposits displayed wide variations in composition,  
 444 both with depth and between different boreholes. This  
 445 is demonstrated in Fig. 6, where the physico-chemical

parameter profiles show very strong variations that are  
 consistent with water–rock interactions in a fracture-  
 dominated flow system. In the case of La Zarza, the  
 data is also consistent with modified water–rock  
 interactions due to the presence of cavities related to  
 previous mining. Variations in the major-element  
 concentrations were also observed as a function of  
 depth and, more significantly, between boreholes. For  
 example, Cl concentration in the La Zarza ground-  
 water varies laterally between 10 and 155  $\text{mg l}^{-1}$ ,  
 whereas variability with depth accounts for less than  
 10  $\text{mg l}^{-1}$ .

The physico-chemical parameters indicate impor-  
 tant differences between the groundwater at the two  
 deposits. The La Zarza groundwater, with Eh between  
 –30 and +400 mV (one point of +600 mV  
 was even measured), is oxidizing whereas the Masa  
 Valverde groundwater, with Eh between –285 and  
 –230 mV, is highly reducing. The groundwater pH  
 also shows differences between the two deposits; the

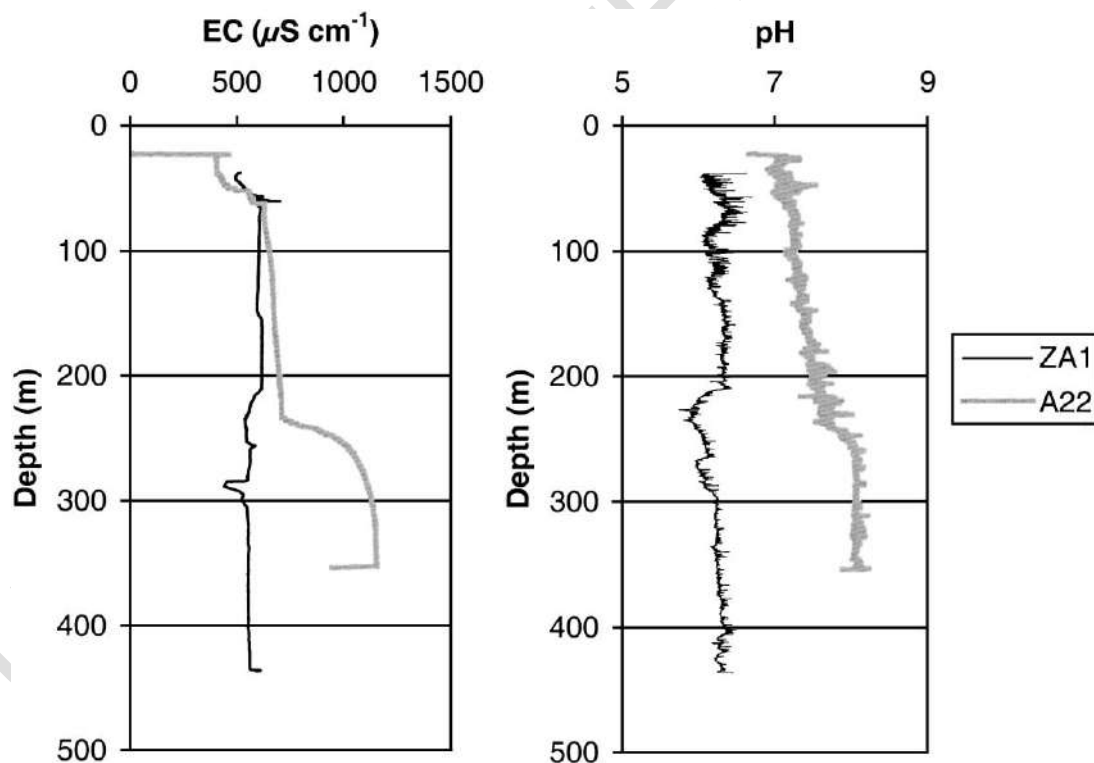


Fig. 6. Selected pH and electrical conductivity profiles obtained in exploration boreholes with the Idronaut Ocean Seven 302 probe. Examples from boreholes ZA1 (La Zarza) and A22 (Masa Valverde).

466 La Zarza groundwater, with a pH between 6.38 and  
467 7.95 (average 6.82) apart from one point at pH 3.28,  
468 is more acid than the Masa Valverde groundwater,  
469 with a pH ranging between 6.45 and 8.46 (average  
470 7.71).

471 Although groundwater conductivity is similar at  
472 the two deposits, with variations between 530 and  
473 1200  $\mu\text{S cm}^{-1}$  (average 735  $\mu\text{S cm}^{-1}$ ) at La Zarza  
474 and between 125 and 1125  $\mu\text{S cm}^{-1}$  (average 678  $\mu\text{S}$   
475  $\text{cm}^{-1}$ ) at Masa Valverde, one finds differences in the  
476 major cation and anion contents. The Masa Valverde  
477 groundwater is bicarbonate dominated, with higher  
478 Na–K and lower Ca–Mg than the La Zarza ground-  
479 water (Fig. 7a and b). The relative proportion of  
480 cations is more variable at Masa Valverde than at La  
481 Zarza, whereas the relative proportion of anions is  
482 more variable at La Zarza than at Masa Valverde. This  
483 variation is related mainly to sulphate concentrations.  
484 The Masa Valverde groundwater, despite the sulphidic  
485 nature of the ore, shows low sulphate concentrations  
486 (some samples were even below the detection limit of  
487 0.1  $\text{mg l}^{-1}$ ), as opposed to the La Zarza groundwater,  
488 which contains significant sulphate concentrations.

489 As regards  $\text{H}_2\text{S}$  concentration in the groundwater,  
490 this was determined in two boreholes at the La Zarza  
491 deposit—0.5 to 1.3  $\text{mg l}^{-1}$  in ZA2, and traces too  
492 low for analysis in ZA28—but was below the detec-  
493 tion limit in all groundwater samples from the Masa  
494 Valverde deposit.

#### 4.2. Waters sampled away from the main ore zones

497 Groundwater sampled from springs and domestic  
498 wells away from the deposits yielded pH values  
499 between 6.4 and 7.9 and Eh values in the range of  
500 +200–360 mV. These values are closer to those of  
501 the La Zarza groundwater than the Masa Valverde  
502 groundwater. Similarly, the relative major cation and  
503 anion concentration patterns in the spring and well  
504 groundwater are similar to those of the La Zarza  
505 groundwater, with sulphate concentrations between  
506 15 and 500  $\text{mg l}^{-1}$  and a relative proportion of alkali  
507 earth elements (Ca–Mg) higher than the alkaline ions  
508 (Na–K). A water sample taken from the Odiel River,  
509 just below its confluence with the Pajaron River,  
510 yielded a very low pH and high dissolved-element  
511 concentrations (Table 1), which agrees with other  
512 measurements performed in this stream (Nelson and

Lamothe, 1993; Elbaz-Poulichet and Dupuy, 1999). 513  
Such extremely acid and metal-rich water, which is 514  
also reported from other streams in the area such as 515  
the Rio Tinto (Elbaz-Poulichet and Leblanc, 1969), 516  
results from intensive pollution due to sulphide-min- 517  
eral oxidation. 518

#### 4.3. Metal concentrations in the groundwater

519  
520  
Most of the samples analysed by ICP-MS showed 521  
detectable total-metal concentrations that varied both 522  
with depth and laterally between boreholes. The mea- 523  
sured concentrations for all the metals ranged through 524  
more than two orders of magnitude and, for any given 525  
borehole, the variability of some metal concentrations 526  
was as high as a single order of magnitude (e.g., As 527  
and Ni in La Zarza borehole ZA3 ranged from 2 to 25 528  
 $\text{mg l}^{-2}$  and from 2 to 11  $\mu\text{g l}^{-1}$ , respectively). 529

The concentration range for  $\sum(\text{Zn} + \text{Cu} + \text{Pb} + \text{Cd}$  530  
 $+ \text{As} + \text{Ni} + \text{Co})$  was found to be of a same order of 531  
magnitude for all the groundwater, whether at La 532  
Zarza or at Masa Valverde, or away from the de- 533  
posits (Fig. 8). A similar situation was also observed 534  
for the individual metals—the groundwater concen- 535  
tration range of each metal was similar regardless of 536  
the provenance of the groundwater. Thus, it was 537  
impossible, on the basis of a particular metal, to 538  
distinguish groundwater from the vicinity of a specific 539  
deposit from groundwater of another deposit or even 540  
from groundwater distant from a deposit (Fig. 9). 541

Comparison between total metal concentration in 542  
the La Zarza groundwater and the mean composition 543  
of the La Zarza ore (Fig. 9) shows clearly that, for all 544  
metals except Ni, the measured groundwater concen- 545  
trations are below those to be expected from stochio- 546  
metric dissolution. In other words, the groundwater 547  
metal concentrations are lower than expected from 548  
sulphates if one assumes that all sulphide minerals are 549  
oxidized at the same rate and with no subsequent 550  
precipitation. A major exception at La Zarza is the 551  
groundwater from borehole ZA20, which is charac- 552  
terised by a low pH. 553

#### 4.4. Comparison of the VIP and ICP-MS results

554  
555  
Comparison between the metal concentrations 556  
determined with the VIP System and those determined 557  
by ICP-MS was possible for 15 of the groundwater 558

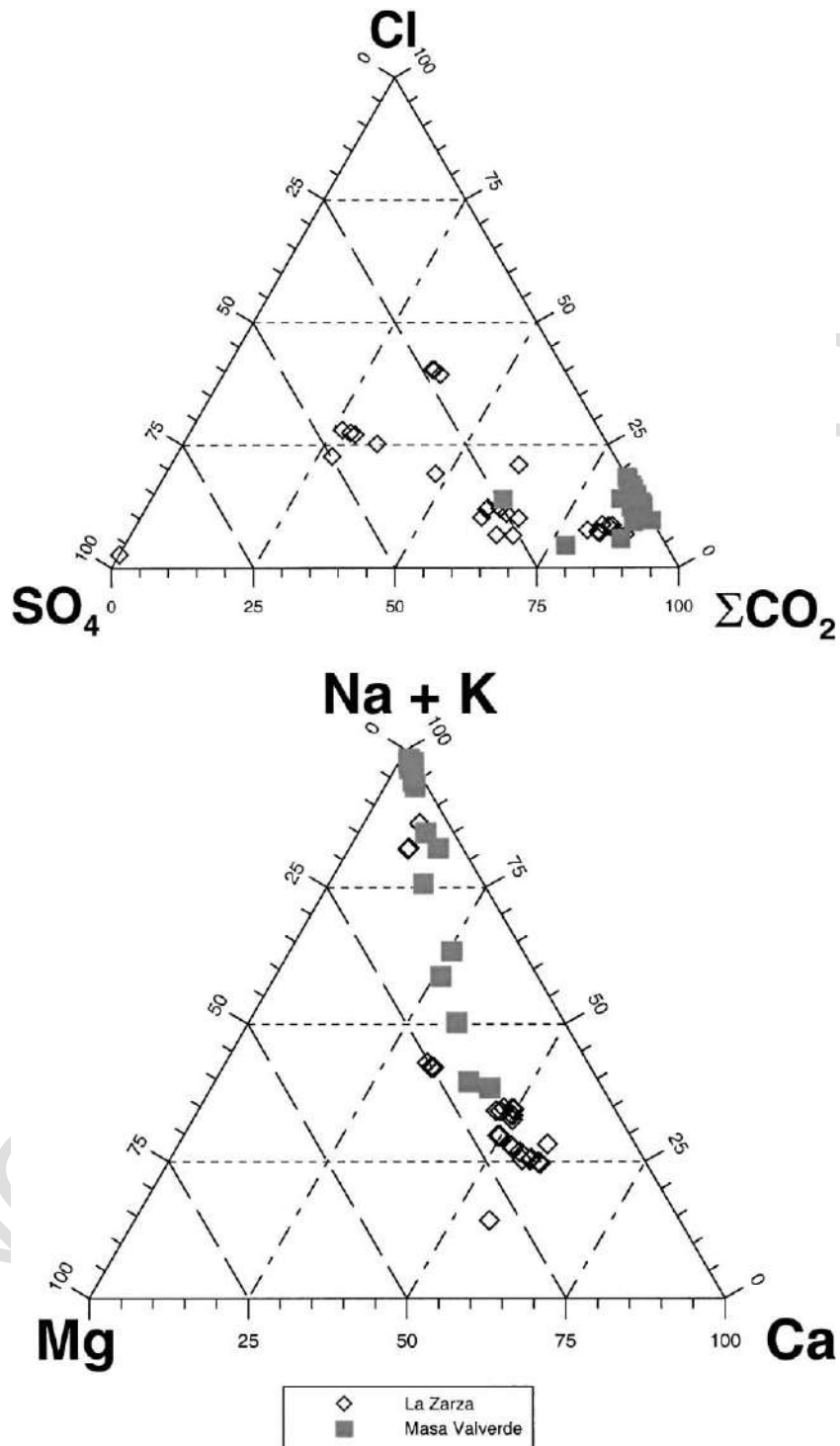


Fig. 7. Relative proportions of (A) Cl,  $\text{H}_2\text{CO}_3 + \text{HCO}_3$  ( $\Sigma\text{CO}_2$ ),  $\text{SO}_4$ , and (B) Na + K, Ca and Mg in groundwater at the La Zarza and Masa Valverde deposits.

t1.1 Table 1

t1.2 Chemical compositions of selected groundwater sampling points at and away from the La Zarza and Masa Valverde deposits

t1.3 Hole	La Zarza												Masa Valverde								
	ZA2		ZA3				ZA20	ZA26	P4	P6	A4	A8	A13	A18	A19	A25	M5	Odiel River			
t1.4																					
t1.5 Depth (m)	61.5	190	286	324	368	200	245	270	430	40	65			140	111	140	140	140	140		
t1.6 pH	7.21	6.95	6.96	6.99	6.97	6.59	6.61	6.62	6.62	3.28	6.79	7	6.94	8.35	6.45	7.09	8.26	7.99	8.06	6.9	3
t1.7 Eh (mV)	-32	-38	-36	-74	86	259	363	416	180	602	298	na	367	-280	-228	-245	-278	-265	-275		
t1.8 EC ( $\mu\text{S cm}^{-1}$ )	599	545	541	614	607	1005	1008	1000	978	721	1188	na	1180	727	124	484	967	922	1125	na	na
t1.9 Alk ( $\text{meq l}^{-1}$ )	5.72	5.8	5.84	5.45	5.37	2.05	2.23	2.38	3.06	nd	2.94	na	na	7.99	0.71	5.34	7.53	7.49	9.1	na	na
t1.10 Na ( $\text{mg l}^{-1}$ )	29.5	27.9	27.8	30.3	29.1	57.2	57.1	57.7	57.8	9.5	86.9	47.6	61.7	68.4	16.4	91.3	269	230	302	42.4	21.7
t1.11 K	4.3	4.8	5	4.7	4.2	1.3	1.2	1.2	nd	1.2	1.6	nd	7.1	1.4	1.1	13.5	2.7	2.3	3.2	2.3	3.2
t1.12 Ca	74.1	73.4	72.8	81.9	79.1	97.3	97.5	98.6	117.2	41.9	123	75.8	157	71	7	20.5	6.6	11.5	3.8	126	144
t1.13 Mg	25.6	23.2	22.6	23.7	22.4	40.9	40.6	40.5	40.6	22.4	46.9	30	68.2	36	3.1	13.1	2.7	4.7	1.2	63.8	124
t1.14 Cl	22.4	31.5	30.7	34.1	33.7	133	133	135	139	9	149	73.9	59.6	32.7	9.8	34.8	102	92.2	126	26	23
t1.15 SO <sub>4</sub>	53.8	46.3	45.1	32.8	29.2	214	213	217	223	318	327	116	480.2	41.4	16.9	nd	nd	nd	nd	559	1320
t1.16 H <sub>2</sub> S	1.34	0.82	0.54	0.54	0.54	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
t1.17 Si	12.2	11.8	11.7	12.6	12	8.9	8.8	8.7	8.6	13.4	8.9	na	9.2	9.8	5.6	5.4	7.6	7.8	8.6	na	na
t1.18 Fe	nd	0.04	nd	nd	0.05	0.05	0.12	nd	1.73	30.6	0.29	na	0.13	0.1	1.6	3.68	0.01	0.32	0.11	na	na
t1.19 Mn ( $\mu\text{g l}^{-1}$ )	1017	973	950	905	891	2571	2436	2377	2442	3094	3500	830	20.8	279	270	587	9.1	114	18.9	1705	0.53
t1.20 Cu	0.2	0.3	0.3	0.01	0.01	1.7	1.6	2.2	0.01	1710	2.3	0.95	11	0.3	0.16	0.1	0.4	0.1	0.3	3.28	8886
t1.21 Zn	3	1.4	0.9	6.1	1.7	45.3	40	57.9	20.3	2313	28.1	2.8	18.3	12	5.88	8	4	2.3	5.3	11.7	21618
t1.22 Cd	0.04	0.001	0	0.04	0.001	0.29	1.2	0.69	0.03	10.1	0.17	nd	0.093	nd	0.05	nd	nd	nd	0.05	0.005	102
t1.23 Pb	0.25	0.27	0.22	0.19	0.1	0.29	0.45	0.26	0.14	454	0.22	nd	0.16	0.14	0.42	0.29	2	0.29	1.5	0.13	156
t1.24 Co	0.3	0.27	0.31	0.32	0.26	7.6	7.5	7.8	0.6	34.8	3.9	2.62	0.14	0.84	0.99	0.31	0.03	0.16	0.06	0.74	533
t1.25 Ni	2.1	1.9	2	2	1.6	10.9	10.6	9.8	2.1	22.8	6.6	6.49	1.6	2	4	1.7	0.2	0.4	0.4	4.3	268
t1.26 As	11	8.5	8.2	18	11.9	2.5	2.2	2	25.4	7.2	na	1.02	na	0.27	na	0.4	1.7	1.1	0.86	1.49	7.96
t1.27 Mo	0.69	na	na	na	na	na	na	na	na	na	na	na	na	na	0.29	na	na	na	na	na	na
t1.28 Sb	0.12	na	na	na	na	na	na	na	na	na	na	na	na	na	0.06	na	na	na	na	na	na

t1.29 n.d.: not detected; n.a.: not analysed.

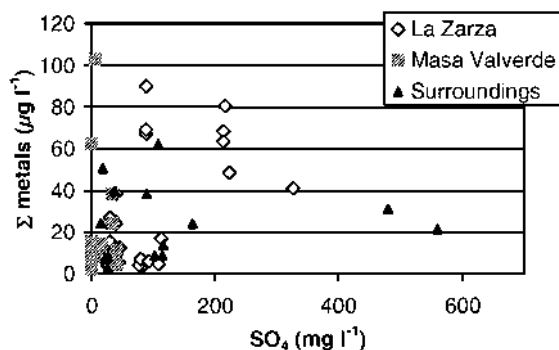


Fig. 8. The  $\sum(\text{Zn} + \text{Cu} + \text{Pb} + \text{Cd} + \text{As} + \text{Ni} + \text{Co})$  versus  $\text{SO}_4$  concentration in groundwater at the La Zarza and Masa Valverde deposits.

559 samples (Fig. 10)—13 samples for Cu, Pb, Zn and Cd  
 560 (one of these also for Mn) from the La Zarza deposit,  
 561 and 2 samples for Mn at the Masa Valverde deposit.

562 *Copper* was detected by the VIP System in two of  
 563 the samples, but at concentrations representing only  
 564 5.8% and 6.1% of the values determined by ICP-MS.

The VIP System detection limit for Cu being  $15 \text{ ng l}^{-1}$ , it can be estimated that the mobile fractions of Cu for the other samples were less than 3% of the Cu total concentrations determined by ICP-MS.

*Zinc* was detected by the VIP System in all samples except two from La Zarza borehole ZA28. The concentrations of the mobile Zn species represented 0.5–21% (average 7.9%) of the total Zn concentrations determined by ICP-MS. The lack of detectable Zn in borehole ZA28 samples indicates that the amount of the mobile Zn species at this site was less than 0.5% of the total Zn concentrations determined by ICP-MS.

*Cadmium*, when detected by the VIP System, represented 7.5–27% (average 14%) of the total Cd concentrations determined by ICP-MS. When no mobile Cd species was detected, it accounted for less than 1% of that determined by ICP-MS.

*Lead* was detected in all samples by the VIP System, with the concentrations of the mobile Pb species representing 8–100% (average 67%) of the total Pb concentration measured by ICP-MS.

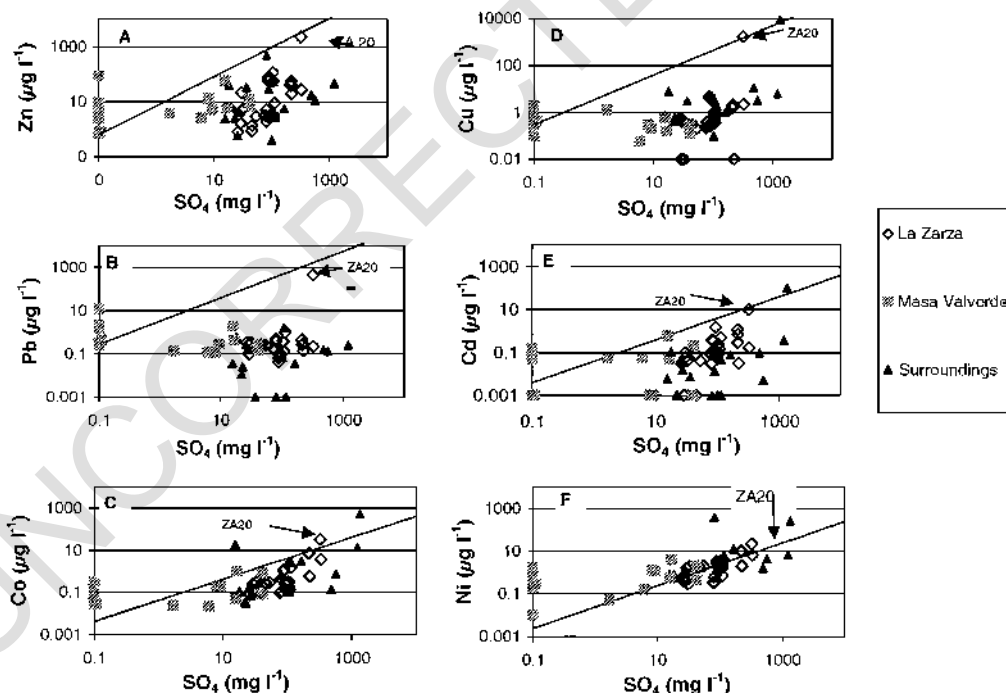


Fig. 9. (Metal,  $\text{SO}_4$ ) diagrams: (A) Zn, (B) Pb, (C) Co, (D) Cu, (E) Cd, (F) Ni. Lines on each diagram represent stoichiometric dissolution of the La Zarza ore calculated from the bulk sulphides composition (S: 30.14%; Zn: 1.15%; Cu: 0.73%; Pb: 0.54%; Cd: 55 ppm; Co: 60 ppm; Ni: 20 ppm).

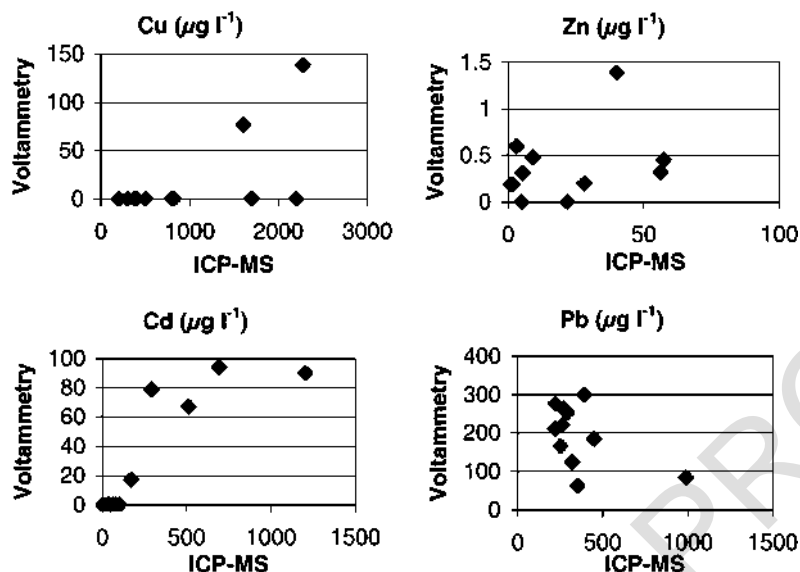


Fig. 10. VIP System versus ICP-MS determinations for Cu, Zn, Cd and Pb concentrations in groundwater at the La Zarza deposit.

586 *Manganese* data is limited to only three samples  
 587 (one from La Zarza and two from Masa Valverde)  
 588 analysed by both the VIP System and ICP-MS. The  
 589 mobile Mn concentrations determined by the VIP Sys-  
 590 tem represented 100% (La Zarza) and 64% (Masa Val-  
 591 verde) of the total Mn concentration determined by  
 592 ICP-MS.

593 These percentages provide interesting information  
 594 regarding the nature of the metals in the groundwater.  
 595 They clearly indicate that the Cu, Cd and Zn mobile  
 596 fractions (free ions and small labile complexes of <4  
 597 nm, including inorganic complexes such as hydrox-  
 598 ides, chlorides, carbonates or sulphates) represent only  
 599 a small fraction of the total metal concentrations. The  
 600 Pb and Mn mobile fractions, however, are more sig-  
 601 nificant.

## 602 5. Discussion

### 603 604 5.1. Chemical and hydrological differences between 605 La Zarza and Masa Valverde groundwater

606 As stated earlier, groundwater from the La Zarza  
 607 deposit and groundwater from Masa Valverde deposit  
 608 show differences in chemical composition, particu-  
 609 larly as regards pH, redox conditions and relative

610 proportions of major cations and anions. This differ-  
 611 ence is illustrated clearly by comparison of the Na/Cl  
 612 ratios (Fig. 11A). The Masa Valverde deposit data  
 613 show a strong correlation ( $R^2=0.94$ ) between Na and  
 614 Cl, which differs from the equivalent correlation  
 615 ( $R^2=0.80$ ) given by the La Zarza deposit data (ex-  
 616 cepting borehole ZA28). This suggests that the  
 617 groundwater chemical compositions result from mix-  
 618 ing trends between a (Na+Cl)-depleted end-member  
 619 and two different (Na+Cl)-rich end-members.

620 One hypothesis for the nature of the dilute end-  
 621 member is simply that of a shallow flow subsequent to  
 622 rainfall. In the case of Masa Valverde, this hypothesis  
 623 is strengthened by the presence of  $SO_4$  above the limit  
 624 of detection in the groundwater samples with the  
 625 lower Na and Cl concentrations (Fig. 11B), indicating  
 626 that the dilute end-member contains oxygen that could  
 627 cause oxidation of the sulphide minerals. The  $SO_4$   
 628 concentration would then indicate low oxygen con-  
 629 sumption by soil respiration and thus rapid circulation  
 630 of the water, such as can occur locally through faults  
 631 (or possibly through a deficient well cementation,  
 632 considering that exploration boreholes do not require  
 633 the same finish as hydrological wells).

634 Further geochemical analysis, including isotopic  
 635 investigations, would be necessary to fully explain  
 636 the origin of the salinity of each (Na+Cl)-rich



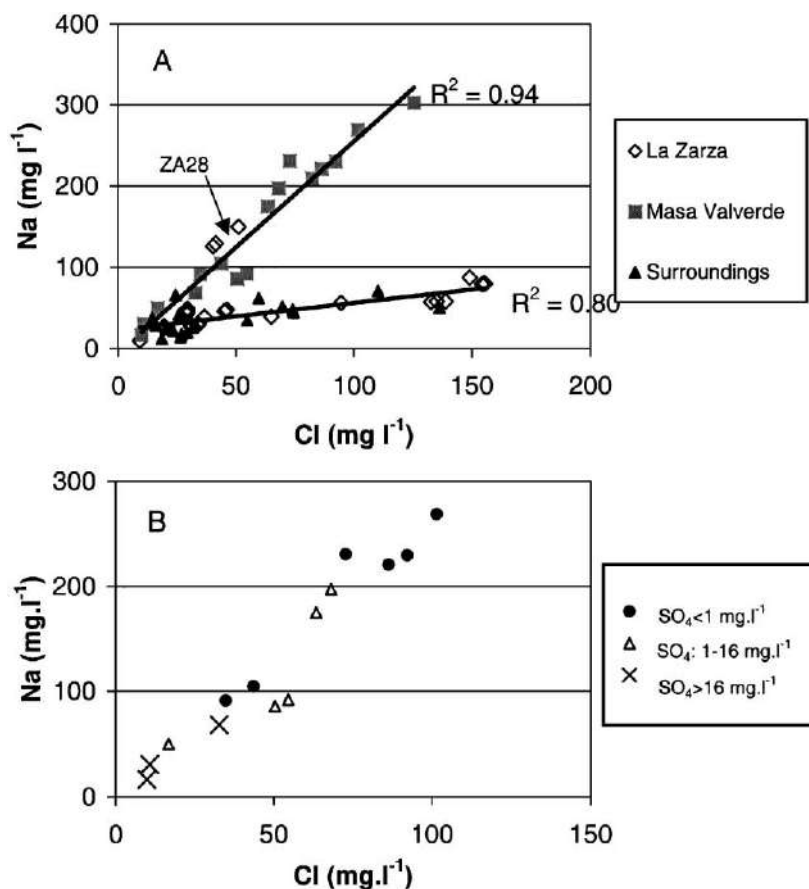


Fig. 11. Na versus Cl concentration in groundwater (A) at the La Zarza and Masa Valverde deposits, and away from these deposits, (B) at the Masa Valverde deposit. The size of the circles relates to the  $\text{SO}_4$  concentration.

637 end-member. However, the presence of two distinct  
 638 (Na+Cl)-rich end-members is in accordance with  
 639 the hydrogeological observations. In particular, the  
 640 piezometric level at La Zarza indicates a predom-  
 641 inance of local flow, whereas at Masa Valverde it  
 642 reveals the occurrence of deeper flow. This concept  
 643 is strengthened by the redox and pH data that  
 644 suggest interaction of an  $\text{O}_2$ -free water with the  
 645 sulphide deposit. In other words, when the deep  
 646 groundwater with the (Na+Cl)-rich end-member  
 647 composition reaches the Masa Valverde deposit,  
 648 the dissolved electron acceptors have been con-  
 649 sumed, probably through the oxidation of dissolved  
 650 or solid organic matter present in both water and  
 651 rock, and consequently part of the waters are  $\text{SO}_4$ -  
 652 free despite interactions with the sulphide deposit.

Data from La Zarza borehole ZA28, which plots on  
 the Masa Valverde mixing line, also accords with the  
 above hypothesis. This borehole, 2.4 km southeast of  
 the La Zarza deposit, is in a relatively depressed  
 topographically and is slightly artesian. It is probably  
 these differences in the hydrogeological conditions,  
 with respect to the other La Zarza exploration bore-  
 holes, that explain the deep flow chemical signature of  
 ZA28 groundwater.

Whatever the origin of the two (Na+Cl)-rich end-  
 members, they appear to form a significant part of the  
 IPB groundwater because (1) the composition of the  
 ZA28 groundwater to the southeast of the La Zarza  
 deposit plots on the Masa Valverde groundwater  
 trend, and (2) the average composition of the ground-  
 water collected at the Neves Corvo deposit (Portugal)

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669 is Na 67 and Cl 76 mg l<sup>-1</sup> (Grimes and de Carvalho,  
670 1994), which plots on the La Zarza deposit mixing  
671 line.

672

## 673 5.2. Chemical speciation and water–rock reactions

674 Thermodynamic calculations on the La Zarza and  
675 Masa Valverde groundwaters, using the EQ3NR geo-  
676 chemical code (Wolery, 1992), gave results that show  
677 certain similarities (Fig. 12) despite the differences in  
678 both apparent residence time and redox conditions.  
679 The groundwater is close to equilibrium with respect  
680 to chalcedony, which indicates water–rock reactions  
681 and, in particular, the dissolution of silicate minerals  
682 from host rocks by the dilute end-member. Ground-  
683 water at both sites is also close to equilibrium, or  
684 slightly undersaturated, with respect to carbonate  
685 minerals (calcite, rhodocrosite and siderite). At Masa  
686 Valverde, it is possible to distinguish a difference  
687 between SO<sub>4</sub>-free samples and SO<sub>4</sub>-bearing samples,  
688 namely between water containing a significant pro-  
689 portion of the dilute end-member and water appa-  
690 rently less affected by such dilution. In the former  
691 case, the water is close to equilibrium with calcite,  
692 whereas in the latter case it may be undersaturated  
693 with respect to the same phase, indicating that re-  
694 equilibration after acidification through sulphide-min-  
695 eral oxidation may not be complete. These calcula-  
696 tions, made at both sites, demonstrate the occurrence  
697 of water–rock reactions and thus at least a partial  
698 equilibrium of the groundwater with respect to a  
699 mineral assemblage.

700 As regards metal behaviour, the saturation state  
701 with respect to sulphide minerals is worth examining.  
702 At the La Zarza deposit, only the groundwater in  
703 borehole ZA2 contains detectable sulphide concentra-  
704 tions. Application of the EQ3NR geochemical code to  
705 this borehole indicates extensive oversaturation with  
706 respect to both pyrite (saturation index (S.I.)=9) and  
707 chalcopyrite (Fig. 13), and moderate oversaturation  
708 with respect to galena (Fig. 13). These oversaturations  
709 may have several single or combined explanations.  
710 For example, because during modelling of chemical  
711 speciation, EQ3NR considers the total concentration  
712 as being only the mobile fraction of elements, macro-  
713 molecules and colloids/small particles (for which the  
714 necessary thermodynamic data are not available) will  
715 contribute to an apparent oversaturation; this is in

accordance with the VIP results for Cu. Other explan- 716  
ations could be the oxidation of sulphide minerals, 717  
and a pH increase subsequent to reaction with carbo- 718  
nate minerals after oxidation of sulphide minerals. 719  
The water is shown to be slightly undersaturated with 720  
respect to sphalerite (Fig. 13), whereas in reality the 721  
undersaturation may be higher than calculated when 722  
one considers that the comparison between the VIP 723  
and ICP-MS results that indicate the presence of Zn as 724  
macromolecules or colloids, which are not taken into 725  
account by the EQ3NR code. This undersaturation can 726  
be explained by the dilution deduced from the Na–Cl 727  
graphs. 728

As noted above, despite the very low solubility of 729  
sulphide minerals and the absence of detectable sul- 730  
phide–mineral oxidation in some samples, metal con- 731  
centrations in the Masa Valverde groundwater show a 732  
same order-of-magnitude range as in the La Zarza 733  
groundwater and in groundwater away from both 734  
deposits. The groundwater saturation state with res- 735  
pect to sulphide minerals cannot be measured directly 736  
due to its lack of detectable H<sub>2</sub>S; however, a first 737  
approximation of H<sub>2</sub>S concentration can be made by 738  
assuming the groundwater to be in equilibrium with 739  
pyrite and examining this equilibrium with respect to 740  
other minerals. Results of calculations carried out 741  
using EQ3NR indicate H<sub>2</sub>S concentrations between 742  
0.3 and 7.0 µg l<sup>-1</sup>. These concentrations are in good 743  
agreement with the fact that H<sub>2</sub>S could not be deter- 744  
mined by titration with HgCl<sub>2</sub> (i.e., a detection thresh- 745  
old no better than 30 µg l<sup>-1</sup>). Therefore, the Masa 746  
Valverde groundwater must be either close to equili- 747  
brium or undersaturated with respect to pyrite, and 748  
equilibrium seems to be a reasonable hypothesis, at 749  
least for SO<sub>4</sub>-free waters. Assuming equilibrium, 750  
therefore, the estimated H<sub>2</sub>S concentration was used 751  
to calculate the equilibrium state with respect to other 752  
sulphide minerals. The results indicate equilibrium 753  
with respect to sphalerite, but oversaturation by sev- 754  
eral orders of magnitude with respect to chalcopyrite 755  
and, to a lesser degree, galena (Fig. 13). 756

Dissolved Pb and Cu concentrations, based on the 757  
assumption of equilibrium with respect to galena and 758  
chalcopyrite, were calculated and compared with the 759  
measured concentrations (Fig. 14). In SO<sub>4</sub>-free waters 760  
these measured concentrations were about 2–3 orders 761  
of magnitude above expected values for Pb, and up to 762  
9–10 orders of magnitude above expected values for 763

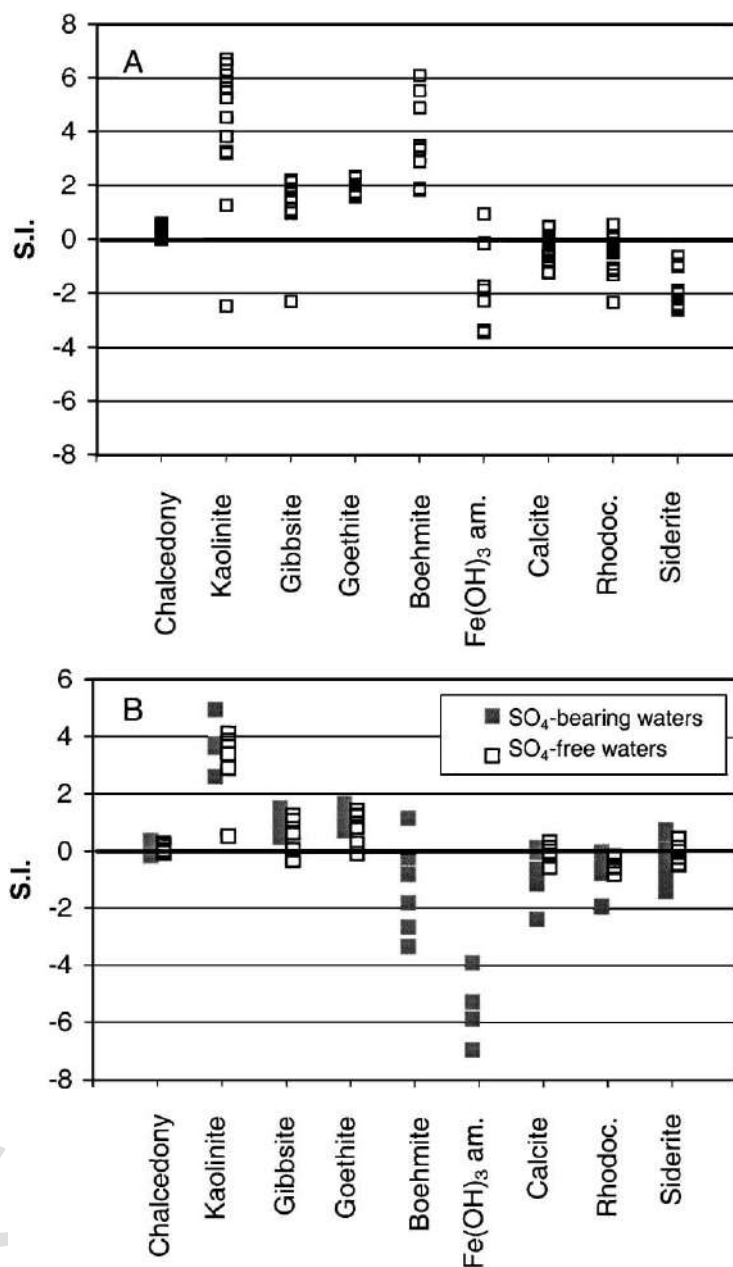


Fig. 12. Saturation index plot calculated using the EQ3NR code (Wolery, 1992) with respect to silicates, oxides, hydroxides and carbonate (calcite, rhodocrosite, siderite) minerals for groundwater at (A) the La Zarza deposit, and (B) the Masa Valverde deposit.

764 Cu. In SO<sub>4</sub>-bearing waters, the difference between the  
 765 expected and measured Cu concentrations was drasti-  
 766 cally reduced during modelling because EQ3NR  
 767 automatically converted part of the SO<sub>4</sub> into thiosul-  
 768 phates (S<sub>2</sub>O<sub>3</sub>) in accordance with the redox potential.

Although thiosulphates could (a) be present, because  
 they are a metastable species with increasing stability  
 in the presence of pyrite above pH=7 (Xu and  
 Schoonen, 1995), and (b) have been oxidized into  
 sulphates after sampling and before SO<sub>4</sub> determina-

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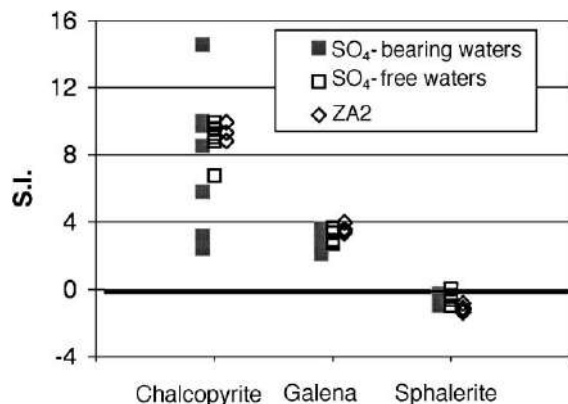


Fig. 13. Saturation index plot calculated using the EQ3NR code (Wolery, 1992) with base-metal sulphide minerals, for groundwater at the Masa Valverde deposit and borehole ZA2, assuming equilibrium with respect to pyrite.

774 tion, this factor was not investigated by the project.  
 775 Fig. 14 illustrates how their presence could effectively  
 776 enhance Cu solubility, but it does not prove their  
 777 presence. Moreover, colloidal and dissolved organic  
 778 matter derived from host-rock/water interaction is also  
 779 a very efficient sink for metals such as Cu, Pb and Zn  
 780 (Bruland, 1988; Apte et al., 1995; Benedetti et al.,  
 781 1996; Sauvé et al., 1998) as well as other forms of  
 782 colloids.

783 Clearly, metal speciation differs from one site to  
 784 the other. On the one hand, for the La Zarza ground-  
 785 water, comparison of the VIP and ICP-MS results,

along with the thermodynamic calculations for bore- 786  
 hole ZA2, indicates that Cu, Zn and Cd are present in 787  
 significant amounts as macromolecules or adsorbed 788  
 on colloids/small particles, and that Pb is dissolved. 789  
 On the other hand, for the Masa Valverde ground- 790  
 water, assuming the hypothesis of equilibrium at least 791  
 for SO<sub>4</sub>-free waters, it is Cu and Pb that occur as 792  
 macromolecules or colloids whereas Zn is assumed to 793  
 be dissolved. The very nature of the colloids/small 794  
 particles may explain this difference, because the 795  
 colloid/small-particle form able to adsorb metals 796  
 can be assumed by a variety of species. At both 797  
 deposits, Si and Mn colloidal species in groundwater 798  
 are probably not important because of equilibrium 799  
 with respect to chalcedony and rhodocrosite. How- 800  
 ever, the presence of Mn colloidal species in the 801  
 Masa Valverde groundwater cannot be totally ex- 802  
 cluded in view of the VIP results. Colloidal Al- 803  
 bearing species may occur in groundwater at both 804  
 sites, as suggested by the oversaturation with respect 805  
 to kaolinite, gibbsite and boehmite, which is more 806  
 marked at La Zarza than at Masa Valverde. The 807  
 occurrence of Fe-bearing species subsequent to sul- 808  
 phide oxidation at La Zarza, which is supported by 809  
 over-saturation with respect to goethite. 810

### 5.3. Implications for mineral exploration

811  
 812  
 Significant metal concentrations are observed in 813  
 the Masa Valverde groundwater, even where this is 814

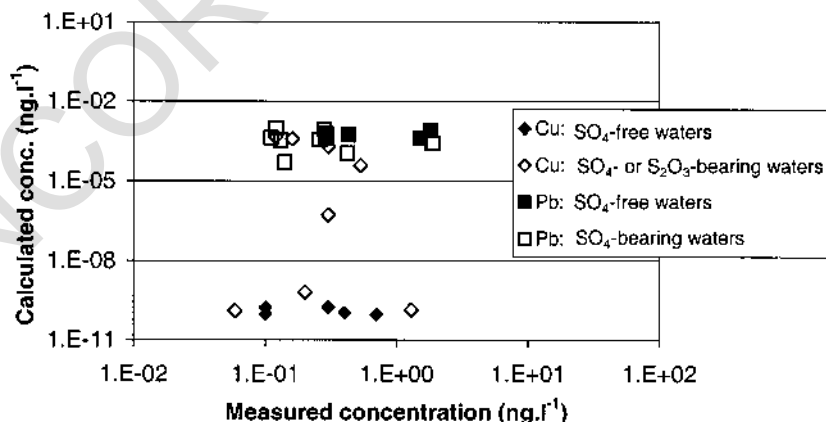


Fig. 14. Cu and Pb concentrations expected from equilibrium of the groundwater at the Masa Valverde deposit with respect to pyrite, chalcopyrite and galena, versus total metal concentrations measured by ICP-MS.

815 SO<sub>4</sub>-free water (i.e., where no significant oxidation is  
816 detected). If it is assumed that these concentrations  
817 result from the presence of the sulphide deposit at  
818 depths of more than 400 m, then they present two  
819 major implications for mineral exploration. Firstly,  
820 they widen the field of potential hydrogeochemical  
821 methods for 'deep orebody' exploration, at least on the  
822 local scale. Secondly, they better constrain the possible  
823 mechanisms for the formation of surface anomalies on  
824 which other geochemical methods of 'deep orebody'  
825 exploration are based. These geochemical methods  
826 include enzyme leach and MMI (mobile metal ion)  
827 selective digestion, with which successful recent case  
828 studies have been recorded (e.g., Clark et al., 1997;  
829 Bajc, 1998), as well as the promising use of new  
830 devices to trap metals transferred to the surface from  
831 buried ore deposits (Malmqvist and Kristiansson,  
832 1982; Wang et al., 1997; Pauwels et al., 1999).  
833 Although the dispersion models giving the observed  
834 patterns of geochemical response at the surface are not  
835 well understood, it is considered that groundwater  
836 composition, and particularly groundwater–rock inter-  
837 actions creating chemical-composition anomalies, are  
838 partly responsible for the formation of the surface  
839 geochemical anomalies.

840  
841 *5.4. Implications for the application of exploration*  
842 *hydrochemistry in areas with previous mining con-*  
843 *tamination*

844 The determination of proximity criteria is essen-  
845 tial for the successful use of groundwater chemistry  
846 as an exploration tool. However, as mentioned ear-  
847 lier, the range of total metal concentrations in  
848 groundwater is similar at La Zarza and Masa Valve-  
849 rde, as well as away from the deposits. It is thus  
850 impossible, either from the total metal concentration  
851 or from the concentration of any particular metal, to  
852 discriminate between SO<sub>4</sub>-bearing groundwater types  
853 (e.g., groundwater in contact with an undisturbed ore  
854 deposit, groundwater in contact with a partly exploi-  
855 ted deposit, or groundwater baseline concentration  
856 that results from previous mining activity upstream),  
857 sulphate concentrations of all of them mainly attest-  
858 ing to sulphide mineral oxidation.

859 We have also seen that groundwater metal contents  
860 are in part controlled by the formation of complexes  
861 and/or by adsorption onto colloids/small particles. The

surface complexation model (e.g., Stumm, 1982; 862  
Dzombak and Morel, 1987) allows adsorption to be 863  
taken into account as a classic complexation reaction, 864  
and so adsorption as well as complexation is a 865  
reaction with a protonable ligand, implying a depend- 866  
ence on the pH, which must be therefore considered as 867  
one of the variables. Data presented in several (metal/ 868  
(H<sup>+</sup>)<sup>2</sup>, metal/(H<sup>+</sup>)<sup>2</sup>) diagrams (Fig. 15) show that it is 869  
possible to distinguish SO<sub>4</sub>-bearing groundwater sam- 870  
ples collected in the vicinities of the two deposits from 871  
SO<sub>4</sub>-bearing groundwater samples collected away 872  
from the two deposits. The more significant plots 873  
are (Cu/(H<sup>+</sup>)<sup>2</sup>, Pb/(H<sup>+</sup>)<sup>2</sup>), (Cu/(H<sup>+</sup>)<sup>2</sup>, Cd/(H<sup>+</sup>)<sup>2</sup>), 874  
and (Ni/(H<sup>+</sup>)<sup>2</sup>, Mn/(H<sup>+</sup>)<sup>2</sup>) in Fig. 15, which show 875  
that, at a given pH, groundwater proximity to the ore 876  
deposits is clearly indicated by higher Cd and Pb 877  
concentrations relative to Cu, and higher Mn relative 878  
to Ni. This means that in areas where the baseline 879  
quality of groundwater reflects past mining activities, 880  
the chemical composition of the groundwater can 881  
provide relevant information for ore deposit explora- 882  
tion, provided a sufficiently complete database is 883  
available. 884

885  
886 *5.5. Implication for studies of environmental pre-*  
887 *mining conditions*

888 Total metal concentration, rate of transport, overall 889  
mobility in water, and metal bioavailability all depend 890  
on metal speciation (e.g., Buffle and de Vitre, 1994; 891  
Tessier and Turner, 1995), which is thus a factor 892  
requiring increasing attention. Nevertheless, the pre- 893  
sent results, particularly those of the SO<sub>4</sub>-free ground- 894  
water at Masa Valverde, illustrate that total metal 895  
concentration is drastically more important than mo- 896  
bile metal species. Even though the studied metal 897  
concentrations do not exceed drinking-water stand- 898  
ards, they are far from negligible, even where there 899  
has been no significant oxidation. A natural baseline- 900  
quality study before the commencement of mining 901  
operations appears, therefore, to be of prime impor- 902  
tance in order to determine realistic achievable targets 903  
for remediation.

904 This then poses the problem of suitable methods for 905  
estimating natural total-metal background concentra- 906  
tions in water at abandoned mine sites. A priori, the 907  
natural metal concentrations can be estimated through 908  
examination of historical records, comparison with

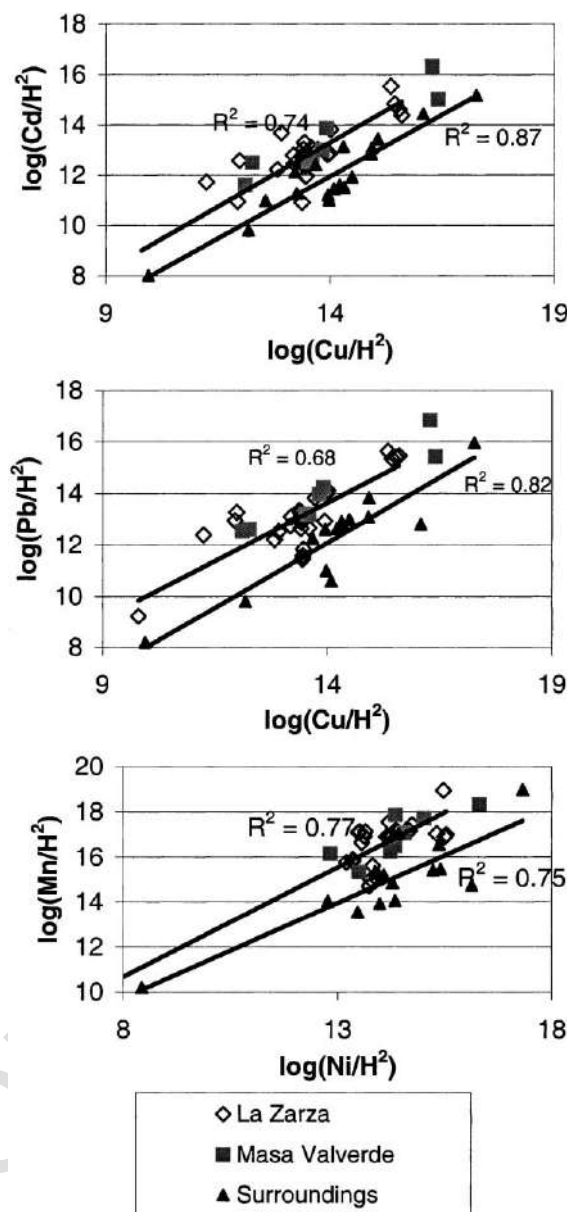


Fig. 15. ( $\log(\text{metal}/\text{H}^2)$ ,  $\log(\text{metal}/\text{H}^2)$ ) plots illustrating differences in the metal behaviour of groundwater in the immediate vicinity of the deposits with respect to the baseline quality of the area.

909 non-mined areas and/or using predictive geochemical  
 910 modelling (Runnells et al., 1992). Predictive geochem-  
 911 ical modelling for surface water in the case of acid  
 912 drainage probably indicates an upper limit for total  
 913 metal contents, at least where the reaction kinetics are  
 914 not taken into account (Runnells et al., 1992). Con-

versely, assuming equilibrium conditions, the ground-  
 water results described above illustrate how predictive  
 geochemical modelling will indicate a lower limit for  
 total metal concentrations because the formation of  
 colloids and adsorption on small particles is not taken  
 into account by the geochemical codes.

915  
 916  
 917  
 918  
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 920

921 **6. Conclusions**

922 The differing major-element chemistry of the  
 923 groundwater at the La Zarza and Masa Valverde  
 924 massive sulphide deposits is due mainly to the differ-  
 925 ent hydrogeological situations and to previous mining  
 926 activity at one site. The La Zarza deposit is located in  
 927 an area of hydrological recharge, has been partly  
 928 exploited, and its groundwater has a lower pH and  
 929 higher Eh and SO<sub>4</sub> than the groundwater at the Masa  
 930 Valverde deposit which, deeply buried, is located in  
 931 an area of water discharge and is unworked. The  
 932 respective pathway of each groundwater type is indi-  
 933 cated by its Na/Cl ratio, with an increase in Na  
 934 concentration during deep circulation.

935 Despite these differences, the metals and trace-  
 936 element chemistry of the groundwater at the two de-  
 937 posits is, with a few exceptions, similar. Moreover, it  
 938 does not differ drastically from the baseline quality of  
 939 groundwater in this area of intense past mining  
 940 activity. Total metal concentrations in the groundwater  
 941 at both deposits are enhanced by the formation of  
 942 complexes and/or by metal adsorption on colloids or  
 943 small particles. This has been demonstrated by com-  
 944 paring ICP-MS data with data obtained using (i) a  
 945 special analytical technique—the Voltammetric In situ  
 946 Profiling (VIP) System, and (ii) calculation with the  
 947 EQ3NR geochemical code. At the deep and undis-  
 948 turbed Masa Valverde deposit where redox conditions  
 949 are very low, the total metal concentrations in the  
 950 groundwater are several orders of magnitude (up to  
 951 10<sup>8</sup>–10<sup>9</sup> for Cu) higher than would be expected from  
 952 the very low solubility of sulphide minerals. The  
 953 results have implications as regards both mineral  
 954 exploration and the environment.

955 Where mineral exploration is concerned, the total  
 956 metal concentrations appear to be significantly en-  
 957 hanced in groundwater, even when the sulphides are  
 958 unoxidized. This fact increases the potential of  
 959 groundwater chemical composition as an ore-deposit  
 960 exploration technique.

961 Where the environment is concerned, knowledge of  
 962 the natural concentrations of metals in the groundwater  
 963 prior to mining operations is of particular importance  
 964 for preparing realistic and technically achievable reme-  
 965 diation plans. For new ventures, the relevant data can  
 966 be acquired through baseline quality monitoring before  
 967 exploitation. For sites already contaminated by exploi-

tation, it should be borne in mind that predictive  
 geochemical modelling can underestimate the metal  
 concentrations because the geochemical codes lack  
 data concerning metal adsorption on colloids or small  
 particles.

7. **Uncited reference**

Pinedo Vara, 1963

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