

Geochemical characterisation of surface waters and precipitates in Nenthorn historic gold mine, East Otago, New Zealand

L David Ok Tedi Mining Limited, Papua New Guinea

Abstract

Nenthorn is one of the historically mined gold districts in East Otago, Southern New Zealand. After mining ceased in the early 1900s, the mine battery and adits have exposed fresh schists and mineralised gold-bearing quartz vein that has undergone continuous chemical weathering and alteration reactions mainly involving, arsenopyrite (AsFeS) and calcite (CaCO₃); producing alkaline waters (pH range of 7.5 to 8) with elevated trace elements. Oxidation and dissolution of sulphide (ore) minerals usually results in elevated sulphate and other heavy metal concentration in mine waterways, hence creating a potential environmental concern. However, with semi-arid climates like East Otago, the occurrence of ochreous precipitates and efflorescence are common. Water samples and precipitates were collected from the mine workings and the adjacent creek to determine the major and trace element content in a one-time sampling program. The analytical data shows elevated concentration of trace elements in precipitates than the water samples, however, the study site was identified as not extremely concentrated or contaminated with heavy metals. The ochreous precipitates samples used for this study most likely formed from the precipitation of supergene alteration minerals like iron hydroxysulphates and iron oxyhydroxides, and primary minerals like arsenopyrite due to the elevated concentration of Iron, Arsenic, and Manganese. The sorption of metals like Copper, Lead, and Zinc to oxyhydroxides of Iron and Manganese sulphates could explain the absence of these metals in the water samples. The circumneutral pH of the water is caused by calcite dissolution, leading to very high Calcium (Ca) concentration in all the samples analysed, however highly undersaturated concerning halite, gypsum, and calcite. Conclusively, it was observed that in the Nenthorn area, arsenic concentration is above the maximum acceptable values for inorganic determinants of health significance in New Zealand. Contamination of surface waters quality in the abandoned Nenthorn mines is small enough that it does not affect the Deighton Creek just downstream. However the study does reflect the potential for even small mineral deposits to actively engage with the surrounding geochemical environment.

Keywords: *Historic gold mine, trace elements, heavy metals, arsenopyrite, iron oxyhydroxides*

1 Background-Nenthorn historic gold mine

Nenthorn is located in the Waitaki District in East Otago, South Island, New Zealand. This historic gold mine site is now a conservation area (Figure 1) that is managed by the department of conservation (DOC). Deighton Creek channels through the gorge adjacent to the old mine workings and feed the Nenthorn stream southeast of the mine. Nenthorn stream is a major tributary of Taieri River from eastward of the Moonlight hills (Ryder & Mandy 2020). Nenthorn stream is well-known for its herpetological and botany conservation values (Bibby 1997), and is considered by Dunedin City Council as the area of significant biodiversity value (Ryder & Mandy 2020). Otago has one of the diverse climates of any region in New Zealand. The region is within the latitudes of prevailing westerlies with strong winds experienced along the coastal areas and dissipates as it progress inland. The highest rainfall is experienced within the summer months (Macara, 2015).



Figure 1 (a) Google Map location of Nenthorn with reference to Dunedin and Macraes mine; (b) Nenthorn conservation area managed by DOC

Nenthorn is one of the significant orogenic gold districts mined historically. It is hosted within the Otago schist, a regional metasedimentary belt that is categorised as orogenic gold deposits (Craw and Norris, 1991; Craw 2003; Martin & Cox 2016), which includes the current Macraes mine located 30km from Nenthorn. It has operated from 1988 to 1904 and exploration work has been ongoing up till 2010 (Martin & Simon 2016). Gold-bearing quartz occurred with major ore minerals scheelite (CaWO_4), stibnite (Sb_2S_3), and arsenopyrite (FeAsS), along with minor sulphide like pyrite (FeS_2), sphalerite (ZnFeS), and galena (PbS). The catchment lithology of the Nenthorn area is mostly quartzofeldspathic schist and minor metabasites with cover sediments or volcanic (Craw et al. 2009; Craw & McKeag 1987; Martin et al. 2016).

Since the closure of this mine in the early 1900's, not much study has been conducted to quantify the distribution of trace element within the surface waters and determine the precipitates formed within the exposed wall of the historic mine shaft and audit.

Based on an environmental perspective, metals and metalloids like lead (pb), cadmium (cd), copper (Cu), chromium (Cr), iron (Fe), nickel (Ni), aluminium (Al), manganese (Mn) and arsenic (As) are vital in mine-related waters since they are toxic for the ecosystem when present in high concentration. This University research is the first environmental geochemistry study conducted on the closed historic mine to:

1. Determine the geochemistry of the surface water and precipitates based on the concentration of major and trace elements and
2. Identify the mechanism that influences the distribution of metals and metalloids within the surface waters and precipitates.

A total of 7 surface waters and 3 precipitates within the historic mine workings and adjacent Deighton Creek were examined. The water samples were filtered, acidified and sent to the University of Otago, centre for Trace Element Laboratory for trace element concentrations. The anion analysis for this study includes chloride and sulphate measurements which were conducted at Hill Laboratory.

The precipitates were initially tested for elemental composition using a Portable X-Ray Fluorescence Spectrometry (pXRF) and tested for crystalline property using X-ray diffraction instrument (XRD). The remaining solid from the crushed precipitates were prepared for trace element analysis. The results were semi quantitative due to the inhomogeneous and porosity of each sample.

2 Methodology

2.1 Water sampling

The water samples analysed for this study were collected from 4 different locations. The samples were collected on the 11th of February, 2021. Four samples were collected along Deighton Creek, two were collected from the main mine shaft while the other two samples were from the mine adits. Deighton Creek's flow rate was not measured at the time of sampling. The sampling locations at Deighton Creek and the mine workings are shown in Figure 2 while the descriptions are outlined in Table 1. Water samples for anions (sulphate and chloride) measurements were collected using three 150 ml bottles while the other 5 water samples were collected in 125 ml for the trace elements and major cations. The insitu measurements for the water samples were the pH and temperature which was taken at the sampling site using an Oakton waterproof pH metre.

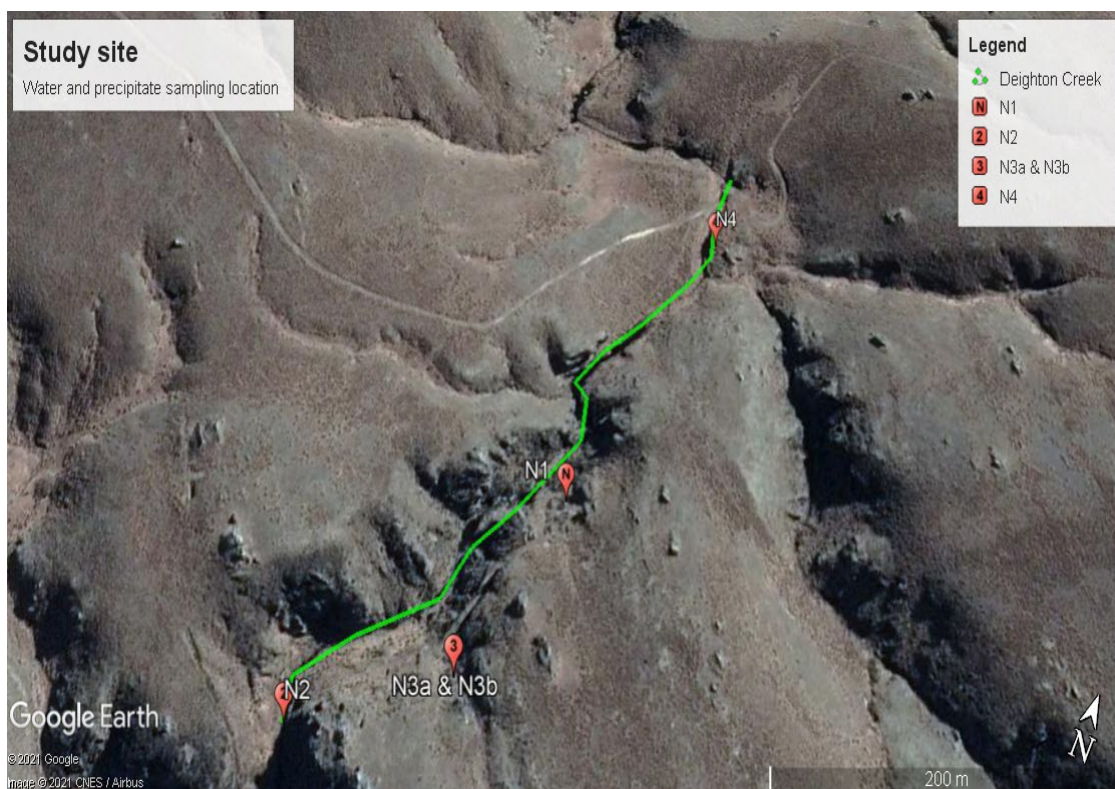


Figure 2 Location of Nenthorn Battery and Deighton Creek where the water samples and precipitates were collected. The precipitates were collected only in the mine workings

Table 1 Description of the locations of the water samples from upstream Deighton Creek to downstream and the subsequent mine workings

Name	Description
N2	This sample was collected from Deighton Creek, upstream of the mine. Stream sediments and the exposed outcrops were observed to be of schist. Primary studies of this area identified a few mineralised faults crosscutting the stream. One of the main faults transects about 50m upstream of this water sampling site. This is the mineralized quartz fault zone that was excavated for gold in the late 1900s (Martin & Cox 2016).
N3 (a and b)	The sample was collected in the adits. The sample was collected on the floor and wall of the tunnel, mainly a water-wet patch. The tunnel wall, backs, and face were extremely oxidized with gunge of precipitates of mostly oxides as observed from the clayish texture and reddish-orange colour.
N1	The sample was collected in the main mineshaft of the Nenthorn historic gold mine. Water filled the shaft to the surface and overflowed to the entrance of the shaft. The surrounding walls were highly weathered and extremely oxidized clayish material of schist origin.
N4	This sample was collected from Deighton creek, downstream of the mine. Its location is at a low altitude with hills on the sides. Water sediments consist of eroded material from the hills as well as being transported from upstream.

2.1.1 Laboratory measurements

The water samples were filtered through 0.45 µm pore diameter filter papers composed of a mixture of cellulose (Millipore HAWP) of 47 mm diameter and pumped using a vacuum pump. The filter system was cleansed with Milli-Q water after and before the acid rinsed with concentrated nitric acid (HNO₃) in between the actual filtration of each sample. Small amounts of the actual water from each sample were also added into the filter system, rinsed, and filtered out before the actual filtering of each sample. After the filtration process, the samples were put through the acidification process to preserve the trace elements in the solution and reduce microbial activity, precipitation, and sorption losses to the walls of the bottles. The water samples for this study were acidified to 2% weight with quartz-distilled concentrated nitric acid (i.e. 1 g of HNO₃ per 50 g of water sample) after the filtration process. A split for each sample was sent to the University of Otago, centre for Trace Element Laboratory for trace element concentrations using the Agilent 7500 quadrupole ICP-MS.

To minimize and avoid contamination of the samples, all preparation work was carried out in the clean laboratory in laminar flow hoods. Appropriate collection and processing steps were undertaken to avoid sample contamination or prevent the samples from cross-contamination.

The anion analysis for this study includes chloride and sulphate measurements which were conducted at Hill Laboratory. The samples were filtered at Christchurch and analysed by Ion Chromatography, APHA 1-10 4110 B methods. Testing was conducted from 19th to 20th April 2021.

2.2 Precipitates sampling

The precipitate samples (Figure 3) were scooped from the tunnel wall and placed into a 50 ml DigiTube using a plastic spatula. Three samples only were collected from the main shaft (N1) and the adit (N3a and b). The samples at N3 were chipped off from the wall and the back of the tunnel. N3a was a sample at the

end of the adit (back) and N3b was collected from the sidewall of the adit (where the dripping water or N3b was sampled). Each solid sample was labelled and packed separately in a zip lock bag and transported back to the department for analysis.

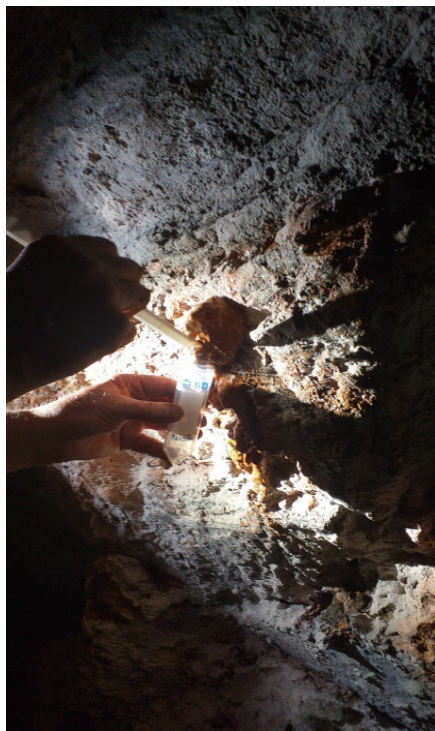


Figure 3 Precipitate and efflorescence formation on the mine's adit where N3b was sampled

2.2.1 *pXRF and XRD preparation*

Chemical analyses of the three precipitates samples were acquired through an Olympus Innov-X Systems model XPD-4000 field portable X-ray fluorescence instrument (fp-XRF) contained in the Otago University's Geology department. The measurements were taken in soil mode and at a 30s beam interval for all measurements. Before the measurements, each sample was dried in the oven at 60°C temperature for 24 hours. After the drying process, they were crushed into a fine silt size of ~150 µm for pXRF and XRD using a mini porcelain mortar and pestle grinding bowl. Diffraction patterns were analysed numerically with PANalytical software.

The remaining solid from the crushed precipitates were prepared for trace element analysis. The preparation process includes digestion and dilution before the samples were sent to the Centre for Trace Element for ICP-MS. The samples were digested for 24 hrs at 105°C, dissolved with 5ml of hydrochloric acid and centrifuge (1 sample only) at a speed of 4000 rpm for 5 to 10 minutes. This was followed by the dilution process where 5 ml of 2 % HNO₃ was added to each sample and left to dry for 24 hrs at 90°C, packed in ICP-MS vials and dispatched to Centre for Trace Elements for ICP-MS test.

3 Results

3.1 Major and trace elements

Major cation (Ca, Na, K, and Mg), trace element concentration, and anions were measured for the water samples respectively. Water for both Deighton Creek and mine workings were near-neutral with pH of 7.5, 8.5, 8.5, 7.6, and 7.69 respectively; from upstream (N2) to downstream (N4) of the mine. All water samples

had a significant concentration of trace elements. Heavy metals and metalloids (Al, As, Cd, Cr, Cu, Fe, Ni, Mn, Pb, and Zn) for both the mine workings and Deighton Creek reported were above detection limits. Figures 4 to 7 are plots for some of the elements, including the anions (Cl and SO₄) and the major cations ternary diagram. The results are presented in parts per billion (ppb) except for anions data that are presented in parts per million (ppm).

The major cations tend to co-vary across the study site. However, waters collected from the mine adit (N3a and b) tend to be elevated about Deighton Creek. For example, Ca reported concentrations of 21100 ppb in N3a and 20300 ppb in N3b while in Deighton Creek, it reported a distinctively lower concentration of 2480ppb at upstream (N2) and 2440 ppb for downstream (N4) respectively. Magnesium concentration trend is similar to Ca, yet not considerably high in concentration compare to Ca for the adit waters. Mg is lower in N1 compare to the rest of the samples whereas N3a and b are higher than Deighton Creek. Moreover, Na concentration in all 8 water samples is fairly steady with the highest concentration levels generated by N3a and N3b (7710 ppb and 7560 ppb respectively), followed by N1 with 6350 ppb and slightly decreases downstream of Deighton Creek (5810 to 5170 ppb).

With the other trace elements, the results also co-vary between the mine workings and Deighton Creek. Iron concentration for N3b shows the highest concentration for all the water samples with 708 ppb Fe. Unlike Ca concentration for N3a having slightly the same concentration with N3b site, Fe concentration for N3b (water puddles from the edit's floor) is somewhat lower with 181 ppb Fe. N1 reported the lowest concentration of Fe (28.7 ppb) while upstream Deighton Creek reported 254 ppb Fe and downstream is 264 ppb Fe. Similarly, As concentration reported the highest for N3b with 94.8 ppb, N3a had 74.7 ppb and N1 with 31.8 ppb. The lowest arsenic concentration was generated from the creek with concentration decreasing downstream.

Furthermore, the anions (Cl and SO₄) concentration for this study is more homogenous for the Deighton Creek and slightly high in mine shafts water samples. N3a and b had no anions data due to low water samples at the time of sampling. In terms of major cations composition in the water samples, a ternary cation plot is shown in Figure 8. Three of the samples (Deighton creek and mine shaft) plot close to the Na + K apex, especially N1 is closer to seawater, whereas the mine adit waters plot closer to the Ca apex and river water composition.

3.1.1 *Deighton Creek*

Deighton Creek (N2 and N4) from above and below the mine area samples have relatively similar trace and major cation elemental concentrations. Na is the major cation with a considerably similar concentration of 5810 ppb upstream N2 and 5770 ppb downstream N4 of Deighton Creek. Figure 4 shows the trace elements in a column graph display for Deighton. As can be seen, the highest metal concentration is Fe, followed by Al and Strontium (Sr). Given that Deighton Creek had analyses for Cl, the milliequivalents calculation was made for Cl: Na ratio in both of the samples and it shows the influence of seawater.

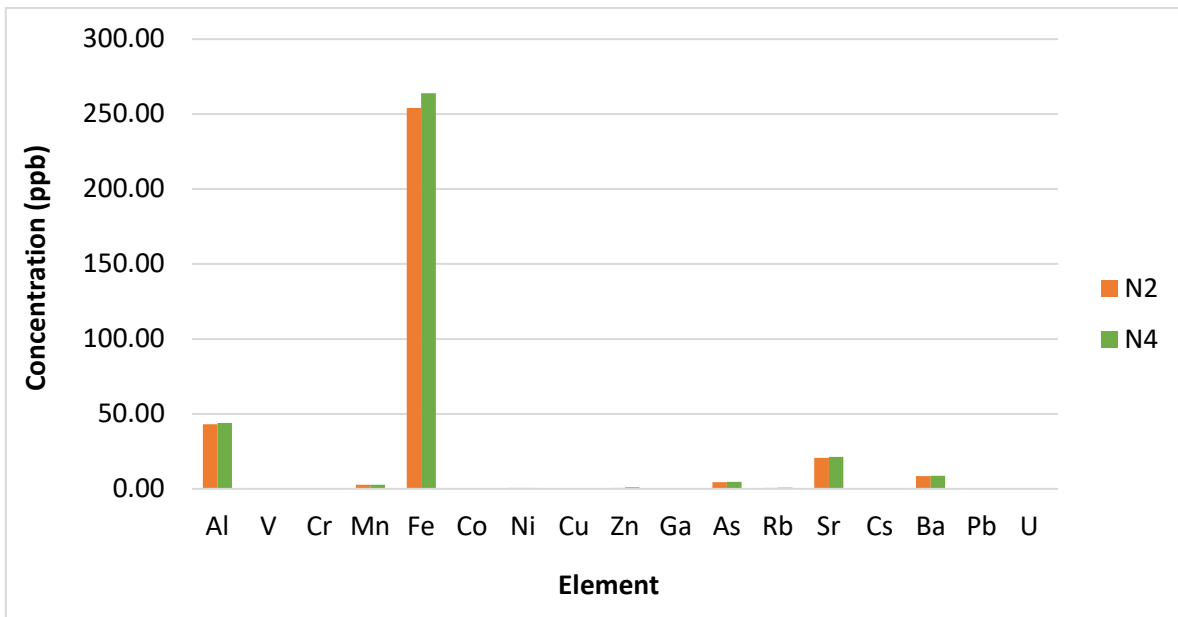


Figure 4 Trace element concentrations of Deighton Creek water samples upstream (N2) and downstream (N4) of the mine

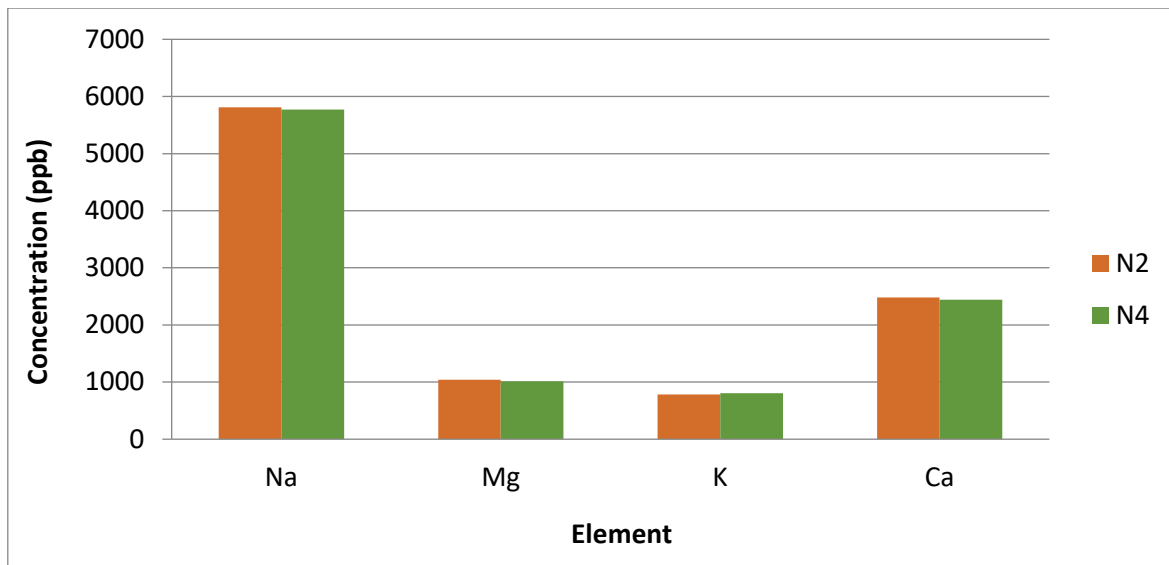


Figure 5 The major cation concentrations for Deighton Creek upstream (N2) and downstream (N4) of the mine

3.1.2 Nenthorn mine working waters

The sample collected directly from the mine adit and shaft varies distinctively from Deighton Creek, both major cations and trace elements. The mine shaft reported high concentration compare to the mine adit (N1). Na does not vary distinctly like Ca but has a slightly lower concentration in the adit compare to the shaft water (Figure 6). Most of the trace elements for the mine waters are below 1 ppb (Figure 7), except for As, Fe, Al, and Mn. Iron is the highest in N3b with 708 ppb and lowest in N1 with 28.70 ppb. Similarly, arsenic had 134 ppb for N3b and lowest at N1 with 31.80 ppb As. The water from the adit wall showed an

elevated concentration of all the elements analysed for this study. Mine shaft shows result more like the creek than N3a and b which had similar concentration.

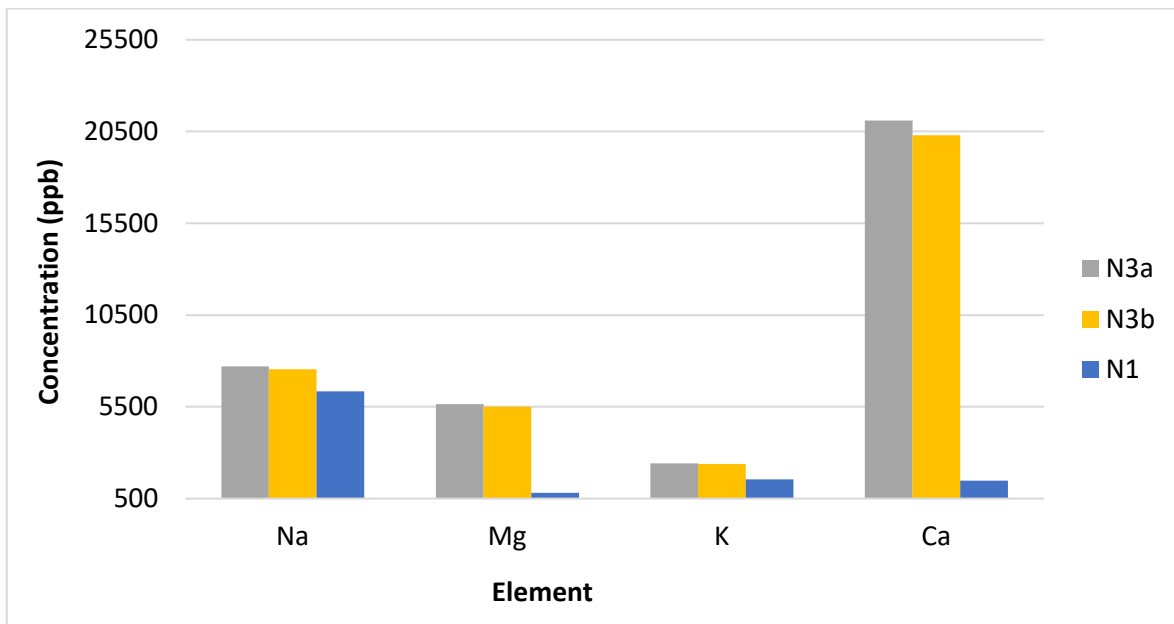


Figure 6 Major cations concentration for Nenthorn's mine adit (N3a and b) and shaft (N1)

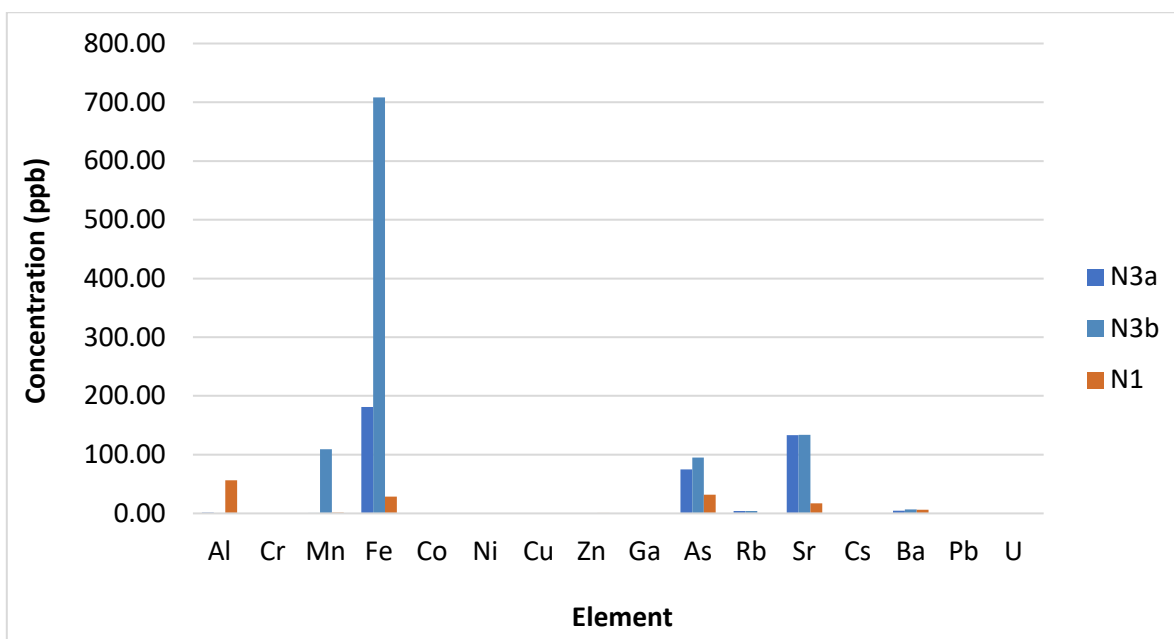


Figure 7 Trace elements concentrations for Nenthorn's mine adit (N3a & b) and shaft (N1)

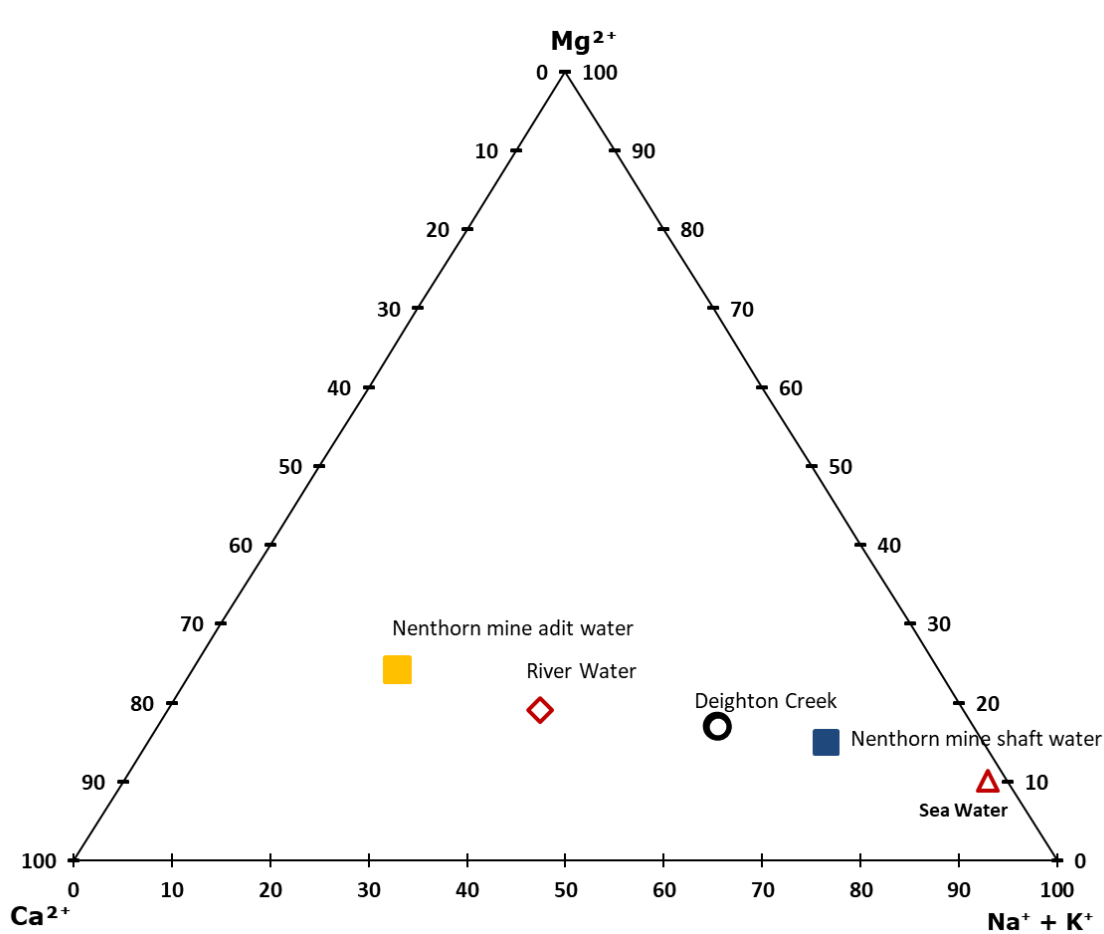


Figure 8 Ternary plot with sample locations from Deighton Creek (N2 and N4) and Nenthorn mine workings (N1 = Blue and N3a/b = Orange shaded square). Three of the samples plotted close to $\text{Na} + \text{K}$ apex, especially N1 closer to sea water composition while the adit waters plotted close to Ca apex and river water composition. River and seawater data source (Chester, 2009)

3.2 Geochemistry of the precipitates

The precipitates were initially tested for elemental composition using the pXRF which the results are plotted in Table 2. However, these results are semi quantitative due to the inhomogeneous and porosity of each sample. For example, N1 had more quartz than N3a and N3b, leading to valuable dilution of the precipitate concentration. Although the data are semi-quantitative, pXRF measured some weight percentage (wt. %) of metals like Fe, As and Mn with the highest recorded for N3a with 1.32 wt. % As, 29.94 wt. % Fe and 1.067 wt. % Mn respectively. These results were close to the mass % calculated for the same three elements using the ICP-MS results. All precipitates samples are amorphous solids as shown by the XRD analyses, producing peaks with low intensity or more diffuse compare to crystalline material that would generate high peak intensity. Fe had the highest elemental concentration of 7.6 %, 22.23 %, and 25.51 % Fe for N1, N3a, and N3b respectively. The second most abundant element is As with 0.27 % As in N1, 0.91 % in N3a, and 1.13 % in N3b. Mn is present in N3a with 1.14 %, 0.77% in N3b but is below the detection limit in N1. Other elements with > 1000 ppm are Al (in N1) and Ca with 1.13 % and 0.72 % at N3a and N3b respectively. Not all elements were detected in all three solids, especially the heavy metals.

Table 2 Bulk analyses for the chemical composition of the precipitates analysed using the pXRF. As can be seen in wt. %, there exists a substantial amount of As, Fe, and Mn within all three of the solid samples analysed. The other metals are lower than the detection limit

Sample ID	Description	Units %	As	Fe	Cr	Cu	H g	Ni	Pb	Sb	Cd	Zn
N3-a	Audit back, extremely friable, mucky and clayish gunge, extremely oxidised	–	1.32	29.94	0.02	0.00	0.00	0.00	0.01	0.01	0.01	0.00
N3b	Audit roof, extremely friable, mucky, and clayish gunge, extremely oxidised. Collected whilst water still dripping	–	0.78	19.26	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00
N1-main	Quartz with oxidised clay silt-sandy texture, less mucky than the other two	–	0.26	7.71	0.02	0.01	<LOD	0.01	0.01	0.01	0.01	<LOD

4 Discussion

4.1 Geochemistry of surface water

The geochemistry of surface water is influenced by several sources and mechanisms such as carbonate dissolution, silicate weathering, and the lithologies within a drainage system. With mine-associated waters, the characteristics of surface water tend to vary greatly, subject to the location of tailing impoundments, ore and waste rock type, weathering, and climatic effects such as rain patterns. All the water in this study has a pH greater than 7 with mean pH of 7.83. Despite the occurrence of pyrite and arsenopyrite oxidation which resulted in the precipitate formation, there is negligible acidification of the discharge waters based on the pH. Samples from Deighton Creek, upstream (N2), and downstream (N4) of the mine have almost identical concentrations.

In general, the major element concentrations are higher in the Nenthorn adit samples compared to Deighton Creek. In terms of the potentially toxic elements (Al, As, Cd, Cr, Cu, Fe, Ni, Mn, Pb, and Zn), the water dripping from the adit wall (N3b) has a higher concentration compared to the other sites. Ca and Sr are high in concentration in N3a and N3b samples compared to the other samples. This may be due to the dissolution of carbonate in the surrounding host rock. Any acid produced by pyrite oxidation would tend to

be neutralised by the abundant presence of calcite that is present in joints and fracture surfaces and within the host rock (Craw, 2000). The dominance of calcite dissolution in water chemistry related to unoxidised rocks would result in high acid neutralising potential that would exceed the acidity that can be generated by sulphide minerals such as pyrite and arsenopyrite (Weightman et al. 2020). When there are no fast-acting neutralisation minerals such as calcite in a groundwater system or stream and minerals such as quartz and silicates are predominant, the movement of the acid plume would be as fast as the flow of water (Zeman, 2004).

The ternary cation diagram in Figure 8 displays the $\text{Ca}^{2+} - \text{Mg}^{2+} - (\text{Na}^+ + \text{K}^+)$ milliequivalents of water from Deighton Creek and Nenthorn mine workings. All waters are low in Mg and range in Ca, however, have a significant amount of $(\text{Na}^+ + \text{K}^+)$. Mine shaft water plot very close to seawater whilst Deighton creek plot in between seawater and river water (Chester 2009). For the adit waters, Fe and Ca were evident for both N3a and N3b, thus plot more closely to Ca apex.

The Ca/Na ratios of mean crustal continental rocks are close to 0.6 and low Ca/Na molar ratios are expected in waters draining principally from silicate rocks due to greater solubility of sodium relative to calcium (Taylor & McLennan 1985). The water samples are shown on a plot of Mg/Na vs. Ca/Na in Figure 9. The result of this study support well this observation and the data collected from numerous studies that focused on waters channelling from silicate lithologies (Plumlee 1999; Jamieson et al. 2015; White & Blum 1995). Based on the 7 water samples for this study, the mine adit samples are characterised by high Ca/Na and Mg/Na ratio whilst the Nenthorn shaft (N1) has low Ca/Na and that is similar to Deighton Creek. This indicates that there is an influence of carbonate dissolution on the audit samples. In addition, the cations composition of the samples is similar to the lithology of the catchment within Nenthorn, which is dominated by Torlesse terrane derived from Otago schists whose principal minerals are quartz, muscovite, feldspar, and biotite (Mortimer & Roser 1992).

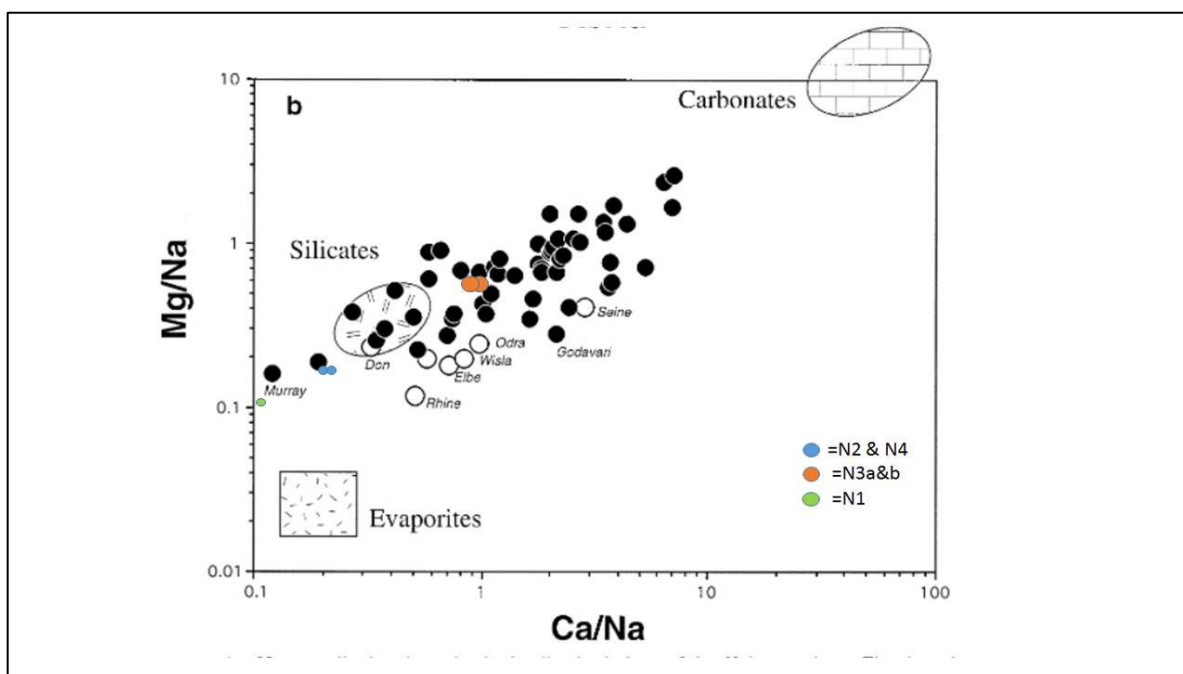


Figure 9 This diagram shows Deighton Creek (blue solid circles) and mine workings waters (Orange circle=adit, Green circle=mine shaft) samples amongst other rivers draining in different lithologies. Deighton Creek and Nenthorn mineshaft water samples plotted within the silicate

endmember whilst adit waters plotted further towards the Carbonates endmember. This diagram has been modified from Gaillardet et al. 1999 to include the ratios for this study

4.1.1 *Geochemistry of precipitates*

The solid samples consist principally of amorphous material as indicated by XRD analysis. Quartz is present in the sample that was collected from the main shaft (N1). Fe-oxyhydroxides (HFO) are fine-grained (micrometre scale) and X-ray amorphous. HFO's occurrence is common in the Macraes mine region (Mains & Craw 2005; Kerr & Craw 2020). HFO forms from the remnants of the historic mine processing residues and modern processing systems. Products of mine waste/pit wall weathering are Fe-oxyhydroxides, jarosite, and clays (Diehl et al. 2006). Iron and arsenic were dominant in the precipitates. High composition of Fe indicates sulphide weathering and leaching of minerals from the exposed adit walls. Table 2 shows the analytical data for the 3 precipitates samples for this study. Based on the calculated mass distribution, the heavy metals in precipitate samples display the following trend:

- Main shaft (N1) : Fe > Al > As > Ni > Cu > Pb > Zn > Cr > Cd > Mn
- Adit back (N3a) : Fe > Mn > As > Ni while other metals are below detection limit
- Adit wall (N3b) : Fe > As > Mn > Ca > Zn > Ni > Pb while other metals below detection limit

According to Weightman et al (2020), near-neutral to alkaline pH of the waste rock waters ensure that Fe³⁺ and Al resulting from alteration reactions are insoluble, yet minor colloids of Fe oxyhydroxides are transferred locally within the waters and deposited with aragonite precipitates. Groundwater-driven reactions of unaltered waste rock minerals such as chlorite produce alteration minerals like kaolinite and Fe oxyhydroxides; also dissolved components in surface groundwater.

4.1.2 *Mechanisms influencing the surface water geochemistry*

The main mechanisms influencing the co-vary concentration of major and trace elements in Nenthorn mine workings and Deighton Creek are dissolution of the primary ore minerals from host rock and precipitation of secondary minerals. However, seasonal variations and the semi-arid climatic condition of the Nenthorn area also could influence the surface water geochemistry. According to Craw and Kerr (2017), groundwaters would have near-neutral pH and overall evolution from Na-Cl rainwaters to Calcium hydrogen carbonate (Ca-HCO₃) waters. A comparison of Na to Cl was made to see the influence of seawater on the water samples for this study. Using mEq Cl to Na, the results shows, 0.7366, 0.7148, and 0.75298 for three of the water samples from upstream N2 to downstream N4. This ratio shows Cl and Na dominant thus indicative of seawater influence.

In addition, carbonate speciation was estimated and it shows a high proportion of Hydrogen carbonate (HCO₃) water for all three of the water samples, suggestive of river water chemistry. The estimated proportions for HCO₃ are 0.9448, 0.9266, and 0.9490 corresponding to upstream N2, mine shaft, and downstream N4 waters. The saturation state for calcite was also calculated and the ionic activity potential resulted in a negative value, indicating the waters were highly undersaturated concerning halite, gypsum, and calcite. Generally, if there is an increase in Na and Cl, this indicates halite dissolution, whereas when Na only increases without Cl, it normally is inferred as Na released from silicate weathering. With the water samples, silica was not measured, however, given that the water being categorised as highly undersaturated, the Na and Cl increase would not be due to halite dissolution. The other factor that could contribute to the elevated concentration of Na in the waters would be silicate weathering.

Cations tend to be easily exchanged than anions and pH does control the exchange process. The concentration of chemical species in natural water systems and water quality is influenced by mineral dissolution and alteration (Abanda & Hannigan 2007). The significance of anions for this study is to

determine the sulphate concentration of the mine waters which is an important aspect of mine rock-water geochemistry. Sulphate is major anions used in studies that compare tailings and waste rock waters, inclusive of abundant mine waters such as Nenthorn mine. According to Weightman et al. (2020), pyrite oxidation has caused dissolved sulphate concentrations to rise to 3000 mg/L over a decade with chlorite dissolution resulted in dissolved Mg^{2+} (600 mg/L). Given the semi-arid climate, evaporative precipitation of sulphate minerals would contribute to an engineered water treatment system. Based on the geochemical models, evaporative precipitation of gypsum can eradicate sulphate from both water types, particularly if carbonate precipitate was repressed by dropping the pH of the water to 6 within an engineered treatment system that has considerable evaporation. Sulphate is assumed to be derived from the dissolution of sulphide minerals like pyrite and arsenopyrite.

5 Conclusion

This study investigated the distribution of potentially toxic trace elements (As, Cd, Cr, Cu, Fe, Ni, Mn, Pb, and Zn) in surface water and precipitates in Nenthorn historic orogenic gold mine. The abandoned mine and adjacent Deighton Creek waters are circumneutral but are elevated in several trace elements as a result of water-rock interaction. Precipitate samples were mostly amorphous and appear to sequester the metals of environmental interest, with the possible exception of As. Nenthorn mining working precipitates can be classified as the buffering zone where much of the primary sulphide minerals were adsorbed and precipitated and are not transferred throughout the water system.

Moreover, the concentration of elements in the waters is higher within the mine working relative to Deighton Creek. The surface waters of Nenthorn are enriched with potentially toxic trace metals, most significantly arsenic. New Zealand's natural arsenic background concentration in topsoil is around 17.4ppm, whereas the precipitates have excess of 0.2 wt. % As. The drinking water, the maximum acceptable value for arsenic is 10 ppb, whereas the mine waters have > 20 ppb As. This indicates that there is a potential health and environmental risk associated with water puddles and surface water at Nenthorn historic gold mine. Iron hydroxides are only stable under aerobic conditions ($pH > 4$), therefore biochemical changes in conditions could continue to release As due to reductive dissolution. Seasonal rainfall and high evaporation rate could influence sulphide weathering at Nenthorn. In any case, the contamination of surface waters quality in the abandoned Nenthorn mine is small enough that it does not affect the Deighton Creek just downstream. However, this study has shown that a large mine with a greater footprint is likely to have a more significant effect on trace elements in the downstream waters.

Acknowledgement

I would like to thank my supervisors at the University of Otago, New Zealand; Dr Candace Martin, Dr Michael Palin and Dr Doug Mackenzie for the supervision, guidance and support provided in completing this project. Also, I would like to thank the Ministry of Foreign Affairs New Zealand for the scholarship that funded this project and my study at University of Otago through the Manaaki Scholarship.

References

- Abanda, PA, & Hannigan, RE 2007, 'Mineral control of minor, trace, and rare earth elements during black shale weathering at near-neutral pH', In D. Sarkar, R. Datta and R. Harrigan (Eds.), *Developments in Environmental Science*, pp.273-303, DOI: 10.1016/S1474-8177(07)05011-5.
- Bibby, CJ, 1997, 'Macraes Ecological District: Survey report for the Protected Natural Areas Programme. New Zealand Protected Natural Areas Programme', *Department of Conservation*, Dunedin, pp. 158.
- Chester, R 2009, 'The transport of material to the oceans: the fluvial pathway in Marine geochemistry', *John Wiley & Sons*, pp. 11-52.

- Craw, D, & Kerr, G 2017, 'Geochemistry and mineralogy of contrasting supergene gold alteration zones, southern New Zealand', *Applied Geochemistry* vol. 85, pp. 19-34, DOI: <https://doi.org/10.1016/j.apgeochem.2017.08.005>.
- Craw, D, Mortensen, J & Mackenzie, D 2009, 'Source of Metals for Gold Deposits in the Otago Schist', In Proceeding from the AusIMM New Zealand Branch Annual Conference', <https://www.researchgate.net/publication/283084333>.
- Craw, D 2003, 'Geochemical changes in mine tailings during a transition to pressure-oxidation process discharge, Macraes mine, New Zealand', *Journal of Geochemical Exploration*, vol. 80, no. 1, pp. 81-94. Doi: 10.1016/s0375-6742(03)00184-5.
- Craw, D 2000, 'Water-rock interaction and acid neutralization in a large schist debris dam, Otago, New Zealand', *Chemical Geology*, vol.171, no. 1-2, pp. 17-32, Doi: 10.1016/s0009-2541(00)00231-x.
- Craw, D, & Norris, RJ 1991, 'Metamorphogenic Au-W veins and regional tectonics: Mineralisation throughout the uplift history of the Haast Schist, New Zealand', *New Zealand Journal of Geology and Geophysics*, vol. 34, pp. 373-383.
- Craw, D, & McKeag, SA 1987, 'Near-surface hydrothermal activity in the eastern Otago schist (Note)', *New Zealand Journal of Geology and Geophysics* vol. 30, no. 4, pp. 437-443, DOI: 10.1080/00288306.1987.10427547.
- Diehl, FS, Hageman, LP, Smith, SK, Koenig, AE, Fey, DL, & Lowers, HA 2006, 'What's weathering in Mine Waste? Mineralogic Evidence for Sources of Metals in Leachates', In *Proceedings of the U.S. EPA Hard Rock Mining Conference*, Tucson, Arizona, DOI: [10.2138/rmg.2000.40.7](https://doi.org/10.2138/rmg.2000.40.7).
- Gaillardet, J, Dupré, B, Louvat, P, & Allegre, CJ 1999, 'Global silicate weathering and CO₂ consumption rates are deduced from the chemistry of large rivers', *Chemical Geology*, vol. 159, no. 1, pp. 3-30.
- Jamieson, HE, Walker, SR, & Parsons, MB 2015, 'Mineralogical characterization of mine waste', *Applied Geochemistry*, vol. 57, pp. 85-105, Doi:10.1016/j.apgeochem.2014.12.014.
- Kerr, G, & Craw, D 2020, 'Metal redistribution during cementation of historic processing residues, Macraes gold mine, New Zealand', *New Zealand Journal of Geology and Geophysics*, vol. 0028-8306, pp. 1-13, DOI: 10.1080/00288306.2020.1787472.
- Macara, GR 2015, 'The climate and weather of Otago', *NIWA Science and Technology Series*, vol. 67, pp. 44, <https://niwa.co.nz/regionalclimatologies/otago>.
- Mackie, C, Mackenzie, DJ, Craw, D, 2009, 'Structural and lithological controls on gold mineralisation at Otarehua on the northeastern margin of the Otago Schist, *New Zealand Journal of Geology and Geophysics*, vol. 52, pp. 43–57, <https://doi.org/10.1080/00288300909509877>.
- Mains, D, & Craw, D 2005, 'Composition and mineralogy of historic gold processing residues, east Otago, New Zealand. *New Zealand Journal of Geology and Geophysics*', vol. 48, no. 4, pp. 641-647, doi:10.1080/00288306.2005.9515138.
- Martin, A.P, & Simon, C. 2016, 'On forty-five years of gold exploration at Barewood and Nenthorn, compared with twenty years prior to mining at Macraes, east Otago, New Zealand', In *A.B. Christie (Ed), Mineral deposits of New Zealand: Exploration and research*, pp. 199-206, Australasian Institute of Mining and Metallurgy.
- Mortimer, N, & Roser, B. P 1992, 'Geochemical evidence for the position of the Caples–Torlesse boundary in the Otago Schist, New Zealand', *Journal of the Geological Society*, vol. 149, no. 6, pp. 967-977.
- Plumlee, G.S 1999, 'The environmental geology of mineral deposits', In: Plumlee, G. S, Logsdon, M.J. (Eds.), and the Environmental Geochemistry of Mineral Deposits,' Part A: Processes, Techniques, and Health Issues: *Reviews in Economic Geology*, vol. 6A, pp. 71–116.
- Ryder, G & Mandy, T October 2020, 'Review of Values, Freshwater Restoration Programmes, and Research Needs within the Taieri Catchment', Department of Conservation, <https://www.doc.govt.nz/.../taieri-river-review.pdf>.
- Taylor, SR, & McLennan, SM 1985, 'The continental crust: its composition and evolution'.
- Weightman, E, Craw, D, Rufaut, C, Kerr, G, & Scott, J 2020, 'Chemical evolution and evaporation of shallow groundwaters discharging from a gold mine, southern New Zealand', *Applied Geochemistry*, vol. 122, no.15. doi:10.1016/j.apgeochem.2020.104766.
- Weightman, E, Craw, D, Snow, T, Christenson, H, & Kerr, G 2020, 'Stratigraphy and mineralogy of tailings at Macraes gold mine, southern New Zealand', *New Zealand Journal of Geology and Geophysics*, vol. 17, Doi: 10.1080/00288306.2021.1931360.
- White, AF, & Blum, AE 1995, 'Effects of climate on chemical weathering in watersheds', *Geochimica et Cosmochimica Acta*, vol. 59, no. 9, pp. 1729-1747.
- Zeman, JS O 2004, 'Introduction to environmental hydrogeochemistry', Chapter 3-7, no. 3, Masaryk University in Brno, Faculty of Science.