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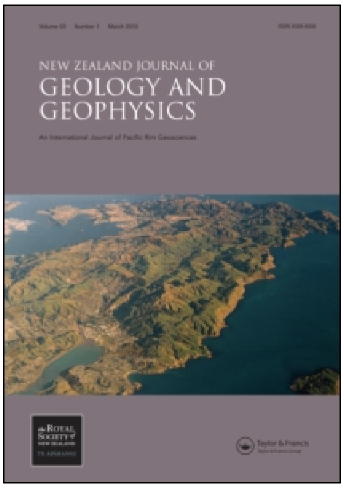

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# Correlation of acid base accounting characteristics with the Geology of commonly mined coal measures, West Coast and Southland, New Zealand

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Assessment of the potential for waste rock at coal mine sites to produce acid mine drainage is an important part of mine planning and operations and is commonly assessed using acid base accounting analyses. The underlying factor that controls mine drainage chemistry is the mineralogical composition of the coal measures sequences which in turn is controlled by several geological factors including provenance, depositional environment, diagenetic processes and tectonic setting. Therefore, coal mine drainage chemistry is directly linked to the geology of coal measures sequences.

Our research uses acid base accounting data to identify relationships between coal measures geology and acid production potential for Brunner, Paparoa and Morley Coal Measures as well as Gore Lignite Measures. Our data is from several sources and reflects areas in these sets of coal measures where mining or exploration is underway. In general Brunner Coal Measures are strongly acid producing especially fine grained rocks and this relates to a coastal depositional environment, common diagenetic pyrite, overlying transgressive marine rocks and compositional maturity. Morley and Paparoa Coal Measures are mostly non-acid forming relating to fluvial - lucustrine depositional environments, overlying coal measures, diagenetic carbonates, and possibly carbonates from source rocks. Gore Lignite Measures are mostly non-acid forming, however, some acid forming rocks are present. Gore Lignite Measures are delta plane deposits with occasional marine influence.

Datasets from Brunner, Paparoa and Morley Coal Measures as well as Gore Lignite Measures also demonstrate some of the limitations of acid base accounting analyses. For example, oxidation steps in acid base accounting analyses designed to dissolve pyrite also react with organic material and this causes a false positive analysis. Other assumptions common in acid base accounting such as use of total S content to calculate pyrite related acidity are inappropriate for some samples because of other forms of S in these samples. Despite the interferences, standard acid base accounting tests and procedures are very useful for first pass predictions of mine drainage chemistry and datasets from commonly mined New Zealand coal measures can be successfully related to geological processes.

**Keywords:** acid mine drainage; AMD; acid base accounting; neutralisation potential; acid producing potential

## Introduction

Prediction of environmental impact including mine drainage chemistry is an important process when planning a new mine. Mine drainage chemistry can be predicted qualitatively by analysis of factors such as regional geology, hydrogeology, mine type and examination of historic mine drainage chemistry (Brady et al. 2000; Pope et al. 2005; Pope et al. 2006; Cravotta III 2008a; Cravotta III 2008b; Pope et al. 2010). Mine drainage chemistry can also be predicted quantitatively by investigation of the geochemistry of rocks to be disturbed by mining (Kleinmann 2000; Skousen et al. 2000; Skousen et al. 2002). Combined qualitative and quantitative approaches provide the best prediction of mine drainage chemistry and have implications for mine, feasibility, operations, economics and closure.

Methods for the quantitative prediction of mine drainage chemistry have been developed throughout the last three decades beginning with tests developed at mine sites to meet local, regional or national requirements (Sobek et al. 1978; Smart et al. 2002; Weber et al. 2005) and these tests have progressed toward internationally recognised standard methods (American Society for Testing and Materials International [ASTM] 2007; Bucknam et al. 2009; Kaartinen & Wahlstrom 2009). Quantitative mine drainage prediction tests that can be completed rapidly and assess the total reactive component of the rock are called static or acid base accounting (ABA) tests. These tests commonly include assessment of the acid producing potential, neutralisation potential, and water soluble acidity. Quantitative prediction of mine drainage chemistry from acid base accounting tests can be refined by long term leaching tests also called kinetic tests. Kinetic tests primarily measure changes in rock leachate chemistry with time and can be performed under controlled conditions in the laboratory or under natural conditions in the field.

Mining companies in New Zealand accumulate site specific datasets of acid base accounting analyses for their deposits related to environmental planning and management of their operations (Lindsay et al. 2002; Hughes et al. 2004).

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However, these datasets are often kept in-house by mining companies and are seldom interpreted in a regional context. Our objective is to present results of acid base accounting analyses from rocks disturbed by coal mining in Southland and the West Coast of the South Island. Some samples have been collected specifically to provide regional context for the acid base accounting characteristics of these rock types, but most have been contributed by mining companies and were collected for mine consent, management, development or operations. Our research examines relationships between the acid base accounting properties of rocks and geological factors that operate at regional to local scales. Identification and interpretation of regional and local geological controls on acid base accounting have implications for mine drainage prediction, mine planning and consenting of future mines. Our research also examines limitations to the applicability of common static test methods and identifies areas where kinetic tests or other advanced testing procedures are required.

Our results and interpretations have implications for mine consenting and planning on the West Coast of the South Island and in Southland. Over 10 Mt of acid forming rock is mined in the South Island of New Zealand per year. Improvements to predictions of the chemistry of mine drainages based on regional geological factors are an important qualitative mine drainage planning tool and regulatory tool.

## Background

### Mineralogical control on mine drainage chemistry

Mine drainage chemistry is controlled by the mineralogical composition of rocks disturbed by mining. Interactions between minerals in rocks disturbed by mining and surface water are complex and varied (Eq. 1–8). In addition there are several site specific mineralogical factors that can influence mine drainage chemistry including, grain-size, reactivity (Weisener & Weber 2010), and mineral chemistry. Other non mineralogical factors such as climate, particle size, rock strength, mine type, mine management and hydrogeology (Pope et al. 2010) can also impact mine drainage chemistry, however, all of these factors are secondary to mineralogy.

Oxidation and hydrolysis reactions relating to the breakdown of sulphide minerals are the most common cause of acidity in mine drainage environments (Eq. 1). The breakdown of pyrite ($\mathrm{FeS_2}$) is an important acid forming reaction because pyrite is abundant in coal measures and rocks surrounding many metalliferous mines. Pyrite breakdown produces Fe(III) which has low solubility at $\mathrm{pH} > 3.5$ and forms secondary minerals such as ferrihydrite ($\mathrm{Fe(OH)_3}$) releasing more acid. Pyrite oxidation is more rapid at low pH (2–3.5). In this pH range dissolved FeIII concentrations can be elevated and cause catalytic oxidation reactions for FeII. In addition, biological catalysis of oxidation reactions is most effective in this pH range (Evangelou 1998).

$$\mathrm{FeS_2} + 15/4\mathrm{O_2} + 7/2\mathrm{H_2O} = \mathrm{Fe(OH)_3(s)} + 2\mathrm{H_2SO_4} \qquad (1)$$

Breakdown of other sulphide minerals such as monosulphides, galena (PbS) or sphalerite (ZnS), do not release acid. However, these reactions can produce elevated dissolved trace element concentrations or precipitation of trace element rich secondary minerals (Eq. 2, 3).

$$\mathrm{PbS} + 2\mathrm{O_2} = \mathrm{PbSO_4} \qquad (2)$$

$$\mathrm{ZnS} + 2\mathrm{O_2} = \mathrm{Zn^{2+}} + \mathrm{SO_4^{2-}} \qquad (3)$$

Dissolution of aluminosilicate minerals can also influence mine drainage chemistry by acid neutralisation, contribution of dissolved components (Eq. 4) and formation of secondary minerals that can store and release acidity (Eq. 5).

$$\mathrm{NaAlSi_3O_8} + 4\mathrm{H^+} + 4\mathrm{H_2O} = 3\mathrm{H_4SiO_4^0} + \mathrm{Na^+} + \mathrm{Al^{3+}} \qquad (4)$$

$$\mathrm{KFe_3(SO_4)_2(OH)_6} + 3\,\mathrm{H_2O} = \mathrm{K^+} + \mathrm{Fe(\,OH)_3} + 2\mathrm{SO_4^{2-}} + 3\mathrm{H^+} \qquad (5)$$

Neutralisation potential from rocks disturbed by mining is primarily provided by carbonate minerals such as aragonite, calcite ($\mathrm{CaCO_3}$), dolomite ($\mathrm{CaMg(CO_3)_2}$), magnesite ($\mathrm{MgCO_3}$) and rhodochrosite ($\mathrm{MnCO_3}$) through open system carbonate dissolution and high solubility of cations released (Eq. 6). Siderite ($\mathrm{FeCO_3}$), a common carbonate mineral, has no net neutralising effect because its dissolution (Eq. 7a) is followed by FeII oxidation (Eq. 7b) and subsequent hydrolysis of FeIII (Eq. 7c) (Skousen et al. 1997; Weber et al. 2005; Haney et al. 2006). Carbonate minerals can be rich in trace elements such as Cu, Zn, Cd, and thus neutralisation reactions can also release these trace elements.

$$\mathrm{CaCO_3} + 2\mathrm{H^+} = \mathrm{Ca^{2+}} + \mathrm{H_2O} + \mathrm{CO_2(g)} \qquad (6)$$

$$\mathrm{FeCO_3} + 2\mathrm{H^+} = \mathrm{Fe^{2+}} + \mathrm{CO_2} + \mathrm{H_2O} \qquad (7a)$$

$$\mathrm{Fe^{2+}} + {}^{1}/_{4}\mathrm{O_2} + \mathrm{H^+} = \mathrm{Fe^{3+}}{}^{1}/_{2}\mathrm{H_2O} \qquad (7b)$$

$$\mathrm{Fe^{3+}} + 3\mathrm{H_2O} = \mathrm{FeOH_3} + 3\mathrm{H^+} \qquad (7c)$$

Silicate minerals can provide neutralisation potential through supply of soluble base cations (Eq. 8). Neutralisation potential from silicate minerals can exceed that from carbonate minerals in some rocks (Weber et al. 2005). In general, the kinetics of silicate dissolution is much slower and these reactions are often only effective if acid production is also slow.

$$\mathrm{Mg_2SiO_4} + 4\mathrm{H^+} = 2\mathrm{Mg^{2+}} + \mathrm{H_4SiO_4} \qquad (8)$$

### Geological control of mineralogy

Coal mining in Southland and on the West Coast of the South Island occurs in several different coal fields but within a restricted number of different geological formations. These include the Brunner and Paparoa Coal Measures on the West Coast, and, Morley Coal Measures and Gore Lignite Measures in Southland (Fig. 1, 2). The mineralogy of these geological formations is controlled by several factors including tectonic setting, provenance, depositional process and environment, diagenesis (Table 1), and localised hydrothermal alteration.

### Brunner Coal Measures

Brunner Coal Measures are predominantly Eocene and were deposited at the beginning of a tectonic controlled marine transgression in a fluvial to estuarine environment. The coal measures unconformably overlie Cambrian to Ordovician Greenland Group rocks, Devonian to Cretaceous granitoids, and Cretaceous to Paleocene Pororari Group and Paparoa Coal Measures. Brunner Coal Measures are typically a relatively thin sequence containing muddy sediments and a single coal seam, however, locally thicker troughs or fault controlled depressions occur that contain sandy sediments and multiple coal seams (Suggate 1959; Nathan 1986). Sandstones are commonly coarse to gritty, poorly rounded and chemically mature, containing little more than quartz and muscovite with locally abundant feldspar and are derived from underlying sedimentary and granitic rocks. (Suggate 1959; Nathan 1986; Titheridge 1988; Titheridge 1992; Flores & Sykes 1996). Diagenetic modifications to the Brunner Coal Measures include quartz overgrowth/cementation, kaolinitic alteration/replacement, and pyritic development, either disseminated or as a cement (Weisener & Weber 2010). The occurrence and distribution of pyrite in Brunner sandstones, which has an important control on acid mine drainage, can be related to interbedded marine or brackish sediment horizons, the proximity of overlying marine beds or hydraulic interconnection to marine fluids after burial. (Suggate 1959; Newman & Newman 1992). In the Reefton district, sparse occurrences of carbonate nodules (siderite, dolomite, and calcite) are present (Newman 1988). Marine rocks (Kaiata Formation) conformably overlying the Brunner Coal Measures are an important control on acid generation and these rocks are commonly disturbed during mining (Hughes et al. 2004). In the Greymouth area, a thick calcareous and pyrite bearing sandstone (Island Sandstone Member) is present, whereas further north, a dark, carbonaceous and pyritic mudstone (Kaiata Mudstone Member) rests on the coal measures.

### Paparoa Coal Measures

Paparoa Coal Measures are Cretaceous to Paleocene and were deposited in a fluvial to lucustrine environment in fault controlled basin. Localisation of river in fault controlled subsidence zones allowed thick accumulations of clean peat (Newman & Newman 1992; Moore et al. 2006). The coal measures unconformably overlie Early Cretaceous conglomerates (Pororari Group) or similar basement rocks to those beneath Brunner Coal Measures. Members hosting coal seams are generally quartzose and lithic in composition. Only parts of one major unit (Rewanui Member) is feldspar rich, attributed to sediment supply from a granitic source (Newman 1985; Boyd & Lewis 1995). Most rock fragments are derived from the Greenland Group, which contains disseminated carbonate minerals associated with mesothermal alteration (Christie & Brathwaite 2003). From a geochemical viewpoint, the Paparoa Coal Measures tend to be acid neutralising. Diagenetic minerals include common chlorite in the sandstones and mudstones, kaolinite, and minor carbonate (siderite > dolomite > calcite) in both the coal measures and the coal (Boyd 1993; Boyd & Lewis 1995). Paparoa coal contains minor pyrite but this is seldom present in the surrounding sediments.

### Gore Lignite Measures

Gore Lignite Measures are Oligocene to Miocene (Pocknall 1990) and deposited in a river delta-plain environment in a regressive tectonic setting (Isaac & Lindqvist 1990) then were buried to between 350 m in the south to 800 m in the northwest (Suggate & Isaac 1990). Interfingering with marine rocks (Chatton Formation) occurs at the base of the Gore Lignite Measures as indicated by marine fossils at Croydon (Stein et al. 2009) and probably in other parts of the sequence where bioturbation and rare marine fossils have been identified (Isaac & Lindqvist 1990). Sediment for the Gore Lignite Measures is derived from the Otago Schist, local basement volcanic and volcaniclastic rocks, and erosion of local Late Cretaceous to early Tertiary sediments (Isaac & Lindqvist 1990; Youngson et al. 2006). Diagenetic alteration of Gore Lignite Measures and overlying/interbedded gravels include alteration of sediment components to smectite or chlorite (Craw et al. 2008), occasional silicification plant remains (Isaac & Lindqvist 1990), rare carbonate cementation and irregularly distributed sulphide cementation of sandstone and conglomerates (Youngson 1995; Falconer & Craw 2005; Falconer et al. 2006). Controls on sulphide distribution are poorly understood in the Gore Lignite Measures and overlying gravels.

### Morley Coal Measures

Morley Coal Measures are Late Cretaceous (Raine 1989; Warnes 1990) and sediment deposited episodically in a fault bounded intermontaine fluvial environment (Sykes 1988; Shearer 1995). The Morley Coal Measures conformably overlie the New Brighton Conglomerate and are unconformably overlain by the Eocene Beaumont Coal Measures (Raine 1989; Warnes 1990). Sediment for the Morley Coal Measures is derived mostly from igneous and metamorphic sources (Sykes 1988). Diagenetic alteration includes kaolinite, montmorillonite (Craw et al. 2008) and carbonate cement. Pyrite is reported as a minor mineral matter

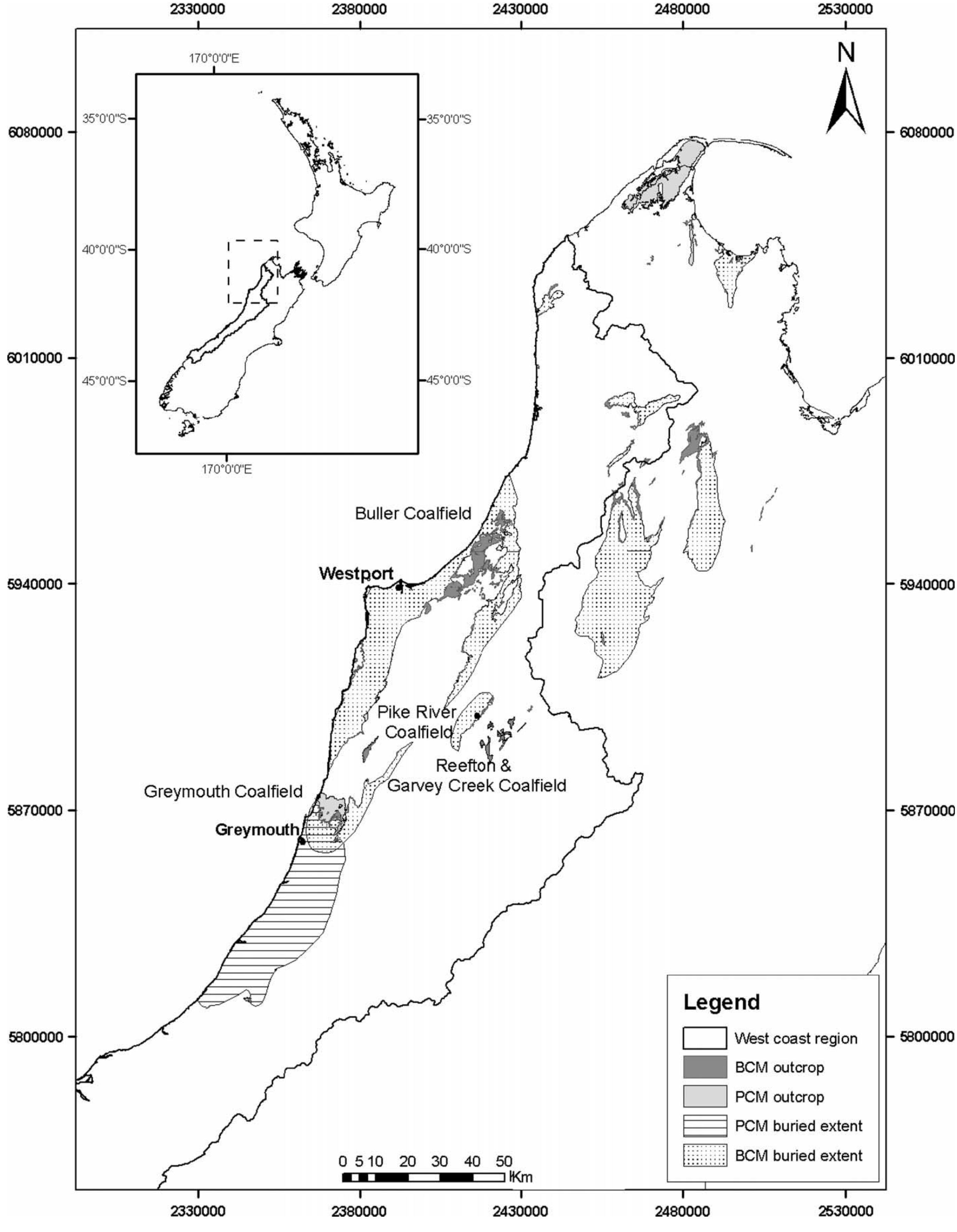

**Fig. 1** Extent of Paparoa and Brunner Coal Measures (PCM and BCM respectively) on the West Coast of the South Island.

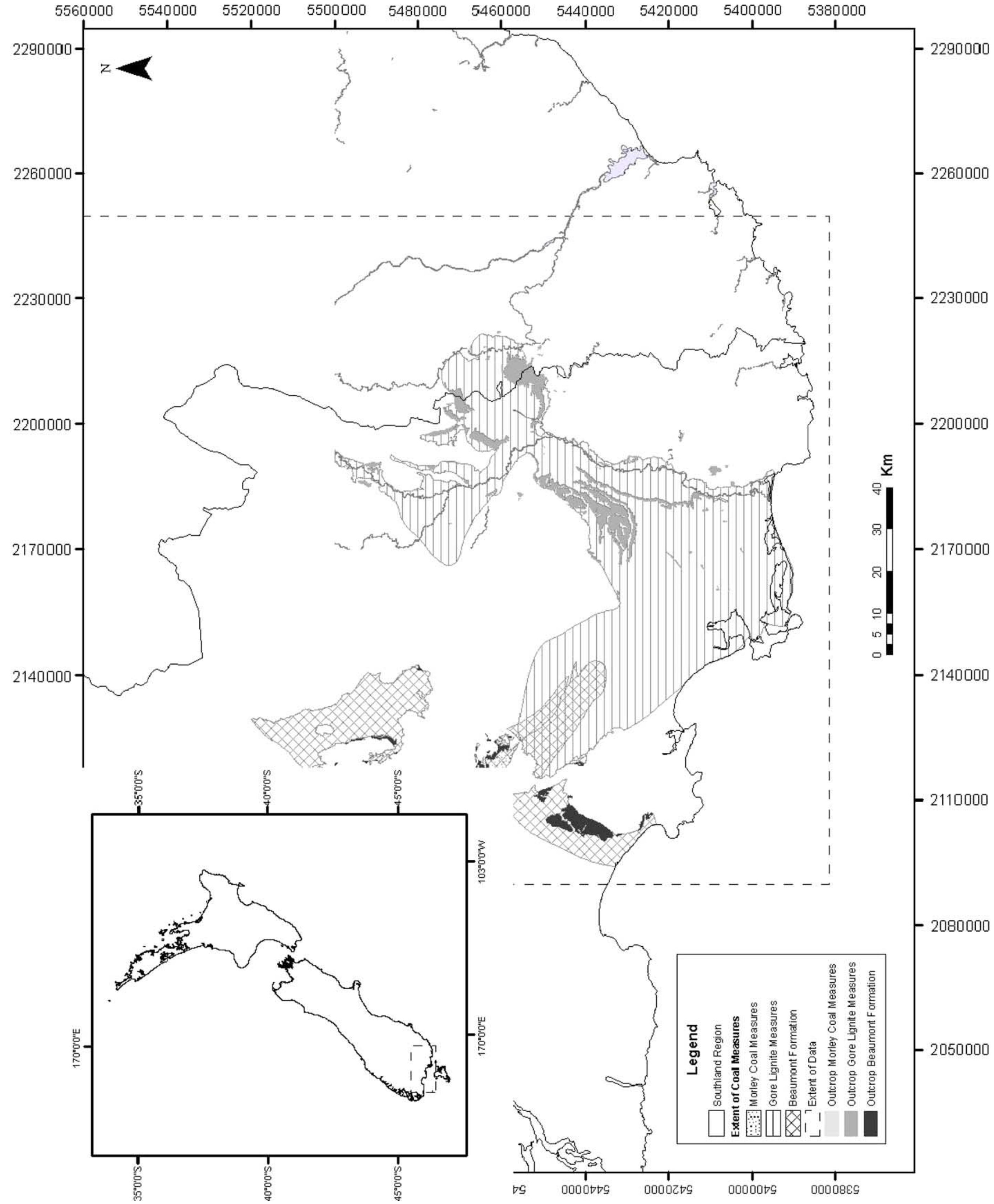

**Fig. 2** Extent of Morley Coal Measures and Gore Lignite Measures in Southland.

**Table 1** Regional geological factors for commonly mined coal measures sequences in Southland and on the West Coast

| Formation | Age | Tectonic Setting | Provenance | Depositional Environment | Diagenetic Phases |
|---|---|---|---|---|---|
| Gore Lignite Measures | Miocene | Regression | Otago Schist Murihiku Rocks<br>Maco Coal Measures | Delta Plain | Smectite, chlorite, quartz, pyrite |
| Morley Coal Measures | Cretaceous | Regression | Igneous (volcanic and plutonic)<br>Metamorphic | Fluvial | Kaolinite, montmorillonite |
| Brunner Coal Measures | Eocene | Transgression | Greenland Group Granite | Delta to estuary | Kaolinite, pyrite, rare carbonate |
| Paparoa Coal Measures | Cretaceous | Uncertain | Greenland Group Granites<br>Takaka terrane schist | Fluvial to lucustrine | Siderite and other carbonates, kaolinite, quartz, illite, muscovite |

component in coal but is not reported in the coal measures (Sykes 1988).

Rocks that are disturbed by coal mining on the West Coast and in Southland also include Kaiata Formation that has a substantial acid base accounting data set (Hughes et al. 2004), and others such as the Rotokohu Coal measures, Beaumont Coal Measures and Orauea Mudstone for which there is minimal acid base accounting data.

## Methods

### *Sampling*

Rock samples to characterise acid producing and neutralising potential of Coal Measures rocks have been collected by mining companies, students, consultants and researchers with sampling strategies that differ depending on the purpose of the study. Suites of rocks collected to characterise a deposit will be different from those collected during mine operations or management. During deposit characterisation, samples are collected with two purposes:

1. to characterise mine drainage implications of the volumetrically significant rock types; and,
2. to determine the abundance and distribution of rocks that are strongly acid producing or acid neutralising but may be less volumetrically significant.

In contrast, after deposit characterisation has been completed for all volumetrically significant rock types, less exhaustive sampling and analysis is required that focuses on rock types that produce or neutralise acid. Despite variations in the sample collection strategies, analytical procedures and analysis methods are similar and regional trends can be identified. It is important to understand the purpose of each sample so that appropriate weighting is applied to interpretation of results. For example, results from a suite of samples collected because they have anomalously abundant sulphides or carbonate contents are interpreted differently from a suite of representative rock type samples.

### *Analyses*

Acid base accounting analyses are used to quantify the acid forming potential or acid neutralising potential of rocks that will be disturbed by mining. Acid base accounting tests have the advantage of simplicity and low cost but the disadvantage of analytical interferences and they lack universal applicability.

Acid Neutralising Capacity (ANC) is a titrimetric test that measures the capacity of rocks to neutralise acid. In general, a sample is reacted with a strong acid ($\mathrm{pH} < 1.5$) and the resulting mixture is titrated back to neutral pH to determine the amount of acid consumed by the sample. There are several variations on this method (Sobek et al. 1978; Smart et al. 2002).

Maximum Potential Acidity (MPA) is a calculation based on sulphur analysis that determines the acid production potential of a rock. This test makes several assumptions: that all measured sulphur occurs as pyrite, that all pyrite will be completely oxidised and that products are hydrolised to form acid, $Fe(OH)_3$ (Eq. 1). During pyrite oxidation, two moles of S in $FeS_2$ produce two moles of $H_2SO_4$ and therefore the S content (w%) can be used to calculate acid generated ($kgH_2SO_4/t$) (Eq. 9).

$$\begin{aligned}&\text{Acidity generated }(\mathrm{KgH_2SO_4/t}) = \\ &\quad \frac{\mathrm{S\,w\%} \times 10 \times 2\ (\mathrm{moles\,H_2SO_4}) \times 98.07(\mathrm{g/mol})}{2(\mathrm{moles\ S}) \times 32.06(\mathrm{g/mol})} \\ &\quad = \mathrm{S\ w\%} \times 30.6\end{aligned} \tag{9}$$

Therefore a conversion factor of 30.6 can be used to calculate the acid generation in $kgH_2SO_4/t$ from the S content in weight%.

Typically, total sulphur measured by Leco infrared analyser is used for the calculation of maximum potential acidity. However, in some rocks sulphur can be present in non-acid forming species such as sulphate minerals (e.g. gypsum), organic sulphur or non-acid forming sulphides (Eq. 2, 3). If these non-acid forming sulphur species are present but not identified, and total sulphur analyses (such as Leco) is used for calculation of MPA then the potential acidity will be over estimated. Alternative methods that are more selective for pyrite sulphur are also available (Sullivan et al. 1999; Sullivan et al. 2000).

Net acid production potential (NAPP) is a commonly quoted value in acid base accounting and is calculated by subtracting ANC from MPA expressed in $kgH_2SO_4/t$. Negative values are net neutralising and positive values net acid forming. In addition, the ratio of ANC to MPA is also commonly used to identify the samples with highly acid neutralising or acid producing mineralogy.

Net acid generation (NAG) test (Miller et al. 1997; Smart et al. 2002) evaluates the acid generation without calculation of MPA or ANC. This test involves the addition of 250 mL (15 vol%) peroxide to 2.5 g of crushed sample to cause oxidation of sulphides. Acid generated by oxidation can be partially neutralised by reactions with carbonates and silicates and net acid generation is quantified by two parameters, the NAG pH (the pH of the NAG liquor after reaction) and the NAG acidity in $kgH_2SO_4/t$ (back titration of the NAG liquor to either pH4.5 or pH7). Additional data can be derived from NAG style tests by analysis of pH changes with time and analysis of the reaction liquor (Smart et al. 2002; Weber et al. 2006). Rocks that contain excess ANC typically produce an NAG pH $>6.5$. Organic matter in a sample can also oxidise and produce false acid indication with pH $<2.5$.

Paste pH involves mixing a crushed sample with water and measuring the pH. It measures the water soluble acidity within a sample and therefore includes adsorbed protons, soluble acidic salts and adsorbed metals that hydrolyse (Lin et al. 2000).The pH does not directly measure the potential of a sample to produce acid with continued weathering because sulphide minerals require oxidation to release acid but paste pH can be used to indicate acid producing samples. Paste pH is most commonly used for site specific operational management where it can be used as a screening tool to characterise waste rocks with different mine drainage implications.

## Results

Acid base accounting analyses have been completed at many of the coal mines and exploration targets in the South Island by many different organisations, mining companies, exploration companies, research organisations and universities through student projects (Table 2). All datasets are restricted geographically to areas where mining or exploration activity takes place and therefore do not have broad or uniform spatial distribution throughout coal measures sequences. Most datasets include complete vertical sampling of the coal measures sequences. The intention of this research is to relate acid base accounting analyses from many sources to regional geological processes and identify factors that determine the acid producing potential of coal bearing strata (Table 2).

### *Brunner Coal Measures*

Acid base accounting from the Brunner Coal Measures is available for the Buller and Garvey Creek coalfields. In the Buller Coalfield about 220 samples of Brunner Coal Measures have been analysed by Solid Energy New Zealand Ltd, mostly from the Stockton open cast mine and mostly from drill core. About 100 of these samples have a complete suite of acid base accounting analyses and the remainder of the Stockton samples have been analysed for MPA and NAG. Several additional grab samples have been analysed for acid base accounting from the Buller Coalfield in the Denniston area (de Joux 2003) and other acid base accounting data sets are kept in-house by mining companies and are unavailable for publication.

In the Garvey Creek Coalfield, Solid Energy New Zealand Ltd and New Zealand Coal and Carbon Ltd have

**Table 2** Summary data for acid base accounting parameters for commonly mined coal measures sequences in Southland and on the West Coast

| | MPA ($KgH_2SO_4/t$) | | | | ANC ($KgH_2SO_4/t$) | | | | NAG Acidity ($KgH_2SO_4/t$) | | | | Paste pH | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Formation | n | Min | Mean | Max | n | Min | Mean | Max | n | Min | Mean | Max | n | Min | Mean | Max |
| Gore Lignite Measures | 80 | < | 12.6 | 169.1 | 64<br>63* | < | 21.7<br>7.6* | 877.5<br>33* | 41 | < | 6.3 | 36 | 58 | 3.5 | 5.08 | 8.5 |
| Morley Coal Measures | 17 | < | 2.3 | 7 | 16 | < | 12.1 | 37.2 | 16 | < | 5.0 | 24.7 | 16 | 5.8 | 6.57 | 9.1 |
| Brunner Coal Measures | 364 | < | 22.4 | 385 | 167 | < | 2.9 | 125 | 366 | < | 26.6 | 223 | 334 | 2.96 | 4.51 | 9.4 |
| Paparoa Coal Measures | 51 | < | 0.80 | 4.6 | 25 | 2.5 | 5.9 | 24.4 | 10 | < | 48.3 | 114 | 38 | 6.04 | 7.27 | 8.4 |

MPA—maximum potential acidity, ANC—acid neutralising capacity, NAG—net acid generation capacity. < indicates below detection. Gore Lignite Measures ANC data are skewed by one sample with very high ANC * indicates the high value is not included.

completed 130 analyses at the Island Block and Echo mine sites respectively. Forty-five samples have complete acid base accounting and the remainder have MPA analysis and some with NAG analysis. In addition, a student thesis (Mackenzie in prep) contains another 25 complete acid base accounting analyses from Echo and Island Block mine sites.

Acid base accounting analyses from the Brunner Coal Measures generally indicate a potential for acid formation as these rocks weather (Table 2). There is excess MPA (average 22.5 $kgH_2SO_4/t$ from 364 samples) compared to ANC (average 2.9 $kgH_2SO_4/t$ from 167 samples). In addition, NAG values indicate significant acid production potential (average 26.6 $kgH_2SO_4/t$ from 366 samples) and paste pH values are lower for Brunner Coal Measures than other coal measures. Sampling strategies and descriptions for many samples in Brunner Coal Measures are not well reported because these samples have been collected in multiple campaigns by different workers.

### *Paparoa Coal Measures*

Forty-nine acid base accounting analyses of the Paparoa Coal Measures are available from Solid Energy New Zealand Ltd, 19 have complete acid base accounting analyses and the remainder have a suite of partial tests completed. These analyses are from Strongman Mine area and from exploration targets in the Rewanui member of the Paparoa Coal Measures.

Acid producing potential from Paparoa Coal Measures is low. There is excess ANC (average 5.9 $kgH_2SO_4/t$ from 25 samples) compared to MPA (average 0.7 $kgH_2SO_4/t$ from 51 samples). In contrast, NAG acidity values indicate substantial acid producing potential (average 47.0 $kgH_2SO_4/t$ from 10 samples). Paste pH values for Paparoa Coal Measures are high on average (pH 7.28 from 38 samples).

### *Gore Lignite Measures*

Eighty-eight acid base accounting analyses of Gore Lignite drill core have been completed by CRL Energy Ltd. and Solid Energy New Zealand Ltd. These are from three deposits, Waimumu, Croydon and Mataura. Several additional grab samples have been collected from the Newvale mine by students (Mulliner 2006).

Averaged data for Gore Lignite Measures is difficult to interpret. There is acid forming potential in the Gore Lignite Measures because MPA values are consistent (average 12.6 $kgH_2SO_4/t$ from 80 samples). However, there is also substantial acid neutralising potential because the ANC is high (average 21.2 $kgH_2SO_4/t$ from 64 samples). In general, MPA values and ANC values are elevated because sampling strategies have targeted sulphide bearing rocks and carbonate bearing rocks (Table 2). NAG acidity values indicate small amounts of acid (average 6.4 $kgH_2SO_4/t$ from 41 samples) and paste pH values indicate low soluble acid values (average 5.08 from 58 samples).

### *Morley Coal Measures*

Acid base accounting analyses for 16 samples from the Morley Coal Measures are available. Nine of these come from the Ohai Mine and were collected by Solid Energy New Zealand Ltd and seven are from the Nightcaps Mine collected by CRL Energy Ltd.

The Morley coal measures have low acid forming potential. There is excess ANC (average 12.1 $kgH_2SO_4/t$ from 16 samples) compared to MPA (average 2.5 $kgH_2SO_4/t$ from 17 samples). NAG acidity values indicate small amounts of acid (average 5.0 $kgH_2SO_4/t$ from 16 samples) and paste pH values are close to neutral (average 6.57 from 16 samples).

## Discussion

Acid base accounting data are often summarised on diagrams that include ANC, MPA (NAPP) and NAG data. The objective is to discriminate potentially acid forming (PAF) samples from non-acid forming (NAF) samples and examine trends or relationships between samples. Acid base accounting analyses are useful because they are rapid, low cost tests. However, they are subject to interferences and therefore care must be taken in the interpretation of acid base accounting data. Our analysis of results includes evaluation of the strengths and weaknesses of different acid base accounting tests for West Coast and Southland coal measures rocks.

### *Brunner Coal Measures*

Acid base accounting data for the Brunner Coal Measures indicate that most samples are potentially acid forming (Table 2, Fig. 3 a–d). This means that mining (or other disturbance such as road cuts, landslides, tunnels, dewatering/drainage, construction sites etc) in the Brunner Coal Measures will produce acid. Acid producing potential in Brunner Coal Measures relates well to geological information. A coastal depositional environment and transgressional tectonic setting cause marine rocks to interfinger with and overlie the Brunner Coal Measures. These marine sediments and the related sea water are a source of S for sulphide precipitation immediately after sediment deposition and by subsequent diagenetic processes. Prolonged and slow depositional processes mean that Brunner Coal Measures are compositionally mature with low detrital carbonate content despite carbonates in Greenland Group source rocks and therefore these rocks have a low ANC. At some mine sites, samples collected for operational management do not include ANC analysis because the low values are considered insignificant.

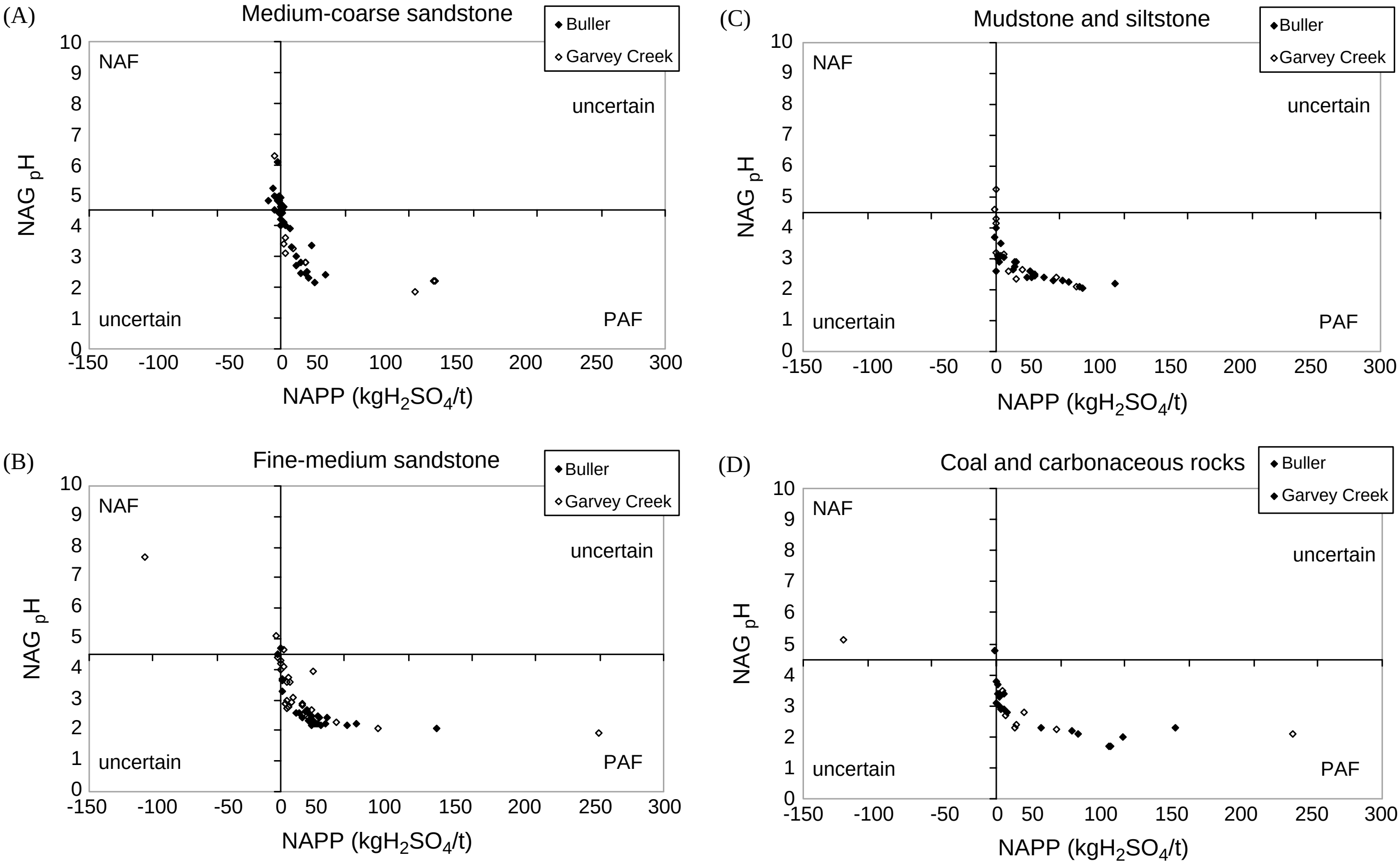

**Fig. 3** Comparison of NAG pH to NAPP acid producing potential for different rock types in Brunner Coal Measures rocks at Buller and Garvey Creek Coalfields. **(A)** Medium–coarse sandstone; **(B)** Fine–medium sandstone; **(C)** Mudstone and siltstone; **(D)** Coal and carbonaceous rocks. PAF—potentially acid forming, NAF—non-acid forming, uncertain – additional study required to determine acid producing/neutralising characteristics.

Acid producing potential increases as grain-size decreases, medium–coarse sandstone < fine–medium sandstone < mudstone (Fig. 3a–c). Coal and carbonaceous rocks have variable acid producing potential (Fig. 3d) and in general sulphides in the roof of coal seams are more abundant in areas where sandstone is the roof rock (Suggate 1959). Buller and Garvey Creek coalfields have similar acid base accounting data. However, in Garvey Creek Coalfield three samples of coarse sandstone are strongly acid producing (NAPP > 100 $kgH_2SO_4/t$) and rare samples are strongly acid neutralising (NAPP < -100 $kgH_2SO_4/t$) (Fig. 3). Depending on the field context of these samples there could be opportunities to manage acid mine drainage (AMD) by selective handling of these rock types. At Stockton coalfield portable test procedures such as paste pH are calibrated with other acid base accounting including NAG testing to make operational decisions on waste rock management (Weber et al. 2006).

It is common to measure and report NAG acid production potential values and these should correlate well with NAPP acid production potential. In theory, it is very unlikely that NAG acid production potential will exceed NAPP acid production potential because NAPP includes a stoichiometric maximum acidity based on S analysis and oxidation of pyrite. Data from the Brunner Coal Measures indicates weak correlation between NAG and NAPP acid production values (Fig. 4). At low acid production potential (NAPP < 20 $kgH_2SO_4/t$) almost all NAG values exceed NAPP values by 5–20 $kgH_2SO_4/t$. At moderate to high acid production potential (NAPP > 20 $kgH_2SO_4/t$) most NAG values exceed NAPP values but there are some samples where NAPP < NAG.

The most likely explanation for NAG values in excess of NAPP values is that organic material in the samples react during sample oxidation and produce titratable organic acids (Smart et al. 2002). As little as 3% organic material in a sample could have a significant impact on NAG results (Stewart 2003; Weber 2003; Stewart et al. 2009). Organic rich samples (coal and carbonaceous rocks) from the Brunner Coal Measures including coal and carbonaceous rocks all plot with NAG >> NAPP (Fig. 4b). This means that in the Brunner Coal Measures NAG acid production

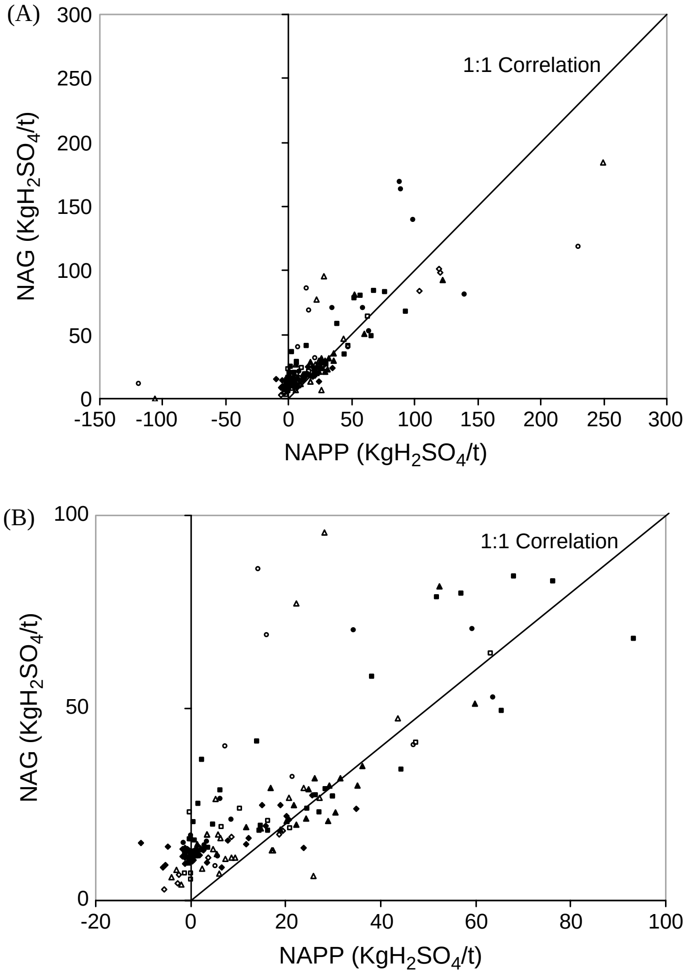

**Fig. 4** **(A)** Comparison of NAG acid production potential to NAPP acid production potential at Buller (closed symbols) and Garvey Creek (open symbols) Coalfields. **(B)** Scale up of axis region of Fig. 4A. Diamonds––medium–coarse sandstone, triangles––fine–medium sandstone, squares––mudstone–siltstone, circles––coal and carbonaceous rocks.

potential provides a false high acid production potential in samples with organic material. In summary, NAG analysis of Brunner Coal Measures can be useful for operational management (Weber et al. 2006; Hughes et al. 2007), however, calculations of acid loading into catchments or treatment systems should be made with caution, and only from rock types that do not contain substantial organic material.

### *Paparoa and Morley Coal Measures*

Acid base accounting analysis of Paparoa and Morley Coal Measures generally indicate NAF (non-acid forming) rock or uncertain results (Table 2, Fig. 5). Non-acid forming character of these coal measures matches well with geological information from these formations. Paparoa and Morley Coal Measures are deposited in fluvial to lacustrine environments away from marine influences and are overlain unconformably by younger coal measures. Elevated ANC in the Paparoa Coal Measures and Morley Coal Measures is probably related to diagenetic carbonate minerals and possibly detrital carbonate from Greenland Group rock fragments in the Paparoa Coal Measures (Eq. 6). Trace pyrite is present in Paparoa and Morley coal but uncommon in Paparoa and Morley Coal Measures sediments. Diagenetic carbonates are abundant in the Paparoa Coal Measures though much of this is identified as siderite with subordinate calcite and dolomite (Newman 1988; Boyd & Lewis 1995).

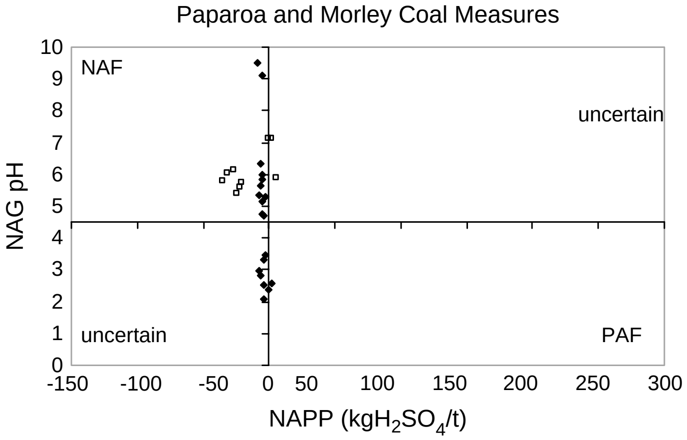

**Fig. 5** Comparison of NAG pH to NAPP acid producing potential for Paparoa (diamonds) and Morely (squares) Coal Measures. PAF—potentially acid forming, NAF— non-acid forming.

NAG acid production potential values indicate false positive potential for acid formation (Table 2) because of organic rock components in a similar manner to Brunner Coal Measures. In addition, interpretation of the acid production potential of several samples of Paparoa and Morley Coal Measures is difficult (Fig. 5). Several samples have low NAG pH and negative NAPP values. This indicates an acid reaction during oxidation to give pH $< 4.5$, but insufficient S (assumed to be present as $FeS_2$) to produce acid. There are several possibilities for this uncertain result including oxidation of organic components releasing acid, release of acid on oxidation of FeII from other minerals or analytical errors. Analytical procedures can produce poor results because some supplies of peroxide (the oxidant in NAG testing) contains phosphoric acid that reduces pH in the NAG procedure to about pH3.5. It is likely the cause of the low NAG pH in these samples was caused by oxidation of organic material which can produce a pH of $< 2.5$ (Weber 2003).

In addition, two samples from the Morely Coal Measures have positive NAPP with a NAG pH greater than 4.5. This means the samples contain enough S (assumed to be $FeS_2$) to make acid, however, when the sample is oxidised no acid occurs. The simplest explanation for this is that the

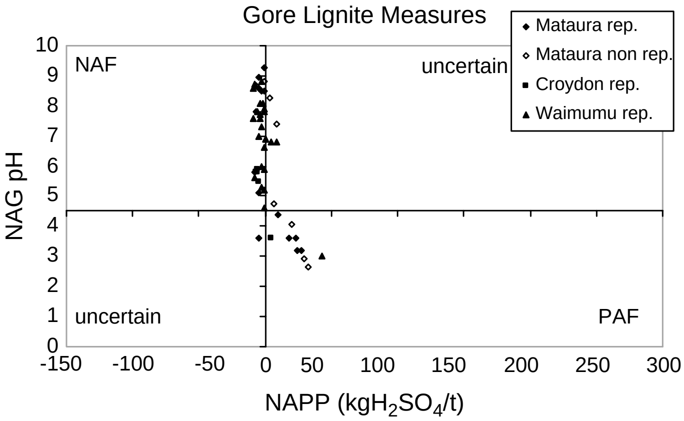

**Fig. 6** Comparison of NAG pH to NAPP acid producing potential for the Gore Lignite Measures. PAF— potentially acid forming, NAF—non-acid forming.

samples contain S that is not present as $FeS_2$, but is present as sulphate (gypsum, alunite etc) or as organic S. Additional investigation of these rocks including sulphur speciation is required to fully interpret the acid base accounting data.

### *Gore Lignite Measures*

Acid base accounting analyses from the gore lignite measures indicate highly variable results (Fig. 6). Most samples have slightly negative NAPP values and NAG pH $> 4.5$ indicating NAF rocks are abundant. The geological setting for the Gore Lignite Measures is consistent with a non-acid forming sequence of rocks. These lignite measures were deposited in a river delta environment during regression and are overlain by terrestrial gravels. There is evidence of marine influence in the interburden rocks because marine fossils are found, however, these are not common. Overlying terrestrial rocks contain occasional sulphide bearing zones and these relate to the presence of paleo salt lakes (Falconer & Craw 2005). This sulphur source might also contribute S to the Gore Lignite Measures and cause irregular distribution of sulphides related rare acid mine drainage issues.

Several samples from Mataura indicate acid producing potential in both representative and non-representative samples. Non-representative samples are collected to identify rock types that either have anomalous acid producing or acid neutralising potential based on hand specimen observations. One sample each from Croydon and Waimumu also indicates acid forming potential. The significance of potentially acid forming samples in the Gore Lignite Measures requires additional examination of their stratigraphic location within proposed mining horizons and correlation of lithological features that might assist in mine site waste management.

Several samples from Croydon for which ANC analyses were not completed (therefore cannot be plotted on NAG pH vs NAPP) indicate that there could be a lithological relationship between carbonaceous mudstone and acid forming potential. The average MPA of samples described as carbonaceous mud or lignitic mud is 57 ($n = 11$) and the average for samples that are not described as carbonaceous mud is 2.5 ($n = 18$) . These sets of samples include analysis of representative and non representative samples.

Several samples from Mataura and Waimumu have positive NAPP values but when oxidised do not produce acid and therefore have NAG pH greater than 4.5. Some of these samples from Mataura have been analysed for pyritic sulphur (Sullivan et al. 1999; Sullivan et al. 2000) and in general the amount of pyritic sulphur is about half of the total sulphur. This means that using total S to calculate the amount of pyrite in Gore Lignite Measures could overestimate the acid producing potential and more accurate results would be obtained by analysing pyrite bound S. The additional S in these samples is probably present as organic sulphur or gypsum (confirmed by x-ray diffraction for one sample).

## Summary and conclusion

The potential for acid mine drainage from four sets of coal measures in the South Island has been has been analysed and related to geological history of the rocks. Geological factors including depositional environment, provenance, diagenetic processes and tectonic setting all influence the mineralogy of coal measures sediments at a regional scale. The mineralogical make up of coal measures sequences directly and predictably influences the acid producing potential or acid neutralising potential of coal measures rocks when disturbed by mining.

Depositional environment is an important control on the potential for acidic drainage from coal mines because the presence or absence of marine rocks closely associated with coal measures is a critical factor that influences the acid producing potential of rocks. For coal measures deposited in coastal environments, tectonic setting is also important and determines if coal measures are overlain by marine rocks or terrestrial rocks. In general, if the coal measures are deposited during regression and therefore are not overlain by transgressive marine sediments, the S content of the coal measures is minimal and therefore the potential to produce acid is low. Conversely when coal is deposited in a coastal environment and in a transgression with marine rocks directly overlying, coal measures have an elevated S content and elevated pyrite content which forms acid mine drainages. Other geological factors such as provenance and diagenetic minerals observed in the Brunner, Paparoa, Morley Coal Measures and Gore Lignite Measures correlate well with the potential of these rocks to form acid when disturbed.

Brunner Coal Measures have the most acid forming potential of the sediments studied and acid base accounting results from Garvey Creek Coalfield are only slightly different to those from the Buller Coalfield. High acid producing potential in the Brunner Coal Measures relates to two factors, elevated pyrite content with S sourced from overlying marine rocks and low carbonate content related to slow deposition and sediment reworking. The large dataset of Brunner Coal Measures acid base accounting data can be used to identify lithological control of acid producing potential such as increasing acid potential with decreasing grain-size from sand to mudstones.

Paparoa and Morley Coal Measures have low acid producing potential due to deposition in fluvial settings. The relationship between the coal measures and formations immediately underlying and overlying appears transgressive. Therefore Paparoa and Morley Coal Measures are overlain by terrestrial sediments rather than marine sediments. Diagentic minerals include carbonates in these rocks and therefore acid neutralising capacity is present. Ambiguous acid base accounting results for some samples probably reflect the presence of non-pyritic sulphur in some samples and acid leaching from organic components or soluble Fe(II) bearing minerals. The data available for the Paparoa and Morley Coal Measures is restricted in area and number of samples and the interpretations here should be compared to new data as these become available.

Gore Lignite Measures have mostly non-acid forming rocks with occasional acid forming samples. This reflects rare marine influences within the Gore Lignite Measures and possibly aerosol derived $SO_4$ in some areas. There is evidence of lithological control of acid base accounting characteristics at Croydon. Additional information on the acid base accounting is required for the Gore Lignite Measures.

In summary, correlation of geological processes with mining related environmental issues provides a robust qualitative predictive tool for companies exploring for coal deposits. This approach can be applied more broadly than to the four sets of coal measures investigated here to other important sets of coal measures in New Zealand and elsewhere.

The datasets indicate the benefits and pitfalls of collection and interpretation of acid base accounting analyses in coal measures sequences. In general, trends can be identified in acid base accounting data that are useful for mine drainage prediction and management. However, there are interferences that hamper interpretation of acid base accounting data. NAG acid production potential and NAG pH can produce false positive acid production because of organic material in coal measures sequences. The impact of these interferences can be identified in Brunner Coal Measures where NAG acid production potential exceeds NAPP acid production potential. In addition, this interference causes some NAPP negative samples of Paparoa Coal Measures to have false low NAG pH. MPA analyses in Gore Lignite Measures could overestimate the acid production potential because some of the S in these rocks is not present as pyrite. Gypsum has been identified by XRD in some samples.

In general, useful information can be gained from acid base accounting analyses, but interpretations should be made with care. Acid load calculations should only be made from samples that are well characterised, this might include other tests such as organic carbon content, pyrite specific S analysis or X-ray diffraction. However, after rocks within a deposit are characterised with a suite of acid base accounting analyses, and assuming interferences are identified and quantified, these methods are a low cost tool for monitoring and management. Other acid base accounting tests such as paste pH are useful screening tools during operational management, however have limited values for prediction of mine drainage chemistry.

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