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Mineralogy and heavy metal content of secondary mineral salts: A case study from the Witwatersrand Gold Basin, South Africa.

Mafuza Maya [1,3], Malcom Sutton[1], Hlanganani Tutu[2], Isabel Weiersbye [1],

[1]School of Animal, Plant and Environmental Sciences; University of Witwatersrand

[2]Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand

[3]Council for Geoscience

Corresponding author: Email: mayamaf@gmail.com

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Abstract

Secondary minerals associated with acid mine drainage play an important role in metal cycling and may pose a geochemical hazard. The occurrence of secondary minerals indicates prevailing and past geochemical conditions. Detecting and characterising secondary minerals is necessary to the planning of remediation programmes. This paper investigates the mineralogical and heavy metal contents of mineral salts associated with acid mine drainage in the East Rand area of the Witwatersrand Basin. Powdered X-ray diffraction was used to identify and quantify mineralogical phases and a scanning electron microscope was used to determine the morphology of the identified minerals. Major cations and anions were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Ion Chromatography (IC). Geochemical modelling was used to predict the saturation of the minerals.

Efflorescent crusts contained high levels of trace metals. Enrichment of trace metals, electrical conductivity and sulphate were highest in white salts. A high metal content was associated with low pH values in mineral salts. The salts were dominated by quartz and clay minerals of the smectite group. Tamarugite, apjohnite and jarosite were the predominant sulphate minerals in the salts. These minerals are very acidic and will accelerate weathering in the surrounding soils. Geochemical modelling yielded precipitated hydrated sulphate, halite and goethite. The information gathered during this study will be useful in managing salinity and high metal contents in receiving waters and soils associated with gold mining activities.

1. Introduction

Mining activities in the Witwatersrand Basin have resulted in six billion tonnes of mine waste (AngloGold Ashanti, 2004). Part of this mine waste includes more than 270 tailings facilities covering an area of about 400 to 500 km^2 (Oelofse *et al.*, 2007) Outdated and often poor mining methods have left auriferous Wits sediments in ponds above the surface. It is estimated that surface tailings contain about 30 million tonnes of sulphur and 430 000 tonnes of uranium in the tailings storage facilities (Weiersbye and Witkowski., 2006). It is estimated that 25 million litres of contaminated water is discharged daily into surface water bodies and 100 tonnes of efflorescent salt is deposited into the surrounding environment (Hobbs and Cobbing, 2007; Straker *et al.*, 2008). Decanting mine water and mine waste tailings are characterised by secondary minerals. Iron oxidises upon exposure to air and precipitates along the flow paths, leaving visually observable precipitates on river beds and banks. During dry periods, the fluctuating water table causes highly saline groundwater to evaporate near the surface, leaving behind visible efflorescent salts. Naicker *et al.* (2003) characterised groundwater reserves as heavily contaminated and acidified as a result of the weathering of pyrite-rich tailings dams. These authors noted that the water table fluctuates seasonally, resulting in seepage zones marked by the precipitation of limonite, a bright red crust. Secondary mineral precipitates also represent the evolution of acid mine drainage and play an important role in the cycling of metals and pollutants in the environment. Straker *et al.* (2008) successfully mapped secondary minerals associated with seepage zones to characterise groundwater pollution in gold mining areas.

Some efflorescent minerals are relatively insoluble and present negligible environmental hazards (for example, gypsum) while others may be readily soluble and contain high concentrations of potentially toxic metals. During periods of rainfall, such salts are washed further afield and into surface water bodies. Dissolution of salts lowers the stream pH and increases the metal load. According to Harris *et al.* (2003), the first flush drainage waters contain high concentrations of Cu, Fe, Zn and sulphate material. In the central Witwatersrand Basin, Tutu *et al.* (2008) reported that pollution levels varied seasonally, with high pollution levels occurring in summer during the rainy season.

The high concentrations of heavy metals in the efflorescent salts pose a significant geochemical hazard to human health and the environment. This hazard is compounded by the fact that these mineral salts occur in sensitive areas such as residential areas, cultivated fields and water courses. The role of secondary minerals in metal cycling and their relationship to acid mine drainage make them suitable to be used as indicators of groundwater pollution and as monitoring agents (Valente and Leal Gomes, 2009). The aim of this paper is to identify and describe secondary mineral precipitates associated with polluted groundwater in the Witwatersrand Basin. The primary objectives are 1) to identify and describe secondary mineral crusts in the area and 2) to determine and evaluate the environmental threat posed by the minerals in the surrounding environment.

2. Methodology

The sampling campaign was conducted in the East Rand Basin of the Witwatersrand Basin. The study area (Figure 1) forms part of the Ekurhuleni Metropolitan Municipality. The sampling campaign mainly targeted newly formed mineral crusts (Figure 2). Efflorescent salts, rock coatings, ochreous precipitates and soil composite crusts were collected. To ensure that representative samples were obtained, sampling materials with varying colours, textural variations and differing proximities to tailings facilities were considered during sampling. Sampling took place at the end of the dry season, when salt precipitation was expected to predominate. Samples were selected at depths of 0–5 cm and comprised approximately 50–150 g of dry and crumbly crusts collected by means of a stainless steel spatula. The samples were subsequently air dried under ambient laboratory conditions and sieved to remove large pieces of debris and stones.

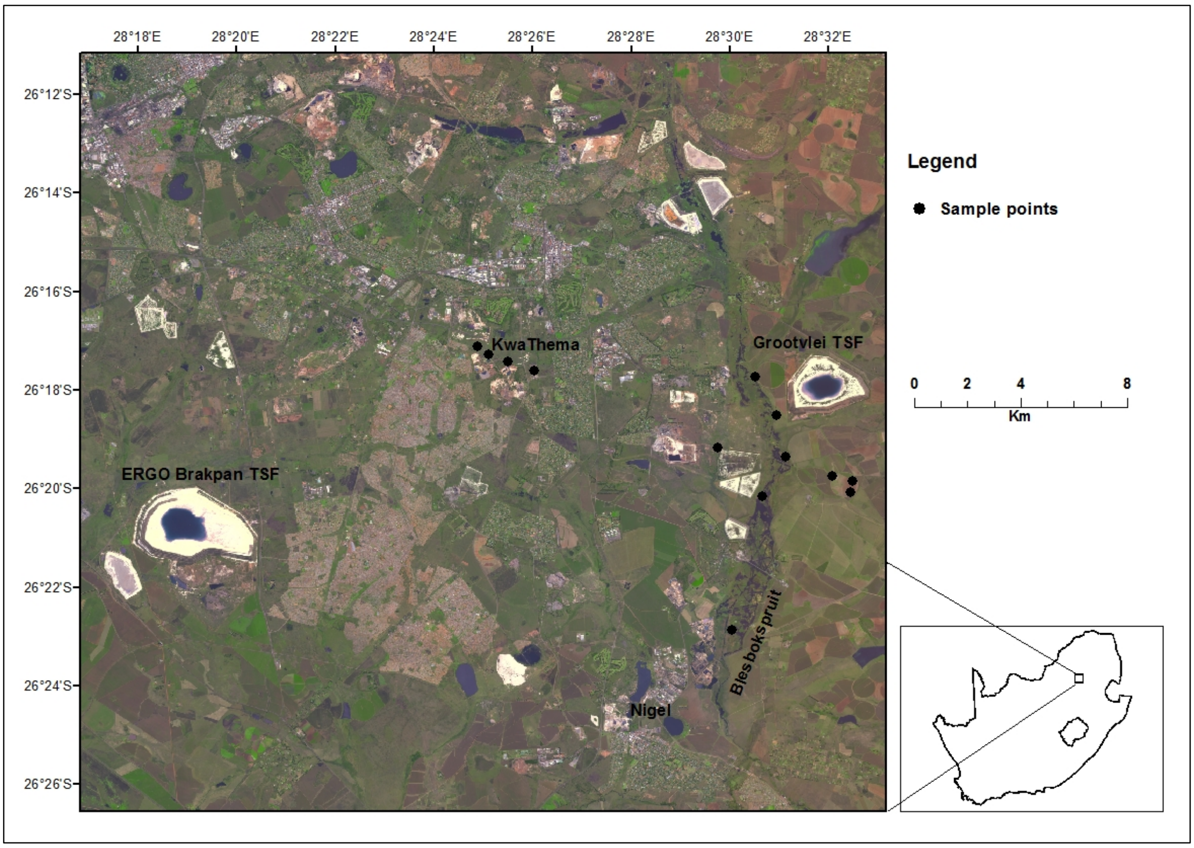

Figure 1. Study area showing selected sample points.

Prior to analysis, a Munsell soil colour chart was used to characterise the colour of the samples. After drying, the samples were gently crushed by hand using an alumina mortar and pestle to obtain a -75 µm fraction. The powdered samples were lightly pressed into aluminium sample holders for insertion into the X-ray diffraction (XRD) analyser, a Philips D500 diffractometer. The crystal structure and chemistry of salt precipitates were determined by scanning electron microscopy. The FE-SEM Zeiss Model Ultra, operating at 3 kV and fitted with an Oxford energy dispersive X-ray detector system (EDS), was used. Dry samples were fixed on Al-SEM plates using electronic conductive carbon tapes.

Figure 2. Sampled secondary minerals in the environment.

Approximately 1 g of the sample was dissolved in 20 ml distilled water, shaken for 30 minutes and centrifuged for 15 minutes to settle down. The leachate was analysed for anions and major elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Ion Chromatography (IC). The electrical conductivity and pH of the leaches solution were determined. The four acid method ($HF / HClO_4$ digestion) was used to target mineral phases and to dissolve trace elements from crystalline phases. This method is effective in dissolving sulphide phases such as pyrite. Approximately 0.20 g of the crushed sample material was digested in 30 ml fluoropolymer sample containers (with 3 ml HCl, 2 ml HNO_3, 1 ml $HClO_4$ and 2 ml HF). The digestion mixture was analysed for major and trace elements by ICP-MS. In order to identify mineral precipitates that would occur when the salt efflorescent dissolves in water, saturation indices were determined using PHREEQC software and the Wateq4f database. In the experiment, evaporation was initiated with 1 000 g of water.

3. Results and discussion

3.1 Geochemical characteristics of salts

The chemical characteristics of the crusts are tabulated in Table 1. Generally, the trace elements Ni, Cr, Co, Zn, As and U were present in higher concentrations in the salt crust than in the tailings and groundwater. Overall, the chemical results are typical of what could be expected in areas subjected to acid mine drainage. High levels of Cr, V, Pb, Mn and Fe occurred in wetlands and cultivated areas. Tailings footprints were characterised by high levels of Co, Ni, Cd, Cu and As.

Table 1. Mean values of selected heavy metals (n = 40; all elements in mg/kg).

Element	**Crusts**	**Water quality (DWA, 2012)**	**Tailings (DWA, 2011)**	**Crustal abundance (Taylor and McLennan, 1995)**
As	47	-	72	1.5
Co	255	41	26	10
Cu	83	-	37	25
Cr	164	5	273	35
Ni	577	301	56	20
Pb	27	16	63	20
U	80	8	76	2.8
V	60	1	40	60
Zn	306	572	81	71

Major anions, pH and EC concentrations are shown in Table 2. For comparison purposes, surface water, groundwater and tailings concentrations from the study area have also been included in the table. The pH values range from 2.65 to 8.2. High pH values are associated with wetland samples. Similar values were reported by Phaleng (2009) for the Blesbokspruit sediments and water. Figure 3 shows that the metal content of the salt crusts varies according to sample colour. For Co, U, As and Ni, high median values are associated with white samples while V and Cr showed high mean values in red samples. Yellow and brown samples show similar metal contents.

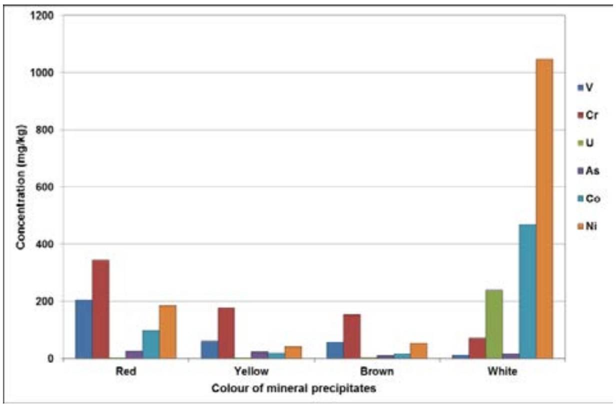

Figure 1. Median values of selected elements in different salt precipitates (n = 40).

Table 2. Concentrations of major anions, pH and EC in mineral salts. (n = 40).

	Crusts		**Tailings soil (DWA, 2011)**		**Surface water (SRK Consulting, 2012)**		**Background borehole water (SRK Consulting, 2012)**	
	Mean	**Median**	**Mean**	**Median**	**Mean**	**Median**	**Mean**	**Median**
pH	5.4	5.7	2.9	2.6	3.1	3.2	7.2	7.3
EC	5 163	1 934	704	652	269	169	109	88
CI (mg/l)	4 495	617	625	370	95	76	81	75
SO_4^{2-} (mg/l)	106 269	25 164	4 902	4 402	1 534	742	280	183
NO_3 (mg/l)	627	48	0.3	0.2	8.1	2.3	3.0	3.0

The Ficklin diagram (Figure 4) shows the total sum of the base metals against the pH of the analysed samples. Salts are classified into near-neutral extreme-metals and acid extreme-metals. This pattern suggests that pH exerts a major influence on the behaviour of these elements.

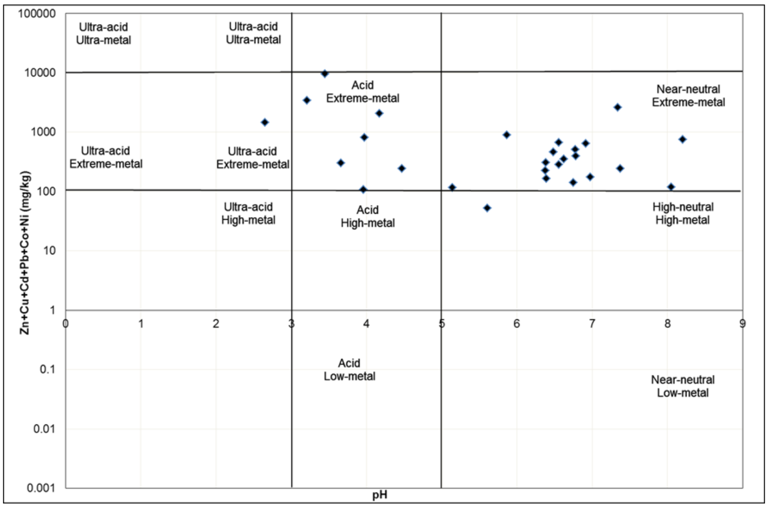

Figure 4. Ficklin diagram presenting the various samples.

In general, sewerage and fertilisers are the common sources of nitrates in the environment. In the study area, elevated nitrate levels occurred in residential and wetland areas. These levels are directly related to a sewerage plant that discharges effluent into the Blesbokspruit stream. Phosphate content showed a distribution pattern similar to that of nitrates, although low concentrations of phosphate were recorded in cultivated soils. High levels of sulphates were associated with tailings and residential areas.

3.2 Mineralogical content of mineral salts

A total of 12 precipitates were analysed by X-Ray Diffraction and the results are presented in Figure 5. Jarosite and gypsum are the most common sulphate minerals in the samples. Gypsum was found to be recurring with jachymovite, a uranium sulphate mineral. Jachymovite occurred in traces. Hexahydrite was found in higher concentrations in brown crusts than in white crusts. Apjohnite, or manganese aluminium sulphate salts, occurred in high concentrations in white mineral crusts only. In most samples, tamarugite and apjohnite were associated with high contents of Cd, U, Ni and As. The most chemically diverse minerals detected were fluellite and ammonium manganese fluoride.

In addition to an XRD analysis, the mineral crusts were subjected to analysis by Scanning Electron Microprobe (SEM). The sulphate minerals identified by XRD and SEM-ES (EDS) are summarized in Table 3. Alunogen was present in colloidal form. Tamarugite showed compact, platy crystals and was also recognised as intergrowths in the apjohnite and hexahydrite matrices. Apjohnite showed thin needle-like crystals forming fibrous aggregates. Jarosite appeared to occur in colloidal form and was poorly crystallised. Jarosite also occurred as a coating to gypsum grains. Gypsum was recognised as single crystals in an alunogen-bloedite matrix and was sometimes covered by halite. It was observed that the crystal matrix of the minerals was dominated by chlorine, proving that the salts were the result of evaporation. Fine crystalline habits and the rough texture (disorder lattices) indicated evaporation from highly supersaturated groundwater. The crystal sizes of apjohnite, blodite, wupatkiite and tamarugite were generally small, indicating fast crystallisation processes. The poor crystalline nature of jarosite, alunogen and hexahydrite were indicative of their high solubility.

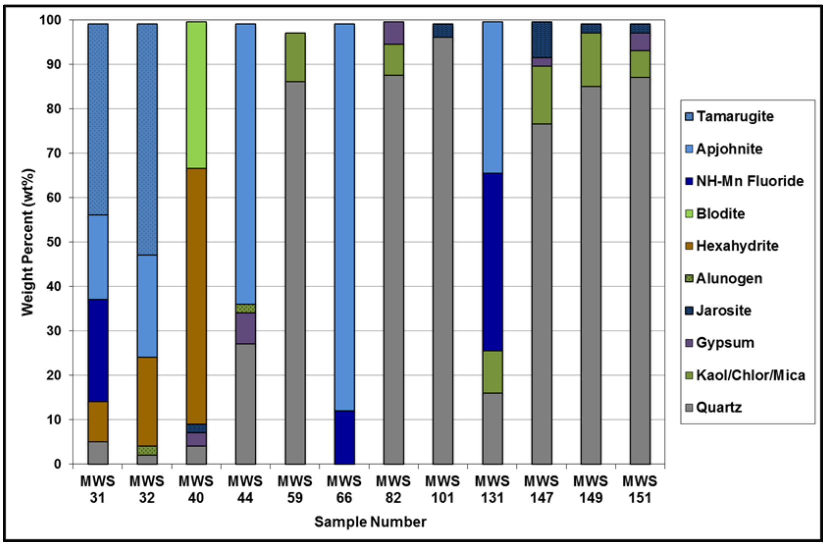

Figure 2. Mineral weight percentages of representative mineral precipitates of the study area.

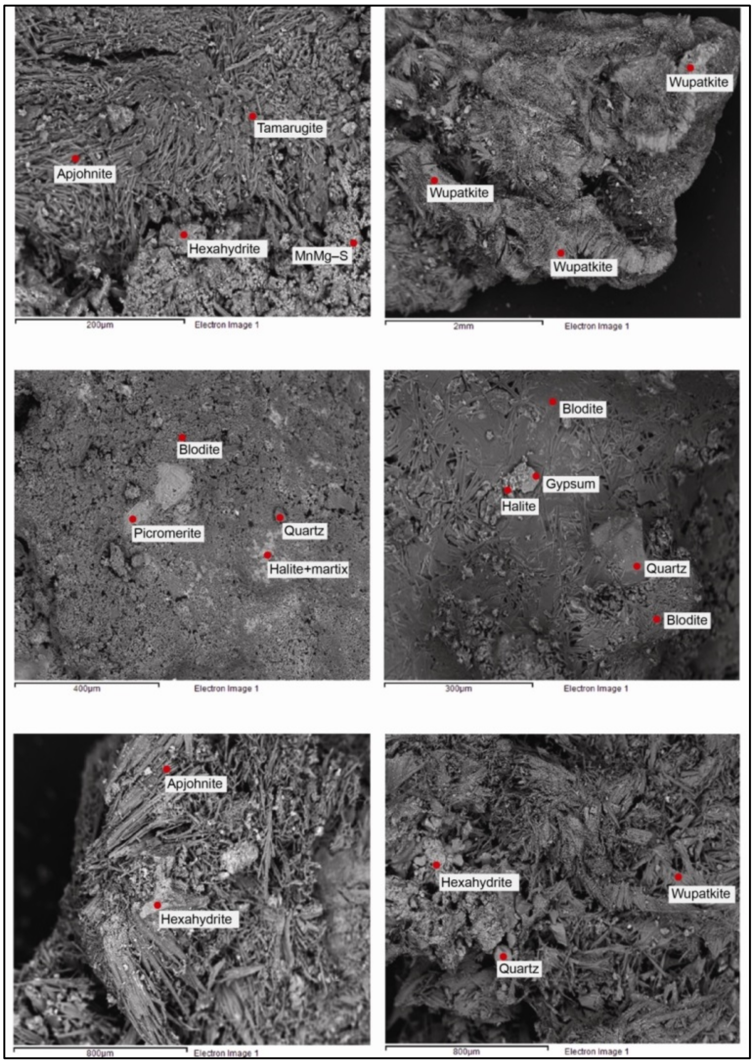

Figure 3. SEM-ES (EDS) images of mineral crusts, illustrating the crystal structure of the minerals.

3.3 Environmental significance

Figure 6 shows that, for most samples, Al, Fe, Mg were the dominant metals released upon dissolution. Variations in minor and trace element concentrations between different mineral precipitates suggest that the processes that transformed one sulphate mineral to another also redistributed these minor and trace elements.

The results obtained from the analysis of the dissolved crusts (pH, EC, metal and sulphate content) were modelled using the PHREEQC geochemical modelling code (Parkhurst and Appelo, 1999). Forward modelling was applied to predict the evaporation sequences of the minerals. The predicted minerals were compared with those obtained by XRD and SEM-ES (EDS). Table 3 tabulates predicted mineral phases and observed mineral phases. Detected and predicted mineral phases correspond very well and differences in minerals such as fibroferrite and apjhonite may be attributed to the fact that these minerals are not found in the database used for prediction.

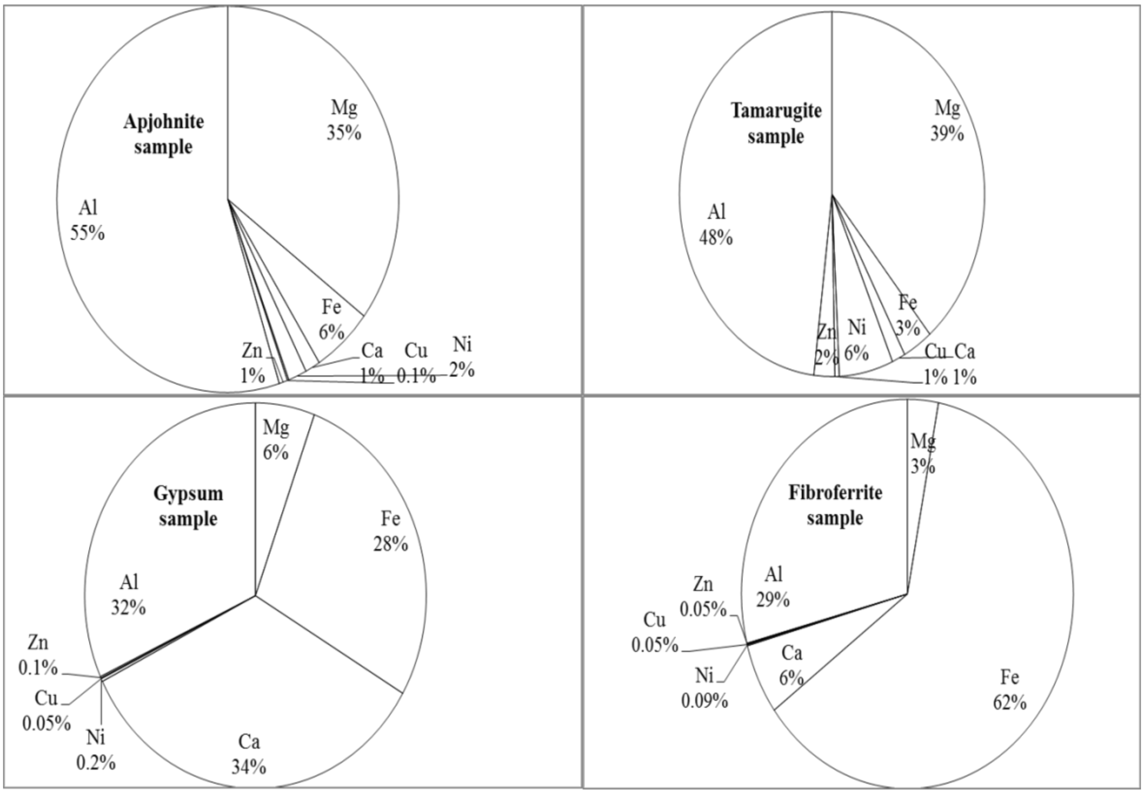

Figure 4. Relative cation abundances in solutions produced by dissolving mineral crusts. Concentrations are in mol% of the total metals.

Evaporation results show that, upon dissolution, iron and sulphate remain the dominant ions. The difference between detected and predicted minerals shows the incorporation of metals in these minerals. Dissolution releases metals and acid components that have been incorporated in the minerals. The dominance of jarosite after dissolution indicates persistent acidic conditions.

Table 3. Predicted versus detected minerals of selected mineral precipitates

Sample	**Predicted**	**Detected (XRD, SEM-ES (EDX)**
MWS 38	Fluorite Gypsum Jarosite-K Magnesite	Hexhydrite Fibroferrite Epsomite
MWS 51	FeS_2 Gypsum	Aragonite Jarosite
MWS 68	Celestite Gypsum Jarosite-SS, Jarosite-K	Gypsum Apjhonite Alunogen
MWS 116	Fluorite Jarosite Rhodochrosite	Aragonite Hematite
MWS 149	Gypsum	Gypsum Jarosite

4. Conclusion

Four types of salt precipitates were identified using the Munsell colour chart as red, yellow, brown/grey and white precipitates. Precipitate groups showed high variations in terms of bulk chemistry. The content of major ions in all precipitates was similar. Red and, to a lesser extent, yellow, precipitates are highly enriched in V, Cr, Cu and As. White precipitates showed high levels of enrichment in Co, Ni, Zn and U. Lead (Pb) is the only element that showed enrichment in brown crusts. Sulphate (SO_4^{2-}) and chlorine (Cl^-) showed high enrichment in all types of salt precipitates. These anions, together with soluble cations, were responsible for the high EC levels of the precipitates. Bulk chemistry and geochemical modelling revealed that elements such as Co, Cr, Ni, Pb, Zn and U occur in particulate solids at higher pH conditions and as free cationic species in low pH conditions.

The mineralogy of the salt precipitates is enriched in sulphate and aluminous components. Sulphate mineral groups are Na, Mg and the sulphite mineral blodite, the Mg sulphate minerals hexahydrite and starkeyite, the Al sulphate minerals alunogen, tamarugite and wupatkiite and apjohnite, the Fe sulphate mineral jarosite and the Ca sulphate mineral gypsum. Generally, ochre precipitates consist mainly of jarosite and hematite. Ammonia and phosphate are the common components of the efflorescent precipitates. The ammonia component indicates evaporation from saline groundwater while the phosphate component illustrates the ability of the salts to act as hyper-accumulators of metals. Dissolution with water and the evaporation experiment showed gypsum and jarosite to be the dominant minerals, indicating that iron and sulphate are the major ions responsible for acidity during precipitation and the dissolution of mineral salts.

5. Acknowledgements

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