

Pollution implications of Save River water from weathering and dissolution of metal hosting minerals at Dorowa phosphate mine, Zimbabwe

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ABSTRACT

The study set out to determine the weathering and dissolution of metal hosting minerals at Dorowa for purposes of deducing pollution potential to the nearby Save River. Phosphate rock is mined at Dorowa for the production of phosphate fertilizer. The major minerals found in the ring complex are feldspars, pyroxenes, apatite, magnetite and calcite. Chemical analysis established that the rocks are associated with metals that include copper, lead, zinc, cobalt, nickel, tin and cadmium. Among the many minerals present apatite and calcite host metals more than the other minerals due to their crystal structure. This study investigated the weathering and dissolution of these two minerals. Both apatite and calcite dissolve in natural environmental conditions prevalent at Dorowa. From the analysis the study concludes that the potential availability of metals trapped in the calcite and apatite structures is high. The understanding of weathering and dissolution of metal hosting minerals is important in predicting quality of water around the study area, because most villagers use the Save River as their primary drinking water source.

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1. Introduction

Igneous rock phosphates are currently being mined at Dorowa mine in Zimbabwe. Mortvedt and Sikora (1992) and Kpomblekou and Tabatabai (1994) reported that these rock phosphates contain harmful elements (heavy metals and radioactive elements) that are toxic to human, plant and animal health. Substantial work on the mineralogy of the Dorowa ring complex has been carried out by Mennel (1946), Johnson (1961), Barber (1991), Walsh et al. (2001), Fernandes (1989) and Govere et al. (2005) but the pollution potential of the minerals around Save River has not been evaluated. This work discusses the weathering/dissolution of apatite and calcite, which are the minerals that were identified as host to metals, as these processes are responsible for releasing the metals bound in the minerals into the environment. The phosphates at Dorowa are mined from an alkaline ring complex that possesses structural, petrological, mineralogical and geochemical features similar to other phosphate deposits known in the world (Notholt et al., 1989). Thus the study at Dorowa can be applied to other phosphate deposits of igneous origin.

This work makes use of the available literature describing experimental studies of rates and mechanisms of the precipitation and dissolution of carbonate and phosphate minerals with particular references to calcite and apatite. The literature on dissolution of carbonates and phosphates (White and Brantley, 1995; Pokrovsky and Schott, 2000, 2001; Oelkers and Schott, 2001; Oelkers, 2001; Chou et al., 1989; Arvidson and Mackenzie, 1999; Lane and Mackenzie, 1990, 1991; Tribble et al., 1995; Valsami-Jones et al., 1998; Guidry and Mackenzie, 2000; Welch et al., 2002) was used to deduce potential dissolution of calcite and apatite at Dorowa. Consequently the data was used to derive water pollution implications for the Save River.

2. Materials and methods

2.1. Description of the study area

The study area is Dorowa mine (Fig. 1), located in the Buhera District of Zimbabwe at around 19°04'S; 31°46'E. The mine is exploiting a carbonatite of Mesozoic age that is associated with foyaite, ijolite and pulaskite (Barber, 1991). The rocks have been extensively mineralized with phlogopite, vermiculite and apatite. The main rock being mined at Dorowa is fluoro-apatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ which comprises more than 50% of the apatite. Carbonate and hydroxyl apatite rocks are also present (Fernandes, 1978). Mining is concentrated in two main centres within a syenite

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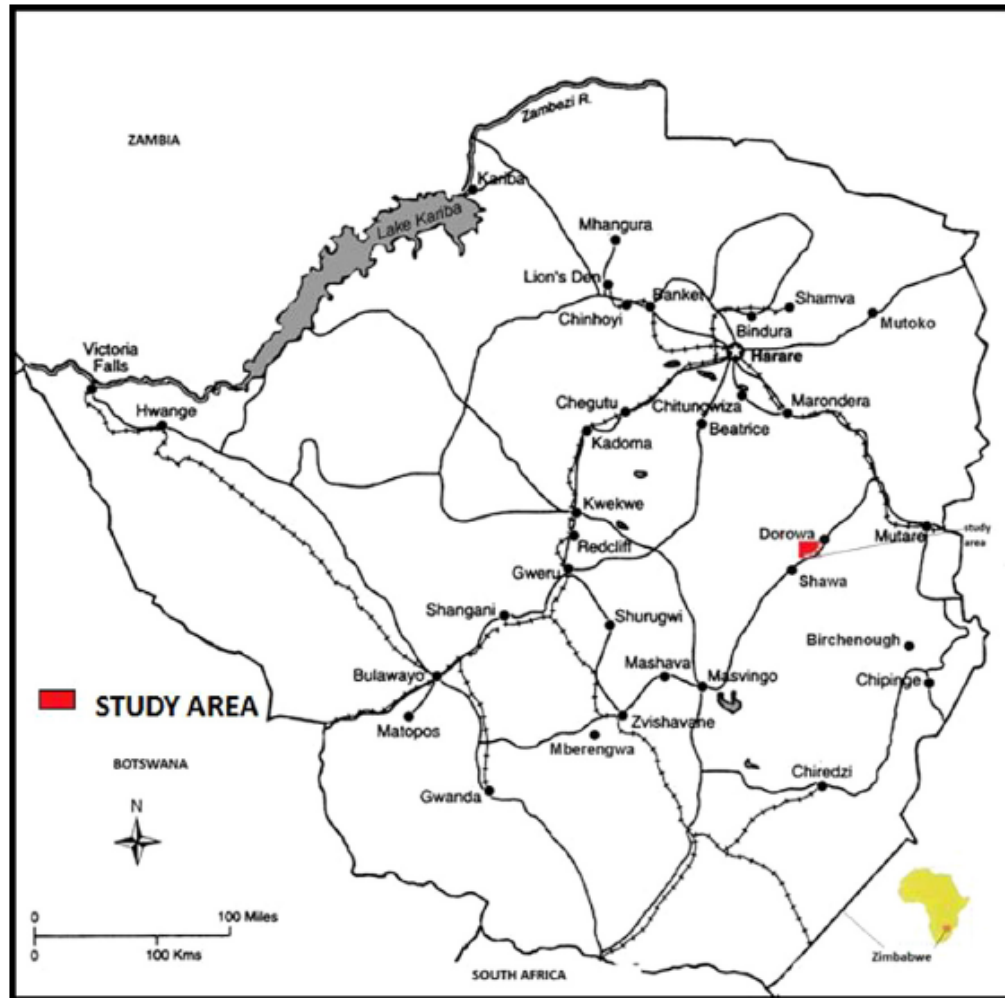


Fig. 1. Study area Dorowa Zimbabwe.

fenite at Dorowa known as the North and South pit. In the North pit apatite occurs as vermiculite apatite in the form of dykes, veins and stringers (Johnson, 1961) whilst in the South pit it occurs as apatite pyroxene.

2.2. Sampling

Pyroxenites, igneous carbonatites, iron oxides rocks and alkaline syenites are the main rock types in the study area (Fernandes, 1989; Barber, 1991). Carbonates and feldspar veins as well as ultramafic dykes also occur in the study area. During sampling an attempt was made to sample from all the major rocks that could be visually distinguished. Based on the mineralogy, fourteen (14) rock samples were analysed. These included five syenites, three pyroxenites, two apatite rocks, two dolerites, a magnetite rock and a carbonatite. These were collected from the two pits at the mine but the majority came from the North pit Fig. 2.

2.3. Analytical methods

The rocks were crushed and split into fractions by coning and quartering. In all cases it was ensured that the total sample for a rock was sufficient to properly characterize the rock described. The minimum size of the samples before coning and quartering was 2.3 kg. The crushed rock samples were ground and pulverized to pass through a 180 μm sieve. To minimize contamination of the samples with elements of interest, an agate mortar and pestle was used for grinding and pulverizing the samples.

X-ray diffraction was used to identify the major minerals present. The X-ray diffraction (XRD) patterns were recorded on un-oriented powder using an X'Pert Quantify Diffractometer with a Gonio Scan Axis and Cu anode. The start position [2°Th.] was 3.0100 whilst the end position [2°Th.] was 79.9900. A continuous scan with step size [2°Th.] of 0.0200 and scan step time of 0.5000s was used. The generator settings were 30 mA and 40 kV.

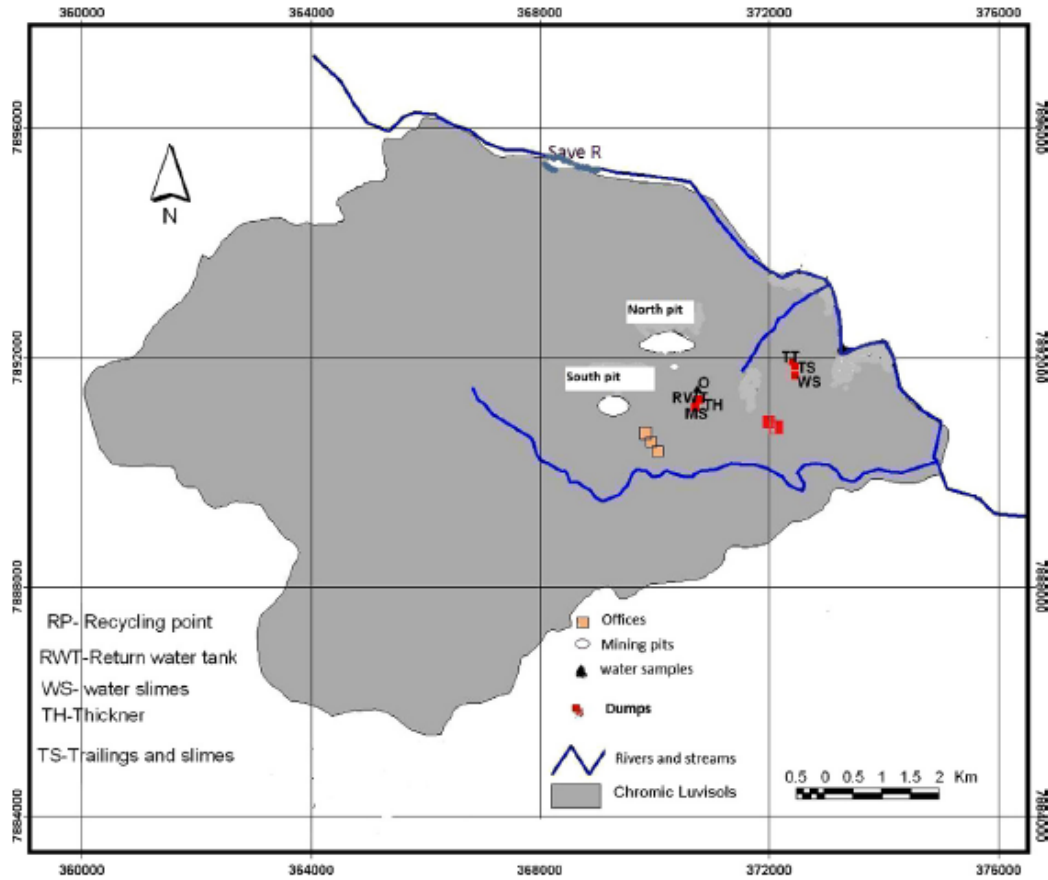


Fig. 2. Sketch map of the mine showing the relative position of the pits sampled.

The method used identifies all phases greater than 2% in the sample. The phases were indexed using Diffrac-AT software linked to a JCPDS database. XRD scans were matched, based on the so-called “figure-of-merit” with a standard mineral database [ICDD PDF2 (2002)] loaded in the X’Pert machine. All phases presumed to be present in a sample were evaluated by verifying peak by peak to see if there was a close match with the powder diffraction file.

The rock samples were also digested in 3:1 concentrated HCl and HNO₃ (aqua regia) and analysed with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for metal levels. Seven metals, namely copper, cobalt, nickel, zinc, lead, tin and cadmium were determined. Quality control included reagent blanks, duplicate samples, in-house reference materials and certified international reference materials (Ramsey et al., 1995). The precision and bias of the chemical analysis was less than 10%.

Table 1
Minerals present in the different rock samples as determined by XRD.

Sample name	Minerals	Rock name
Meck 1	Calcium carbonate, fluoro-apatite	Syenite
Meck 2	Ce-rich fluorapatite, augite, albite, montmorillonite	Dolerite
Meck 3	Albite intermediate, sodium tecto-alumosilicate, diopside, apatite	Apatite pyroxenite
Meck 4	Iron diiron(III) oxide, magnetite low, syn iron III hydrogen oxide, magnetite	Magnetite
Meck 5	Albite, ordered augite	Syenite
Meck 6	Diopside aluminian, syn augite, albite, fluorapatite, bytownite, enstatite	Pyroxenite
Meck 7	Hydroxyl apatite, syn iron di iron(III) oxide	Apatite rock
Meck 8	Augite, hydroxyl apatite, syn albite ordered	Pyroxenite
Meck 9	Calcite, montmorillonite-15A	Carbonitite
Meck 10	Diopside, hydroxyl apatite, albite,	Dolerite
Meck 11	Albite, calcium augite, lazurite, nepheline	Syenite
Meck 12	Albite ordered, anorthoclase disordered, montmorillonite	Syenite
Meck 13	Albite, ordered orthoclase, augite,	Syenite
Meck 14	Hydroxyl apatite, syn actinolite, magnetite, syn SiO ₂ , quartz	Apatite

3. Results

3.1. XRD results

Phases observed in the 14 samples are summarized in Table 1. The major minerals are feldspars, pyroxenes, apatite magnetite and calcite. Small peaks corresponding to clays were also observed, however these peaks were in most cases insufficient to determine the mineral present. The XRD results show the prevalence of apatite bearing minerals, (apatite, fluoro-apatite and hydroxyl apatite)

in the Dorowa Complex rocks. These observations compare well with the work done by previous researchers (Mennel, 1946; Johnson, 1961; Barber, 1991; Fernandes, 1989) and observations on igneous rock phosphates elsewhere in the world (Notholt et al., 1989).

3.2. ICP-MS results

The ICP-MS results shows that most rocks at Dorowa are associated with the metals copper, cobalt, lead, zinc, nickel, tin and cad-

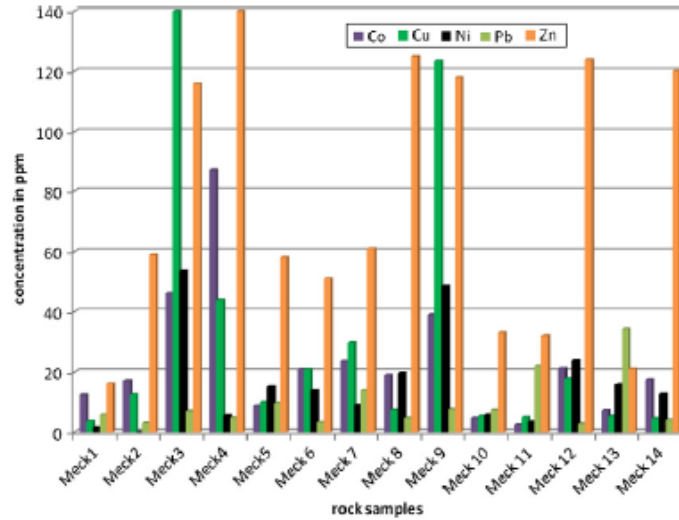


Fig. 3. Metal levels in the different rock samples. Cadmium and tin though present in the rocks are in low concentration.

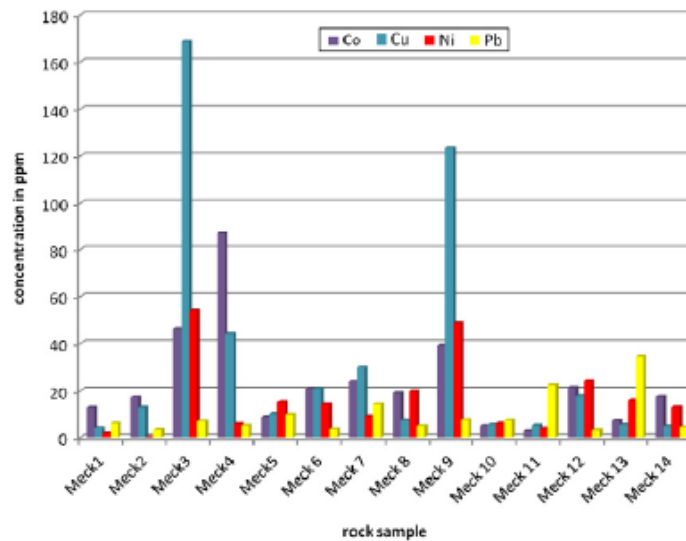


Fig. 4. Metal levels in the different rock samples. Zinc levels are generally high in all the rocks thus zinc was removed to clearly show the trend exhibited by the rocks.

Table 2
Chemical formulae for the minerals that are likely to host metals as observed in this study.

Mineral	Formula
Calcium carbonate	Ca (CO ₃)
Ce-rich fluorapatite	Ca _{9.653} Ce _{0.327} Na _{0.02} (Si _{0.127} F _{5.08} O ₂₄ F _{1.46} (OH) _{0.52})
Apatite	Ca ₅ (F, Cl)P ₃ O ₁₂
Fluorapatite	Ca ₅ (PO ₄) ₃ F _{0.4} Cl ₁
Hydroxyl apatite	Ca _{5.42} Si _{0.18} H _{0.4} (PO ₄) ₃ (OH) _{1.00}
Hydroxyl apatite	Ca _{10.042} (PO ₄) _{5.982} (OH) _{2.282}

mium. Figs. 3 and 4 show the metals associated with the different rocks analysed. The data shows that the rocks Meck 3, Meck 4, Meck 9 have the highest metal levels. Analysis of the XRD results in Table 1 show that these rocks contain magnetite, calcite and apatite. Rocks with no or low apatite and calcite have the low metal levels (Meck 1, Meck 10 and Meck 11). The rocks with fluoroapatite (Meck, 1, Meck2, and Meck6) have generally lower metal concentrations than those with hydroxyl apatite (Meck 7, Meck 8 and Meck 14).

4. Discussion

4.1. Metal-hosting minerals

Meck et al. (submitted for publication) analysed the phases identified in this study and established that the potential metal host among the many minerals present are apatite and calcite respectively. Table 1 and Figs. 3 and 4 confirm that calcite and apatite are likely to host metals more than the other minerals. The data presented in Table 2 shows that the various apatites found in the study area have a site that is hosting trace elements. This further confirms that these apatites have a potential for hosting and subsequently releasing the metals. In Table 2 the sites that would be occupied by metals are those occupied by Ca, Na, Sr and Ce in the given formulae. The dissolution and weathering of apatite and calcite is discussed here in order to ascertain how the metals may be released.

Lasaga et al. (1994) noted that dissolution rates and mechanisms are a function of mineral composition and environmental conditions. Accordingly the dissolution of mineral likely to host metals (Tables 1 and 2) are used to discuss the potential pollution of the Save River under prevailing conditions. Some of the variables that will affect the rate of dissolution/weathering include general solubility, temperature, pH, organic acid concentrations and surface area (Guidry and Mackenzie, 2000). These will be discussed in this report for the study area.

4.2. Apatite weathering and dissolution

Work on dissolution of apatite include that by Lane and Mackenzie (1990, 1991), Tribble et al. (1995), Valsami-Jones et al. (1998), Guidry and Mackenzie (2000), Welch et al. (2002) and Guidry and Mackenzie (2003). Apatite is generally soluble and though usually present only in trace amounts, it dissolves several orders of magnitude more quickly than most silicates (Nezat et al., 2008). Consequently it can be weathered from surface soils in only a few thousand years (Merrill, 1896). According to Atlas and Pytkowicz (1977), the neutral ammonium citrate (NAC) solubilities of igneous apatites are generally about 1–2% P₂O₅. The NAC for Dorowa phosphates was established by Fernandes (1978) as 0.8%. Though low for release of agricultural phosphorus, 0.8% NAC solubility is still of concern where the phosphate contains metals as is the case with Dorowa. At prevailing conditions (NAC 0.8%) the phosphates will dissolve and release metals.

The processing of the ore at Dorowa definitely makes the apatites more soluble. Atlas and Pytkowicz (1977) reported that the

surface area of apatite particles had a pronounced effect on solubility. Grinding provides 'fresh' particle surfaces, increases geometric surface area, and increases solubility. Studies by the International Fertilizer Development Center (IFDC) of phosphate rocks with high NAC solubilities indicated that NAC solubilities of phosphate rocks can increase from about 60% to 120% with grinding to minus 200 mesh. The grinding of phosphate rocks at Dorowa produces slimes that are less than 45 µm and tailings in the range 45–300 µm thereby increases the solubility. Surface area effects on the solubility are reported in full by Greenwald (1942).

Smith et al. (1974) described incongruent dissolution and surface complexes of hydroxyl apatite. At Dorowa several rocks contain hydroxyl apatite (Table 1) thus incongruent dissolution peculiar to these apatites is expected. Guidry and Mackenzie (2003) noted that from pH of 2 to 6, the rate of release from dissolution of all apatite components [calcium (Ca), phosphorus (P), and fluoride (F)] increased with decreasing pH for igneous fluorapatite (FAP). From pH of 6 to 8.5, the FAP dissolution rate is pH independent. The pH of the waters around Dorowa is around 7–8 thus it can be concluded that the dissolution of FAP at Dorowa is not influenced by pH. A surface, not diffusion controlled dissolution reaction is thus expected at Dorowa as suggested by Guidry and Mackenzie (2003) and Welch et al. (2002). According to Guidry and Mackenzie (2003), both the surface area of igneous rock available for weathering and the average temperature are important factors in determining the apatite dissolution. Temperatures at Dorowa which are around 25 °C on average encourage apatite dissolution.

The Oral Environment (2008) noted that fluorapatite is less soluble and has a lower solubility product (about 20% less soluble than hydroxyl apatite) when the solubilities, measured as the concentration of calcium, are compared. The main apatite at Dorowa is fluoroapatite, though carbonate and hydroxyl apatite are also present (Fernandes, 1978). This implies that the apatite would dissolve at different rates and with major apatite releasing the metals slower than the minor apatites. The Oral Environment (2008) and Greenwald (1942) report an increase in phosphate solubility with increasing carbonate. Thus the abundant carbonates (calcite, magnesite and dolomite) at Dorowa will likely increase the solubility of apatite.

4.3. Calcite weathering and dissolution

Calcite belongs to the carbonate group of minerals which are amongst the most reactive minerals on the earth's surface. According to Konhauser (2007) rates of calcite dissolution are transport controlled at pH less than 4. Therefore at Dorowa where pH is between 7 and 8 the dissolution rates are not transport controlled. Calcite dissolves congruently at rates that are orders of magnitude faster than that of silicate minerals and at much higher pH values (Morse, 1983). Thus the high pH at Dorowa is not a hindrance to calcite weathering. Water carrying small amounts of carbonic acid readily dissolves calcium carbonate rocks with which it comes in contact. Mass balance from the experiments by White (1998) indicated that calcite was completely dissolved in a short time when it leached out of the column material after 2 years where solubilities of several minerals were being tested. White (1998) concluded that this is consistent with the lack of measurable calcite in the naturally weathered granitoids in the watersheds. The rapid weathering of calcite implies that metals that may have been bound in the lattice are easily released into the environment.

Unlike feldspars where the weathering products might accumulate on the mineral surface causing the rate of dissolution to decrease, the carbonate ions that detach from the crystal surface are chemically altered to bicarbonate (Konhauser, 2007) which facilitates more dissolution.

Merrill (1896) stated that the alkaline carbonates are among the most soluble substances known. For example the carbonate of soda requires for solution only six times its weight of water at ordinary temperatures unlike silica, which, even in its most soluble form requires ten thousand times its weight of water for solution. The carbonates at Dorowa are alkaline therefore likely to dissolve more readily.

5. Conclusions

The reactions of apatite are complex and involve non-equilibrium processes (Atlas and Pytkowicz, 1977; Dietz et al., 1964; Smith et al., 1974) and those of calcite are simple. Nevertheless both apatite and calcite dissolve in natural environmental conditions prevalent at Dorowa. The conditions prevalent at Dorowa that will abet dissolution include the grinding of the apatite rock, the alkaline nature of the carbonates, and the co-existence of apatite and calcite and high temperatures. The alkaline pH at Dorowa is one of the few factors does not aid the dissolution of apatite. Since both the apatite and calcite at Dorowa will easily dissolve and release metals bound in their structures, the pollution potential of the Save River is high.

This study of the dissolution rates of minerals hosting metals has yielded information that can be used in modelling water quality. Garrels and Mackenzie (1971), Garrels et al. (1975), Holland (1984), Delaney (1998) and Guidry et al. (2000) have shown that the weathering of apatite controls the long-term availability of phosphorus. Since both apatite and calcite are hosting the metals it therefore implies that their weathering/ dissolution will also control metal availability thereby control long-term pollution potential. The metals in the Save River have not reached significant levels to cause threats to the environment at the moment but there is need to monitor the water as there is potential threat resulting from accumulation.

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