# HYDROGEOCHEMICAL MODELING: APPARENT CONTROLS ON SOLUTION TRANSPORT FOR Zn, Pb AND Cu IN THE SUPERGENE ZONE OF TOLFA MOUNTAINS VOLCANIC DISTRICT (LATIUM, CENTRAL ITALY)

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RIASSUNTO. — Sono stati studiati quattordici campioni di acque del distretto vulcanico tolfetano nel Lazio, alcuni dei quali sono stati raccolti da drenaggi acidi di miniera, altri da sorgenti, altri che hanno attraversato rocce trachitiche alterate e non e altri infine che hanno percorso sedimenti flyschoidi.

I costituenti fondamentali sono stati analizzati con metodi di routine, mentre Zn, Pb e Cu sono determinati mediante voltammetria.

Le concentrazioni trovate per i metalli base sono alte rispetto a quelle di acque naturali non contaminate, ma molto basse rispetto a quelle tipiche di acque provenienti da aree mineralizzate.

Dall'esame dei dati analitici le acque, indipendentemente dalla loro origine, mostrano due stadi simili di evoluzione. Il primo è dato dalla neutralizzazione, per interazione con rocce incassanti, dell'acidità solforica originata dall'alterazione supergenica di solfuri. Come conseguenza si ha un forte aumento di pH non necessariamente coerente con il contenuto in solidi solubili, in quanto composti poco solubili possono precipitare. Durante il secondo stadio si ha un mescolamento con acque provenienti da rocce incassanti fresche e non mineralizzate; in seguito a ciò il contenuto in solfati diminuisce e il pH è controllato da un sistema tampone dovuto agli equilibri tra l'anidride carbonica disciolta e i bicarbonati e, in secondo luogo, i carbonati solubili.

Inoltre, il modello idrogeochimico, proposto con il metodo della speciazione ed il calcolo delle attività, ha dato alcuni risultati interessanti. Fra i tre elementi considerati solo il rame sembra essere condizionato, per quanto riguarda la solubilità, dalla precipitazione di composti insolubili come azzurrite e malachite. Le acque, caratterizzate da pH < 4,5, comprese quelle arricchite in solfati, sono sempre lontane dalla saturazione rispetto ai composti limitanti la solubilità di zinco, piombo e rame, evidenziando una scarsa assunzione, nel loro percorso, di metalli base.

In ogni caso, viene evidenziato il ruolo svolto dal chimismo dell'acqua nella discussione dell'andamento notato, che può esssere molto frequente solo in relazione alla limitata formazione di composti con metalli base da parte di acque con alte velocità di percolamento attraverso zone contenenti solfuri in via di ossidazione.

ABSTRACT. — Fourteen water samples from acid mine drainages, streams and, altered and unaltered trachytes and flysch sediments, coming from Tolfa Mountains volcanic district have been studied. Fundamental constituents were analyzed by routine procedures, while Zn, Pb and Cu determinations were carried out by voltammetric techniques.

The concentration levels exhibited by base-metals are higher relative to natural unpolluted waters and by far lower in comparison to the typical contents reported for waters from mineralized areas.

From the analytical data it is apparent that the waters, independently from their origin, display a similar two-steps evolution trend. The first stage involves the neutralization, by interaction with country rocks, of the sulfuric acidity originated by supergene alteration of sulphide minerals. The most impressive consequence is a dramatic pH-increasing not necessarily sympathetic with dissolved solid contents, as sparingly soluble compounds may be

lost. During the second stage mixing with waters from unaltered, unmineralized country rocks occurs; then the sulphate concentration decreases and pH is controlled as well as buffered by equilibria among carbon dioxide dissolved species viz. bicarbonate and subordinately carbonate.

Moreover, hydrogeochemical modeling performed by speciation and activity calculations yields some interesting results. Among the three elements considered only copper appears to be limited in its solubility by precipitation of insoluble compounds, i.e. malachite and azurite. Waters characterized by pHs < 4.5, also those sulphate-enriched, are always by far undersaturated with respect to the most effective solubility-limiting compounds of Zn, Pb and Cu, thus indicating meagre base-metal uptakes.

However, in discussion such features which have been too often only accounted for by scant occurrences of base-metals coupled with high seeping rate of the waters through the oxidation zone of sulphide mineralizations, the role played by water chemism is emphasized.

## Introduction

Hydrogeochemical methods, considered as a whole, represent one among the most used tools in ore bodies prospecting. However, although such methods continue to improve their reliability owing to the impressive data base made available by geochemical researches, misinterpretations are by far to be ruled out. As a result it is not rare that the analytical data gathered throughout hard work lead to biased evaluations, e.g. between base-metal mineralizations and barren pyrite ore bodies.

Up to now the strategy adopted by prospectors to decrease the failures consists both in determining many trace-elements instead of a few, and in data treatment by means of sophisticated statistics. There is general agreement among geochemists, however, that the constraints for hydrogeochemical prospecting stem from the lack of knowledge for those processes which control the transport and the attenuation of base-metals during their mobilization from the source.

Elements hydrogeochemistry, particularly for trace-elements, is really by far complicated than that we can represent by means of a schematic and theoretical model, since many variables are not adequately known. Apart from the rate of waters mixing and circulation, absorption onto organic and mineral solids (both stationary and suspended), kinetics of metal speciation reactions, environmental redox conditions and formation of high-stability complexes with organic matter play a role as neglected as important in governing the metal concentrations in natural waters.

The AA. are well aware that geochemical modeling of waters is not a cure-all. However, despite its limitations it represents an obligatory step to attain a satisfactory understanding of the behavior of heavy-metals in natural solutions, in order to improve their hydrogeochemical prospecting meaning.

The study area has been chosen owing to the extensive literature which deals with its more striking features. Besides that, as mine workings were abandoned a long ago, the hydrogeochemistry of the area should be only governed by natural equilibria, that is without interferences caused by on-site milling of minerals and leaching of waters throughout recent dumps.

## Geologic setting of study area

Tolfa Mountains volcanic district (fig. 1) is located about 70 km north of Rome. Its main feature is represented by an extensive acid volcanism which, according to K/Ar age measurements carried out on the different volcanites outcropping may be referred to the Upper Pliocene (LOMBARDI et al., 1974). Volcanics, that according to the local geological situation may overlay either the flysch formation of Cretaceous-Palaeogene age or Early-Pliocene clastic terranes, range from quartz-latites to rhyolites.

Following volcanite emplacements, hydrothermal fluids upwelling through fault pattern metasomatized both the Sycilide flysch formation and volcanics. As regards the former terranes, hydrothermal alteration produced a heavy loss of carbonate component, while volcanic rocks were severely kaolinitized, alunitized and silicified. Mineralizing processes generated abundant deposits of phanerocrystalline calcite, while sulphide-minerals were mainly disseminated in hydrothermal calcite as well as altered flysch, only locally being concentrated in veins.
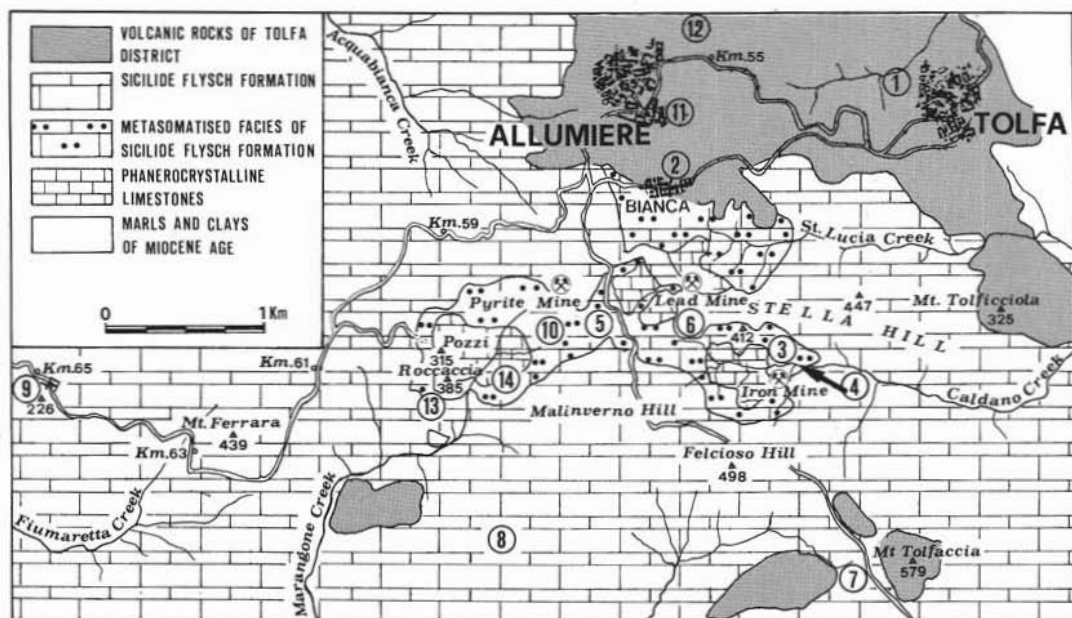
Fig. 1. — Geologic sketch map of the study area showing the position of the sampling sites.

The most important sulphide-minerals occurring are pyrite, galena, sphalerite and chalcopyrite; subordinate occurrences of other minerals, however, are also reported.

The complex of mine workings at Tolfa commenced in the last century and have been completely abandoned in 1950s, since they were uneconomical.

More detailed information on geo-chronology, geochemistry and mineral deposits of the study area are reported by NEGRETTI et al. (1966), FAZZINI et al. (1972), FERRINI (1975) and BARBIERI et al. (1978).

## Experimental

### Sampling and « in situ » measurements

All samples were stored in polyethylene bottles previously soakes with 6N HCl. Water samples were collected taking care that bottom sediments were not disturbed; surface waters were sampled, where possible, in the middle of homogeneous streams.

The aliquot of each sample to be analysed for metals was acidified to 0.1 % (v/v) with HCl, in order to prevent metal absorptions onto the walls of the bottle and avoid precipitations normally occurring due to Eh change and/or loss of volatile components.

pH, temperature and conductivity were measured in the field.

### Chemical analyses

Water samples were filtered through 0.45 μm Millipore filters before being analysed. Na and K concentrations were determined by flame spectrophotometry, working with Li as internal standard. Sulphate, chloride and bicarbonate contents were measured following the procedures after GREENBERG et al. (1975), by turbidi-metric, potentiometric and titrimetric techni-ques, respectively. Ca, Mg, Fe and Mn determinations were run with a Perkin-Elmer atomic absorption spectrophotometer, following the manufacturer's handbook. Zn, Pb and Cu contents were measured polaro-graphically, by the differential pulse anodic stripping voltammetry technique. In par-ticular the method for Zn determination was after BLUTSTEIN and BOND (1976) and that for Pb and Cu after CALDERONI (1981).

As the most important source of errors in geochemical modeling of natural waters stems from the inadequate quality of data base, analytical results were checked by running

TABLE 1

*Physicochemical data for the analysed waters*

| Sample | pH | Specific conduct. ($\mu$mho·cm$^{-1}$) | Na | K | Ca | Mg | Fe | Mn | Zn | Pb | Cu | HCO$_3$ | Cl | SO$_4$ | I $\times 10^{-4}$ |
|--------|-----|------|------|------|-------|------|--------|------|-------|------|------|------|------|-------|-----|
| **STREAMS :** | | | | | | | | | | | | | | | |
| T 3 | 7.3 | 590.1 | 16.6 | 0.9 | 96.3 | 31.1 | 0.20 | 150 | 25.0 | 2.0 | 10.0 | 5.39 | 0.67 | 1.94 | 127 |
| T 4 | 7.3 | 660.0 | 15.5 | 2.7 | 93.4 | 30.1 | 0.44 | 80 | 32.3 | 1.8 | 8.0 | 4.00 | 0.69 | 3.09 | 129 |
| T 14 | 7.8 | 671.5 | 17.0 | 3.4 | 83.4 | 14.6 | 0.04 | 20 | 13.6 | 1.0 | 5.0 | 3.50 | 0.76 | 2.19 | 101 |
| **GROUNDWATERS FROM TRACHITES :** | | | | | | | | | | | | | | | |
| T 1 | 4.3 | 120.0 | 12.9 | 3.2 | 4.3 | 10.4 | 0.86 | 10 | 35 | 2.1 | 25 | - | 0.71 | 1.00 | 27 |
| T 2 | 4.1 | 155.5 | 17.7 | 2.9 | 1.8 | 10.3 | 0.02 | 30 | 29 | 2.0 | 17 | - | 0.93 | 1.04 | 29 |
| T 11 | 4.2 | 138.2 | 14.4 | 4.4 | 8.8 | 10.9 | 1.10 | 15 | 32 | 3.8 | 31 | - | 0.90 | 1.25 | 30 |
| T 7 | 7.0 | 427.0 | 31.1 | 37.5 | 23.2 | 22.8 | 0.05 | 9 | 11.0 | 1.5 | 7.0 | 2.39 | 1.66 | 1.11 | 73 |
| **GROUNDWATERS FROM FLYSCH SEDIMENTS :** | | | | | | | | | | | | | | | |
| T 8 | 7.1 | 720.5 | 17.3 | 1.3 | 80.7 | 19.7 | 0.04 | 21 | 15 | 0.9 | 3.0 | 3.90 | 1.28 | 1.15 | 98 |
| T 9 | 6.6 | 760.0 | 26.4 | 0.8 | 131.8 | 23.2 | 0.05 | 15 | 24 | 1.0 | 6.1 | 6.81 | 1.71 | 1.21 | 145 |
| T 10 | 7.5 | 560.5 | 16.3 | 1.1 | 75.7 | 24.4 | 0.03 | 10 | 16 | 1.5 | 12.5 | 3.94 | 0.81 | 2.04 | 105 |
| T 13 | 6.6 | 990.0 | 20.2 | 2.0 | 126.6 | 47.1 | 5.00 | 860 | 46 | 2.0 | 10.3 | 6.19 | 1.42 | 3.76 | 182 |
| **MINE DRAINAGES :** | | | | | | | | | | | | | | | |
| T 5 | 6.2 | 1130 | 18.7 | 1.6 | 224.6 | 15.5 | 5.3 | 690 | 225.0 | 7.1 | 130 | 4.88 | 0.95 | 7.92 | 241 |
| T 6 | 2.7 | 1530 | 15.4 | 2.6 | 205.1 | 73.0 | 108.0 | 3300 | 24.0 | 9.1 | 503 | - | 0.50 | 22.36 | 433 |
| T 12 | 2.8 | 960.4 | 16.8 | 2.4 | 54.1 | 16.5 | 84.5 | 40 | 232.1 | 15.0 | 34.3 | - | 1.04 | 8.10 | 160 |

Concentrations are given as follows: HCO$_3$, Cl and SO$_4$ as meq l$^{-1}$; Fe and fundamental cations as mg l$^{-1}$ (ppm); Mn, Zn, Pb and Cu as $\mu$g l$^{-1}$ (ppb).

various independent measurements, particularly for trace-elements. Such a cautious procedure is imperative, as « wild » results for trace-elements are hardly noticed while, on the contrary, significative errors relative to the fundamental constituents are easily detected by a large cation-anion imbalance.

## Results and discussion

Locations of the sampling sites are indicated in fig. 1. Table 1 lists the results of the physicochemical measurements carried out for the sampled waters; calculated ionic strengths (I) are also reported. At first glance analytical data point out notable differences among the water chemisms; such a picture, however, is mainly due to the wide range exhibited by pH, sulphates and alkaline-earth metals. On the contrary it is apparent that alkali metals and chloride contents are by far less scattered. Samples T-1, T-2, T-6, T-11 and T-12 appear to be HCO$_3^-$-depleted, since very acid natural waters contain only traces of both dissociated and undissociated carbon dioxide species. Consequently their

high H$_3$O$^+$ activity should depend on processes other than carbonate and bicarbonate dissociation equilibria, these latter representing the most common source of acidity. The most important sulphide minerals occurring in the study area, i.e. iron sulphides, galena and sphalerite, are all oxidingeable by chemical interaction with aerated waters; such a process, however, by introducing important amounts of H$_3$O$^+$ to the hydrosphere, can determine and keep acid pHs.

Main chemism features are emphasized in fig. 2, which shows the concentration of fundamental cations and anions, expressed as percent of the total dissolved solids, plotted in Piper's trilinear diagram. From the graph it is apparent that in respect of cations (left triangle) the waters are differentiated into two groups, one including samples from streams, mine workings drainages and flysch sediments, and the other containing water samples from trachytes. Otherwise, anions triangle points out three groups of waters, i.e. from trachytes, flysch sediments and streams, and mine drainages. This latter feature is kept after plotting the repre-
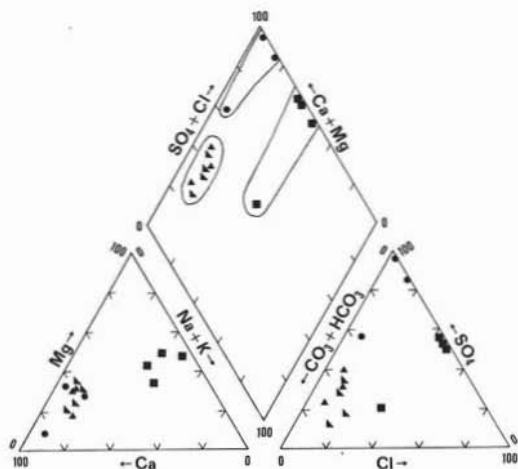
Fig. 2. — Fundamental constituents of the analysed waters plotted in Piper's trilinear diagram. Symbols as follow: ● = water from mine drainages; ■ = groundwater from trachytes; ▲ = surface waters; ▲ = groundwater from flysch sediments. Three groups of waters are evidenciated in the diamond-shaped field of the graph.

sentative points of the waters from the lower triangles in the diamond-shaped field. From fig. 2 it is also apparent that samples T-5 and T-7 (belonging to the group of waters from mine drainages and trachytes, respectively) display a peculiar chemism, their representative points being shifted downward relative to the remaining samples of the two groups. Such a feature is mainly a consequence of the pH of the two water samples, which in both cases is by far higher relative to the typical pHs for the two groups. As regards sample T-7, the pH exhibited (7.0) may be regarded as that due only to the dissolved carbon dioxide species, as the water which circulates in unaltered, unmineralized trachyte, is neither $SO_4^{2-}$-nor $Ca^{2+}$-enriched. On the contrary sample T-5 in spite of its pH (6.2) exhibits high sulphate and calcium contents, this likely meaning that the acidity of the water in the sampling site was already almost totally neutralized by interaction with country rocks carbonate-bearing. Piper's plot also shows that the waters from flysch sediments and streams are quite indistinguishable on the basis of major chemical constituents. Likely this is because water inputs to streams from the oxidation zone of ore bodies are not so

important to affect significantly the chemism of surface waters, the latter being mostly originated by groundwater from unmineralized flysch sediments aquifers.

Fig. 3 shows the relationship between pH and sulphate content for the sampled waters; according to NAUMOV et al. (1972) these two variables are very effective to elucidate the chemical evolution of waters from mineralized areas. The dashed curves a and b drawn in the graph indicate the overall evolution trend for the water from sulphide-bearing trachytes and acid mine drainages, respectively. For both groups of waters the first and most striking change involves pH, this being increased of various units essentially owing to interaction with country rocks and, by far subordinately, dilution with surface waters. In this stage dilution does not play an important role, as the scarce decreasing in sulphate contents demonstrates. During the following evolution stage sulphate-rich, mild-acid waters are essentially diluted and $SO_4^{2-}$ concentration levels approach the background value for the area, i.e. about 1 meq $l^{-1}$. This latter stage is not so evident for the waters from sulphide-bearing trachytes, since their primitive sulphate content is quite comparable to that of surface waters. It is noteworthy that such a low sulphate content means that waters from trachytes received only scant $H_3O^+$ by sulphide oxidation processes and the true cause of
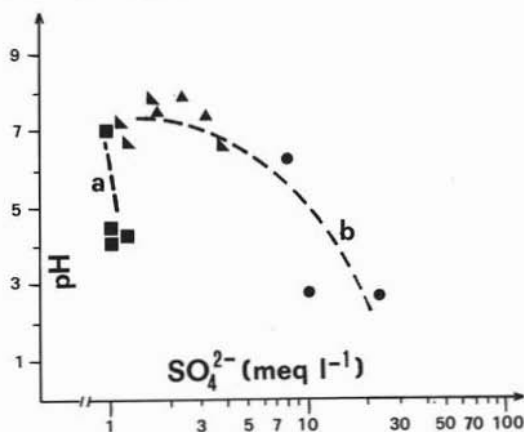


Fig. 3. — Relationship between pH and sulphate content for the examined waters. Dashed curves a and b indicate the evolution trend for the water from trachytes and mine drainages, respectively. Symbols as in fig. 2.

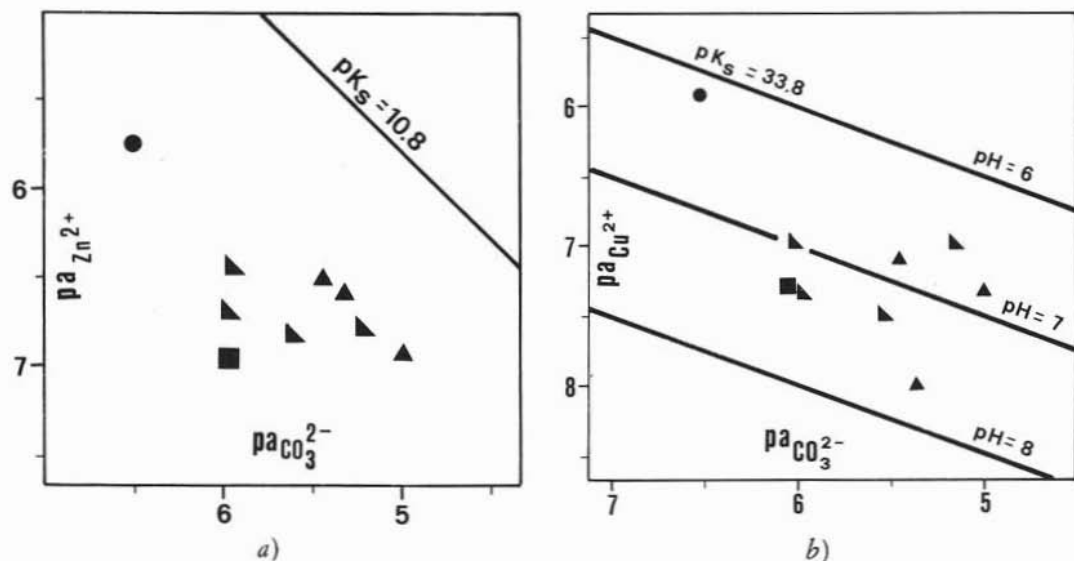Fig. 4 *a, b, c, d, e, f.* — Saturation status for the sampled waters in respect of ionic activity products of $ZnCO_3$ (*a*), $Cu_2(OH)_2CO_3$ (*b*), $Cu_3(OH)_4(CO_3)_2$ (*c*), $CuCO_3$ (*d*), $PbCO_3$ (*e*) and $PbSO_4$ (*f*). Three iso-pH saturation curves were drawn for those solids whose formation is directly pH-dependent; selected $pK_s$ value is reported along each saturation curve.

their significant acid pHs ($\overline{pH} = 4.2$) just depends on their low ionic strengths ($I = 28.6 \cdot 10^{-4}$) which allow the protons to display an activity coefficient close to the unity. From this point of view the chemical evolution of the waters from trachytes could be accounted for by simple mixing with higher pH- and I-inflows, as this mechanism can increase pH by both dilution and decreasing the activity coefficient of $H_3O^+$. Finally, at the end of the second stage the waters do not display any important differences; pH is controlled and buffered to some extent by equilibria among dissolved carbon dioxide species and the chemical composition gives the background values for the area.

The above discussion applays to the major dissolved constituents of the waters; in fact the mechanisms which control the transport and the change in concentration of trace-metals are a different matter. Let's note that the concentration levels found at Tolfa for all base-metals but Pb (table 1) are by far lower than those reported by WEDEPOHL (1974) for waters from various mineralized areas. Lead abundances, although often comparable, are meaningless for our purposes owing to the short-range mobility of this element, its solubility being markadly affected by sparingly soluble solids which normally lower equilibrium activity of $Pb^{2+}$ well below 2 $\mu gl^{-1}$ (HEM, 1970). On the other hand waters from Tolfa display base-metal contents significantly higher than those relative to uncontaminated continental waters from unmineralized areas (WEDEPOHL, 1974).

Such features, which indicate just a meagre base-metals uptake, can be determined by different causes, e.g. high seeping rate of the water through the oxidation zone and scant occurrence of sulphides other than those of iron in the mineralized bodies. Moreover, detailed investigations after GIBLIN (1978) demonstrated that if water seeps down through the « subsurface zone » of the ore body (characterized by absence of both oxygen and carbon dioxide) the base-metals previously mobilized from supergene zone may be lost to a severe extent.
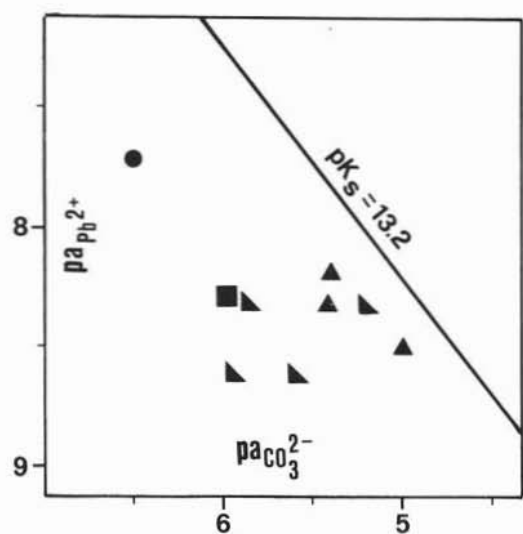
There are many evidences, however, that mobilization of base-metals is not only dependent on the above reported mechanisms; in fact, although often understimated, the chemism of the water play a major role. This arises because according to the abundance of the fundamental anions ($Cl^-$, $SO_4^{2-}$, $HCO_3^-$, $CO_3^{2-}$ and $OH^-$) different
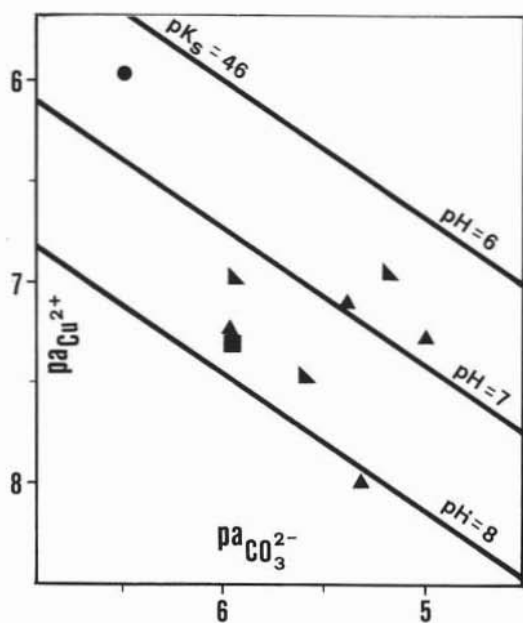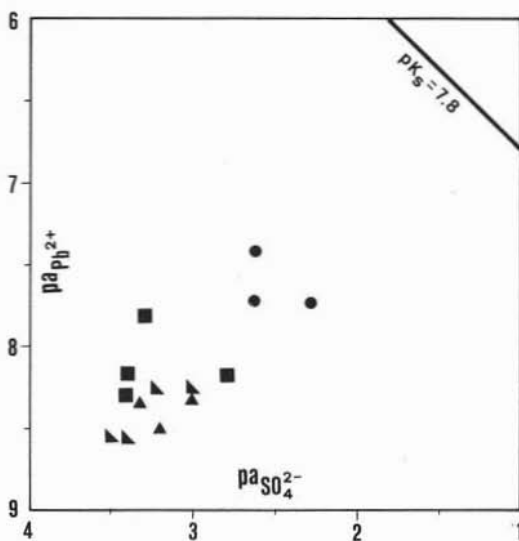
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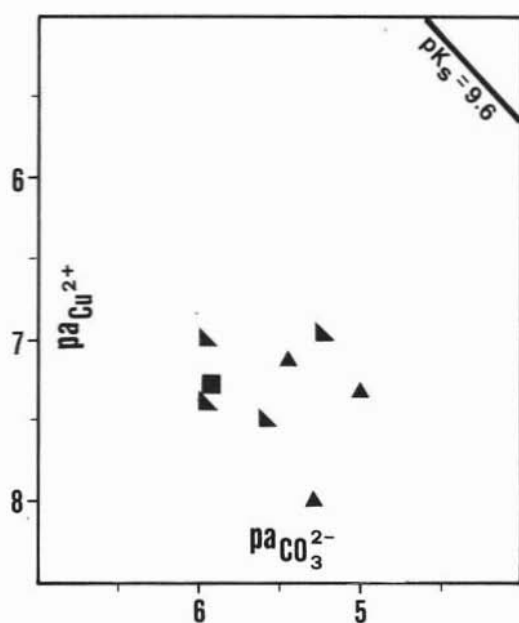


d)



e)



f)

amounts of both insoluble compounds and aqueous complexes with metals are formed. At present a considerable data base dealing with solubility products and stability constants is available so that it is possible to implement a speciation scheme for Zn, Pb and Cu to shed some light on the chemical species responsible for their solution transport. In addition this is also a viable method to determine the percentage of unbound metals, which represents the only fraction really available for equilibria with solubility-limiting compounds.

The speciation calculations herein adopted have been previously reported (CALDERONI et al., 1984); they rely on the assumption that the activity of trace-metals compared with that of the ligands is by far subordinate,

## TABLE 2
### Calculated distribution pattern for Zn, Pb and Cu chemical species

| Sample | FREE ION | | | BOUND METAL | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Zn | Pb | Cu | Zn | | | | Pb | | | | Cu | | | |
| | | | | Cl | $SO_4$ | $CO_3$ | OH | Cl | $SO_4$ | $CO_3$ | OH | Cl | $SO_4$ | $CO_3$ | OH |
| T 3 | 80 | 1 | 4 | – | 6 | 14 | – | – | – | 90 | 9 | – | – | 71 | 25 |
| T 4 | 79 | 1 | 5 | – | 10 | 11 | – | – | – | 88 | 11 | – | 1 | 66 | 28 |
| T 14 | 69 | – | 1 | – | 7 | 24 | – | – | – | 87 | 13 | – | – | 38 | 61 |
| T 1 | 93 | 86 | 93 | – | 7 | – | – | 2 | 11 | – | 1 | – | 7 | – | – |
| T 2 | 93 | 85 | 93 | – | 7 | – | – | 2 | 12 | – | 1 | – | 7 | – | – |
| T 7 | 78 | 3 | 13 | – | 5 | 3 | 14 | – | – | 82 | 15 | – | 1 | 63 | 23 |
| T 11 | 92 | 83 | 92 | – | 8 | – | – | 2 | 14 | – | 1 | – | 8 | – | – |
| T 8 | 75 | 2 | 8 | – | 4 | 7 | 14 | – | – | 88 | 10 | – | – | 72 | 20 |
| T 9 | 87 | 4 | 17 | – | 4 | 4 | 5 | – | – | 89 | 7 | – | 1 | 73 | 9 |
| T 10 | 55 | 1 | 2 | – | 5 | 12 | 28 | – | – | 88 | 11 | – | – | 60 | 38 |
| T 13 | 82 | 4 | 18 | – | 10 | 3 | 5 | – | 1 | 88 | 7 | – | 2 | 75 | 5 |
| T 5 | 77 | 12 | 41 | – | 22 | 1 | – | – | 15 | 65 | 8 | – | 12 | 41 | 6 |
| T 6 | 58 | 33 | 62 | – | 42 | – | – | – | 67 | – | – | – | 38 | – | – |
| T 12 | 78 | 59 | 78 | – | 22 | – | – | 2 | 39 | – | – | – | 22 | – | – |

Besides free ions, results give the sum of the considered complexes for each individual ligand. All the data are reported as %; dashes indicate complex percentages less than 1 %.

so that the competion among the oligo-elements in giving complexes can be neglected. In particular Zn-, Pb- and Cu-complexes with the ligands $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$ and $OH^-$ were considered, whereas those involving $HCO_3^-$ were neglected as this latter ligand does not complex to any extent the three metals (BILINSKI et al., 1976). According to the ionic strength displayed by water samples, two extended Debye - Huckel equations were employed to calculate activity coefficient ($\gamma$) for the single ions; neutral complexes were assigned the $\gamma$-values experimentally determined by REARDON and LANGMUIR (1976) and finally, $\gamma$-values for ion-pairs $+1$ and $+2$ charged were assumed to match those calculated in the corresponding waters for $HCO_3^-$ and $CO_3^{2-}$, respectively (LONG and ANGINO, 1977). As usual when the metals display low concentrations, poly-nuclear complexes were not considered; owing to its unimportance third order association was considered in a few cases, just for chloro- and hydroxo-complexes. All the thermodynamic data used to carry out the calculations were selected from the com-prehensive lists after SILLEN and MARTELL (1964, 1971).

Table 2 shows the results of the speciation calculations for Zn, Pb and Cu expressed as percentage of the total metal that is free ($Me^{2+}$) and bound by the four ligands considered; abundancens below 1 % were omitted. Individual complexes were not listed as a more detailed resolution in the speciation scheme is worthless for practical purposes. At first glance it is apparent that chemical species distribution patterns displayed by the three elements are quite different and, furthermore, for the same element the chemical species responsible for solution transport change according to the chemism of each group of waters. Relative to both Pb and Cu, Zn is the element whose speciation pattern is least affected by water chemism, $Zn^{2+}$, which is the most abundant Zn-species, being roughly constant in almost all the waters. $Cl^-$ does not contribute to Zn mobilization, likely owing to the com-bined effects of its low activity and weak association constants relative to Zn chloro-complexes. $ZnSO_4$ ion-pair is well-known to

play a major role in determining Zn mobilization; at Tolfa, however, although such a feature is significantly exhibited by $SO_4^{2-}$-enriched samples, viz. T-5, T-6, T-12 and T-13, it does not become ever predominant. Zn complexation by $CO_3^{2-}$ and $OH^-$ gains importance, to a different extent, sympathetically with pH raising, likely owing to the increased activity of those two ligands.

Pb behavior appears to be more complicated. A constant feature is that the abundance of $Pb^{2+}$ (free ion) is strictly pH-dependent: as shown by water samples from trachytes and mine drainages, when pH increases $Pb^{2+}$ activity is notably reduced. In addition high $SO_4^{2-}$ activities are needed to form $PbSO_4$ ion-pair, whose activity, in turn, is held very low by the formation of very sparingly soluble $PbSO_4$. At pHs close to 7 the abundance of $Pb^{2+}$ drops down dramatically and, on the contrary, carbonato- and hydroxo-complexes are formed, the former representing the predominant species in all the waters with pHs near to neutrality or weakly alkaline. It is noteworthy that because of the sparing solubility of both $PbSO_4$ and $PbCO_3$, Pb mobilization will increase just in the presence of very high $Cl^-$ activities, as the latter ligand displays low association constants with $Pb^{2+}$.

As far as Cu behavior is concerned, interesting analogies with Pb are exhibited, thus likely accounts for the controversial understanding of their respective mobility (MANN and DEUTSCHER, 1980). In fact also the abundance of $Cu^{2+}$ (free ion) is pH-dependent, even though to a less extent relative to $Pb^{2+}$, whereas $CuSO_4$ ion-pair formation is just less sensitive to sulphate activity increasing, compared with $PbSO_4$. $Cl^-$, at the concentration levels found at Tolfa, does not bound any Cu and, conformably with Pb speciation scheme, $CO_3^{2-}$ is the predominant ligand in bounding copper, although $OH^-$ gains some additional importance.

By taking into consideration the percentage of unbound metals ($Me^{2+}$), which represents the only fraction involved in solubility equilibria, it is possible to examine the saturation status of the waters with reference to the solids that, owing to their low ionic activity products, can affect the solubility of Zn, Pb and Cu. The graphical rapresentation herein adopted consists of plotting the antilog of $Me^{2+}$ activity vs. that of the ligand for each compound considered. Selected value for the ionic activity product ($pK_s$) is written along the saturation curve; for those solids whose formation is directly pH-dependent three iso-pH saturation curves were drawn. Fig. 4 $a$, $b$, $c$, $d$, $e$ and $f$ are relative to the saturation status of the waters in respect of $ZnCO_3$ (smithsonite), $Cu_2(OH)_2CO_3$ (malachite), $Cu_3(OH)_2(CO_3)_2$ (azurite), $CuCO_3$ (tenorite), $PbCO_3$ (cerussite) and $PbSO_4$ (anglesite), respectively. The graphs show that among the three elements considered only copper is affected in its solubility by formation of sparingly soluble compounds, i.e. basic copper carbonate (fig. 4 $b$ and $c$). $Zn^{2+}$ activity is always lower than the value required to satisfy the equilibrium with $ZnCO_3$, which represents the most insoluble Zn-compound (fig. 4 $a$). Although no water samples display a $Pb^{2+}$ activity to allow the formation of $PbCO_3$ (fig. 4 $e$), there are at least three points that fall very close to the $PbCO_3$ saturation curve. Finally, $PbSO_4$ solubility product is by far greater than $Pb^{2+}$ and $SO_4^{2-}$ ionic activity products found for the waters, this likely means that anglesite is ruled out from controling Pb solubility (fig. 4 $f$).

The above predictions dealing with the occurrence of solid compounds limiting the solubility of the three elements, which were obtained *via* calculations, receive some degree of support by the findings of secondary minerals in the study area. At Tolfa, according to FERRINI (1975), malachite and azurite represent the most spread alteration minerals. While secondary Zn-minerals were never found, scant occurrences of both cerussite and anglesite, the latter by far subordinate, are also reported.

Our theoretical results, however, fairly agree with field evidences as regards Cu and Zn. The scant occurrences of cerussite and anglesite can be reasonably accounted for by very peculiar environmental conditions, since, as reported by FERRINI (1975), such secondary Pb-minerals just occur as concretions onto galena crystals, at whose interface exceeding $Pb^{2+}$ activity is likely attainable.

Anyhow our data predict that at Tolfa cerussite and by far more anglesite are metastable phases in the aquatic environment, thus being in good agreement with the reported occurrences.

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