

LOW-TEMPERATURE SECONDARY MINERALS FROM TARBELA

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ABSTRACT

Several types of sulphates and other minerals, believed to have formed at low temperatures, were found in a remedial excavation site overlooking Tunnel 3 and 4 on the right bank of the Tarbela Dam. Identified with the help of optical properties, XRD and chemical analyses, these include gypsum, pickeringite, potassium alum, hydrated iron sulphate, epsomite, lecontite, natroalunite, huntite, halloysite, (?) leonite and (?) starkeyite. Optical and chemical data for most of the samples studied are presented in the paper.

The sulphates are thought to have formed in connection with the weathering and alteration of pyrite commonly present in the metasediments of the host Salkhala formation. The huntite has formed by the action of ground water on dolomitic rocks, or gabbros and pyroxene/biotite peridotites, and the halloysite from alkali feldspar-rich intrusive rocks of the Tarbela "alkaline" complex.

INTRODUCTION

The Tarbela area comprises Precambrian Salkhala and Tanawal Formations intruded by Permean Tarbela "alkaline" complex (D.R.C. Kempe, pers. com.). The Tanawal Fm., consisting mainly of quartzites becoming more pelitic and talcosic near the base, is thrust upon the Salkhala Fm. The latter consists of alternating beds of pelitic and crystalline limestone, poorly cemented and disturbed arenaceous limestone, carbonaceous slates/schists and minor phyllitic horizons. Beds of fractured, white marble are found at the base of the carbonaceous horizons. Underlying this limestone-carbonaceous series is a more massive chloritic schist sequence containing "amorphous" gypsum beds (alabaster).

Pods of weathered and chloritized basic sill-like intrusions with evidence of much hydrothermal alteration occur along thrust zones in the Tanawal Fm. The general thrusting is in a northwesterly direction. The Salkhala Fm. is also faulted, folded and intruded. The weaker carbonaceous horizons show tight folding and

cross-shearing, the vergence being generally northwesterly. Just near the Dam on the east bank, step-faulting with an east-west strike downthrown to the south was observed in these rocks.

Both the formations have been intruded by gabbroic rocks, minor granitic rocks, and associated albitites constituting the Tarbela "alkaline" complex downstream of the Dam axis (Kempe and Jan, 1970; Jan *et al.*, 1981). Near the large intrusions, limited contact metamorphism overprints the generally low grade regional metamorphism. There is a considerable amount of metasomatism associated with the gabbroic intrusions; albitization of sediments (adinoles), and development of scapolite, at places several centimeters long, in limestones are common. The albitites were considered igneous by Jan *et al.* (1981) but the possibility of them being metasomatic cannot be ruled out.

LOW TEMPERATURE MINERALS

Detailed studies related to engineering geology have been carried out in Tarbela for over 25 years. During one such investigation in 1984 we noted a variety of secondary minerals formed at low temperature and pressure. The area examined in detail for this purpose formed a part of a remedial excavation overlooking Tunnels 3 and 4 of the Tarbela Dam Project. It is situated on the right bank just downstream of the dam axis and adjacent to the outcrops of basic intrusions. It is no longer exposed, being covered by the stabilising works and gunited. In the 15 samples collected for further studies, a variety of secondary minerals were identified with the help of optical studies, x-ray diffractometry (powdered samples) and chemical analyses (atomic absorption). The following minerals were identified (some doubtfully), with ideal formulae taken from Palache *et al.* (1951) and Fleischer *et al.* (1984):

1. Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
2. Pickeringite $\text{MgAl}_2(\text{SO}_4) \cdot 22\text{H}_2\text{O}$
3. Potassium alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
4. ? Leonite $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
5. ? Starkeyite $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$
6. Hydrated sulphate of iron similar in composition to carphosiderite $(\text{H}_2\text{O} \cdot \text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O})$ of Palache *et al.* (1951, p. 566)
7. Epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or leconite $(\text{K}, \text{NH}_4)\text{Na}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$
8. Natroalunite $(\text{Na}, \text{K})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$
9. Huntite $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$
10. Halloysite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Gypsum

Gypsum is ubiquitous in several habits in the area, occurring finely disseminated within the host rock or along tight jointing, open jointing, or within micro-fault planes cross-cutting the cleavage/bedding fabric. It also occurs in an euhedral crystalline (selenite?) form crystallized out from the seepage water within drainage pipes installed as part of the stabilization works. Contact twinning producing "swallow tails" or "arrow heads" are recognizable.

The thickest deposits of gypsum were seen near the contact with overlying and underlying limestone in hard, distorted and folded carbonaceous slate containing large boudins of pyrite vein. The pyrite-rich masses are up to a meter in thickness and are boundinaged and folded in conformity with the overall tectonics. In some locations the gypsum occurs as an "opaque", milky plating up to 1.5 mm thick on the open cleavage and fracture surfaces.

Elsewhere in the more graphitic horizons of the carbonaceous sequence, high lustre transparent, tabular crystalline gypsum coating within tight cleavage surfaces and along jointing was observed in a high concentration. Within the same area fibrous gypsum (satin spar, exhibiting a pearly sheen) was seen as infill along the minor shear planes parallel to "major" faulting. The higher concentrations of gypsum in the locality appear to be associated with the carbonaceous horizons containing pyrite, either as large veins or minor 2 to 3 mm thick veined enclosures, or in granular pockets upto a maximum of 60 cm overall size.

Three principal phases occur in the calcium sulphate-water system: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemi-hydrate or basanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), and anhydrite (CaSO_4). The temperature of transition of gypsum to anhydrite in pure water is 42°C but it may persist metastably above this temperaure. In the presence of NaCl and CaCO_3 , with increasing pressure the transition temperature is lowered considerably (Conley and Bundy, 1958). Conversion of gypsum to anhydrite via hemi-hydrate involves the release of water and decrease of volume (and vice versa) which can cause local dislocations. The presence of anhydrite, however, has not been identified in the area.

Pickeringite, Potassium Alum and associated sulphates

Significant quantities of these were observed within hard carbonaceous slates with a slight graphitic slickensiding in one locality on the north upstream side of the east-west step faulting. No associated intrusions or their alteration product were found, nor the presence of abundant pyrite. The sulphates here tightly infill open cross-cut joints and cleavage partings. The thickness of the infills reaches up to 1.5 cm, most are less than a centimeter, are light bluey green (aquamarin) in colour, and completely soluble in water.

Optical and XRD studies reveal the presence of more than one sulphate species in the infills. The most abundant minerals are ferroan pickeringite and potassium alum which are intimately associated. The pickeringite typically forms fibres up to a centimeter in length. It has a positive elongation, $Z \wedge C 30^\circ$,

$\alpha = 1.480$, $\beta = 1.484$, $\gamma = 1.487$ (all ± 0.002) and $2V \sim 60^\circ$. The bluish green colour, refractive indices and the higher value of Fe_2O_3 as compared to MgO would suggest that the mineral should be called halotrichite; however, the name pickeringite is preferred on the basis of XRD data. The potassium alum is isometric with a refractive index of 1.456.

Small quantities ($< 2\%$) of two more sulphates are associated with the pickeringite and potassium alum. One of these with a minimum refractive index of 1.463 and maximum of 1.476 might be starkeyite. This mineral is distinctly zoned chemically under the microscope and forms about a millimeter thick coating on one side of the infills but in some infills it is associated with the other sulphates. X-ray diffraction data also reveal minor peaks of leonite but this mineral was not studied optically.

Bulk analysis of the infills for some elements contains Fe_2O_3 (total) = 3.71%, $\text{MnO} = 0.01\%$, $\text{MgO} = 1.21\%$, $\text{CaO} = 0.54\%$, $\text{Na}_2\text{O} = 0.02\%$, $\text{K}_2\text{O} = 3.87\%$, $\text{H}_2\text{O} + \text{SO}_3 + \text{CO}_2$ (i.e. ignition loss) = 74.26%, $\text{Zn} = 55$ ppm, and $\text{Cu} = 15$ ppm. The small amount of CaO in the analysis is due to the presence of a small quantity of tiny carbonate (? calcite) grains associated with the sulphates.

Also found to the north of the E-W step faulting is a yellow evaporate emanating from a drain hole. The parent rock at depth is unknown. This rather soft material lost a considerable amount of water and hardened when left for a year at room temperature. Microscopic examination suggests that it consists of several mineral species including minor carbonate and (?) quartz, but the grains are too fine-grained to work with satisfactorily. Three of the minerals appear to be phosphates. One of these is isotropic and, based on XRD data, is potassium alum; another is fibrous with a low interference colour (? pickeringite/halotrichite); and the third has rhombic to subrounded outlines in crushed grains with upper first order interference colour. Fig. 1 is the x-ray diffraction pattern of this material whose bulk analysis contains 4.20% Fe_2O_3 (total), 0.07% MnO , 2.36% MgO , 0.72% CaO , 0.40% Na_2O , 0.02% K_2O , 53.24% volatiles (ignition loss after a year exposure), 12 ppm Zn and 30 ppm Cu .

Hydrated Fe sulphate

Some light bluish amorphous-looking sulphate encrustation was observed in an open joint infilling in a sulphurous open cavity area above a massive pyrite vein set within a slickensided hard graphitic schist. This material tastes astringent, not soluble in water but dissolved by dilute HCl , and turns earthy brown-grey upon slight heating. It is composed of 45.45% total Fe_2O_3 , 0.00% MnO , 1.05% MgO , 0.67% CaO , 0.03% Na_2O , 0.01% K_2O , 50.28% volatiles (ignition loss), 31 ppm Zn , and 109 ppm Cu . The chemical composition of this material is similar to that of carphosiderite (cf. Dana's System of Mineralogy, 1951, vol. II, p. 566), however, its refractive indices ($\alpha = 1.473$, $\gamma = 1.486$) are much lower than those (1.728 to 1.816) of carphosiderite.

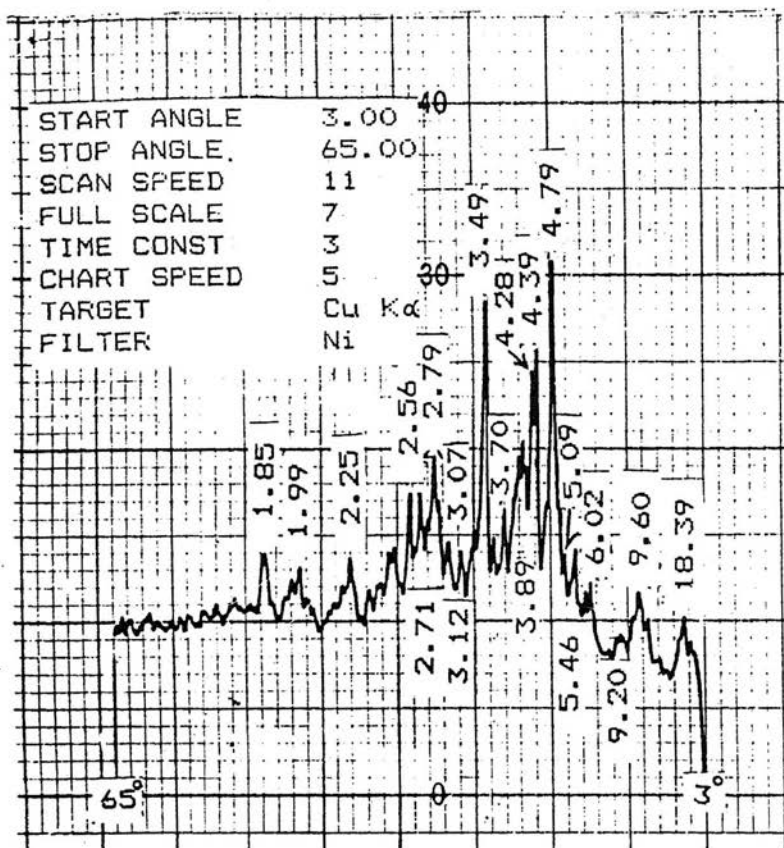


Fig. 1. XRD powder data for yellowish evaporate

Also found in the area is a dark reddish brown material of a low specific gravity, and not soluble in water. This amorphous (glassy) substance has refractive indices in the range of 1.626 to 1.655 and is chemically similar to carphosiderite. It contains 52.27% Fe_2O_3 , 0.01% MnO , 2.3% MgO , 1.17% CaO , 0.32% Na_2O , 0.04% K_2O , 12.84% H_2O^- , 19 ppm Zn, and has an ignition loss of 30.76%.

Epsomite/Lecontite and associated phases

This material was seen at the base of Tanawal Fm. and formed some days after excavation, growing out of the rocks in fine, curved silken tassels. A "massive" deposit of fine fibres was also associated with tight isoclinal fold in chloritic phyllites having a southerly vergence. Associated with this growth was an afflorescence of gypsum, and a variety of unidentified minerals including traces of a (?) carbonate. The unidentified minerals include at least two isotropic sulphate species of different refractive indices, and a third sulphate with upper second to

third order interference colour and refractive indices around 1.448. The very small grain size of these prohibited their exact determination.

Optical data for the fine tassels, up to a centimeter in length ($\alpha = 1.438$, $\beta = 1.451$, $\gamma = 1.456$, $2V \sim 47^\circ$) suggest that they are lecontite or epsomite; the latter name is preferred due to the fine fibrous to wooly nature of the mineral and the closeness of its optic axial angle to epsomite (cf. Fleischer *et al.*, 1984). However, there might be some lecontite in the associated minerals. The occurrence of these two minerals could be widespread as unidentified white encrustations are common in the carbonaceous slates as well as phyllites and limestones. The epsomite could be derived from or associated with the formation of the ubiquitous gypsum.

Natroalunite

Natroalunite occurs in fault breccia in carbonaceous slates and in some places forms up to a few centimeter across, stretched rounded masses. In one case it forms several centimeter broad masses of brownish yellow colour imparted by a minor amount of red iron oxide/hydroxide. The mineral has one refractive index of 1.574 and the identification was confirmed by XRD. It is full of tiny granules and dust of brownish red hematite or Fe-hydroxide.

Huntite

This mineral is found in carbonaceous slates and forms up to 2 cm thick masses of chalky appearance. Like typical huntite (cf. Deer *et al.*, 1962, vol. 5), it is pure white, soft and friable, porous and crumbles into water. It is so fine-grained that optical data could not be obtained satisfactorily but the aggregates show colour fringes when immersed in an oil of 1.618 refractive index. The mineral was confirmed by XRD and chemistry. The chemical analysis is typical of huntite (cf. Deer *et al.*) and contains 0.20% Fe₂O₃ total (? as impurities), 0.10% MnO, 32.86% MgO, 16.57% CaO, 0.45% Na₂O, 0.06% K₂O, 1.27% H₂O⁻, 46.26% CO₂ (ignition loss), 56 ppm Zn and no Cu (total = 97.67). The Mg: Ca ratio (2.8:1) is close to the 3:1 ratio in theoretical formula.

Lying close to huntite concentrations are up to 0.7 mm thick pyrite-rich veins with variable amount of plagioclase. Both the minerals are fresh and the β refractive index (1.535) of the plagioclase suggests an albitic composition with $An=7.5$.

Halloysite

Halloysite is a hydrated member of the kandite (kaolinite) group of clay minerals. It consists of layers of kaolinite composition, Si₄Al₄O₁₀(OH)₈, separated by single molecular layers of water which due to disordered stacking of layers and sheet mismatch cause the layers to curve, resulting in a tabular structure. On dehydration these tubes split, collapse and unroll, causing a 7 to 15% volume reduction (Gillott, 1968).

The Tarbela mineral, identified by XRD, has a soapy and waxy feel, and can be chalky depending on moisture content. It has a conchoidal fracture when dry. Two types were found, one white one blue, the white is more common. It occurs as discontinuous bands and fracture-fillings in the top and bottom of the carbonaceous horizons. It also fills joints along fault planes that may be parallel or oblique to bedding.

Also believed to be halloysite are individually distributed round to egg-shaped, white chalky "inclusions" in a fine matrix set in breccia zones along parallel planes on either side of fault. In contrast to the veins and joint infillings which soften on wetting, the encountered "inclusions" were always dry and hard, displaying conchoidal fracture and being very absorbant. However, at least one of these "inclusions" consists of albite (XRD data), another of altered feldspar+clay (n 1.577), and a third of scapolite with a subordinate amount of carbonate. Partial chemical analyses of these substances are as follows :

Altered albite : 1.09% Fe_2O_3 total, 1.72% MgO, 1.41% CaO, 5.53%, Na_2O , 1.85% K_2O , 0.53% H_2O^- , 46.25% volatiles, 28 ppm Zn, 184 ppm Cu.

Scapolite : 0.26% Fe_2O_3 total, 0.02% MnO, 1.94% MgO, 7.58% CaO, 7.85% Na_2O , 0.43% K_2O , 0.60% H_2O^- , 6.63% volatiles, 25 ppm Zn and 40 ppm Cu. Assuming that all the Ca, Na and K are contained in the scapolite, the meionite content of the analysis is about 34 mole per cent. This value closely matches that (36) derived from refractive indices ($\epsilon = 1.544$, $\omega = 1.563$) (cf. Deer *et al.*, 1962, vol. 3). These two materials are not a product of low temperature alteration and their presence has been previously described by Jan *et al.* (1981) from the Tarbela "alkaline" complex. In this complex, scapolite is a common mineral in metasomatised calcareous rocks on contact with gabbros, as is a variety of albitites. It is possible that these rocks are present in the fault zone or have been brought to surface along fault planes.

DISCUSSION

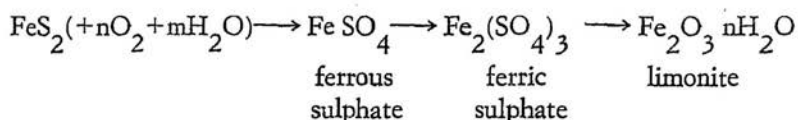
Pyrite is an important mineral in the area, especially in carbonaceous rocks, and is believed to have a direct bearing on the formation of the low temperature sulphate minerals described in this paper. Its occurrence and weathering characteristics are therefore summarised in the following.

Pyrite is widespread in the area, occurring as euhedral crystals scattered throughout certain phyllites and calcareous rocks. It is concentrated as thin, pinched out veins associated with quartz, and thick massive aggregates and pockets of sandy grains within the carbonaceous horizons. Above the massive aggregates in isolated places occur vugs with euhedral pyrite crystals. The possible presence of pyrrhotite Fe_7S_8 (magnetic and scratchable with knife) was not tested, but isolated chalcopyrite Cu Fe S_2 showing peacock iridescence was noted.

The weathering of iron sulphides by oxidation can take place by both atmospheric oxygen containing 21% free O_2 and dissolved oxygen in water which can be up to 35% (3% by volume). Thus, percolating waters in aerated conditions

will provide ample oxygen. In addition, the OH¹ and H¹ components of water provide further active chemical reagents, more particularly the H¹ which increases with temperature. The OH¹ H¹ dissociation increases with temperature and doubles between 0° and 30°C. This dissociation is further increased by the presence of free CO₂. In CO₂-saturated water, the H¹ concentration increases 300 or more times. Sufficiently high temperatures and the presence of CO₂ can be expected to exist near the rock surface to promote oxidation of pyrite.

The weathering of the iron sulphide progresses from the low valency ferrous towards high valency ferric hydroxides, ending up in the most stable mineral limonite :



The sulphuric acid generated in the oxidation/weathering of pyrite must have played an important role in the formation of the various sulphate minerals at Tarbela. During passage through igneous rocks, carbonaceous schists and calcareous rocks, it reacted with appropriate components to produce the sulphates. The action of sulphurous vapours associated with hydrothermally altered zones could also be a source. A survey of literature summarised in Palache *et al.* (1951) and Deer *et al.* (1962, vol. 5) suggests that all the sulphate minerals can be associated with pyrite weathering and oxidation. It is possible that the ponding of water in Tarbela Dam and consequent seepage of water in the neighbouring rocks has enhanced the process.

Huntite, a relatively uncommon carbonate, has been found in vugs in magnesite-deweylite rock in Nevada and is believed to have precipitated as a very fine powder from cool groundwaters which became magnesium-rich in traversing the magnesite deposit (Faust, 1953). In the Torrens Dolomite of south Australia, it occurs in sporadic nodules in fault zones and in brecciated shales at a depth of < 10 m beneath the present surface (Skinner, 1958). It also occurs in mines, caves, and as veinlets in the weathered crust of slightly serpentinized dolomite. The composition of this mineral suggests that it formed at the expense of either dolomitic rocks or clinopyroxene ultramafites (see Jan *et al.*, 1981) by the action of groundwaters or waters seeping from the Tarbela Dam.

The clay minerals (halloysite) may have formed from the alteration of acidic and feldspathic rocks (microgranites and/or albitites; see Jan *et al.*, 1981) under acidic conditions. It seems likely that they have been transported through faults as their presence is invariably the first indication of faulting. However, as they are easily transported by water, they would only be observed in fresh excavations for a limited period.

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