

# DISPERSION PATTERNS OF HEAVY METALS IN MAHANAGDONG HYDROTHERMAL SYSTEM, LEYTE, PHILIPPINES

Noel D. Salonga and June Rizza V. Paraon

PNOC Energy Development Corporation, Merritt Road, Ft. Bonifacio, 1201 Makati City, Philippines

## ABSTRACT

*Mahanagdong area in Leyte hosts an active hydrothermal system within high-angle fractures system. The fluids have maximum temperature of 300°C, salinity of 0.20m in terms of Cl, and gas contents of 3.0% by weight. The  $\delta^{18}\text{O}$  in water of -3.0 to -1.0‰ indicates mixing of about 65-80% groundwater with 20-35% original magmatic components. With  $\text{H}_2\text{S}$  as the dominant sulfur species, the present-day hydrothermal system appropriately belongs to low-sulfidation, epithermal environment.*

*Mahanagdong hydrothermal system will unlikely support deposition of metals transported in bisulfide complexes, like gold, silver and mercury, because the fluids have already attained near neutral-pH level probably through the process of water and rock interaction. The low total sulfur content of the fluids (0.004m) may be primarily transporting arsenic complexes, the most abundant heavy metal species in Mahanagdong fluids. Arsenic increases with decline in temperature and is expected to disperse further in supergene environment.*

*Metals transported by Cl complexes such as zinc and lead tend to decrease from the hot and saline central part of the field towards the cooler and diluted peripheral sectors. Degassing and increase in pH, the consequences of boiling, appear to favor deposition of these metals. On the other hand, iron and copper, which are also transported by Cl complexes, have lower correlation with temperature, salinity and fluid pH. Their mobility is also controlled by other factors, such as the redox state. Having low solubilities, iron and copper are the most dominant metal forming minerals, in form of pyrite and chalcopyrite, in Mahanagdong.*

## 1.0 INTRODUCTION

The study of the dispersion of heavy metals in hydrothermal fluids is important in two branches of applied geochemistry -exploration and environmental geochemistry. Moreover, models of metal deposition based on chemical equilibria and solubility equations contribute to a better understanding of the present-day ore deposits.

Vast numbers of works have been devoted to the geochemistry of geothermal fluids and mineral alteration. However, detailed works on the mobilisation of heavy metals within the active hydrothermal systems have only been recently initiated.

In this paper, the numerous deep wells in Mahanagdong active hydrothermal system in Central Leyte (Fig. 1) provided a three dimensional perspective of the heavy metal dispersion within a high-temperature convecting fluid system. The objective of this study is to determine the factors affecting metal dispersion and deposition in hydrothermal environment

## 2.0 METAL SOLUBILITIES

Heavy metals are transported in hydrothermal system as chloride ( $\text{MeCl}_2$ ) and bisulfide ( $\text{Me}(\text{HS})_2$ ) complexes (Barnes, 1979; Hedenquist, 1985; Corbett and Leach, 1995).

## 2.1 Bisulfide Complex

Metal deposition from sulfide complexes has the following typical reaction:



Any processes that reduce  $\text{HS}^-$  and  $\text{H}_2\text{S}$  will increase the degree of metal saturation in this complex and cause deposition. These processes include the following:

- **Boiling** -- causes liberation of  $\text{H}_2\text{S}$ .
- **Dilution** -- an initially saturated solution would precipitate approximately half of its metals from  $\text{Me}(\text{HS})_3$  if diluted with 1:1 sulfide-free water with other conditions remaining constant.
- **Decreasing pH** -- about 90% of the complexed metal should deposit if the pH were to drop by 2.0 pH units from  $\text{pK}_{\text{H}_2\text{S}}$ .
- **Oxidation** -- or slight increase in  $f\text{O}_2$  is the most effective means in causing deposition because it decreases both the total sulfide concentration and pH, unless well buffered by the rock.

Gold is transported as a bisulfide complex ( $\text{Au}(\text{HS})_2$ ) over all conditions within mesothermal and epithermal environments (<300-350°C), and probably as a chloride complex ( $\text{AuCl}$ ) at higher temperatures. Silver is also transported mainly as a bisulfide in dilute conditions and as chloride complex in hotter more saline conditions. Arsenic and mercury have very stable bisulfide complexes however, these are deposited at lower temperature.

## 2.2 Chloride Complex

The typical reaction for metal deposition in chloride complex is as follows:



The following processes increase the degree of saturation or the extent of deposition of the sulfides:

- **Increased  $\text{H}_2\text{S}$  concentration** -- due, for example, to sulfate reduction.
- **Increased pH** -- caused by either reaction of the fluids with the rock or boiling off acid gases.
- **Decrease in salinity** -- 1:1 dilution by  $\text{Cl}^-$  free water causes deposition of 85% of the metal in solution, other conditions remaining constant.
- **Decreased temperature** -- temperature decrease of 100°C generally deposits approximately 90% of the metal.

Lead and zinc are transported as chloride complexes under most hydrothermal conditions and their deposition is caused by decrease in temperatures, salinity and pressure. Copper chloride complex is apparently the dominant stoichiometry at all temperatures, and is less soluble than lead and zinc, therefore copper mineralisation is dominant over other base metals at both porphyry and epithermal levels. On the other hand, iron complexes are stable in weakly acidic solutions of  $10^{-2}$  m or less sulfide.

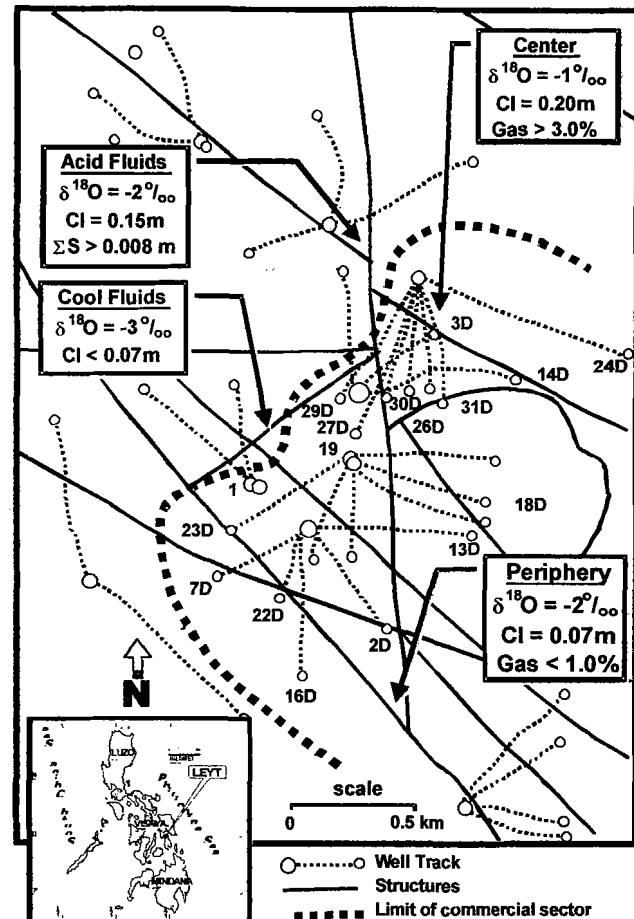


Figure 1. General map of Mahanagdong hydrothermal system in Central Leyte showing the major structures, well tracks and fluid characteristics. Only the wells included in this paper were labeled

### 3.0 THE MAHANAGDONG SYSTEM

#### 3.1 Reservoir Rock and Permeability

Mahanagdong hydrothermal system developed as a consequence of subduction of the Philippine Plate against the Philippine Trench, and of the differential movements along the Philippine Fault Zone. Volcanism and episodes of sedimentation built-up the rock units in the area composed of metamorphic basement, conglomerate complex, impermeable claystone unit, and young lavas and pyroclastics of andesitic composition.

The spatial and vertical distributions of the rock units control the size of the hydrothermal reservoir. In the western part of the field, the fluid flow appears to terminate on the claystone and metamorphic units where lithological permeability is poor. Likewise, ascend of the fluids to the surface stops upon encountering a more than one-km thick of impermeable sequence of lavas and pyroclastics.

High-angle structures related with the Philippine Fault provide the channels for fluid movements in the reservoir (Fig. 1). In the southern sector of the field, the presence of interconnected northeast and northwest trending fractures enhanced fluid mixing and influenced the direction of the fluid outflow towards the southeast. In the northern areas, the absence of the same structural fabrics confined fluid movement, and consequently suppressed fluid and rock interaction.

#### 3.2 Hydrothermal Fluid Flow

The centre of Mahanagdong hydrothermal has temperature of above 300°C with salinity of around 0.20 m Cl (represented by well MG-3D in Table 1 and Figure 1). This parent fluid has high CO<sub>2</sub> content of greater than 3.0% by weight. Its δ<sup>18</sup>O in water of -1.0‰ represents mixing of 65% groundwater with 35% magmatic components (Salonga and Bayon, 1997).

Towards the north, the fluids are acidic with more than 0.008 m total sulfur. Salinity ranges from 0.8 to 1.0m Cl and CO<sub>2</sub> ranges from 0.5 to 1.7% by weight. These fluids have temperatures of 260-280°C and have slightly depleted δ<sup>18</sup>O that range from -3.0 to -2.0‰. The high amount of Mg in acidic fluids indicates that the fluids have not yet attained full equilibrium with the reservoir rocks.

On the other hand, the fluids flowing towards the south have alkaline to neutral-pH level with less than 0.004m total sulfur. The temperature range is 260 to 280°C and the salinity is 0.07 to 0.08 m Cl. The CO<sub>2</sub> level in this area is below 1.0% by weight. The fluids have slightly depleted δ<sup>18</sup>O ranging from -3.0 to -2.0‰, translating to mixing of 75% groundwater with 25% original magmatic components.

In the western part of the field, fluids have temperatures of less than 240°C, the coolest among the production wells. These are also the most diluted fluids with salinity of less than 0.07m Cl and the most isotopically depleted with less than -3.0‰ δ<sup>18</sup>O. All of these indicate the presence of cooler type of fluids in the western part of the field with more than 80% groundwater component.

#### 3.3 Alteration Minerals

Mahanagdong reservoir displays mineral alteration assemblages that are intimately related with reservoir temperature and fluid chemistry (Fig. 2). The core of the system with temperature greater than 300°C is marked by biotite, illite, actinolite, abundant pyrite, anhydrite and calcite. Outside of this core where temperature ranges from 300 to 270°C, the alteration assemblage is composed of illite, wairakite, epidote, abundant pyrite,

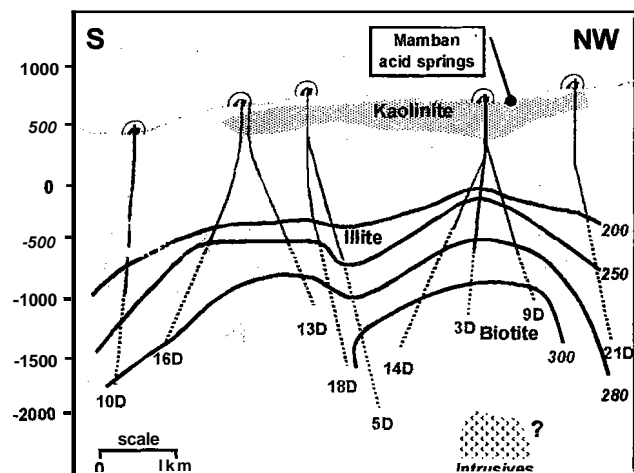


Figure 2. Cross-section across Mahanagdong traversing the Northwest-Central-Southern areas. Shown are the well tracks of selected wells, the measured temperature contours and the key minerals for each mineral alteration zones. Elevation in mRSI.

Table 1. Results of chemical analysis of fluid samples from Mahanagdong. Reservoir pH is calculated using speciation software called WATCH. T(Quartz) is based on quartz geothermometer.

Well Name	Lab pH	Res pH	Cl [m]	CO <sub>2</sub> %w	T(Quartz) (°C)	Zn	Cu	As	Fe	Hg	Pb
MG-1	6.87	5.60	0.08	0.4	272	26	20	3473	139	5	116
MG-2D	6.44	5.80	0.08	0.3	265	22	19	3855	244	3	81
MG-3D	5.90	4.80	0.17	1.3	292	40	29	445	89	6	151
MG-7D	7.11	5.60	0.08	0.4	276	35	23	3091	79	2	110
MG-13D	7.22	6.30	0.08	1.4	286	17	22	1095	55	1	80
MG-16D	6.90	5.80	0.08	0.2	271	27	23	3902	90	3	83
MG-18D	7.00	5.90	0.07	1.7	269	20	18	1770	119	4	82
MG-19	5.88	5.80	0.07	0.6	265	15	14	2261	76	3	99
MG-22D	6.94	5.80	0.08	0.3	264	23	20	3266	83	3	90
MG-23D	6.75	5.70	0.08	0.7	271	34	19	3543	135	5	105
MG-24D	6.35	5.10	0.09	3.6	290	37	26	621	86	2	133
MG-26D	7.78	6.00	0.07	3.3	245	5	18	2891	136	3	58
MG-27D	6.74	5.30	0.09	0.5	282	32	14	2794	112	4	75
MG-29D	6.40	5.20	0.13	0.7	281	25	17	2556	73	2	120
MG-30D	6.75	5.10	0.11	0.5	285	44	17	2124	101	4	101
MG-31D	6.52	5.30	0.11	1.3	274	26	26	3203	162	3	121

anhydrite and calcite. Interestingly, these secondary mineral assemblages, classified under the phyllic to inner propylitic zones, are present in both acid and neutral-pH reservoirs.

The southern part of the field developed a convecting system of thermal fluids possibly due to the interconnected fractures in this sector. The alteration minerals belong to propylitic zone, exemplified by the dominance of calcite over anhydrite, the predominance of epidote and wairakite, and the occurrence of pyrite in lesser quantities.

Acid minerals generally occur in two regimes. There are deeper thin zones in the north with active high-temperature acid minerals such as pyrophyllite and diaspore, associated with abundant pyrite, and traces of chalcopyrite (Zaide-Delfin and Dulce, 1996). There are also shallow acid altered zones above the illite-smectite line composed of dickite, kaolinite and native sulfur all formed in the presence of cooler condensates rich in H<sub>2</sub>S and CO<sub>2</sub>.

### 3.4 Heavy Metals

Table 1 presents the results of the analysis of water samples from deep hot wells in Mahanagdong. All of the samples have neutral to near-neutral laboratory pH, while the calculated reservoir pH ranges from 4.90 to 5.80. [It was unfortunate that no samples from acid and cooler wells were obtained for this project because they were no longer discharging. Also, gold and silver analysis were not performed because of limitations in our laboratory.]

Zinc (5-44 µg/L) and lead (75-151 µg/L) showed distinct direct correlation with fluid temperature and salinity (Table 2), and inverse correlation with reservoir pH. In other words, there is an apparent increase in dissolved Zn and Pb with increase in temperature, salinity and alkalinity in the fluids.

Copper (14-29 µg/L) and iron (55-244 µg/L) showed poor correlation with temperature and no correlation at all with fluid salinity and pH. On the other hand, mercury (1-6 µg/L) did not have correlation with any of the three parameters.

The most abundant and the most interesting heavy metal in this study is arsenic (445-3902 µg/L). In Mahanagdong, arsenic has inverse correlation with temperature but has direct correlation with reservoir pH. However, it did not have any clear correlation with fluid salinity.

Table 2. Correlation factors (r<sup>2</sup>) of the linear regressions of the plots of the different metal species against fluid pH, temperature and salinity.

Metal Species	T(Quartz)	Res pH	Cl
Zinc	0.36	0.30	0.17
Lead	0.41	0.32	0.26
Arsenic	0.46	0.33	0.01
Mercury	0.02	0.001	0.07
Iron	0.19	0.04	0.008
Copper	0.16	0.09	0.01

## 4.0 GENERAL DISCUSSION

### 4.1 Geologic Environment

The present deep wells in Mahanagdong did not encounter the supposedly hot intrusive supplying the heat, volatiles and metals to the hydrothermal system. Fresh SO<sub>2</sub> and HCl can no longer be traced in the well discharges, and porphyry-type and mesothermal sulfide deposits typical on the fringes of batholiths (temperature of above 350°C) are not encountered in the rock cuttings.

The known reservoir of thermal fluids has maximum temperature of 300°C, salinity of 0.20 m Cl, and gas content of 3.0%. Isotopic data also provided evidence that the hydrothermal system is dominated by groundwater (65-80%) with a fraction of original magmatic constituents (20-35%). Most sulfurs in the fluids occur as H<sub>2</sub>S, although substantial amounts of H<sub>2</sub>SO<sub>4</sub> were detected in the northern part of the field.

The above geochemical characteristics of Mahanagdong satisfy the criteria of a low-sulfidation, epithermal environment. The fluids in the central and the southern areas have been neutralized by the process of fluid and rock interaction as evident on the chemically equilibrated nature of the fluids and on the well-developed secondary mineral assemblages. The H<sub>2</sub>SO<sub>4</sub>-bearing northern sector, a hybrid of low and high sulfidation systems, is possibly still in the process of neutralization.

### 4.2 Physical Processes

The inter-relations of temperature, pH and salinity (Fig. 3) demonstrate the processes occurring in Mahanagdong system. At deep conditions, the hottest parent fluids has slightly acidic pH (4.90) because of the presence of acidic gases (mainly CO<sub>2</sub>). [Note that the acid well has slightly lower pH of 4.60 owing to the high dissolved H<sub>2</sub>S.]

From a temperature of 300°C, the parent fluids boil down to 280°C allowing the acidic gases to exsolve from the solution. This process raised the pH to 5.40, which is close to the neutral level at that temperature (represented by the equilibrium line in the graph). Moreover, the process of boiling also enriched the salinity of the fluids.

As the fluids migrate away from the centre, there is a progressive decline in temperature and salinity suggesting that mixing with dilute groundwater takes place.

Dilution process is also illustrated by the decline in the isotopic and gas composition of fluids. The net effect of this process is the shift of fluid pH to neutral and slightly alkaline level.

### 4.3 Chloride Complexes

Calculations of saturation of metal-Cl complexes enable predictions of their mobility and deposition. In PbS (galena), for example:

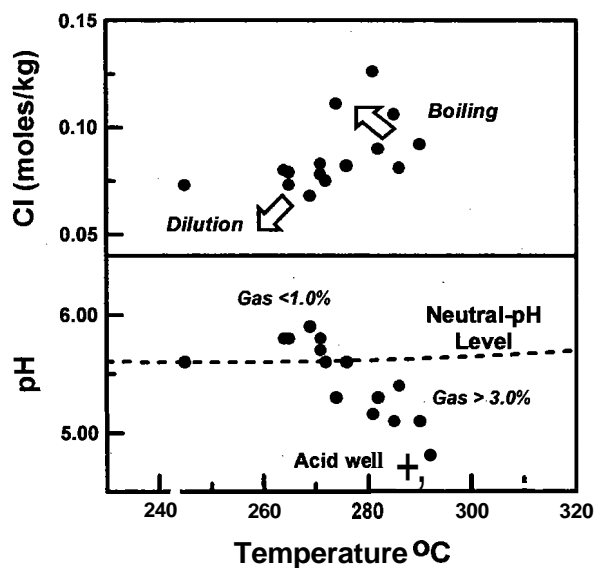


Figure 3. Physical processes in Mahanagdong hydrothermal system (based on T (Quartz) in Table 1), salinity and pH. The plot of an acidic well was plotted for reference.

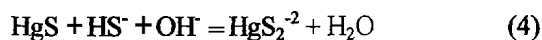
has equilibrium equation expressed in terms of  $H^+$  (acidity), salinity ( $Cl^-$ ) and temperature. The main assumption for this simple calculation is that the metal reservoir concentrations occur mainly as  $Cl^-$  complex. The saturation index of each complex species is computed based on the differences of equilibrium and actual concentrations [ $\text{Log}(Q/K)$ ] and the results are presented in Figure 4.

$CuCl$ ,  $FeCl_2$ ,  $ZnCl_2$  and  $PbCl_2$  complexes all have positive and increasing saturation indices with decline in temperature, with the exception of two outliers both of which are steam-rich wells. These trends suggest that in the presence of sufficient  $H_2S$ , there is a big potential of deposition of sphalerite ( $ZnS$ ), galena and Fe-Cu sulfides. In the cases of Zn and Pb, the decrease of concentration with decline in temperature indicates that substantial amounts of the metals have precipitated from the hot saline center to the cooler peripheral sector.

Iron and copper contents in the fluids, on the other hand, did not show clear trend with decline in temperature. It is possible that there are other factors controlling their concentrations, like the redox state of the fluids. And that it is more common to find Cu co-existing with Fe in sulfides suggests a more complicated equilibrium is involved in their deposition. Figure 5 illustrates the effect of  $fO_2$  on the type of Fe and Cu minerals that may form in Mahanagdong. Pyrite and chalcopyrite are the favoured sulfides. Petrographic studies proved that these are indeed the most dominant sulfides in Mahanagdong (Dulce, et al., 1996).

#### 4.4 Bisulfide Complex

Calculations of saturation index was also done in Mercury based on:



the equilibrium equation of which is dependent on sulfur, pH and temperature. Figure 6 shows that in most conditions, the Mahanagdong fluids are unsaturated with metacinnabar, possibly because of low total sulfur in the system and the near-neutral pH level of the fluids.

There is virtually no hydrothermal solubility data now available for the arsenides; thus, the reservoir concentration of arsenic is just plotted with temperature (Fig. 6). The plot clearly illustrates that arsenic has a high geochemical mobility in Mahanagdong system. The metal is expected to be transported further in the supergene environment and surface hot springs.

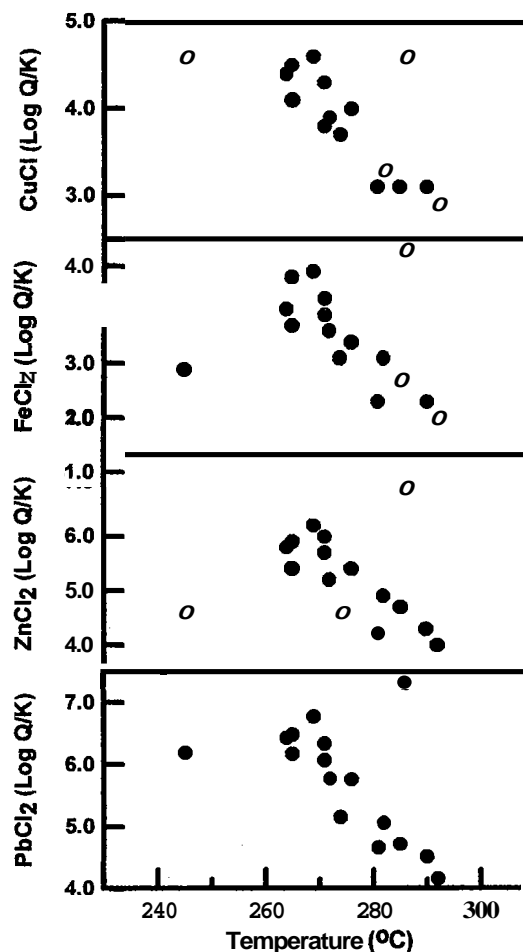


Figure 4. Saturation indices for the different metal-chloride complexes. Note that the saturation level has  $\text{Log}(Q/K)$  of zero.

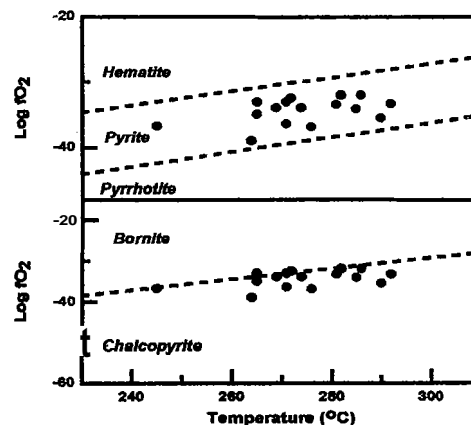


Figure 5. The effects of temperature and redox state of the fluids (in terms of  $fO_2$ ) to the mineral phases of Cu and Fe sulfides. Fugacities of oxygen were calculated using WATCH software.

Even without gold and silver analysis in the fluids, it is logical to predict that only trace amount of Ag and Au may occur in Mahanagdong fluids. Bulk of these heavy metals may have precipitated in hotter and deeper environment, where the low-pH and high-sulfur (>0.2m) conditions are more favourable. [It may be interesting to study the mobility of bisulfide complexes at the acidic northern sector. but we lack actual samples. There is, however, a study in progress on precious metal deposition in Palinpinon field, Negros with similar environment as Mahanagdong].

## 5.0 CONCLUSIONS

- The active hydrothermal system in Mahanagdong belongs to low-sulfidation, epithermal environment on the basis of fluid temperature and degree of fluid neutralization due to water and rock interaction (Fig. 7).
- Boiling in the central part of the field and mixing of diluted cooler fluids in the peripheral areas are the major processes controlling the dispersion patterns of the heavy metals in Mahanagdong. These processes modify fluid temperature, salinity and acidity, which are major factors controlling heavy metal dispersion.
- Deposition of heavy metals in bisulfide complexes, like gold, silver and mercury, is not favoured in Mahanagdong because of near-neutral pH level of fluids.
- Arsenic, the most abundant heavy metal in the fluids, has high mobility in the system. It is expected to circulate further in supergene environment.
- Dispersion patterns of lead and zinc Cl-complexes are affected by changes in fluid temperature, alkalinity and salinity.
- Iron and copper are the major mineral-forming heavy metal in Mahanagdong. Their mobilisation in the system is also dependent on the redox state of the fluids.

## REFERENCES

- Barnes, H.L., 1979. Solubilities of Ore Minerals. In Barnes (ed.) at Geochemistry of Hydrothermal Ore Deposits. p. 404-454.
- Corbett, G.J. and T.M. Leach, 1995. SW Pacific Rim Au/Cu Systems: Structure, Alteration and Mineralisation. Manila, 152pp.

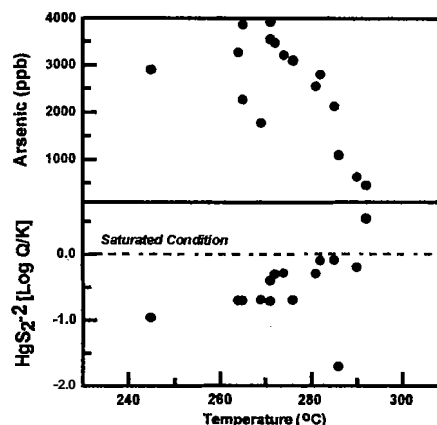


Figure 6. Saturation index of bisulfide complex of mercury (lower) and concentration of arsenic (upper) against fluid temperature.

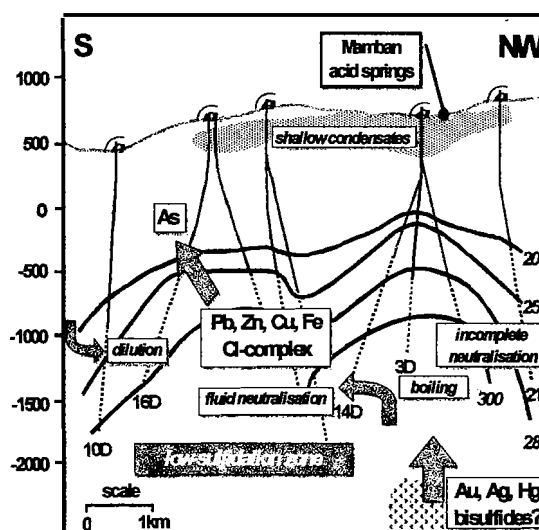


Figure 7. Schematic diagram showing the different physical processes and the dispersion patterns of the heavy metals in Mahanagdong. Elevation in mRSL.

Dulce, R.G., J.B. Rosell and M.C. Zaide-Delfin, **1996**. Sulfide minerals as indicators of acid-Cl-SO<sub>4</sub> fluids. **Proc. PNOC-EDC 17<sup>th</sup> Annual Geothermal Conference**, p. **137-149**.

Hedenquist, J.W. and R.W. Henley, **1985**. Epithermal Gold. Earth Resources Foundation, University of Sydney 311pp.

Helgeson, H.C., **1969**. Thermodynamics of hydrothermal systems at elevated temperature and pressures. *American Journal of Science*. p. **729-801**.

Martinez, M.M., **1998**. Mineral alteration in acid and neutral-pH reservoir: The case of Mahanagdong geothermal field, Leyte. **Proc. 19<sup>th</sup> Annual PNOC-EDC Geothermal Conference**. p.**299-309**.

Salonga, N.D. and F.E.B. Bayon, **1997**. Acid fluids and sulfur isotope systematic in some of the geothermal fields in the Philippines. **Proc. 1997 Geological Convention, Manila**.